

Coupled manganese carbonate mineralization and molybdenum cycling in the oxygenated Neoproterozoic ocean

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Supplementary Information

Supplementary Notes

1. Geological setting

The South China Plate was assembled at ca. 870 Ma through the amalgamation of the Yangtze and Cathaysia blocks (Fig. 1a), only to undergo rifting at ca. 820 Ma¹. This event led to the formation of several rift basins along the plate edges within a passive continental margin setting, such as the Nanhua Basin. Paleogeographic reconstructions have delineated the Yangtze Block's margins into distinct zones, transitioning from inner shelf, intra-shelf basin, shelf margin, to slope–basin facies

23 toward the basins (Fig. 1a)². The peripheral regions of the Yangtze Block contain complete Ediacaran
24 Period sequences, exemplified by the Doushantuo and Dengying formations. The Doushantuo
25 Formation, in particular, comprises four members (Fig. 1c)². Member I is characterized by cap
26 carbonates, 3–7-m-thick, that unconformably overlies the Cryogenian Nantuo glacial diamictites.
27 Member II comprises ~80 m of organic-rich shales interbedded with thin dolostone layers. Member
28 III consists of ~60 m of chert-bearing dolostone interbedded with organic-rich shale. Finally, Member
29 IV has ~10 m of organic-rich black shales underlying the thick dolostones of the Dengying Formation.

30 Paleogeographic reconstruction shows that our section is located in the rift basin along the
31 northern margin of the Yangtze Block. Petrologically, our Mn carbonates are closely associated with
32 black shales, suggesting deposition in a relatively low-energy sedimentary environment². Moreover,
33 our section is located in a deep-water sedimentary environment as evidenced by abundant gravity-
34 driven sedimentary structures of meter-scale slump folds as a result of soft sediment deformation³.
35 Collectively, the geological findings suggest that our section of the Doushantuo Member IV is located
36 in the slope setting in continental margin rift basin with high water depth rather than in shallow
37 platform environment.

38

39 **2. Detailed methods**

40 The petrological observation was performed under transmitted and reflected light model using Nikon
41 LHS2H100C21 optical microscopy. For whole-rock mineralogical examination, samples were
42 crushed to < 200 mesh in an agate mortar prior to analysis. A Rigaku Dmax Rapid II X-ray
43 diffractometer (XRD) was used with a rotating anode Mo target X-ray source (Mo K α = 0.71073 Å)
44 at an accelerating voltage of 50 kV and beam current of 90 mA. Data processing and mineral
45 identification were performed using the Jade 6.0 software. For high resolution *in situ* mineralogical

determination, we employed micro-Raman spectroscopy (LabRAM HR Evolution) on thin sections. A diode pumped solid state laser of wavelength of 532 nm (green) and a 50 × objective lens was used for imaging and Raman examination. The spectrometer was calibrated using a Si wafer (wavenumber 520 cm⁻¹). Spectra were acquired over the range 100–2000 cm⁻¹, with an acquisition time of 1 min and triplicate scans. Spectral resolution was better than 0.65 cm⁻¹. Mineral identification was based on the RRUFF Database (<http://rruff.info/>): 1083 cm⁻¹ for kutnohorite, 1086–1088 cm⁻¹, for rhodochrosite, 633 cm⁻¹ for todorokite, 1350 cm⁻¹ and 1605 cm⁻¹ for carbonaceous matter, and 344 cm⁻¹ and 380 cm⁻¹ for pyrite. All petrological and mineralogical examinations were performed at the State Key Laboratory for Mineral Deposit Research and MOE Key Laboratory of Surficial Geochemistry at Nanjing University, Nanjing, China.

For N isotopes, 10% HCl was added to the bulk powders (~2 g) and reacted for at least 48 h to completely remove the carbonate fraction. The supernatant was removed by centrifuging at 3000 rev/min for 10 min, and the solid residue was retained and washed with deionized water at least five times until the pH of the solution reached 7. The carbonate-free residues were dried and ground again to fine powder. Decarbonated and homogeneous powders (1–50 mg) were loaded into capsules and flash combusted at 960°C in a Thermo Fisher Elemental Analyzer coupled to a Thermo EA–Isolink–Delta V Plus stable isotope ratio mass spectrometer (IRMS) via a Thermo ConFlo III Interface at the International Center for Isotope Effects Research in Nanjing University, Nanjing, China. Nitrogen isotope results are reported as δ values relative to atmospheric N₂ (0‰; air). An international reference standard (acetanilide; $\delta^{15}\text{N} = -5.07\text{‰}$; total nitrogen [TN]=10.36 wt.%) was used to monitor the analytical uncertainties, and the precisions are better than $\pm 0.3\text{‰}$.

The extraction of pyrite was undertaken at the State Key Laboratory of Palaeobiology and Stratigraphy in the Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences,

69 Nanjing, China. Powders (1–6 g) were prepared for pyrite extraction using the Cr reduction method⁴.
70 The H₂S generated from pyrite reduction was transported into a silver nitrate (3%; v/v) trap using N₂
71 as a carrier gas. The pyrite contents were determined stoichiometrically by weight from the
72 precipitated Ag₂S. Sequential extraction of other Fe species, including Fe_{carb} (Fe in carbonate), Fe_{ox}
73 (Fe in oxides), and Fe_{mag} (Fe in magnetite) followed the protocols of Poulton and Canfield⁵. These
74 used a 1 M Na acetate solution for Fe_{carb}, 0.3 M dithionite and 0.2 M Na citrate solutions for Fe_{ox},
75 and 0.2 M ammonium oxalate and 0.17 M oxalic acid solutions for Fe_{mag}. The sequential extracts
76 were analyzed by inductively coupled plasma optical emission spectrometry (ICP–OES; Thermo ICP
77 6300) with a precision of ±0.5% at the MOE Key Laboratory of Surficial Geochemistry in Nanjing
78 University, Nanjing, China.

