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Terminal Mesoproterozoic (1.1–1.0 Ga) shallow ocean oxygenation and the rise of crown-group eukaryotes

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Abstract

At the end of the Mesoproterozoic Era (1.1–1.0 Ga), crown-group eukaryotes including rhodophytes and chlorophytes diversified and began to dominate the marine ecosystem. It is commonly thought that the oxygenation of Earth's surface environment was the driver behind this eukaryotic evolution and ecosystem change, but there is currently little evidence for an increase in biospheric oxygenation across the Meso-Neoproterozoic transition. Here, we report mineralogical and geochemical data from the ca. 1.1 Ga Nanfen Formation, North China, to explore possible causal relationships between marine redox conditions and terminal Mesoproterozoic biotic innovation. Elevated Ba concentrations and the occurrence of authigenic barite in the Nanfen Formation indicate an increase in seawater sulfate concentrations, likely caused by enhanced oxidative weathering of the continents. In addition, carbonate I/(Ca+Mg) ratios of up to 15 μmol/mol, coupled with a negative shift in carbonate $\delta^{13}C$, indicate oxidation of iodide and dissolved organic carbon as a result of enhanced water column oxygenation on the North China Platform. These geochemical trends occur coincident with increased P/Al ratios, suggesting that enhanced P bioavailability ultimately drove more extensive oxygenation. These results, in combination with highly fractionated carbonate Cr isotope data from time-equivalent strata in West Africa and extensive Mn deposits in Western Australia, suggest widespread oxic shallow ocean conditions during the terminal Mesoproterozoic. This suggests that shallow ocean oxygenation likely created favorable conditions for the diversification of crown-group eukaryotes at ca. 1.1 Ga.

Key words: North China; Nanfen Formation; eukaryotic evolution; I/(Ca+Mg); redox conditions

1. Introduction

The presence of free O_2 in Earth's surface environment is one of the prerequisites for the evolution of eukaryotes (e.g., Planavsky et al., 2014). It has been hypothesized that the Great Oxidation Event (2.43–2.22 Ga; Poulton et al., 2021) paved the way for the origination of eukaryotes, while the subsequent Neoproterozoic Oxygenation Event (0.8–0.5 Ga; Och and Shields, 2012) triggered the evolution of early animals (Canfield et al., 2007; Lyons et al., 2014, 2021). However, for the billion-year interval of the mid-Proterozoic (1.8–0.8 Ga), the relationship between the evolution of eukaryotes and marine redox change remains poorly resolved.

The general lack of significant chromium (Cr) isotope fractionation in ironstones (Planavsky et al., 2014) and shales (Cole et al., 2016), as well as highly fractionated Fe isotopes in ironstones (Wang et al., 2022), have been suggested to indicate low atmospheric oxygen levels of < 1% PAL (Present Atmospheric Level) during the mid-Proterozoic, which may have led to the evolutionary 'stasis' of eukaryotes and the delayed appearance of animals. However, highly fractionated Cr isotopes in ~1.3–1.1 Ga shales (Canfield et al., 2018) and carbonates (Gilleaudeau et al., 2016), as well as the development of oxygen minimum zones (Zhang et al., 2016a) and the lack of recycled carbon in black shales at ~1.4 Ga (Canfield et al., 2021), suggest higher atmospheric oxygen levels (≥ 4% PAL), at concentrations sufficient for the respiration demands of eukaryotes (including metazoans). Alongside this debate on absolute atmospheric oxygen concentrations, increasing evidence supports pulsed oxygenation events (e.g., ~1.57 Ga and ~1.4 Ga) in mid-Proterozoic shallow oceans (e.g., Hardisty et al., 2017; Zhang et al., 2018; Shang et al., 2019; Kendall, 2021; Luo et al., 2021; Fang et al., 2022; Xie et al., 2023; Xu et al., 2023), with eukaryotic evolution being promoted during the oxygenation pulses (e.g., Zhang et al., 2018; Wei et al., 2021a). However, the identification of global oxygenation 'events' is also complicated by emerging evidence for widespread ocean redox heterogeneity linked to regional climate variability (Zhang et al., 2015; Song et al., 2023).

The terminal Mesoproterozoic (1.1–1.0 Ga) represents a critical interval for both eukaryotic and marine redox evolution. Across this interval, early fossils of multicellular chlorophyte (green algae) and rhodophyte (red algae) have been identified from the Nanfen Formation in North China (Tang et al., 2020a) and from the Hunting Formation in northeastern Canada (Butterfield, 2000; Gibson et al., 2018), respectively. These fossils represent early forms of crown-group eukaryotes and mark divergence points for several key branches of eukaryotes in geologic history (Brocks et al., 2023).

