



Article Pyrite Sulfur Isotope Systematics Suggest Low Marine Sulfate Levels across the Ediacaran–Cambrian Transition

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Abstract: The Ediacaran–Cambrian (E–C) transition was a critical period in Earth's history, and it was characterized by variable but potentially significant increases in atmospheric oxygen levels (pO₂). Sulfate is an essential oxidant and plays a key role in regulating Earth's surface redox conditions. However, there is uncertainty regarding seawater sulfate levels during the E–C transition. To address this issue, organic carbon ($\delta^{13}C_{org}$) and pyrite sulfur isotope ($\delta^{34}S_{py}$) analyses of the Heyu section (the Dengying Formation) in the Sichuan Basin, South China, were carried out. The $\delta^{13}C_{org}$ varies between -36.4% and -27.4%, and $\delta^{34}S_{py}$ ranges from -6.6% to 27.3%. The TOC and pyrite content ranges from 0.13 wt.% to 4.28 wt.% and from 0.01 wt.% to 0.94 wt.%, respectively. The marine sulfate concentration was modeled using a one-dimensional diffusion–advection–reaction model (1D-DAR). The modeling results indicate that the seawater sulfate level remained at a relatively low level of ~2–6 mM. The increased pyrite burial at extensive marine anoxia during the terminal Ediacaran period was likely a driver of such a low sulfate level.

Keywords: marine sulfate concentration; pyrite sulfur isotope; sulfur cycle; the Dengying Formation



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1. Introduction

Marine redox conditions changed dramatically during the Ediacaran–Cambrian (E–C) transition [1–10]. A series of studies based on sedimentary rock archives and chemostratigraphic records from South China have shown apparent spatial and temporal heterogeneity in marine biogeochemistry in E–C oceans [1,11–16]. The surface ocean was oxic, and the deep ocean was anoxic and ferruginous, with intermittent sulfidic conditions in the mid-dle [9,17–19]. For example, although exposure to erosional unconformities is common at the platform, the E–C successions of shallow marine facies of the Nanhua Basin, e.g., the Gaojiashan section [12] and the Xiaotan section [4,14,18,20], show predominantly oxic conditions. Deep water records, such as those for the Yinjiang section [21] and the Silikou section [21–23], indicate anoxic conditions.

Seawater sulfate is strongly affected by marine redox conditions. In contrast with the consensus for marine redox, oceanic sulfate concentrations during the E–C transition differ by an order of magnitude between multiple works [24–33]. There are two contrasting views on this matter: the high-level hypothesis and the low-level hypothesis. The high-level assumption is largely based on the analysis of halite fluid inclusion, which is a potential proxy for the estimation of seawater sulfate levels. This hypothesis proposes that seawater sulfate levels might have risen significantly. Halite samples from Oman and Pakistan suggest a sulfate level of >16 mM during the E–C transition [25,27,30]. However, evaporites are commonly deposited in supratidal environments with limited connections to the open ocean. They would interact with sulfate-enriched brine during diagenesis; thus, this hypothesis requires further tests [29].

Alternatively, the low-level hypothesis is based on frequent changes in the carbonateassociated sulfate sulfur isotope ($\delta^{34}S_{CAS}$) [26,28,31,32]. At low levels of seawater sulfate, i.e., a small sulfate reservoir, the sulfur isotopic composition of seawater sulfate ($\delta^{34}S_{sw}$) is more sensitive to inputs or outputs and thus commonly undergoes frequent changes in $\delta^{34}S_{CAS}$ [34]. Conversely, a high sulfate concentration or a large reservoir can more easily buffer external changes, resulting in relatively stable levels of $\delta^{34}S_{CAS}$ over a specific time period [28]. The $\delta^{34}S_{CAS}$ values reported from Namibia, California, and Mexico's E–C successions all display rapid changes and suggest a relatively low marine sulfate level of <2 mM [31,35]. Notably, authigenic carbonate or diagenesis can also generate a frequent change in $\delta^{34}S_{CAS}$ [36,37]. Some $\delta^{34}S_{CAS}$ variations during the E–C transition have been caused by local changes in carbonate deposition or diagenesis, rather than changes in a marine sulfur reservoir [38].

Several models are commonly used to measure the transportation, concentration, and diagenetic profiles of sulfate in sediments, such as the diffusion–bioturbation–irrigation model, the diagenetic model, and the one-dimensional diffusion–advection–reaction model (1D-DAR) [39–41]. The 1D-DAR model can be helpful in identifying the controlling factors in bulk sample $\delta^{34}S_{py}$ records and in estimating sulfate levels in ancient clastic rocks under non-sulfidic water conditions [41–44]. This study analyzed the succession in the Sichuan Basin, South China (the Dengying Formation at the Heyu section), and marine sulfate concentrations were modeled during the terminal Ediacaran period using the 1D-DAR model.

