

Multiple ocean oxygenation events during the Ediacaran Period: Mo isotope evidence from the Nanhua Basin, South China

Lin Yuan^{a,*}, Ying Zhou^a, Xi Chen^b, Maoyan Zhu^{c,d}, Simon W. Poulton^e, Zheyu Tian^a, Da Li^f, Matthew Thirlwall^g, Graham A. Shields^a

^a*Department of Earth Sciences, University College London, London, WC1E 6BT, UK*

^b*Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China*

^c*State Key Laboratory of Palaeobiology and Stratigraphy and Center for Excellence in Life and Palaeoenvironment, Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences, Nanjing 210008, China*

^d*College of Earth and Planetary Sciences, University of Chinese Academy of Sciences, Beijing 100049, China*

^e*School of Earth and Environment, University of Leeds, Leeds, LS2 9JT, UK*

^f*School of Marine Science and Engineering, Nanjing Normal University, Nanjing 210023, Jiangsu, China*

^g*Department of Earth Sciences, Royal Holloway, University of London, Egham, TW20 0EX*

*Corresponding author at: Department of Earth Sciences, University College London, Gower Street, London, UK, WC1E 6BT

E-mail address: lin.yuan.19@ucl.ac.uk (Lin Yuan)

This manuscript has been submitted for publication in *Precambrian Research*. Please note that, despite having undergone peer-review, the manuscript has yet to be formally accepted for publication. Subsequent version of this manuscript may have slightly different content. If accepted, the final version of this manuscript will be available via the 'Peer-reviewed Publication DOI' link on the right-hand side of this webpage. Please feel free to contact any of the authors; we welcome your feedback.

Abstract

The Ediacaran Period (ca. 635–539 Ma) was an eventful interval in Earth history, during which a succession of biological and environmental changes, including episodic ocean oxygenation events (OOEs), may have paved the way for the Cambrian radiations of animal life. To better understand the evolution of ocean redox conditions and to estimate the extent of seafloor oxygenation during this period, we analysed molybdenum (Mo) isotope compositions and redox sensitive element (RSE) concentrations from a continuous, mid-slope section of the Doushantuo Formation (ca. 635–560 Ma) of the Nanhua Basin on the South China Craton. Alongside an updated compilation of published Mo isotope and RSE data, our new data show that three OOEs occurred within a generally anoxic Ediacaran ocean, with the last, particularly extensive event occurring during deposition of Doushantuo Member IV. Here, these findings suggest that the global balance of redox-related Mo sinks shifted dynamically in response to these transient OOEs, which correlate well with the first appearance of Ediacaran fossil groups and so may have triggered or stimulated biotic innovations and radiations. Moreover, the spatial distribution of the Mo data from multiple sections supports episodic expansion of a euxinic wedge on the slopes of the Nanhua Basin, consistent with pyrite burial as a potential cause of the OOEs.

Keywords: Ediacaran Period, molybdenum isotopes, redox sensitive elements, ocean oxygenation, Doushantuo Formation, Nanhua Basin

1. Introduction

The Ediacaran Period (~635–539 Ma) marks a turning point when several important evolutionary and environmental events occurred that set the stage for the subsequent progression towards the modern Earth system. This includes the appearance of complex multicellular eukaryotes in the form of the Ediacaran biota (Narbonne 2005; Droser et al., 2017), which reached their maximum diversity at around 560 Ma (Xiao et al., 2009). Most eukaryotes, especially the overwhelming majority of metazoans, require oxygen for various physiological processes (Summons et al., 2006; Acquisti et al., 2007; Narbonne 2004; Canfield et al., 2007, Sperling et al., 2013). Moreover, the diversification of animals is plausibly linked to a stepwise rise in oceanic (and possibly atmospheric) oxygenation during the late Ediacaran Period (Canfield et al., 2007; Frei et al., 2009; Knoll, 2011; Lenton et al., 2014; Chen et al., 2015; Bowyer et al., 2017; Cole et al., 2020).

It is commonly thought that some 1.5 billion years after the ‘Great Oxidation Event’ (GOE, ~2.3 Ga) (Holland, 2002; Canfield, 2005), there was a second significant increase in Earth surface oxygenation (termed the ‘Neoproterozoic Oxygenation Event’, NOE) at ~0.8–0.5 Ga (Shields-Zhou and Och, 2011). Indeed, some data suggest that oceanic oxygen levels during the NOE may have risen to near present levels (Zhang et al., 2019). In more detail, however, abundant evidence shows that Ediacaran ocean oxygenation events (OOEs) were only transient (Canfield et al., 2007; Sahoo et al., 2012, 2016; Zhang et al., 2019; Xu et al., 2022), while ferruginous (Fe²⁺ containing) or euxinic (sulphidic) anoxic environments (Canfield et al., 2008; Li et al., 2010; Kurzweil et al., 2015; Wood et al., 2015; Zhang et al., 2018) continued to be widespread. Although enrichments of redox-sensitive element (RSE) on the South China Craton (particularly the Doushantuo Formation) imply that oceans

