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The molybdenum cycle in the oxygenated Neoproterozoic ocean was coupled to manganese carbonate mineralization

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The Neoproterozoic oxygenation event is a milestone in Earth's history, yet the redox structure and elemental cycling of the Neoproterozoic ocean remain debated. Here, we investigated iron speciation, molybdenum, and nitrogen isotopes in black shales and manganese carbonates from the upper Ediacaran Doushantuo Formation, South China, to examine the links between redox state, manganese mineralization, and molybdenum cycling. In both lithologies, high pyritic iron ratios (> 0.8) indicate a localized euxinic zone, while estimated seawater molybdenum (1.9‰) and sediment nitrogen isotopic compositions (4.19 \pm 1.96‰) resemble modern values, suggesting oxygenated surface waters over euxinic depths. Negative molybdenum isotope in manganese(II) carbonates points to manganese(IV) oxide reduction, acting as a molybdenum shuttle from oxygenated surface to euxinic deep waters. Periodic euxinic contractions drove manganese(II) oxidation and mineralization, shaping molybdenum cycling. This study highlights essential manganese(II) oxidation for manganese carbonate mineralization and offers new insights into molybdenum geochemistry and ancient ocean oxygenation events.

The Neoproterozoic oxygenation event (NOE; ca. 0.80-0.55 Ga) is a milestone for the co-evolution of life and Earth's habitability, with an obvious rise in atmospheric and oceanic oxygen (O₂) levels from the early to late Ediacaran^{1,2}. This shift created favorable environmental conditions for the emergence of multicellular organisms, including metazoans³⁻⁵. Representative evidence for the progressive oxidation of the Ediacaran Ocean includes an increase in redox-sensitive trace elements⁶, elevated oceanic sulfate (SO₄²⁻) and phosphorus (P) availability^{1,4}, and an aerobic component to the nitrogen (N) cycle7. However, other geochemical proxies, such as high proportions of highly reactive iron (Fe) minerals and heavy isotopic compositions of pyrite ($\delta^{34}S_{py}$) in sediments, paradoxically indicate widespread anoxic to euxinic deep Ediacaran seawaters^{8,9}. The main challenge lies in determining whether mid-to-deep ocean waters were ferruginous, euxinic, or oxic beneath oxygenated surface layers. Furthermore, it remains unclear whether the previously reported oxygenated, ferruginous, or euxinic conditions of the paleo-ocean during the NOE were global phenomena or restricted to local environments^{7,9}. These conflicting signals complicate the spatial redox picture of the Ediacaran Ocean. Reconciling these divergent paleoenvironmental proxies is essential for understanding the spatial redox structure and associated biogeochemical cycling, as well as their role in shaping early life during the NOE.

South China provides an ideal area for investigating this key scientific issue due to its extensive sedimentary records. A globally unique, black shale-hosted, manganese (Mn) carbonate deposit occurs at the upper Ediacaran Doushantuo Formation, along the northern margin of the Yangtze Block, which is potential to provide new insights into constraining the oceanic redox state. The mineralization of Mn(II) carbonates (from herein referred to as Mn carbonates) is thought to require the reduction of Mn(III, IV) oxides (from herein referred to as Mn oxides), with organic matter, ferrous Fe or methane being electron donors¹⁰⁻¹². Consequently, it is believed that Mn carbonates are indicative of an oxygenated ocean¹³⁻¹⁵. However, other studies suggested that Mn carbonate minerals can precipitate directly from O2-deficient seawater containing high levels of dissolved Mn (>200 $\mu\text{M})$ without undergoing Mn redox cycling $^{16,17}\!\!\!$. This controversy surrounding the Neoproterozoic Mn carbonate precipitation pattern further complicates our understanding of the unclear redox configuration of the sedimentary basin during the deposition of the Doushantuo Formation.

¹State Key Laboratory for Mineral Deposits Research, Frontiers Science Center for Critical Earth Material Cycling, School of Earth Sciences and Engineering, Nanjing University, Nanjing, China. ²School of Resources and Safety Engineering, Chongqing University, Chongqing, China. ³College of Resources and Environmental Engineering, Guizhou University, Guiyang, China. ⁴Department of Earth & Atmospheric Sciences, University of Alberta, Edmonton, AB, Canada. ©e-mail: jcao@nju.edu.cn; kaihu@nju.edu.cn In this study, we utilized a combination of three geochemical proxies to elucidate the paleo-ocean's redox state and Mn carbonate mineralization regime. Nitrogen isotopes ($\delta^{15}N_{sed}$) and Fe speciation constrain the redox conditions of surface¹⁸ and bottom waters¹⁹, respectively, offering insights into the water column's redox profile. Additionally, molybdenum (Mo) isotopes ($\delta^{98}Mo$) were used to track ancient marine redox conditions and Mn cycling due to the strong affinity for Mn oxides²⁰. Particularly, we explored the influence of Mn oxide shuttles on $\delta^{98}Mo$ values and further reconstructed contemporaneous seawater molybdenum isotopic compositions ($\delta^{98}Mo_{sw}$), which provide constraints on the Mn mineralization process and the redox conditions of Neoproterozoic oceans comprehensively. The distinct $\delta^{98}Mo$ values in turn allow us to reveal the variable Mo cycling patterns under the fluctuating redox state of Neoproterozoic oceans.

The study area is located in Chengkou County, situated in the Chongqing region, along the northern margin of the Yangtze Block, South China (Fig. 1a, b). Regionally, the Doushantuo Formation can be correlated with its counterpart along the southeastern margin of the Yangtze Block (Supplementary Note 1). The uppermost layer of the Doushantuo Formation (i.e., Member IV; $<557.8 \pm 0.8 \text{ Ma}$)²¹ is characterized by organicrich black shales (Fig. 1c). Mn carbonates with variable thicknesses (ranging from 0.35 to 2.80 m) occur within Member IV of the Doushantuo Formation along the margins of the rift basin, while they are absent in the deeper central basin^{22,23}. Five Mn ore exploration areas occur in the Chengkou region, with our samples being collected from the Xiuqi Mn ore exploration area (Fig. 1b). Our findings demonstrate that Mn(II) oxidation are prerequisite for Mn carbonate mineralization in the Doushantuo Formation. Periodic contractions of euxinic deep zone in stratified slope setting drove Mn(II) oxidation and associated Mo cycling.