Although increased ocean oxygenation has been suggested as a potential driver of this evolutionary innovation (Gibson et al., 2018; Tang et al., 2020a), direct evidence for ocean oxygenation at 1.1–1.0 Ga is lacking (Mills et al., 2022). Highly fractionated Cr isotopes from ca. 1.1 Ga carbonates in West Africa may suggest atmospheric oxygen levels higher than 0.1%–1% PAL (Gilleaudeau et al., 2016). However, due to the low oxygen threshold (0.1%–1% PAL) for Cr isotope fractionation, implications for the coeval redox state of the ocean are largely unknown, and indeed, few studies have directly assessed water column redox conditions across the 1.1–1.0 Ga interval (e.g., Guilbaud et al., 2020). For example, while there is limited evidence for transitions between ferruginous and euxinic conditions in the epeiric sea setting of the ~1.1 Ga Taoudeni Basin, Morocco (Beghin et al., 2017; Guilbaud et al., 2020), the extent of shallow water oxygenation has not been investigated. Thus, new geochemical proxy data are required to more specifically elucidate marine redox conditions at 1.1–1.0 Ga.

To address this limitation, we have analyzed the mineralogy, I/(Ca+Mg) ratios, Ba concentrations, P/Al ratios and C-O isotope compositions of drill core samples from the Nanfen Formation (ca. 1.1 Ga) in North China. These new data provide constraints on oxygen levels in the terminal Mesoproterozoic shallow ocean with implications for spatiotemporal redox heterogeneity and its potential impact on eukaryotic evolution.

2. Geological setting

The Nanfen Formation is well exposed in the Benxi region of eastern Liaoning Province, NE of the North China Craton, and our study focuses on three drill cores from this region. The formation belongs to the Xihe Group, which contains the Diaoyutai, Nanfen and Qiaotou formations in ascending order (Fig. 1; LBGMR, 1989). The Nanfen Formation conformably overlies quartz sandstones of the Diaoyutai Formation, and disconformably underlies sandstones of the Qiaotou Formation. Based on the youngest detrital zircon age peak of 1136 ± 11 Ma (n = 33 analysis points) from the Diaoyutai Formation (Zhao et al. 2020), and ~945–920 Ma mafic sills intruded into the Qiaotou Formation (Zhang et al. 2016b; Zhao et al. 2020), the Nanfen Formation is constrained between ~1136 Ma and ~945 Ma (~1.1 Ga; Fig. 1; Zhao et al., 2020). Cyclostratigraphic study indicates that the sampled interval (Fig. 1C) of this study consists of 20.5 long eccentricity (405 kyr) cycles, representing ~8.3 Myr with an average depositional rate of ~21 m/Myr (Bao et al., 2023).

In Liaoning Province, the Nanfen Formation is subdivided into three members (Fig. 1; LBGMR, 1989). Member I consists of greenish-grey to red siltstones and sandy shales near the bottom, pale blue laminated argillaceous limestones in the middle part, and purplish red limestones near the top. Member II is composed of purplish red, thin-bedded calcareous mudstone interbedded with pale blue limestone. Member III is dominated by yellowish-green shale and sandstone (Zhao et al., 2020; Bao et al., 2023). The shale and argillaceous limestone in this formation show well-preserved horizontal laminations but lack wave-agitated structures or cross-bedding, suggesting deposition in a shallow sea below fair-weather wave base. Based on its distinct lithology, the formation can be correlated across the Benxi region of east Liaoning Province and the Dalian region of south Liaoning Province.

Macroscopic fossils have been widely identified in the Xihe Group of Liaoning Province (Fig. 1). This includes abundant carbonaceous compressions of *Chuaria*, *Tawuia* and *Proterocladus* (green algae) in siltstone and shale from the Diaoyutai Formation in the Dalian region (Lin, 1984; Li et al., 2023). In the lowermost Nanfen Formation, abundant *Proterocladus* fossils have been identified in dark grey and yellowish-green silty shale and mudstone in the Dalian region (Tang et al., 2020a). The studied carbonate interval immediately overlies this fossil-bearing interval. Abundant carbonaceous compressions of *Chuaria*, *Tawuia*, *Shouhsienia* and *Proterocladus* are present in yellowish-green shales from the upper part of the Nanfen formation in the Dalian (Duan, 1982; Lin and Xing, 1984) and Benxi regions (LBGMR, 1989). In the upper Qiaotou Formation, *Chuaria* has been identified in shale interbeds (Hong et al., 1991).

3. Materials and methods

Carbonate samples were collected from three drill cores in Qianjinling, Benxi City, NE China. Correlations between the drill cores has been discussed in Bao et al. (2023), and is shown in Figure 1. After cleaning in ultrapure (18.2 MΩ) water, dried samples were cut for thin sections and powdered for geochemical analyses. Petrographic analysis was conducted on thin sections with a Zeiss Axio Scope A1 microscope. Microstructures were investigated on thin sections using a Zeiss Supra 55 field emission scanning electron microscope (FESEM) under 20 kV accelerating voltage with a working distance of 15 mm in the FESEM Laboratory, China University of Geosciences (Beijing). A secondary electron imaging detector was used to characterize topographic features, where an AsB detector was used to reveal compositional differences (backscattered electron, BSE, image), and an Oxford NordlysNano electron backscatter diffraction (EBSD) acquisition camera was used to identify the mineralogy. Prior to analysis, samples were coated with ~8 nm thick carbon for better electrical conduction.