were widely oxygenated soon in the wake of Marinoan glaciation (Sahoo et al., 2012, 2016), oxygen levels likely waxed and waned throughout the NOE period (Fike et al., 2006; Canfield et al., 2008; McFadden et al., 2008; Kendall et al., 2015; Sperling et al., 2015; Tostevin et al., 2019; Tostevin and Mills, 2020; Wei et al., 2021). Furthermore, oceanic redox structure, especially around productive margins, may have been highly variable (Li et al., 2015). Overall, the detailed timing and intensity of Ediacaran oxygenation, as well as resultant changes in the marine redox landscape, remain unclear (Och and Shields-Zhou, 2012; Sperling et al., 2013; Lyons et al., 2014; Och et al., 2016). Thus, further detailed studies utilising redox proxies that address local to more regional redox heterogeneity are required, such as the proxies outlined below.

A sequential extraction procedure for acquiring the relative proportion of iron mineral species in ancient sediments, iron speciation, is widely used to investigate the local to regional redox state of ocean basins (Poulton and Canfield, 2005; 2011). The ratio of Fe_{HR}/Fe_T (Fe_{HR} , highly reactive iron, normalized to Fe_T , total iron) has been extensively calibrated as a tool of indicating water column anoxia in both ancient and modern marine settings (Raiswell and Canfield, 1998; Raiswell et al., 2001; Poulton and Raiswell, 2002; Clarkson et al., 2014). Fe_{HR}/Fe_T ratios lower than 0.22 suggest probable oxic water column conditions, while $Fe_{HR}/Fe_T > 0.38$ implies water column anoxia, with intermediate Fe_{HR}/Fe_T ratios considered equivocal (Poulton and Canfield, 2011). For anoxic conditions, euxinia can be distinguished from ferruginous conditions by considering the extent of the pyritisation of the highly reactive iron pool (Fe_{PY}/Fe_{HR} ; Poulton et al., 2004; Poulton and Canfield, 2011). Recent work on the euxinic Lake Cadagno (Xiong et al., 2019) and euxinic Holocene sediments from the Eastern Mediterranean Sea (Benkovitz et al., 2020), combined with existing criteria (Anderson and Raiswell, 2004; März et al., 2008), suggest that $Fe_{PY}/Fe_{HR} < 0.6$ provides strong support for ferruginous water column conditions, $Fe_{PY}/Fe_{HR} > 0.8$ implies euxinic conditions, while ratios of 0.6–0.8 are considered equivocal and require additional evidence, such as trace metal concentrations and isotope compositions, to recognise the precise redox state of the water column (Poulton, 2021).

Redox-sensitive element concentrations are used for tracing not only local but also global ocean redox states (Sahoo et al., 2012, 2016; Ostrander et al., 2019). Most RSEs are transferred to the ocean in the form of aqueous oxyanions derived from the oxidative weathering of RSE-bearing minerals (Dunk et al., 2002; Miller et al., 2011), while marine sediments represent the major RSE sink, governed largely by the redox condition of the local depositional environment. RSE contents in marine sediments beneath oxic waters generally approximate crustal values (Mo ~1.1 ppm, U ~1.7 ppm, V ~98 ppm; Wedepohl, 1995) without authigenic enrichment, as most of the RSEs remain in dissolved form in oxic seawater, which today has Mo ~110 nM (Ho et al., 2018), U ~14 nM, and V ~40 nM (Morford and Emerson, 1999). The exception is in authigenic Fe-Mn oxide particles, onto which RSEs, Mo and V in particular, may be sequestered via adsorption (Tribovillard et al., 2006).

Under reducing marine states, the burial fluxes of many RSEs (e.g., Mo, U and V) exceed those in oxygenated settings by several orders of magnitude (Sahoo et al., 2012). As RSE enrichments in anoxic marine sediments generally report dissolved RSE concentrations in seawater, the extent of RSE enrichment in sediments during anoxic deposition can be applied to trace ocean redox state (Scott et al., 2008; Algeo et al., 2006; Och and Shields-Zhou, 2012). Under anoxic (both sulphidic and ferruginous) conditions, dissolved U may be efficiently captured in shales, following quantitative reduction from U(VI) to U(IV) (Tribovillard et al., 2012; Massey et al., 2014; Brüske et al., 2020). Similarly, under suboxic or anoxic conditions, pentavalent vanadate is reduced to tetravalent vanadyl susceptible to incorporation into organic matter (Breit and Wanty, 1991). Further reduction to

insoluble trivalent V species is kinetically slow (Wanty and Goldhaber, 1992) and does not induce sedimentary V enrichment, even in the modern euxinic Framvaren Fjord, which has the highest marine H₂S concentration of 8 mM (Scott et al., 2017). By contrast, Mo precipitation initiates due to thiolation by H₂S, rather than reduction, and thiomolybdates are prone to further particle scavenging (Helz et al., 1996) or sulphide formation (Helz, 2021).

