Shallow seawater oxygenation at ~1.44 Ga: A reflection of local seafloor oxygen oases or extensive water-column oxygenation?

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Abstract

It has been suggested that local marine oxygen oases could have formed during the Archean through the oxygenic photosynthesis of microbial mats residing in stromatolites. The ensuing mid-Proterozoic (~1.8–0.8 Ga) was characterized by overall low atmospheric oxygen levels and pervasive oceanic anoxia below a shallow chemocline, but with increasing evidence for several intervals of transient oxygenation. However, since some of the oxygenation intervals have largely been documented by stromatolites, it remains unclear whether these oxygenation signals represent local seafloor oxygen oases or extensive seawater oxygenation. To address this issue, we have conducted a comparative investigation of the mineralogy and geochemistry of stromatolite-rich and stromatolite-poor sections formed during a prominent oxygenation interval in the ~1.44 Ga Tieling Formation of North China. Similar iodine concentration and cerium anomaly characteristics in the stromatolite column and inter-column carbonates suggest that no significant difference existed in terms of redox conditions between the stromatolites and the surrounding water column. Furthermore, the stromatolite-rich interval exhibits lower I/(Ca+Mg) values relative to the contemporaneous stromatolite-poor interval. This indicates that the photosynthetic oxygen production capacity of microbial mats developed in the Tieling Formation was limited, and insufficient to elevate seafloor oxygen levels significantly.

After considering our high-resolution I/(Ca+Mg) and carbonate-carbon isotope data alongside seawater redox investigations of other contemporary basins, we argue that the ~1.44 Ga interval of oxygenation may represent an extensive shallow seawater oxygenation event across multiple basins, but with local redox heterogeneity. Our study therefore provides new insight into the nature of oxygenation events recorded by stromatolites during the mid-Proterozoic.

Keywords: stromatolites; microbial mats; photosynthetic oxygen production capacity; redox conditions; Tieling Formation; North China

1. Introduction

The rise of oxygen on the early Earth exerted a crucial influence on planetary habitability (Canfield, 2005; Lyons et al., 2014). The mid-Proterozoic (~1.8–0.8 Ga), situated between the Great Oxidation Event (GOE; Holland, 2002; Poulton et al., 2021) and the Neoproterozoic Oxygenation Event (NOE; Och and Shields-Zhou, 2012), represents an important transitional period in Earth's surface oxygenation history (Canfield, 2005; Lyons et al., 2014, 2021). In recent years, increasing evidence shows that the mid-Proterozoic atmosphere-ocean system may have experienced prominent fluctuations in redox conditions, with several transient oxygenation events occurring against a backdrop of overall low atmospheric oxygen levels and pervasive oceanic anoxia below a shallow chemocline (e.g., Mukherjee and Large, 2016; Zhang et al., 2016, 2018; Hardisty et al., 2017; Shang et al., 2019; Ye et al., 2021; Luo et al.,

2021; Xie et al., 2023). In order to better understand these prominent seawater redox fluctuations during the mid-Proterozoic, we further constrain seawater oxygen concentrations using the redox state classification proposed by Uahengo et al. (2020): anoxic ($[O_2]$ < ~1–3 μM), suboxic ($[O_2]$ < ~10 μM), dysoxic (~10 μM < $[O_2]$ < 20–70 μM) and oxic ($[O_2]$ > 20–70 μM).

Previous studies have suggested that during the Archean, when atmospheric oxygen levels were extremely low (< 10^{-5} present atmospheric levels, PAL; Zahnle et al., 2006), local oxygen oases were commonly formed through oxygenic photosynthesis in microbial mats developed in stromatolites (e.g., Olson et al., 2013; Riding et al., 2014; Sumner et al., 2015; Heard et al., 2022). Although atmospheric oxygen levels in the mid-Proterozoic were higher than in the Archean, oxygen concentrations were still maintained at an overall low level (<0.1%–1% PAL; Planavsky et al., 2014; Cole et al., 2016; Wang et al., 2022). Furthermore, biogeochemical models have demonstrated that when atmospheric oxygen levels are low (e.g., < 2.5% PAL), local seawater redox conditions are largely controlled by primary productivity (Reinhard et al., 2016). This poses a challenge for discerning whether oxygenation events recorded by stromatolites in the mid-Proterozoic signify seafloor oxygen oases or more extensive seawater oxygenation.

Recent studies have inferred dysoxic conditions in shallow seawater at ~1.44 Ga, mainly based on increased I/(Ca+Mg) values and negative Ce anomalies revealed in the Tieling Formation of North China (Hardisty et al., 2017; Wei et al., 2021; Yu et al., 2022). In addition, positive Cr isotope anomalies within a short interval of the Tieling

89 Formation, potentially indicating a brief increase in atmospheric oxygen levels (> 1%
90 PAL), have also been identified (Wei et al., 2021). However, this archive of
91 oxygenation largely derives from studies of stromatolites, and the photosynthetic
92 oxygen production capacity of microbial mats developed in the Tieling Formation has
93 not been evaluated, leading to uncertainty about the nature and spatial extent of the
94 ~1.44 Ga oxygenation event.

95 To address this, we have conducted a comparative investigation of the
96 mineralogy and geochemistry of stromatolite-rich and stromatolite-poor sections of
97 the Tieling Formation. This enables us to distinguish local seafloor oxygen oasis
98 conditions from extensive seawater oxygenation, thus providing new insight into the
99 nature of oxygenation events recorded by stromatolites in the mid-Proterozoic.

100

101 **2. Geological setting**

102 Associated with the tectonic evolution from the breakup of supercontinent Nuna
103 (Zhao et al., 2003, 2004, 2011; Zhang et al., 2009, 2012, 2017) to the assembly of
104 supercontinent Rodinia (Li et al., 2008), a very thick stratigraphic succession (~9 km)
105 was deposited on the North China Platform during the Proterozoic (Fig. 1A). This
106 stratigraphic succession is widely distributed and regionally well preserved, with a
107 low metamorphic grade generally below prehnite-pumpellyite facies (Chu et al.,
108 2007). The mid-Proterozoic sedimentary succession can be divided into three groups,
109 including the Changcheng (1660–1600 Ma), Jixian (1600–1400 Ma) and Qingbaikou
110 (1000–800 Ma) groups in ascending order, with a hiatus of up to ~400 Myr between

111 the Jixian and Qingbaikou groups (Gao et al., 2009). The Jixian Group is dominated
112 by epicontinental sea deposits and consists of six formations, including the
113 Gaoyuzhuang, Yangzhuang, Wumishan, Hongshuizhuang, Tieling and Xiamaling
114 formations in ascending order (Wang et al., 1985).

