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Dynamic redox fluctuations and transient oxygenation during deposition of the ~1.56 Ga Gaoyuzhuang Formation, North China Craton

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Abstract

There is increasing evidence that the redox state of the Mesoproterozoic (1.6-1.0 Ga) ocean was much more dynamic than previously recognized, although the trajectory of Earth surface oxygenation over this immense interval of time remains poorly understood. In order to further constrain oceanic oxygenation dynamics, we present a high-resolution, multi-proxy geochemical study of carbonate-rich rocks from the Mesoproterozoic Gaoyuzhuang Formation, North China Craton, which represents a critical Mesoproterozoic section due to its association with the earliest known, decimetre-scale eukaryotes. Combined with Fe-speciation analyses, our approach utilizes sequential leaching to target primary carbonate-phase, and utilizes an improved enrichment factor calculation for application of U (U_{EF}^{*}) and Mo (Mo_{EF}^{*}) systematics to carbonate-rich rocks. Rather than recording a series of discrete oxygenation pulses, our data suggest a prolonged interval of enhanced oxygenation, from the upper part of Member I to the lower part of Member III in the Gaoyuzhuang Formation. However, this only oxygenated surface waters to shallow subtidal depths. Subsequently, a more distinct oxygenation pulse occurred below the Gaoyuzhuang fossil horizon of Member III (~750 m), which oxygenated the water column to around storm wave base. However, this enhanced oxygenation appears to have ceased during deposition of Member IV in the Gaoyuzhuang Formation, with a decline in surface water oxygenation, at least on a local or regional scale, raising uncertainty over the broader scale trajectory of Earth surface oxygenation. Based on the oceanic redox evolution recorded by the whole formation, we speculate that the prolonged stable oxygenation of shallower waters, rather than a discrete oxygenation event, may have permitted the evolution of the large-scale Gaoyuzhuang eukaryotes.

Key words: Mesoproterozoic; Extracted leaching; Carbonate geochemistry; Oxygenation

1. Introduction

The Mesoproterozoic era (1.6-1.0 Ga) has commonly been regarded as a relatively static period in early Earth evolution (often termed the "Boring Billion"), characterized by limited eukaryotic biodiversity and evolution, relatively stable oceanic carbon cycling, and generally low atmospheric and oceanic oxygen levels (Brasier and Lindsay, 1998; Brocks et al., 2023; Cole et al., 2016; Lyons et al., 2014; Planavsky et al., 2014, 2018; Knoll, 2014; Mukherjee et al., 2018). However, recent research has provided significant nuance to the suggestion of stable environment conditions in the Mesoproterozoic, with evidence for considerable ocean redox variability, both temporally and spatially (e.g., Zhang et al., 2015; Wang et al., 2017; Zhang et al., 2018; Shang et al., 2019; Wang et al., 2020; Song et al., 2023; Tang et al., 2025). Similarly, the fossil record has continued to reveal new insight into the evolution of multicellular eukaryotes during the Mesoproterozoic (e.g., Yan and Zhu, 1992; Butterfield, 2015; Zhu et al., 2016; Miao et al., 2021).

In particular, episodic oxygenation events have been documented against the backdrop of overall low oxygen levels in the Mesoproterozoic. These intervals include the 1.60-1.57 Ga Gaoyuzhuang Formation, North China Craton (Zhang et al., 2018; Shang et al., 2019; Luo et al., 2021; Xie et al., 2023), the 1.46-1.45 Ga Hongshuizhuang Formation, North China Craton (Shi et al., 2021), the 1.42-1.36 Ga Velkerri Formation, North Australian Craton (Mukherjee and Large, 2016; Mitchell et al., 2021), the 1.40-1.35 Ga Xiamaling Formation, North China Craton (Zhang et al., 2015; Wang et al., 2017; Song et al., 2023), and the 1.1-1.0 Ga Nanfen Formation, North China Craton

(Tang et al., 2025). Several of these oxygenation intervals have also been linked to recent paleontological discoveries, including the occurrence of decimetre-scale multicellular fossils in the Gaoyuzhuang Formation (Zhu et al., 2016; Chen et al., 2023), and multicellular chlorophyte (green algae) and rhodophyte (red algae) in the Nanfen Formation (Tang et al., 2020).

The Gaoyuzhuang Formation has received particular attention, in part due to the increased size of multicellular fossils found in the middle section of this unit (Zhu et al., 2016; Chen et al., 2023). The Gaoyuzhuang Formation records over 1,500 m of peritidal to shallow-marine carbonates with distinctive microbialite biostromes (Guo et al., 2013). Evidence for oxygenation during deposition of the Gaoyuzhuang Formation comes from progressively negative Ce anomalies associated with negative $\delta^{13}C_{carb}$ excursions (Zhang et al., 2018), along with I/(Ca+Mg) spikes, $\delta^{98}Mo$ excursions, and positive Cr isotope values that may potentially indicate transient atmospheric O_2 rises to ≥4% PAL (Shang et al., 2019; Luo et al., 2021; Tang et al., 2022; Xie et al., 2023). These geochemical signals have led to the suggestion that oxygenation pulses may have been directly linked to the appearance of the decimetre-scale Gaoyuzhuang eukaryotes (Zhang et al., 2018; Luo et al., 2025). However, current understanding of the evolution of redox conditions during deposition of the Gaoyuzhuang Formation remains incomplete. In particular, while oxygenation pulses have been invoked at various points through the succession (e.g., Zhang et al., 2018; Shang et al., 2019; Luo et al., 2021), the temporal extent of these pulses and their intensity remain poorly constrained, which clearly limits understanding of potential links to biological evolution at this time.

To provide further insight into the evolution of ocean redox conditions during deposition of the Gaoyuzhuang Formation, we present a high resolution, multi-proxy geochemical investigation of a continuous section spanning almost the entire formation. We focus on detailed iron speciation analyses, and utilize a new approach for considering redox sensitive trace metal (RSTM) data in carbonate lithologies, alongside consideration of RSTM's in carbonate-hosted phases. Following this improved analytical approach, we then consider these data in terms of variability in relative sea level, to provide a highly resolved reconstruction of oxygenation dynamics during deposition of the Gaoyuzhuang Formation.

2. Geological setting

The North China Craton contains the Eastern Block, Western Block, and the Trans-North China Orogen (Zhao et al., 2005). After the assembly of the Nuna supercontinent, three major Mesoproterozoic rift zones existed, namely the Xiong'er, Yanliao and Zha'ertai-Baiyun Obo-Huade rift systems (Fig. 1a; Zhao et al., 2002; Zhang et al., 2012). The Yanliao rift zone is located in the Yanshan region of the northern margin of the North China Craton. The region preserves a thick succession of late Paleoproterozoic to Neoproterozoic sedimentary strata, which are formally divided into the Changcheng, Jixian and Qingbaikou systems. Amongst these, the Jixian Section in the Yanshan region near Jixian city, Tianjin Province, is ocated near the depositional center of the Yanliao Basin. This section has been extensively studied through sedimentological, paleontological and geochronological investigations, providing a strong foundation for further research (Fig. 1a, b, d; Chu et al., 2007; Li et al., 2003). It comprises five formations, including the Gaoyuzhuang, Yangzhuang, Wumishan, Hongshuizhuang and Tieling formations from bottom to top (Fig. 1c).

