

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

Corresponding Author: Dr Jian Cao

This file contains all editorial decision letters in order by version, followed by all author rebuttals in order by version.

Attachments originally included by the reviewers as part of their assessment can be found at the end of this file.

Version 0:

Decision Letter:

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Dear Dr Cao,

Your manuscript titled "Coupled oxygenation, manganese carbonate mineralization, and Mo cycling during the Neoproterozoic ocean" has now been seen by 2 reviewers, and we include their comments at the end of this message. They find your work of interest, but some important points are raised. We are interested in the possibility of publishing your study in Communications Earth & Environment, but would like to consider your responses to these concerns and assess a revised manuscript before we make a final decision on publication.

We therefore invite you to revise and resubmit your manuscript, along with a point-by-point response that takes into account the points raised. Please highlight all changes in the manuscript text file.

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**** Present a compelling and clear assessment of the extent to which the $\delta^{15}\text{N}$ can be spatially extrapolated, addressing the reviewer's #1 discussion point.**

**** Justify your estimation of the Ediacaran $\delta^{98}\text{Mo}$ values.**

**** Provide more petrographic details about your samples either on the main text or in the Supplementary Data.**

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Please do not hesitate to contact us if you have any questions or would like to discuss these revisions further. We look forward to seeing the revised manuscript and thank you for the opportunity to review your work.

Best regards,

Carolina Ortiz Guerrero, Ph.D.
Associate Editor
Communications Earth & Environment

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and also in our style and formatting guide [Communications Earth & Environment formatting guide](https://www.nature.com/documents/commsj-phys-style-formatting-guide-accept.pdf) .

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Please refer to our data policies at http://www.nature.com/authors/policies/availability.html.

REVIEWER COMMENTS:

Reviewer #1 (Remarks to the Author):

In this manuscript, the authors provided iron (Fe) speciation, molybdenum (Mo) and nitrogen (N) data from black shales and associated Mn(II) carbonates in the upper Ediacaran Doushantuo Formation, South China. The data are well presented and reasonably explained. The topic of the manuscript fits the journal and the results provide important insights on the coupled relationship between oceanic oxygenation, Mn mineralization, and Mo geochemical cycling during the Neoproterozoic Oxygenation Event. I suggest a minor revision for the paper before it can be accepted for publication. Detailed comments including:

1. Nitrogen isotope explanation: Combined with anoxic iron speciation results, the authors attributed positive $\delta^{15}\text{N}$ signatures to partial denitrification in a redox-stratified water column, which is reasonable. In this case, I suggest the authors consider the $\delta^{15}\text{N}$ signatures as a regional signal. In a global perspective, more explanations and comments for logic are better provided, if taking the signal as evidence for oxidation level of the surface water (lines 99-101) and the oceanic redox structure (lines 260-262) by comparison with $\delta^{15}\text{N}$ signatures of the well-oxygenated modern ocean.

2. Global $\delta^{98}\text{Mo}_{\text{sw}}$ estimation: The authors cited the isotopic offset ($\Delta^{98}\text{Mo}_{\text{seawater-sediment}} = 0.5 \pm 0.3\text{‰}$) between the dissolved Mo species and authigenic solid Mo reported from the Black Sea and added 0.5‰ to the extrapolated sedimentary $\delta^{98}\text{Mo}$ value ($\sim +1.4\text{‰}$) when estimating the Ediacaran global $\delta^{98}\text{Mo}_{\text{sw}}$ (lines 158-160). This is interesting and important, yet rarely used in previous Mo isotope studies of sulfidic successions, because $\Delta^{98}\text{Mo}_{\text{seawater-sediment}}$ in the Black Sea implicates sedimentary $\delta^{98}\text{Mo}$ values close to the open ocean and heavier aqueous $\delta^{98}\text{Mo}$ values of the bottom water. The authors are suggested to reconsider the estimation of the Ediacaran global $\delta^{98}\text{Mo}_{\text{sw}}$, either modify the value or provide more evidence to support their estimation. This also helps to understand the maximum offset they calculated for Mn oxide shuttle (lines 180-185).

3. Minors:

Lines 102-103: Reliability of iron speciation results is normally screened by $\text{FeT} > 0.5 \text{ wt.}\%$ rather than $\text{FeT/Al} > 0.5$ (Clarkson, M. O., Poulton, S. W., Guilbaud, R., and Wood, R. A., 2014, Assessing the utility of Fe/Al and Fe-speciation to record water column redox conditions in carbonate-rich sediments: *Chemical Geology*, v. 382, p. 111-122.)

Lines 114-115: Negative $\delta^{13}\text{C}_{\text{carb}}$ values are quite common for the upper Doushantuo Formation though seawater $\delta^{13}\text{C}_{\text{carb}}$ values are still debated.

Reviewer #2 (Remarks to the Author):

Zhang et al. presented geochemical proxies to study ocean chemistry during the Neoproterozoic oxygenation event (NOE). They analyzed manganese-bearing carbonate rocks and black shales from the upper Ediacaran Doushantuo Formation in South China. The authors found that the redox structure of the paleo-ocean during the NOE was similar to the modern oxygenated ocean, with localized euxinic zones. They also concluded that Mn(II) oxidation in oxygenated environments is crucial for the formation of Mn carbonate. However, there are some important issues that need to be addressed before the manuscript can be accepted for publication.

Major comments:

1. The authors claim that the formation of manganese carbonate mineralization requires the prior precipitation of manganese oxides. Nevertheless, it is important for the authors to acknowledge that manganese carbonates can precipitate in an oxygen-depleted environment. How can the assertions made in the article be aligned with those put forward by Liu et al (2020)?

W. Liu et al, Anoxic photogeochemical oxidation of manganese carbonate yields manganese oxide. *Proc. Natl. Acad. Sci. U.S.A.* 117, 22698-22704 (2020).

2. It would be beneficial for the authors to delve into a more detailed discussion of ocean chemistry over time or in the Neoproterozoic in the paper's introduction. This would provide context since the authors are questioning the oxygenation levels of the oceans during the NOE (Lines 46-47). Clarifying the specific ocean referenced would be helpful, as surface waters have primarily been oxygenated since the Paleoproterozoic. Conversely, mid and deep waters exhibited variations between ferruginous, euxinic, and oxic conditions towards the Neoproterozoic, until the ocean became predominantly oxic near the Phanerozoic.

3. It would be helpful for the authors to provide a brief petrography section (it could go into a supplementary document). There are samples with approximately 35% Mn (e.g., ID-3-15; Table S1-data), and given this high content, is there no precipitation of oxide phases, such as pyrolusite, cryptomelane, etc.? Also, why is there a 2.71% Mn content (ID-3-23) in a sample of black shale? Solving these questions can help to understand some trends in the isotopic data presented.

4. It's important to consider the depositional systems of the Ediacaran Doushantuo Formation in order to fully understand

some of the authors' conclusions. For instance, when the authors mention the contraction of the euxinic zone at the platform margin (Line 238), it's worth noting that platform margins typically feature shallow water depths of up to 200m. Even in the Neoproterozoic era, these shallow marine environments should have been oxygenated.

Specific comments

1. Line 19-20: "High Fe speciation ratios ($F_{py}/F_{HR} > 0.8$) imply a localized marginal deep euxinic zone." Please specify which samples (black shales, Mn-carbonate, or both?) showed high Fe speciation ratios.
2. Line 20-21: "The estimated Ediacaran seawater Mo isotopic ($\delta^{98}\text{Mosw} = 1.9\text{‰}$) and Ediacaran sedimentary N isotopic compositions ($\delta^{15}\text{N}_{\text{sed}} = 4.19 \pm 1.96\text{‰}$) both closely resembled the modern $\delta^{98}\text{Mosw}$ (2.34‰) and $\delta^{15}\text{N}_{\text{sed}}$ (5‰) values, corroborating an oxygenated surface seawater overlay euxinic bottom water". As with the above, please specify if these isotopic valleys are from black shales or, Mn-carbonate or both.
3. Line 34: Please provide the section's name (Introduction?) before the main text.
4. Line 51: I suggest that the authors delete "widely" from the sentence since, as the authors themselves state below, there is disagreement about the conditions of precipitation of manganese carbonates.
5. Line 115-118: "Our finding of residual Mn oxides (i.e., todorokite; ref.25) in the studied Mn(II) carbonates, coupled with the positive cerium anomalies¹⁹, unequivocally indicate that the formation of these Mn carbonates did not involve direct precipitation of Mn(II) in anoxic waters. Instead, it likely involved the reduction of a Mn oxide precursor". What is the origin of todorokite? Could it be a post-diagenetic or even supergene mineral?
6. Line 119: Please explain the probable precursor of the Mn oxide in the text.
7. Line 124-126: In mildly reducing and non-sulfidic anoxic waters, vanadate is transformed into vanadyl ions (VO_2^-) and hydroxyl forms. Under strongly reducing conditions in a euxinic environment with free H_2S , V^{3+} phases are further reduced to insoluble hydroxide forms.
8. Line 142: "However, there is no significant enrichment of Mn in those shales". Please explain why some shales have higher Mn values than the crustal averages (e.g. PAAS and UCC; around 0.1%).
9. Line 233: Please, exclude "indeed" of the sentence
10. Line 236: " $R^2 = 0.590$ " is not a strong correlation.
11. Line 298-299: "Simplified stratigraphy of the Doushantuo 298 Formation on the Yangtze Platform (modified from refs.18,20)." Do the numbers 1,2,3 and 4 refer to the members?
12. Figure 3: Please revise Figure 3. In Figure 3b, there is an arrow referring to Figure 2b; I believe it is Figure 3c. Figure 3d also needs to be better referenced.

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Decision Letter:

<*** REMEMBER TO ATTACH REVISIONS CHECKLIST (WORD)***>

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Dear Dr Cao,

Your revised manuscript titled "Coupled oxygenation, manganese carbonate mineralization, and Mo cycling in the Neoproterozoic ocean" has now been seen by our original reviewers, whose comments appear below. In light of their advice we are delighted to say that we are happy, in principle, to publish a suitably revised version in Communications Earth & Environment.

We therefore ask that you edit your manuscript to comply with our format requirements and to maximise the accessibility and therefore the impact of your work.

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We hope to hear from you within two weeks; please let us know if you need more time.

Best regards,

Carolina Ortiz Guerrero, Ph.D.
Associate Editor
Communications Earth & Environment

REVIEWERS' COMMENTS:

Reviewer #1 (Remarks to the Author):

The authors have carefully revised the manuscript following the comments I provided on the last version, and clearly explained how they revised the manuscript in the response letter. I have no further comments on the revised version. This is a nice contribution to understanding both the Neoproterozoic paleoenvironment and manganese mineralization. Therefore, I recommend acceptance and a quick publication of the manuscript.

Reviewer #2 (Remarks to the Author):

The author has thoroughly addressed all my concerns and made the necessary adjustments. I recommend accepting the manuscript.