115 The Tieling Formation is dominated by shallow marine carbonates and can be
116 subdivided into two members. Member I primarily consists of manganese-rich
117 dolostone and thin green shale interbeds with hummocky bedding at the Jixian,
118 Chengde and Kuancheng sections (Fig. 2A–2C), with locally developed sedimentary
119 manganese deposits along the northeastern margin of the Yanliao Basin (Yan et al.,
120 2024). These sedimentary structures suggest that Member I was mainly deposited in a
121 deep subtidal environment (Mei et al., 2008; Tang et al., 2017). Member II is
122 dominated by stromatolitic (Fig. 2D–2F) and thinly-bedded limestone at the Jixian
123 section, indicative of deposition in shallow subtidal to intertidal environments (Mei et
124 al., 2008; Tang et al., 2017). Northward to the Chengde and Kuancheng sections,
125 however, Member II is primarily composed of thinly-bedded limestone with
126 intraclastics and green and red shale interbeds (Fig. 2G and 2H), suggesting a deep to
127 shallow subtidal environment. The Tieling Formation shows notable distinctions in
128 lithology from both the underlying Hongshuizhuang Formation and the overlying
129 Xiamaling Formation. The two members of the Tieling Formation are also easily
130 distinguished, allowing their identification and correlation across the North China
131 Platform.

132 The age of the Tieling Formation is well-constrained. Two U-Pb zircon ages of

1445 ± 12 Ma and 1442 ± 10 Ma from K-bentonite layers in the basal part of Member II at Jixian were obtained by laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS; Guo et al., 2019), and a U-Pb zircon age of 1418 ± 14 Ma from a bentonite layer in the basal part of Member I of the overlying Xiamaling Formation at Xiahuayuan was also determined by LA-ICP-MS analysis (Lyu et al., 2021). Therefore, the depositional age of the Tieling Formation can be constrained to between 1.45 Ga and 1.42 Ga. In addition, the two widely distributed K-bentonite layers in the basal part of Member II of the Tieling Formation also serve as important isochronous markers for correlating the Tieling Formation across different regions in North China.

3. Materials and methods

In this paper, a total of 590 carbonate samples from three sections documenting the Tieling Formation were analyzed, among which 268 samples are from Jixian (N: 40°04′54.05″, E: 117°25′51.25″; Fig. 1B), 200 are from Chengde (N: 40°43′19.54″, E: 118°11′50.59″; Fig. 1C), and 122 are from Kuancheng (N: 40°34′37.31″, E: 118°21′27.06″; Fig. 1D). All samples were cut into chips and only their fresh central parts were used for mineralogical and geochemical analyses. After the sample chips were cleaned and dried, ~300 mg of sample powder was obtained for each sample by a diamond drill.

Microfabrics were observed using a Zeiss Axio Scope A1 microscope on thin sections. Ultrastructures were analyzed using a Zeiss Supra 55 field emission

scanning electron microscope (FESEM) under 20 kV accelerating voltage with a working distance of 15 mm at the State Key Laboratory of Biogeology and Environment Geology, China University of Geosciences (Beijing). Samples were coated with ~10 nm thick carbon for better electric conduction before ultrastructural analysis. A secondary electron imaging detector (SE2) was used to characterize the topographic features. Semi-quantitative element concentrations in micron-size spots were analyzed by an Oxford energy dispersive X-ray spectrometer (EDS) connected to FESEM, operated at 20 kV with a working distance of 15 mm and a beam diameter of about 2 μm.

Iodine (I), major elements (Ca, Mg, Mn, Sr), rare earth elements and yttrium (REE+Y) were measured using an ICP-MS/MS (Thermo iCAP^{TM} TQ) at the National Research Center for Geoanalysis, Beijing. For iodine analysis, ~24 mg of powder was rinsed with 18.25 MΩ Milli-Q (MQ) water and then dried. The dried powder was weighed into a 15-mL centrifuge tube. To completely dissolve the carbonate minerals, 4 mL of 3% HNO_3 was added, and the supernatant was obtained by centrifugation. A 1 mL aliquot of the supernatant was transferred to a new 15-mL centrifuge tube, followed by the addition of 1 mL of 3% tertiary amine solution (to stabilize iodine; Lu et al., 2010) and 4 mL of MQ water for iodine analysis. Rhodium (Rh) and rhenium (Re), each at 2 ppb, were used as internal standards, with JDo-1 used as an external standard during the iodine analysis. The sensitivity of iodine was tuned to about 50 kcps for a 1 ppb standard in the ICP-MS/MS. The analytical uncertainties for iodine, monitored by repeat analyses of dolostone standard JDo-1, were less than 5.4% (Table

S1). For major element and REE+Y analyses, supernatant aliquots of 0.1 mL and 1 mL were separately taken and diluted to 6 mL with 3% HNO_3. The analytical uncertainties for Ca, Mg, Mn and Sr, monitored by repeat analyses of JDo-1, were less than 4% (Table S1). The precision of ICP-MS/MS analyses for REE+Y was generally better than 90%.

Although using 3% HNO_3 to digest relatively pure carbonate has been shown to produce no obvious influence on REE+Y compositions (Nothdurft et al., 2004), we nevertheless selected 21 samples and used 0.3 M acetic acid to completely dissolve carbonate minerals for further REE+Y analysis, ensuring the reliability of the results. Upon comparing the REE+Y results obtained from the two different digestion procedures, we found that they were identical within analytical uncertainty (Table S2 and S3), thus confirming the reliability of the results obtained using the 3% HNO_3 method. The REE+Y results were normalized to Post-Archean Australian Shale (PAAS; McLennan, 1989), and labeled with the subscript SN. To avoid any potential influence on the Ce anomaly caused by a positive La anomaly in seawater, Ce anomalies were calculated as: $Ce/Ce_{(SN)}^* = Ce_{(SN)}/(Pr_{(SN)}^2/Nd_{(SN)})$ (Lawrence et al., 2006).