The Gaoyuzhuang Formation is the basal unit of the Jixian Group and occurs widely in the Yanliao Basin, mainly at two locations, the Yanqing section and Jixian section (Xie et al., 2024). This study focuses on the Jixian section, located in Jizhou District (Fig. 1d, e). The Gaoyuzhuang Formation has experienced only low-grade metamorphism (generally below prehnite-pumpellyite facies), and was deposited in deep subtidal to supratidal environments in the Yanliao Basin in the North China Craton. The Gaoyuzhuang Formation has been divided into four lithological members, which mainly consist of dolostone and partly dolomitic limestone over an interval of ~1560 m (Fig. 1c). What's more, the existence of Paleo-Mesoproterozoic supercontinent Columbia has undergone a long-period accretion between 1.6 Ga and 1.3 Ga (Zhao et al., 2002; Pisarevsky et al., 2014; Nordsvan et al., 2018), but the position of North China Craton within Columbia is still highly debated due to the paucity of available high-quality paleomagnetic and reliable geological constraints. Cai et al. (2020) reported new paleomagnetic results from ca. 1.68-1.63 Ga mafic dyke swarms and incorporated the North China Craton into a paleogeographic reconstruction of the Columbia supercontinent. Their results show that the reconstruction places the North China Craton at low palaeolatitudes during the early Mesoproterozoic. Although an exact palaeolatitude for ~1.6-1.5 Ga cannot be uniquely determined, these results give more evidence to support a tropical to subtropical setting for the North China Craton, consistent with previous Proterozoic paleomagnetic constraints (e.g., Zhao et al., 2004). What's more, the development of thick and laterally extensive carbonate successions in different sections, stratigraphically coherent $\delta^{13}C_{carb}$ trends, seawater-like REE signatures, and Mo isotopic signatures could also indicate that the Gaoyuzhuang Formation was deposited in an open to semi-open marine basin rather than a strongly restricted environment (Chen et al., 1981; Chu et al., 2007; Guo et al., 2013; Zhang et al., 2018; Luo et al., 2021).

The sea level is followed by Luo et al. (2021), showing a systematic variation (Fig. 2). Member I is characterized by supratidal to shallow subtidal, recording predominantly shallow-water deposition, followed by a relative deepening into Member II and the lower part of Member III, reaching shallow to deep-subtidal conditions (Fig. 2). At the middle of Member III, as its deepest, it is likely deposited near or below storm wave base, while from the middle of Member III to Member IV, it indicates a gradual shallowing trend, with deposition returning toward shallower subtidal environment.

Member I mainly comprises thick-bedded dolostone, with thin quartz sandstones in the lowermost part, representing a very shallow coastal environment. The upper part has Mn-rich dolostone with local chert bands, indicating deepening into a subtidal setting (Fig. 2; Guo et al., 2013). Member II is characterized by Mn-rich siltstone and Mn-bearing carbonates, with increasing clay contents in the upper part of the member indicating a further increase in water depth (Fig. 2; Guo et al., 2010). Member III consists of calcareous mudstone with dolomitic nodules and thin argillaceous dolostone in the lower part, combined with limestone and dolostone with shale interlayers. The upper part of the member III contains molar-tooth structures and columnar stromatolites (Mei, 2007; Guo et al., 2013). Notably, the multicellular eukaryotic fossils are reported from the middle and upper part of this member (Fig. 2; Zhu et al., 2016; Chen et al., 2023). Member IV comprises bituminous dolostone in the lower part, and thick-bedded coarse crystalline dolostone in the upper part. Our samples cover the bottom of Member I to the lower part of Member IV (Mei, 2007).

The age of the Gaoyuzhuang Formation is well constrained by zircon U-Pb ages of 1560 ± 5 Ma and 1582 ± 12 Ma from tuffaceous beds within the lower to the middle part of Member III (Li et al., 2010; Tian et al., 2015). Recently, a new SIMS zircon age of 1588.8 ± 6.5 Ma from a volcanic tuff in Qianxi County, about 11 m above the macrofossil horizon in the upper part of Member III, has also been reported (Chen et al., 2024).

3. Methods

A total of 163 samples were analysed, covering the bottom to the top of the Gaoyuzhuang Formation. The samples dominantly comprise limestones, with a few being dolomitic (Table S1). All samples were collected from unaltered host rock areas without obvious late-stage structural veins. Surface weathered layers were removed prior to crushing to powder (<100 mesh) in an agate mortar.

3.1. Bulk-rock geochemical analyses

Bulk-rock major element concentrations were measured on fused glass disks using a Rigaku ZSX100e X-ray Fluorescence spectrometer (XRF). The analytical uncertainties for major elements varied from 1% to 5%, based on repeat analyses of the international standards, BHOV-2 and AGV-2. Trace element abundances of bulk rock were measured on a Perkin-Elmer Sciex ELAN 6000 ICP-MS. Approximately 50 mg of sample was digested in a solution of HF and HNO_3 in high-pressure Teflon vessels for 7 days at ~100°C. Instrumental stability was maintained through continuous monitoring using a Rhodium-spiked internal standard solution. For quality assurance and data calibration, certified reference materials, including United States Geological Survey standards G-2, W-2, MRG-1 and AGV-1, and Chinese national rock standards GSD-12, GSR-1, GSR-2 and GSR-3, were analyzed concurrently with the samples. The accuracy of ICP-MS analyses was better than 5% for all elements of interest. The analyses were performed at the Guangzhou Tuoyan Testing Technology Co., Ltd.