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Detailed Response (R) Reviewers

Please note that all key revisions have been highlighted by blue for easy tracking in the revised manuscript.

Response to Reviewer #1

In this manuscript, the authors provided iron (Fe) speciation, molybdenum (Mo) and nitrogen (N) data from black shales and associated Mn(II) carbonates in the upper Ediacaran Doushantuo Formation, South China. The data are well presented and reasonably explained. The topic of the manuscript fits the journal and the results provide important insights on the coupled relationship between oceanic oxygenation, Mn mineralization, and Mo geochemical cycling during the Neoproterozoic Oxygenation Event. I suggest a minor revision for the paper before it can be accepted for publication. Detailed comments including:

R: Thank you very much for your careful reviews, constructive comments, and positive evaluation on our work. As noted, your comments have been addressed in detail. Please see the responses below and the revised manuscript for details.

1. Nitrogen isotope explanation: Combined with anoxic iron speciation results, the authors attributed positive $\delta^{15}\text{N}$ signatures to partial denitrification in a redox-stratified water column, which is reasonable. In this case, I suggest the authors consider the $\delta^{15}\text{N}$ signatures as a regional signal. In a global perspective, more explanations and comments for logic are better provided, if taking the signal as evidence for oxidation level of the surface water (lines 99-101) and the oceanic redox structure (lines 260-262) by comparison with $\delta^{15}\text{N}$ signatures of the well-oxygenated modern ocean.

R: Thank you very much for your constructive comments, along which we added more comments for clarity. According to your comments, on the basis of the data obtained in this paper, we further 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) (Cremonese et al., 2013; Ader et al., 2014; Kikumoto et al., 2014; Spangenberg et al., 2014). It can be found that these data are generally consistent with those obtained in this paper, suggestive of a global redox signal rather than a local one (Ader et al., 2014). In detail, almost all Ediacaran sedimentary N isotope values are higher than 0‰ and comparable to those of modern marine sediments (Tesdal et al., 2011), indicating that the Ediacaran ocean had a large nitrate reservoir and the surface ocean was generally oxygenated with a deeper redox interface. Under this condition, the N-cycle pattern is similar to that of the modern ocean, suggesting that the oxidation degree of the surface seawater and the oceanic redox structure during this period may have been much similar to those of the modern ocean.

Please see the added comments above for clarity in Lines 112-118 on Page 6 of the main text, and Fig. S3 in Supplementary Materials for clarity.

2. Global $\delta^{98}\text{Mo}_{\text{sw}}$ estimation: The authors cited the isotopic offset ($\Delta^{98}\text{Mo}_{\text{seawater-sediment}} = 0.5 \pm 0.3\text{‰}$) between the dissolved Mo species and authigenic solid Mo reported from the Black Sea and added 0.5‰ to the extrapolated sedimentary $\delta^{98}\text{Mo}$ value ($\sim +1.4\text{‰}$) when estimating the Ediacaran global $\delta^{98}\text{Mo}_{\text{sw}}$ (lines 158-160). This is interesting and important, yet rarely used in previous Mo isotope studies of sulfidic successions, because $\Delta^{98}\text{Mo}_{\text{seawater-sediment}}$ in the Black Sea implicates sedimentary

$\delta^{98}\text{Mo}$ values close to the open ocean and heavier aqueous $\delta^{98}\text{Mo}$ values of the bottom water. The authors are suggested to reconsider the estimation of the Ediacaran global $\delta^{98}\text{Mo}_{\text{sw}}$, either modify the value or provide more evidence to support their estimation. This also helps to understand the maximum offset they calculated for Mn oxide shuttle (lines 180-185).

R: Thank you very much for your expert comments. If the Mo isotope value ($\sim 1.4\text{‰}$) calculated through the linear regression equation between Mn contents and Mo isotopes in euxinic black shales is considered to be the Mo isotopic composition of contemporaneous seawater, it is significantly lower than the maximum Mo isotope value ($\sim 2\text{‰}$; Kendall et al., 2015; Ostrander et al., 2019) detected in black shales of the Doushantuo Formation Member IV by predecessors. This does not conform to the basic principle of sedimentary Mo isotope geochemistry, that is, the Mo isotope value of sediments is generally lower than or equal to that of contemporaneous seawater. The heaviest Mo isotope value in strong euxinic sediments is thus approximately representative of that of seawater (Wei et al., 2021), since light Mo preferentially sinks to sediments while heavy Mo tends to reside in seawater. It can be concluded that the original estimated Mo isotope value of $\sim 1.4\text{‰}$ cannot reliably represent the Mo isotope compositions of contemporaneous seawater, which is significantly lower than the true seawater Mo isotope compositions ($\sim 2\text{‰}$). Notably, studies have shown that there is a small fractionation ($\sim 0.5 \pm 0.3\text{‰}$) of Mo isotope value between the sediment and ambient strong euxinic waters (e.g., modern Black Sea) (Arnold, et al., 2004; Nagler et al., 2011; Bruske et al., 2020), which shed lights on reconciling these contradictory estimations. Hereby, we conservatively employed this fractionation (0.5‰) to recalculate the seawater Mo isotope compositions during the deposition of the Doushantuo Formation Member IV. The calculated results are higher than 1.9‰ , which is comparable to the highest Mo isotopes ($\sim 2\text{‰}$) measured in the equivalent black shales in South China. This aligns with the basic principle of sedimentary Mo isotope geochemistry (Neubert et al., 2008; Nagler et al., 2011), that is, the maximum sediment Mo isotope value is basically similar to that of ambient seawater.

Please see the added comments above in Lines 192-212 on Pages 9-10 of the main text and Lines 151-154 on Page 7 in the Supplementary Materials for clarity.

3. Minors:

Lines 102-103: Reliability of iron speciation results is normally screened by $\text{Fe}_\text{T} > 0.5 \text{ wt.}\%$ rather than $\text{Fe}_\text{T}/\text{Al} > 0.5$ (Clarkson, M. O., Poulton, S. W., Guilbaud, R., and Wood, R. A., 2014, Assessing the utility of Fe/Al and Fe-speciation to record water column redox conditions in carbonate-rich sediments: *Chemical Geology*, v. 382, p. 111-122.)

R: We replaced the proxy of “ $\text{Fe}_\text{T}/\text{Al}$ ” with “ Fe_T ”. Please see Lines 119-121 on Page 6 in the revised main text and Lines 125-130 on Page 6 in the Supplementary Materials for details.

Lines 114-115: Negative $\delta^{13}\text{C}_{\text{carb}}$ values are quite common for the upper Doushantuo Formation though seawater $\delta^{13}\text{C}_{\text{carb}}$ values are still debated.

R: Thank you very much for your constructive comments, along which we added more comments for clarity. As you commented, the C isotopic compositions of Neoproterozoic seawater are still debated. However, a few investigations proposed that the seawater C isotopic value might be normally close to or slightly higher than 0‰ (Hoffman and Lamothe, 2019; Cui et al., 2022). Notably, the negative C isotope values of the Mn carbonates (low to -11‰) in the Doushantuo Formation Member IV of this study is generally lower than those of speculated Ediacaran seawater and contemporaneous carbonate rocks in other cratons (Yang et al., 2021). In addition, the C isotope values of Mn carbonates (low to -11‰) are significantly lower than that of coexisted dolostone

(around 0‰) and there is a negative correlation between Mn contents and C isotope values (Zhang et al., 2021, 2024). This indicates a mechanism of Mn oxides reduction coupled with organic C mineralization (Okita et al., 1988; Polgári et al., 1991). Therefore, the abnormally low C isotopic values of Mn carbonates in the Doushantuo Formation Member IV of this study are related to the formation of Mn carbonate minerals, which is indicative of Mn carbonate formation mechanism.

Please see the added comments above for clarity in Lines 131-136 on Pages 6-7 for details.

Response to Reviewer #2

Zhang et al. presented geochemical proxies to study ocean chemistry during the Neoproterozoic oxygenation event (NOE). They analyzed manganese-bearing carbonate rocks and black shales from the upper Ediacaran Doushantuo Formation in South China. The authors found that the redox structure of the paleo-ocean during the NOE was similar to the modern oxygenated ocean, with localized euxinic zones. They also concluded that Mn(II) oxidation in oxygenated environments is crucial for the formation of Mn carbonate. However, there are some important issues that need to be addressed before the manuscript can be accepted for publication.

R: Thank you very much for your positive evaluation and careful reviews on our manuscript. Your time and effort expended on the manuscript are greatly appreciated. As noted, your comments have been addressed point by point. Please see the responses below and the revised manuscript for details.

Major comments:

1. The authors claim that the formation of manganese carbonate mineralization requires the prior precipitation of manganese oxides. Nevertheless, it is important for the authors to acknowledge that manganese carbonates can precipitate in an oxygen-depleted environment.

R: Thank you very much for your expert comments. We agree with you that Mn carbonates can precipitate in an oxygen-depleted environment, which is another pathway for the formation of Mn carbonate minerals in addition to the mechanism of our study and has been verified in many cases (Wittkop et al., 2020). This, however, is not the primary origin of the Mn carbonates of this study. Multiple lines of evidence, including the extremely negative C isotopic compositions (low to -11‰), positive Ce anomaly, Mn oxide residues (i.e., todorokite) (Zhang et al., 2021, 2022), enrichment pattern of Mo-U, and the obviously low Mo isotopic compositions, collectively suggest a Mn oxide precursor for the formation of the Mn carbonate minerals in the Doushantuo Formation Member IV, South China.

Please see the added comments above for clarity in Lines 131-170 on Pages 6-8 for details.

How can the assertions made in the article be aligned with those put forward by Liu et al (2020)? W. Liu et al, Anoxic photogeochemical oxidation of manganese carbonate yields manganese oxide. Proc. Natl. Acad. Sci. U.S.A. 117, 22698-22704 (2020).

R: The simulation experiment of Liu et al. (2020) argued that the photochemical oxidation of rhodochrosite can also produce high-valent Mn hydroxide under the condition of ultraviolet irradiation (with wavelength of ~230 nm), and this process might be dominant in the Archean with low atmospheric O₂ concentrations. However, this pathway is 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 have increased significantly compared with those pre-GOE. The increase of atmospheric oxygen concentration promoted the establishment of stratospheric ozone shield, which

filtered high-energy ultraviolet light (Farquhar et al., 2000). 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 tend to be the main ways of Mn oxide formation before the precipitation of Mn carbonate minerals in this period (Morgan et al., 2005). This aligns with the temporally coupled relationship between sedimentary Mn and atmospheric O₂ concentrations (Maynard, 2010).

Please see the added comments above for clarity in Lines 277-293 on Pages 13-14 for details.