Other factors affect the extent of RSE drawdown including, particularly, the content of these elements in the open ocean, as well as the connectivity of ocean basins to the open ocean (Algeo and Maynard, 2004; Lyons and Severmann, 2006). Basin restriction generally reduces the extent of RSE enrichments (Algeo et al., 2006; Lyons et al., 2009), which means that the upper limits of enrichments within an interval do not only have local significance (Sahoo et al., 2012). Therefore, high RSE enrichments recorded in euxinic shales provide strong evidence for a broadly oxygenated ocean, since such enrichments in locally anoxic settings require high availability of RSE sourced from a largely oxygenated open ocean (Scott et al., 2008; Sahoo et al., 2012, 2016).

Molybdenum (Mo) isotopes have developed into a strong paleoredox proxy for evaluating the spatial extent of different oceanic redox conditions, due to the redox controlled switches between different depositional mechanisms and ensuing changes in isotope fractionations (e.g., Arnold et al., 2004; Kendall et al., 2017). In the modern oxygenated ocean, Mo scavenging by Fe-Mn oxides comprises a large portion of the global Mo sink. This process is slow, and the product is significantly enriched in the lighter Mo isotopes (Barling et al., 2001), which causes modern open ocean seawater (OSW) to be homogeneously enriched in the heavier Mo isotopes, with a $\delta^{98}\text{Mo}_{\text{OSW}}$ composition of around +2.34‰ (Nakagawa et al., 2012). Similarly, high $\delta^{98}\text{Mo}$ values have been reported from sediments deposited during the early Cambrian (Chen et al., 2015), early Devonian (Dahl et al., 2010), and the Paleocene–Eocene thermal maximum (Dickson et al., 2012), which are interpreted to reflect a modern-like extent of oxygenated seafloor. These interpretations are based on the observation that isotopic fractionations are commonly much smaller under suboxic through to anoxic conditions (Poulson et al., 2009). Therefore, when such settings expand, the $\delta^{98}\text{Mo}_{\text{OSW}}$ value tends to decrease, as shown near the end of the Permian Period (Zhang et al., 2021) and during the Late Cretaceous Ocean Anoxic Event (OAE) 2 (Goldberg et al., 2016; Dickson et al., 2021).

Here, we use these redox systematics to interpret a combined data set of local to potentially global redox proxies, including Mo isotopes, RSEs and Fe-speciation, from a newly discovered and dated mid-slope section named Xiajiaomeng West (XJMW), Guizhou Province, South China. Combined with data from previous studies on Ediacaran sections positioned at various water depths across the Nanhua Basin, these new data from the Doushantuo Formation provide supporting evidence for the occurrence of OOE through the Ediacaran Period, and allow a detailed investigation of the temporal and spatial evolution of redox conditions on productive ocean margins during the Ediacaran Period.