Carbonate carbon and oxygen isotopes ($\delta^{13}C$ and $\delta^{18}O$) were analyzed using a Delta V Advantage IRMS at Northwest University (Xi'an, China), following the method described in Zhang et al. (2022). Approximately 100 ± 20 μg of sample powder was weighed into a 10 mL glass vial and sealed with a septum, then flushed with 99.999% helium for 5 min to avoid contamination by natural air. Then, about

100 μL of concentrated phosphoric acid was added at 70 °C to fully release carbon dioxide from the sample. The carbon dioxide analytic gas was isolated via gas chromatography, and water was removed using a Nafion trap. Carbon and oxygen isotope values were processed using Vienna Pee Dee Belemnite (VPDB) standards, with an analytical precision of better than 0.15‰.

4. Results

4.1. Mineralogical and geochemical features of the stromatolite-column and inter-column carbonates

Both stromatolite-column and inter-column carbonates are well developed in the Tieling stromatolites, with concentrated glauconite along the boundaries between stromatolite-column and inter-column carbonates in Member II of the Tieling Formation at the Jixian section (Fig. 3A and 3B). Macroscopic observations show that the stromatolite-column carbonate is about 25 cm in height and approximately 2.5 cm in width; stromatolite inter-column carbonate is about 1 cm in width (Fig. 3A). Microscopic observations show that the stromatolite-column carbonate is characterized by alternating light and dark laminae (Fig. 3C and 3D). The light laminae consist mainly of carbonate mud trapped by microbial mats (Tosti and Riding, 2017) and herringbone calcite (Tang et al., 2017), while the dark laminae are dominated by microbial mat-induced micrite (Fig. 3C and 3D). By contrast, the stromatolite inter-column carbonate consists primarily of carbonate mud (Fig. 3E). Glauconite is dark green in color (Fig. 3F), and exhibits a lamellar structure (Fig. 3G).

Further, EDS analysis reveals that the major element compositions in glauconite are K, Mg, Al, Si, Fe and O (Fig. 3H), consistent with previous results (cf. Tang et al., 2017).

A total of 61 stromatolite-column and inter-column carbonate samples from the stromatolite-rich interval at the Jixian section were analyzed for iodine, major elements, REE+Y, carbon and oxygen isotopes (Table S2 and S3). We use the T-test in statistics to analyze whether there exists significant differences in I/(Ca+Mg), $Ce/Ce_{(SN)}$* and $\delta^{13}C$ values between the stromatolite-column and inter-column carbonate samples. The T-test results indicate that no significant difference exists in I/(Ca+Mg) value between stromatolite-column carbonate (0.11 ± 0.03 μmol/mol, n = 33) and stromatolite inter-column carbonate (0.11 ± 0.07 μmol/mol, n = 28) (p > 0.05; Fig. 4A), and both are lower than the Precambrian baseline of 0.5 μmol/mol (Lu et al., 2017). Although T-test results suggest that $Ce/Ce_{(SN)}$* and $\delta^{13}C$ values differ significantly between stromatolite-column (0.89 ± 0.03, –0.5 ± 0.2‰, respectively, n = 33) and stromatolite inter-column carbonates (0.93 ± 0.05, –0.1 ± 0.6‰, respectively, n = 28) (p < 0.05; Fig. 4B and 4C), the gap between their means is actually rather small and they are nearly identical within analytical uncertainty. I/(Ca+Mg) values in both stromatolite-column and inter-column carbonates show a close positive correlation with I, but not with ($CaCO_3$+$MgCO_3$), Sr, $\delta^{18}O$ or Mg/Ca (Fig. 5A–5E). No obvious co-variations are observed between Th and $Ce/Ce_{(SN)}$*, Th and Y/Ho, Th and Pr_{SN}/Yb_{SN}, $Ce/Ce_{(SN)}$* and Sr, or $Ce/Ce_{(SN)}$* and $\delta^{18}O$ in either the stromatolite-column or inter-column carbonates (Fig. 5F–5J). The REE+Y distributions in stromatolite-column and inter-column carbonates show left-skewed

243 patterns, with positive La anomalies and high Y/Ho ratios (> 36 ppm/ppm; Fig. 5K).
244 $\delta^{13}C$ values in both stromatolite-column and inter-column carbonates show no
245 significant correlation with $\delta^{18}O$ (Fig. 5L).
246
247 *4.2. Geochemical features of the Tieling Formation in different sections*
248 We analyzed 529 stratigraphically continuous samples for iodine and major
249 elements, and 297 samples for carbon and oxygen isotopes in carbonates from the
250 stromatolite-rich Jixian section, and stromatolite-poor Chengde and Kuancheng
251 sections (Table S4). The results show that the I/(Ca+Mg) values in stromatolite-poor
252 carbonates from the Chengde and Kuancheng sections are generally higher than 0.5
253 μmol/mol (Fig. 6). At the Jixian section, however, although relatively high I/(Ca+Mg)
254 values (>0.5 μmol/mol) are observed in stromatolite-poor intervals (at 0–160 m and
255 ~265–275m), the stromatolite-rich interval (~180–270 m) has relatively low
256 I/(Ca+Mg) values (<0.5 μmol/mol) (Fig. 6). Furthermore, the $\delta^{13}C$ values across
257 different sections show similar features, varying from ~–3‰ to ~+0.5‰ at Jixian,
258 ~–2.5‰ to ~+1.5‰ at Chengde, and ~–2.5‰ to ~+0.7‰ at Kuancheng, with a
259 comparable positive excursion of ~+4‰ (Fig. 6). In all sections, I/(Ca+Mg) values
260 show a close co-variation with I, but not with ($CaCO_3$+$MgCO_3$), Sr, $\delta^{18}O$ or Mg/Ca
261 (Fig. 7A–7E). In addition, no obvious co-variation is observed between their $\delta^{13}C$ and
262 $\delta^{18}O$ compositions (Fig. 7F).
263
264 **5. Discussion**

265 *5.1. Geochemical data evaluation*

266 The liberation of iodine from organic matter during chemical analysis may
267 artificially inflate carbonate I/(Ca+Mg) values. However, some studies suggest that
268 iodine in organic matter is tightly bound and difficult to release (Zhou et al., 2017). In
269 this study, our samples were grey-white in color (with low organic matter content; Fig.
270 2), indicating that iodine release from organic matter likely had a negligible impact on
271 I/(Ca+Mg) values. Furthermore, most of our samples are relatively pure carbonates,
272 as evidenced by high ($CaCO_3$+$MgCO_3$) contents (Table S2 and S4), suggesting that
273 the detrital component is unlikely to have contributed a significant amount of iodine.
274 In addition, the 3% HNO_3 solution used to dissolve the samples would further
275 minimize iodine release from the detrital fraction (cf. Lu et al., 2010; Zhou et al.,
276 2017; Wörndle et al., 2019). The I/(Ca+Mg) values in our samples show a high
277 correlation with I, but not with ($CaCO_3$+$MgCO_3$) (Fig. 5A and 5B; Fig. 7A and 7B),
278 indicating that the I/(Ca+Mg) values are primarily controlled by iodine content in the
279 carbonates, rather than by the carbonate concentration in the samples.