2. Geologic Setting and Samples

The South China Block formed from an amalgamation of the Yangtze and Cathaysia blocks in the early Neoproterozoic era [45] (Figure 1A). During the breakup of the Rodinia supercontinent in the early Neoproterozoic era, the Nanhua rift [45,46], the South Qinling rift [47,48], and the Kangdian rift were formed around the Yangtze Block. Due to the ultimate breakup of Rodinia or the slab pull in the drift, the Yangtze Block is in an extensional setting, resulting in widespread rifting activity during the E–C transition [45,46,49]. Because of this rifting activity, the northern Yangtze Block formed a rift basin during the Ediacaran period. In contrast, the southern Yangtze Block was characterized by a stable shallow-water platform with several intracratonic sub-basins [50–53].

The Ediacaran successions of the Yangtze Block include the Doushantuo Formation (carbonate and mudstone) and the Dengying Formation (carbonate) in shallow water facies. In the deep-water facies, Ediacaran successions consist of Doushantuo Formations (siltstone) in the lower part and Liuchapo/Laobao Formations (cherts) in the upper part. Meanwhile, the Dengying Formation is unconformably overlain in the shallow water facies by the Maidiping/Kuanchuanpu Formations.

The Heyu section (HY) is located 20 km east of Chengkou County in Sichuan Province (Figure 1B,C). This section is situated to the north of the Yangtze Block and is a typical succession of the Southern Qinling Mountains. At the HY section, the Ediacaran Dengying Formation is about 74 m thick and is mainly constituted by chert in the lower parts and siliceous dolostone in the upper parts, suggesting an upward shallowing sequence.

The Dengying Formation can be simply divided into upper and lower parts at the HY section. The lower part (I) is about 39 m thick and mainly consists of chert (Figure 2A). Under a microscope, rhythmic laminae composed of fine quartz and black carbonaceous mud can be seen (Figure 2C). Its characteristics are similar to those of the Liuchapo Formation in the Nanhua Basin, suggesting a deep-water deposition. The upper part of the Dengying Formation (II) is 35 m thick and mainly composed of thin-layered siliceous dolostone interbedded with thin-layered siliceous dolostone (Figure 2B,D). The dolostone deposition gradually increases from the bottom to the top. Synsedimentary sliding plastic deformation structures can be seen at the top of this part [48]. Carbonaceous shale or cherts of the Early Cambrian Maidiping Formation overlay the top of the Dengying Formation. In total, 22 chert and dolostone samples were collected from the HY section.



Figure 1. Palaeogeographic map and stratigraphic column. (**A**) Global paleogeography at ~540 Ma. (**B**) Paleogeographic map of the Yangtze Block during the Ediacaran–Cambrian transition (modified from [52]). (**C**) Lithological column of the Heyu section (modified from [48]).



Figure 2. Field and microscopic photographs of the Heyu section. (**A**) Mid-thick bedded chert. (**B**) Thin-bedded chert and siliceous dolostone. (**C**) Carbonaceous shale. (**D**) Organic-rich siliceous dolostone.

3. Methods

Cherts and dolostones from the HY section were sampled continuously at ~1–2 m intervals. All samples were split into two parts. One part was prepared for thin section cutting, while the other part was prepared for powdering. Fresh rock chips were ground into powder (<200 mesh) using an agate mortar. An aliquot of about 1 g powder was decarbonated using 5 vol.% HCl in a centrifuge tube. After 24 h, the acid solution was centrifugated, and the supernatant was removed. The residues were washed three times using deionized water and then thoroughly dried for TOC and carbon isotope analysis. For pyrite content and $\delta^{34}S_{py}$ analysis, 0.5–2 g powder was weighed, and the pyrite in the powder was reduced to a Ag_2S precipitate using the chromium reduction method. A $CrCl_2$ solution was prepared with 50–100 g of zinc pellets, 30 mL of 1 M CrCl₂, and 70 mL of 12 M HCl. The samples and the CrCl₂ solution were mixed and heated to induce a reaction. The duration of the reaction was at least 2 h. Ag₂S precipitates were dried and weighed for measurements. TOC, $\delta^{13}C_{org}$, and $\delta^{34}S_{py}$ were measured using an Organic Elemental Analyzer (FLASH 2000, Waltham, MA, USA) and a Delta V Advantage Isotope Ratio Mass Spectrometer at the Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences. Organic carbon isotope compositions were reported in the delta notation per mil deviation from the Vienna Pee Dee Belemnite (VPDB) standard, with an analytical error of <0.1%. $\delta^{34}S_{py}$ was expressed using the delta notation as per mil deviation from the Vienna Canyon Diablo Troilite (VCDT), with an analytical error <0.2‰.