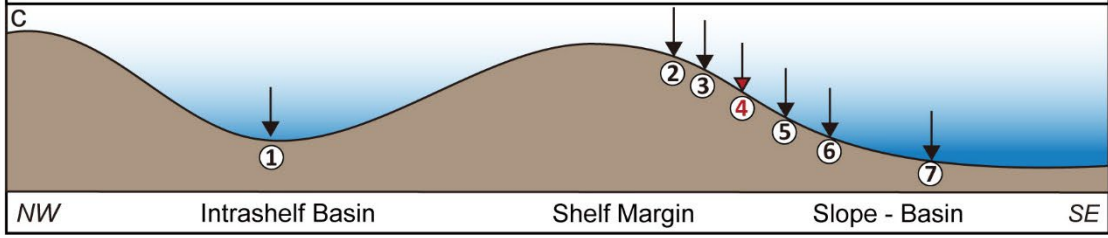
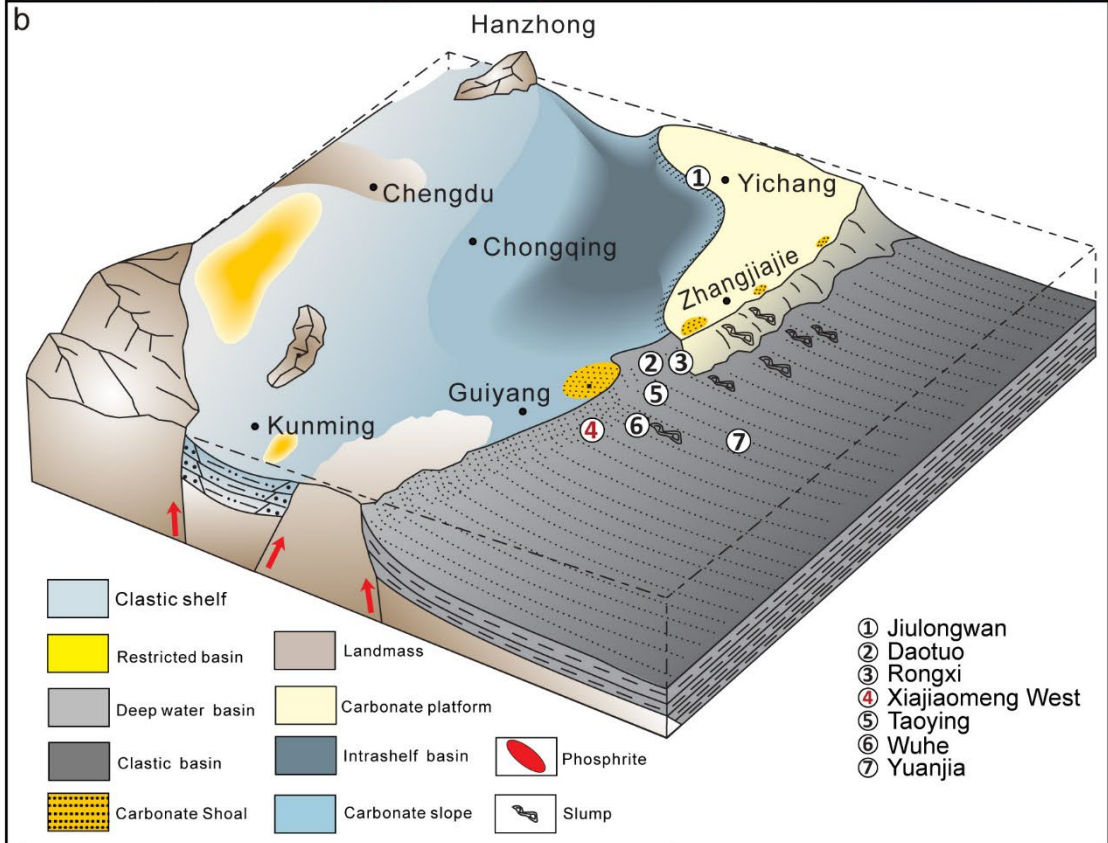
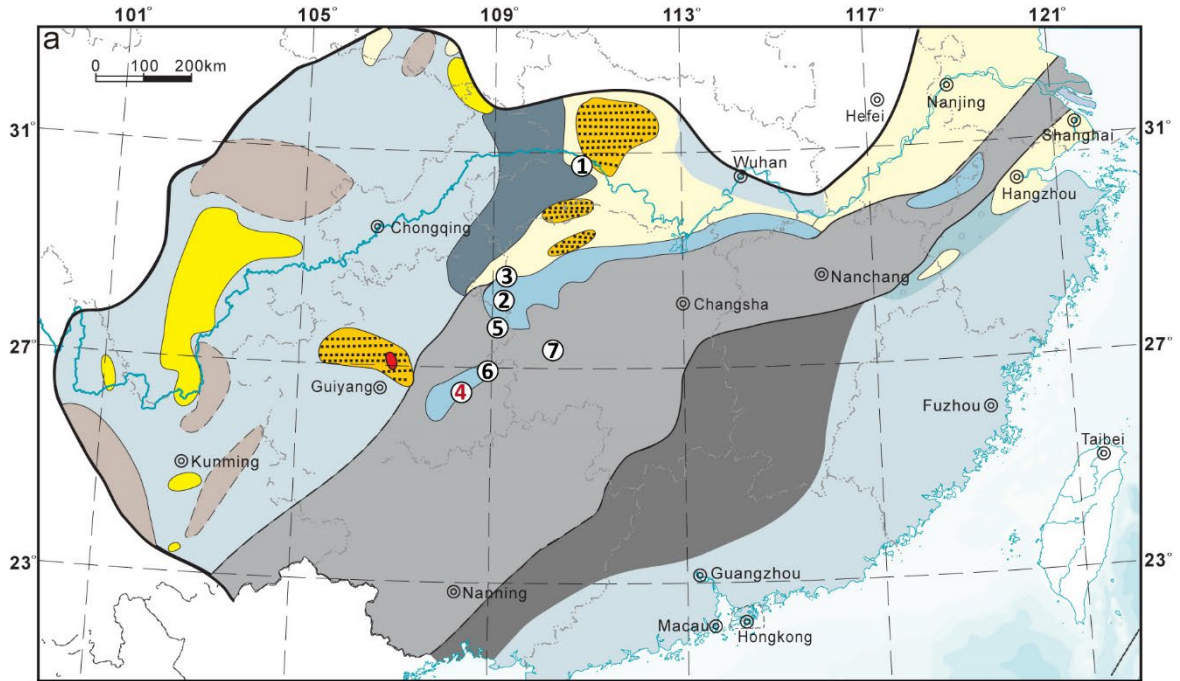


Fig. 1. (a) A reconstructed paleogeographic map of South China Craton during the deposition time of Doushantuo Formation, modified from Lu et al. (2013). (b) A 3D paleogeographic reconstruction of the Nanhua Basin together with the depositional environment. The figure is modified from Zhu et al. (2019) and see the legend of color in the reference paper. (c) Cross-section view of the paleogeographic reconstruction of the Nanhua Basin.

