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Key Points:

- The redox conditions along the continental marginal slope were stratified and fluctuating in the late Ediacaran ocean
- Paleoclimate variations influenced the basin's hydrochemistry and biological activity, driving shifts in the redox chemocline
- The shifts in the slope's redox chemocline regulated distinct oceanic manganese cycling and mineralization processes in South China

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Manganese Cycling Driven by Fluctuating Redox Chemocline in the Ediacaran Ocean

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Abstract The Ediacaran Period, immediately following the Neoproterozoic Cryogenian glaciations, marked a crucial phase in the Earth's evolutionary history. The paleo-oceanic environment helped shape the habitability, yet the links between oceanic redox state, hydrochemistry, biological activity, and elemental cycling during this time remain poorly understood. Here, we address this scientific issue based on highresolution geochemical data from black shale-hosted, manganese (Mn)-rich carbonates within the upper Ediacaran Doushantuo Formation, located on the northern margin of the Yangtze Block, South China. Multiple redox proxies indicate that while the open ocean may have been intermittently oxygenated during the late Ediacaran glaciation, the continental margin slope was characterized by redox stratified conditions with a fluctuating redox interface. These fluctuations were driven by climatic shifts. During the deposition of black shales, a relatively warm and humid climate caused a notable increase in freshwater runoff and glacial meltwater, raising water levels and lowering salinity. The influx of bioessential elements carried by terrestrial runoff promoted primary productivity. By contrast, the deposition of the Mn(II) carbonates occurred under colder, more arid conditions, with limited terrigenous nutrient input, leading to lower organic carbon production. This resulted in the deepening of the redox chemocline over the continental shelf, promoting Mn(II) oxidation and subsequent mineralization. Paleoclimate-driven redox fluctuations were key in controlling elemental cycling during the late Ediacaran. This may offer insights into similar processes throughout Earth's history.

Plain Language Summary If the late Ediacaran ocean is oxygenated or reducing remains a topic of debate. Here we propose a stratified scenario with an intermittently fluctuating redox interface between O_2 -bearing surface waters and O_2 -depleted deep waters on the continental margin slope as represented by the Doushantuo Formation of South China. We further establish coupled links between the ancient oceanic redox state, paleoclimate, marine hydrochemistry, biological activity, and Mn-cycle during this period based on multiple geochemical proxies. Warm and humid climate supplied nutrient elements that fueled high primary productivity, sustaining higher redox interface and widespread H_2S -bearing conditions conducive to black shale deposition. In contrast, a colder, more arid climate limited nutrient supply and productivity, leading to diminished organic carbon synthesis, descending redox interface, and contracted deep O_2 -depleted zone, which favored Mn(II) carbonate formation. The fluctuating redox interface created optimal conditions for Mn(II) oxidation, Mn(IV) reduction, and Mn(II) carbonate mineralization during the transformative phase of oxygenation event in the late Ediacaran. This might be general throughout geological history.

1. Introduction

The aftermath of the Cryogenian Period, which ended around 635 million years ago (Ma) (Hoffman et al., 1998), was a transformative time for both redox changes and the evolution of life on Earth (Canfield et al., 2007). Extensive fossil evidence of eukaryotes and metazoans (Waggoner, 2003), as well as intermittent fluctuations in the carbon cycle (Fike et al., 2006; Husson et al., 2020), has led to a general consensus that the global oceans were predominantly oxygenated during this time (Ader et al., 2014; Sahoo et al., 2012; Wang, Ling, et al., 2018). This oxygenation is believed to have been related to a Neoproterozoic oxygenation event (NOE), which occurred between ca. 800 and 500 Ma (Alcott et al., 2019).

However, various geochemical proxies have suggested that the Ediacaran oceans remained largely anoxic, with strong stratification and a shallow redox interface (Li et al., 2010; Planavsky et al., 2011; Poulton & Canfield, 2011). These findings challenge the previous understanding and indicate a complex pattern of redox conditions during this period. The potential reasons for this discrepancy include—but are not limited to—the following factors. First, most of the geochemical data comes from shallow, proximal facies in continental shelf setting, where hydrological complexity leads to strong spatial heterogeneity in redox conditions, making it difficult to infer the redox state of the entire ocean. Second, different geochemical proxies often yield contrasting conclusions. For example, nitrogen (N) isotopic composition of sediment is only a valuable indicator of surface water redox conditions (Canfield et al., 2010; Wang, Jiang, et al., 2018), while iron (Fe) speciation is more indicative of deep-water redox states (Poulton & Canfield, 2011). Consequently, the apparent contradictions in paleo-ocean redox models may arise from the localized nature of redox conditions captured by different geochemical proxies. To resolve these uncertainties, integrating multiple robust proxies—such as N isotope, Fe speciation, and others—will be essential for constructing a coherent and comprehensive view of the paleo-oceanic redox state. This, in turn, is crucial for understanding the evolution of life and the cycling of critical elements in the late Neoproterozoic ocean.

Black shales and carbonate rocks of the Ediacaran Doushantuo Formation (ca. 635–551 Ma) in South China represent distinct sedimentary environments that offer valuable insights into post-Cryogenian paleo-oceanic conditions and critical element cycling. Of particular interest are the Mn(II) carbonates (from herein referred to as Mn carbonates), which are bounded by Mn-deficient black shale in the upper Doushantuo Formation, and restricted to the rift basin periphery at the northern margin of the Yangtze Block. These Mn carbonates have not been observed in Ediacaran formations elsewhere in the world (Zhang et al., 2024), making them prime candidates for investigating unique Mn geochemical cycles and the broader paleo-oceanic environment. The accumulation of these Mn carbonates may also provide a new perspective on reconstructing the oceanic redox state in deep time. However, the paleo-oceanic redox conditions that prevailed during Ediacaran Mn carbonate mineralization remain controversial.

Due to the insufficient consideration of molybdenum (Mo) isotopic fractionation caused by Mn cycle and sulfide sequestration, underestimated Mo isotope data suggest that the extent of ocean oxygenation during the period of Mn mineralization was comparable to Mesozoic oceanic anoxic events (OAEs) (Tan et al., 2023). Based on this, a metallogenic model was proposed in which hydrothermal Mn(II) was directly incorporated into Mn carbonate minerals without Mn(II) oxidation in an anoxic setting (Gao et al., 2021). However, this model contradicts our previous findings of abnormally negative inorganic carbon isotopic compositions and residual Mn(IV) oxide phases (from herein referred to as Mn oxides), indicating that Mn oxides were served as the precursors to the Mn carbonates (Zhang et al., 2022, 2024). This discrepancy challenges the notion of an anoxic sedimentary environment proposed by Mo isotope data, as Mn(II) requires a high redox potential to oxidize (Wittkop et al., 2020). Whether the contemporaneous oceanic redox state could support Mn(II) oxidation remains unresolved.

Furthermore, previous research has also highlighted that both the black shales and Mn carbonates of the upper Doushantuo Formation were frequently influenced by hydrothermal fluids (Wang, Li, et al., 2020), which are believed to have introduced Mn(II) for Mn carbonate formation (Gao et al., 2021; Zhang et al., 2021). However, the reason for Mn enrichment in carbonate rocks but depletion in the closely associated black shales remains unclear. It is plausible that other external factors, such as paleo-redox conditions, may have played a crucial role in controlling Mn cycling and mineralization during this period. Further investigations are warranted to resolve these complexities.

In this study, we investigated the oceanic redox state during the deposition of the upper Doushantuo Formation and its implications for Mn cycling. Our approach integrated a suite of hydrochemical and redox-sensitive proxies alongside and mineralogical proxies such as pyrite morphology and size. By reconstructing shifts in paleoclimatic conditions during the deposition of black shales and Mn carbonates, we were able to elucidate the interconnections between the paleo-hydrological conditions, paleo-oceanic redox state, and Mn geochemical cycling. Our results offer valuable insights into the redox structure of the late Ediacaran ocean and offer a plausible explanation for the unique development of black shale-hosted Mn carbonate deposits at the northern margin of the Yangtze Block. Overall, this investigation, with more comprehensive methods and samples being used than prior works and new perspectives on ocean redox changes and critical metal mineralization, enhances our understanding of the ancient oceanic conditions and critical metal (e.g., Mn) cycling processes, contributing





Figure 1. Geological and paleogeographic maps of the Yangtze Block in the late Ediacaran. (a) Paleogeography of Earth at *ca.* 550 Ma (modified after Merdith et al., 2021). Af = Afghanistan; ANS = Arabian–Nubian Shield; Ant = Antarctica; Aus = Australia; DML–CLN = Dronning Maud Land–Coats Land; I = India; I-A = Indo-Antarctica; K = Kalahari; KMT = Krygyz Middle Tianshan; KNT = Krygyz North Tianshan; Lha = Lhasa; NC = North China; Qa = Qaidam; Qi = Qilian; SC = South China; SM = Sahara Metacraton; T = Tarim; WAC = West African Craton. (b) Summary of the timing of sequences and events in the Neoproterozoic era. GC/TSA/CA = Gucheng/Tiesiao/Changan formations; DTP = Datangpo Formation; NT = Nantuo Formation; DST = Doushantuo Formation; DY = Dengying Formation. (c) Paleogeographic map of the Yangtze Block during the Ediacaran (modified after Jiang et al., 2011). The blue rectangle shows the study area. (d) Stratigraphy of the Doushantuo Formation. The right-hand-side section shows Member IV of the Doushantuo Formation in the study area. The gray and solid red circles represent the sample locations of the black shales and Mn carbonates, respectively.

to a fuller understanding of Earth's evolving habitability. Moreover, this study contributed to the broader knowledge of Mn carbonate mineralization processes that may have occurred across other geological eras.