280 Carbonate I/(Ca+Mg) values are susceptible to diagenetic alteration and
281 dolomitization (Lu et al., 2010; Hardisty et al., 2014, 2017; Zhou et al., 2015;
282 Wörndle et al., 2019). During diagenesis (e.g., meteoric or hydrothermal fluid
283 alteration), iodate (IO_3^-) in carbonate is readily reduced to iodide (I^-) and expelled
284 from the carbonate lattice, resulting in lower I/(Ca+Mg) ratios (Lu et al., 2010;
285 Hardisty et al., 2017). Since meteoric water alteration can cause the expulsion of Sr
286 from marine carbonates and the enrichment of Mn, the Mn/Sr ratio is often used to

assess the extent of alteration by meteoric water (Kaufman and Knoll, 1995). However, since Member I of the Tieling Formation is dominated by Mn-rich carbonates, we instead use the Sr content to evaluate potential alteration caused by meteoric water. In addition, $\delta^{18}O$ values are sensitive to diagenesis, and hydrothermal fluid alteration commonly decreases $\delta^{18}O$ values (Kaufman and Knoll, 1995). In our study, most samples have high Sr contents (> 40 ppm) and relatively high $\delta^{18}O$ values (> –10‰), with I/(Ca+Mg) values that do not co-vary with either Sr or $\delta^{18}O$ (Fig. 5C and 5D; Fig. 7C and 7D), suggesting that the I/(Ca+Mg) values have not been significantly influenced by diagenetic alteration.

Although some studies suggest that early diagenetic dolostone could record primary I/(Ca+Mg) signals more robustly than limestone, strong dolomitization during late diagenesis could substantially reduce iodate contents (Hardisty et al., 2017; Hashim et al., 2022). In our samples, no obvious negative correlation is observed between I/(Ca+Mg) and Mg/Ca (Fig. 5E and Fig. 7E), likely indicating that the I/(Ca+Mg) values have not been notably altered by dolomitization. Thus, the I/(Ca+Mg) values obtained from stromatolite-column and inter-column carbonates, along with the other I/(Ca+Mg) values from the Tieling Formation at the Jixian, Chengde and Kuancheng sections, may record primary seawater signals.

Non-skeletal carbonates can serve as reliable archives of seawater REE+Y signals (Webb et al., 2009). However, contamination from non-carbonate components, especially terrestrial sediments, may substantially affect carbonate REE+Y patterns normalized by PAAS (Ling et al., 2013). In our study, Th concentrations in both the

309 stromatolite-column and inter-column carbonates show no obvious correlation with
310 $Ce/Ce_{(SN)}$*, Y/Ho or Pr_{SN}/Yb_{SN} (Fig. 5F–5H), suggesting a negligible influence of
311 terrestrial sediments on the REE+Y patterns (cf. Tang et al., 2016). Likewise,
312 $Ce/Ce_{(SN)}$* ratios do not co-vary with Sr or $\delta^{18}O$ either (Fig. 5I and 5J), suggesting
313 that diagenetic alteration of $Ce/Ce_{(SN)}$* was limited. Further, REE+Y patterns display
314 a left-skewed shape, with an obvious positive La anomaly and high Y/Ho ratios (> 36
315 ppm/ppm; Fig. 5K), resembling those of modern seawater (cf. Ling et al., 2013).
316 Therefore, the REE+Y data can be used to track primary seawater signals.

317 Diagenesis also has the potential to change primary $\delta^{13}C$ and $\delta^{18}O$ compositions
318 in carbonates (Bekker et al., 2006). In our study, however, no clear co-variations are
319 observed between $\delta^{13}C$ and $\delta^{18}O$, and all $\delta^{18}O$ values are heavier than –10‰ (Fig. 5L
320 and Fig. 7F), suggesting that the $\delta^{13}C$ values have not been significantly altered by
321 diagenesis (cf. Guo et al., 2013). Thus, the $\delta^{13}C$ values of the Tieling Formation can
322 be reliably used to reconstruct contemporary seawater conditions.

323

324 *5.2. Evaluation of the photosynthetic oxygen production capacity of microbial*
325 *mats*

326 Microscopic observations show that the stromatolite-column carbonates are
327 primarily composed of water-column precipitated carbonate mud trapped by microbial
328 mats (Tosti and Riding, 2017), seafloor-precipitated herringbone calcite (Tang et al.,
329 2017), and seafloor-precipitated micrite induced by microbial mats (Fig. 3C and 3D).
330 By contrast, the stromatolite inter-column carbonates are dominated by water-column

precipitated carbonate mud (Tosti and Riding, 2017; Fig. 3E). Because most of the carbonate mud in stromatolite-column and inter-column carbonates originated from water-column precipitation (Tosti and Riding, 2017), it can serve as a valuable archive for tracking water column redox conditions (cf. Fang et al., 2022). Similarly, since the microbial mat-induced micrite in stromatolite-column carbonates largely resulted from seafloor precipitation driven by microbial mat activity (cf. Dupraz et al., 2009), it can be considered a reliable archive of local seafloor redox conditions (cf. Li et al., 2023). By comparing the differences in redox proxies between stromatolite-column and inter-column carbonates, it is possible to evaluate the oxygen levels at the seafloor, and then reflect the photosynthetic oxygen production capacity of microbial mats and discern whether the oxygenation recorded in stromatolites signifies local seafloor oxygen oases or water-column oxygenation. It should be noted that the criterion for this study to judge the strong photosynthetic oxygen production capacity of microbial mats is that the oxygen levels at the seafloor can be significantly elevated; otherwise, the photosynthetic oxygen production capacity of microbial mats will be regarded as weak.