3.2. Iron speciation

Iron speciation analyses were performed following the sequential extraction procedure of Poulton and Canfield (2005) in the Cohen Geochemistry Laboratory, University of Leeds. The extraction targeted the fraction of total iron (Fe_T) considered highly reactive (Fe_{HR}) towards sulfide-promoted reductive dissolution (Raiswell and Canfield, 1998; Poulton et al., 2004). Highly reactive iron includes carbonate-associated iron (Fe_{carb}; targeted with Na-acetate at pH 4.5 and 50°C for 48 h), ferric(oxyhydr)oxides (Fe_{ox}; targeted with Na-dithionite at pH 4.8 for 2 h), and magnetite (Fe_{mag}; targeted with ammonium oxalate for 6 h). Sulfide-bound iron, including acid volatile sulfide (Fe_{AVS}; extracted with boiling 6 N HCl) and pyrite (Fe_{py};

extracted with boiling chromous chloride), were extracted via the sequential method of Canfield et al. (1986). Quality assurance was achieved through repeat analyses of international standard, WHIT (Alcott et al., 2020), with all procedural stages giving relative standard deviations (RSDs) of <5%. Iron speciation analyses on carbonate samples require additional care due to the potential for significant diagenetic overprinting (for example during deep burial dolomitization), which led Clarkson et al. (2014) to suggest a general Fe_T threshold of 0.5 wt.% for robust interpretation of Fe speciation data. Many of our samples have Fe_T <0.5 wt.% (Table S2). We have evaluated the high Fe_T and low Fe_T samples, which has no bias in distribution (see details in Supplementary material). Nevertheless, there is no discernable difference in the interpretation of Fe speciation data for low and high Fe_T samples (see below), and thus for completion, we include data for all analysed samples here.

3.3. Total organic carbon analyses

Total organic carbon (TOC) contents of 115 samples were obtained using a LECO CS-344 carbon-sulfur Analyzer at the Guangzhou Tuoyan Testing Technology Co., Ltd. Approximately 0.25-0.50 g powdered samples were placed in polypropylene centrifuge tubes and slowly treated with 5 mL of diluted HCl (1+9, ~1 M) to remove inorganic carbon, and then samples were repeatedly washed with ultrapure 18.2 MΩ H_2O until the pH was above 4. Sample analyses were calibrated against reference material IFP160000 (the certified TOC value is 3.28 ± 0.14 wt.%), with an RSD of <5%.

3.4. Carbon and oxygen isotope analyses

Carbon ($\delta^{13}C_{carb}$) and oxygen ($\delta^{18}O$) isotopes were analyzed by Iso-Analytical

Limited (UK). Samples were digested with phosphoric acid in Exetainer™ vials at 90°C for 3 h, followed by a 24 h reaction at room temperature to ensure complete carbonate conversion to CO_2. The evolved CO_2 was analyzed for carbon and oxygen isotopic ratios using Continuous Flow Isotope Ratio Mass Spectrometry (CF-IRMS; Europa Scientific 20-20 IRMS), with data reported relative to the VPDB standard. Reference materials included NBS-18 carbonatite (IAEA standard; $\delta^{13}C$ = -5.01‰, $\delta^{18}O$ = -23.2‰), and laboratory standards IA-R022 ($\delta^{13}C$ = -28.63‰, $\delta^{18}O$ = -22.69‰), IA-R066 ($\delta^{13}C$ = +2.33‰, $\delta^{18}O$ = -1.52‰), IA-R040 ($\delta^{13}C$ = -0.72‰, $\delta^{18}O$ = -17.07‰), and ILC1 ($\delta^{13}C$ = +2.17‰, $\delta^{18}O$ = -3.99‰). Samples and standard acid digests were measured concurrently using IA-R022, eliminating the need for temperature-dependent fractionation corrections. Analytical precision was <3% for both $\delta^{13}C$ (>97% accuracy) and $\delta^{18}O$ (>99% accuracy).

3.5. Elemental concentrations in carbonate phases

During the formation of authigenic carbonates, detrital material and other authigenic phases (e.g., Fe and Mn (oxyhydr)oxides, organic matter, and sulfide minerals formed in the water column or during diagenesis) may significantly influence the trace element contents of carbonate rocks (Nance and Taylor, 1976; Frimmel, 2009). We therefore utilized a sequential extraction technique to quantify the abundance of trace elements in carbonate phases (Bayon et al., 2002), utilizing sequential extraction methods from Rongemaille et al. (2011) and Jia et al. (2023). First, ~500 mg of powder was dried in an oven for 24 h prior to analysis. The powders were then washed for 3 h using 5 ml of 1 mol/L CH_3COONH_4 at room-temperature, to remove exchangeable elements. Following this, the samples were treated with 1 N ultrapure Acetic Acid (AA) for 16 h to remove carbonate minerals and to extract the carbonate fraction. The supernatant was then evaporated to dryness and re-dissolved in 2% HNO_3 prior to analysis. Trace element concentrations were determined using a Thermo Fisher X series 2 ICP-MS at Guizhou Tongwei Analytical Technology Co., Ltd.

4. Results

All geochemical data are listed in the Information (Tables S1-S3). To aid discussion, we divide the Gaoyuzhuang Formation into 6 intervals (Interval A-F) based on variability in $\delta^{13}C_{carb}$ values and geochemical data. Interval A covers the majority of Member I, and at the base of this interval, our new $\delta^{13}C_{carb}$ data show a previously undocumented, short-lived negative excursion, from ~-0.5‰ down to ~-1.8‰ (Fig. 2). This is followed by an increase to relatively stable values of -0.29 to 0.32‰, with an average of 0.07‰. Towards the top of this member (at ~300 m), there appears to be a further distinct $\delta^{13}C_{carb}$ excursion to ~-0.9‰ (Fig. 2). However, the lack of samples from the uppermost part of the Interval A precludes understanding of whether this represents a distinct isotope excursion, or the start of the more highly resolved excursion evident across Interval B (see below). While the identification and analysis of additional samples from the top of Member I is required to resolve this issue, we note that the lowermost samples from Interval B have higher isotope values than the upper samples from Interval A, potentially suggesting that these latter samples may document a discrete, previously unrecognized $\delta^{13}C_{carb}$

excursion.

Total Fe varies considerably throughout Interval A (0.29-1.28 wt.%), while Fe_{HR}/Fe_T values are persistently high (a feature of the entire section; Fig. 2), plotting above the 0.38 threshold for the recognition of water column anoxia (Poulton and Canfield, 2011; note that some values slightly exceed the maximum value possible (1.0), which reflects increased errors in the measurement of Fe phases when Fe contents are low). However, the interpretation of low Fe_T (i.e., <0.5 wt.%) and higher Fe_T samples remains constant throughout the section (Fig. 2), suggesting that Fe speciation analyses have not been compromised by Fe addition during diagenesis (see Section 5.1 for an evaluation of potential diagenetic modification of primary geochemical signals). In terms of the degree of sulfidation of the Fe_{HR} fraction, Fe_{py}/Fe_{HR} values (where Fe_{py} includes minor Fe present as Fe_{AVS} in some samples; Table S3) are very low (~0) throughout Interval A (Fig. 2). Carbonate-phase Fe contents (Fe_{carb}) show considerable scatter (521-3700 ppm), but there is an overall increase through the interval, consistent with increasing total Mn (0.05-2.04 wt.%) and Mn_{carb} (44.6-2870 ppm) contents, with peak values for these Mn pools occurring in association with the transition to lower $\delta^{13}C_{carb}$ values towards the top (Fig. 2). Several samples have elevated Mo_{EF}^* and U_{EF}^* values (>1), particularly at the bottom ($Mo_{EF}^* = 0.38$-2.52; $U_{EF}^* = 0.93$-1.67) and top ($Mo_{EF}^* = 1.17$-3.02; $U_{EF}^* = 0.97$-1.23) of Interval A where more negative $\delta^{13}C_{carb}$ values occur, while TOC contents are relatively low throughout (up to 0.2 wt.%) (Fig. 2).