2. Geological Setting

The South China Plate was isolated at ~30°N during the Neoproterozoic (Figure 1a; Hoffman & Li, 2009) and amalgamated by the Yangtze and Cathaysia blocks at *ca*. 870 Ma (Figure 1b; Li et al., 2008). With the breakup of the Rodinian supercontinent at *ca*. 820 Ma (Figure 1b; Wang & Li, 2003), the Yangtze Block subsequently separated from the Cathaysia Block. The South China Plate was thus in an extensional tectonic environment until the end of the Neoproterozoic. Several extensional rift basins were formed at the periphery of the Yangtze Block (Jiang et al., 2011; Xiao et al., 2021, Figure 1c). The sedimentary record of multiple glacial–interglacial ages in the Neoproterozoic were preserved in these rift basins, including the Gucheng/Tiesiao/Changan formations (Sturtian glaciation; 720–663 Ma), the Datangpo Formation (interglacial; 663–654 Ma), the Nantuo Formation (Marinoan glaciation; 654–635 Ma), and the Doushantuo and Denying formations (post-glaciations; 635–551 and 551–541 Ma) (Figure 1b; Zhou et al., 2004; Jiang et al., 2011; Shields-Zhou et al., 2012). Following the Marinoan glaciation, continuous and complete Ediacaran sequences were deposited within these extensional basins, including the Doushantuo, Dengying (shallow-water facies), and Liuchapo (deep-water facies) formations (Jiang et al., 2011). Small bilaterian (Chen et al., 2013) and possible animal embryo fossils in the Doushantuo Formation (Cohen et al., 2009; Xiao et al., 1998) appear to record key stages in the evolution of the Earth's ecosystems leading up to the Cambrian explosion of life.

Paleogeographic reconstructions indicate that the Ediacaran strata of the Yangtze Block can be divided into four facies belts across the shelf-to-basin transects based on lithology: inner shelf (intertidal-shallow subtidal carbonate platform), intrashelf basin (deep subtidal carbonate and shale), outer shelf (peritidal shoal complex with erosional/exposure surface), and slope-basin (thick black shale with minor carbonate) (Figure 1c; Jiang et al., 2011). The Doushantuo Formation was mainly deposited in a marginal marine sedimentary environment (Vernhet, 2007), with lithologies ranging from carbonates in shallow water platform to fine siliciclastic rocks in deep water slope and basin (Jiang et al., 2011). The formation consists of four members (I–IV), spanning from bottom to top (Figure 1d).

Member I is a 3–7 m-thick cap carbonate that has been dated to 635.2 ± 0.6 Ma (Condon et al., 2005). It is separated from the underlying glacial diamictite of the Nantuo Formation by an unconformity. Member II (~80 m thick) is characterized by alternating organic-rich shales and dolostone beds with abundant pea-sized chert nodules (Xiao et al., 2010). Member III (~60 m thick) consists of massive and laminated cherty dolostones, interbedded with organic-rich black shales. Member IV (~10 m thick) has been dated to 551.1 ± 0.7 Ma (Condon et al., 2005) and mainly consists of organic-rich black shales, which in turn, are overlain by a thick layer of dolostones of the Dengying Formation. However, due to subsequent erosion, only the deep-water facies black shales with a few authigenic calcite nodules from Member IV are preserved (Cui et al., 2017, 2022). The black shales, overlain by thick dolostones of the Dengying Formation, serve as key marker beds for regional stratigraphic correlations within the Doushantuo Formation Member IV in South China. These shales are absent in more proximal shelf areas (i.e., the inner shelf and outer shelf), where the time-equivalent strata consist of carbonates or phosphorite-rich sequences (Jiang et al., 2011).

Our study area is located in the Chengkou region of Chongqing, South China. The samples were deposited in relatively deep slope/basin facies within a sub-rift basin controlled by syngenetic normal faults during extension along the northern margin of the Yangtze Block (Wang, Li, et al., 2020, Figure 1c). Of particular note are the laminated Mn carbonates, ranging from 0.35 to 2.80 m thicknesses, which are interbedded within black shales of the Member IV of the Doushantuo Formation in study area (Figure 1d), a feature not observed elsewhere in South China. The black shales, characterized by horizontal bedding, primarily consist of organic matter and fine-grained siliciclastic material that are cemented by diagenetic carbonate minerals (Zhang et al., 2024), indicative of a deep and low-energy marine setting. By contrast, the Mn carbonates are characterized by granular rhodochrosite (MnCO₃) cemented by kutnohorite ([Mn, Ca] [CO₃]₂) (Zhang et al., 2022, 2024). Additionally, these Mn carbonates contain abundant spherical biological structures, such as oolites and oncolites with graded bedding, and stromatolites, which suggest deposition in a shallow, high-energy marine environment (Zhang et al., 2022, 2024). The repetitive transitions between the shallow-water Mn carbonates and deep-water black shales indicate episodic variations in the sedimentary environment and hydrodynamic conditions during their deposition (Jiang et al., 2011).

3. Materials and Methods

A total of 35 fresh core samples were collected (XQ-1 to -35) at the town of Xiuqi, southeast of Chengkou County, northwestern Chongqing (Figure 1c). This includes 12 organic-rich black shales and 23 Mn-rich carbonate rocks. The samples were thoroughly washed with deionized water and dried to remove surficial contamination. All samples were divided into two fractions; one was used to make thin-sections for mineralogical investigations, while the other was powdered to 200 mesh for geochemical analysis.

Systematic mineralogical and geochemical analyses, including pyrite (FeS_2) morphology, major and trace elements, total organic carbon (TOC), total nitrogen (TN), and total sulfur (TS) contents, N isotopes, and Fe speciation, were conducted at the State Key Laboratory for Mineral Deposits Research, International Center for Isotope Effects Research, and MOE Key Laboratory of Surficial Geochemistry, Nanjing University, Nanjing, China. The extraction of pyrite for Fe speciation analysis was carried out at the State Key Laboratory of Paleobiology and Stratigraphy in the Nanjing Institute of Geology and Palaeontology.

Pyrite morphology. The morphology and size distribution of framboidal pyrite were investigated in thin-sections by optical microscopy (Nikon LHS2H100C21) under reflected light and by a field emission scanning electron microscope (FE-SEM; Zeiss-Supra55) equipped with an energy dispersive X-ray spectrometer (EDS) operated in secondary electron mode. The diameters of the framboidal pyrite were measured directly by the SEM. To obtain a statistically robust pyrite size distribution, more than 2,800 data were collected.



Major and trace elements. Major element analyses of whole-rock samples were conducted by X-ray fluorescence (XRF) spectrometry (Thermo Scientific ARL 9900), with an operating voltage of 15 kV and beam current of 70 mA. The major element data and details of the analytical procedures were presented in Zhang et al. (2022). The chemical index of alteration (CIA) value calculated through major elements (aluminum, Al; calcium, Ca, phosphorous, P; sodium, Na; and potassium, K) follows the equation as: CIA = $[Al_2O_3/(Al_2O_3 + CaO^* + Na_2O + K_2O_{corr})] \times 100$, where all the oxides are in molar units, and CaO* is only the CaO in the silicate fraction (Fedo et al., 1995) and not CaO in apatite and carbonate. The correction procedure for CaO* is as follows: (a) CaO is first corrected for that residing in apatite using P_2O_5 (CaO' = CaO - $10/3 \times P_2O_5$); (b) if CaO' is greater than Na₂O, the final CaO* value is set to be equal to Na₂O, but if CaO' is less than Na₂O, the final CaO* value is set to be equal to CaO' (McLennan, 1993).