Carbonate I/(Ca+Mg), as a proxy for tracing the redox conditions of paleo-oceans, has been widely applied to reconstruct the redox conditions of shallow seawater, from the Archean to the modern oceans (e.g., Hardisty et al., 2017; Lu et al., 2018; Fang et al., 2024). In modern oceans, iodine exists only in the forms of thermodynamically stable iodate (IO_3^-) and iodide (I^-) (Lu et al., 2010; Hardisty et al., 2017). Iodate reduction can be caused by microbial activity or reaction with sulfide or

353 dissolved ferrous iron (Councell et al., 1997; Jiang et al., 2023). Although the
354 mechanism for iodide oxidation is currently unknown, it is certain that its oxidation is
355 unlikely to be caused by free O_2, which is thermodynamically unfavorable for iodine
356 oxidation (Luther et al., 1995). In terms of thermodynamics, iodine oxidation requires
357 the participation of reactive oxygen species, such as hydrogen peroxide and OH
358 radicals (Luther, 2023). Although the pathways for iodate formation are not clear, the
359 observations show that 1) IO_3^- is reduced to I^- when seawater oxygen levels decrease,
360 and IO_3^- concentrations show a positive correlation with dissolved oxygen contents in
361 seawater (Lu et al., 2010); 2) laboratory experiments have confirmed that only IO_3^-
362 can incorporate into the carbonate lattice with a fixed coefficient, whereas I^- is
363 completely excluded (Lu et al., 2010). These enable carbonate I/(Ca+Mg) values to
364 reflect IO_3^- concentrations in seawater and to be used for reconstruction of seawater
365 oxygen levels. In general, the higher carbonate I/(Ca+Mg) values reflect the higher
366 oxygen levels in seawater.

367 Previous studies have indicated that carbonate I/(Ca+Mg) values are not only
368 influenced by *in-situ* redox conditions, but also by the overall redox conditions of
369 surrounding water bodies, primarily because the reduction of IO_3^- occurs much more
370 rapidly than oxidation of I^- (Zhou et al., 2014; Lu et al., 2016; Hardisty et al., 2017).
371 For example, in well-oxygenated modern surface oceans (~250 μM) with an oxygen
372 minimum zone below, carbonate I/Ca values show relatively low values (< 2.6
373 μmol/mol; Lu et al., 2016). By contrast, in a well-oxygenated surface ocean without
374 an oxygen minimum zone, carbonate I/Ca values are relatively high (> 2.6 μmol/mol;

375 Lu et al., 2016). Thus, in this study, the impact of surrounding water bodies on
376 I/(Ca+Mg) values between the stromatolite-rich and stromatolite-poor sections may
377 be seriously considered. However, due to the close proximity of stromatolite-column
378 and inter-column carbonates at the same section, any influence from surrounding
379 anoxic water bodies would similarly lower their I/(Ca+Mg) values, but with a
380 negligible effect on the difference between these values.

381 It is important to note that although the reduction of IO_3^- occurs much more
382 rapidly than the oxidation of I^-, it does not necessarily mean that transient
383 oxygenation of the environment cannot be recorded by carbonate I/(Ca+Mg). For
384 instance, assuming that seawater oxygen level rises from 0 μM (anoxic) to 20 μM
385 (oxic), then theoretically the iodate concentration needs to reach ~0.25 μM (cf. Lu et
386 al., 2016) before carbonate I/(Ca+Mg) can record this oxygenation. Based on the
387 iodine oxidation rates estimated from experiments (118–189 nM/yr; cf. Hardisty et al.,
388 2020), we can deduce that such an oxygen level only requires maintaining for about
389 two years, then carbonate I/(Ca+Mg) can accurately record it. Thus, this likely implies
390 that once transient oxygenation occurs on the geological time scale, carbonate
391 I/(Ca+Mg) can record it almost simultaneously.

392 Based on the above-mentioned principles in using carbonate I/(Ca+Mg) to trace
393 the seawater redox conditions, we can reasonably deduce that if the photosynthetic
394 oxygen production capacity of microbial mats is strong, then the oxygen levels and
395 IO_3^- concentration at the seafloor will be significantly elevated. Consequently, if the
396 high IO_3^- concentration at the seafloor can be recorded by microbial mat-induced

397 micrite, then the stromatolite-column carbonate will have higher I/(Ca+Mg) values
398 than stromatolite inter-column carbonate because microbial mat-induced micrite is the
399 main difference between them. However, our data show that the I/(Ca+Mg) values in
400 the stromatolite-column carbonate (0.11 ± 0.03 μmol/mol, n = 33) are nearly identical
401 with those in the stromatolite inter-column carbonate (0.11 ± 0.07 μmol/mol, n = 28)
402 (Fig. 4A). The potential causes for this scenario could be: 1) the photosynthetic
403 oxygen production capacity of microbial mats was strong, but the incorporation of
404 herringbone calcite formed in ferruginous seawater (cf. Sumner and Grotzinger, 1996)
405 into the stromatolite-column carbonate led to low I/(Ca+Mg) values; 2) the
406 photosynthetic oxygen production capacity of microbial mats was strong, but
407 microbial mat-induced micrite in the stromatolite-column carbonate does not record
408 high iodate content caused by oxygenation; or 3) the photosynthetic oxygen
409 production capacity of microbial mats was weak, resulting in low oxygen level and
410 low iodate concentrations at the seafloor, thereby leading to low I/(Ca+Mg) values in
411 microbial mat-induced micrite of the stromatolite-column carbonates.

412 Microscopic observations and geochemical analyses indicate that I/(Ca+Mg)
413 values in the stromatolite-column carbonate have no obvious change (Fig. 4A),
414 regardless of the relative abundance of herringbone calcite (Fig. 3C and 3D). Thus,
415 the incorporation of herringbone calcite into stromatolite-column carbonate may have
416 not affected the I/(Ca+Mg) values. The capacity of microbial mat-induced micrite to
417 record high I/(Ca+Mg) values in an oxygenated seafloor environment largely depends
418 on the pathways of microbial mat-induced mineralization. Oxygenic photosynthesis

(which causes such phenomena as carbonate encrustation of cyanobacteria and sheath mineralization) and anaerobic respiration in microbial mats are the two major processes leading to the formation of microbial induced micrite by increasing pH in the micro-environment (cf. Dupraz et al., 2009). Because micrite induced by oxygenic photosynthesis is formed in the environment where oxygen was present (cf. Dupraz et al., 2009), thus it can record relatively high I/(Ca+Mg) values. By contrast, micrite induced by anaerobic respiration requires the absence of oxygen (cf. Dupraz et al., 2009), it can only record low I/(Ca+Mg) values. Although at the moment we cannot determine which kind of microbially-induced mineralization was the dominant pathway, the presence of abundant herringbone calcite (Fig. 3D) and glauconite (Fig. 3F) in the stromatolite carbonates gives an indication that the seafloor environment was not highly oxygenated at this time, because their formation needs Fe^{2+} (cf. Sumner and Grotzinger, 1996; Tang et al., 2017). Therefore, the similar I/(Ca+Mg) values between stromatolite-column and inter-column carbonates more likely point to a low oxygen concentration at the seafloor and a limited photosynthetic oxygen production capacity for the microbial mats in the Tieling Formation.