Pyrite crystals were analyzed using a field emission environment scanning electron microscope (FSEM, FEI Quanta 250FEG, Waltham, MA, USA) with an accelerating scanning voltage of 20 kV at the State Key Laboratory of Oil and Gas Reservoir Geology and Exploitation (Chengdu University of Technology). The thin section was placed inside the field emission scanning electron microscope, which was tuned to the backscattering mode. The color of the pyrite is brighter than that of the enclosing rock due to the difference in composition. The pyrite's morphology was observed and counted in order from top to bottom and from left to right to avoid human errors. Typically, >200 framboids were measured directly on-screen per sample.

4. Results

We analyzed the TOC, $\delta^{13}C_{org}$, pyrite content, and $\delta^{34}S_{py}$ of 22 samples from the HY section. All data are shown in Figure 3 and Table 1.



Figure 3. Stratigraphic column, geochemical profiles, and diameter of framboidal pyrite in the Heyu section.

Sample No.	Height (m)	$\delta^{13}C_{org}$ (‰)	TOC (%)	δ ³⁴ S _{py} (‰)	Pyrite (%)	Diameter (µm)
HY-LCP-1	1.3	-29.6	2.44	n.a.	0.04	7.64
HY-LCP-2	4.8	-33.4	2.98	-6.6	0.02	8.46
HY-LCP-3	8.2	-34.4	2.69	n.a.	0.02	13.63
HY-LCP-4	11.6	-29.5	1.60	5.3	0.12	n.a.
HY-LCP-5	15.0	-34.3	3.14	10.4	0.20	9.78
HY-LCP-6	18.4	-27.4	0.13	n.a.	0.08	n.a.
HY-LCP-7	21.8	-34.8	1.49	n.a.	0.16	n.a.
HY-LCP-8	25.2	-34.6	1.10	4.7	0.23	6.95
HY-LCP-9	28.6	-35.1	1.20	n.a.	0.03	n.a.
HY-LCP-10	32.0	-35.2	0.75	-0.9	0.01	n.a.
HY-LCP-11	35.4	-30.7	1.67	n.a.	0.05	16.79
HY-LCP-12	38.8	-36.4	3.22	n.a.	0.08	n.a.
HY-LCP-13	42.2	-35.6	2.40	20.5	0.94	9.03
HY-LCP-14	45.6	-30.7	3.13	n.a.	0.57	n.a.
HY-LCP-15	49.0	-35.4	4.28	n.a.	0.61	8.31
HY-LCP-16	52.4	-34.3	1.97	n.a.	0.25	n.a.
HY-LCP-17	55.8	-35.4	2.56	27.3	0.17	n.a.
HY-LCP-18	59.2	-34.3	2.47	24.1	0.30	8.48
HY-LCP-19	62.6	-30.4	2.03	n.a.	0.55	n.a.
HY-LCP-20	66.0	-35.4	3.08	26.5	0.64	7.67
HY-LCP-21	69.4	-35.1	2.78	n.a.	0.18	8.08
HY-LCP-22	72.8	-34.2	1.16	n.a.	0.04	n.a.

Table 1. Geochemical results from the Dengying Formation.

n.a. = not available.

The TOC content at the lower part of the Dengying Formation decreased gradually, while the content in the upper part was relatively high. For Member I, the TOC ranged from 0.13% to 3.22%, with an average value of 1.84%. For Member II, the TOC ranged from 1.16% to 4.28%, with an average value of 2.59%.

The $\delta^{13}C_{org}$ of Member I ranged between -36.4% and -27.4%, with an average value of -32.9%. The $\delta^{13}C_{org}$ of Member II ranged between -35.6% and -30.4%, with an average value of -34.1%.

The pyrite content of Member I ranged from 0.01% to 0.23%, with an average value of 0.09%. The pyrite content of Member II varied between 0.04% and 0.94%, with an average value of 0.43%.

The $\delta^{34}S_{py}$ content of Member I oscillated between -6.6% and 10.4%, whereas the $\delta^{34}S_{py}$ of Member II showed relatively high values, ranging from 20.5‰ to 27.3‰, with a mean value of 24.6‰.

The microscopic characteristics of pyrite are shown in Figure 4. Framboidal pyrite and euhedral or semihedral pyrite developed in the Heyu section. The size of the framboidal pyrite ranged between 6.95 μ m and 16.79 μ m (mean = 9.53 μ m).



Figure 4. Microphotographs of pyrite from the Dengying Formation. (**A**) Disseminated pyrite. (**B**) Euhedral pyrite and semihedral pyrite.