79 For molybdenum contents and isotopic compositions, sample powders were weighed to provide
80 120 ng of Mo. A ⁹⁷Mo–¹⁰⁰Mo double-spike was added to the sample powders followed by digestion
81 with 4 mL of HF and 2 mL of HNO₃ in closed beakers at 140°C overnight. N-benzoyl-N-phenyl
82 hydroxylamine chromatographic resin was used for Mo separation and purification following the
83 protocols of Li⁶. The Mo isotopic measurements employed a Thermo-Fisher Scientific Neptune Plus
84 multi-collector inductively coupled plasma mass spectrometer (MC–ICP–MS)⁷. Isotopic results are
85 reported using δ notation in per mil (‰) relative to the NIST SRM 3134 standard:

$$86 \quad \delta^{98}\text{Mo} = [({}^{98}\text{Mo}/{}^{95}\text{Mo})_{\text{sample}}/({}^{98}\text{Mo}/{}^{95}\text{Mo})_{\text{NIST3134}} - 1] \times 1000 + 0.25 \quad (1)$$

87 The external reproducibility of the δ⁹⁸Mo values for NIST SRM 3134 were 0.00 ± 0.05‰ (2SD;
88 n = 17). The δ⁹⁸Mo values of the United States Geological Survey (USGS) rock reference material
89 AGV-2 and seawater IAPSO were determined to be −0.16 ± 0.04‰ (2SD; n = 1) and +2.09 ± 0.03‰
90 (2SD; n = 2) relative to NIST SRM 3134 = 0‰, respectively. These Mo isotope and content data are
91 consistent with the certified values and those reported by previous studies^{6,8,9}. Repeated digestion and

analysis of individual samples yielded a reproducibility of $\leq \pm 0.1\%$ (2 SD). The Mo procedural blank was 0.54 ± 0.18 ng (2SD; $n = 3$), which is much less than the total Mo contents in the samples and standards. All isotopic data are recalculated relative to the NIST SRM 3134 standard solution ($+0.25\%$)¹⁰. The chemical separation and mass spectrometric analyses of Mo isotopes were conducted at the State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou, China.

3. Nitrogen isotopes

Nitrogen is a key bio-essential element and a redox-sensitive element for paleoenvironmental reconstructions. The cycling of N and its isotopic fractionation are controlled by redox conditions and biological metabolic activity (Supplementary Fig. S4)¹¹. Nitrogen-fixing prokaryotes capture atmospheric N_2 ($\delta^{15}N = 0\%$) within the euphotic zone and are the primary source of N in the ocean, which is slightly isotopically fractionated ($\epsilon = -2\%$ to $+1\%$)¹². Lower $\delta^{15}N$ values (-2% to $+1\%$) of fixed N that does not undergo other cycling would be recorded in sediments in anoxic oceans, such as the modern Black Sea.

Nitrate is the primary form of N, and biologically fixed N is quantitatively converted to nitrate with no net isotopic fractionation, which produces a large reservoir of nitrate in the oxygenated ocean¹³. Under these conditions, denitrifying bacteria mediate denitrification to release isotopically light N ($\delta^{15}N = -20\%$) with a large isotopic fractionation ($\epsilon = -25\%$) in local O_2 -depleted zones¹⁴. The remaining isotopically heavy N ($\delta^{15}N = +5\%$) is retained in the sediments¹⁵. This may explain the heavier N isotopic compositions of modern marine sediments, particularly in O_2 minimum zones or euxinic wedges on oxygenated continental margins where denitrification occurs¹⁴.

In line accordance with these fractionation model, higher $\delta^{15}N_{sed}$ values generally indicate that

115 there is a large reservoir of nitrate and local denitrification, as represented by the oxygenated ocean
116 (e.g., the modern ocean). Conversely, lighter N isotopic compositions are indicative of either limited
117 nitrate or complete denitrification in O₂-depleted marine environments, such as the ocean during
118 oceanic anoxic events (OAEs).

119

120 **4. Iron speciation**

121 Iron speciation is a proxy of the redox state of deep-water masses and can be used to distinguish
122 between anoxic and euxinic conditions. Highly reactive Fe (Fe_{HR})^{16,17}, including Fe_{py} (e.g.,
123 mackinawite and pyrite), Fe_{carb} (e.g., ankerite and siderite), Fe_{ox} (e.g., goethite and hematite), and
124 Fe_{mag} (e.g., magnetite), can be involved in both biotic and abiotic geochemical cycling under different
125 redox conditions at continental margins⁵. Studies have demonstrated that anoxic conditions are
126 characterized by higher Fe_{HR} and the Fe_{HR}/Fe_T ratios increase as dissolved O₂ concentrations
127 decrease^{18,19}. In theory, Fe_{HR}/Fe_T<0.22 and Fe_{HR}/Fe_T>0.38 distinguish oxic and anoxic bottom waters,
128 respectively^{20,21}. Under anoxic conditions (i.e., Fe_{HR}/Fe_T>0.38), the proportion of Fe_{py} within Fe_{HR}
129 also increases with increasing concentrations of free H₂S. Fe_{py}/Fe_{HR}>0.7–0.8 indicates a euxinic
130 environment, whereas Fe_{py}/Fe_{HR}<0.7–0.8 represents non-sulfidic anoxic conditions (e.g.,
131 ferruginous)^{20,22}.