2. Study sites and samples

2.1. The Doushantuo Formation on the South China Craton

The South China Craton consists of two blocks, Yangtze and Cathaysia, between which the Nanhua Basin developed as a failed intracratonic rift basin at ~820 Ma (Wang and Li, 2003). Ediacaran sedimentary successions, comprising the Doushantuo and Dengying formations, are well preserved over the Yangtze platform, with the underlying Doushantuo Formation representing a considerably greater proportion of Ediacaran time (Condon et al., 2005). The Nanhua Basin comprises a large platform facies, a transition belt, and a basin facies, representing a shelf-to-basin transect from the northwest to the southeast (Fig. 1a and 1b). The precise paleobathymetric reconstructions of Zhu et al. (2003) have reflected that the shallow-water platform was characterised by multiple intra-shelf basins and carbonate barriers on its margins. The Doushantuo Formation was deposited on the southeastern margin of the Yangtze platform with some connection to the open ocean (Jiang et al., 2011; Sahoo et al., 2012). It is underlain by the Nantuo Formation, which mainly comprises glaciogenic diamictites deposited towards the end of the Cryogenian Period, and is overlain by the Dengying/Liuchapo formations that were deposited during the terminal part of the Ediacaran Period.

The Doushantuo Formation in the Yangtze Gorges area has been commonly divided into four distinct lithological members (I–IV from base to top), which are likely correlative with sections of the same formation name along the basin margin (McFadden et al., 2008; Jiang et al., 2011). Member I, a cap carbonate (dolostone), overlies the Nantuo diamictite and can be up to ~5 m thick in the Yangtze Gorges area. There is an ash bed just above the top of Member I in the Yangtze Gorges area which has been dated at 635.23 ± 0.57 Ma (Condon et al., 2005), with a 634.57 ± 0.88 Ma age from the uppermost Nantuo Formation (Zhou et al., 2019). These two ages are similar to ages from other well-known basal Ediacaran sections, including $<636.41 \pm 0.45$ Ma from Tasmania, Australia (Calver et al., 2013), $<635.21 \pm 0.59$ Ma in northern Namibia (Prave et al., 2016), and $>632.3 \pm 5.9$ Ma in northwestern Canada (Rooney et al., 2015). The two ages from the South China Craton are almost indistinguishable within analytical error, and together they indicate that the boundary of Cryogenian–Ediacaran is at approximately 635 Ma (Xiao and Narbonne, 2020).

Member II comprises interbedded black shale and dolostone with abundant chert nodules and pyrite. U-Pb zircon dating from about six meters from the base of this member gives an age of ~632 Ma (Condon et al., 2005). Member III is mainly composed of carbonates, largely ribbon-banded limestones and marls, with irregular chert bands and fewer shale layers. Member IV is dominated by organic-rich black shale, which is overlain by the Dengying/Liuchapo Formation. The end of Member IV deposition at the Jiuqunao (Jijiawan) section in the Yangtze Gorges area is dated by a zircon age of ~551 Ma from an ash layer, which was reported to be 1 m below the top of Member IV (Condon et al., 2005; Zhang et al., 2005). More recently, this has been re-dated to 550.1 ± 0.6 Ma by Yang et al.

(2021). In the Doushantuo Formation, biostratigraphic correlations can be made using fossil assemblages, including macroscopic carbonaceous compressions of multicellular algae, and acanthomorphic acritarchs (Xiao et al., 2004; Yuan et al., 2011; Xiao et al., 2014; Qu et al., 2018; Quyang et al., 2019). The overlying Dengying/Liuchapo Formation preserves biomineralizing metazoan fossils including Shibantan and Gaojiashan Biota (Xiao et al., 2005; Cai et al., 2010; Chen et al., 2014).

The upper part of the Doushantuo Formation (Members III and IV) records the world largest negative carbon isotope excursion in Earth history, called the 'DOUshantuo Negative Carbon isotope Excursion' (DOUNCE) in South China (Lu et al., 2013). The top of Doushantuo Member IV marks the end of the DOUNCE ($>\sim 550$ Ma; Yang et al., 2021) and this excursion is considered as being equivalent to worldwide $\delta^{13}\text{C}$ excursions: the Shuram $\delta^{13}\text{C}$ excursion in Oman (Fike et al., 2006), the Wonoka $\delta^{13}\text{C}$ excursion in southern Australia (Calver, 2000), and the Krol B $\delta^{13}\text{C}$ excursion in northern India (Kaufman et al., 2006), all recorded from upper Ediacaran successions. Different models exist to interpret negative carbon isotope excursions, such as the remineralisation of a putative, large dissolved organic carbon pool (Rothman et al., 2003). However, Bristow and Kennedy (2008) pointed out that such an event would have exhausted ocean oxidant supply on a timescale of ~ 800 kyrs, much shorter than the likely duration of the anomaly. This issue can potentially be resolved if surplus sulphate weathering coupled with pyrite burial replenished the requisite oxidant (Shields et al., 2019). Alternative models include authigenic carbonate deposition (Schrag et al., 2013; Laakso and Schrag 2020), while some argue for a local or diagenetic origin for the $\delta^{13}\text{C}$ excursions (e.g., Busch et al., 2022).