2. It would be beneficial for the authors to delve into a more detailed discussion of ocean chemistry over time or in the Neoproterozoic in the paper's introduction. This would provide context since the authors are questioning the oxygenation levels of the oceans during the NOE (Lines 46-47). Clarifying the specific ocean referenced would be helpful, as surface waters have primarily been oxygenated since the Paleoproterozoic. Conversely, mid and deep waters exhibited variations between ferruginous, euxinic, and oxic conditions towards the Neoproterozoic, until the ocean became predominantly oxic near the Phanerozoic.

R: The atmospheric O₂ concentration persistently increased from the early to late Ediacaran and the *p*O₂ in the atmosphere reached 60–100% of the present atmospheric level (PAL) at the end-Ediacaran (Ding et al., 2019). Some proxies indicate a progressively oxygenated Neoproterozoic ocean (Fike et al., 2006; Sahoo et al., 2012; Ader et al., 2014; Dodd et al., 2023). However, other geochemical proxies suggest the existence of a predominantly anoxic and strongly stratified Ediacaran ocean with a very shallow redox interface (Li et al., 2010; Planavsky et al., 2011; Poulton & Canfield, 2011). These findings indicate a complex pattern of redox conditions during this period. Surface waters have primarily been oxygenated since the Paleoproterozoic. Conversely, mid and deep waters exhibited variations between ferruginous, euxinic, and oxic conditions towards the Neoproterozoic, until the ocean became predominantly oxic during the early Phanerozoic. The main challenge lies in determining whether mid-to-deep ocean waters were ferruginous, euxinic, or oxic beneath oxygenated surface layers in Neoproterozoic ocean. 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 (Li et al., 2010; Ader et al., 2014). Clarifying the specific ocean redox configurations is crucial to understand the ocean chemistry and associated biogeochemical cycling and mineralization.

Please see the added comments above for clarity in Lines 32-46 on Pages 2-3 for clarity.

3. It would be helpful for the authors to provide a brief petrography section (it could go into a supplementary document).

R: We added brief petrographic description in result section and corresponding petrographic photographs for different lithologies in Supplementary Materials. Please see Lines 80-87 on Page 4 and Lines 346-354 on Pages 16-17 of the main text, Lines 33-48 on Pages 2-3 and Fig. S1 in the Supplementary Materials for clarity.

There are samples with approximately 35% Mn (e.g., ID-3-15; Table S1-data), and given this high content, is there no precipitation of oxide phases, such as pyrolusite, cryptomelane, etc.?

R: We have not found other Mn oxide mineral phases (e.g., pyrolusite and cryptomelane as you commented) in the samples with the highest Mn contents (e.g., ID-3-15). Instead, only a few Mn grains of todorokites were found in individual Mn carbonates (Zhang et al., 2022), which are the

residual after non-quantitative reduction of Mn oxides rather than the products of secondary oxidation of Mn carbonate minerals. Otherwise, the precipitation of Mn oxide phases prone to be preserved in Mn carbonates with the highest Mn contents.

Please see the added comments above for clarity in Lines 85-87 on Page 4 and Lines 136-145 on Page 7 for details.

Also, why is there a 2.71% Mn content (ID-3-23) in a sample of black shale? Solving these questions can help to understand some trends in the isotopic data presented.

R: There is a black shale with high Mn contents in our samples, which is named Mn-bearing black shale (Fig. 1c). This is because the Mn-bearing black shale is very close to the lower Mn carbonate rock and located at the transition boundary between Mn carbonates and black shales. Hence, the high Mn contents in this shale is the result of the existence of a small amount of Mn carbonate minerals (Zhang et al., 2021). The enrichment mechanism of Mn in this shale is consistent with that of Mn carbonates, that is, the reduction of Mn oxides with organic matter as electron donor. This strictly follows the trend that Mn contents are negatively correlated with C isotope values.

Please see the added comments above for clarity and Lines 134-136 on Page 7 for details.

4. It's important to consider the depositional systems of the Ediacaran Doushantuo Formation in order to fully understand some of the authors' conclusions. For instance, when the authors mention the contraction of the euxinic zone at the platform margin (Line 238), it's worth noting that platform margins typically feature shallow water depths of up to 200m. Even in the Neoproterozoic era, these shallow marine environments should have been oxygenated.

R: We agree with you that the shallow part of the ocean should have been oxygenated in the Neoproterozoic era. Notably, paleogeographic reconstruction shows that our section is located in the rift basin along the northern margin of the Yangtze Block. Petrologically, our Mn carbonates are closely associated with black shales. The black shales are a fine-grained sediment deposited in a relatively low energy sedimentary environment (Jiang et al., 2011), indicating that our section is located at a deep-water sedimentary environment. In addition, a previous study reported abundant gravity-driven sedimentary structures of meter-scale slump folds as a result of soft sediment deformation in the Doushantuo Member IV of this study (Wang et al., 2020), also suggesting that our section is located in the slope setting of continental margin rift basin rather than in a shallow platform environment. Therefore, the stratified redox structure of oxygenated surface layer and anoxic deep water is reasonable in such depositional systems, which are also supported by N isotopes and Fe speciation proxies.

Please see the added comments above for clarity in Lines 305-310 on Pages 14-15 of the main text and Lines 23-30 on Pages 1-2 of the Supplementary Materials for details.

Specific comments

1. Line 19-20: "High Fe speciation ratios ($\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}} > 0.8$) imply a localized marginal deep euxinic zone." Please specify which samples (black shales, Mn-carbonate, or both?) showed high Fe speciation ratios.

R: Both. Please see the clarification in Lines 18-21 on Page 1.

2. Line 20-21: "The estimated Ediacaran seawater Mo isotopic ($\delta^{98}\text{Mo}_{\text{sw}} = 1.9\text{‰}$) and Ediacaran sedimentary N isotopic compositions ($\delta^{15}\text{N}_{\text{sed}} = 4.19 \pm 1.96\text{‰}$) both closely resembled the modern $\delta^{98}\text{Mo}_{\text{sw}}$ (2.34‰) and $\delta^{15}\text{N}_{\text{sed}}$ (5‰) values, corroborating an oxygenated surface seawater overlay

euxinic bottom water". As with the above, please specify if these isotopic valleys are from black shales or, Mn-carbonate or both.

R: Both. Please see Lines 18-21 on Page 1 for the clarification.

3. Line 34: Please provide the section's name (Introduction?) before the main text.

R: Provided (i.e., Introduction). Please see Line 31 on Page 2.

4. Line 51: I suggest that the authors delete "widely" from the sentence since, as the authors themselves state below, there is disagreement about the conditions of precipitation of manganese carbonates.

R: Deleted for the precision of the science. Please see Lines 53-54 on Page 3.

5. Line 115-118: "Our finding of residual Mn oxides (i.e., todorokite; ref.25) in the studied Mn(II) carbonates, coupled with the positive cerium anomalies¹⁹, unequivocally indicate that the formation of these Mn carbonates did not involve direct precipitation of Mn(II) in anoxic waters. Instead, it likely involved the reduction of a Mn oxide precursor". What is the origin of todorokite? Could it be a post-diagenetic or even supergene mineral?

R: Our previous work showed that the todorokite was derived from the oxidation of Mn(II) by microorganisms during the formation of Mn carbonate minerals (Zhang et al., 2022). Subsequently, Mn oxide was reduced to dissolved Mn(II) using organic carbon as the electron donor. The todorokite is thus the residual Mn oxide retained in Mn carbonates after non-quantitative reduction. Todorokite is unlikely a post-diagenetic or even supergene mineral. This is because the todorokite only occurs in some Mn carbonates and is located between Mn carbonate minerals and is closely associated with fine-grained pyrite (Fig. S1). The well-preserved pyrite around todorokite suggests that the todorokite was not the product of diagenetic oxidation since pyrite is more readily oxidized than Mn(II)-bearing minerals (Zhang et al., 2022). Otherwise, the fine-grained syngenetic pyrite cannot be well preserved. In addition, our samples are extracted from cores buried more than 700 m deep with no signs of exposure. This excludes the possibility of post-diagenetic or even supergene oxidation of Mn carbonate to form Mn oxides.

Please see the added comments above for clarity in Lines 137-145 on Page 7 for details.

6. Line 119: Please explain the probable precursor of the Mn oxide in the text.

R: Todorokite. Please see the clarification in Lines 148-149 on Page 7.

7. Line 124-126: In mildly reducing and non-sulfidic anoxic waters, vanadate is transformed into vanadyl ions (VO_2^-) and hydroxyl forms. Under strongly reducing conditions in a euxinic environment with free H_2S , V^{3+} phases are further reduced to insoluble hydroxide forms.

R: Thank you very much for your constructive comments, along which we added the transformation of V in varied redox environments. Please see Lines 156-158 on Page 8 for details.

8. Line 142: "However, there is no significant enrichment of Mn in those shales". Please explain why some shales have higher Mn values than the crustal averages (e.g. PAAS and UCC; around 0.1%).

R: In order to avoid misunderstanding and confusion, we revised this sentence to "there is no extreme enrichment of Mn in the shales as observed in the Mn carbonates." As you commented, the Mn contents of black shales are indeed higher than that of PAAS and UCC. This is because the

charging of the deep hydrothermal fluids during the deposition of the Doushantuo Formation Member IV provides a large amount of Mn in study area (Gao et al., 2021; Zhang et al., 2021), which elevates the dissolved Mn concentration in the seawater in the rift basin. Under these conditions of high Mn background concentrations, the Mn contents of black shales will increase and be higher than those of PAAS and UCC. However, the Mn contents of black shales are significantly lower than those of Mn carbonates, reflecting varied degrees of Mn biogeochemical cycle and enrichment processes for these two lithologies. Overall, the input of hydrothermal Mn is the cause of the increase of Mn contents in the black shales in this study.

Please see the added comments above for clarity in Lines 177-180 on Page 9 for details.

9. Line 233: Please, exclude "indeed" of the sentence

R: Excluded. Please see Lines 299-301 on Page 14.

10. Line 236: " $R^2 = 0.590$ " is not a strong correlation.

R: Revised to "Notably, Mn oxides exert a greater impact on $\delta^{98}\text{Mo}$ 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; Fig. S6d)." for clarity and precision of the science. Please see Lines 301-303 on Page 14.

11. Line 298-299: "Simplified stratigraphy of the Doushantuo Formation on the Yangtze Platform (modified from refs.18,20)." Do the numbers 1,2,3 and 4 refer to the members?

R: The numbers I–IV in Fig. 1c refer to the members I–IV of the Doushantuo Formation as you commented. We added annotation in the caption of Fig. 1 for clarity. Please see Lines 375-376 on Page 18 for details.

12. Figure 3: Please revise Figure 3. In Figure 3b, there is an arrow referring to Figure 2b; I believe it is Figure 3c. Figure 3d also needs to be better referenced.