We present no new $\delta^{13}C_{carb}$ or Fe speciation data for Interval B, which represents the boundary between members I and II. However, published $\delta^{13}C_{carb}$ values show a negative excursion (from ~0.3 to ~-2.61‰), while Fe_{HR}/Fe_T ratios remain high and Fe_{py}/Fe_{HR} ratios remain low (Fig. 2; Luo et al., 2021). Both Fe_T and Fe_{carb} contents increase in Interval B (0.6-1.33 wt.% and 2270-7000 ppm), alongside major increases in total Mn (1.08 to 2.61 wt.%) and Mn_{carb} (6420 to 19400 ppm) (Fig. 2). However, U_{EF}^* (0.98-1.19) and Mo_{EF}^* (0.79-1.24) values are commonly close to unity or only slightly enriched, while TOC values generally remain low, with the exception of two samples with considerably elevated values (2.46 and 2.53 wt.%; Fig. 2).

Interval C corresponds to Member II of the Gaoyuzhuang Formation. The $\delta^{13}C_{carb}$ values range from -0.7‰ to -0.3‰, similar to the middle of Interval A, but there is an overall decrease to lower values towards the top of the interval (Fig. 2). The Fe_{HR}/Fe_T values remain elevated, while Fe_{py}/Fe_{HR} values are persistently very low (Fig. 2). Total and carbonate-phase Fe contents share similar patterns, with an initial drop to lower values towards the center of the interval (0.14-0.23 wt.% and 1190-1810 ppm, respectively), followed by a rise to higher values towards the top (0.39-0.79 wt.% and 1540-4620 ppm, respectively). Total Mn and Mn_{carb} contents show a similar pattern, with an initial decline to lower values, followed by a distinct increase in the upper half of the interval (Fig. 2). Mo_{EF}^* values show considerable scatter, reaching a maximum value of 16.1. By contrast, U_{EF}^* values remain persistently low, with no evidence of enrichment (Fig. 2).

During Interval D, a second negative $\delta^{13}C_{carb}$ excursion occurs, while elevated Fe_{HR}/Fe_T and low Fe_{py}/Fe_{HR} ratios persist (Fig. 2). Total Fe and carbonate-phase Fe contents generally decrease relative to the top of Interval C, with similar trends apparent for total Mn and Mn_{carb}. The U_{EF}^{*} values rise slightly (to 1.26), while Mo_{EF}^{*} values remain low, at ~0.96 (Fig. 2).

In Interval E, following an initial rise in $\delta^{13}C_{carb}$ values (from -1.6‰ to -0.9‰), another negative excursion then occurs, to values as low as -2.9‰ (Fig. 2). Fe_{HR}/Fe_{T} values are persistently high, and some samples towards the top of the interval display slightly elevated (up to 0.22) Fe_{py}/Fe_{HR} ratios, coincident with elevated TOC contents (up to 0.46 wt.%; Fig. 2). Total Fe and Fe_{carb} contents also vary considerably (0.04-1.32 wt.% and 1110-4590 ppm, respectively), while total Mn remains low and Mn_{carb} contents decrease further towards the top of the interval. Mo_{EF}^{*} and U_{EF}^{*} values both increase (1.18-9.35 and 0.72-1.30, respectively) towards the top of this interval.

During Interval F, covering the middle of Member III to the bottom of Member IV, $\delta^{13}C_{carb}$ values are generally maintained at relatively high values, but with some scatter (-1.4‰ to 0.1‰), while the ranges in Fe_{HR}/Fe_{T}, Fe_{py}/Fe_{HR}, Mn, Mn_{carb} and TOC remain similar to the underlying interval (Fig. 2). However, total Fe values show a progressive decline from the lower to the top of Interval F (1.56-0.01 wt.%), with Fe_{carb} decreasing and then remaining at relatively low values (850-3200 ppm; Fig. 2). These samples are also generally enriched in Mo and U (1.05-31.11 and 1.02-1.47, respectively), although Mo_{EF}^{*} decreases to persistently low values towards the top of this interval (1.05-1.61; Fig. 2)

5. Discussion

5.1. Evaluation of primary geochemical signatures

Prior to evaluating the evolution of ocean redox chemistry through the Gaoyuzhuang Formation, the potential for diagenetic modification of primary geochemical signals in these carbonate-rich lithologies requires consideration. In this context, Zhang et al. (2018) described well-preserved depositional textures for the Jixian section, including coated grains, micritic matrices and algal laminae. In particular, cathodoluminescence analysis revealed predominantly non-luminescent carbonate grains, with bright luminescent cements and zoned replacive dolomites exhibiting dull cores and bright rims. Collectively, this indicates early diagenetic alteration during shallow burial without pervasive late-stage overprinting (Zhang et al., 2018). Luo et al. (2021) also analyzed the morphology of carbonate minerals in the dolostones from the Gaoyuzhuang Formation in the same locality as the present study, with the limited occurrence of euhedral Fe-oxides and an absence of late-stage cements or fabric-destructive characteristics indicating minimal later stage alteration.

For our samples in particular, the $\delta^{13}C_{carb}$ data predominantly preserve contemporaneous seawater signatures, as evidenced by $\delta^{18}O$ values higher than -10‰, which have a weak correlation with $\delta^{13}C_{carb}$ values (Fig. 3a). In addition, strontium (Sr) is sensitive to diagenetic alteration in carbonate rocks, whereby Sr^{2+} may substitute for Ca^{2+} in marine carbonates but is depleted during fluid alteration (Brand and Veizer, 1981). However, with the exception of three samples with low MgO and CaO values, Mg/Ca ratios have only a weak negative relationship with Sr/Ca ratios (Fig. 3b), suggesting that diagenetic alteration had a limited overall impact on the geochemical composition of these carbonate samples. What's more, we also examine the elemental and isotopic correlations to the diagenetic degree: Mn/Sr ratio versus $\delta^{13}C_{carb}$ value and Mn/Sr ratio versus $\delta^{18}O$ value (Fig. 3c, d). Based on the Mn-rich bearing horizons during Member I-II, it can be divided the samples into two groups, Mn-rich samples and non-Mn-rich samples. For the non-Mn-rich samples, cross-plots show no systematic correlation between Mn/Sr and $\delta^{13}C_{carb}$ (Fig. 3c), which is consistent with the weakly correlation between Mn/Sr and $\delta^{18}O$ (Fig. 3d). What's more, the several samples, possessing relatively high carbonate-phase Mn contents, have a strong correlation with $\delta^{13}C_{carb}$ and $\delta^{18}O$, which indicated that these samples might be affected by preferential alteration during diagenesis. Together with these findings, it shows that these samples experienced low-degree diagenetic alteration, which represents the primary geochemical signatures.