Whole-rock trace element data were obtained by Zhang et al. (2021). The enrichment factor (EF) of a trace element (X) is defined as $X_{EF} = [X/AI]_{sample}/[X/AI]_{UCC}$, and an authigenic trance element (X) content is defined as $X = [X]_{sample} - [X]_{UCC}/[AI]_{UCC} \times [AI]_{sample}$ (Zhou et al., 2012). The standard used for normalization in this study is average upper continental crust (UCC; Taylor & McLennan, 1985). The samples were reacted with 10% HCl for at least 48 hr to completely remove the carbonate component. The treated solutions were centrifuged at 3,000 rev/min for 10 min, and the solid residue was retained and washed with deionized water until the pH of the solution approached neutrality. The carbonate-free residues were re-ground to fine powders, which were then digested in hydrofluoric acid (HF) and nitric acid (HNO₃) in high-pressure Teflon bombs prior to analysis (Zhang et al., 2021). The major and minor element contents of the decarbonated samples were determined by inductively coupled plasma optical emission spectrometry (ICP-OES; Thermo ICP 6300) with a precision of ±0.5% (ISD) and Thermo Scientific ELEMENT XR inductively coupled plasma mass spectrometer (ICP–MS) with a precision better than ±5% (ISD), respectively.

TOC, TN, and TS contents. The TOC, TN, and TS contents were determined using a Vario MACRO elemental analyzer (ECS 4024 CHNSO; Costech, Italy). Approximately 30 mg of carbonate-free samples were wrapped in tin foil for elemental analysis. The laboratory standard material sulfadiazine (S8626-25G; TOC = 47.99 wt.%, TN = 22.37 wt.%, and TS = 12.81 wt.%) was analyzed after every eight samples to monitor the data quality; the analytical precision was better than ± 0.1 wt.% (1SD). The whole-rock TOC, TN, and TS contents were corrected to take into the account the mass fraction of carbonate in each sample. Detailed analytical procedures were presented in Zhang et al. (2021).

Nitrogen and organic C isotopes. Decarbonated homogeneous powders (1–50 mg) were loaded into capsules and flash combusted at 960°C in a Thermo Fisher Elemental Analyzer coupled to a Thermo EA-Isolink-Delta V Plus stable isotope ratio mass spectrometer (IRMS) via a Thermo Conflo III Interface. Nitrogen isotope (δ^{15} N) data are reported as δ values relative to atmospheric N₂ (0% $_{\circ}$). The international reference standard (acetanilide; δ^{15} N = -5.07% $_{\circ}$, TN = 10.36 wt.%) was used to monitor the analytical uncertainties, and the precisions of the δ^{15} N values were better than ±0.3% $_{\circ}$ (1SD). Organic C isotopic compositions ($\delta^{13}C_{org}$) were determined using a Flash 2000 HT Elemental Analyzer (EA) coupled to a ConFlo IV-Thermo MAT 253 stable isotope ratio mass spectrometer (IRMS). The working standard (L-glutamic acid; USGS40) with $\delta^{13}C_{org} = -26.39%_{\circ}$ (relative to VPDB) was used for calibration during the analyses. The precision was better than ±0.2% $_{\circ}$ (1SD). See Zhang et al. (2022) for detailed descriptions of these analytical protocols.

Iron speciation. The total Fe (Fe_T) contents were measured by XRF spectrometry. Fe_{HR} refers to the Fe-bearing minerals that are considered to be highly reactive during biological or abiological reduction under anoxic conditions (Canfield et al., 1992; Poulton et al., 2004), including Fe sulfide (Fe_{py}) such as mackinawite and pyrite; Fe in carbonate (Fe_{carb}) such as ankerite and siderite; Fe oxides (Fe_{ox}) such as goethite and hematite, and Fe in magnetite (Fe_{mag}) (Poulton & Canfield, 2005). The pyrite contents were determined stoichiometrically by weight from the precipitated Ag₂S after chromium chloride reduction. Powders (1–6 g) were prepared for pyrite extraction using the Cr reduction method (Canfield et al., 1986). Pyrite extraction was performed under N₂ gas by the addition of 12 M HCl and 1 M reduced chromium chloride. The reaction was allowed to proceed for at least 2 hr, with the sulfide collected as Ag₂S. The Ag₂S was generated from the H₂S produced by pyrite reduction in a AgNO₃ (3%; v/v) trap.

Other Fe species, including Fe_{carb} , Fe_{ox} , and Fe_{mag} , were extracted sequentially as per the protocol of Poulton and Canfield (2005) using 1 M sodium acetate (Fe_{carb}), 0.3 M dithionite and 0.2 M sodium citrate (Fe_{ox}), and 0.2 M





Figure 2. Morphology and size distribution of pyrite framboids in the Doushantuo Formation Member IV, South China. (a) Pyrite framboids in black shale (reflected light; XQ-34). (b) Pyrite framboids in Mn carbonate (reflected light; XQ-13). (c)–(d) Microscopic characteristics of pyrite framboids in black shale and Mn carbonate (SEM images in secondary electron mode; XQ-31 and -6, respectively). (e) Size distribution of the pyrite framboids.

ammonium oxalate and 0.17 M oxalic acid (Fe_{mag}). The sequential extracts were analyzed using ICP–OES (Thermo ICP 6300) with a precision of $\pm 0.5\%$ (1SD).

4. Results

4.1. Pyrite Morphology

Pyrite within the black shales and Mn carbonates of the Doushantuo Formation Member IV are predominantly framboidal in morphology (Figures 2a–2d), often surrounded by clay minerals and laminated organic matter in the black shales (Figure 2c). Using SEM, we measured the sizes of 2,837 pyrite framboids. These framboids have small diameters, ranging from 3 to 7 μ m, with the average size of 5.17 ± 2.38 μ m. Additionally, 96.72% of the pyrite framboids have diameters <10 μ m (Figure 2e).



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4.2. Geochemistry

The geochemical data are provided in Figure 3 and Table S1 in Zhang and Cao (2024). The Mn contents of the black shales range from 0.16 to 3.46 wt.% (with average of 0.79 wt.%), significantly lower than those of the Mn carbonates, where it ranges from 5.06 to 36.77 wt.% (with average of 20.79 wt.%). Conversely, the Fe content is higher in the black shales, ranging from 2.87 to 5.66 wt.% (with average of 4.26 wt.%) compared to the Mn carbonates, which range from 0.41 to 6.17 wt.% (with average of 1.85 wt.%).

Key redox-sensitive indicators, such as Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} , also differ between the two lithologies. The Fe_{HR}/Fe_T ratio varies from 0.80 to 0.96 (with an average of 0.92) in the black shales, compared to 0.18 to 0.98 (with an average of 0.69) in the Mn carbonates. Similarly, the Fe_{py}/Fe_{HR} ratio ranges from 0.79 to 0.96 (with an average of 0.93) for the black shales and 0.11 to 0.95 (with an average of 0.79) for the Mn carbonates.

Notably, the $\delta^{15}N$ and $\delta^{13}C_{org}$ values are similar between the black shales and Mn carbonates, with $\delta^{15}N$ values averaging +4.20% and +4.14%, and $\delta^{13}C_{org}$ values averaging -31.51% and -31.29%, respectively.







Other geochemical indicators further highlight contrasts between the two facies. The Mo/TOC ratios range from 2.42 to 7.75 ppm/wt.% (average of 4.57 ppm/wt.%) for the black shales and 3.86 to 118.79 ppm/wt.% (average of 21.48 ppm/wt.%) for the Mn carbonate residue after acid dissolution. The Mo_{EF} and uranium (U)_{EF} range from 7.32 to 50.37 (averaging 21.99) and 1.62 to 26.26 (averaging 9.15) for the black shales, and from 4.87 to 577.00 (averaging 82.56) and 0.87 to 9.50 (averaging 2.96) for the Mn carbonate residues. The strontium (Sr)/barium (Ba) ratios range from 0.03 to 0.26 (average of 0.11) for the black shales and from 0.08 to 0.75 (average of 0.27) for the Mn carbonates. The TS/TOC ratios range from 0.29 to 2.74 (averaging 1.25) for the black shales and 0.64 to 15.42 (averaging 3.01) for the Mn carbonates. The authigenic copper (Cu_{auth}) concentrations range from 26.11 to 333.62 ppm (with an average of 180.03 ppm) in the black shales and from 5.65 to 188.30 ppm (with an average of 49.11 ppm) in the Mn carbonates. The CIA values range from 56.89 to 64.53 (with the average of 58.69) for the black shales and 37.39 to 65.18 (with the average of 54.64) for the Mn carbonates.

5. Discussion

5.1. Hydrological Conditions

5.1.1. Variations of Sedimentary Water Source in Marginal Rift Basin

Paleomagnetic data indicate that after the breakup of Rodinia, the South China Plate became isolated from other paleo-continents and was surrounded by open oceans (Figure 1a; Zhang et al., 2015; Sahoo et al., 2016). Consequently, both freshwater from land and bulk seawater jointly influenced the hydrochemistry in the sub-rift basin along the north margin of Yangtze Block of this study (Cheng et al., 2021; Dávila et al., 2002). Increased exchange between the water in continental margin rift basin and the open ocean amplified the effects of seawater on sediment, reflecting in stronger marine geochemical signals, such as elevated Mo concentration (Cheng et al., 2021).