132 Despite the general applicability of the above scheme, a sudden increase in sedimentation rate
133 (e.g., gravity flow) and loss of highly reactive Fe may result in lower Fe_{HR}/Fe_T values²³. In addition,
134 carbonate-rich sediments with low Fe_T (< 0.5 wt.%) routinely give spuriously high Fe_{HR}/Fe_T ratios²⁴.
135 These two effects would both create misleading Fe_{HR}/Fe_T ratios, rendering the Fe speciation an
136 ineffective proxy^{23,24,25}. Therefore, iron speciation proxy, in particular for Fe_{HR}/Fe_T ratios of
137 carbonate-rich sediments, should be viewed with caution to investigate bottom water redox state.

138

139 **5. Molybdenum cycling and isotopic fractionation**

140 Molybdenum isotopes are a reliable proxy for paleo-marine redox conditions²⁶. With a residence time
141 of Mo in the ocean of around 440 kyr²⁷, which is 300 times the oceanic mixing timescale (1–2 kyr)²⁸,
142 it is assumed that specific geological periods have similar global seawater Mo isotopic compositions²⁹.
143 Molybdenum is a bio-essential element and constitutes a vital component of biological nitrogenase³⁰.
144 It is also a significant redox-sensitive element and exists predominantly in dissolved form as the
145 tetrahedrally coordinated conservative molybdate anion in oxidized environments. It is not readily
146 enriched in precipitates except when Fe–Mn oxides (e.g., oceanic Fe–Mn crusts) are present to adsorb
147 and concentrate Mo³¹. Recent studies have identified significant fractionation of Mo isotopes owing
148 to the preferential adsorption of isotopically light Mo by Fe–Mn oxides ($\Delta_{\text{sw-oxide}}=3\text{‰}$ for Mn oxides
149 and 1.1‰–1.4‰ for Fe oxides), causing a shift toward isotopically heavier, dissolved Mo in the water
150 column^{32,33}.

151 By contrast, Mo tends to accumulate as octahedrally coordinated, particle-reactive
152 oxythiomolybdate that is produced sequentially from molybdate by the capture of reactive particles
153 (e.g., sulfides and organic matter) under euxinic conditions. The sulfide-dependent Mo isotopic
154 fractionation varies widely. Under weakly euxinic conditions ($\text{H}_2\text{S}_{\text{aq}} < 11 \text{ }\mu\text{M}$), isotopically lighter Mo
155 converts preferentially to $\text{MoO}_x\text{S}_{4-x}^{2-}$ ($x=1-3$), which is associated with a moderate level of isotopic
156 fractionation (with average of 0.7‰)³⁴. Above this threshold ($\text{H}_2\text{S}_{\text{aq}} > 11 \text{ }\mu\text{M}$), Mo is near-
157 quantitatively converted to tetrathiomolybdate ($\text{MoS}_2/\text{MoS}_4^{2-}$) and transferred to the sediment with
158 small isotopic fractionation. Therefore, sedimentary Mo signals in strongly euxinic environments
159 often approximate the lowest Mo isotopic compositions of contemporaneous seawater²⁶. Nevertheless,
160 whether sedimentary Mo records can represent the Mo isotopic compositions of seawater requires

161 more consideration.

162 Furthermore, post-depositional diagenesis and metamorphism do not modify the isotopic
163 composition of Mo³⁵. As such, ancient sedimentary rocks accurately record deep-time Mo cycling.

164

165 **6. Modeling the Mo isotopic compositions of Fe–Mn oxides**

166 The adsorption of Mo onto Fe and Mn oxides exerts variable Mo isotopic fractionation. The
167 fractionation induced by Mn oxides (3‰)³² is greater than that induced by Fe oxides (1.11‰ for
168 ferrihydrite and 1.40‰ for goethite)³³. We used a simple mass-balance model that calculates the
169 $\delta^{98}\text{Mo}$ values affected by Fe and Mn oxides (Supplementary Fig. S5)³⁶. The Mo isotopic compositions
170 of Fe and Mn oxides are:

$$171 \quad \delta^{98}\text{Mo}_{\text{Fe}} = \delta^{98}\text{Mo}_{\text{sw}} - \Delta_{\text{Fe}} \quad (2)$$

$$172 \quad \delta^{98}\text{Mo}_{\text{Mn}} = \delta^{98}\text{Mo}_{\text{sw}} - \Delta_{\text{Mn}} \quad (3)$$

173 where $\delta^{98}\text{Mo}_{\text{sw}}$ represents the isotopic composition of contemporaneous seawater, and Δ_{Fe} and Δ_{Mn}
174 are fractionation values for Fe and Mn oxides, respectively. We used 1.2‰ for Δ_{Fe} and 3‰ for Δ_{Mn} .