Major elements were quantitatively analyzed for 122 samples using an Oxford EDS connected to the FESEM, operated at 20 kV and 120-μm aperture diameter with a working distance of ~15 mm, in the FESEM Laboratory. In order to reduce bias caused by sample heterogeneity, three areas with size of 1.2 mm × 0.9 mm, rather than points in each thin section, were analyzed for each sample. About one million counts were acquired in ~3 min for each area to reduce the uncertainty on major element concentrations. Apatite, biotite and barite in MINM25-53 were used as reference standards. Duplicate analyses of individual areas of the standards gave an analytical error of <1% (Table S1).

Carbonate iodine concentrations in 110 samples were determined using MC-ICP-MS. Major and trace elements, including Ca, Mg, Mn and Sr were analyzed using ICP-MS at the National Research Center for Geoanalysis, Beijing, following the method described in Fang et al. (2024). In brief, ~4 mg of dry powder was rinsed three times in Milli-Q water and digested using 4 mL of 3% nitric acid in 15 mL centrifuge tubes. Following a 0.5-hour digestion, the supernatant was collected and 1 mL was used for iodine analysis, where 3% of tertiary amine solution was added to stabilize the iodine (Lu et al., 2010). The supernatant was then diluted to 1:6000. For Ca, Mg, Mn and Sr contents, 0.2 mL of the original supernatant was diluted to 1:51000 with 3% nitric acid. The analytical uncertainty for iodine, as monitored by the standard JDo-1 and duplicate samples, was ≤6% (Table S2). The analytical uncertainties monitored by JDo-1 for Ca, Mg, Mn and Sr were ≤5% (Table S2). Samples with high I/(Ca+Mg) were analyzed multiple times to confirm their high values (Table S3).

For carbon and oxygen isotope analyses, sample powders were drilled from 110 polished slabs, avoiding recrystallized areas and veins. Analyses were conducted at the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences (Wuhan). About 150–400 μg of powder was placed in a 10 mL Na-glass vial, sealed with a butyl rubber septum, and reacted with 100% phosphoric acid at 72 °C after flushing with helium. Evolved CO_2 gas was analyzed for $\delta^{13}C$ and $\delta^{18}O$ using a MAT 253 mass spectrometer coupled directly to a Finnigan Gasbench II interface (Thermo Scientific). Isotopic values are reported in per mil relative to the Vienna Pee Dee belemnite (VPDB) standard. Analytical precision was better than ±0.1‰ for $\delta^{13}C$ and $\delta^{18}O$ based on replicate analyses of two laboratory standards (GBW 04416 and GBW 04417), where the $\delta^{13}C$ and $\delta^{18}O$ compositions of these standards are +1.6‰ and −11.6‰, and −6.1‰ and −24.1‰, respectively. Samples with low $\delta^{18}O$ values were analyzed multiple times to confirm their low values (Table S4).

4. Results

Calcite crystals in the studied samples are commonly less than 10 μm in size (Fig. 2A and B). Most calcite crystals are rounded in shape without abrasion (Fig. 2A and B), and were likely derived from water-column precipitated carbonate mud (cf. Fang et al., 2022). Globular apatite aggregates are abundant in the pale blue argillaceous limestone (Fig. 2B and C). In addition, barite with anhedral morphology and corrugated boundaries is common (Fig. 2D and E). The lower and upper parts of the studied interval comprise carbonate red beds (Fig. 1B) with abundant authigenic hematite with a euhedral morphology (Fig. 2F–I).

The most prominent geochemical feature of the Nanfen Formation carbonates is the presence of two intervals of high I/(Ca+Mg) ratios, up to ~12 μmol/mol and ~15 μmol/mol, respectively (Fig. 3; Table S3), which are the highest recorded values from Precambrian carbonates, comparable with those found in modern settings (Fig. 4). Based on fluctuations in I/(Ca+Mg) ratios, the studied section can be subdivided into five intervals (interval I–V) as shown in Fig. 3. The first increase in I/(Ca+Mg) (interval II) lasted for ~3.2 Myr and is associated with an ~6‰ negative $\delta^{13}C$ excursion, whereas the second increase in I/(Ca+Mg) (interval IV) lasted for ~1.2 Myr and occurs coincident with an ~2‰ negative $\delta^{13}C$ excursion. In both cases, high I/(Ca+Mg) ratios start at the rising limb of the negative $\delta^{13}C$ excursion.