5. Discussion

5.1. Syndepositional Early Diagenetic Origin of Pyrite in the Dengying Formation

Variation in $\delta^{34}S_{py}$ is closely related to changes in marine redox conditions and seawater sulfate concentrations [43,54–59]. For example, the $\delta^{34}S_{py}$ from the oxic and high-sulfate Phanerozoic ocean commonly shows a low and negative value, whereas the $\delta^{34}S_{py}$ from the anoxic and low-sulfate Proterozoic ocean is predominantly characterized by a relatively high and positive value [28,34,53]. However, recent works show that local depositional conditions, diagenetic processes, or metamorphic conditions may differentially affect bulksample $\delta^{34}S_{py}$ records. During diagenesis, the iron released from smectite or chlorite can interact with hydrogen sulfide to precipitate pyrite [60]; meanwhile, in late hydrothermal alterations, such as the thermochemical sulfate reduction (TSR), reactions can profoundly increase the levels of $\delta^{34}S_{py}$ [61]. Therefore, the timing and location of pyrite formation should be confirmed before offering an interpretation.

Multiple lines of evidence show that the pyrite from the Dengying Formation is authigenic. First, framboidal pyrite commonly occurs along the bedding plane, and no fluid conduits or hydrothermal veins are observed in connection with pyrite laminae. The size and morphology of pyrite crystals are similar to those of authigenic pyrite reported in modern marine sediments [62]. The particle size of framboidal pyrite in the Heyu section ranges from 6.95 μ m to 16.79 μ m, which is much larger than that of the pyrite in sulfidic oceans. Second, the wide range of variation in $\delta^{34}S_{py}$ (ranging from -6.6% to 27.3‰), which sharply contrasts with the narrow range and low $\delta^{34}S_{py}$ values of hydrothermal fluids, also suggests the diagenetic origin of pyrite [41,63]. Euhedral pyrite and hemihedral pyrite are similar in size to framboidal pyrite; they are formed by the recrystallization of framboidal pyrite. When the pore water system is not well connected to the overlying water column, framboidal pyrite gradually transforms into euhedral and semihedral pyrite in the sediments [64,65]. Thus, the pyrites from the Dengying Formation were mainly precipitated at the sediment–water interface (SWI) or within the porewater during diagenesis.

5.2. Modeling of the Bulk-Sample $\delta^{34}S_{py}$ and Pyrite Content of the Yangtze Block

5.2.1. Model Description

The 1D-DAR model simulates the formation of syndepositional pyrites in pore water based on the geochemical conditions at the water–sediment interface and the geochemical cycling process of sulfur in sediments [39,40,42]. The behaviors of organic matter, sulfate,

active iron, and H₂S in sediments can be characterized as diffusion, convection, and reaction processes using the 1D-DAR model. The boundary of pyrite concentration and sulfur isotopes can be constrained based on the sulfate concentration at the water–sediment interface, seawater sulfur isotopes, the dissimilatory sulfate reduction (DSR) rate, the sedimentation rate, the proportion of re-oxidized H₂S, and the active iron concentration.

The dissimilatory sulfate reduction (DSR) at the HY section occurs at or below SWI. As such, the pyrite, including most framboidal pyrite, may be mainly precipitated in sediment porewater. The 1D-DAR model can simulate this process. We made several assumptions to simplify the numerical calculations and constrain the pyrite concentration and the $\delta^{34}S_{py}$ boundary. First, we did not consider the disproportionation during DSR, and all of the H₂S was derived directly from DSR. We also assumed that H₂S oxidizes to produce sulfate without intermediate sulfides to ensure that no H₂S comes from the disproportionation reaction of intermediate because DSR alone can generate fractionation as significant as that produced by the disproportionation reaction.

Moreover, we set the constant isotopic fractionation in the model at 47% as a boundary condition representing the maximum possible sulfur isotope fractionation. Such a value is in line with observed fractionations in pure cultures from DSR. Second, we assumed that the DSR rate is linearly correlated with the TOC content. Most organic matter settled to the SWI cannot be utilized directly by a sulfate-reducing microbe, even though the DSR organisms prefer fresh and labile organic matter. Therefore, the relationship between TOC and the DSR rate may not be linear. Our assumption would thus generate an optimistic estimation of the TOC and pyrite formation. Third, we assumed that the sulfate derived from H₂S oxidation returned to the seawater sulfate pool. This assumption indicates a sulfate concentration with a constant initial value during modeling.