A previous study proposed that there was an intermittent and fluctuating hydrography in the study area during the deposition of the Doushantuo Formation Member IV (Tan et al., 2023). Nevertheless, whether there were significant hydrographic differences between distinct lithologic sedimentary periods remains unclear. The Mo/TOC ratio for fine-grained siliciclastic sediment is considered a robust proxy for evaluating the degree of seawater influence on shelf margin basins. Sediments in modern sedimentary basins with variable degrees of connectivity to the open ocean, such as the Black Sea and Saanich Inlet, exhibit different Mo/TOC ratios because the abundance of Mo in seawater is higher than that in freshwater (Figure 4a; Algeo et al., 2007). Thus, increasing seawater input into a rift basin typically results in higher Mo/TOC values (Algeo & Lyons, 2006; Cheng et al., 2016).

To mitigate the influence of carbonate components on Mo/TOC ratios, we measured Mo and TOC concentrations from decarbonated Mn carbonate powders. The results show that Mo/TOC ratios of the black shales are significantly lower than those of decarbonated Mn carbonates; this indicates that the sedimentary waters from which the Mn carbonates precipitated were significantly influenced by seawater compared to those during black shales deposition (Figure 4a).

Similarly, the relative enrichment of Mo to U is an effective indicator of seawater input in a shelf margin basin. In well connected, sulfidic basins, Mo is preferentially enriched over U, and $M_{o_{EF}}/U_{EF}$ ratios increase from 0.1 to 0.3 seawater ratio (SW) to 1–3 SW, due to the replenishment of seawater Mo (Algeo & Tribovillard, 2009). Conversely, in sulfidic basins with limited marine Mo input, the $M_{o_{EF}}/U_{EF}$ values remain lower than the normal ~1SW (Tribovillard et al., 2012). The $M_{o_{EF}}$ values of the black shales are consistently low, showing minimal variation, and the distribution pattern of these black shales follows the $M_{o_{EF}}$ – U_{EF} variation trend characteristic of a highly restricted basin (Figure 4b). By contrast, the decarbonated Mn carbonate samples are distributed in the area associated with the particulate shuttle process, where Mn oxides transfer Mo from shallow, oxic waters to deeper, anoxic waters. These Mn carbonate samples exhibit higher $M_{o_{EF}}$ than the black shales, indicating a weakly restricted or unrestricted sedimentary setting with relatively good connectivity to the open ocean (Figure 4b). Collectively, these observations indicate fluctuating hydrological conditions across different lithologies in the upper Doushantuo Formation, with varying degrees of open marine influence.

5.1.2. Paleo-Salinity Variations

Paleo-salinity serves as an indirect indicator of the source of water in continental marginal basins like in this study, reflecting the salinity differences between terrestrial runoff and seawater. Proxies such as sedimentary Sr/Ba (Zhang et al., 2017) and TS/TOC ratios (Berner & Raiswell, 1984; Hieshima & Pratt, 1991) are commonly used to reconstruct paleo-salinity conditions. This is because the Sr concentration in seawater is much higher than that in freshwater, while the Ba concentration in seawater are 10–1,000 times higher than in freshwater (Wei & Algeo, 2020). Additionally, sulfate (SO₄²⁻) concentrations in seawater are 10–1,000 times higher than in freshwater (Wei & Algeo, 2020). Therefore, higher salinity levels are typically associated with elevated Sr/Ba and TS/TOC ratios (Wei & Algeo, 2020). However, one challenge is that Sr can substitute for Ca in carbonate minerals due to their similar ionic radii, potentially leading to artificially high Sr/Ba ratios in carbonate-rich sediments (Vahrenkamp & Swart, 1990). To account for this effect, we compared Sr concentrations and carbonate abundances. The results showed that there was no significant correlation between these two parameters ($R^2 = 0.07$; Figure 5a); this indicates that the carbonate fraction did not cause anomalous Sr enrichment, validating the use of Sr/Ba ratios in our paleo-salinity analysis.

The Sr/Ba and TS/TOC ratios of the black shales are significantly lower than those of the Mn carbonates (p < 0.05; Figures 5b–5d), implying that the water salinity fluctuated during the deposition of the Doushantuo Formation Member IV. This variation indicates a lower salinity for the black shales and higher salinity for the Mn carbonates. These changes in salinity align with the relative effects of the open seawater and freshwater inputs (see above). Specifically, the higher salinity associated with the Mn carbonates points to increased seawater influence, whereas the lower salinity in the black shales reflects a stronger influence of terrestrial runoff and limited marine input.

5.1.3. Variable Chemical Index of Alteration

The CIA reflects the chemical weathering intensity of sediments from continental sources (Wang, Du, et al., 2020). Higher temperatures and precipitation levels increase chemical weathering, leaching away more mobile elements such as Ca and Na, while the more resistant element (e.g., Al) is retained within terrigenous detrital material. As a result, higher CIA values normally correspond to warmer and more humid climatic conditions (Retallack et al., 2004; Von Blanckenburg et al., 2015). Notably, K-metasomatism, the process where pore water interacts with kaolinite to form secondary illite, increases K contents in sediments and can distort CIA values. To account for this, the weathering trend in the A–CN–K (Al₂O₃–CaO^{*} + Na₂O–K₂O) diagram should intersect the A–CN axis (Figure 6a; Fedo et al., 1995), and a correction of K content is necessary before the CIA calculations. The correction is applied using the formula: $K_2O_{corr} = [m \times Al_2O_3 + m \times (CaO^* + Na_2O)]/(1 - m)$, where $m = K_2O/(Al_2O_3 + CaO^* + Na_2O + K_2O)$ (Panahi et al., 2000). Our samples from the Doushantuo Formation Member IV in South China showed evidence of K-metasomatism (Figure 6a), necessitating K



Figure 5. Paleo-salinity proxy data for the Doushantuo Formation Member IV, South China. (a) Plot of carbonate abundance versus Sr concentrations. (b) Box-and-whisker plots of Sr/Ba ratios. (c) Box-and-whisker plots of Sr/Ba ratios (data were taken from Gao et al., 2021). (d) Box-and-whisker plots of S/TOC ratios. The single sample *t*-test were performed for all statistical differences.

correction. To eliminate the effects of carbonate, the samples were treated with diluted acid to remove the carbonate content. A strong positive correlation between $\text{CIA}_{\text{whole-rock}}$ and $\text{CIA}_{\text{decarbonated}}$ values ($R^2 = 0.92$, p < 0.01; Figure 6b) confirms that the carbonate fraction had minimal effect on the CIA values. Thus, the CIA values calculated from terrigenous detrital components, including those in carbonate rocks, effectively record paleoclimate conditions and can be compared directly with those from black shales.



Figure 6. CIA values of the Doushantuo Formation Member IV, South China. (a) A-CN-K (Al_2O_3 -CaO* + Na_2O - K_2O) ternary diagram. The solid black arrow parallel to the A-CN axis represents the ideal weathering trend without K-metasomatism. (b) Plot of corrected whole-rock CIA values (CIA_{whole-rock}) versus corrected CIA values of decarbonated samples (CIA_{decarbonated}). (c) Box-and-whisker plot of corrected CIA values for the Mn carbonates and black shales. The single sample *t*-test were performed for the statistical difference.

The CIA values of the Mn carbonates span a wider range but with a lower average value than that of the black shales (p < 0.05; Figure 6c). This indicates that the sediments forming the black shales experienced a higher degree of chemical weathering, indicative of a warmer and more humid paleoclimate during that period. Contrastingly, the paleoclimate during deposition of the Mn carbonates was relatively cold and arid. The wider range of CIA values for the Mn carbonates also points to frequent fluctuations in paleoclimate during that period. These findings highlight a strong relationship between hydrological and hydrochemical conditions and paleoclimate. During the warmer and more humid period associated with the deposition of the black shales, a higher influx of freshwater led to lower water salinity. Conversely, during the colder and drier period that characterized Mn carbonate deposition, freshwater influx diminished, resulting in an increase in water salinity. This relationship suggests that paleoclimate changes had a direct influence on the sedimentary environment and water chemistry during the deposition of the Doushantuo Formation Member IV of this study.

In theory, the black shales were deposited in a deeper and lower energy setting than the Mn carbonates (Jiang et al., 2011). The fluctuating hydrological conditions suggest that the increase in water depth during black shale deposition was more likely due to an influx of freshwater rather than high-salinity seawater. Increased precipitation during warmer and more humid periods would lead to more terrestrial runoff, contributing freshwater to the basin. However, such precipitation alone cannot account for the significant facies shift from shallow-water carbonates to deeper-water black shales. Temporally, the Doushantuo Formation of this study corresponded to the Great Late Ediacaran Ice Age, a diachronous but continuously glaciation event from ca. >580 to <560 Ma, as continents migrated through polar and temperate latitudes (Wang, Shen, et al., 2023, Wang, Yin, et al., 2023). The relatively warmer conditions during black shale deposition would have favored the melting of ice sheets in mid-to-high latitudes, which, in turn, would have introduced a large volume of freshwater ratio the oceans. This influx of glacial meltwater would have contributed to a rise in sea level and a decrease in seawater salinity, creating the deeper-water condition necessary for black shale deposition. On the other hand, during relatively colder and more arid periods, Mn carbonates were deposited in shallow water. We thus proposed that the variations of the sedimentary environment (i.e., water depth and salinity) were in response to the change of paleoclimate during the Great Late Ediacaran Glaciation.