Results

Petrography and minerology

Lithologically, our samples are divided into black shales and Mn carbonates. The black shales contain widely distributed laminar organic matter (Supplementary Fig. S1a) and are composed of detrital quartz, dolomite intraclasts, and pyrite (Supplementary Fig. S1b). In the Mn carbonates, spherical and ellipsoidal Mn carbonate minerals are distributed throughout the



Fig. 1 | **Location and geological setting of study area. a** Paleogeographic map of the Yangtze Platform during the Ediacaran Period (modified from ref. 55). **b** Geological map of the northern margin of the Yangtze Platform (modified from ref. 22).

c Simplified stratigraphy of the Doushantuo Formation on the Yangtze Platform (modified from refs. 22,55). Numbers I–IV refer to the members I–IV of the Doushantuo Formation.



Fig. 2 | Iron speciation results and enrichment factors of redox-sensitive elements for Member IV of the Doushantuo Formation. a Box-and-whisker plot of Fe_T. b Plot of Fe_{HR}/Fe_T versus Fe_{py}/Fe_{HR}. c Box-and-whisker plots of U_{EF}, Mo_{EF}, and V_{EF}. d Plot of U_{EF} versus Mo_{EF}.

samples, and a combination of powder X-ray diffraction and in situ Raman spectroscopy analyses identified these spherical and ellipsoidal structures as rhodochrosite cemented by kutnohorite (Supplementary Fig. S1c–f). Notably, only fine-grained todorokite, a Mn oxide detected by Raman spectra, was found within the individual Mn carbonate, closely associated with fine pyrite (Supplementary Fig. S1g, h).

Elemental geochemistry

The geochemical results are presented in Supplementary Data 1 and Supplementary Fig. S2. The Mn contents of the Mn carbonates are markedly higher compared with the black shales (averages of 20.18 ± 7.98 wt.% and 0.68 ± 0.83 wt.%, respectively). The redox-sensitive elements uranium (U), Mo, and vanadium (V) are enriched in all samples. The U_{EF} values of the Mn carbonates and black shales are similar (averages of 6.71 and 6.54, respectively), whereas Mo_{EF} and V_{EF} values are higher for the Mn carbonates (averages of 96.11 and 13.77, respectively) compared with the black shales (averages of 22.49 and 5.07, respectively).

Nitrogen isotopes, Fe speciation, and Mo isotopes

The $\delta^{15}N_{sed}$ values of the Mn carbonates and black shales are semblable (averages of 4.65‰ and 4.31‰, respectively). The Fe speciation ratios of the Mn carbonates are slightly lower than those of the black shales, with Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} of 0.53–0.98 and 0.79–0.95 for the Mn carbonates and 0.90–0.96 and 0.79–0.95 for the black shales, respectively. The δ^{98} Mo values are negative (–1.30‰ to –0.04‰, with an average of –0.74‰) for the Mn carbonates, but positive (0.05‰ to 1.00‰, with an average of 0.43‰) for the black shales.

Discussion

The $\delta^{15}N_{sed}$ measurements for both Mn carbonates and black shales consistently exceed 0‰, with averages of 4.65‰ and 4.31‰ (Supplementary

Data 1 and Supplementary Fig. S2), respectively, indicating an oxygenated upper water column. This is because quantitative nitrification in an oxygenated ocean maintains a large nitrate reservoir. Partial denitrification then releases isotopically light N2 in the redox transition zone, resulting in high $\delta^{15}N_{sed}$ values^{7,24}. Conversely, in anoxic settings where nitrate is scarce, limited denitrification occurs, preserving more biologically fixed N and resulting in $\delta^{15}N_{sed}$ values of ~0‰ (see Supplementary Note 3)²⁵. Notably, our $\delta^{15}N_{sed}$ values are slightly lower than those in the modern ocean (5%)²⁴, suggesting slightly less oxidation in the surface water column compared to the present counterpart⁷. Furthermore, we compiled Ediacaran sedimentary N isotope data from multiple paleocontinents, including the Amazon craton (Brazil), Nanhua Basin (South China), northwest Canada, and northeast Svalbard, across different sedimentary environments (i.e., shelf margin and inner shelf)^{7,26-28}. Notably, both our data and the compiled N isotopic datasets are consistent with, though slightly lighter than, modern marine sediments (Supplementary Fig. S3), indicating oxygenated shallow seawater and a redox structure similar to that of the modern ocean. The consistency of Ediacaran N isotopic compositions across multiple cratons likely reflects a global rather than local redox signal.

With the exception of two Mn carbonates, most of our samples, deposited under low accumulation rates, have Fe_T contents exceeding 0.5 wt.% (Fig. 2a). This suggests that Fe speciation is a reliable redox proxy for the bottom waters (see Supplementary Note 4)^{19,29}. All samples have Fe_{HR}/Fe_T > 0.38 and Fe_{py}/Fe_{HR} > 0.7 (Fig. 2b), indicative of anoxic conditions with free hydrogen sulfide (H₂S) in bottom water. These conditions result in Fe sulfides being the primary form of reactive Fe under euxinic conditions (Fig. 2b)¹⁹.

Collectively, the positive $\delta^{15}N_{sed}$ values and high Fe speciation ratios suggest that the water column was characterized by upper oxygenated waters overlying anoxic bottom waters (Supplementary Fig. S4).



Fig. 3 | Correlations between Mn contents and V_{EF} and δ^{98} Mo values. a Mn contents versus V_{EF} values for all samples. b Mn contents versus δ^{98} Mo values for all samples. c Mn contents versus δ^{98} Mo values for Mn-depleted black shales.