First, the 1D-DAR model, which is in a steady state below the water–sediment interface, constrains porewater sulfate. Sulfate is supplied from overlying seawater via diffusion and is consumed by the DSR process. During sedimentation, the water–sediment interface moves upwards, and the porewater sulfate concentration can be calculated as follows.

$$\frac{\partial \left[{}^{i}\mathrm{SO}_{4} \right]}{\partial t} = D_{s} \left(\frac{\partial^{2} \left[{}^{i}\mathrm{SO}_{4} \right]}{\partial z^{2}} \right) - s \left(\frac{\partial \left[{}^{i}\mathrm{SO}_{4} \right]}{\partial z} \right) - R_{DSR}^{i} \left[{}^{i}\mathrm{SO}_{4} \right] [\mathrm{CH}_{2}\mathrm{O}] \tag{1}$$

The left side of the equation represents the variation in the porewater sulfate concentration with time/distance, and the right side corresponds to the diffusion, advection, and reaction of sulfate in the sediment. D_s is the sulfate diffusion coefficient, s is the sedimentation rate, and [SO₄] and [CH₂O] represent the sulfate concentration and organic matter content in the sediment, respectively. *t* is the sedimentation time, z represents the distance from the water–sediment interface, R^I_{dsr} is the reaction constant of DSR, and the superscript i represents ³²S or ³⁴S. Expressions $D_s \left(\frac{\partial^2[^iSO_4]}{\partial z^2}\right)$, $-s \left(\frac{\partial[^iSO_4]}{\partial z}\right)$, and $-R^i_{DSR}[^iSO_4]$ [CH₂O] correspond to the processes of sulfate diffusion, advection, and reaction under WSI, respectively.

In porewater, sulfate is continuously reduced to H_2S , reacting with active iron ([Fe]) to generate pyrite. Similarly to the sulfate concentration, porewater H_2S is consumed within the sediment by diffusion, advection, and pyrite precipitation. The porewater H_2S profile can be simulated by using the following:

$$\frac{\partial \left[{}^{i}H_{2}S \right]}{\partial t} = R_{DSR}^{i} \left[{}^{i}SO_{4} \right] \left[CH_{2}O \right] + D_{H_{2}S} \left(\frac{\partial^{2} \left[{}^{i}H_{2}S \right]}{\partial z^{2}} \right) - s \left(\frac{\partial \left[{}^{i}H_{2}S \right]}{\partial z} \right) - R_{PY}^{i} \left[{}^{i}H_{2}S \right] \left[Fe \right] / 2$$

$$(2)$$

where D_{H2S} is the diffusion coefficient of H_2S , and R_{PY} is the constant rate of pyrite formation. We assume that the organic carbon ([CH₂O]) and active iron ([Fe]) are mainly consumed by DSR and pyrite precipitation, respectively. Because one mole Fe requires

two moles H_2S to form pyrite, the stoichiometric ratio of 0.5 should be considered in the reaction terms.

Below the sediment–water interface, organic matter is gradually depleted by the DSR process. This behavior continues until the organic matter or sulfate is completely depleted. In conjunction with the DSR process, the time/depth dependence of $[CH_2O]$ can be expressed as:

$$\frac{\partial [CH_2O]}{\partial t} = -R_{DSR}^{32} \left[{}^{32}SO_4 \right] [CH_2O] - R_{DSR}^{34} \left[{}^{34}SO_4 \right] [CH_2O]$$
(3)

The consumption process of organic matter is principally involved with the reaction process, and is almost independent of diffusion and convection effects. $-R_{DSR}^{32}[^{32}SO_4][CH_2O]$ and $-R_{DSR}^{34}[^{34}SO_4][CH_2O]$ imply the depletion of organic matter by sulfates of the ^{32}S and ^{34}S in pore water, respectively.

Likewise, the expression for the active iron content [Fe] is as follows:

$$\frac{\partial [Fe]}{\partial t} = -R_{PY}^{32} \left[\frac{3^2 H_2 S}{Fe} \right] [Fe]/2 - R_{PY}^{34} \left[\frac{3^4 H_2 S}{Fe} \right] [Fe]/2$$
(4)

For the sake of simplicity, $\delta^{34}S_{py}$ can be expressed as $\delta^{34}S_{py} = [ln(^{34}S/^{32}S)sam/(^{34}S/^{32}S)std] \times 1000$, where subscripts sam and std represent the sample and standard, respectively. Even if the natural log definition of $\delta^{34}S_{py}$ differs from the traditional definition, the difference between the two calculations is <5% when $\delta^{34}S_{py}$ is under 100%. Both $\delta^{34}S_{py}$ and pyrite content ([pyrite]) are cumulative values for all pyrite formed in the sediments because the pyrite precipitates in a depth range. The relationship between $\delta^{34}S_{py}$ and pyrite content [pyrite] can be calculated as follows.

$$\delta^{34}S_{PY} = \frac{\int {}_{0}^{z} \delta^{34}S_{PY}[H_2S][Fe]dz}{\int {}_{0}^{z} [H_2S][Fe]dz}$$
(5)

$$[pyrite] = \left(\int_{0}^{z} R_{PY}[H_2S][Fe]dz\right) / (2s)$$
(6)