R: We revised "Fig. 2c" to "Fig. 3c" in Fig. 3 and specified the data source of Fig. 3d in the caption (i.e., Tan et al., 2023). Please see the newly revised Fig. 3 on Page 26 and Lines 384-385 on Page 18 for details.

References cited

- 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).
- Arnold, G.L. et al. Molybdenum isotope evidence for widespread anoxia in mid-Proterozoic oceans. *Science* **304**, 87–90 (2004).
- Brüske, A. et al. Correlated molybdenum and uranium isotope signatures in modern anoxic sediments: Implications for their use as paleoredox proxy. *Geochim. Cosmochim. Acta* **270**, 449–474 (2020).
- 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).
- Cui, H. et al. An authigenic response to Ediacaran surface oxidation: Remarkable micron - scale isotopic heterogeneity revealed by SIMS. *Precambrian Res.* **377**, 106676 (2022).
- Ding, W. et al. Early animal evolution and highly oxygenated seafloor niches hosted by microbial mats. *Sci. Rep.* **9**, 13628 (2019).
- Dodd, S.M. et al. Uncovering the Ediacaran phosphorus cycle. *Nature* **618**, 974–980 (2023).
- Farquhar, J. et al. Atmospheric influence of Earth's earliest sulfur cycle. *Science*, **289**, 756–758 (2000).
- Fike, D.A. et al. Oxidation of the Ediacaran Ocean. *Nature* **444**, 744–747 (2006).
- 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).
- Hoffman, P.F. & Lamothe, K.G. Seawater-buffered diagenesis, destruction of carbon isotope excursions, and the composition of DIC in Neoproterozoic oceans. *P. Natl. Acad. Sci. USA* **116**, 18874–18879 (2019).
- 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).
- 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).
- 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).
- Li, C. et al. A stratified redox model for the Ediacaran ocean. *Science* **328**, 80–83 (2010).
- Liu, W. et al. Anoxic photogeochemical oxidation of manganese carbonate yields manganese oxide. *Proc. Natl. Acad. Sci. U.S.A.* **117**, 22698–22704 (2020).
- 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).
- Morgan, J.J. Kinetics of reaction between O₂ and Mn(II) species in aqueous solutions. *Geochim. Cosmochim. Acta* **69**, 35–48 (2005).
- 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).
- Neubert, N. et al. Sulfidity controls molybdenum isotope fractionation into euxinic sediments: Evidence from the modern Black Sea. *Geology* **36**, 775–778 (2008).
- 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).

- 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).
- Planavsky, N.J. et al. Widespread iron-rich conditions in the mid-Proterozoic ocean. *Nature* **477**, 448–451 (2011).
- Polgári, M. et al. Stable isotope evidence for the origin of the Úrkút manganese ore deposit, Hungary. *J. Sediment. Petrol.* **61**, 384–393 (1991).
- Poulton, S.W. & Canfield, D.E. Ferruginous conditions: a dominant feature of the ocean through Earth's history. *Elements* **7**, 107–112 (2011).
- Sahoo, S.K. et al. Ocean oxygenation in the wake of the Marinoan glaciation. *Nature* **489**, 546–549 (2012).
- 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).
- Tesdal, J.E. et al. Nitrogen isotopes in bulk marine sediment: linking seafloor observations with subseafloor records. *Biogeosciences* **10**, 101–118 (2013).
- 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**, 104056 (2020).
- 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).
- Wittkop, C. et al. Evaluating a primary carbonate pathway for manganese enrichments in reducing environments. *Earth Planet. Sci. Lett.* **538**, 116201 (2020).
- 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. Ea.* **129**, e2023JB028307 (2024).
- Zhang, B. et al. Dynamic biogeochemical cycling and mineralization of manganese of hydrothermal origin after the Marinoan glaciation. *Chem. Geol.* **584**, 120502 (2021).
- 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).

Detailed Response (R) Reviewers

Please note that all key revisions have been highlighted by blue for easy tracking in the revised manuscript.

Response to Reviewer #1

In this manuscript, the authors provided iron (Fe) speciation, molybdenum (Mo) and nitrogen (N) data from black shales and associated Mn(II) carbonates in the upper Ediacaran Doushantuo Formation, South China. The data are well presented and reasonably explained. The topic of the manuscript fits the journal and the results provide important insights on the coupled relationship between oceanic oxygenation, Mn mineralization, and Mo geochemical cycling during the Neoproterozoic Oxygenation Event. I suggest a minor revision for the paper before it can be accepted for publication. Detailed comments including:

R: Thank you very much for your careful reviews, constructive comments, and positive evaluation on our work. As noted, your comments have been addressed in detail. Please see the responses below and the revised manuscript for details.

1. Nitrogen isotope explanation: Combined with anoxic iron speciation results, the authors attributed positive $\delta^{15}\text{N}$ signatures to partial denitrification in a redox-stratified water column, which is reasonable. In this case, I suggest the authors consider the $\delta^{15}\text{N}$ signatures as a regional signal. In a global perspective, more explanations and comments for logic are better provided, if taking the signal as evidence for oxidation level of the surface water (lines 99-101) and the oceanic redox structure (lines 260-262) by comparison with $\delta^{15}\text{N}$ signatures of the well-oxygenated modern ocean.

R: Thank you very much for your constructive comments, along which we added more comments for clarity. According to your comments, on the basis of the data obtained in this paper, we further 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) (Cremonese et al., 2013; Ader et al., 2014; Kikumoto et al., 2014; Spangenberg et al., 2014). It can be found that these data are generally consistent with those obtained in this paper, suggestive of a global redox signal rather than a local one (Ader et al., 2014). In detail, almost all Ediacaran sedimentary N isotope values are higher than 0‰ and comparable to those of modern marine sediments (Tesdal et al., 2011), indicating that the Ediacaran ocean had a large nitrate reservoir and the surface ocean was generally oxygenated with a deeper redox interface. Under this condition, the N-cycle pattern is similar to that of the modern ocean, suggesting that the oxidation degree of the surface seawater and the oceanic redox structure during this period may have been much similar to those of the modern ocean.

Please see the added comments above for clarity in Lines 112-118 on Page 6 of the main text, and Fig. S3 in Supplementary Materials for clarity.

2. Global $\delta^{98}\text{Mo}_{\text{sw}}$ estimation: The authors cited the isotopic offset ($\Delta^{98}\text{Mo}_{\text{seawater-sediment}} = 0.5 \pm 0.3\text{‰}$) between the dissolved Mo species and authigenic solid Mo reported from the Black Sea and added 0.5‰ to the extrapolated sedimentary $\delta^{98}\text{Mo}$ value ($\sim +1.4\text{‰}$) when estimating the Ediacaran global $\delta^{98}\text{Mo}_{\text{sw}}$ (lines 158-160). This is interesting and important, yet rarely used in previous Mo isotope studies of sulfidic successions, because $\Delta^{98}\text{Mo}_{\text{seawater-sediment}}$ in the Black Sea implicates sedimentary

$\delta^{98}\text{Mo}$ values close to the open ocean and heavier aqueous $\delta^{98}\text{Mo}$ values of the bottom water. The authors are suggested to reconsider the estimation of the Ediacaran global $\delta^{98}\text{Mo}_{\text{sw}}$, either modify the value or provide more evidence to support their estimation. This also helps to understand the maximum offset they calculated for Mn oxide shuttle (lines 180-185).

R: Thank you very much for your expert comments. If the Mo isotope value ($\sim 1.4\text{‰}$) calculated through the linear regression equation between Mn contents and Mo isotopes in euxinic black shales is considered to be the Mo isotopic composition of contemporaneous seawater, it is significantly lower than the maximum Mo isotope value ($\sim 2\text{‰}$; Kendall et al., 2015; Ostrander et al., 2019) detected in black shales of the Doushantuo Formation Member IV by predecessors. This does not conform to the basic principle of sedimentary Mo isotope geochemistry, that is, the Mo isotope value of sediments is generally lower than or equal to that of contemporaneous seawater. The heaviest Mo isotope value in strong euxinic sediments is thus approximately representative of that of seawater (Wei et al., 2021), since light Mo preferentially sinks to sediments while heavy Mo tends to reside in seawater. It can be concluded that the original estimated Mo isotope value of $\sim 1.4\text{‰}$ cannot reliably represent the Mo isotope compositions of contemporaneous seawater, which is significantly lower than the true seawater Mo isotope compositions ($\sim 2\text{‰}$). Notably, studies have shown that there is a small fractionation ($\sim 0.5 \pm 0.3\text{‰}$) of Mo isotope value between the sediment and ambient strong euxinic waters (e.g., modern Black Sea) (Arnold, et al., 2004; Nagler et al., 2011; Bruske et al., 2020), which shed lights on reconciling these contradictory estimations. Hereby, we conservatively employed this fractionation (0.5‰) to recalculate the seawater Mo isotope compositions during the deposition of the Doushantuo Formation Member IV. The calculated results are higher than 1.9‰ , which is comparable to the highest Mo isotopes ($\sim 2\text{‰}$) measured in the equivalent black shales in South China. This aligns with the basic principle of sedimentary Mo isotope geochemistry (Neubert et al., 2008; Nagler et al., 2011), that is, the maximum sediment Mo isotope value is basically similar to that of ambient seawater.

Please see the added comments above in Lines 192-212 on Pages 9-10 of the main text and Lines 151-154 on Page 7 in the Supplementary Materials for clarity.

3. Minors:

Lines 102-103: Reliability of iron speciation results is normally screened by $\text{Fe}_\text{T} > 0.5 \text{ wt.}\%$ rather than $\text{Fe}_\text{T}/\text{Al} > 0.5$ (Clarkson, M. O., Poulton, S. W., Guilbaud, R., and Wood, R. A., 2014, Assessing the utility of Fe/Al and Fe-speciation to record water column redox conditions in carbonate-rich sediments: Chemical Geology, v. 382, p. 111-122.)

R: We replaced the proxy of “ $\text{Fe}_\text{T}/\text{Al}$ ” with “ Fe_T ”. Please see Lines 119-121 on Page 6 in the revised main text and Lines 125-130 on Page 6 in the Supplementary Materials for details.

Lines 114-115: Negative $\delta^{13}\text{C}_{\text{carb}}$ values are quite common for the upper Doushantuo Formation though seawater $\delta^{13}\text{C}_{\text{carb}}$ values are still debated.

R: Thank you very much for your constructive comments, along which we added more comments for clarity. As you commented, the C isotopic compositions of Neoproterozoic seawater are still debated. However, a few investigations proposed that the seawater C isotopic value might be normally close to or slightly higher than 0‰ (Hoffman and Lamothe, 2019; Cui et al., 2022). Notably, the negative C isotope values of the Mn carbonates (low to -11‰) in the Doushantuo Formation Member IV of this study is generally lower than those of speculated Ediacaran seawater and contemporaneous carbonate rocks in other cratons (Yang et al., 2021). In addition, the C isotope values of Mn carbonates (low to -11‰) are significantly lower than that of coexisted dolostone

(around 0‰) and there is a negative correlation between Mn contents and C isotope values (Zhang et al., 2021, 2024). This indicates a mechanism of Mn oxides reduction coupled with organic C mineralization (Okita et al., 1988; Polgári et al., 1991). Therefore, the abnormally low C isotopic values of Mn carbonates in the Doushantuo Formation Member IV of this study are related to the formation of Mn carbonate minerals, which is indicative of Mn carbonate formation mechanism.