Typically, Mn carbonates precipitated directly from anoxic water with high dissolved Mn concentrations can retain contemporaneous seawater geochemical signals¹⁷, such as carbon (C) isotopes ($\delta^{13}C_{carb}$). However, Mn carbonates in the Doushantuo Formation exhibit distinctly negative $\delta^{13}C_{carb}$ values (as low to -11%)²³, which are significantly lighter than normal Ediacaran seawater (≥ 0 %)^{30,31}, equivalent sequence in other sections^{32,33}, and associated Mn-depleted dolostones²³. Additionally, there is a negative correlation between Mn contents and C isotope values in both Mn carbonates and nearby Mn-bearing black shales containing small amounts of Mn carbonate minerals in this study^{23,33}, indicating a reduction of Mn oxides coupled with organic C mineralization^{34,35}. Furthermore, our finding of residual Mn oxides (i.e., todorokite)³⁶ within individual Mn carbonates, along with positive cerium (Ce) anomalies²³, indicates that todorokite is likely primary, not a product of post-diagenetic or supergene alteration. Two lines of evidence further support this assertion. First, todorokite only appears in individual Mn carbonates, rather than in samples with particularly high Mn contents, and is found between Mn carbonate minerals in close association with fine-grained pyrite (Supplementary Fig. S1). The wellpreserved pyrite suggests that todorokite did not result from diagenetic oxidation, as pyrite would oxidize more readily than Mn(II) minerals³⁶. Second, our samples were extracted from cores buried more than 700 m deep with no signs of exposure, ruling out supergene oxidation of Mn carbonates to form Mn oxides. Therefore, we posit that Mn carbonates in the Doushantuo Member IV in this study did not form through direct



d Mn contents versus δ^{98} Mo values for euxinic black shales in other sections in the study area (data from ref. 42).

precipitation in anoxic waters but rather involved the reduction of a Mn oxide precursor¹⁵.

Here, we present additional robust evidence supporting the presence of high-valent todorokite precursors in the formation of Mn carbonate. First, the Mo_{EF} and V_{EF} exceed the U_{EF} in Mn carbonates (Fig. 2c). Furthermore, our samples plot within the particulate shuttle field on a plot of U_{EF} - Mo_{EF} (Fig. 2d), indicating that Mn oxides facilitated the enrichment of Mo and V. This enrichment is attributed to the greater affinity of Mo and V for Mn oxides, which has minimal effect on U enrichment^{20,37}.

Second, we observe a positive correlation between V_{EF} values and Mn contents ($R^2 = 0.5023$, p < 0.01; Fig. 3a), providing further evidence for the presence of Mn oxides. This correlation results from V's stronger affinity for Mn oxides compared to Mo³⁸. In this context, Mn oxides facilitate the transport of soluble V⁵⁺ from the oxic water column to euxinic deep waters, where V subsequently settles into the sediment pile as insoluble V³⁺ hydroxides. Consequently, V_{EF} is proposed as a qualitative tracer for Mn oxide shuttles³⁷.

Third, the δ^{98} Mo values for Mn carbonates are consistently negative, reaching a minimum value of -1.3% (Supplementary Data 1), in contrast to the positive values observed in Mn-depleted black shales (up to 1.0‰; Supplementary Figs. S2, 3b). Importantly, there is a strong negative correlation between Mn contents and δ^{98} Mo values ($R^2 = 0.8073$, p < 0.01; Fig. 3b), indicating the probable involvement of Mn oxide shuttles. This correlation is attributed to the preferential sequestration of isotopically

lighter Mo from seawater by Mn oxides, leading to large isotopic fractionations³⁹. Consequently, the Mn carbonates inherit the isotopically light Mo signals from their Mn oxide precursors¹⁴.

Collectively, while the direct precipitation of Mn carbonate minerals in an oxygen-depleted environment - another possible pathway for their formation that has been verified in many cases¹⁶ - cannot be completely ruled out, our findings support the conclusion that the Mn carbonates in the Doushantuo Formation primarily originated from the reduction of Mn oxide precursors.

Previous studies reported near 0% or slightly negative δ^{98} Mo values of organic-rich shale within Doushantuo Formation Member IV in several sections in South China^{37,40}, which were ascribed to the operation of Mn oxide shuttles in oxygenated marine waters or non-quantitative thiomolybdate formation. The former suggests an oxygenated environment, while the latter indicates a weakly euxinic one. Although the Mn contents of black shale are indeed higher than that of Post-Archean Australian Shale (PAAS) and/or Upper Continental Crust (UCC) due to the influx of deep hydrothermal fluids, which elevated the Mn background concentration in ambient seawater^{23,41}, there is no extreme enrichment of Mn in the shales as observed in the Mn carbonates. Whether these low δ^{98} Mo values arise from the operation of Mn oxide shuttles requires further investigation. By contrast, other studies have reported heavy δ^{98} Mo values (~1‰) in black shales of Member IV in our study area⁴², which they attributed to relatively O₂depleted depositional conditions. The geological implication of the distinct δ^{98} Mo values in the black shale in Member IV remains unclear, leading to the above conflicting interpretations. Clarifying what sedimentary Mo isotopes represent is crucial for constraining the ocean's redox state. Accordingly, reconstructing δ^{98} Mo_{sw} values could provide new insights into the paleo-oceanic redox configuration (Supplementary Note 5).