Detrital contamination is an additional factor that requires consideration. To avoid contamination from the non-carbonate components, we utilized a sequential leaching approach to target carbonate-phase trace elements (see Methods). Titanium (Ti) and thorium (Th) are expected to be negligible in pure carbonate phases, but are commonly elevated in detrital silicates. This contrast makes them sensitive proxies for detecting even minor detrital contamination in the carbonate-phase leaches (Webb and Kamber, 2000; Nothdurft et al., 2004). Therefore, we applied an end-member calculation to demonstrate the significance of detrital contamination, which assumes that all measured carbonate-phase Ti comes from the detrital phase (Li et al., 2025b). The maximum potential detrital contribution for carbonate-associated Th (Th_{carb}) can be then calculated:

$$Th_{det} = (Th/Ti)_{det} \times Ti_{meas} \quad (1)$$

$$Th_{carb} = Th_{meas} - Th_{det} \quad (2)$$

where Th_{det} represents the concentrations of Th in the detrital phase, and $(Th/Ti)_{det}$ expresses the Th/Ti mass ratio of the detrital components. We adopted an end-member value for the detrital Th/Ti ratio $(Th/Ti)_{det}$ of 0.0027 (Rudnick and Gao, 2003), which represents an extreme estimate for crustal compositions. Ti_{meas} and Th_{meas} represent the measured Ti and Th values in the carbonate-phase leachate. The resulting Th_{carb} values are compared to the measured leachate Th concentrations (Th_{meas}) in Table S2. The close agreement between calculated and measured values confirms that the detrital contribution is negligible, and thus the measured trace element concentrations in the carbonate-phase leachate dominantly represent primary signatures.

5.2. Oceanic redox evolution through the Gaoyuzhuang Formation

Redox-sensitive trace elements such as Mo and U are commonly used to evaluate paleo-redox conditions in the ocean (Algeo and Tribovillard, 2009). However, calculation of EF values in chemical sediments such as carbonates commonly leads to elevated values due to low detrital Al contents (Tribovillard et al., 2006; Krewer et al., 2024). We thus applied an improved EF calculation (EF^*) that accounts for the low Al contents of chemical sediments, and allows direct comparison with EF trends derived from siliciclastic sediments (Krewer et al., 2024):

$$Element_{excess} = Element_{sample} - (Al_{sample} \times Element_{UCC}/Al_{UCC}) \quad (3)$$

$$Element_{EF}^{*} = (Element_{excess} + Element_{UCC}) / Element_{UCC} \quad (4)$$

where $Element_{excess}$ represents the trace metal fraction not associated with the siliciclastic influx, based on normalization to average upper continental crust (UCC; Rudnick and Gao, 2003).

In oxic and weakly dysoxic depositional environments, U usually demonstrates minimal enrichment, as reflected by low U_{EF}^* values (e.g., Li et al., 2025a). Enrichments in U increase under more reducing conditions, with elevated U_{EF}^* values in anoxic settings (Li et al., 2025a). This arises due to the reduction of soluble carbonate complexes to insoluble U(IV), which occurs in anoxic sediments and does not require dissolved sulfide (Anderson et al., 1989). Molybdenum predominantly exists as soluble molybdate (MoO_4^{2-}) under oxic conditions, commonly resulting in limited enrichments in normal oxic marine sediments (Bertine and Turekian, 1973). However, Mo drawdown to the sediments can occur via two primary mechanisms: enhanced fixation through interaction with sulfide, and particulate-phase drawdown (the so-called "particulate shuttle"; Erickson and Helz, 2000; Tribovillard et al., 2004). These distinct removal pathways can be effectively discriminated through Mo_{EF}^*-U_{EF}^* covariation analysis (Algeo and Tribovillard, 2009; Tribovillard et al., 2012; Li et al., 2025a).

Most of the U_{EF}^* values through the Gaoyuzhuang Formation are close to a value of 1, or are slightly enriched (up to ~1.5; Fig. 2). These values are consistent with variable oxic to dysoxic conditions at the sediment-water interface (Li et al., 2025a). Although some Mo_{EF}^* values plot close to 1, many samples are slightly elevated, with several discrete peaks (Fig. 2). A Mo_{EF}^*–U_{EF}^* crossplot shows that while some samples plot in the oxic to dysoxic zone, most samples are more closely associated with the particulate shuttle trajectory (Fig. 4; Li et al., 2025a), suggesting that Mo enrichments dominantly arise due to drawdown in association with Fe-Mn (oxyhydr)oxides precipitating in the water column, rather than due to water column anoxia at the site of deposition (e.g., Algeo and Tribovillard, 2009; Tribovillard et al., 2012).

Iron speciation is also commonly used to reconstruct water column redox conditions, via the enrichment of highly reactive phases due to mobilization and precipitation in the water column (Raiswell and Canfield, 1998; Poulton and Canfield, 2011; Poulton, 2021). Oxic conditions are typically indicated by Fe_{HR}/Fe_T ratios lower than ≤ 0.22, whereas anoxic conditions are commonly indicated by ratios ≥ 0.38 (Poulton and Canfield, 2011). However, it should be recognized that these enrichments may be due to upwelling of anoxic deeper waters into oxic or dysoxic surface waters, or due to deepening of the oxycline into anoxic waters, and thus anoxic conditions at the actual site of deposition are not necessarily indicated (Poulton and Canfield, 2011; Poulton, 2021). For samples that exhibit evidence of Fe^{2+} mobilization under anoxic conditions, the Fe_{py}/Fe_{HR} ratio is then used to distinguish ferruginous and euxinic water column conditions, whereby values above 0.6-0.8 may indicate euxinia, whereas lower values likely record ferruginous conditions (Poulton, 2021).

Throughout the section, all samples are enriched in Fe_{HR}/Fe_T, supporting mobilization of Fe^{2+} under anoxic conditions (Poulton and Canfield, 2011; Raiswell et al., 2018), while low Fe_{py}/Fe_{HR} ratios indicate dominantly ferruginous deeper water conditions (Fig. 2). However, stratigraphic variability in the array of applied geochemical proxies may reflect dynamic redox fluctuations at the chemocline, which we next consider in more detail for Intervals A-F (Fig. 2).