175 Therefore, the $\delta^{98}\text{Mo}$ values of Fe- and Mn-rich sediments can be expressed as follows:

$$176 \quad \delta^{98}\text{Mo} = (\delta^{98}\text{Mo}_{\text{Mn}} + f \times K \times \delta^{98}\text{Mo}_{\text{Fe}}) / (1 + f \times K) \quad (4)$$

177 where f is the Fe/Mn ratio (wt.%/wt.%) of the sediments and K is the ratio of Mo adsorbed onto Fe
178 oxides to Mo adsorbed onto Mn oxides. We used the K value (0.37) derived from the ratios of Mo/Mn
179 and Mo/Fe in modern pelagic sediments³⁶.

180 The Mo isotopic compositions of sediments enriched in Fe and Mn in the modern ocean align
181 with this modeling trend³⁶. Higher Fe contents in black shales compared with Mn carbonates
182 (Supplementary Data 1) are suggestive of potential effects from Fe oxides on the Mo isotopic
183 compositions in this study, because Fe oxides also preferentially adsorb isotopically light Mo from

184 seawater³³. However, the relationship between Mo isotopes and Fe/Mn ratios in the black shales
185 deviates from the expected trend acquired from the model (Supplementary Fig. S5)³⁶. Lower $\delta^{98}\text{Mo}$
186 values compared with the modeling results can be attributed to the effects of the Mn oxide shuttle,
187 whereas higher $\delta^{98}\text{Mo}$ values may result from H₂S-dependent fractionation (Supplementary Fig. S5).
188 This is because Mo isotopic fractionation caused by Fe oxides lies between that caused by Mn oxides
189 and H₂S. This demonstrates that the effects of the Fe oxide shuttle on Mo isotopic fractionation
190 appears to be suppressed in Mn-rich conditions, and the effects of the Fe oxide shuttle on Mo isotopic
191 fractionation in this study are negligible (Supplementary Fig. S5)³⁶.

192

193 **7. Basin restriction proxy**

194 The differential enrichment of Mo and U is a proxy for the extent of open seawater in a continental
195 marginal basin. This is because Mo tends to accumulate preferentially over U in euxinic basins that
196 are significantly affected by the open ocean. Better connectivity between the water mass in the
197 continental marginal basin and the open ocean results in larger Mo reservoirs because of the large Mo
198 reservoir in the open ocean³⁷. The replenishment of seawater Mo progressively increases the
199 $\text{Mo}_{\text{EF}}/\text{U}_{\text{EF}}$ ratios from 0.1–0.3 SW (i.e., the seawater ratio) to 1–3 SW³¹. In contrast, the $\text{Mo}_{\text{EF}}/\text{U}_{\text{EF}}$
200 ratios tend to be lower than that of seawater (1 SW)³⁸ in restricted euxinic basins because of the
201 limited Mo pool. In this study, the Fe speciation indicates that both the Mn carbonates and black
202 shales were deposited in euxinic bottom waters. The Mo_{EF} and U_{EF} values of the black shales are
203 lower and follow the trend observed for a strongly restricted basin (Fig. 4d). Conversely, the Mn
204 carbonates exhibit greater Mo enrichment and plot mainly in the weakly or non-restricted basin field
205 (Fig. 4d). This suggests that the open ocean had a lesser effect during deposition of the black shales
206 compared with during deposition of the Mn carbonates.

207 Similarly, $\text{Mo}_{\text{auth}}/\text{TOC}$ ratios can also be used to trace the restriction of shelf marginal basins,
208 with more open basins having higher $\text{Mo}_{\text{auth}}/\text{TOC}$ ratios (e.g., the Black Sea versus the Saanich Inlet;
209 Fig. 8a)^{39,40}. In this study, the $\text{Mo}_{\text{auth}}/\text{TOC}$ ratios of the black shales are lower than those of the Mn
210 carbonates, and the black shale samples have a more restricted range of ratios (Fig. 6a), suggesting
211 that there were weaker contributions from open seawater during deposition of the black shales.
212 Furthermore, the estimated average deep-water Mo concentration ($[\text{Mo}]_{\text{aq}}$) during deposition of the
213 black shales is slightly higher than that of the modern Black Sea but significantly lower than that
214 during deposition of the Mn carbonates (Fig. 6b). The anomalously high deep-water $[\text{Mo}]_{\text{aq}}$ can be
215 explained by the combined effect of weak water-mass restriction and a high Mo input from the open
216 ocean during deposition of the Mn carbonates⁴¹.