The two intervals with high I/(Ca+Mg) also have particularly high P/Al (wt%/wt%) ratios relative to Post Archean Australian Shale (PAAS; McLennan, 2001), with values of up to 0.2 (interval II) and 0.4 (interval IV) (Fig. 3; Table S5). In other intervals, including the red beds at the base and top of the measured section, P/Al values are much lower (0.01 ± 0.01 wt%/wt% at the base and 0.04 ± 0.04 wt%/wt% at the top; Fig. 3), although many values are still highly elevated relative to PAAS, likely due to the low detrital Al component in these sediments. The Mg/Ca ratios are < 0.12 mol/mol, and Mn/Sr ratios are < 4 ppm/ppm, with neither ratio showing a correlation with I/(Ca+Mg) ratios (Fig. 3). Barium concentrations (0.15 ± 0.47 wt%; Table S5) are commonly higher than PAAS (0.07 wt%; McLennan, 2001) throughout the section, although some samples are below PAAS. However, two peaks in Ba are identified: the first peak in interval I starts at the beginning of the negative $\delta^{13}C$ shift and predates the high I/(Ca+Mg) values, while the second peak in interval V postdates the negative $\delta^{13}C$ shift and high I/(Ca+Mg) values in interval IV (Fig. 3).

5. Discussion

5.1. Data evaluation

Diagenetic processes and dolomitization in pore fluids and during deeper burial mostly occur under anoxic conditions, and may potentially decrease (but not increase) carbonate I/(Ca+Mg) ratios (Hardisty et al., 2017; Wörndle et al., 2019). In our samples, relatively low Mn/Sr (< 4 ppm/ppm) and Mg/Ca (< 0.12 mol/mol) ratios (Fig. 3), and their lack of covariation with I/(Ca+Mg), suggest that the temporal fluctuations in I/(Ca+Mg) were caused by paleoenvironmental change rather than by diagenetic alteration or dolomitization (cf. Wörndle et al., 2019). It has been proposed that dissolution of apatite would release non-carbonate iodine, resulting in higher I/(Ca+Mg) ratio (Zhang et al., 2024). In this study, although the increase in I/(Ca+Mg) ratios is associated with a general increase in P concentrations, I/(Ca+Mg) ratios do not co-vary with P concentrations (R^2 = 0.13; Table S3), indicating that the I/(Ca+Mg) ratios are not obviously contaminated by apatite dissolution.

The oxygen isotope data are remarkably constant (ca. –10‰) throughout most of the measured section (Table S3). It is possible that the $\delta^{18}O$ values reflect analytical artifact by the contamination of H_2O in the laboratory. However, we reanalyzed selected samples and yielded similar results (Table S4). Additionally, two laboratory standards were used to monitor analytical accuracy, further confirming the reliability of these data. While most diagenetic fluids are characterized by low $\delta^{18}O$ (Brand and Veizer, 1980),

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the low $\delta^{18}O$ value of ≤ −10‰ has traditionally been used to indicate strongly diagenetic alteration. However, the well-preserved fabrics (Bao et al., 2023) and minerals (Fig. 2) argue against strong diagenetic alteration. Interestingly, there has been a suggestion of high-latitude glaciation at ca. 1.1 Ga (Geboy et al., 2013), which could potentially explain the low $\delta^{18}O$ values. The Nanfen Formation has been demonstrated to have formed in a high paleo-latitude area (Zhao et al., 2020), and thus possibly in a cold environment. Equilibrium isotope fractionation during marine ice formation results in isotopically light oxygen in residual seawater (O'Neil, 1968), and carbonate formed in such seawater could record very low $\delta^{18}O$ values. However, further evidence, such as oxygen isotope studies of contemporaneous carbonates deposited at similar high paleo-latitudes, is needed to substantiate this potential link. Nevertheless, the lack of correlation between $\delta^{18}O$ and $\delta^{13}C$, as well as between $\delta^{18}O$ and I/(Ca+Mg) (Table S3), suggests that the $\delta^{13}C$ and I/(Ca+Mg) values were likely not significantly alterated and may reflect original seawater signals.