The lowermost part of Interval A was deposited in a supratidal zone, and the water depth then increased to intertidal to very shallow subtidal, indicating extremely shallow-water conditions (Fig. 2). Despite the very shallow water conditions, the lowermost samples in Interval A tend to have slightly elevated Mo_{EF}^* and U_{EF}^* values (Fig. 2) which plot towards the dysoxic field on a Mo_{EF}^*–U_{EF}^* crossplot (Fig. 4). Dysoxic conditions are supported by the lack of Mn enrichment (Fig. 2). We note here that while total Mn dominantly comprises Mn present as both oxides and carbonate phases, Mn_{carb} may represent either a primary carbonate phase formed under anoxic water column conditions (e.g., Wittkop et al., 2020), or precipitation of Mn oxides under oxic water column conditions followed by reduction and reprecipitation as carbonate phases during early diagenesis (e.g., Calvert and Pedersen, 1996). However, since the variability in total Mn contents through the section far exceeds that for the Mn_{carb} fraction (Fig. 2), we interpret changes in these parameters to dominantly reflect changes in Mn oxide precipitation driven by variability in the intensity of water column oxygenation. We additionally note here that Mn oxide precipitation generally requires elevated oxygen levels relative to Fe (oxyhydr)oxide precipitation (e.g., Glasby and Schultz, 1999). Thus, the lack of Mn enrichment in the basal section of Interval A implies that the observed Fe_{HR} enrichments occurred due to upwelling of ferruginous deeper waters into very shallow waters that were not sufficiently oxygenated to promote Mn^{2+} oxidation. However, as the water depth increased slightly towards the top of the interval, total Mn and Mn_{carb} contents increase (Fig. 2), suggesting the onset of better oxygenated conditions. This is supported by Mo_{EF}^*–U_{EF}^* systematics, with most of the data through Interval A plotting along the particulate shuttle trajectory (Fig. 4), as well as the apparent decrease in $\delta^{13}C_{carb}$, which likely reflects oxidation of dissolved organic carbon (e.g., Zhang et al., 2018; Luo et al, 2021, 2025).

The reconstructed sea level curve suggests that the samples in Interval B were deposited at a similar, or slightly deeper, water depth relative to the samples from the top of Interval A (Fig. 2). Relatively stable Fe_{HR}/Fe_T and low Fe_{py}/Fe_{HR} ratios demonstrate that anoxic, ferruginous conditions persisted in deeper waters (Fig. 2). However, Mn and Fe concentrations increase in both the bulk and carbonate fractions, while Mo_{EF}^* and U_{EF}^* values are persistently low (Fig. 2). These combined characteristics suggest the continued enhancement of elevated oxygen levels in shallow waters (impinging on the shallow subtidal zone), relative to Interval A, which specifically promoted the precipitation of Mn oxides (Fig. 4a). The lack of U enrichment suggests that the sediment-water interface was also well oxygenated, while the absence of Mo drawdown via the particulate shuttle (despite elevated Fe-Mn (oxyhydr)oxide deposition), suggests that Mo was likely drawn down via this mechanism in slightly deeper waters. Luo et al. (2021) have conducted detailed petrographic observations, which indicated that primary sedimentary fabrics are well preserved throughout the section, including algal laminae and nodular structures, with no evidence for pervasive recrystallization. What's more, Zhang et al. (2018) have also investigated detailed petrographic work, which shows little evidence for deep burial dolomitization. Our samples are collected close to theirs, which are more likely experienced similar comparable diagenetic alteration. These observations indicate that later diagenetic overprinting is unlikely to account for the lack of U enrichment. Total organic carbon contents are commonly low through Interval B, but there are two samples with very high values (up to 2.53 wt.%; Fig. 2), likely reflecting transient intervals of enhanced productivity, potentially linked to enhanced nutrients inputs that may have driven more expansive oxygenation. The enhanced oxygenation indicated for this interval is supported by the distinct negative $\delta^{13}C_{carb}$ excursion (Luo et al., 2021), which appears to reflect basin-scale oxygenation of shallower waters.

During Interval C, manganese-enriched siltstones interbedded with thick-bedded manganiferous and micritic dolostones were deposited (Mei, 2007). The samples plot close to the particulate shuttle trajectory on a Mo_{EF}^{*}–U_{EF}^{*} crossplot (Fig. 4a), suggesting this mechanism for Mo draw down, rather than sulfide scavenging, while the high Fe_{HR}/Fe_{T} and low Fe_{py}/Fe_{HR} ratios support the continued persistence of ferruginous anoxia in the deeper waters (Fig. 2). In more detail, however, the initial drop in total Mn and Mn_{carb} contents at the base of Interval C coincides with a deepening water column, whereas as water depth subsequently decreased again, Mn enrichments re-occur (Fig. 2). At the same time, there is a distinct decrease in $\delta^{13}C_{carb}$ values, supporting oxidation of dissolved organic carbon in very shallow waters. This suggests the persistence of shallow water oxygenation through Interval C, which did not extend deeper than the shallow sub-tidal zone.

The decrease in $\delta^{13}C_{carb}$ persists and becomes more prevalent in Interval D at the base of Member III (Fig. 2). This excursion occurs coincident with fluctuating, but commonly increased Fe_{HR}/Fe_T and Fe_{carb} contents, but low total Mn and Mn_{carb} contents (Fig. 2). Uranium is moderately enriched, but Mo_{EF}^* values are persistently low (Fig. 2), and as such, there is no indication for significant draw down of Mo via the particulate Fe-Mn (oxyhydr)oxide shuttle (Fig. 4b). Together, these observations indicate persistent shallow water oxygenation. However, since the water depth did not change appreciably relative to the top of Interval B (Fig. 2), the absence of Mn enrichments, coupled with slightly elevated U_{EF}^* values, may indicate a lower level of oxygenation relative to that observed in the underlying sediments.

Following a return to background $\delta^{13}C_{carb}$ values as the water depth increased during the lower part of interval E, a pronounced negative $\delta^{13}C_{carb}$ shift (to the lowest values observed, approaching -3‰) occurs towards the top of this interval (Fig. 2). It is notable that alongside high Fe_T and Fe_{carb} contents, and high Fe_{HR}/Fe_T ratios, both TOC contents and Fe_{py}/Fe_{HR} ratios show significant peaks at this time (Fig. 2). This indicates the relatively rapid development of anoxia in surface sediments, which is supported by persistent enrichments in U (Fig. 2). In more detail, the relationship between Mo_{EF}^* and U_{EF}^* (Fig. 4b) documents two groups of samples, with some aligning with the particulate shuttle draw down pathway, while others plot towards the dysoxic field in the redox pathway, which suggests fluctuating redox conditions in the water column. Overall, however, given that the water depth approaches its deepest extent coincident with this carbon isotope excursion (Fig. 2), the combined data indicate an interval of enhanced shallower water oxygenation that extended to deeper depths than in the underlying strata. This may have been stimulated by an enhanced weathering influx of nutrients (Shang et al., 2019; Chen et al., 2026), that enhanced primary productivity, leading to the observed enrichment in TOC, with remineralization of this TOC promoting dysoxic conditions close to the sediment-water interface and the generation of sulfidic porewaters during diagenesis. Surface water oxygen levels were sufficient to promote the precipitation of Fe (oxyhydr)oxides, but the more reducing conditions relative to Interval B prevented the precipitation of Mn oxides, resulting in low total Mn and Mn_{carb} contents at this precise location (Fig. 2). However, since this interval documents relatively deepwater conditions, it remains likely that shallower waters were sufficiently oxic to promote extensive Mn oxide precipitation at more proximal locations elsewhere.