The presence of Mn oxide precursors led to larger Mo isotopic fractionation. Conversely, the low Mn contents $(0.68 \pm 0.83 \text{ wt.\%})$ in the black shales suggest that Mn oxide shuttles had a negligible effect on the δ^{98} Mo values. We have also ruled out the possible influence of Fe oxides on the δ⁹⁸Mo values of Fe-rich black shales (Supplementary Fig. S5 and Supplementary Note 6). Therefore, black shales can serve as a basis for reconstructing δ^{98} Mo_{sw}⁴³. The regression lines in plots of δ^{98} Mo values versus Mn contents of the euxinic Mn-depleted black shales show intercepts of δ^{98} Mo = 1.35‰–1.45‰ (Fig. 3c, d), indicating that δ^{98} Mo_{sw} may be around 1.45‰ as the heaviest Mo isotope value in strongly euxinic sediments, such as the sulfidic black shales, generally represents the lightest $\delta^{98}Mo_{sw}$ value (since lighter Mo preferentially sinks to sediments)⁴⁴. Notably, the heaviest Mo isotope value for black shales of the Doushantuo Formation Member IV reported in previous studies from South China is about 2‰37,40, which is obviously higher than the estimated $\delta^{98}Mo_{sw}$ values of 1.45‰ and thus suggests an underestimation of $\delta^{98}Mo_{sw}$. Interestingly, in highly euxinic waters (e.g., the modern Black Sea), there is typically an isotopic offset $(\Delta^{98}Mo_{seawater-sediment} = 0.5 \pm 0.3\%)$ between the dissolved Mo species and authigenic solid-phase Mo (see Supplementary Note 5)45. This information helps reconcile the contradictory $\delta^{98}Mo_{sw}$ estimations. Accordingly, we conservatively applied this fractionation (i.e., 0.5‰) to recalculate the δ^{98} Mo_{sw} value during the deposition of the Doushantuo Formation Member IV. The recalculated results imply that the global $\delta^{98}Mo_{sw}$ value during deposition of the upper Doushantuo Formation should be higher than 1.9‰ (i.e., 1.4 + 0.5%), which is consistent with the heaviest Mo isotope values of black shales in South China (i.e., 2‰)^{37,40}. This aligns with the basic principle of sedimentary Mo isotope geochemistry, that is, the heaviest Mo isotope value in sediments is basically similar to that of seawater at the same period^{43,45}. If the fractionation value of 0.5‰ is not introduced, the heaviest Mo isotopes in sediments (~2‰) will be much higher than the calculated seawater Mo isotopic values (i.e., 1.4‰), which is inconsistent with the basic Mo geochemical principle^{43,45}. Hence, it is concluded that our estimation of the Ediacaran δ^{98} Mo value of seawater is more reasonable.

Geological records indicate a correlation between estimated $\delta^{98}Mo_{sw}$ values and atmospheric O₂ levels (Fig. 4a, b). Essentially, higher atmospheric O₂ levels coupled with more oxygenated oceans lead to the sequestration of isotopically light Mo from seawater by oxide shuttles and limited free H₂S⁴⁰. Both mechanisms are known to retain isotopically heavier Mo isotopes in seawater, thereby increasing $\delta^{98}Mo_{sw}$ values. Consequently, the modern oxygenated ocean typically exhibits higher δ^{98} Mo_{sw} values (2.34‰)⁴⁶ compared with O2-depleted oceans (e.g., during the Toarcian OAE; Fig. 4c)^{40,47}, which provides insights into the explanation of the gradually increases in estimated $\delta^{98}Mo_{sw}$ values during the Great Oxidation Event (GOE) and NOE (Fig. 4a, b). Conversely, extremely low $\delta^{98}Mo_{sw}$ values since the Phanerozoic eon correspond to major extinction events and anomalous C isotopic excursions, which are mostly associated with ocean deoxygenation (Fig. 4c). Within this framework, the paleo-oceanic redox state can be accurately reconstructed from the $\delta^{98}Mo_{sw}$ values during the deposition of the upper Doushantuo Formation. The near-modern $\delta^{98}Mo_{sw}$ value during the termination of the Doushantuo Formation suggests slightly less oxygenated seawater than the modern ocean. This can be attributed to the preferential sequestration of isotopically light Mo into sediments in oxidized oceans, resulting in higher $\delta^{98}Mo_{sw}$ values, consistent with the conclusions drawn from the N isotope proxy.

The maximum offset (3.2‰; Fig. 5a) between the lowest δ^{98} Mo value (-1.3‰) of the Mn carbonates and the calculated δ^{98} Mo_{sw} value (1.9‰) slightly exceeds the theoretical Mo isotopic fractionation attributed to the Mn oxide shuttle (3‰; see Supplementary Note 5)³⁹. Similarly, the minimum offset (0.9‰; Fig. 5a) between the highest δ^{98} Mo value (1.0‰) of the black shales and the estimated δ^{98} Mo_{sw} value also surpasses the theoretical sulfide-dependent Mo isotopic fractionation (0.7‰; Supplementary Note 5)⁴⁸. These observations can only be explained by a combined influence of both Mn oxides and sulfide⁴⁹. Specifically, the Mo isotopic fractionation is primarily controlled by the Mn oxide shuttle in the Mn carbonates, whereas sulfide-dependent transformation dominates in the black shales.

Various pathways of Mo sequestration from seawater lead to distinct Mo isotopic fractionations, thereby influencing the contemporaneous $\delta^{98}Mo_{sw}$ values. When Mo sources and sinks in the ocean reach a dynamic equilibrium, contemporaneous $\delta^{98}Mo_{sw}$ values offer insights into changes in the relative proportions of Mo between oxidized and reduced sinks⁴⁶. In this study, the first calculated late Ediacaran $\delta^{98}Mo_{sw}$ value is ~1.9%. We adopted a simple steady-state isotope mass balance model to quantitatively evaluate the origins of the different Mo isotopic signals in the Mn carbonates and black shales. The equations are as follows:

$$\delta^{98} \text{Mo}_{\text{sink}} = \delta^{98} \text{Mo}_{\text{sw}} - (\Delta^{98} \text{Mo}_{\text{oxic}} \times f_{\text{oxic}} + \Delta^{98} \text{Mo}_{\text{mod}} \times f_{\text{sub}} + \Delta^{98} \text{Mo}_{\text{eux}} \times f_{\text{eux}})$$
(1)

$$f_{\text{oxic}} + f_{\text{sub}} + f_{\text{eux}} = 1 \tag{2}$$

where δ^{98} Mo_{sink} and δ^{98} Mo_{sw} represent the Mo isotopic compositions of the sediments and seawater, respectively. f_{oxic} , f_{sub} , and f_{eux} denote the fractions of the oxic, suboxic to weakly euxinic, and strongly euxinic sinks, respectively. This model shows that δ^{98} Mo_{sink} value is influenced by three factors: (1) variations in f_{oxic} , f_{sub} , and f_{eux} (2) changes in Δ^{98} Mo_{oxic}, $\Delta^{98/95}$ Mo_{mod}, and $\Delta^{98/95}$ Mo_{eux}; and (3) alterations in δ^{98} Mo_{sw}. Here, the average δ^{98} Mo values of the Mn carbonates and black shales are -0.73% and 0.43%, respectively (Supplementary Data 1). The estimated contemporaneous δ^{98} Mo_{sw} value ranges from 1.8% to 2.0%. Δ^{98} Mo_{oxic} $(3\%)^{39}$, Δ^{98} Mo_{sub} $(0.7\%)^{48}$, and Δ^{98} Mo_{eux} $(0.5\%)^{45}$ are the Mo isotopic fractionations of the above three distinct Mo sinks, respectively. The variation in f_{oxic} , f_{sub} , and f_{eux} values thus becomes the most potential factor in controlling the δ^{98} Mo_{sink} value.