217

Supplementary Figures

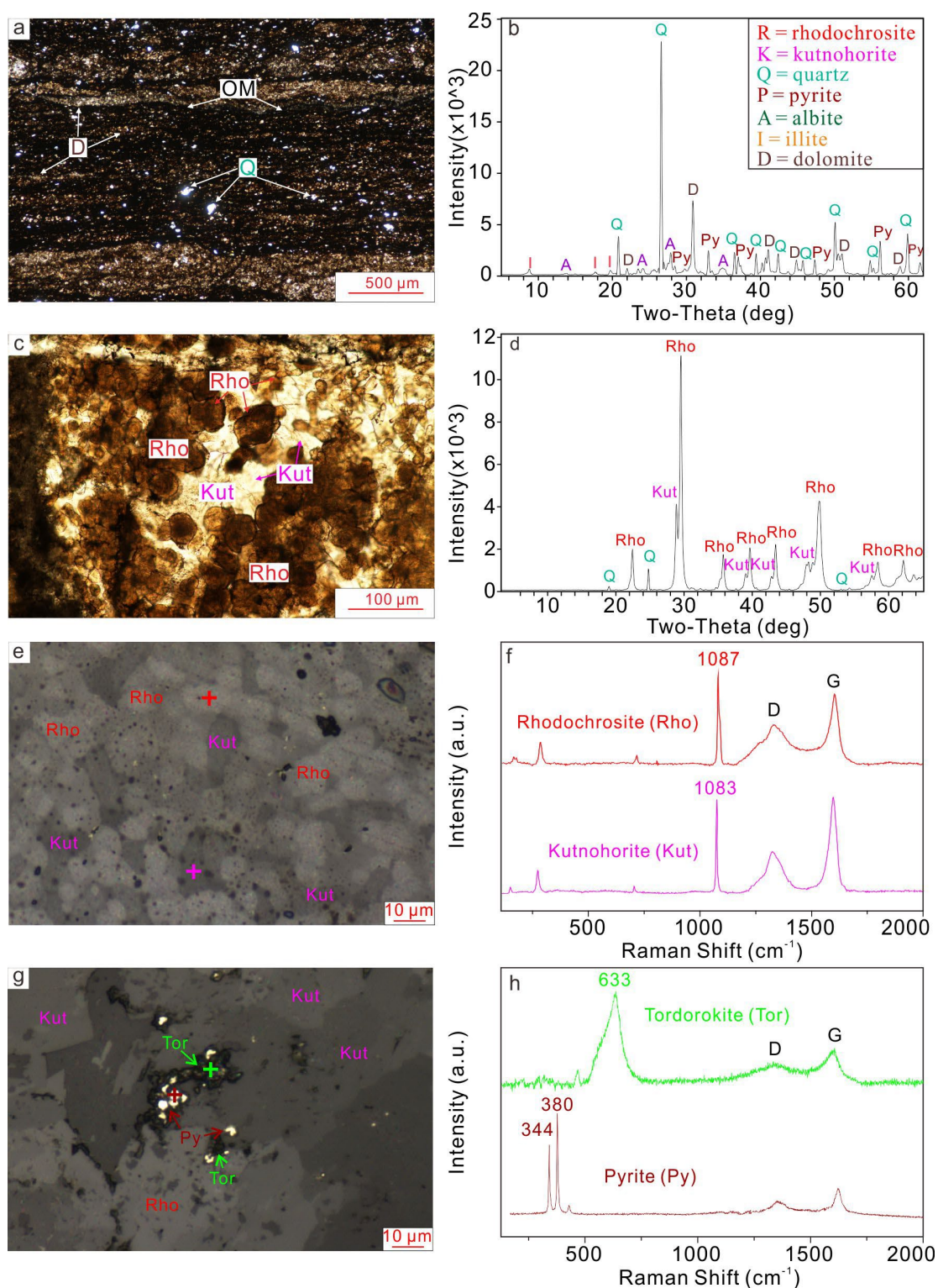


Fig. S1. Petrographic and mineralogical characteristics of the black shales and Mn carbonates in the Doushantuo Formation Member IV in South China. (a) Lamellar organic matter, detrital quartz, and dolomite intraclasts in black shale (cross-polarized light). **(b)** XRD spectrum for a black shale sample. **(c)** Microspherical rhodochrosite cemented by kutnohorite (plane-polarized light). **(d)** XRD spectrum of a Mn carbonate sample. **(e)** Spherical and ellipsoidal Mn carbonate minerals and cements (reflected light). Crosses refer to the locations of Raman analysis points. **(f)** Representative Raman spectra of rhodochrosite and kutnohorite in panel e. **(g)** Todorokite closely associated with

organic matter and pyrite in Mn carbonates (reflected light). Crosses refer to the locations of the Raman analysis points. **(h)** Representative Raman spectra of todorokite and pyrite in panel **(g)**.