After an initial deepening, a gradual rise in sea level occurred in Interval F, with a transition from a basinal setting (below storm wave base), to at least a shallow subtidal setting (Fig. 2). The persistently low Mn contents suggest that oxygen availability did not exceed the threshold required for sustained Mn oxidation (Fig. 2). Compared to the previous interval, $\delta^{13}C_{carb}$ values are relatively stable, and generally plot above the average value for the section (Fig. 2). However, as with Interval E, TOC values show a relatively high degree of variability, ranging from 0.1 to 0.5 wt.%, while there are also small peaks in Fe_{py}/Fe_{HR} (Fig. 2). In addition, while some samples follow the particulate shuttle trajectory on a Mo_{EF}^{*}–U_{EF}^{*} crossplot, many of the samples plot close to the dysoxic zone on the redox pathway (Fig. 4b). Specifically, at the base of the interval, samples exhibit mixed behavior, with some plotting along the particulate shuttle trajectory while others plot within the dysoxic field. However, most samples plot within the dysoxic field at the top of interval (Fig. 4b). This is consistent with total Fe contents, which indicate that Fe (oxyhydr)oxide precipitation decreased through the interval, and thus the particulate shuttle pathway for Mo drawdown diminished (Fig. 2). Alongside the lack of enrichment in Mn, these geochemical data indicate a return to less well oxygenated shallow water conditions.

5.3. Early Mesoproterozoic oxygenation dynamics

The Gaoyuzhuang Formation has provided significant insight into early Mesoproterozoic marine redox evolution. Zhang et al. (2018) suggested that fluctuations in Ce/Ce* values and different REE patterns, especially in relation to the occurrence of negative Ce anomalies and higher LREE/HREE ratios around the fossil horizons in Member III, combined with decreased $(Pr/Yb)_{SN}$ and increased Y/Ho ratios, indicated expanded oxygenation of shallow seawater (Tang et al., 2016). High I/(Ca+Mg) ratios for carbonates in the Gaoyuzhuang Formation have also been taken to indicate oxygen levels potentially higher than 4% PAL, linked to negative $\delta^{13}C_{carb}$ excursions and pulses in phosphorus bioavailability (indicated by higher P/Al ratios; Shang et al., 2019). Luo et al. (2021) subsequently documented three pulsed oxygenation events based on $\delta^{13}C_{carb}$ negative shifts, and these were evaluated by Mo isotope (δ^{98}Mo) measurements, with the suggestion that pulsed oxygenation events progressively increased global ocean oxygenation levels. Similarly, a significant increase in δ^{98}Mo values has also been observed through the lower part of the Gaoyuzhuang Formation in both the Gan'gou and Xinglong sections, which has been explained by uptake of light Mo isotopes to Fe-Mn (oxyhydr)oxides, as a result of the expansion of the oxygenated seawater (Xu et al., 2023). Furthermore, Cr isotope measurements show an increase in δ^{53}Cr (from -0.18‰ to +0.66‰), which has been interpreted to reflect an overall low-oxygen atmosphere but with a transient oxygenation event in Member III (Xie et al., 2023).

Together, these previous studies document multiple transient oxygenation signals based on diverse geochemical proxies, commonly interpreted as discrete oxygenation events. However, our new data, when considered in the context of fluctuations in water depth, specifically support an extensive interval of persistent shallow water oxygenation, followed by a decrease in local oxygenation levels in the upper part of the section, which we explore in more detail below.

The apparent occurrence of dysoxic conditions in supratidal to intertidal sediments deposited at the base of Member I (Interval A), suggests an extremely shallow chemocline, where oxygen levels were likely controlled by diffusion across the air-sea interface. This, in turn, implies extremely low atmospheric oxygen levels. The minor negative $\delta^{13}C_{carb}$ excursion that occurs at this time (Fig. 2) thus likely represents oxidation of dissolved organic carbon under these low oxygen, very shallow water conditions, rather than a discrete oxygenation event.

By contrast, the minor negative $\delta^{13}C_{carb}$ excursion that occurs at the top of Interval A (Fig. 2) appears to represent the onset of a protracted interval of enhanced surface ocean oxygenation. However, rather than representing distinct fluctuations in oxygen levels, the $\delta^{13}C_{carb}$ fluctuations that subsequently occur through Intervals B to D track changes in water depth (see also Luo et al., 2021). Thus, while progressive oxygenation likely occurred through Member II and the lower part of Member III of the Gaoyuzhuang Formation (Luo et al., 2021), this section was more generally characterized by persistent oxygenation to a depth that approached the shallow subtidal zone.

The combined geochemical evidence from the base of Interval E suggests that significant water column oxygenation had not yet extended into the deep subtidal zone. However, the distinct basin-wide $\delta^{13}C_{carb}$ excursion that occurs towards the top of this interval (Luo et al., 2025) suggests an additional discrete pulse of oxygenation, likely driven by an enhanced weathering influx of nutrients (Shang et al., 2019; Chen et al., 2026). This appears to have deepened the chemocline, with the development of a dynamic interface between oxic and dysoxic conditions that extended into basinal waters below storm wave base, while persistently well-oxygenated conditions likely occurred above this depth. However, the apparent return to less well-oxygenated shallower water conditions through Interval F suggests that the prolonged interval of progressively enhanced oxygenation levels eventually ceased, at least on a local or regional scale.

Assuming a constant average sedimentation rate of 4.5 cm/kyr (Liu et al., 2022), the interval of progressively enhanced oxygenation from the top of Member I to the first macrofossil horizon in Member III represents ~10 Myr. This, in turn, suggests that the prolonged persistence of stable shallower water oxygen levels, rather than a rapid pulse of oxygenation, may ultimately have aided the evolution of the first known decimetre-scaled eukaryotes, although it remains intriguing that the fossils are currently only known from relatively deep water facies at this time (Zhu et al., 2016; Zhang et al., 2018). It is also interesting to note that the majority of carbonaceous fossils found in the second interval towards the top of Member III (Fig. 2) tend to be significantly smaller in size (generally 0.5-3.5 mm, with a few reaching 30 mm; Chen et al., 2023). Whether this relates to the apparent decrease in shallower water oxygenation levels suggested by our data requires further consideration.