5.2. Pulsed oxygenation of the shallow ocean

Carbonate I/(Ca+Mg) provides a means of evaluating local redox conditions from which carbonates were precipitated, and has been applied to paleoredox reconstructions of shallow seawater from the Archean to the modern (e.g., Lu et al., 2010, 2017, 2018; Hardisty et al., 2014, 2017; Shang et al., 2019; Wörndle et al., 2019). In the modern ocean, iodate (IO_3^-) and iodide (I^-) are the only two thermodynamically stable iodine forms, and the high iodate that characterizes oxic seawater is reduced to iodide under anoxic seawater conditions (Lu et al., 2010). Laboratory experiments demonstrate that only iodate can substitute into the crystal lattice of carbonates by replacing CO_3^{2-}, whereas iodide is excluded, and this iodate incorporation has a near-constant partition coefficient (Lu et al., 2010). Therefore, carbonate I/(Ca+Mg) ratios can record iodate concentrations in the seawater from which the carbonate formed. The standard reduction potential of IO_3^-/I^- is very close to that of O_2/H_2O (Rue et al., 1997), making carbonate I/(Ca+Mg) a particularly useful proxy for reflecting the oxygenation state of shallow seawater (Lu et al., 2010). In general, higher I/(Ca+Mg) ratios in carbonate commonly implies higher seawater oxygen concentrations (Shang et al., 2019). A statistical study of the Precambrian carbonate I/(Ca+Mg) distribution has suggested that a value of 0.5 μmol/mol can be used as a baseline for Precambrian carbonates (Lu et al., 2017). When there is no other independent evidence indicative of seawater oxygenation, this baseline represents more than 95% of Precambrian carbonate I/(Ca+Mg) ratios formed under anoxic to suboxic seawater conditions. Therefore, if I/(Ca+Mg) ratios in Precambrian carbonates are persistently higher than this baseline value, an increase in oxygen concentrations above a low background level is indicated (cf. Shang et al., 2019; Wei et al., 2021a). In addition, based on comparative studies of modern oxic seawater with that within oxygen minimum zones, an upper I/(Ca+Mg) threshold value of 2.6 μmol/mol has been established (Lu et al., 2016; Hardisty et al., 2017), where ratios higher than 2.6 μmol/mol indicate oxic seawater with $[IO_3^-]$ higher than 0.25 μM (Lu et al., 2016; Hardisty et al., 2017). Therefore, the elevated I/(Ca+Mg) ratios (> 2.6 μmol/mol) in intervals II and IV indicate well-oxygenated shallow water conditions, whereas the low I/(Ca+Mg) ratios (< 0.5 μmol/mol) in other intervals suggest suboxic to anoxic conditions.

As noted above, some of the I/(Ca+Mg) ratios in the Nanfen Formation samples are particularly high, up to ~15 μmol/mol (Fig. 3), which are the highest values recorded for the Precambrian to date (Fig. 4). There are two possible explanations for these high I/(Ca+Mg) ratios. The first is that shallow water oxygen concentrations may have been as high as in the modern ocean, but this appears unlikely given the relatively low atmospheric oxygen concentrations proposed for the entirety of the mid-Proterozoic (Lyons et al., 2021). A second explanation is that the high I/(Ca+Mg) ratios were primarily due to relatively high oxygen concentrations in shallow seawater, with the release of iodine from organic matter remineralization also partially contributing to the elevated I/(Ca+Mg) values (Fig. 5; cf. Wörndle et al., 2019). Prior to the peak in I/(Ca+Mg) ratios in interval II, the negative ~6‰ carbon isotope excursion and the ~0.8 wt% positive shift in Ba concentrations in interval I (Fig. 2) imply that enhanced continental input of sulfate (cf. Cui et al., 2022) activated the remineralization of organic carbon through bacterial sulfate reduction (cf. Xie et al., 2023), resulting in the accumulation of iodide below the redoxcline (cf. Wörndle et al., 2019). This accumulated iodide may have subsequently been oxidized to iodate, resulting in the exceptionally high I/(Ca+Mg) ratios observed in interval II (Fig. 3).

While there is no direct counterpart to this scenario in the modern ocean, the degradation of organic matter can release iodine and increase its concentration locally (Martin et al., 1993), since recycled iodine from marine primary productivity is the most significant source of iodine (Lu et al., 2010). A similar scenario likely occurred at ~0.81 Ga, as recorded in Bitter Springs carbonates, where an increase in I/(Ca+Mg) of up to ~8 μmol/mol is associated with a negative carbon isotope excursion of ~8‰ (Wörndle et al., 2019). Prior to the peak in I/(Ca+Mg) in interval IV, the negative excursion in carbon isotopes (up to ~2‰) is less prominent than in interval I (Fig. 2). This likely indicates that less iodide was transformed from remineralization of organic matter, suggesting that higher oxygen concentrations (likely ≥ 20–70 μM; Shang et al., 2019) in shallow seawater were required to result in the higher I/(Ca+Mg) ratios in this interval (Fig. 3). However, dissolved oxygen concentrations were likely still far below modern levels, since remineralization of organic matter would also have contributed to the high I/(Ca+Mg) ratios.

The elevated Ba concentrations (Fig. 3) and occurrence of barite (Fig. 2) throughout the studied interval provide independent evidence for oxygenation of Earth's surface environment. During the mid-Proterozoic, the ocean was persistently rich in Ba, due to low sulfate concentrations in seawater, but authigenic barite precipitation was rare (Wei et al., 2021b; Cui et al., 2022). Therefore, the occurrence of authigenic barite in the Nanfen Formation implies elevated sulfate concentrations (cf. Cui et al., 2022), likely caused by increased atmospheric oxygen levels and enhanced oxidative weathering of the continents (cf. Daines et al., 2017). This is because, although the oxygen levels required for pyrite oxidation are extremely low, simulations suggest that as atmospheric oxygen levels increase, sulfate input from terrestrial oxidative weathering to the ocean also continues to rise until oxygen levels reach approximately 10% PAL (Daines et al., 2017). The occurrence of barite is consistent with highly fractionated Cr isotope results documented in contemporaneous carbonates from West Africa (Gilleaudeau et al., 2016), and large-scale Mn deposition in West Australia, which exceeds the size of Mn deposits during the Neoproterozoic and during most of the Paleoproterozoic and Phanerozoic (Spinks et al., 2023). However, since low mid-Proterozoic atmospheric oxygen levels were commonly not in equilibrium with the shallow ocean (Reinhard et al., 2016), a direct covariation between Ba contents and I/(Ca+Mg) ratios is not observed.