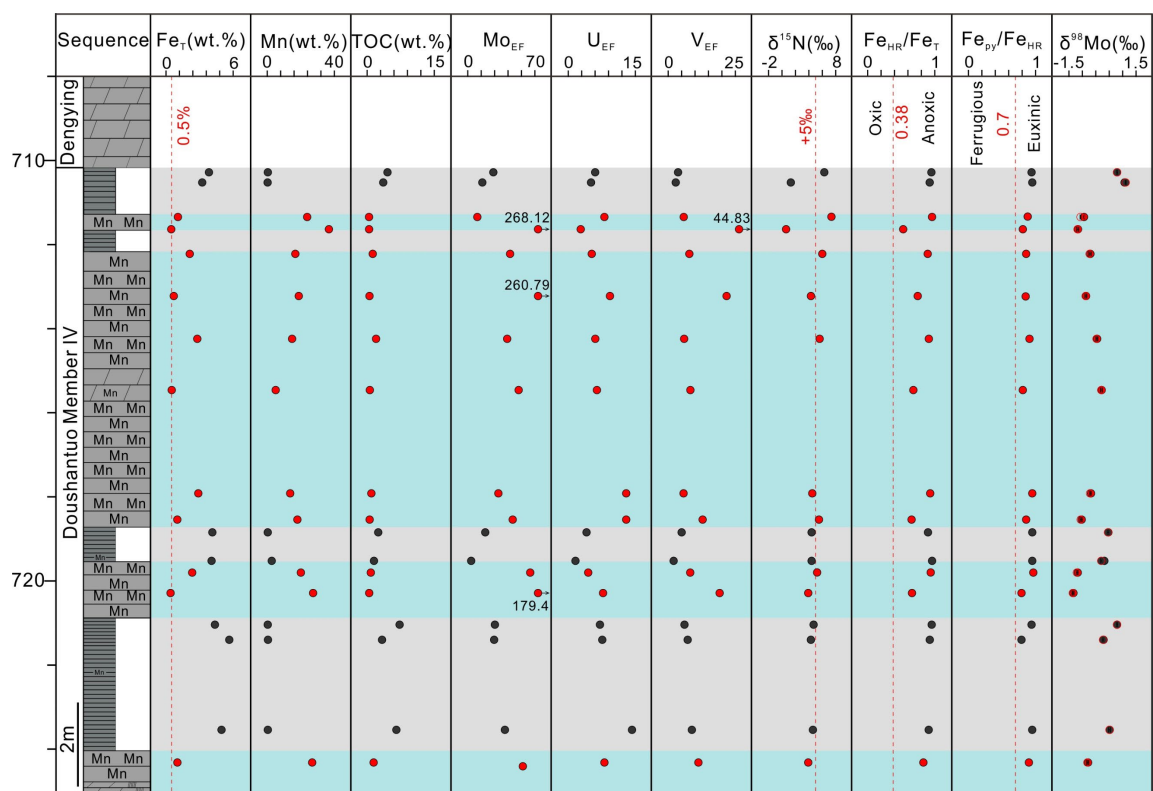


Fig. S2. Chemostratigraphy of the Doushantuo Formation Member IV in South China. Solid circles (Mo isotopes) represent the primary uncorrected results, while open circles represent the results after the authigenic correction. Error bars are smaller than the symbol size for $\delta^{98}\text{Mo}$.