2.2 Studied section: Xiajiaomeng

The XJMW section ($26^{\circ}68'56''\text{N}$, $108^{\circ}33'82''\text{E}$) is located in Guizhou Province and is ~ 70 km to the southwest of the Wuhe section (Fig. 1; red number). The XJMW section incorporates the whole of the Doushantuo Formation, and the lithologies vary from carbonates and calcareous dolomite to shales. In total, 45 samples were collected from an abandoned quarry with freshly exposed surface. Based on a lithological comparison with the four members of the Doushantuo Formation observed in the Yangtze Gorges area, the Doushantuo Formation at XJMW can be similarly divided into four members: Members I–IV. The dolomitic Member I sits above diamictite, and likely represents the “cap dolostone” in this section; Member II begins with the first chert bed. Its lower part is predominantly siliceous with some carbonate interbeds, becoming more shaly upwards, with cherty interbeds; Member III is mostly carbonate with some chert bands; Member IV is dominated by black shale or black marl. Compared with Yangtze Gorges sections, the XJMW section appears to be more siliceous (Table 1; Al content) and was deposited in a middle slope environment in the Nanhua Basin (Fig. 1c). The overall thickness of the sampled section is approximately 38 m, having been shortened somewhat by tectonic shearing and low-grade metamorphism. The only dating result for the slope sections is a zircon U-Pb age of 556.4 ± 0.7 (CA-ID-TIMS) from the lower part of the overlying Liuchapo Formation at the same XJMW section (Yang et al., 2021). This would be consistent with an age of ~ 560 Ma for the end of Doushantuo Member IV. (Yang et al., 2021). For the purpose of this study, we assume an age span of ~ 635 to ~ 560 Ma for the entire Doushantuo Formation and an approximately constant sedimentation rate (Table 1).

3. Methodology

All samples were crushed and ground into powder using a tungsten carbide Tema. RSE concentrations were acquired by X-ray fluorescence (XRF) on a Philips PW2400 Spectrometer (PANalytical, Almelo, the Netherlands) at Royal Holloway University, London, with representative reproducibilities (2SD) of Mo = 0.2 µg/g, U = 0.4 µg/g, and V = 2.4 µg/g. Fe extractions were conducted at the University of Leeds following the methods outlined in Poulton and Canfield (2005) and Canfield et al. (1986). The concentration of Fe in operationally-defined sequential leaches of un sulphidised Fe phases (see Poulton, 2021) were determined by atomic absorption spectroscopy, while the concentration of pyrite Fe was determined gravimetrically after precipitation as Ag₂S. Replicate extractions gave a relative standard deviation of <5% for all steps, and accuracy was ensured using international Fe speciation standard, WHIT (Alcott et al., 2020). Total organic carbon (TOC) was obtained by the difference between total carbon before and after the removal of inorganic carbon (two 10% (vol/vol) HCl washes for 24 h). Samples were analysed on a FLASH EA (elemental analyser) at University College London, and replicate analyses gave a precision of ± 0.12 wt% (2SD).

Mo purification and δ⁹⁸Mo measurements were performed at Nanjing University, China. For Mo isotope analysis, about 10–100 mg of powder containing ~50–200 ng Mo was digested with HNO₃ and HF. A drop of ⁹⁷Mo–¹⁰⁰Mo double spike containing the same amount of Mo was added to the mixture. The mixture was left on a hotplate (150 °C) for ~72 h. The supernatant was separated and dried before being re-dissolved using HCl. The purification of Mo using BPHA resin follows the protocol of Li et al. (2014). Mo isotope compositions were measured on a Thermal Neptune Plus multi-collector ICP-MS. The measurement and mass bias correction by the double spike technique were carried out as described by Archer and Vance (2008). The Mo isotope data are reported relative to the reference standard, NIST-SRM-3134 (δ⁹⁸Mo = +0.25‰; Nägler et al., 2014). The internal reproducibility of δ⁹⁸Mo measurements was better than 0.1‰ (2SE, n = 30).

To assess and compare the authigenic fractions of RSEs, enrichment factors (E_{fs}) were calculated via the equation $X_{EF} = [(X/Al)_{sample} / (X/Al)_{UCC}]$ (Tribovillard et al., 2006; Algeo and Tribovillard, 2009), where X (ppm) and Al (wt%) represent the contents of RSE X and Al, respectively. Data are normalized against abundances of upper continental crust (UCC) outlined in McLennan (2001). In general, $X_{EF} > 3$ corresponds to a detectable authigenic enrichment, while $X_{EF} > 10$ suggests a substantial enrichment (Algeo and Tribovillard, 2009).