5.3. Causes of oxygenation and deoxygenation in shallow 1.1–1.0 Ga oceans

Our data provide insight into the causes of oxygenation and deoxygenation in the 1.1–1.0 Ga shallow ocean. The observed increases in P/Al in intervals II and IV (Fig.

2) may have been caused by an increase in either the source or sink of P. Precipitation of iron (oxyhydr)oxides in ferruginous settings can effectively uptake P from seawater (e.g., Guilbaud et al., 2020), potentially resulting in an increase in the P content of sediments during transitions to ferruginous conditions (Alcott et al., 2022). However, in the Nanfen Formation, red beds rich in hematite, which likely formed under weakly oxygenated conditions via oxidation of Fe(II) (cf. Tang et al., 2020b), are not associated with an increase in P/Al (Fig. 2), indicating that an increase in the P sink was not the main cause for increased P/Al ratios. In addition, the more prominent positive excursion in P/Al ratios correlates with a less pronounced negative excursion in carbon isotope values (e.g., interval IV in Fig. 2), suggesting that organic carbon remineralization was not the primary source of phosphorus.

Instead, it is most likely that enhanced continental weathering of P was the main cause for the increased P/Al ratios. Phosphorus is a major bio-limiting nutrient and likely played a pivotal role in modulating net primary productivity, and therefore redox conditions, over geological timescales (Tyrrell, 1999; Tang et al., 2022a, 2022b; Xie et al., 2024). In the Nanfen Formation, P/Al begins to increase (from 0.01 wt%/wt%) with the onset of the first I/(Ca+Mg) pulse in interval II, and continues to increase (up to 0.17 wt%/wt%) through this interval (Fig. 2). Following this, there is a second major increase in P/Al at the end of interval III and into interval IV (from 0.01 to 0.39 wt%/wt%), and although values then start to decrease through this interval of highly elevated I/(Ca+Mg), P/Al ratios nevertheless remain very high. The peak in P/Al occurs slightly earlier than the I/(Ca+Mg) peak (Fig. 2). This implies that an enhanced continental influx of P caused the pulsed ocean oxygenation (Fig. 5).

It is worth noting that the first peak in Ba concentrations (interval I) predates the peak in I/(Ca+Mg), whereas the second peak (interval V) postdates the peak in

I/(Ca+Mg) (Fig. 2). It is likely that the first increase in I/(Ca+Mg) reflects a response to an increase in atmospheric oxygenation, and this led to increased oceanic oxygenation in the studied region owing to the enhanced chemical weathering influx of P and subsequent stimulation of primary productivity. The second peak (interval IV) then represents an additional increase in atmospheric and oceanic oxygenation, which subsequently led to even more oxidative weathering and a further enhanced influx of Ba, but this oxidative weathering took time to become evident in the rock record and occurred after the peak in oxygenation.

Negative $\delta^{13}C$ anomalies could be a result of oxidation of organic carbon in the ocean (e.g., Rothman et al., 2003) or other forms of reduced carbon such as methane (e.g., Bjerrum and Canfield, 2011), terrestrial organic matter (e.g., Kaufman et al., 2007) and petroleum (e.g., Kroeger and Funnell, 2012), authigenic carbonate precipitation (e.g., Higgins et al., 2018), and/or low primary production (e.g., Kump, 1991), and/or diagenesis (e.g., Oehlert and Swart, 2014). Oxidative weathering of terrestrial organic matter is one possible cause of the negative carbon isotope excursion. If this is the case, this process should be associated with the oxidation of organic iodine, leading to a concurrent increase in the carbonate I/(Ca+Mg) ratio. However, the data indicate that the carbonate I/(Ca+Mg) ratio only begins to increase as the carbon isotope values recover from their lowest point (Fig. 3). Therefore, although other possibilities may also exist, the most parsimonious interpretation for this negative $\delta^{13}C$ anomaly accompanied by a positive shift in I/(Ca+Mg) is the oxidation of the oceanic organic matter (Shang et al., 2019; Wörndle et al., 2019). With the expansion of shallow seawater oxygenation, oxidation of organic carbon was enhanced and became one of the significant oxygen-consuming processes (cf. Shang et al., 2019; Wörndle et al., 2019). In interval II, the negative excursion in carbon isotopes (Fig. 3) suggests that mixing of deep, organic carbon-rich seawater with oxygenated shallow seawater may have contributed to the subsequent transition back to less well-oxygenated seawater. However, the negative carbon isotope excursion stops before the end of high I/(Ca+Mg) values, suggesting that this was not the sole cause of the deoxygenation. Instead, since the decrease in I/(Ca+Mg) is associated with decreasing P/Al ratios (Fig. 3), this suggests that a decreased influx of continental P was the major cause of the deoxygenation of shallow seawater. This process likely also contributed to the decrease in I/(Ca+Mg) in interval IV. In this interval, the magnitude of the negative carbon isotope excursion is lower than in interval II, suggesting that oxidation of organic carbon was not the main cause for the subsequent deoxygenation. Following the pulsed oxygenation in interval IV, the carbon isotope profile remains relatively stable, but the lithology changed to marine red beds (Figs. 2 and 3), suggesting that the oxidation of anoxic Fe(II)-rich deep seawater was also partially responsible for the shallow water deoxygenation (cf. Ye et al., 2023).