5.1.4. Fluctuating Primary Productivity

Paleoclimatic variations not only drive changes in hydrochemical conditions, but they impact the nutrient availability for coastal marine plankton (Sánchez-Baracaldo et al., 2017). As discussed above, the flux of terrestrial runoff into the continental margin rift basin varied significantly during the deposition of the black shales and Mn carbonates. Given that terrestrial runoff transports weathered materials, which contain essential nutrients for biological metabolism (Kang et al., 2023), fluctuations in runoff could directly impact primary productivity in these environments. In the relatively S-depleted Neoproterozoic ocean (Halverson & Hurtgen, 2007; Loyd et al., 2012), SO₄²⁻ derived primarily from continental weathering (Crockford et al., 2016), which is supported by the strong positive correlation observed between Al and TS contents for our samples ($R^2 = 0.80$, p < 0.01; Figure 7a). Hence, S abundance in Neoproterozoic ocean were closely tied to terrestrial weathering fluxes. Combined with above CIA values, our TS contents of the black shales are significantly higher than in the Mn carbonates (p < 0.05; Figure 7b). This suggests that variations in terrestrial weathering and the influx of weathered materials delivered by freshwater likely affected the availability of nutrients, potentially driving changes in primary productivity. In this case, the higher S content in the black shales reflects an enhanced influx of weathering products during periods of increased freshwater input, likely tied to warmer and more humid paleoclimatic conditions.

To verify whether variations in terrestrial weathering flux influenced primary productivity during the deposition of the black shales and Mn carbonates, we further compared the primary productivity levels between the two different sedimentary periods. Copper is mainly bound to organic ligands in oxygenated surface waters, and sinks with organic matter to the sediments. The Cu_{auth} is a reliable proxy for reconstructing paleo-productivity (Piper & Perkins, 2004; Tribovillard et al., 2006). Our data shows a strong positive correlation between Cu_{auth} and TOC ($R^2 = 0.62, p < 0.01$; Figure 7c), suggesting that primary productivity played a primary role in preservation of the sediment organic matter (Tribovillard et al., 2006). Furthermore, the Cu_{auth} concentrations in the black shales are significantly higher than those of the Mn carbonates (p < 0.05; Figure 7d), indicating the primary productivity was higher during the deposition of the black shales compared to the Mn carbonates. These findings support the idea that terrestrial weathering fluxes, which supplied essential nutrients via freshwater input, regulated primary



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Figure 7. Primary productivity proxy data for the Doushantuo Formation Member IV, South China. (a) Plot of Al versus TS. (b) Box-and-whisker plot of TS for the Mn carbonates and black shales. (c) Plot of TOC versus Cu _{auth}. (d) Box-and-whisker plot of Cu _{auth} for the Mn carbonates and black shales. The single sample *t*-test were performed for the statistical difference.

productivity. Hence, during periods of increased weathering, such as the warmer and more humid conditions associated with the black shale deposition, higher nutrient availability likely enhanced primary productivity. Conversely, the colder and more arid conditions during the deposition of the Mn carbonates, with reduced weathering fluxes, resulted in relatively lower primary productivity.

Our results indicate that the relatively warm and humid paleoclimate during deposition of the black shales increased the freshwater flux from terrestrial runoff and glacial meltwater in polar-temperate latitudes. This influx led to reduced salinity and greater water depth. Moreover, increased chemical weathering on land released more nutrients, enhancing primary productivity, which in turn generated large amounts of organic matter preserved in deep-water environments, resulting in organic-rich black shales. In contrast, during colder and more arid periods, decreased freshwater and glacial meltwater fluxes lowered water depth, particularly during the deposition of Mn carbonates. Under these conditions, hydrochemistry was mainly controlled by high-salinity seawater. At the same time, limited supply of nutrients sourced from chemical weathering resulted in low primary productivity, and as a consequence, Mn carbonates were deposited in shallow-water settings with low TOC contents.

5.2. Reconstruction of Fluctuating Redox Configuration

5.2.1. Surface Redox Conditions

The N isotopic proxy is a powerful tool for tracing past surface redox condition (Stüeken et al., 2016). Nitrogen, an essential element for life, is closely linked to environmental redox conditions and biological metabolism, as reflected in the sediment δ^{15} N values (Kang et al., 2023). Nitrogen fixation is the primary source of N in marine ecosystems, while biological assimilation and reduction of nitrate (NO₃⁻) (e.g., denitrification and anammox) act

as major N sinks (Kang et al., 2023). The bioavailability of N species (NO₃⁻ or ammonium, NH₄⁺) and their cycling pathways are controlled by aqueous redox conditions, leading to different degrees of N isotopic fractionation (Stüeken et al., 2016). As a result, δ^{15} N values in sediments can be used to reconstruct the redox state over geological timescales. Importantly, biological N cycling occurs within the photic zone (Canfield et al., 2010; Wang, Jiang, et al., 2018), meaning that δ^{15} N values primarily reflect the redox conditions and N cycling in the surface waters that exchange with atmospheric N₂ (Falkowski, 1997). However, post-depositional processes, including diagenesis and metamorphism, can alter the original δ^{15} N values of sediments, typically by preferentially releasing ¹⁵N-depleted N₂ or NH₃, which may lead to N loss and heavier δ^{15} N values in the sediments (Ader et al., 2014; Stüeken et al., 2016). Therefore, only unmodified primary δ^{15} N values can be used as a reliable proxy for reconstructing past redox condition in the surface ocean (Stüeken et al., 2016). Additionally, covariations between δ^{15} N values, TOC and TN contents are often observed in sediments that have undergone post-depositional alteration (Kikumoto et al., 2014).

In this study, there is a strong positive correlation between TOC and TN contents ($R^2 = 0.80$, p < 0.01), with an intercept close to zero (Figure 8a), indicating that N was mainly derived from biological N fixation rather than external inorganic and clay-bound N sources (Wang, Jiang, et al., 2018). During diagenesis and organic matter maturation, N is generally lost prior to organic C (Chang et al., 2022). Under such conditions, higher (C/N)_{mol} ratios (i.e., greater than the Redfield ratio of 6.6 for planktonic biomass; Redfield, 1934) along with a positive correlation between TOC and (C/N)_{mol} for the sediments are expected. The studied samples exhibit (C/N)_{mol} ratios >6.6, and there is a strong positive correlation between TOC and (C/N)_{mol} values for the black shales ($R^2 = 0.76$, p < 0.01; Figure 8b), suggesting partial N loss from the sediments after deposition. The samples with (C/N)_{mol} < 6.6 are mostly from Mn carbonates, which are poor in organic C (Figure 8b). This may be due to Mn (IV) reduction, wherein anaerobic heterotrophic bacteria oxidize organic carbon and transfer the electrons to Mn (IV), reducing it to dissolved Mn(II) (Zhang et al., 2022).

Sediments also preferentially release ¹²C and ¹⁴N during metamorphism, leading to a positive correlation between $\delta^{13}C_{org}$ and $\delta^{15}N$ values (Pinti et al., 2009). However, no significant positive correlation between $\delta^{13}C_{org}$ and $\delta^{15}N$ values was observed in our samples (Figure 8c), suggesting that metamorphic effects on $\delta^{15}N$ values were negligible. This demonstrates that diagenesis, rather than metamorphism, was predominantly responsible for post-depositional N loss. Similarly, no significant correlations were found between TOC and $\delta^{15}N$, TN and $\delta^{15}N$, or $(C/N)_{mol}$ and $\delta^{15}N$ (Figures 8d–8f). These results imply that while some N loss occurred during diagenesis, it did not significantly modify the $\delta^{15}N$ values of the sediments (Wang, Jiang, et al., 2018). Thus, the $\delta^{15}N$ values in these samples likely represent the primary N isotopic composition inherited from the surface waters.