4. Results

4.1. Redox conditions at the XJMW section

For the XYMW section, all but two samples (XJMW33 and 39) had Fe_T values above 0.5 wt%, which is considered to give a robust Fe speciation signal (Clarkson et al., 2014), and hence these samples were analysed for Fe speciation (Table 1). Almost all XJMW samples have Fe_{HR}/Fe_T values greater than 0.38, suggesting deposition beneath a persistently anoxic water column. The only exception is sample XJMW41, which had an Fe_{HR}/Fe_T ratio of 0.28 in the equivocal anoxic zone. However, the RSE contents of this sample are similar to those of neighbouring samples above and below, indicating probable anoxia (Table 1; Fig. 2). For Member I, Fe_{Py}/Fe_{HR} ratios for all samples were <0.6, indicating that

Member I was deposited under a ferruginous water column. For Member II, the lower part shows a ferruginous signature with $Fe_{Py}/Fe_{HR} < 0.6$, while samples in the upper part lie mostly in the equivocal zone, with Fe_{Py}/Fe_{HR} between 0.6 and 0.8, possibly fluctuating between ferruginous and euxinic conditions. The Fe_{Py}/Fe_{HR} values of Member III range between 0.26 and 0.89, showing oscillating euxinic and ferruginous values. In Member IV, except for XJMW41 (Table 1), all samples have equivocal (0.6–0.8) or euxinic $Fe_{Py}/Fe_{HR} (>0.8)$ ratios.

4.2. RSE concentrations at the XJMW section

As shown in Fig. 2 and Table 1, the different measured redox sensitive elements (Mo, U and V) show roughly the same trend. Based on elevated RSE concentrations, three distinct intervals of enrichment can be identified (Fig. 2): Zone A: basal Member II, Zone B: basal Member III, and Zone C: Member IV. The occurrence of these three RSE-enriched intervals is approximately consistent with previous studies of other sections across the basin transect (Kendall et al., 2015; Sahoo et al., 2016; Ostrander et al., 2019; Ye et al., 2020).

The first high RSE interval (Fig. 2; Table 1) occurs in basal Member II (Mo = 0.4–15 ppm, U = 3–15 ppm, V = 100–1200 ppm). Mo_{EF} , U_{EF} and V_{EF} range from 1–9, from 3–7, and from 3–30, respectively. This interval is followed by a progressive shift to lower RSE concentrations from 7–25 m in the section (Mo = 2–4 ppm, U = 3–5 ppm, V = 80–120 ppm), with concentrations that are similar to crustal values (Mo = 1–2 ppm, U = 2–4 ppm, V = 120–140 ppm). At the base of Member III (Fig. 2; Zone B), RSE concentrations increase again, with Mo contents varying between 1–11 ppm ($Mo_{EF} = 4–9$), U between 1–11 ppm ($U_{EF} = 2–6$), and V between 21–160 ppm ($V_{EF} = 1–2$). Above this interval, RSE values again decrease to near crustal levels. Finally, there is a third large shift in RSE concentrations in Member IV (Zone C), whereby this interval records the highest Mo and U concentrations (Mo = 6–312 ppm, U = 6–48 ppm), while V concentrations are also elevated (115–910 ppm). Efs for these RSEs are also elevated during this interval ($Mo_{EF} = 14–597$, $U_{EF} = 7–72$, $V_{EF} = 2–10$).

4.3. Mo isotope compositions at the XJMW section

The 24 samples from the Doushantuo Formation at the XJMW section show mostly positive $\delta^{98}Mo$ values, up to +1.82‰ (Fig. 2; Table 1), with only one negative value (–0.39‰) in Member II. Mo isotope compositions are elevated during the three RSE-enriched intervals. In Zone A, two samples from the lowermost Member II have relatively low $\delta^{98}Mo$ values (+0.23‰ and +0.37‰, respectively). Between Zone A and Zone B, the $\delta^{98}Mo$ data show a limited range except for one negative value. The $\delta^{98}Mo$ values increase progressively upsection towards Member IV, with the $\delta^{98}Mo$ value showing up to +1.39‰ in Zone B. Moving to Zone C, the $\delta^{98}Mo$ values show a range of +0.64 to +1.82‰, averaging $+1.29 \pm 0.42‰$ (1SD). Throughout the XJMW section, the TOC trend generally covaries with the Mo isotopic data. One important finding is that $\delta^{98}Mo$ values continue to rise through Member IV (Fig. 2), and above the most Mo-enriched sample (312 ppm), which has a relatively low $\delta^{98}Mo$ value (+0.64‰).

Table 1. Geochemical data for Doushantuo Formation at the XJMW section.