As Ce(IV)/Ce(III) has a relatively high reduction potential similar to O_2/H_2O, it also serve as a robust tracer for constraining redox conditions in Precambrian shallow seawater (Lu et al., 2010; Ling et al., 2013). In oxygenated seawater, the oxidation of Ce(III) to Ce(IV) will lead to its enhanced adsorption by reactive particles such as Fe- and Mn-(oxyhydr)oxides (Byrne and Sholkovitz, 1996). For this reason, the removal of Ce in oxygenated seawater will result in negative Ce anomalies in associated

441 chemical sediments, while the particles scavenging Ce will retain positive Ce
442 anomalies (Sholkovitz et al., 1994). Similar to the I/(Ca+Mg) results, no significant
443 difference in $Ce/Ce_{(SN)}$* is observed between the stromatolite-column carbonate (0.89
444 ± 0.03, n = 33) and stromatolite inter-column carbonate (0.93 ± 0.05, n = 28) (Fig.
445 4B), likely supporting a limited photosynthetic oxygen production capacity of
446 microbial mats at this time.

447 In order to further evaluate the photosynthetic oxygen production capacity of
448 microbial mats during this period, high-resolution I/(Ca+Mg) values from
449 stromatolite-rich and stromatolite-poor intervals in the Tieling Formation were
450 analyzed over several sections. The results show that the stromatolite-rich interval has
451 relatively low I/(Ca+Mg) values compared to the stromatolite-poor interval (Fig. 6),
452 likely indicating that the photosynthetic oxygen production capacity of microbial mats
453 was limited. Our study also shows that even the conical stromatolites, which have
454 been shown to generate oxygen bubbles in the Archean (Bosak et al., 2009; Wilmeth
455 et al., 2022), were not sufficient to significantly elevate oxygen levels at the seafloor
456 (against a relatively higher oxygen level background compared to pre-GOE shallow
457 seawater), as evidenced by low I/(Ca+Mg) values (Fig. 6).

458 In summary, multiple lines of evidence suggest a limited photosynthetic oxygen
459 production capacity of microbial mats during the Tieling deposition. However, this
460 does not necessarily mean that all the microbial mats at ~1.44 Ga had limited
461 photosynthetic oxygen production capacity. Thus, a more comprehensive evaluation is
462 needed to explicit the environmental limiting factors (e.g., nutrient and light) and

463 microbial mat types, so that their overall photosynthetic oxygen production capacity
464 at ~1.44 Ga can be accurately determined.
465
466 *5.3. Local seawater redox heterogeneity*
467 In general, even though the photosynthetic oxygen production capacity of
468 microbial mats was limited, the lower I/(Ca+Mg) values observed in the
469 stromatolite-rich interval relative to the stromatolite-poor interval would perhaps not
470 be expected (Fig. 6). Possible interpretations for this may include: 1) the iodate
471 absorbed by microbial mats through their metabolism would result in a partial loss of
472 the iodate concentrations (cf. Zhou et al., 2014); 2) microbial mat degradation could
473 lead to decreased oxygen levels and iodate concentrations (cf. Liu et al., 2020); or 3)
474 the presence of neighboring anoxic water masses could have decreased water-column
475 iodate concentrations (cf. Zhou et al., 2014; Lu et al., 2016; Hardisty et al., 2017).
476 If microbial mats absorbed iodate or their degradation can significantly lower
477 I/(Ca+Mg) values in the stromatolite-rich interval, then we can predict that 1) the
478 stromatolite-rich interval will have lower I/(Ca+Mg) values relative to the
479 stromatolite-poor interval at the same section; 2) the stromatolite-column carbonates
480 will also have lower I/(Ca+Mg) values relative to the stromatolite inter-column
481 carbonates. However, our study shows similar I/(Ca+Mg) values between
482 stromatolite-poor (at ~160–180 m) and stromatolite-rich (at ~180–270 m) intervals at
483 the Jixian section (Fig. 6), similar to the situations observed at stromatolite-column
484 and inter-column carbonates (Fig. 4A), which may in turn indicate that microbial mat

485 iodate absorption and their degradation are unlikely to have significantly decreased
486 I/(Ca+Mg) values. Further, assuming that the stromatolite inter-column carbonate
487 records the seawater $\delta^{13}C$ values (–0.1‰), and the stromatolite-column carbonate
488 reflects a mixed $\delta^{13}C$ signal of seawater and degraded microbial mat (–25‰; cf.
489 Dickens et al., 1995; Shang et al., 2019), then it would require ~98% carbon from
490 seawater and ~2% carbon from microbial mat degradation to produce the observed
491 $\delta^{13}C$ value in stromatolite-column carbonate (–0.5‰). This implies that microbial mat
492 degradation only had a limited contribution to the carbon required for stromatolite
493 formation, and is therefore unlikely to have resulted in the lower I/(Ca+Mg) values.

494 Previous studies have indicated a persistent dysoxic seawater condition, as
495 inferred from $Ce/Ce_{(SN)}*$ data, in the stromatolite-rich interval of the Tieling
496 Formation (Fig. 6; Wei et al., 2021; Yu et al., 2022). In such an environment, however,
497 I/(Ca+Mg) values tend to be low (< 0.5 μmol/mol; Fig. 6). Given that I/(Ca+Mg)
498 values are readily influenced by the overall redox conditions of surrounding water
499 bodies (Zhou et al., 2014; Lu et al., 2016; Hardisty et al., 2017), a plausible
500 explanation would be that the depositional environment remained persistently dysoxic
501 but was intermittently disrupted by ferruginous seawater, thereby decreasing the
502 I/(Ca+Mg) values (Fig. 8). This idea is supported by the presence of abundant
503 herringbone calcite (Fig. 3D) and glauconite (Fig. 3F) in the stromatolites at Jixian,
504 since Fe^{2+} is required for their formation (Sumner and Grotzinger, 1996; Tang et al.,
505 2017). If this explanation is correct, then our data suggest that the sedimentary
506 environment at Chengde and Kuancheng was less disrupted by ferruginous seawater

than at Jixian (Fig. 8). This, in turn, may indicate that seawater redox conditions were rather heterogeneous in the Yanliao Basin.