In strongly stratified oceans with shallow redox interface (e.g., the Black Sea) and ancient anoxic oceans (e.g., during OAEs in the Phanerozoic), N exists mainly as NH_4^+ , while NO_3^- concentrations are extremely low. In these environments, near-quantitative denitrification completely consumes the limited NO_3^- in seawater near the chemocline, resulting in no net isotopic fractionation. Nitrogen fixed by diazotrophs is directly assimilated by organisms and preserved in sediments, which record light $\delta^{15}N$ values, typically ranging from -2% to +1% (Fulton et al., 2012). By contrast, well-oxygenated oceans, such as the modern ocean, maintain a large, stable NO_3^- reservoir produced through near-quantitative nitrification of biologically fixed N, with no net isotopic fractionation (Wang, Jiang, et al., 2018). Under these conditions, non-quantitative denitrification ($\varepsilon = -25\%$) releases ¹⁵N-depleted N₂ ($\delta^{15}N = -20\%$) to the atmosphere, leaving behind residual ¹⁵N-enriched NO_3^- ($\delta^{15}N = +5\%$), which is assimilated by organisms and then incorporated into sediments. As a result, sediments deposited in modern oxygenated oceans are characterized by heavy $\delta^{15}N$ values, ranging from +5% to +6.7% (Tesdal et al., 2013).

The δ^{15} N values of the black shales are comparable to those of the Mn carbonates in the Doushantuo Formation Member IV (Figure 3), indicating that the lithology was not the primary control on the sediment N isotope variations. This also implies that there were no significant differences in redox potential and N cycling pathways in surface waters during deposition of these two different lithologies. The δ^{15} N values are significantly higher than those typically found in sediments deposited in an anoxic ocean (~0%) and comparable to, but slightly lower than, the values observed in modern ocean sediments (+5% to +6.7%). This indicates that the surface waters were oxygenated, though potentially at lower levels than in the modern ocean. During the Ediacaran Period, atmospheric O₂ concentrations persistently increased, with the partial pressure of O₂ (*p*O₂) reaching 60%–100% of the present atmospheric level (PAL) at the end of the Ediacaran (Ding et al., 2019). The gradual increase in





Figure 8. The evaluation indexes of the validity of N isotopic proxy for the Doushantuo Formation Member IV, South China. (a) TOC versus TN, (b) TOC versus $(C/N)_{mol}$, (c) $\delta^{13}C_{org}$ versus $\delta^{15}N$, (d) TOC versus $\delta^{15}N$, (e) TN versus $\delta^{15}N$, and (f) (C/N)_{mol} versus $\delta^{15}N$.

 δ^{15} N values up-section, along with several transient fluctuations in the middle of the studied section (Figure 9), indicate that oxygenation of surface waters gradually increased in parallel with the rise in atmospheric pO_2 .

A compilation of N isotope data for Member IV of the Doushantuo Formation (or the equivalent Lantian Formation) across different geographical locations and sedimentary facies within the Yangtze Block reveals that all the sediments exhibit higher δ^{15} N values than those from anoxic oceans but slightly lower than those from modern, well-oxygenated oceans (Figure 9). This indicates that, by the end of Doushantuo Formation deposition, the surface ocean around the South China Plate was widely oxygenated. This widespread oxygenation likely reflects a global trend in the surface ocean during the Ediacaran Period (Sahoo et al., 2012, 2016; Wang, Jiang, et al., 2018).



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Figure 9. Nitrogen isotope chemostratigraphy of the Doushantuo Formation Member IV for different facies in South China. Data sources: 1 = Yangtze Gorge (Kikumoto et al., 2014); 2 = Yangjiaping (Ader et al., 2014); 3 = Chengkou (this study); 4 = zk2012 (Chen et al., 2019); 5 = Lantian (Wang et al., 2017). DST = Doushantuo Formation; LT = Lantian Formation; DY = Dengying Formation; LCP = Liuchapo Formation. Blue solid circles refer to the data from previous literature. Red and gray solid circles refer to data of Mn carbonates and black shales in this study, respectively. Blue and red dash lines refer to the value of 0% and +5%, respectively.

Regionally, however, δ^{15} N values in our section (Section 3 in Figure 9) are slightly higher than those in the sections from the intrashelf and outer shelf settings (Sections 1 and 2 in Figure 9) but more comparable to the sections from slope and basin settings (Sections 4 and 5 in Figure 9). This pattern suggests that, despite wide-spread oxygenation of the surface ocean, there was still a small spatial N isotopic gradient, with heavier N isotopes in more distal facies (Chen et al., 2019). This could be due to the residence time of N in seawater being similar to the mixing time of the ocean, around ~2 kyr (Brandes & Devol, 2002), which may cause localized heterogeneity in NO₃⁻ reservoirs, especially in more stagnant intrashelf basins. The N isotopic chemostratigraphy, along with lithological evidence from black shales and carbonates (Jiang et al., 2011), collectively suggest that our section was more likely located in a slope facies of a continental marginal sub-rift basin, rather than an isolated intrashelf basin setting. This interpretation is further supported by sedimentary structures, such as slump folds in thin-bedded carbonates (Wang, Li, et al., 2020). The alternating deposition of black shales in deeper water and Mn carbonates in shallower water reflects sea-level fluctuations along the slope, although the magnitude of these changes is difficult to quantify. The hydrochemistry and water depth in this setting were influenced by a combination of terrestrial freshwater input, glacial meltwater, and seawater, creating variable hydrological conditions.

5.2.2. Bottom-Water Redox Conditions

Nitrogen isotope data indicate that the redox state of surface waters during the deposition of the Doushantuo Formation Member IV in South China was similar to that of the modern well-oxygenated ocean (see discussion in Section 5.2.1 above). However, the redox state of the deep waters during this period is still controversial (Sperling et al., 2015). It has been suggested that oxygen minimum zones (OMZs) occur at the shelf margin in the modern well-oxygenated ocean (Figure 1 in Ader et al., 2014). However, more robust evidence is required to confirm whether similar OMZs existed at the continental margins of the Ediacaran oceans.

Authigenic pyrite, which precipitate during the syngenesis (in euxinic water) or diagenesis (in sediments), generally forms through the reaction of dissolved sulfide (H₂S) produced by bacterial sulfate reduction (BSR)





Figure 10. Size parameters of pyrite framboids in the Doushantuo Formation Member IV, South China. Plots of pyrite mean diameter versus (a) standard deviation of pyrite diameter and (b) skewness of pyrite diameter. The pyritic data of Tan et al. (2023) are from same area with this study.

with Fe(II) generated from bacterial Fe(III) reduction under anoxic and sulfidic conditions (Konhauser, 2007). The mineralogical differences between syngenetic and diagenetic pyrite can help distinguish their formation processes. Syngenetic pyrite, precipitated in euxinic waters, is characterized by small framboids with a mean diameter of $5.0 \pm 1.7 \mu m$, and a fraction of larger framboids (>10 µm) accounting for <4% (Wilkin et al., 1996). These framboids are relatively uniform in size because of the short crystallization intervals (on the scale of days) and rapid sedimentation following crystallization (Rickard, 2019). In contrast, diagenetic pyrite, which form during a longer crystallization interval within sediments, is larger, with a mean diameter of $7.7 \pm 4.1 \mu m$, and 10%-50% of the grains exceeding 10 µm (Wilkin et al., 1996). Diagenetic pyrite also exhibits greater size variability, and the larger grains are often euhedral in shape (Cui et al., 2018).

Most of the studied pyrites are framboidal (Figures 2a-2d), with diameters ranging from 3 to 7 µm. The proportion of pyrite framboids with diameters smaller than 10 µm reaches 96.72% (Figure 2e), indicating that the pyrite in Member IV formed in anoxic-euxinic waters during the syngenetic stage. Additionally, the size parameters of framboidal pyrite show that most samples fall within the euxinic area (Figure 10). These observations collectively suggest that local anoxic to euxinic bottom waters existed beneath the oxygenated surface waters in slope setting along the northern margin of the Yangtze Block during deposition of the upper Doushantuo Formation.

Iron speciation is also a reliable proxy for the redox state of bottom waters, particularly when the Fe_T/Al ratio exceeds the average crustal value of 0.5 (Poulton & Canfield, 2011; Sahoo et al., 2012). The Fe_{HR}/Fe_T ratio increases with decreasing dissolved O_2 concentrations (Anderson & Raiswell, 2004; Severmann et al., 2008), since anoxic environments promote Fe_{HR} enrichment. Specifically, $Fe_{HR}/Fe_T < 0.22$ indicate oxic conditions, while $Fe_{HR}/Fe_T > 0.38$ suggest anoxic bottom waters (Poulton & Canfield, 2011; Poulton & Raiswell, 2002). Under anoxic conditions (i.e., $Fe_{HR}/Fe_T > 0.38$) with high H_2S concentrations, highly reactive Fe precipitates as Fe sulfide, such as pyrite. The Fe_{py}/Fe_{HR} ratio further distinguished anoxic settings, with values > 0.7–0.8 indicating euxinic (sulfidic) conditions and values below this threshold representing ferruginous (non-sulfidic) conditions (Lyons & Severmann, 2006; Poulton, 2021; Poulton & Canfield, 2011).