The modeling results show redox evolution curves of Mn carbonate and black shale with certain δ^{98} Mo_{sw} value by plotting $f_{oxic}/(f_{oxic} + f_{OMZ})$ and f_{eux} (Fig. 5b). To obtain light δ^{98} Mo values for the Mn carbonates, f_{oxic} and f_{eux} vary from 80.0% to 89.6% and from 0% to 18.4%, whereas for the black shales, f_{oxic} and f_{eux} range from 29.1% to 42.8% and from 0% to 65.2%, respectively (Fig. 5b; Supplementary Data 1). This suggests that Mo in the Mn carbonates primarily originated from sorption onto precipitating Mn Fig. 4 | Evolution of atmospheric O₂ levels and temporal variations in δ^{98} Mo values of ancient sedimentary rocks throughout geological history. a Evolution of Earth's atmospheric O₂ levels through time³. b Compilation of δ^{98} Mo data for sediments throughout geological history (data from ref. 62 and references therein). c Detailed δ^{98} Mo record of sediments from 800 to 0 Ma (data from ref. 40 and references therein). DST IV = the Doushantuo Formation Member IV.



oxides in the oxygen-rich water (i.e., oxic sink), whereas Mo in the black shales was predominantly enriched under strongly euxinic condition (i.e., strongly euxinic sink). Sensitivity analysis shows that the distinct decreases in sediment δ^{98} Mo_{sink} correspond to the increases in f_{oxic} . These imply greater oxygenation in the seawater during the deposition of Mn carbonates compared to the black shales (Fig. 5b). Furthermore, this model highlights that higher δ^{98} Mo_{sw} values (e.g., 1.8‰ versus 2.0‰) within the same lithology correspond to a higher f_{oxic} values (Fig. 5b), consistent with the higher δ^{98} Mo_{sw} values observed in more oxygenated oceans.

In addition, the relationship between $Mo_{EF}-U_{EF}$, as well as Mo–TOC, illustrates a more pronounced effect from open seawater during the deposition of Mn carbonates compared to black shales (Figs. 2d, 6a; Supplementary Note 7). Due to lower dissolved Mo concentrations in euxinic seawater compared with oxygenated seawater²⁰, the elevated $[Mo]_{aq}$ in the bottom waters (Fig. 6b) during Mn carbonate deposition reflects the contraction of the euxinic zone. This combined effect of open ocean influences and a corresponding shrinking euxinic zone during Mn mineralization can be attributed to the widespread oxygenated Ediacaran ocean⁷.

Notably, the anaerobic photochemical oxidation of Mn carbonate and anoxygenic photosynthesis can also produce Mn oxide under high ultraviolet irradiation during the Archean, especially during the pre-GOE period with low O_2 level^{50,51}. However, these pathways are not applicable in the deposition of the Doushantuo Formation Member IV of this study. This is because the Doushantuo Formation was deposited at the end of NOE when the atmospheric oxygen concentration and oceanic dissolved oxygen content increased to some extent compared with those pre-GOE. The increase of atmospheric O_2 concentration promoted the establishment of a stratospheric ozone shield, which filtered high-energy ultraviolet light⁵². Under this condition, the photochemical oxidation of rhodochrosite is inhibited. In addition, the accumulation of oxygen in the Earth's surface layer is a favorable oxidant for Mn oxidation. The transformation of Mn with varied valence will be mainly regulated by redox conditions. Oxygen-driven biological or abiotic oxidation of Mn tends to be the main way of Mn oxide formation before the precipitation of Mn carbonate minerals in this period⁵³. This aligns with the temporally coupled relationship between sedimentary Mn and atmospheric O_2 concentrations⁵⁴. In this regard, the contraction of the euxinic zone, to some extent, likely transformed local euxinic waters into oxygenated deep waters, serving as the primary driver for the oxidation of dissolved Mn(II) in previously anoxic waters and subsequently triggering Mn mineralization during the deposition of the Doushantuo Formation Member IV.

There is also a positive correlation between authigenic Mo (Mo_{auth}) concentration with pyritic Fe (Fe_{py}) and total organic carbon (TOC) contents (Supplementary Fig. S6a, b). This not only indicates the importance of sulfide (i.e., the transformation of molybdate to oxythiomolybdate as a mechanism of fixing Mo into euxinic sediments) but also organic matter as a primary carrier of Mo. Although Mn oxides transported Mo from shallow to deep waters, the adsorbed Mo was subsequently released into euxinic waters after Mn oxide reduction and then captured by organic matter and sulfides, thus decoupling the Mn and Mo contents (Supplementary Fig. S6c). There is a clear negative correlation between Mn contents and δ^{98} Mo values (Fig. 3b), reflecting the significant influence of Mn oxides on Mo isotopic

Fig. 5 | Mo isotopic fractionation and modeling results. a Mo contents versus δ^{98} Mo values for Mn-rich sediments of various ages. Data for Baltic sapropels, Datangpo Mn ores, and Morro da Mina Mn ores are from ref. 63 and references therein. Data for Black Sea sediments are from ref. 45 and references therein. Dashed lines are the contemporaneous δ^{98} Mo_{sw} values. **b** Modeling results for the δ^{98} Mo values of the Mn carbonates and black shales in response to the various Mo sinks.



fractionation. Notably, Mn oxides exert a greater impact on δ^{98} Mo values in the Mn carbonates compared to that in the black shales, as indicated by the stronger correlation ($R^2 = 0.590$ for Mn carbonates versus 0.266 for black shales; Supplementary Fig. S6d).