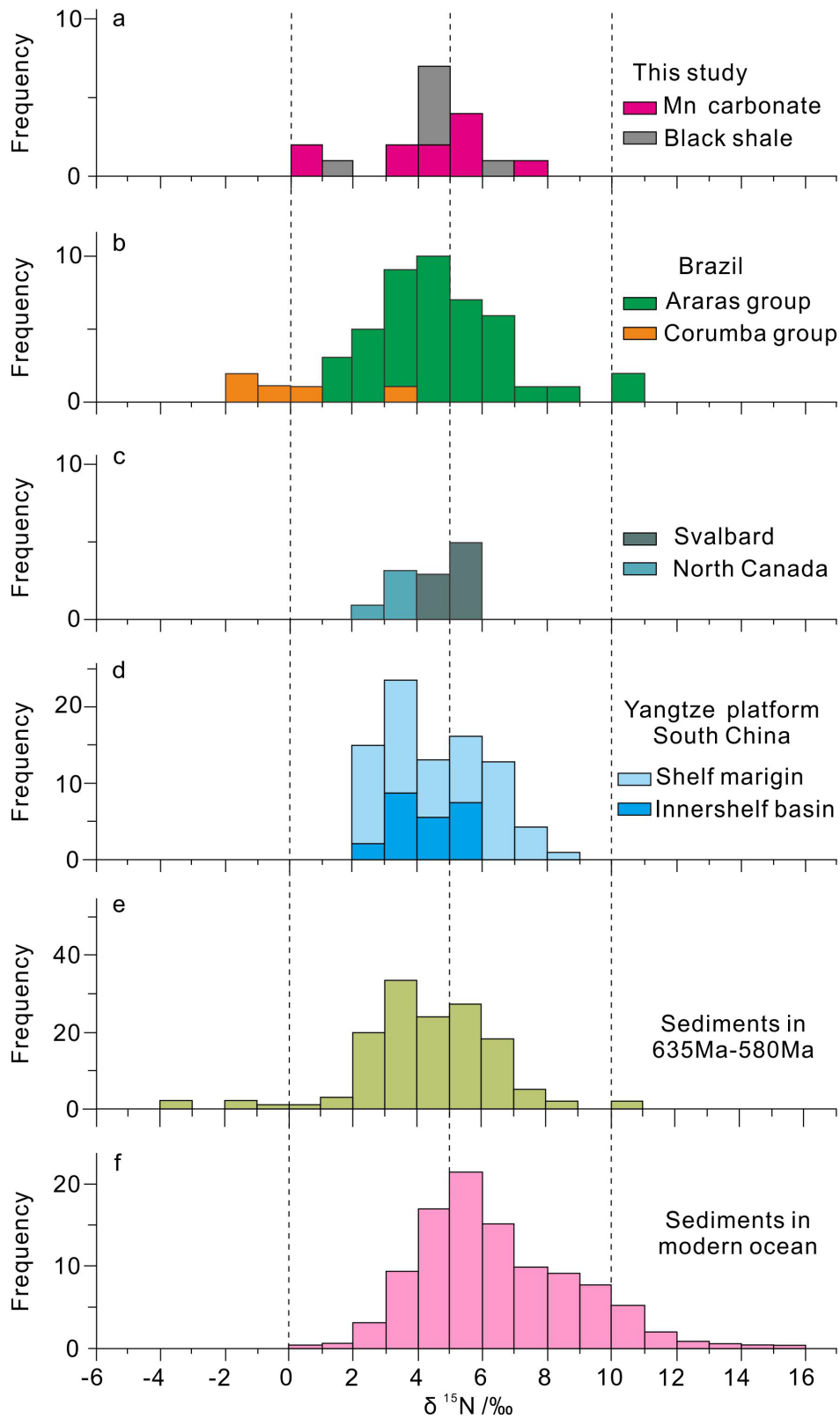


Fig. S3. Comparison of $\delta^{15}\text{N}$ data from modern and late Neoproterozoic oceanic sediments. (a) $\delta^{15}\text{N}$ values of black shales and Mn carbonates in this study. (b) $\delta^{15}\text{N}$ distributions in the Amazon craton, Brazil^{14,42}. (c) $\delta^{15}\text{N}$ data from northwestern Canada and Svalbard¹⁴. (d) $\delta^{15}\text{N}$ data from varied sedimentary environments in the Yangtze platform, South China^{43,44}. (e) Compiled $\delta^{15}\text{N}$ data of late Neoproterozoic sediments^{14,42,43,44}. (f) $\delta^{15}\text{N}$ data of modern marine sediments¹⁵.

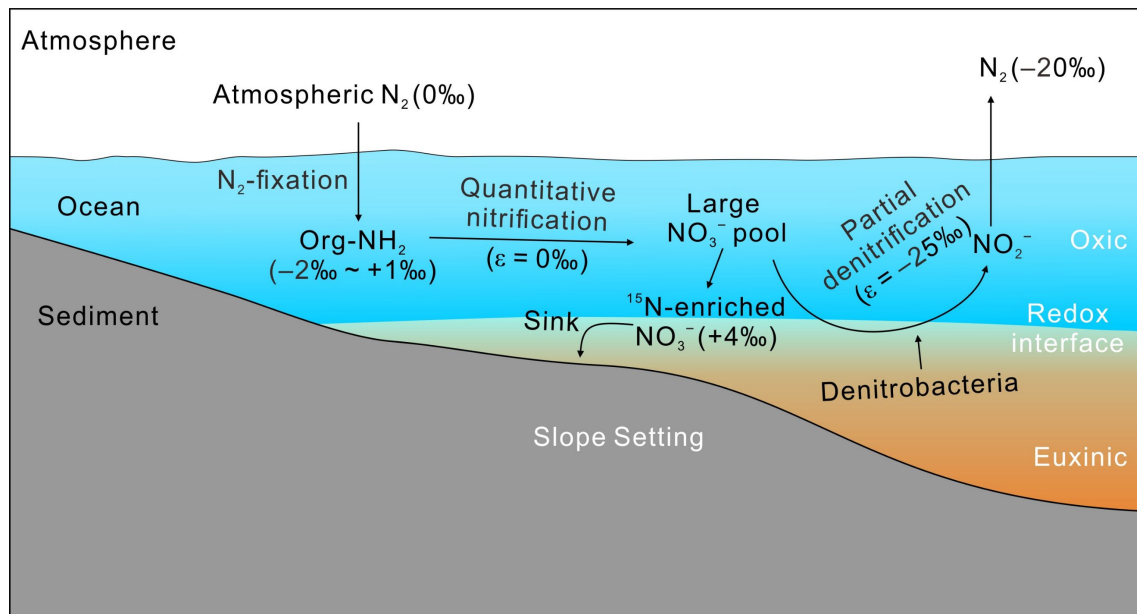


Fig. S4. Schematic diagram of a local redox model in slope setting constructed from various redox proxies and the corresponding biogeochemical N cycle during deposition of the Doushantuo Formation Member IV in South China.