Please see the added comments above for clarity in Lines 131-136 on Pages 6-7 for details.

Response to Reviewer #2

Zhang et al. presented geochemical proxies to study ocean chemistry during the Neoproterozoic oxygenation event (NOE). They analyzed manganese-bearing carbonate rocks and black shales from the upper Ediacaran Doushantuo Formation in South China. The authors found that the redox structure of the paleo-ocean during the NOE was similar to the modern oxygenated ocean, with localized euxinic zones. They also concluded that Mn(II) oxidation in oxygenated environments is crucial for the formation of Mn carbonate. However, there are some important issues that need to be addressed before the manuscript can be accepted for publication.

R: Thank you very much for your positive evaluation and careful reviews on our manuscript. Your time and effort expended on the manuscript are greatly appreciated. As noted, your comments have been addressed point by point. Please see the responses below and the revised manuscript for details.

Major comments:

1. The authors claim that the formation of manganese carbonate mineralization requires the prior precipitation of manganese oxides. Nevertheless, it is important for the authors to acknowledge that manganese carbonates can precipitate in an oxygen-depleted environment.

R: Thank you very much for your expert comments. We agree with you that Mn carbonates can precipitate in an oxygen-depleted environment, which is another pathway for the formation of Mn carbonate minerals in addition to the mechanism of our study and has been verified in many cases (Wittkop et al., 2020). This, however, is not the primary origin of the Mn carbonates of this study. Multiple lines of evidence, including the extremely negative C isotopic compositions (low to -11‰), positive Ce anomaly, Mn oxide residues (i.e., todorokite) (Zhang et al., 2021, 2022), enrichment pattern of Mo–U, and the obviously low Mo isotopic compositions, collectively suggest a Mn oxide precursor for the formation of the Mn carbonate minerals in the Doushantuo Formation Member IV, South China.

Please see the added comments above for clarity in Lines 131-170 on Pages 6-8 for details.

How can the assertions made in the article be aligned with those put forward by Liu et al (2020)? W. Liu et al, Anoxic photogeochemical oxidation of manganese carbonate yields manganese oxide. *Proc. Natl. Acad. Sci. U.S.A.* 117, 22698-22704 (2020).

R: The simulation experiment of Liu et al. (2020) argued that the photochemical oxidation of rhodochrosite can also produce high-valent Mn hydroxide under the condition of ultraviolet irradiation (with wavelength of ~ 230 nm), and this process might be dominant in the Archean with low atmospheric O₂ concentrations. However, this pathway is 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 have increased significantly compared with those pre-GOE. The increase of atmospheric oxygen concentration promoted the establishment of stratospheric ozone shield, which

filtered high-energy ultraviolet light (Farquhar et al., 2000). 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 tend to be the main ways of Mn oxide formation before the precipitation of Mn carbonate minerals in this period (Morgan et al., 2005). This aligns with the temporally coupled relationship between sedimentary Mn and atmospheric O₂ concentrations (Maynard, 2010).

Please see the added comments above for clarity in Lines 277-293 on Pages 13-14 for details.

2. It would be beneficial for the authors to delve into a more detailed discussion of ocean chemistry over time or in the Neoproterozoic in the paper's introduction. This would provide context since the authors are questioning the oxygenation levels of the oceans during the NOE (Lines 46-47). Clarifying the specific ocean referenced would be helpful, as surface waters have primarily been oxygenated since the Paleoproterozoic. Conversely, mid and deep waters exhibited variations between ferruginous, euxinic, and oxic conditions towards the Neoproterozoic, until the ocean became predominantly oxic near the Phanerozoic.

R: The atmospheric O₂ concentration persistently increased from the early to late Ediacaran and the *p*O₂ in the atmosphere reached 60–100% of the present atmospheric level (PAL) at the end-Ediacaran (Ding et al., 2019). Some proxies indicate a progressively oxygenated Neoproterozoic ocean (Fike et al., 2006; Sahoo et al., 2012; Ader et al., 2014; Dodd et al., 2023). However, other geochemical proxies suggest the existence of a predominantly anoxic and strongly stratified Ediacaran ocean with a very shallow redox interface (Li et al., 2010; Planavsky et al., 2011; Poulton & Canfield, 2011). These findings indicate a complex pattern of redox conditions during this period. Surface waters have primarily been oxygenated since the Paleoproterozoic. Conversely, mid and deep waters exhibited variations between ferruginous, euxinic, and oxic conditions towards the Neoproterozoic, until the ocean became predominantly oxic during the early Phanerozoic. The main challenge lies in determining whether mid-to-deep ocean waters were ferruginous, euxinic, or oxic beneath oxygenated surface layers in Neoproterozoic ocean. 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 (Li et al., 2010; Ader et al., 2014). Clarifying the specific ocean redox configurations is crucial to understand the ocean chemistry and associated biogeochemical cycling and mineralization.

Please see the added comments above for clarity in Lines 32-46 on Pages 2-3 for clarity.

3. It would be helpful for the authors to provide a brief petrography section (it could go into a supplementary document).

R: We added brief petrographic description in result section and corresponding petrographic photographs for different lithologies in Supplementary Materials. Please see Lines 80-87 on Page 4 and Lines 346-354 on Pages 16-17 of the main text, Lines 33-48 on Pages 2-3 and Fig. S1 in the Supplementary Materials for clarity.

There are samples with approximately 35% Mn (e.g., ID-3-15; Table S1-data), and given this high content, is there no precipitation of oxide phases, such as pyrolusite, cryptomelane, etc.?

R: We have not found other Mn oxide mineral phases (e.g., pyrolusite and cryptomelane as you commented) in the samples with the highest Mn contents (e.g., ID-3-15). Instead, only a few Mn grains of todorokites were found in individual Mn carbonates (Zhang et al., 2022), which are the

residual after non-quantitative reduction of Mn oxides rather than the products of secondary oxidation of Mn carbonate minerals. Otherwise, the precipitation of Mn oxide phases prone to be preserved in Mn carbonates with the highest Mn contents.

Please see the added comments above for clarity in Lines 85-87 on Page 4 and Lines 136-145 on Page 7 for details.

Also, why is there a 2.71% Mn content (ID-3-23) in a sample of black shale? Solving these questions can help to understand some trends in the isotopic data presented.

R: There is a black shale with high Mn contents in our samples, which is named Mn-bearing black shale (Fig. 1c). This is because the Mn-bearing black shale is very close to the lower Mn carbonate rock and located at the transition boundary between Mn carbonates and black shales. Hence, the high Mn contents in this shale is the result of the existence of a small amount of Mn carbonate minerals (Zhang et al., 2021). The enrichment mechanism of Mn in this shale is consistent with that of Mn carbonates, that is, the reduction of Mn oxides with organic matter as electron donor. This strictly follows the trend that Mn contents are negatively correlated with C isotope values.

Please see the added comments above for clarity and Lines 134-136 on Page 7 for details.

4. It's important to consider the depositional systems of the Ediacaran Doushantuo Formation in order to fully understand some of the authors' conclusions. For instance, when the authors mention the contraction of the euxinic zone at the platform margin (Line 238), it's worth noting that platform margins typically feature shallow water depths of up to 200m. Even in the Neoproterozoic era, these shallow marine environments should have been oxygenated.

R: We agree with you that the shallow part of the ocean should have been oxygenated in the Neoproterozoic era. Notably, paleogeographic reconstruction shows that our section is located in the rift basin along the northern margin of the Yangtze Block. Petrologically, our Mn carbonates are closely associated with black shales. The black shales are a fine-grained sediment deposited in a relatively low energy sedimentary environment (Jiang et al., 2011), indicating that our section is located at a deep-water sedimentary environment. In addition, a previous study reported abundant gravity-driven sedimentary structures of meter-scale slump folds as a result of soft sediment deformation in the Doushantuo Member IV of this study (Wang et al., 2020), also suggesting that our section is located in the slope setting of continental margin rift basin rather than in a shallow platform environment. Therefore, the stratified redox structure of oxygenated surface layer and anoxic deep water is reasonable in such depositional systems, which are also supported by N isotopes and Fe speciation proxies.

Please see the added comments above for clarity in Lines 305-310 on Pages 14-15 of the main text and Lines 23-30 on Pages 1-2 of the Supplementary Materials for details.

Specific comments

1. Line 19-20: "High Fe speciation ratios ($\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}} > 0.8$) imply a localized marginal deep euxinic zone." Please specify which samples (black shales, Mn-carbonate, or both?) showed high Fe speciation ratios.

R: Both. Please see the clarification in Lines 18-21 on Page 1.

2. Line 20-21: "The estimated Ediacaran seawater Mo isotopic ($\delta^{98}\text{Mo}_{\text{sw}} = 1.9\text{‰}$) and Ediacaran sedimentary N isotopic compositions ($\delta^{15}\text{N}_{\text{sed}} = 4.19 \pm 1.96\text{‰}$) both closely resembled the modern $\delta^{98}\text{Mo}_{\text{sw}}$ (2.34‰) and $\delta^{15}\text{N}_{\text{sed}}$ (5‰) values, corroborating an oxygenated surface seawater overlay

euxinic bottom water". As with the above, please specify if these isotopic valleys are from black shales or, Mn-carbonate or both.

R: Both. Please see Lines 18-21 on Page 1 for the clarification.

3. Line 34: Please provide the section's name (Introduction?) before the main text.

R: Provided (i.e., Introduction). Please see Line 31 on Page 2.

4. Line 51: I suggest that the authors delete "widely" from the sentence since, as the authors themselves state below, there is disagreement about the conditions of precipitation of manganese carbonates.

R: Deleted for the precision of the science. Please see Lines 53-54 on Page 3.

5. Line 115-118: "Our finding of residual Mn oxides (i.e., todorokite; ref.25) in the studied Mn(II) carbonates, coupled with the positive cerium anomalies¹⁹, unequivocally indicate that the formation of these Mn carbonates did not involve direct precipitation of Mn(II) in anoxic waters. Instead, it likely involved the reduction of a Mn oxide precursor". What is the origin of todorokite? Could it be a post-diagenetic or even supergene mineral?