5.4. A possible global oxygenation at ~1.44 Ga

Statistical analysis has shown that 95% of I/(Ca+Mg) values for anoxic or suboxic Precambrian intervals (as evidenced independently from other redox proxies; e.g., $Ce/Ce_{(SN)}$*, $\delta^{98}Mo$ and $\delta^{53}Cr$) are below 0.5 μmol/mol (Lu et al., 2017; Shang et al., 2019). Thus, an I/(Ca+Mg) value of 0.5 μmol/mol is commonly taken as a baseline for Precambrian carbonates deposited under anoxic to suboxic conditions. In our study, the relatively high I/(Ca+Mg) values (> 0.5 μmol/mol) are observed at the Jixian (at 0–160 m and ~265–275 m), Chengde and Kuancheng sections (Fig. 6), suggesting the presence of dysoxic conditions in shallow seawater across the Yanliao Basin during the deposition of the Tieling Formation. Considering a limited contribution from photosynthetic oxygen production of microbial mats in the Tieling Formation, these oxygenation signals in our case cannot be explained by local seafloor oxygen oases; instead, they most likely have reflected an extensive water-column oxygenation (Fig. 8).

In addition, other studies have also captured oxygenated signals in shallow seawater at ~1.44 Ga. For instance, a recent study has found obvious Ce anomalies (as low as 0.42) in the contemporaneous Fengjiawan Formation of the Xiong'er Basin on the southern margin of North China, which also suggests dysoxic conditions in shallow seawater at ~1.44 Ga (Yang et al., 2024). This oxygenation interval is

529 comparable to that found in the ~1.45 Ga Kaltasy Formation (Arlan Member) of
530 western Siberia, which is interpreted to have deposited in a deep-water environment
531 with dysoxic conditions (Sperling et al., 2014). Further, manganese-rich deposits are
532 widely developed in Member I of the Tieling Formation of North China and the
533 correlatable Ullawarra Formation of Western Australia, which were interpreted to be
534 formed by the diagenetic reduction of precursor manganese (IV) oxides (Spinks et al.,
535 2023; Yan et al., 2024). This also supports a well-oxygenated surface seawater (> 10
536 μM; cf. Tostevin et al., 2016) at ~1.44 Ga, because large-scale manganese oxidation
537 typically requires the presence of molecular oxygen (cf. Robbins et al., 2023).
538 Considering all these studies, we therefore propose that the ~1.44 Ga interval of
539 oxygenation may represent an extensive oxygenation event across multiple basins.

540 The burial of marine organic carbon is the major source of free oxygen in the
541 Earth surface system, which is commonly accompanied by a positive $\delta^{13}C$ excursion
542 in the seawater (Berner, 2003). Our study also revealed a pronounced positive $\delta^{13}C$
543 excursion (up to ~+4‰) in the Tieling Formation across the Jixian, Chengde and
544 Kuancheng areas (Fig. 6). Such a marked positive $\delta^{13}C$ excursion is comparable to
545 that found in the Fengjiawan Formation (~+2‰; Yang et al., 2024). A simple mass
546 balance calculation shows that a ~4‰ positive excursion in $\delta^{13}C$ would require a
547 burial of ~6.8×10^{17} moles of organic matter ($\delta^{13}C_{org} \approx -25‰$), which would produce
548 oxygen amount equivalent to ~1.8% PAL (~3.9×10^{19} moles; cf. Dickens et al., 1995;
549 Shang et al., 2019). This atmospheric oxygen level has exceeded the background
550 during the mid-Proterozoic (< 0.1%–1% PAL; Planavsky et al., 2014; Cole et al.,

551 2016), thereby indicating a prominent increase in atmospheric oxygen levels at ~1.44
552 Ga, consistent with the positive Cr isotope anomalies identified in a short interval of
553 the Tieling Formation (Fig. 6; Wei et al., 2021). Moreover, an initial $^{187}Os/^{188}Os$ value
554 (0.93 ± 0.14; Liu et al., 2016), higher than that of the mantle (~0.12), has also been
555 recognized in black schists of the ~1.45 Ga Bilute Formation in the Bayan Obo Basin
556 along the northern margin of North China, which is considered to have resulted from
557 enhanced oxidative weathering on the continent due to elevated atmospheric oxygen
558 levels (cf. Chu et al., 2023). Collectively, a notable increase in oxygenation levels of
559 both shallow seawater and the atmosphere at ~1.44 Ga appears highly likely.
560
561 *5.5. Implications for mid-Proterozoic oxygenation*
562 Our study indicates that the photosynthetic oxygen production capacity of
563 microbial mats in the Tieling Formation was limited. Thus, the oxygenation signals
564 recorded by stromatolites in this formation may represent water-column oxygenation
565 rather than local seafloor oxygen oases. Combined with seawater redox investigations
566 of other contemporary basins, we argue that the ~1.44 Ga interval of oxygenation may
567 represent an extensive shallow oxygenation event across multiple basins. However,
568 despite the existence of widespread oxygenation in shallow seawater across multiple
569 basins (possibly global) at ~1.44 Ga, redox heterogeneity is also apparent, even within
570 the Yanliao Basin. This likely implies that redox heterogeneity may have been
571 widespread in the mid-Proterozoic ocean, due to the overall low atmospheric oxygen
572 levels (e.g., Sperling et al., 2014; Reinhard et al., 2016). To better understand the