Hence, we propose two distinct patterns of Mo cycling during the deposition of Mn carbonates and black shales in the upper Doushantuo Formation of South China. Paleogeographic reconstruction suggests that our section was located in a slope setting, evidenced by the co-existence of black shales and Mn carbonates⁵⁵ and abundant gravity-driven sedimentary structures (such as meter-scale slump folds from soft sediment deformation)²². During the contraction of the euxinic zone at the shelf margin slope, an increased influx of oxygenated open seawater oxidized the dissolved Mn(II) in previously anoxic waters to insoluble Mn oxides. The strong affinity of Mo and V for Mn oxides, combined with the preferential

adsorption of isotopically light Mo ($\Delta_1 = 3\%$), caused V and isotopically light Mo to be sequestered into Mn oxides. As Mn oxides were later reduced in the Mn reduction zone, the adsorbed molybdate was released and gradually converted into thiomolybdate in euxinic waters ($\Delta_2 = 0.7\%$), which was then fixed by organic matter and sulfides ($\Delta_3 = 0.5\%$). The Mn(II) released by Mn oxide reduction in the O₂-depleted water column then reprecipitated as Mn carbonate, inheriting negative δ^{98} Mo values. These Mn oxide shuttles preferred enriching Mo and V compared with U (Fig. 7a) and thus appeared to be the main controlling factor on Mo isotopic fractionation during this stage (Supplementary Fig. S5).

By contrast, the broader euxinic zone at the shelf margin experienced minimal influence from oxygenated open seawater during the deposition of the Mn-depleted black shales. The effects of Mn oxides on δ^{98} Mo values (Δ_1) were thus weaker, with euxinic conditions dominating the Mo species



Fig. 6 | Relation between Mo and TOC in Member IV of the Doushantuo Formation. a Plot of sediment Mo versus TOC. b Plot of deep-water $[Mo]_{aq}$ versus sediment Mo_{auth}/TOC ratios. The linear correlation was constrained by geochemical data obtained from the four annotated modern basins with varying restriction⁶⁴.



Fig. 7 | Schematic models of the geochemical cycling of multiple redox-sensitive elements during deposition of the upper Doushantuo Formation. a During the deposition of Mn carbonates. b During the deposition of black shales. The widths of the arrows represent the intensity of elemental flux.

transformations and isotopic fractionations (Δ_2 and Δ_3). Consequently, the black shales record δ^{98} Mo values are slightly lower than δ^{98} Mo_{sw} but higher than those in Mn carbonates (Fig. 7b). With U displaying a low affinity for Mn oxides, the enrichment levels of U in both Mn carbonates and black shales remain consistent. However, the enrichment levels of Mo and V decrease markedly in the black shales compared to the Mn carbonates due to a limited effect of the Mn oxide shuttle.

Our geochemical data from Mn carbonates and associated black shales in the upper Doushantuo Formation, located on the northern margin of the Yangtze Block in South China, revealed key insights into local paleo-oceanic redox conditions, Mn mineralization processes, and Mo cycling during the NOE. The presence of near-modern $\delta^{98}Mo_{sw}$ (1.9‰) and $\delta^{15}N_{sed}$ (4.19 ± 1.96‰) values, alongside elevated Fe speciation ratios, indicate that the paleo-oceanic redox structure resembled that of the modern oxygenated ocean, albeit with localized deep, euxinic zones on the shelf margin. The contraction of these euxinic zones, driven by increased oxygenation, facilitated the oxidation of dissolved Mn to insoluble Mn oxides, which played a critical role in the subsequent Mn carbonate mineralization. This transition between anoxic and oxygenated conditions also regulated Mn-associated Mo cycling, explaining the observed low δ^{98} Mo values in the Mn carbonates. Our findings suggest that Mn carbonates serve as a record of oxidation events in deep time, capturing redox fluctuations during the NOE. These localized shifts in redox conditions were pivotal for Mn cycling and mineralization, as well as for regulating the coupled Mo cycling process.

Methods

Samples

A total of 18 samples were collected, including 11 Mn carbonates and 7 black shales. All samples were washed with Milli-Q water before being ground to powder (200 mesh) using an agate mortar and pestle. The powders were separated into several aliquots for geochemical analyses, including N isotopes, Fe speciation, and Mo contents and isotopes.

Petrographic and mineralogical examination

The petrographic observation was performed using a Nikon LHS2H100C21 optical microscopy under transmitted and reflected light model. Powder X-ray diffraction analyses of bulk samples involved a Rigaku Dmax Rapid II X-ray diffractometer with a rotating anode Mo target X-ray source. Data processing and mineral identification were performed using the Jade 6.0 software. High-resolution in situ micro-mineralogical identification on thin sections was determined using micro-Raman spectroscopy (LabRAM HR Evolution) equipped with a diode-pumped solid-state laser of the wavelength of 532 nm (green). Mineral identification was based on the RRUFF Database (http://rruff.info/) of standard minerals.

Elemental analyses and calculation

The major and trace element data (except for Mo), and TOC contents were obtained from our previous works^{23,36}. Enrichment factors (EFs) and authigenic (auth) trace element contents were standardized relative to the UCC⁵⁶ and are defined as $X_{EF} = [X/A]_{sample}/[X/AI]_{UCC}^{20}$ and $[X]_{auth} = [X]_{sample} - [X]_{UCC}/[AI]_{UCC} \times [AI]_{sample}^{57}$, respectively, where X represents trace elements such as Mo, U, and V.

Isotopic and Fe speciation analyses

Nitrogen isotopes were analyzed by 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. For the extraction of pyrite, we adopted the Cr reduction method proposed by Canfield⁵⁸. Iron speciation, including Fe_{carb} (Fe in carbonate), Fe_{ox} (Fe in oxides), and Fe_{mag} (Fe in magnetite), was determined by sequential extraction following the protocols of Poulton and Canfield⁵⁹. Molybdenum contents and isotopic compositions were determined using the double-spike method according to the protocols of Li⁶⁰. The detailed analytical methods are presented in Supplementary Note 2.

Data availability

The data underlying the research presented in our paper is available in the Supplementary Information and the data table has been deposited in Figshare⁶¹ (Zhang Bin⁶¹, https://doi.org/10.6084/m9.figshare.27135192.v1).