Using the above 1D-DAR equations in conjunction with Matlab Software, the progression of pyrite formation under the water–sediment interface can be simulated. The simulation results are output as $\delta^{34}S_{py}$ -[pyrite] figures. The parameters of the model constrain the boundary of the plot. A range of sulfate concentrations is assumed in the 1D-DAR model, combined with certain conditions for the other boundary parameters (such as seawater sulfur isotope, fractionation during DSR, TOC, active iron concentration, and the sedimentation rate). Hence, a series of $\delta^{34}S_{py}$ -[pyrite] figures based on sulfate variations are simulated and output. The pyrite data measured in the laboratory are confirmed to fall precisely into the interval of the $\delta^{34}S_{py}$ -[pyrite] figures. The over-concentration or dispersion of pyrite data in the laboratory, either inside or outside the boundary, affects the estimation of sulfate at the water–sediment interface. Where the data points for pyrite fit reasonably well within the $\delta^{34}S_{py}$ -[pyrite] figure, the estimated sulfate concentration is considered to be the sulfate concentration during the E–C transition.

5.2.2. Parameter Setup and Boundary Constraints

The seawater sulfur isotope ($\delta^{34}S_{so4}$) was estimated to be +40‰ for the boundary of the 1D-DAR [66–69]. In the terminal Ediacaran (~541 Ma) period, $\delta^{34}S_{so4}$ increases to a value upon ~40‰ at sites including Oman, Namibia, South China, and Siberia [12,34,68,70–72]. Various minerals, including evaporites, francolite, and carbonate, show that levels of $\delta^{34}S_{so4}$ stayed elevated (generally 35‰–40‰) in most basins throughout the early part of the Paleozoic era [58,67–69,73–76]

The isotopic fractionation during DSR ($[F_{DSR}]$) is highly variable, ranging from -25% to -70% [77–85]. Here, we set it at 47‰ as the boundary of the 1D-DAR. This value is in line with observed fractionations in pure cultures from DSR [83]. As the seawater concentration is a marginal value for the 1D-DAR model, isotopic fractionation may be smaller for oceans with a lower sulfate concentration. The isotopic fractionation factors drop to about ~2–3 mM. The sulfate concentrations estimated by the authors are lower than those of modern seawater, but they may not be lower than those in which isotopic fractionation.

The diffusivity of Ds was set to $4.23 \times 10^{-10} \text{ m}^2/\text{s}$, and D_{H2S} was set to $6.14 \times 10^{-10} \text{ m}^2/\text{s}$ [86]. The calculations were performed based on relations derived from the diffusion coefficient in a free solution for pore-water at a temperature of 10 °C. The sedimentation rate (s) is calculated by dividing the stratigraphic thickness by the duration; s is set at 0.05 m/ky for the shallow water environment.

The [CH₂O] is controlled by exported primary productivity (EPP) and governed by the TOC and pyrite content of bulk samples. Primary productivity is high in the modern ocean [87], but only a few macroscopic organisms developed during the Ediacaran– Cambrian transition [88], so the EPP may be low. Here, [CH₂O] is set to 1–30 wt.%, and then EPP is shown to be 0.01–3 mol/m²/yr. [Fe]₀ is set to infinity here (Fe in sediment >2 wt.%).

5.2.3. Modeling Results

The modeling simulations show that bulk-sample $\delta^{34}S_{py}$ records and pyrite concentrations from the Dengying Formation are highly dependent on the availability of organic matter (dashed line) and the proportion of H₂S reoxidation (solid line) during pyrite formation (Figure 5). Seawater sulfate concentration, i.e., [SO₄] at the SWI, can also be simulated using the above parameters. The concentration that [SO₄] is simulated at is approximately ~2–6 mM (Figure 5A–C) for the pyrite formation in the water–sediment interface. Most data fell outside the boundary of 1D-DAR when [SO₄] is simulated by 8 mM (Figure 5D). The simulation of [SO₄] suggests a relatively low sulfate level at the HY section in shallow water during the terminal Ediacaran period.

5.2.4. Sensitivity Tests

Marine sulfate levels may differed significantly between shallow- and deep-water environments during the E–C transition. To test the influence of the sedimentation environment on sulfate concentration calculations, the 1D-DAR model was used to simulate the bulk-sample $\delta^{34}S_{py}$ records in the Dengying Formation at the Wangji section (WJ), which is deposited on the inner shelf [89]. The boundary of 2–6 mM also fit the 1D-DAR model at this time, which implies the presence of relative low sulfate levels during the E–C transition (Figure 5).