R: Our previous work showed that the todorokite was derived from the oxidation of Mn(II) by microorganisms during the formation of Mn carbonate minerals (Zhang et al., 2022). Subsequently, Mn oxide was reduced to dissolved Mn(II) using organic carbon as the electron donor. The todorokite is thus the residual Mn oxide retained in Mn carbonates after non-quantitative reduction. Todorokite is unlikely a post-diagenetic or even supergene mineral. This is because the todorokite only occurs in some Mn carbonates and is located between Mn carbonate minerals and is closely associated with fine-grained pyrite (Fig. S1). The well-preserved pyrite around todorokite suggests that the todorokite was not the product of diagenetic oxidation since pyrite is more readily oxidized than Mn(II)-bearing minerals (Zhang et al., 2022). Otherwise, the fine-grained syngenetic pyrite cannot be well preserved. In addition, our samples are extracted from cores buried more than 700 m deep with no signs of exposure. This excludes the possibility of post-diagenetic or even supergene oxidation of Mn carbonate to form Mn oxides.

Please see the added comments above for clarity in Lines 137-145 on Page 7 for details.

6. Line 119: Please explain the probable precursor of the Mn oxide in the text.

R: Todorokite. Please see the clarification in Lines 148-149 on Page 7.

7. Line 124-126: In mildly reducing and non-sulfidic anoxic waters, vanadate is transformed into vanadyl ions (VO_2^-) and hydroxyl forms. Under strongly reducing conditions in a euxinic environment with free H_2S , V^{3+} phases are further reduced to insoluble hydroxide forms.

R: Thank you very much for your constructive comments, along which we added the transformation of V in varied redox environments. Please see Lines 156-158 on Page 8 for details.

8. Line 142: "However, there is no significant enrichment of Mn in those shales". Please explain why some shales have higher Mn values than the crustal averages (e.g. PAAS and UCC; around 0.1%).

R: In order to avoid misunderstanding and confusion, we revised this sentence to "there is no extreme enrichment of Mn in the shales as observed in the Mn carbonates." As you commented, the Mn contents of black shales are indeed higher than that of PAAS and UCC. This is because the

charging of the deep hydrothermal fluids during the deposition of the Doushantuo Formation Member IV provides a large amount of Mn in study area (Gao et al., 2021; Zhang et al., 2021), which elevates the dissolved Mn concentration in the seawater in the rift basin. Under these conditions of high Mn background concentrations, the Mn contents of black shales will increase and be higher than those of PAAS and UCC. However, the Mn contents of black shales are significantly lower than those of Mn carbonates, reflecting varied degrees of Mn biogeochemical cycle and enrichment processes for these two lithologies. Overall, the input of hydrothermal Mn is the cause of the increase of Mn contents in the black shales in this study.

Please see the added comments above for clarity in Lines 177-180 on Page 9 for details.

9. Line 233: Please, exclude "indeed" of the sentence

R: Excluded. Please see Lines 299-301 on Page 14.

10. Line 236: " $R^2 = 0.590$ " is not a strong correlation.

R: Revised to "Notably, Mn oxides exert a greater impact on $\delta^{98}\text{Mo}$ 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; Fig. S6d)." for clarity and precision of the science. Please see Lines 301-303 on Page 14.

11. Line 298-299: "Simplified stratigraphy of the Doushantuo Formation on the Yangtze Platform (modified from refs.18,20)." Do the numbers 1,2,3 and 4 refer to the members?

R: The numbers I–IV in Fig. 1c refer to the members I–IV of the Doushantuo Formation as you commented. We added annotation in the caption of Fig. 1 for clarity. Please see Lines 375-376 on Page 18 for details.

12. Figure 3: Please revise Figure 3. In Figure 3b, there is an arrow referring to Figure 2b; I believe it is Figure 3c. Figure 3d also needs to be better referenced.

R: We revised "Fig. 2c" to "Fig. 3c" in Fig. 3 and specified the data source of Fig. 3d in the caption (i.e., Tan et al., 2023). Please see the newly revised Fig. 3 on Page 26 and Lines 384-385 on Page 18 for details.

References cited

- 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).
- Arnold, G.L. et al. Molybdenum isotope evidence for widespread anoxia in mid-Proterozoic oceans. *Science* **304**, 87–90 (2004).
- Brüske, A. et al. Correlated molybdenum and uranium isotope signatures in modern anoxic sediments: Implications for their use as paleoredox proxy. *Geochim. Cosmochim. Acta* **270**, 449–474 (2020).
- 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).
- Cui, H. et al. An authigenic response to Ediacaran surface oxidation: Remarkable micron - scale isotopic heterogeneity revealed by SIMS. *Precambrian Res.* **377**, 106676 (2022).
- Ding, W. et al. Early animal evolution and highly oxygenated seafloor niches hosted by microbial mats. *Sci. Rep.* **9**, 13628 (2019).
- Dodd, S.M. et al. Uncovering the Ediacaran phosphorus cycle. *Nature* **618**, 974–980 (2023).
- Farquhar, J. et al. Atmospheric influence of Earth's earliest sulfur cycle. *Science*, **289**, 756–758 (2000).
- Fike, D.A. et al. Oxidation of the Ediacaran Ocean. *Nature* **444**, 744–747 (2006).
- 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).
- Hoffman, P.F. & Lamothe, K.G. Seawater-buffered diagenesis, destruction of carbon isotope excursions, and the composition of DIC in Neoproterozoic oceans. *P. Natl. Acad. Sci. USA* **116**, 18874–18879 (2019).
- 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).
- 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).
- 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).
- Li, C. et al. A stratified redox model for the Ediacaran ocean. *Science* **328**, 80–83 (2010).
- Liu, W. et al. Anoxic photogeochemical oxidation of manganese carbonate yields manganese oxide. *Proc. Natl. Acad. Sci. U.S.A.* **117**, 22698–22704 (2020).
- 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).
- Morgan, J.J. Kinetics of reaction between O₂ and Mn(II) species in aqueous solutions. *Geochim. Cosmochim. Acta* **69**, 35–48 (2005).
- 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).
- Neubert, N. et al. Sulfidity controls molybdenum isotope fractionation into euxinic sediments: Evidence from the modern Black Sea. *Geology* **36**, 775–778 (2008).
- 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).

- 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).
- Planavsky, N.J. et al. Widespread iron-rich conditions in the mid-Proterozoic ocean. *Nature* **477**, 448–451 (2011).
- Polgári, M. et al. Stable isotope evidence for the origin of the Úrkút manganese ore deposit, Hungary. *J. Sediment. Petrol.* **61**, 384–393 (1991).
- Poulton, S.W. & Canfield, D.E. Ferruginous conditions: a dominant feature of the ocean through Earth's history. *Elements* **7**, 107–112 (2011).
- Sahoo, S.K. et al. Ocean oxygenation in the wake of the Marinoan glaciation. *Nature* **489**, 546–549 (2012).
- 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).
- Tesdal, J.E. et al. Nitrogen isotopes in bulk marine sediment: linking seafloor observations with subseafloor records. *Biogeosciences* **10**, 101–118 (2013).
- 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**, 104056 (2020).
- 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).
- Wittkop, C. et al. Evaluating a primary carbonate pathway for manganese enrichments in reducing environments. *Earth Planet. Sci. Lett.* **538**, 116201 (2020).
- 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. Ea.* **129**, e2023JB028307 (2024).
- Zhang, B. et al. Dynamic biogeochemical cycling and mineralization of manganese of hydrothermal origin after the Marinoan glaciation. *Chem. Geol.* **584**, 120502 (2021).
- 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).

Detailed Response (R) Reviewers

Please note that all key revisions have been highlighted by blue for easy tracking in the revised manuscript.

Response to Reviewer #1

In this manuscript, the authors provided iron (Fe) speciation, molybdenum (Mo) and nitrogen (N) data from black shales and associated Mn(II) carbonates in the upper Ediacaran Doushantuo Formation, South China. The data are well presented and reasonably explained. The topic of the manuscript fits the journal and the results provide important insights on the coupled relationship between oceanic oxygenation, Mn mineralization, and Mo geochemical cycling during the Neoproterozoic Oxygenation Event. I suggest a minor revision for the paper before it can be accepted for publication. Detailed comments including:

R: Thank you very much for your careful reviews, constructive comments, and positive evaluation on our work. As noted, your comments have been addressed in detail. Please see the responses below and the revised manuscript for details.

1. Nitrogen isotope explanation: Combined with anoxic iron speciation results, the authors attributed positive $\delta^{15}\text{N}$ signatures to partial denitrification in a redox-stratified water column, which is reasonable. In this case, I suggest the authors consider the $\delta^{15}\text{N}$ signatures as a regional signal. In a global perspective, more explanations and comments for logic are better provided, if taking the signal as evidence for oxidation level of the surface water (lines 99-101) and the oceanic redox structure (lines 260-262) by comparison with $\delta^{15}\text{N}$ signatures of the well-oxygenated modern ocean.

R: Thank you very much for your constructive comments, along which we added more comments for clarity. According to your comments, on the basis of the data obtained in this paper, we further 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) (Cremonese et al., 2013; Ader et al., 2014; Kikumoto et al., 2014; Spangenberg et al., 2014). It can be found that these data are generally consistent with those obtained in this paper, suggestive of a global redox signal rather than a local one (Ader et al., 2014). In detail, almost all Ediacaran sedimentary N isotope values are higher than 0‰ and comparable to those of modern marine sediments (Tesdal et al., 2011), indicating that the Ediacaran ocean had a large nitrate reservoir and the surface ocean was generally oxygenated with a deeper redox interface. Under this condition, the N-cycle pattern is similar to that of the modern ocean, suggesting that the oxidation degree of the surface seawater and the oceanic redox structure during this period may have been much similar to those of the modern ocean.

Please see the added comments above for clarity in Lines 112-118 on Page 6 of the main text, and Fig. S3 in Supplementary Materials for clarity.

2. Global $\delta^{98}\text{Mo}_{\text{sw}}$ estimation: The authors cited the isotopic offset ($\Delta^{98}\text{Mo}_{\text{seawater-sediment}} = 0.5 \pm 0.3\text{‰}$) between the dissolved Mo species and authigenic solid Mo reported from the Black Sea and added 0.5‰ to the extrapolated sedimentary $\delta^{98}\text{Mo}$ value ($\sim +1.4\text{‰}$) when estimating the Ediacaran global $\delta^{98}\text{Mo}_{\text{sw}}$ (lines 158-160). This is interesting and important, yet rarely used in previous Mo isotope studies of sulfidic successions, because $\Delta^{98}\text{Mo}_{\text{seawater-sediment}}$ in the Black Sea implicates sedimentary

$\delta^{98}\text{Mo}$ values close to the open ocean and heavier aqueous $\delta^{98}\text{Mo}$ values of the bottom water. The authors are suggested to reconsider the estimation of the Ediacaran global $\delta^{98}\text{Mo}_{\text{sw}}$, either modify the value or provide more evidence to support their estimation. This also helps to understand the maximum offset they calculated for Mn oxide shuttle (lines 180-185).