The Fe_T/Al values in our samples are consistently >0.5 (Figure 11a), and the majority of the samples have high Fe_{HR}/Fe_T values (>0.38), except for some Mn carbonates, which have values <0.38 (Figure 11b). This indicates that the bottom waters during deposition of the Doushantuo Formation Member IV were predominantly anoxic, but experienced intermittent oxidation events during the deposition of the Mn carbonates. For samples with Fe_{HR}/Fe_T > 0.38, most Fe_{py}/Fe_{HR} values are >0.7 (Figure 11c), indicative of euxinic bottom waters. Notably, the Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} values of the black shales are relatively uniform and significantly higher than those of the Mn carbonates (average of 0.92 vs. 0.69 and 0.93 vs. 0.79, respectively, p < 0.05; Figures 11b and 11c). Contrastingly, the Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} values of the Mn carbonates display a broader range (Figures 11b and 11c).





Figure 11. Iron speciation in different lithologies of the Doushantuo Formation Member IV, South China. (a) Box-and-whisker plots of Fe_T/Al. (b) Box-and-whisker plots of Fe_{HR}/Fe_T. Colors depict the threshold for anoxic conditions (Fe_{HR}/Fe_T > 0.22–0.38) in the bottom water column (Poulton & Canfield, 2011). (c) Box-and-whisker plots of Fe_{py}/Fe_{HR}. The blue–green bar depicts the threshold for euxinic conditions (Fe_{py}/Fe_{HR} > 0.7–0.8) in the bottom water column (Poulton & Canfield, 2011). (d) Plot of Fe_{HR}/Fe_T versus Fe_{py}/Fe_{HR}. The single sample *t*-test were performed for all statistical differences.

This suggests that the black shales were deposited under more stable euxinic conditions with relatively lower dissolved O_2 concentrations, whereas the Mn carbonates reflect more oxygenated bottom waters with an unstable redox state and a fluctuating chemocline (Figure 11d). The low Fe_{HR}/Fe_T (<0.22) values in the Mn carbonates imply a relatively deep chemocline, occasionally near or below the sediment-water interface. The high flux of terrestrial freshwater during deposition of the black shales enhanced the primary productivity and delivered increased amounts of dissolved, weathering-derived SO₄²⁻. This would have enhanced BSR, releasing H₂S into the bottom waters, thus further promoting localized stable euxinic conditions.

Based on the Fe speciation and N isotope results, we proposed a redox-stratified model for the upper Doushantuo Formation in South China, where the surface waters were oxygenated, while deep waters along the continental margin were anoxic to euxinic. However, more evidence is required to determine whether such a stratified redox model is applicable to the entire Ediacaran ocean. To explore this further, we compiled global Fe speciation data from different sedimentary facies following the Marinoan glaciation (Figure 12a). The Fe_{HR}/Fe_T dataset shows that the bottom waters, especially in the deep ocean, were prone to oxygenation after the Gaskiers glaciation (~580 Ma) (Canfield et al., 2007, Figure 12b). This observation appears to contradict the euxinic bottom-water conditions along the slope, as suggested by our data, indicating that the redox state of the global ocean during deposition of the upper Doushantuo Formation was spatially heterogeneous. The presence of both oxygenated deep waters in some regions and euxinic conditions in others suggests that redox conditions were variable and likely influenced by local environmental and geochemical factors.



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Figure 12. Fe_{HR}/Fe_T ratios and deep-water chemistry in the Ediacaran. (a) Fe_{HR}/Fe_T values in different depositional environments (data were taken from Canfield et al., 2008). Blue dash line refers to the threshold Fe_{HR}/Fe_T ratio for oxic and anoxic condition. (b) Redox state of bottom waters obtained from Fe_{HR}/Fe_T ratios (modified from Canfield et al., 2008).

Although the Mo isotopic composition of late Ediacaran seawater, as reported by Tan et al. (2023), suggested limited ocean oxygenation, our data combined with previously compiled records indicate that the redox structure of the Ediacaran ocean, at least for a period after the Gaskiers glaciation, was similar to that of the modern ocean (Ader et al., 2014). This redox structure featured globally oxygenated surface waters and euxinic bottom waters that persisted beneath oxygenated surface waters in slope settings along continental margin. As more profiles are drilled and additional samples are analyzed, we will be able to perform systematic studies across multiple sections. This will help us to create more detailed and convincing reconstructions of the paleo-environmental conditions during this critical interval in Earth's history.

5.3. Links Between the Hydrological Conditions and Redox State

Our geochemical data indicates that the hydrological conditions and redox chemocline fluctuated during deposition of the upper Doushantuo Formation along the northern margin of the Yangtze Block. Significantly, the dynamic fluctuations of the redox chemocline are coupled with changes in hydrological and hydrochemical conditions, which were regulated by paleoclimate during this period. This covariation indicates that there was a genetic relationship between redox chemocline fluctuations in the water column and paleoclimate. Furthermore,





Figure 13. Models for the fluctuating redox state during deposition of the black shales (a) and Mn carbonates (b) as well as various N cycling pathways for negative N isotopic compositions in the Doushantuo Formation Member IV, South China.

climate-driven changes in primary productivity also occurred. Given that organic matter synthesized by primary producers is the most important electron donor to respire electron acceptors in seawater (e.g., O_2 , SO_4^{2-}), fluctuations in primary productivity—mediated by changes in paleoclimate—emerged as the primary actor controlled the expansion or contractions of anoxic and euxinic zone in bottom waters.

In this study, we constructed distinct redox models for the deposition of black shales (Figure 13a) and Mn carbonates (Figure 13b) in the Doushantuo Formation Member IV of South China, emphasizing dynamic fluctuations in the redox chemocline driven by changes in the hydrochemistry and paleoclimate. During deposition of the black shales, the warm and humid paleoclimate fostered a high flux of terrestrial freshwater and glacial meltwater to ocean, leading to an increase in seawater depth. The enhanced input of essential nutrients by rivers fueled coastal primary productivity (Wang, Ling, et al., 2018). The organic matter synthesized by primary producers consumed oxidants in the water column, resulting in the expansion of anoxic conditions and the development of a shallower redox chemocline. In the relatively S-depleted Neoproterozoic oceans (Loyd et al., 2012), SO_4^{2-} derived from continental weathering was reduced by BSR. The subsequent release of H₂S transformed the anoxic environment into a more stable, euxinic bottom-water setting (Figure 13a). In contrast, during deposition of the Mn carbonates, a relatively cold and arid paleoclimate dominated. The sedimentary waters during this period were predominantly affected by high salinity seawater owing to the lower flux of





Figure 14. Schematic diagram of the paleogeography and biogeochemical N and Mn cycles during deposition of the Doushantuo Formation Member IV, South China.

terrestrial freshwater and low salinity glacial meltwater, which resulted in a decrease in water depth and increase in salinity. Reduced terrestrial freshwater and glacial meltwater fluxes, along with effect of high salinity seawater, led to decreased water depth and increased salinity. This period's lower terrestrial nutrient input diminished primary productivity, leading to fewer organic carbon sources and thus the preservation of oxidants in the water column. This caused a contraction of the anoxic zone and deepened the redox chemocline. The relatively small S pool and limited availability of organic matter jointly limited the production of H_2S , leading to a reduced euxinic zone (Figure 13b). These fluctuations in redox state were closely tied to hydrological and hydrochemical variations at the continental margin, reflecting the interactions between paleoclimate-driven changes and biogeochemical processes in this ancient Earth ecosystem.

5.4. Redox Heterogeneity and N Cycling

Our N isotope and compiled Fe speciation data indicate that the Ediacaran oceans were generally oxygenated following the Marinoan glaciation, a condition corresponding to the NOE (Sahoo et al., 2012, 2016; Wang, Jiang, et al., 2018). However, our Fe speciation analyses support a stratified redox structure, particularly in the slope settings at the continental margin, where oxygenated surface water existed above anoxic and euxinic deep bottom water column. Notably, the wide range of Fe_{HR}/Fe_T ratios suggests that the redox chemocline, especially during the deposition of Mn carbonates, fluctuated significantly over time. This intermittent vertical movement of the chemocline provided an ideal environment for the dynamic biogeochemical cycling of redox-sensitive elements (Figures 13 and 14).

Diazotrophic prokaryotes in the oxygenated photic zone of the Ediacaran ocean fixed atmospheric N₂ using the nitrogenase enzyme, leading to limited N isotopic fractionation ($\varepsilon = -2\%$ to +1%). This fixed organic N was almost completely oxidized to NO₃⁻ via quantitative nitrification, which occurred without significant N isotopic fractionation. The near-quantitative nitrification imparted a large and stable NO₃⁻ reservoir throughout the oxygenated portions of the ocean. At the O₂-depleted zone along the continental margin, non-quantitative denitrification of NO₃⁻ took place, which caused a large isotopic fractionation ($\varepsilon = -25\%$; Quan et al., 2013) and released ¹⁵N-depleted N₂ ($\delta^{15}N = -20\%$) to the atmosphere. The residual ¹⁵N-rich NO₃⁻ was then

assimilated by marine microorganisms, incorporated into biomass, and eventually buried in sediments. This process explains the relatively heavy N isotope values observed in the sediments of the Doushantuo Formation Member IV (+2.45% to +7.1%), which are comparable to, but slightly lower than, those found in the modern ocean (Figure 14). This suggests that while the overall redox structure of the surface ocean was oxygenated, the anoxic zones at the continental margin were sites of active denitrification.