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References

- 1. Dodd, S. M. et al. Uncovering the Ediacaran phosphorus cycle. *Nature* **618**, 974–980 (2023).
- 2. Ding, W. et al. Early animal evolution and highly oxygenated seafloor niches hosted by microbial mats. *Sci. Rep.* **9**, 13628 (2019).
- Lyons, T. W. et al. The rise of oxygen in Earth's early ocean and atmosphere. *Nature* 506, 307–315 (2014).
- 4. Fike, D. A. et al. Oxidation of the Ediacaran Ocean. *Nature* **444**, 744–747 (2006).
- Canfield, D. E. et al. Late Neoproterozoic deep-ocean oxygenation and the rise of animal life. Science **315**, 92–95 (2007).
- Sahoo, S. K. et al. Ocean oxygenation in the wake of the Marinoan glaciation. *Nature* 489, 546–549 (2012).
- Ader, M. et al. Ocean redox structure across the Late Neoproterozoic Oxygenation Event: a nitrogen isotope perspective. *Earth Planet. Sci. Lett.* **396**, 1–13 (2014).
- Canfield, D. E. et al. Ferruginous conditions dominated later Neoproterozoic deep-water chemistry. *Science* 321, 949–952 (2008).
- 9. Li, C. et al. A stratified redox model for the Ediacaran Ocean. *Science* **328**, 80–83 (2010).
- Kristensen, E. et al. Temporal behavior of manganese and iron in a sandy coastal sediment exposed to water column anoxia. *Estuar. Coast.* 26, 690–699 (2003).
- Johnson, J. E. et al. Manganese mineralogy and diagenesis in the sedimentary rock record. *Geochim. Cosmochim Acta* **173**, 210–231 (2016).
- Huang, Q. et al. Thermochemical oxidation of methane by manganese oxides in hydrothermal sediments. *Commun. Earth Environ.* 4, 224 (2023).
- Calvert, S. & Pedersen, T. Sedimentary geochemistry of manganese; implications for the environment of formation of manganiferous black shales. *Econ. Geol.* **91**, 36–47 (1996).
- Planavsky, N. J. et al. Evidence for oxygenic photosynthesis half a billion years before the Great Oxidation Event. *Nat. Geosci.* 7, 283–286 (2014).
- Yan, H. et al. Mineral paragenesis in Paleozoic manganese ore deposits: Depositional versus post-depositional formation processes. *Geochim. Cosmochim. Acta* 325, 65–86 (2022).
- Wittkop, C. et al. Evaluating a primary carbonate pathway for manganese enrichments in reducing environments. *Earth Planet. Sci. Lett.* 538, 116201 (2020).
- Chen, F. G. et al. Carbonate-hosted manganese deposits and ocean anoxia. *Earth Planet. Sci. Lett.* 622, 118385 (2023).
- Stüeken, E. E. et al. The evolution of Earth's biogeochemical nitrogen cycle. *Earth-Sci. Rev.* 160, 220–239 (2016).
- Poulton, S. W. & Canfield, D. E. Ferruginous conditions: a dominant feature of the ocean through Earth's history. *Elements* 7, 107–112 (2011).

- Algeo, T. J. & Tribovillard, N. Environmental analysis of paleoceanographic systems based on molybdenum–uranium covariation. *Chem. Geol.* 268, 211–225 (2009).
- 21. Sui, Y. et al. Astronomical time scale for the middle-upper Doushantuo Formation of Ediacaran in South China: implications for the duration of the Shuram/Wonoka negative δ^{13} C excursion. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **532**, 109273 (2019).
- Wang, H. et al. Ediacaran extension along the northern margin of the Yangtze Platform, South China: constraints from the lithofacies and geochemistry of the Doushantuo Formation. *Mar. Petrol. Geol.* **112**, 1–17 (2020).
- Zhang, B. et al. Dynamic biogeochemical cycling and mineralization of manganese of hydrothermal origin after the Marinoan glaciation. *Chem. Geol.* 584, 120502 (2021).
- Tesdal, J. E. et al. Nitrogen isotopes in bulk marine sediment: linking seafloor observations with subseafloor records. *Biogeosciences* 10, 101–118 (2013).
- 25. Fulton, J. M. et al. Black Sea nitrogen cycling and the preservation of phytoplankton δ^{15} N signals during the Holocene. *Global Biogeochem. Cy.* **26**, 1–15 (2012).
- Cremonese, L. et al. Marine biogeochemical cycling during the early Cambrian constrained by a nitrogen and organic carbon isotope study of the Xiaotan section, South China. *Precambrian Res.* 225, 148–165 (2013).
- Kikumoto, R. et al. Nitrogen isotope chemostratigraphy of the Ediacaran and Early Cambrian platform sequence at Three Gorges, South China. *Gondwana Res.* 25, 1057–1069 (2014).
- Spangenberg, J. E. et al. Redox variations and bioproductivity in the Ediacaran: evidence from inorganic and organic geochemistry of the Corumbá Group, Brazil. *Gondwana Res.* 26, 1186–1207 (2014).
- Clarkson, M. O. et al. Assessing the utility of Fe/Al and Fe-speciation to record water column redox conditions in carbonate-rich sediments. *Chem. Geol.* 382, 111–122 (2014).
- Hoffman, P. F. & Lamothe, K. G. Seawater-buffered diagenesis, destruction of carbon isotope excursions, and the composition of DIC in Neoproterozoic oceans. *Proc. Natl Acad. Sci. USA* **116**, 18874–18879 (2019).
- Cui, H. et al. An authigenic response to Ediacaran surface oxidation: remarkable micron-scale isotopic heterogeneity revealed by SIMS. *Precambrian Res.* 377, 106676 (2022).
- 32. Yang, C. et al. The tempo of Ediacaran evolution. *Sci. Adv.* **7**, eabi9643 (2021).
- Zhang, B. et al. A new negative carbon isotope interval caused by manganese redox cycling after the Shuram excursion. *J. Geophys. Res Sol. Earth* **129**, e2023JB028307 (2024).
- Okita, P. M. et al. Isotopic evidence for organic matter oxidation by manganese reduction in the formation of stratiform manganese carbonate ore. *Geochim. Cosmochim. Acta* 52, 2679–2685 (1988).
- Polgári, M. et al. Stable isotope evidence for the origin of the Úrkút manganese ore deposit, Hungary. J. Sediment. Petrol. 61, 384–393 (1991).
- Zhang, B. et al. Microbially-mediated Mn redox cycling and Mn carbonate precipitation in the Marinoan glacial aftermath, South China. *Glob. Planet. Change* **217**, 103950 (2022).
- Ostrander, C. M. et al. Multiple negative molybdenum isotope excursions in the Doushantuo Formation (South China) fingerprint complex redox-related processes in the Ediacaran Nanhua Basin. *Geochim. Cosmochim. Acta* 261, 191–209 (2019).
- Brinza, L. et al. Experimental and simulation adsorption of Mo and V onto ferrihydrite. Sci. Rep UK 9, 1365 (2019).
- Barling, J. & Anbar, A. D. Molybdenum isotope fractionation during adsorption by manganese oxides. *Earth Planet. Sci. Lett.* **217**, 315–329 (2004).
- Kendall, B. et al. Uranium and molybdenum isotope evidence for an episode of widespread ocean oxygenation during the late Ediacaran Period. *Geochim. Cosmochim. Acta* **156**, 173–193 (2015).