5.4. Implications for eukaryote evolution

A study of modern ocean eukaryotes suggests that oxygen levels of at least 8 μM (2.7% PAL) are required for the evolution of crown-group eukaryotes, (Mills et al., 2024), which may be slightly lower than the levels needed for simpler Precambrian eukaryotes. Since the I/(Ca+Mg) proxy is only suitable for application to carbonates, we are not able to use our approach to deduce oxygen levels in the siliciclastics in which the fossils occur (Fig. 1). Nevertheless, our identification of fluctuating oxygenation levels at this time, including transitions to particularly high oxygen levels, suggests that the 1.1–1.0 Ga interval was characterized by the periodic development of conditions that were permissible for eukaryote evolution. Indeed, the initial rise of crown-group eukaryotes, as reflected in the appearance of multicellular chlorophytes in the ca. 1.1 Ga Nanfen Formation and the oldest rhodophytes in the ca. 1.05 Ga Hunting Formation, Canada (Butterfield, 2000; Gibson et al., 2018), broadly corresponds to this interval of enhanced pulses of oxygenation (Fig. 4). This reinforces the role of oxygen as a potential evolutionary driver for the initial rise of crown-group eukaryotes in the terminal Mesoproterozoic.

It should be noted that our data suggest that enhanced oxygenation of shallow seawater was relatively short-lived, and the redox conditions in shallow oceans fluctuated considerably. According to the astrochronological timescale (Fig. 2; Bao et al., 2023), the first pulse in oxygenation (interval II) persisted for ~3.2 Myr, while the second pulse (interval IV) lasted only for ~1.2 Myr. Although this time allowed for an increase in complexity, it was likely not sufficient for significant changes in diversity, as such changes require the construction and occupation of new morphospace (Lowery and Fraass, 2019) and/or ecosystems (Alvarez et al., 2019) through novel innovations, which are much slower than the development of complexity. Similar scenarios have been observed in other pulsed oxygenation events during the mid-Proterozoic, such as the 1.57 Ga (Zhang et al., 2018; Shang et al., 2019) and 1.4 Ga oxygenation events (Zhang et al., 2016a, 2021). It is therefore likely that the unstable redox conditions impeded the evolutionary trajectory of eukaryotes.

6. Conclusions

Two prominent peaks in I/(Ca+Mg) ratios, marking significant oxygenation events in Earth's history, have been identified in the ~1.1 Ga Nanfen Formation, North China. These events are manifest as two pulsed oxygen increases in the shallow ocean, lasting ~3.2 Myr and ~1.2 Myr, respectively. Increased inputs of continentally-derived P likely drove enhanced productivity and ultimately oxygen production across these two intervals. However, subsequent deoxygenation of seawater as the pulsed increases in the supply of P from enhanced continental weathering waned, likely occurred via the oxidation of organic carbon and the intrusion of deep, Fe(II)-rich seawater. Our data thus reveal that the oxygenation state of mid-Proterozoic shallow seawater was highly dynamic, building on a growing body of evidence for highly heterogeneous mid-Proterozoic sub-surface redox conditions. The initial rise of crown group eukaryotes appears to be linked to enhanced pulses of shallow water oxygenation at ~1.1 Ga, suggesting that environmental oxygenation played a crucial role in facilitating early eukaryotic evolution. However, unstable ocean redox conditions on longer timescales likely hindered the evolutionary trajectory of these organisms.

CRediT authorship contribution statement

All authors have contributed to this work. D.J. Tang designed the study. X.L. Li, H.Q. Zhao and S.H. Zhang collected the samples. D.J. Tang, H.Y. Zhou, L.M. Zhou and H.Y. Song performed the experiments. D.J. Tang drafted the manuscript, which all other authors substantively revised.