More broadly, the Gaoyuzhuang Formation clearly documents an interval of enhanced oxygenation, which appears to have been repeated across several intervals of the Mesoproterozoic (Shi et al., 2021; Mukherjee and Large, 2016; Mitchell et al., 2021; Zhang et al., 2015; Wang et al., 2017; Song et al., 2023; Tang et al., 2025). However, there currently appears to be limited evidence for either a stepwise increase in Earth surface oxygenation levels (as documented by both the Great Oxidation Episode and the Paleozoic Oxygenation Event; Farquhar et al., 2000; Canfield, 2005; Krause et al., 2018; Poulton et al., 2021) or intense global fluctuations in atmospheric and oceanic oxygenation (as documented by the Neoproterozoic Oxygenation Event; Krause et al., 2022). Thus, it currently remains unclear whether the fluctuating and heterogeneous oxygenation levels documented during the Mesoproterozoic are best considered to reflect paleogeographic and climatic/temporal variability (e.g., Song et al., 2023), which have likely influenced regional oxygenation levels since the first biological production of oxygen, or a global stepwise increase in oxygenation levels that would be required to invoke a ‘Mesoproterozoic Oxygenation Event’ (e.g., Zhang et al., 2021;

Xie et al., 2023), or a combination of both.

6. Conclusions

Our high-resolution $\delta^{13}C_{carb}$, total Fe-Mn, iron speciation, carbonate-phase Fe-Mn contents and Mo_{EF}^{*}-U_{EF}^{*} data provide nuanced insight into the oxygenation history of the ~1.56 Ga Gaoyuzhuang Formation. At the base of the Gaoyuzhaung Formation, very low shallow water oxygen levels are indicated, with oxygen levels likely reflecting equilibrium with very low atmospheric oxygen levels. A protracted interval of progressively enhanced shallower water oxygenation then occurred, lasting ~10 Myr. This initially resulted in increased water column oxygenation, but only to the depth of the shallow subtidal zone. Discrete horizons that document negative $\delta^{13}C_{carb}$ values through this interval thus likely reflect changes in water depth, and resultant oxidation of dissolved organic carbon at the chemocline, rather than distinct, isolated oxygenation pulses, although this does not preclude a general progressive increase in oxygen levels.

By contrast, a specific pulse in oxygen levels appears to have occurred in the lower part of Member III of the Gaoyuzhuang Formation, likely stimulated by an enhanced weathering influx of nutrients (Shang et al., 2019; Chen et al., 2026). This deepened the chemocline to below storm wave base, resulting in fluctuating redox conditions (between oxic and dysoxic) in the Jixian section. We speculate that the prolonged interval of progressively enhanced oxygenation levels (rather than a rapid pulse) may have created an environment permissive for the evolution of large decimetre-scale eukaryotes. However, at least on a local to regional scale, the intensity of shallow water oxygenation appears to have declined towards the top of the Gaoyuzhuang Formation, creating uncertainty over the subsequent global-scale trajectory of Earth surface oxygenation through the Mesoproterozoic.

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Figure Captions:

Figure 1. Geological framework of the study areas and sampling sites. (a) Schematic map of the North China Craton showing Mesoproterozoic strata (modified after Zhai and Liu, 2003; Zhao and Zhai, 2013); (b) Simplified map of the tectonic units of China; (c) General stratigraphic column showing the Changcheng and Jixian groups, and a more detailed stratigraphic column for the Gaoyuzhuang Formation; (d) Simplified paleogeographic map of North China during the early Mesoproterozoic, showing the location of the study area (modified after Xie et al., 2024); (e) Simplified geological map of the Jixian area, north of Tianjin (modified after Xie et al., 2024). Samples in this study are from Member I to the bottom segment of Member IV in the Gaoyuzhuang Formation (modified after Luo et al., 2021).

Figure 2. Geochemical profiles through the Gaoyuzhuang Formation in the Jixian sections. The geochemical data comprises $\delta^{13}C_{carb}$, Fe_{HR}/Fe_T, Fe_{py}/Fe_{HR}, total Fe and Mn, Fe and Mn in carbonate phases (determined via sequential leaching), TOC, Mo_{EF}^* and U_{EF}^* values. Published $\delta^{13}C_{carb}$ data (shown as grey symbols) for the Jixian section are from Zhang et al. (2018) and Luo et al. (2021), while data from the current study are shown in yellow symbols. Grey circles on other plots are data from Luo et al. (2021). The vertical dashed line on the $\delta^{13}C_{carb}$ plot represents the average value of the Jixian section. Solid black lines on the Mo_{EF}^* and U_{EF}^* plots represent an enrichment factor of 1, with values above this representing element enrichment. The brown stars represent the approximate position of the Gaoyuzhuang fossils (Zhu

et al., 2016; Chen et al., 2023). Triangles represent the tuff horizons, which gave ages of 1582 ± 12 Ma in the lower part of Member III (Tian et al., 2020), and 1588.8 ± 6.5 Ma at the top of Member III (Chen et al., 2024). The brown curves on the total Fe, Fe and Mn in carbonate phases, and TOC plots represent estimated scatterplot smoothing lines (LOESS, 0.2). The relative sea level curve is from Luo et al. (2021).

Figure 3. Cross-plots of (a) $\delta^{13}C_{carb}$ values versus $\delta^{18}O$, (b) Sr/Ca versus Mg/Ca, (c) Mn/Sr versus $\delta^{13}C_{carb}$, and (d) Mn/Sr versus $\delta^{18}O$, to examine the potential influence of diagenesis on the studied samples. Both data plots show no correlation. Sr, Mg and Ca contents in (a) and (b) represent total analyses of the bulk-rocks, while Mn and Sr contents in (c) and (d) represent analyses of the extracted leaching carbonate-phase. The blue circles in (c) and (d) represent the samples from non-Mn-rich horizons, while yellow circles in (c) and (d) represent the samples from Mn-rich horizons.

Figure 4. Mo_{EF}^{*}–U_{EF}^{*} covariation for different stratigraphic intervals through the Jixian section. The diagonal dashed lines represent proportions of the seawater (SW) Mo/U molar ratio. The dashed arrows illustrate different Mo accumulation pathways. The *particulate shuttle* represents uptake of Mo during the water column precipitation of Fe–Mn (oxyhydr)oxides, and the *redox variation* trajectory tracks oxic, dysoxic, anoxic, and euxinic water column conditions (modified after Algeo and Tribovillard, 2009 and Li et al., 2025a).