- Gao, Z. F. et al. Insights into hydrothermal controls and processes leading to the formation of the late Ediacaran Gaoyan stratiform manganese-carbonate deposit, Southwest China. *Ore Geol. Rev.* 139, 104524 (2021).
- Tan, Z. Z. et al. Molybdenum isotope evidence from restricted-basin mudstones for an intermediate extent of oxygenation in the late Ediacaran Ocean. *Chem. Geol.* 623, 121410 (2023).
- Neubert, N. et al. Sulfidity controls molybdenum isotope fractionation into euxinic sediments: evidence from the modern Black Sea. *Geology* 36, 775–778 (2008).
- 44. Wei, G. Y. et al. Global marine redox evolution from the late Neoproterozoic to the early Paleozoic constrained by the integration of Mo and U isotope records. *Earth Sci. Rev.* **214**, 103506 (2021).
- Nägler, T. F. et al. Molybdenum isotope fractionation in pelagic euxinia: evidence from the modern Black and Baltic Seas. *Chem. Geol.* 289, 1–11 (2011).
- Siebert, C. et al. Molybdenum isotope records as a potential new proxy for paleoceanography. *Earth Planet. Sci. Lett.* **211**, 159–171 (2003).
- Dickson, A. J. A molybdenum-isotope perspective on Phanerozoic deoxygenation events. *Nat. Geosci.* 10, 721–726 (2017).
- Kendall, B. et al. The stable isotope geochemistry of molybdenum. *Rev. Mineral. Geochem.* 82, 683–732 (2017).
- Qin, Z. et al. Molybdenum isotope-based redox deviation driven by continental margin euxinia during the early Cambrian. *Geochim. Cosmochim. Acta* 325, 152–169 (2022).
- Daye, M. et al. Light-driven anaerobic microbial oxidation of manganese. *Nature* 576, 311–314 (2019).
- Liu, W. et al. Anoxic photogeochemical oxidation of manganese carbonate yields manganese oxide. *Proc. Natl Acad. Sci. USA* **117**, 22698–22704 (2020).
- 52. Farquhar, J. et al. Atmospheric influence of Earth's earliest sulfur cycle. *Science* **289**, 756–758 (2000).
- Morgan, J. J. Kinetics of reaction between O₂ and Mn(II) species in aqueous solutions. *Geochim. Cosmochim. Acta* 69, 35–48 (2005).
- Maynard, J. B. The chemistry of manganese ores through time: a signal of increasing diversity of Earth-surface environments. *Econ. Geol.* **105**, 535–552 (2010).
- Jiang, G. Q. et al. Stratigraphy and paleogeography of the Ediacaran Doushantuo formation (ca. 635–551 Ma) in south China. *Gondwana Res.* **19**, 831–849 (2011).
- Taylor, S. R. & McLennan, S. M. The Continental Crust: Its Composition and Evolution. An Examination of the Geochemical Record Preserved in Sedimentary Rocks 312 (Blackwell Scientific Publications, Oxford, 1985).
- 57. Zhou, L. et al. U/Mo ratios and $\delta^{98/95}$ Mo as local and global redox proxies during mass extinction events. *Chem. Geol.* **324–325**, 99–107 (2012).
- Canfield, D. E. et al. The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chem. Geol.* 54, 149–155 (1986).
- Poulton, S. W. & Canfield, D. E. Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. *Chem. Geol.* **214**, 209–221 (2005).
- Li, J. et al. Measurement of the isotopic composition of molybdenum in geological samples by MC-ICP-MS using a novel chromatographic extraction Technique. *Geostand. Geoanal. Res.* 38, 345–354 (2014).
- Zhang, B. Coupled oxygenation, manganese carbonate mineralization, and Mo cycling during the Neoproterozoic ocean. figshare https://doi. org/10.6084/m9.figshare.27135192.v1 (2024).

- Wang, Z. F. et al. Tracing Earth's oxygenation events using metal stable isotopes. *Earth Sci.* (in Chinese with English abstract) CN 42-1874/P, 1–37 (2021).
- 63. Tan, Z. Z. et al. Geochemistry and molybdenum isotopes of the basal Datangpo formation: implications for ocean-redox conditions and organic matter accumulation during the Cryogenian interglaciation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **563**, 110169 (2021).
- Algeo, T. J. & Rowe, H. Paleoceanographic applications of tracemetal concentration data. *Chem. Geol.* 324–325, 6–18 (2012).

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Author contributions

B.Z., J.C., and K.H. designed and conceived the study; Z.B., Z.W.L., R.J.Z., Y.Z., and C.H.S. collected the samples; B.Z., and R.J.Z. contributed to the data curation; B.Z., J.C., K.H., and K.O.K. contributed to writing and editing the original draft.

Competing interests

The authors declare no competing interests.

Additional information

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