As sulfate concentration records show significant spatial heterogeneity due to local variations in depositional conditions, the low seawater sulfate level in deep-water facies was also tested in the Yangtze Block. Here, we collected isotopic data of other bulk samples from the Yinjiang section (YJ) [21,90], the Longbizui section (LBZ) [15,91–93], and the Xugongping section (XGP) [94], which were all deposited in the deep-water environment of the Yangtze Block. The Liuchapo Formation (isochronous strata with the Dengying Formation) at the Yinjiang section is 40 m thick and consists of gray-black laminated chert, depositing in a slope environment [21,90]. At the Longbizui section, the Liuchapo Formation is ca. 70 m thick, composed of chert with intercalated siliceous shale, and deposited in a slope environment [15,91–93]. The Liuchapo Formation at the Xugongping section is approximately 40 m thick and consists of cherts with minor siliceous shale interbeds in the middle part [94]. The Yinjiang, Longbizui, and Xugongping sections experienced predominantly ferruginous conditions during the E–C transition [21,94]. Some pyrite samples precipitated from the intermittent euxinia environment in the Xugongping section

were excluded from the analysis. At simulated sulphate concentrations of 2 (Figure 6A), 3 (Figure 6B), and 6 (Figure 6C), $\delta^{34}S_{py}$ -[pyrite] figures were output via the 1D-DAR model. The modeling results show that the [SO₄] at ~3 mM may match the sulfate concentrations of the seawater (Figure 6B).



Figure 5. Modeling results for sulfate concentrations in shallow water during the E–C transition. (**A**) The modeling results show a value of 2 mM in shallow water. (**B**) The modeling results show a value of 4 mM in shallow water. (**C**) The modeling results show a value of 6 mM in shallow water. (**D**) The modeling results show a value of 8 mM in shallow water. In the figures, the horizontal axis represents the pyrite sulfur isotopic composition, and the vertical axis indicates the pyrite content. The blue, pink, and purple solid lines indicate that the proportion of H₂S reoxidation was 30%, 60%, and 99%, respectively. The orange, gray, and black dashed lines indicate that the organic matter flux was 0.1, 1, and 3 mol/m²/yr, respectively. The boundary conditions of the model are shown in the figures. The data in the Wangji section are taken from [89].



Figure 6. Modeling results of sulfate concentrations during the E–C transition in deep water. (**A**) Modeling results showing 2 mM in shallow water. (**B**) Modeling results showing 4 mM in shallow water. (**C**) Modeling results showing 6 mM in shallow water. In the figures, the horizontal axis represents the pyrite sulfur isotopic composition, and the vertical axis indicates the pyrite content. The pink, yellow, and purple solid lines indicate that the proportion of H₂S reoxidation was 60%, 80%, and 99%, respectively. The orange, gray, green, and black dashed lines indicate that the organic matter flux was 0.1, 1, 2, and 3 mol/m²/yr, respectively. The boundary conditions of the model are shown in the figures. The data in the Longbizui section are taken from [15,90–92]. The data in the Yinjiang section are taken from [21,93]. The data in the Xugongping section are taken from [94].

In addition, because the initial $\delta^{34}S_{sw}$ and biological isotope fractionation impacted the bulk-sample $\delta^{34}S_{pv}$ records, we ran sensitivity tests. Almost all data were fitted for the boundary of the 1D-DAR model when the sulfate concentration was set at 4 mM. The results show that low sulfate concentrations during the E-C transition were not sensitive to variations in these parameters (Figure 7). Only a few data from the Wangji section fell outside of the boundary, as indicated in in Figure 7A,C. Even though the isotopic fractionation factors may drop to about 3 mM [78], the sulfate concentration may be higher than 2 mM and lower than that of the modern ocean. Figure 7A shows that the sulfate fractionation factor over 35‰ is valid for the boundary of the 1D-DAR model. The superheavy pyrite isotope in Figure 7C may have been caused by the low sulfate concentration of seawater, the enhanced burial of pyrite, the dilution effect of pure dolostones formed at a high sedimentation rate, or thermochemical sulfate reduction (TSR) rather than BSR [89,95]. As there is no clear evidence in sedimentation characters for a significant impact by hydrothermal fluids in the section or in South China, the TSR origin for high values of $\delta^{34}S_{pv}$ may not be preferred. Ocean anoxic events indicated by high $\delta^{15}N$ signals and low $\delta^{238}U$ signals worldwide may promote pyrite burial and enhance the value of $\delta^{34}S_{py}$. The value of $\delta^{34}S_{py}$ shows the same trend as the value of $\delta^{34}S_{sw}$, suggesting that low sulfate concentrations may be a factor involved in producing high values of $\delta^{34}S_{pv}$. More information is needed to assess this phenomenon [89,95].