The presence of significantly lighter N isotopes (-1.27% to +2.45%) in certain samples from the Doushantuo Formation Member IV (Figure 3) suggests anomalies in N cycling. By integrating Fe speciation data, we reconstructed distinct N cycling processes associated with redox fluctuations. In black shale samples (XQ-1 and XQ-2), where lighter N values were recorded, high Fe speciation ratios indicate euxinic bottom-water conditions. This setting likely supported a limited NO₃⁻ reservoir, similar to the ocean during Mesozoic oceanic anoxic events (Junium & Arthur, 2007) or in the modern Black Sea (Fulton et al., 2012). Under such conditions, the biological N fixation by diazotrophs, which preferentially fix isotopically light N₂, exceeded denitrification, leading to the direct preservation of these light N isotopes in the sediments (Chen et al., 2019). By contrast, for the Mn carbonates with similarly light N isotopes (e.g., XQ-5 and XQ-14 to XQ-18), low Fe_{HR}/Fe_T ratios indicate that the redox chemocline was deeper, possibly near or below the sediment-water interface. Under this circumstance, contraction of the anoxic zone limited the synthesis of denitrification enzymes (Codispoti et al., 2001), causing stagnation in denitrification. The isotopically light N fixed by the diazotrophs underwent near-quantitative nitrification, which then led to the complete incorporation of this light N into the sediments, further explaining the observed light N isotopic signatures. Despite these variations, the dominant N cycling processes during this time were biological N fixation, quantitative nitrification, and non-quantitative denitrification.

5.5. Manganese Cycling and Mineralization

Manganese is also an important redox-sensitive element that can be used to trace Earth's oxidation history and the evolution of life, in addition to the proxies discussed above (Spinks et al., 2023). Traditionally, the formation of Mn carbonates has been understood to require two key processes. First, Mn(II) is oxidized to Mn(IV) oxides in oxygenated environments. These Mn oxides are then deposited and undergo microbial reduction back to dissolved Mn(II) during diagenesis, forming Mn carbonates within sediments (Dong et al., 2023; Yu et al., 2016). This model has made ancient Mn carbonates valuable indicators of oxidative events throughout Earth's history (Calvert & Pedersen, 1996; Maynard, 2010). However, recent laboratory experiments and studies of modern analogs, such as stratified lakes, suggest an alternative pathway for Mn carbonates formation. These studies demonstrate that Mn(II) can be directly incorporated into Mn carbonate minerals in anoxic conditions, without requiring the oxidation to Mn(IV) (Wittkop et al., 2020). This leads to a model where Mn carbonates can precipitate directly from dissolved Mn(II) under anoxic conditions, bypassing the traditional oxidation-reduction cycle (Gao et al., 2021).

The black shale-hosted Mn carbonates in the Doushantuo Formation Member IV of South China, discovered along the northern margin of the Yangtze Block, represent the only known Mn carbonate deposits in Ediacaran strata in this region (Zhang et al., 2024). Our previous findings on these Mn carbonates revealed several striking geochemical signatures, including extremely negative C isotopic compositions (down to -11%) and positive cerium (Ce) anomaly (Zhang et al., 2021), along with residual Mn oxide residues such as todorokite (Zhang et al., 2022). These findings collectively indicate that Mn(IV) oxides, likely formed in an oxygenated setting, were precursors for the Mn carbonates, which later formed under reducing conditions (Zhang et al., 2022, 2024). Our redox proxies further support this interpretation, showing that Mn was significantly enriched in Mn carbonates deposited in environments that experienced periodic oxygenation, as evidenced by frequent fluctuations in the redox chemocline. In contrast, contemporaneous black shales, deposited under more stable anoxic and euxinic conditions, show Mn depletion. The enrichment patterns of Mo and U in the Mn carbonates also suggest the involvement of a Mn oxides particulate shuttle, further supporting the hypothesis of Mn cycling between oxidized and reduced forms (Figure 4b). Thus, the formation of these Mn carbonates involved a two-step process: initial Mn(II) oxidation under oxygenated conditions, followed by reduction of Mn(IV) in oxygen-depleted waters (Calvert & Pedersen, 1996; Maynard, 2010). This emphasizes that Mn carbonates can serve as robust indicators of past oxidation events.

Previous studies of black shale-hosted Mn carbonates of different ages have suggested that local oxidation of anoxic bottom waters could be driven by episodic ventilation. This model proposes that intermittent influxes of

oxygenated surface waters create brief oxygenated conditions, allowing for Mn(II) oxidation (Dong et al., 2023; Yu et al., 2016). However, this theory is controversial, particularly in its ability to account for the large-scale, economically significant Mn ore deposits. The key limitation of the episodic ventilation model is whether such events could produce enough Mn(IV) oxides to form extensive Mn carbonate deposits. In the context of the Doushantuo Formation of this study, the episodic ventilation model appears insufficient. Notably, the Mn carbonates of the Doushantuo Formation Member IV are distributed along the rift basin margin but were absent in the basin center (Wang, Li, et al., 2020). This spatial pattern indicates that the deep-water ventilation is not a viable explanation for Mn carbonates formation in this region. Instead, the stratified redox model with a fluctuating redox chemocline at the continental margin, as proposed in this study, offers a more comprehensive explanation for the localized Mn carbonate deposits.

We propose a geochemical model for Mn cycling during the deposition of the Mn carbonates in the Doushantuo Formation Member IV of South China, driven by the fluctuating and stratified redox conditions (Figure 14). In this model, Mn was introduced into the anoxic bottom waters via hydrothermal fluids along syngenetic normal faults, as indicated by previous geochemical evidence such as the positive europium (Eu) anomaly and hydrothermal alabandite deposits (Zhang et al., 2021). During deposition of the black shales, the water column was characterized by expanded euxinic conditions that were unfavorable for the oxidation of dissolved Mn(II). Consequently, Mn(II) remained dispersed within the anoxic water, forming a large reservoir of dissolved Mn (Figure 14). However, as the climate shifted toward colder and more arid conditions, the flux of freshwater decreased. This decrease, coupled with lower primary productivity, led to a contraction of the oxidation of Mn(II). Dissolved Mn(II) was oxidized to insoluble Mn oxides above the chemocline, leading to initial enrichment of dispersed Mn(II) (Figure 14). These Mn oxides, being insoluble, settled down into the deeper water column. Upon crossing the redox interface, the Mn oxides were reduced back to Mn(II) by the anoxic conditions in the bottom waters. This reduced Mn(II) was subsequently incorporated into the Mn carbonates, completing the Mn cycling process.

In summary, the mineralization of black shale-hosted Mn carbonate ore in the Doushantuo Formation of South China was driven by the coupling of various factors. The influx of hydrothermal Mn(II), along with local fluctuations in the redox chemocline, was necessary for large-scale Mn carbonate deposition. These fluctuations were primarily controlled by changes in paleoclimate and hydrochemistry conditions, which played a key role in regulating Mn cycling. These dynamic interactions coupled hydrothermal Mn input likely explains why black shale-hosted Mn carbonate deposits are uniquely found at the northern margin of the Yangtze Block during the Ediacaran Period.

6. Conclusions

The Mn carbonates in the Doushantuo Formation Member IV along the northern margin of the Yangtze Block formed due to complex interactions between environmental conditions, biological activities, and elemental cycling after the Cryogenian. Although the ocean may have experienced episodes of oxygenation after the Marinoan glaciation, the slope facies waters at the continental margin remained redox-stratified, with a fluctuating redox chemocline. Variations in paleoclimate altered the hydrological and hydrochemical conditions, influencing nutrient availability and primary productivity. The relatively low primary productivity during Mn mineralization led to contraction of the anoxic bottom-water zone and deepening of the redox chemocline, which provided ideal conditions for oxidation of soluble Mn(II). These redox fluctuations, driven by changes in primary productivity, were critical in driving Mn cycling. The large Mn pool coupled with localized redox condition fluctuations were instrumental in shaping the cycling of key elements in the Earth's transitional period. This explains why black shale-hosted Mn carbonate deposits only accumulated along the northern margin of the Yangtze Block during the Ediacaran Period. The interplay of such processes might be general throughout the Earth evolution, particularly for the time across the critical oxygenation events.

Conflict of Interest

The authors declare no conflicts of interest relevant to this study.

Data Availability Statement

The raw data files used in this paper are available at (Zhang & Cao, 2024).

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