R: Thank you very much for your expert comments. If the Mo isotope value ($\sim 1.4\text{‰}$) calculated through the linear regression equation between Mn contents and Mo isotopes in euxinic black shales is considered to be the Mo isotopic composition of contemporaneous seawater, it is significantly lower than the maximum Mo isotope value ($\sim 2\text{‰}$; Kendall et al., 2015; Ostrander et al., 2019) detected in black shales of the Doushantuo Formation Member IV by predecessors. This does not conform to the basic principle of sedimentary Mo isotope geochemistry, that is, the Mo isotope value of sediments is generally lower than or equal to that of contemporaneous seawater. The heaviest Mo isotope value in strong euxinic sediments is thus approximately representative of that of seawater (Wei et al., 2021), since light Mo preferentially sinks to sediments while heavy Mo tends to reside in seawater. It can be concluded that the original estimated Mo isotope value of $\sim 1.4\text{‰}$ cannot reliably represent the Mo isotope compositions of contemporaneous seawater, which is significantly lower than the true seawater Mo isotope compositions ($\sim 2\text{‰}$). Notably, studies have shown that there is a small fractionation ($\sim 0.5 \pm 0.3\text{‰}$) of Mo isotope value between the sediment and ambient strong euxinic waters (e.g., modern Black Sea) (Arnold, et al., 2004; Nagler et al., 2011; Bruske et al., 2020), which shed lights on reconciling these contradictory estimations. Hereby, we conservatively employed this fractionation (0.5‰) to recalculate the seawater Mo isotope compositions during the deposition of the Doushantuo Formation Member IV. The calculated results are higher than 1.9‰ , which is comparable to the highest Mo isotopes ($\sim 2\text{‰}$) measured in the equivalent black shales in South China. This aligns with the basic principle of sedimentary Mo isotope geochemistry (Neubert et al., 2008; Nagler et al., 2011), that is, the maximum sediment Mo isotope value is basically similar to that of ambient seawater.

Please see the added comments above in Lines 192-212 on Pages 9-10 of the main text and Lines 151-154 on Page 7 in the Supplementary Materials for clarity.

3. Minors:

Lines 102-103: Reliability of iron speciation results is normally screened by $\text{Fe}_\text{T} > 0.5 \text{ wt.}\%$ rather than $\text{Fe}_\text{T}/\text{Al} > 0.5$ (Clarkson, M. O., Poulton, S. W., Guilbaud, R., and Wood, R. A., 2014, Assessing the utility of Fe/Al and Fe-speciation to record water column redox conditions in carbonate-rich sediments: *Chemical Geology*, v. 382, p. 111-122.)

R: We replaced the proxy of “ $\text{Fe}_\text{T}/\text{Al}$ ” with “ Fe_T ”. Please see Lines 119-121 on Page 6 in the revised main text and Lines 125-130 on Page 6 in the Supplementary Materials for details.

Lines 114-115: Negative $\delta^{13}\text{C}_{\text{carb}}$ values are quite common for the upper Doushantuo Formation though seawater $\delta^{13}\text{C}_{\text{carb}}$ values are still debated.

R: Thank you very much for your constructive comments, along which we added more comments for clarity. As you commented, the C isotopic compositions of Neoproterozoic seawater are still debated. However, a few investigations proposed that the seawater C isotopic value might be normally close to or slightly higher than 0‰ (Hoffman and Lamothe, 2019; Cui et al., 2022). Notably, the negative C isotope values of the Mn carbonates (low to -11‰) in the Doushantuo Formation Member IV of this study is generally lower than those of speculated Ediacaran seawater and contemporaneous carbonate rocks in other cratons (Yang et al., 2021). In addition, the C isotope values of Mn carbonates (low to -11‰) are significantly lower than that of coexisted dolostone

(around 0‰) and there is a negative correlation between Mn contents and C isotope values (Zhang et al., 2021, 2024). This indicates a mechanism of Mn oxides reduction coupled with organic C mineralization (Okita et al., 1988; Polgári et al., 1991). Therefore, the abnormally low C isotopic values of Mn carbonates in the Doushantuo Formation Member IV of this study are related to the formation of Mn carbonate minerals, which is indicative of Mn carbonate formation mechanism.

Please see the added comments above for clarity in Lines 131-136 on Pages 6-7 for details.

Response to Reviewer #2

Zhang et al. presented geochemical proxies to study ocean chemistry during the Neoproterozoic oxygenation event (NOE). They analyzed manganese-bearing carbonate rocks and black shales from the upper Ediacaran Doushantuo Formation in South China. The authors found that the redox structure of the paleo-ocean during the NOE was similar to the modern oxygenated ocean, with localized euxinic zones. They also concluded that Mn(II) oxidation in oxygenated environments is crucial for the formation of Mn carbonate. However, there are some important issues that need to be addressed before the manuscript can be accepted for publication.

R: Thank you very much for your positive evaluation and careful reviews on our manuscript. Your time and effort expended on the manuscript are greatly appreciated. As noted, your comments have been addressed point by point. Please see the responses below and the revised manuscript for details.

Major comments:

1. The authors claim that the formation of manganese carbonate mineralization requires the prior precipitation of manganese oxides. Nevertheless, it is important for the authors to acknowledge that manganese carbonates can precipitate in an oxygen-depleted environment.

R: Thank you very much for your expert comments. We agree with you that Mn carbonates can precipitate in an oxygen-depleted environment, which is another pathway for the formation of Mn carbonate minerals in addition to the mechanism of our study and has been verified in many cases (Wittkop et al., 2020). This, however, is not the primary origin of the Mn carbonates of this study. Multiple lines of evidence, including the extremely negative C isotopic compositions (low to -11‰), positive Ce anomaly, Mn oxide residues (i.e., todorokite) (Zhang et al., 2021, 2022), enrichment pattern of Mo–U, and the obviously low Mo isotopic compositions, collectively suggest a Mn oxide precursor for the formation of the Mn carbonate minerals in the Doushantuo Formation Member IV, South China.

Please see the added comments above for clarity in Lines 131-170 on Pages 6-8 for details.

How can the assertions made in the article be aligned with those put forward by Liu et al (2020)? W. Liu et al, Anoxic photogeochemical oxidation of manganese carbonate yields manganese oxide. *Proc. Natl. Acad. Sci. U.S.A.* 117, 22698-22704 (2020).

R: The simulation experiment of Liu et al. (2020) argued that the photochemical oxidation of rhodochrosite can also produce high-valent Mn hydroxide under the condition of ultraviolet irradiation (with wavelength of ~ 230 nm), and this process might be dominant in the Archean with low atmospheric O₂ concentrations. However, this pathway is 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 have increased significantly compared with those pre-GOE. The increase of atmospheric oxygen concentration promoted the establishment of stratospheric ozone shield, which

filtered high-energy ultraviolet light (Farquhar et al., 2000). 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 tend to be the main ways of Mn oxide formation before the precipitation of Mn carbonate minerals in this period (Morgan et al., 2005). This aligns with the temporally coupled relationship between sedimentary Mn and atmospheric O₂ concentrations (Maynard, 2010).

Please see the added comments above for clarity in Lines 277-293 on Pages 13-14 for details.

2. It would be beneficial for the authors to delve into a more detailed discussion of ocean chemistry over time or in the Neoproterozoic in the paper's introduction. This would provide context since the authors are questioning the oxygenation levels of the oceans during the NOE (Lines 46-47). Clarifying the specific ocean referenced would be helpful, as surface waters have primarily been oxygenated since the Paleoproterozoic. Conversely, mid and deep waters exhibited variations between ferruginous, euxinic, and oxic conditions towards the Neoproterozoic, until the ocean became predominantly oxic near the Phanerozoic.

R: The atmospheric O₂ concentration persistently increased from the early to late Ediacaran and the *p*O₂ in the atmosphere reached 60–100% of the present atmospheric level (PAL) at the end-Ediacaran (Ding et al., 2019). Some proxies indicate a progressively oxygenated Neoproterozoic ocean (Fike et al., 2006; Sahoo et al., 2012; Ader et al., 2014; Dodd et al., 2023). However, other geochemical proxies suggest the existence of a predominantly anoxic and strongly stratified Ediacaran ocean with a very shallow redox interface (Li et al., 2010; Planavsky et al., 2011; Poulton & Canfield, 2011). These findings indicate a complex pattern of redox conditions during this period. Surface waters have primarily been oxygenated since the Paleoproterozoic. Conversely, mid and deep waters exhibited variations between ferruginous, euxinic, and oxic conditions towards the Neoproterozoic, until the ocean became predominantly oxic during the early Phanerozoic. The main challenge lies in determining whether mid-to-deep ocean waters were ferruginous, euxinic, or oxic beneath oxygenated surface layers in Neoproterozoic ocean. 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 (Li et al., 2010; Ader et al., 2014). Clarifying the specific ocean redox configurations is crucial to understand the ocean chemistry and associated biogeochemical cycling and mineralization.

Please see the added comments above for clarity in Lines 32-46 on Pages 2-3 for clarity.

3. It would be helpful for the authors to provide a brief petrography section (it could go into a supplementary document).

R: We added brief petrographic description in result section and corresponding petrographic photographs for different lithologies in Supplementary Materials. Please see Lines 80-87 on Page 4 and Lines 346-354 on Pages 16-17 of the main text, Lines 33-48 on Pages 2-3 and Fig. S1 in the Supplementary Materials for clarity.

There are samples with approximately 35% Mn (e.g., ID-3-15; Table S1-data), and given this high content, is there no precipitation of oxide phases, such as pyrolusite, cryptomelane, etc.?

R: We have not found other Mn oxide mineral phases (e.g., pyrolusite and cryptomelane as you commented) in the samples with the highest Mn contents (e.g., ID-3-15). Instead, only a few Mn grains of todorokites were found in individual Mn carbonates (Zhang et al., 2022), which are the

residual after non-quantitative reduction of Mn oxides rather than the products of secondary oxidation of Mn carbonate minerals. Otherwise, the precipitation of Mn oxide phases prone to be preserved in Mn carbonates with the highest Mn contents.

Please see the added comments above for clarity in Lines 85-87 on Page 4 and Lines 136-145 on Page 7 for details.

Also, why is there a 2.71% Mn content (ID-3-23) in a sample of black shale? Solving these questions can help to understand some trends in the isotopic data presented.

R: There is a black shale with high Mn contents in our samples, which is named Mn-bearing black shale (Fig. 1c). This is because the Mn-bearing black shale is very close to the lower Mn carbonate rock and located at the transition boundary between Mn carbonates and black shales. Hence, the high Mn contents in this shale is the result of the existence of a small amount of Mn carbonate minerals (Zhang et al., 2021). The enrichment mechanism of Mn in this shale is consistent with that of Mn carbonates, that is, the reduction of Mn oxides with organic matter as electron donor. This strictly follows the trend that Mn contents are negatively correlated with C isotope values.