5.3. Implications for Marine Sulfate Levels in the Terminal Ediacaran Ocean

Marine sulfate is essential in regulating the redox and marine carbon cycle. For example, the Shuram/Wonoka/DOUNCE negative carbon isotope excursion in the mid-Ediacaran period, the largest negative carbon isotope excursion in the Earth's history, has been interpreted as a consequence of dissolved organic carbon (DOC) remineralization associated with DSR [89,96]. Sulfate levels may have been high in the early- to middle-Ediacaran period. It is proposed that intense continental weathering during the melting of the Marinoan "Snowball Earth" glaciation led to an immediate rise in seawater sulfate levels in the early Ediacaran era [42,82]. Numerical analyses of δ^{34} Scas from the Doushantuo Formation in South China suggest a high sulfate level of ~10 mM in the inner shelf, but a low sulfate concentration of <3 mM in the deep ocean [97].



Figure 7. The 1D-DAR model sensitivity tests of variable $\delta^{34}S_{sw}$, [Fe]₀, and biological fractionation. (**A**) and (**B**) show the modeling results of different biological fractionations. (**C**) and (**D**) show the modeling results of different $\delta^{34}S_{sw}$ values. (**E**) and (**F**) show the modeling results of different [Fe]₀ values. The data in the Wangji section are taken from [82]. The blue, pink, and purple solid lines indicate that the proportion of H₂S reoxidation was 30%, 60%, and 99%, respectively. The orange, gray, and black dashed lines indicate that the organic matter flux was 0.1, 1, and 3 mol/m²/yr, respectively. The boundary conditions of the model are shown in the figures. The data in the Wangji section are taken from [89].

Compared with the relatively high sulfate levels in the early-to-mid-Ediacaran era, the modeling results suggest low marine sulfate levels during the E–C transition (Figure 8). A low sulfate concentration is consistent with the results from multiple sulfur isotope datasets from South China, which also suggest a low sulfate concentration of <4 mM [98]. Moreover, low marine sulfate levels are consistent with the rapid changes in δ^{34} Scas data

reported from the Ediacaran-Cambrian succession in Mexico and California. Frequent changes in δ^{34} Scas levels commonly result from the weak buffering abilities of seawater sulfate [31]. Notably, the suggestion of low sulfate concentrations is not contradicted by pervasively distributed evaporites of the Yangtze Platform in the terminal Ediacaran era [99–101]. Gypsum precipitation only requires ion products between Ca^{2+} and SO_4^{2-} exceeding 23 mM². In the carbonate-oversaturated Precambrian ocean, the ion product would easily reach this threshold value if seawater sulfate measured ~2 mM [99]. Canfield and Farquhar, 2009, argue that oceanic sulfate levels may have been as high as 10 mM in the terminal Ediacaran era. They propose that the reoxidation of H₂S caused by pervasive bioturbation may have significantly reduced the amount of pyrite burial, increasing sulfate concentrations in the seawater. However, due to bioturbation's bilateral "dual" roles in the sedimentary sulfur cycle, the increase in sulfate concentrations caused by bioturbation may be overestimated [102]. Bioturbation supplies not only oxygen but also sulfate into the sediment. With the increased levels of sulfate in the sediment, the sulfate reduction and in situ pyrite precipitation were promoted within the sediments [102]. This process may have enhanced sulfide burial and reduced the sulfate concentration of seawater.



Figure 8. Conceptual model of the marine sulfur cycle and sulfate levels during the Ediacaran–Cambrian transition.

The low levels of marine sulfate were likely caused by extensive marine anoxia during the terminal Ediacaran period. It is estimated that >21% of the seafloor might be anoxic [103]. Moreover, ⁸⁷Sr/⁸⁶Sr data from South China [104], Siberia [71,105], and Namibia [106] also indicate that chemical weathering was reduced during the E–C transition compared to the Shuram excursion. Under the conditions of expanded anoxic water and reduced continental weathering, most sulfate in the seawater was moved into the sediment in the presence of pyrite during the microbial sulfate reduction process. Large amounts of pyrite burial may have caused an increase in Earth's surface redox and paved the way for the diversification of the metazoan in the Cambrian period [107].

6. Conclusions

This study reports new pyrite and organic carbon isotope data for the Heyu section in the shallow water of the Yangtze Block, South China. $\delta^{13}C_{org}$ content varies between -36.4% and -27.4%, and $\delta^{34}S_{py}$ content ranges from -6.6% to 27.3%. The TOC and pyrite content ranges from 0.13 wt.% to 4.28 wt.% and from 0.01 wt.% to 0.94 wt.%, respectively. The diameter of pyrite from the Dengying Formation ranges from 6.95 µm to 16.79 µm, showing that these pyrites were mainly precipitated at the sediment–water interface (SWI) or within porewater during early diagenesis. Additionally, the numerical modeling of these bulk-sample $\delta^{34}S_{py}$ variations shows a low marine sulfate concentration during the E–C transition, with values of ~2–6 mM in shallow water. Low seawater sulfate levels might have been caused by extensive sulfate consumption in the terminal Ediacaran period.

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