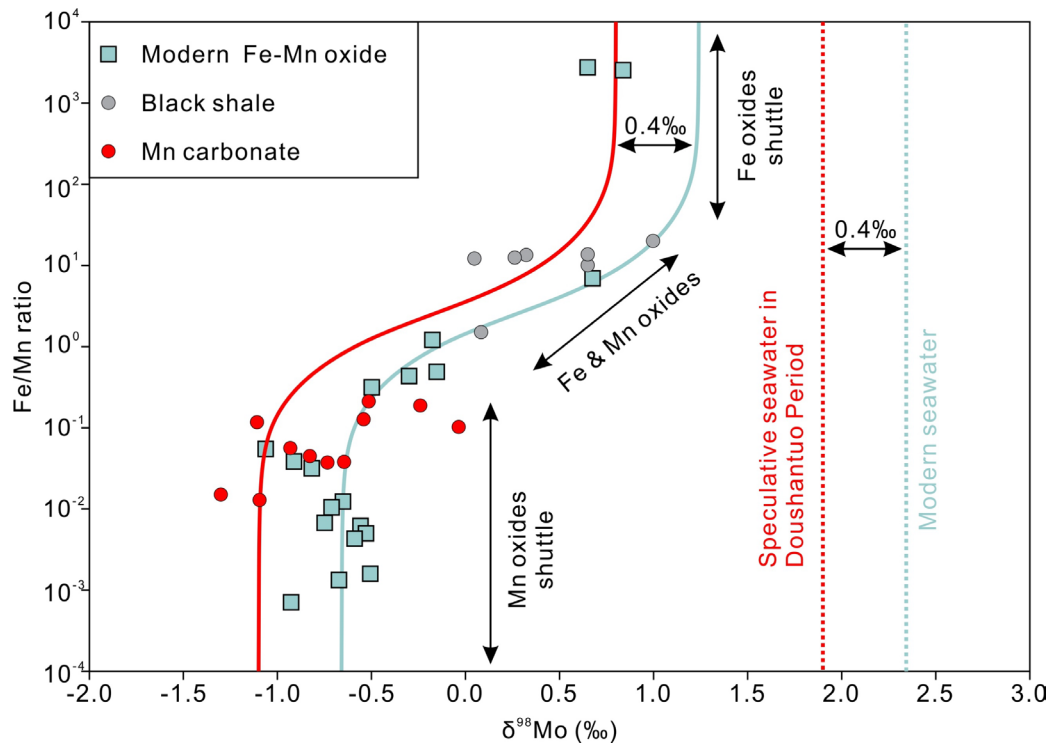


Fig. S5. Modeled sedimentary $\delta^{98}\text{Mo}$ values in relation to varying Fe/Mn ratios. Light green and red solid lines are the modeling results based on the adsorption of Mo onto Fe and Mn oxides from modern³⁷ and the Doushantuo period seawater, respectively. Light green and red dashed lines represent the $\delta^{98}\text{Mo}$ values of modern and the Doushantuo period seawater, respectively.

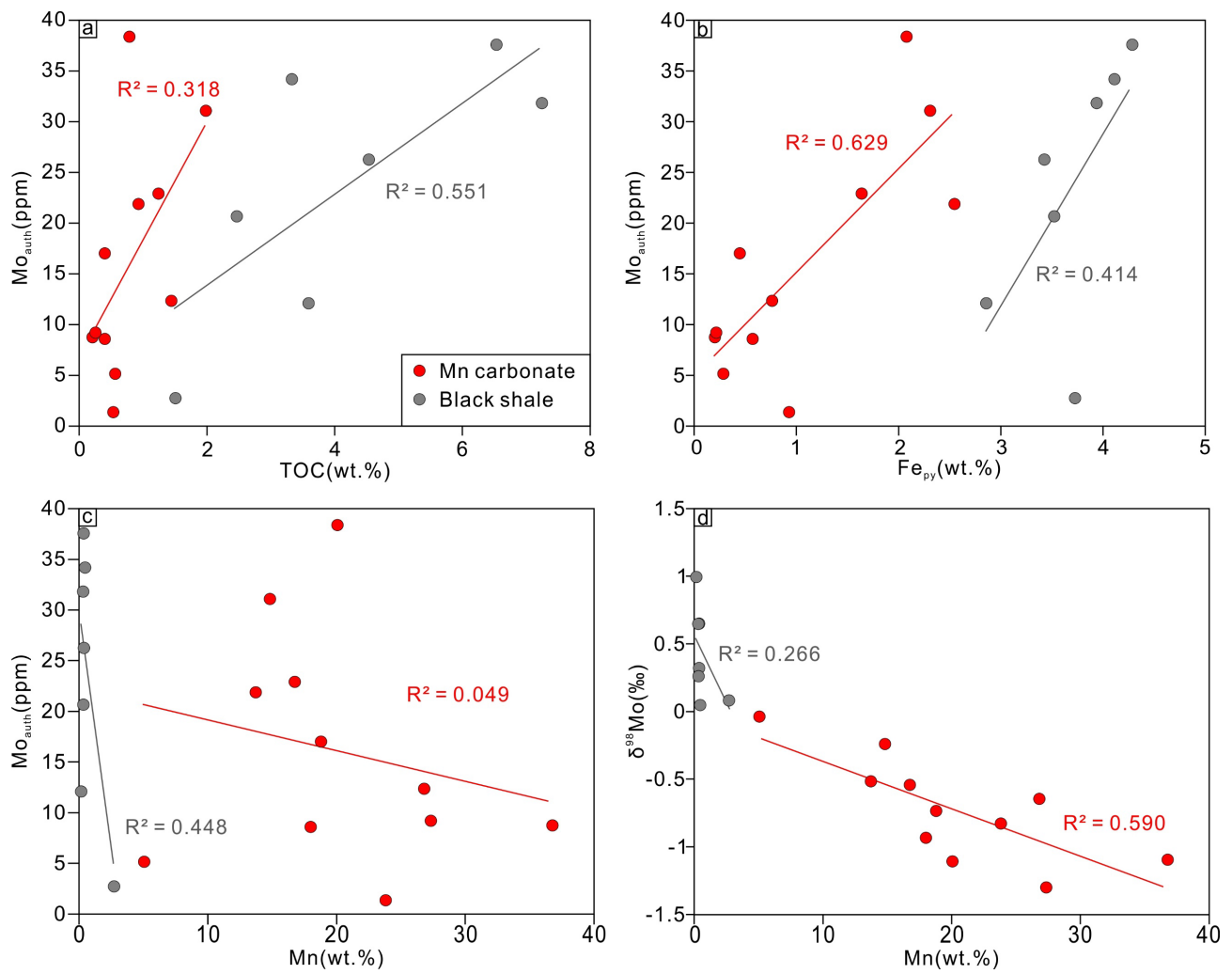


Fig. S6. Correlations between different geochemical results for the Doushantuo Formation Member IV of South China. (a) Plots of TOC versus Mo_{auth} contents. **(b)** Plots of Fe_{py} versus Mo_{auth} contents. **(c)** Plots of Mn versus Mo_{auth} contents. **(d)** Plots of Mn contents versus $\delta^{98}\text{Mo}$ values.

Supplementary Data 1

Table S1-S2. Separated Excel file with raw geochemical data (Table S1) and Mo isotopic steady-state isotope mass balance model results (Table S2) in this study are included in Supplementary Data 1.

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