Declaration of competing interest

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

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Supplementary materials

Supplementary material, including all data, associated with this article can be found in the online version, at https://doi.org/10.17632/w5xjdhc5xw.2

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Figure captions

Figure 1. Geological background and stratigraphic succession of the ca. 1.1 Ga Nanfen Formation in the Benxi region, North China. (A) Tectonic subdivision of the North China Craton (Zhao et al. 2005). (B) Geological map showing the location of the three studied drill cores (Bao et al., 2023). (C) Simplified stratigraphic succession and subdivision of the Nanfen Formation, based on the correlation of three drill cores (modified from Bao et al., 2023). The fossil information is adopted from Duan (1982); Lin (1984); Lin and Xing (1984); LBGMR (1989); Hong et al. (1991); Tang et al. (2020a); Li et al. (2023). The studied drill core interval and depositional environments are marked on the right of panel C.

Figure 2. Representative petrographic features of the Nanfen Formation samples. (A) Photomicrograph (plane-polarized light) of a pale blue argillaceous limestone from the middle Nanfen Formation (Sample ID: B380406A2; Stratigraphic height: 115.66 m), showing its carbonate mud composition. (B) BSE image of the same sample in panel A, showing the composition of carbonate mud (Cal), chert (Qz) and apatite grains (Ap). (C) EDS elemental mapping of panel B, showing the distribution of P, Si, Ca and K. (D) BSE image of red argillaceous limestone (red bed) from the upper Nanfen Formation (Sample ID: A040201A2; Stratigraphic height: 242.80 m), showing the occurrence of anhedral barite crystals (Brt) with corrugated boundaries. (E) EDS elemental mapping of panel E, showing the distribution of Ba, Ca, S and O. (F) Photomicrograph (plane-polarized light) of the sample in panel D, showing red hematite in a carbonate matrix. (G) BSE image of panel F with high magnification, showing hexagonal morphology of a hematite polyhedron. (H) EDS analysis of the hematite particle in panel G (red circle), showing high contents of Fe and O. (I) Electron backscattered diffraction analysis, confirmed the mineralogy of hematite in panel G.

Figure 3. Profiles of I/(Ca+Mg), Mg/Ca, Mn/Sr, $\delta^{13}C$, $\delta^{18}O$, Ba, P and P/Al from carbonates in the Nanfen Formation (Member I) at Benxi, North China (see the studied interval in Fig. 1). Long eccentricity cycles (405 kyr; Bao et al., 2023) are shown to the right of the stratigraphic column. The smoothed thick lines represent the LOESS curves (span = 0.1). The vertical red dashed line at 0.5 μmol/mol on the I/(Ca+Mg) profile marks the suboxic–anoxic Precambrian I/(Ca+Mg) baseline (Lu et al., 2017), and the red dashed line at 2.6 μmol/mol represents the lower limit for oxic conditions ($[O_2] \geq$ 20–70 μM; Shang et al., 2019). Positive shifts in I/(Ca+Mg) broadly coincide with the

recovery from negative shifts in $\delta^{13}C_{carb}$ and higher [P] and P/Al. The Ba and P/Al composition of PAAS are 0.067 wt% and 0.007 (wt%/wt%), respectively (McLennan, 2001).

Figure 4. Secular variation in I/(Ca+Mg) through time (B, modified from Xie et al., 2023) relative to the long-term atmospheric pO_2 curve (A, from Lyons et al., 2021). The I/(Ca+Mg) data are sourced from Glock et al. (2014), Lu et al. (2016, 2018), Hardisty et al. (2017), He et al. (2020), Huang et al. (2022), Shang et al. (2019), Wei et al. (2019, 2021), Wörndle et al. (2019), Ding et al. (2022), Yu et al. (2022) and Yuan et al. (2022). (C) Phylogenetic tree of the domain Eukarya with black, red and green lines highlighting crown-group branches (Brocks et al., 2023). LECA – the last common ancestor of all extant eukaryotes, rapidly evolved during the 1.1–1.0 Ga interval (Brocks et al., 2023).

Figure 5. Schematic model showing episodic oxygenation of shallow seawater and fluctuations in I/(Ca+Mg) ratios during deposition of the Nanfen formation. (A) Enhanced continental P input enhanced primary productivity in shallow seawater, resulting in oxygenation. Increased continental sulfate input promoted microbial sulfate reduction below the redoxcline, leading to the accumulation of iodide in anoxic seawater and authigenic barite precipitation. The mixing of oxic shallow seawater and upwelling of iodide-rich, anoxic seawater resulted in the oxidation of iodide to iodate and therefore high I/(Ca+Mg) ratios. This process generated spatiotemporal redox heterogeneity that created niches for crown-group eukaryotes. (B) A decrease in continental P input, oxidation of organic carbon, and the upwelling of Fe(II)-rich seawater led to a decrease in oxygen concentrations in shallow seawater and therefore

low I/(Ca+Mg) ratios. The highly fluctuating redox conditions may have prevented continual rapid eukaryote evolution on longer timescales.