Please see the added comments above for clarity and Lines 134-136 on Page 7 for details.

4. It's important to consider the depositional systems of the Ediacaran Doushantuo Formation in order to fully understand some of the authors' conclusions. For instance, when the authors mention the contraction of the euxinic zone at the platform margin (Line 238), it's worth noting that platform margins typically feature shallow water depths of up to 200m. Even in the Neoproterozoic era, these shallow marine environments should have been oxygenated.

R: We agree with you that the shallow part of the ocean should have been oxygenated in the Neoproterozoic era. Notably, paleogeographic reconstruction shows that our section is located in the rift basin along the northern margin of the Yangtze Block. Petrologically, our Mn carbonates are closely associated with black shales. The black shales are a fine-grained sediment deposited in a relatively low energy sedimentary environment (Jiang et al., 2011), indicating that our section is located at a deep-water sedimentary environment. In addition, a previous study reported abundant gravity-driven sedimentary structures of meter-scale slump folds as a result of soft sediment deformation in the Doushantuo Member IV of this study (Wang et al., 2020), also suggesting that our section is located in the slope setting of continental margin rift basin rather than in a shallow platform environment. Therefore, the stratified redox structure of oxygenated surface layer and anoxic deep water is reasonable in such depositional systems, which are also supported by N isotopes and Fe speciation proxies.

Please see the added comments above for clarity in Lines 305-310 on Pages 14-15 of the main text and Lines 23-30 on Pages 1-2 of the Supplementary Materials for details.

Specific comments

1. Line 19-20: "High Fe speciation ratios ($\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}} > 0.8$) imply a localized marginal deep euxinic zone." Please specify which samples (black shales, Mn-carbonate, or both?) showed high Fe speciation ratios.

R: Both. Please see the clarification in Lines 18-21 on Page 1.

2. Line 20-21: "The estimated Ediacaran seawater Mo isotopic ($\delta^{98}\text{Mo}_{\text{sw}} = 1.9\text{‰}$) and Ediacaran sedimentary N isotopic compositions ($\delta^{15}\text{N}_{\text{sed}} = 4.19 \pm 1.96\text{‰}$) both closely resembled the modern $\delta^{98}\text{Mo}_{\text{sw}}$ (2.34‰) and $\delta^{15}\text{N}_{\text{sed}}$ (5‰) values, corroborating an oxygenated surface seawater overlay

euxinic bottom water". As with the above, please specify if these isotopic valleys are from black shales or, Mn-carbonate or both.

R: Both. Please see Lines 18-21 on Page 1 for the clarification.

3. Line 34: Please provide the section's name (Introduction?) before the main text.

R: Provided (i.e., Introduction). Please see Line 31 on Page 2.

4. Line 51: I suggest that the authors delete "widely" from the sentence since, as the authors themselves state below, there is disagreement about the conditions of precipitation of manganese carbonates.

R: Deleted for the precision of the science. Please see Lines 53-54 on Page 3.

5. Line 115-118: "Our finding of residual Mn oxides (i.e., todorokite; ref.25) in the studied Mn(II) carbonates, coupled with the positive cerium anomalies¹⁹, unequivocally indicate that the formation of these Mn carbonates did not involve direct precipitation of Mn(II) in anoxic waters. Instead, it likely involved the reduction of a Mn oxide precursor". What is the origin of todorokite? Could it be a post-diagenetic or even supergene mineral?

R: Our previous work showed that the todorokite was derived from the oxidation of Mn(II) by microorganisms during the formation of Mn carbonate minerals (Zhang et al., 2022). Subsequently, Mn oxide was reduced to dissolved Mn(II) using organic carbon as the electron donor. The todorokite is thus the residual Mn oxide retained in Mn carbonates after non-quantitative reduction. Todorokite is unlikely a post-diagenetic or even supergene mineral. This is because the todorokite only occurs in some Mn carbonates and is located between Mn carbonate minerals and is closely associated with fine-grained pyrite (Fig. S1). The well-preserved pyrite around todorokite suggests that the todorokite was not the product of diagenetic oxidation since pyrite is more readily oxidized than Mn(II)-bearing minerals (Zhang et al., 2022). Otherwise, the fine-grained syngenetic pyrite cannot be well preserved. In addition, our samples are extracted from cores buried more than 700 m deep with no signs of exposure. This excludes the possibility of post-diagenetic or even supergene oxidation of Mn carbonate to form Mn oxides.

Please see the added comments above for clarity in Lines 137-145 on Page 7 for details.

6. Line 119: Please explain the probable precursor of the Mn oxide in the text.

R: Todorokite. Please see the clarification in Lines 148-149 on Page 7.

7. Line 124-126: In mildly reducing and non-sulfidic anoxic waters, vanadate is transformed into vanadyl ions (VO_2^-) and hydroxyl forms. Under strongly reducing conditions in a euxinic environment with free H_2S , V^{3+} phases are further reduced to insoluble hydroxide forms.

R: Thank you very much for your constructive comments, along which we added the transformation of V in varied redox environments. Please see Lines 156-158 on Page 8 for details.

8. Line 142: "However, there is no significant enrichment of Mn in those shales". Please explain why some shales have higher Mn values than the crustal averages (e.g. PAAS and UCC; around 0.1%).

R: In order to avoid misunderstanding and confusion, we revised this sentence to "there is no extreme enrichment of Mn in the shales as observed in the Mn carbonates." As you commented, the Mn contents of black shales are indeed higher than that of PAAS and UCC. This is because the

charging of the deep hydrothermal fluids during the deposition of the Doushantuo Formation Member IV provides a large amount of Mn in study area (Gao et al., 2021; Zhang et al., 2021), which elevates the dissolved Mn concentration in the seawater in the rift basin. Under these conditions of high Mn background concentrations, the Mn contents of black shales will increase and be higher than those of PAAS and UCC. However, the Mn contents of black shales are significantly lower than those of Mn carbonates, reflecting varied degrees of Mn biogeochemical cycle and enrichment processes for these two lithologies. Overall, the input of hydrothermal Mn is the cause of the increase of Mn contents in the black shales in this study.

Please see the added comments above for clarity in Lines 177-180 on Page 9 for details.

9. Line 233: Please, exclude "indeed" of the sentence

R: Excluded. Please see Lines 299-301 on Page 14.

10. Line 236: " $R^2 = 0.590$ " is not a strong correlation.

R: Revised to "Notably, Mn oxides exert a greater impact on $\delta^{98}\text{Mo}$ 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; Fig. S6d)." for clarity and precision of the science. Please see Lines 301-303 on Page 14.

11. Line 298-299: "Simplified stratigraphy of the Doushantuo Formation on the Yangtze Platform (modified from refs.18,20)." Do the numbers 1,2,3 and 4 refer to the members?

R: The numbers I–IV in Fig. 1c refer to the members I–IV of the Doushantuo Formation as you commented. We added annotation in the caption of Fig. 1 for clarity. Please see Lines 375-376 on Page 18 for details.

12. Figure 3: Please revise Figure 3. In Figure 3b, there is an arrow referring to Figure 2b; I believe it is Figure 3c. Figure 3d also needs to be better referenced.

R: We revised "Fig. 2c" to "Fig. 3c" in Fig. 3 and specified the data source of Fig. 3d in the caption (i.e., Tan et al., 2023). Please see the newly revised Fig. 3 on Page 26 and Lines 384-385 on Page 18 for details.

References cited

- 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).
- Arnold, G.L. et al. Molybdenum isotope evidence for widespread anoxia in mid-Proterozoic oceans. *Science* **304**, 87–90 (2004).
- Brüske, A. et al. Correlated molybdenum and uranium isotope signatures in modern anoxic sediments: Implications for their use as paleoredox proxy. *Geochim. Cosmochim. Acta* **270**, 449–474 (2020).
- 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).
- Cui, H. et al. An authigenic response to Ediacaran surface oxidation: Remarkable micron - scale isotopic heterogeneity revealed by SIMS. *Precambrian Res.* **377**, 106676 (2022).
- Ding, W. et al. Early animal evolution and highly oxygenated seafloor niches hosted by microbial mats. *Sci. Rep.* **9**, 13628 (2019).
- Dodd, S.M. et al. Uncovering the Ediacaran phosphorus cycle. *Nature* **618**, 974–980 (2023).
- Farquhar, J. et al. Atmospheric influence of Earth's earliest sulfur cycle. *Science*, **289**, 756–758 (2000).
- Fike, D.A. et al. Oxidation of the Ediacaran Ocean. *Nature* **444**, 744–747 (2006).
- 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).
- Hoffman, P.F. & Lamothe, K.G. Seawater-buffered diagenesis, destruction of carbon isotope excursions, and the composition of DIC in Neoproterozoic oceans. *P. Natl. Acad. Sci. USA* **116**, 18874–18879 (2019).
- 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).
- 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).
- 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).
- Li, C. et al. A stratified redox model for the Ediacaran ocean. *Science* **328**, 80–83 (2010).
- Liu, W. et al. Anoxic photogeochemical oxidation of manganese carbonate yields manganese oxide. *Proc. Natl. Acad. Sci. U.S.A.* **117**, 22698–22704 (2020).
- 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).
- Morgan, J.J. Kinetics of reaction between O₂ and Mn(II) species in aqueous solutions. *Geochim. Cosmochim. Acta* **69**, 35–48 (2005).
- 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).
- Neubert, N. et al. Sulfidity controls molybdenum isotope fractionation into euxinic sediments: Evidence from the modern Black Sea. *Geology* **36**, 775–778 (2008).
- 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).

- 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).
- Planavsky, N.J. et al. Widespread iron-rich conditions in the mid-Proterozoic ocean. *Nature* **477**, 448–451 (2011).
- Polgári, M. et al. Stable isotope evidence for the origin of the Úrkút manganese ore deposit, Hungary. *J. Sediment. Petrol.* **61**, 384–393 (1991).
- Poulton, S.W. & Canfield, D.E. Ferruginous conditions: a dominant feature of the ocean through Earth's history. *Elements* **7**, 107–112 (2011).
- Sahoo, S.K. et al. Ocean oxygenation in the wake of the Marinoan glaciation. *Nature* **489**, 546–549 (2012).
- 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).
- Tesdal, J.E. et al. Nitrogen isotopes in bulk marine sediment: linking seafloor observations with subseafloor records. *Biogeosciences* **10**, 101–118 (2013).
- 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**, 104056 (2020).
- 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).
- Wittkop, C. et al. Evaluating a primary carbonate pathway for manganese enrichments in reducing environments. *Earth Planet. Sci. Lett.* **538**, 116201 (2020).
- 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. Ea.* **129**, e2023JB028307 (2024).
- Zhang, B. et al. Dynamic biogeochemical cycling and mineralization of manganese of hydrothermal origin after the Marinoan glaciation. *Chem. Geol.* **584**, 120502 (2021).
- 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).