573 nature of oxygenation during the mid-Proterozoic, a comprehensive assessment of
574 redox heterogeneity in shallow seawater is required.
575
576 **6. Conclusions**
577 Based on the mineralogical and geochemical investigations of stromatolite-rich
578 and stromatolite-poor sections of the Tieling Formation in the Yanliao Basin, North
579 China, three major conclusions can be made:
580 1. Stromatolite column and inter-column carbonate precipitates in the Tieling
581 Formation show similar features, both in I/(Ca+Mg) and $Ce/Ce_{(SN)}$* ratios. In
582 comparison with the stromatolite-poor interval, the stromatolite-rich interval displays
583 relatively low I/(Ca+Mg) values. This likely indicates that the photosynthetic oxygen
584 production capacity of microbial mats developed in the Tieling Formation was limited
585 and in isolation, and may not be sufficient to elevate seafloor oxygen levels
586 significantly.
587 2. In comparison with the stromatolite-poor interval in the Chengde and
588 Kuancheng regions, the stromatolite-rich interval at Jixian exhibits relatively low
589 I/(Ca+Mg) values, suggesting a local redox heterogeneity in shallow seawater, at least
590 in the Yanliao Basin at ~1.44 Ga.
591 3. The high-resolution I/(Ca+Mg) and $\delta^{13}C$ data from the Tieling Formation,
592 when combined with the seawater redox conditions constrained from other
593 contemporary basins, suggest that the seawater oxygenation at ~1.44 Ga may
594 represent an extensive oxygenation of shallow seawater across multiple basins, likely

595 implying a global phenomenon.

596

597 **CRediT authorship contribution statement**

598 All authors have contributed to this work. L. Xu and D.J. Tang designed the
599 study. L. Xu, D.J. Tang, L.F. Sun, B.Z. Xie and X.Q. Zhou collected the samples. L.
600 Xu, D.J. Tang, L.M. Zhou, K.J. Huang and L.F. Sun performed the experiments. L.
601 Xu drafted the manuscript, which all other authors substantively revised.

602

603 **Declaration of Competing Interest**

604 The authors declare that they have no known competing financial interests or
605 personal relationships that could have appeared to influence the work reported in this
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607

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621

622 **Supplementary materials**

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Figure Captions

Figure 1. Geological setting of the study area. (A) Distribution of the mid-Proterozoic rifts in North China (modified from Zhai and Liu, 2003). (B–D) Simplified map showing the geology of the Jixian, Chengde and Kuancheng area (modified from GMC, 2013).

Figure 2. Macroscopic depositional features of the Tieling Formation. (A) Thinly-bedded dolostone in the middle Member I (Jixian section). (B) Dolostone with green shale beds in the lower Member I (Chengde section). (C) Dolostone with green shale beds in the lower Member I (Kuancheng section). (D) Hilly stromatolite in the middle Member II (Jixian section). (E) Columnar stromatolite in the middle Member II (Jixian section). (F) Conical stromatolite (denoted by arrows and red dashed line) in the upper Member II (Jixian section). (G) Intraclastic limestone in the lower Member II (Chengde section). (H) Thinly-bedded limestone with red and green shale interbeds in the lower Member II (Kuancheng section).

Figure 3. Major mineralogical features of stromatolite-column (SC), stromatolite inter-column (SIC) and glauconite (Gl). (A) Macroscopic depositional features of stromatolite-column and inter-column carbonate precipitation. (B) Thin-section features of stromatolite-column and inter-column carbonate precipitation. (C)

Microscopic features of stromatolite-column carbonate precipitation. The light laminae (LL) are dominated by carbonate mud trapped by microbial mats, while the dark laminae (DL) are composed of microbial mat-induced micrite. (D) Features of LL and DL stromatolite-column carbonates under cross polarized light. LL are dominated by seafloor-precipitated herringbone calcite, while DL are composed of microbial mat-induced micrite. (E) Carbonate mud in stromatolite inter-column. (F) Microscopic features of glauconite concentrated at the boundaries between stromatolite-column and inter-column carbonates. (G) SEM image of glauconite showing lamellar structures. (H) EDS spectrum showing that the major element composition in glauconite is K, Mg, Al, Si, Fe and O.

Figure 4. Geochemical data of the stromatolite-column and inter-column carbonates. (A–C) I/(Ca+Mg), $Ce/Ce_{(SN)}$* and $\delta^{13}C$ results in the stromatolite-column and inter-column carbonates of the Tieling Formation, Jixian section.

Figure 5. Geochemical analyses of the stromatolite-column and inter-column carbonates. (A) I/(Ca+Mg) vs. I. (B) I/(Ca+Mg) vs. ($CaCO_3$+$MgCO_3$). (C) I/(Ca+Mg) vs. Sr. (D) I/(Ca+Mg) vs. $\delta^{18}O$. (E) I/(Ca+Mg) vs. Mg/Ca. (F) $Ce/Ce_{(SN)}$* vs. Th. (G) Y/Ho vs. Th. (H) Pr_{SN}/Yb_{SN} vs. Th. (I) $Ce/Ce_{(SN)}$* vs. Sr. (J) $Ce/Ce_{(SN)}$* vs. $\delta^{18}O$. (K) REE+Y distribution patterns of stromatolite-column and inter-column carbonates. (L) $\delta^{13}C$ vs. $\delta^{18}O$.

Figure 6. Geochemical data of the Tieling Formation. The upper and lower red correlation lines are based on the notable distinctions of the Tieling Formation in lithology from both the underlying Hongshuizhuang Formation and the overlying Xiamaling Formation. The middle red correlation line is based on the stratigraphic sequence, volcanic ash and $\delta^{13}C$ characteristics. The blue shaded interval correlation is based on the $\delta^{13}C$ characteristics. $Ce/Ce_{(SN)}*$ and $\delta^{53}Cr_{auth}$ of the Tieling Formation at the Jixian section are from Wei et al. (2021). The geochronological data of the Tieling Formation at the Jixian section are adopted from: a: Guo et al., 2019; b: Lyu et al., 2021.

Figure 7. Cross plots of geochemical data from the Tieling Formation. (A) I/(Ca+Mg) vs. I. (B) I/(Ca+Mg) vs. ($CaCO_3$+$MgCO_3$). (C) I/(Ca+Mg) vs. Sr. (D) I/(Ca+Mg) vs. $\delta^{18}O$. (E) I/(Ca+Mg) vs. Mg/Ca. (F) $\delta^{13}C$ vs. $\delta^{18}O$.

Figure 8. Paleogeographic and redox condition maps of the study area. (A) Simplified paleogeographic map showing possible sources of ferruginous seawater during deposition of the Tieling Formation (modified from Wang et al., 1985). (B) Schematic model showing increased ocean-surface oxygen levels with local redox heterogeneity during deposition of the Tieling Formation (see text for further details).