Unit	Sample	Height (m)	Age (Ma)	$\delta^{98}\text{Mo}$ (‰)	TOC (%)	Al (%)	Mo (ppm)	U (ppm)	V (ppm)	$\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$	$\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}}$
Member I	XJMW1	0	635		0.07	7.54	0.3	2.8	66	0.61	0.39
Member I	XJMW2	0.5	634		0.04	3.47	0.4	2.5	43	0.83	0.12
Member I	XJMW3	1.4	633		0.06	1.43	0.9	1.5	13	0.93	0.04
Member II	XJMW4	3	632		0.35	3.06	0.4	7.1	1199	0.88	0.05
Member II	XJMW5	3.6	631		0.05	3.24	1.0	6.2	413	0.94	0.12
Member II	XJMW6	4.6	629	0.234	0.21	8.57	15	14	315	0.77	0.5
Member II	XJMW7	5.6	627	0.368	0.73	7.44	11	7.9	250	0.87	0.44
Member II	XJMW8	6.6	625		0.04	3.63	1.7	5.3	189	0.9	0.24
Member II	XJMW9	8.3	621		0.25	1.46	0.3	3.0	66	0.93	0.07
Member II	XJMW10	9.3	619		0.12	8.76	0.1	6.3	162	0.72	0.6
Member II	XJMW11	11.3	615		0.04	1.38	0.3	0.8	58	0.91	0.11
Member II	XJMW12	12.3	613		0.11	7.42	0.8	1.5	85	0.84	0.75
Member II	XJMW13	14	609		0.09	5.24	0.8	1.2	54	0.81	0.63
Member II	XJMW14	15	607	-0.388	1.69	7.19	1.3	2.2	99	0.88	0.76
Member II	XJMW15	16.4	604		0.13	6.77	0.9	1.6	76	0.52	0.54
Member II	XJMW16	17.4	602	0.672	1.50	7.82	1.2	2.4	95	0.78	0.69
Member II	XJMW17	18.4	600	0.692	0.00	8.03	1.7	2.8	104	0.54	0.44
Member II	XJMW18	20.4	596	0.253	1.33	6.42	2.3	3.5	95	0.85	0.79
Member II	XJMW19	20.8	595		0.80	5.14	2.1	3.0	69	0.91	0.59
Member II	XJMW20	21.1	595	0.434	2.42	7.68	3.6	5.4	105	0.96	0.77
Member II	XJMW21	22.7	591	0.205	1.47	7.17	1.8	3.1	98	0.91	0.78
Member II	XJMW22	22.8	591	0.309		5.26	1.6	1.4	74	0.96	0.76
Member II	XJMW23	23.6	590		0.54	5.14	0.9	2.9	75	0.82	0.72
Member III	XJMW24	24.6	588		0.45	1.94	0.5	1.2	27	0.92	0.38
Member III	XJMW25	26.1	584	0.569	3.45	7.40	9.2	8.8	169	1	0.78
Member III	XJMW26	26.3	584	0.644	2.24	6.86	5.5	6.5	160	0.95	0.85
Member III	XJMW27	26.7	583		0.59	0.74	1.1	0.9	21	0.98	0.26
Member III	XJMW28	27	583	1.386	4.13	5.74	5.6	11	141	0.85	0.81

Member III	XJMW29	27.5	582		2.35	1.88	2.1	1.8	37	0.96	0.45
Member III	XJMW30	27.8	581	1.148	3.05	6.54	11	5.9	106	0.87	0.88
Member III	XJMW31	28.3	580	0.270	0.04	5.46	2.4	3.9	88	0.94	0.78
Member III	XJMW32	29.1	578	0.228	0.33	4.41	2.9	2.3	59	0.94	0.89
Member III	XJMW33	30.1	576		0.05	0.51	0.6	1.7	52		
Member III	XJMW34	30.9	575		0.24	1.82	1.0	3.9	150	0.73	0.51
Member III	XJMW35	31	574		0.11	1.83	0.6	7.8	153	1	0.37
Member III	XJMW36	32.5	571		0.03	2.38	1.1	3.7	397	0.92	0.62
Member IV	XJMW37	33	570	0.640	0.37	6.68	312	48	910	0.89	0.88
Member IV	XJMW38	35	566	1.349	0.09	2.36	6.4	9.2	324	0.99	0.75
Member IV	XJMW39	37	562	0.857	0.30	0.83	94	21	115		
Member IV	XJMW40	37.1	562	1.393	1.54	2.32	34	6.0	128	1	0.85
Member IV	XJMW45	37.2	562	0.805	5.96	2.68	31	21	128	1	0.63
Member IV	XJMW41	37.5	561	1.821	6.19	4.82	66	19	140	0.28	0.77
Member IV	XJMW42	37.65	561	1.722	6.60	5.34	58	19	136	0.99	0.69
Member IV	XJMW43	37.8	560	1.549	7.32	5.07	56	24	140	1	0.71
Member IV	XJMW44	38	560	1.443	7.58	4.86	51	18	133	0.96	0.74

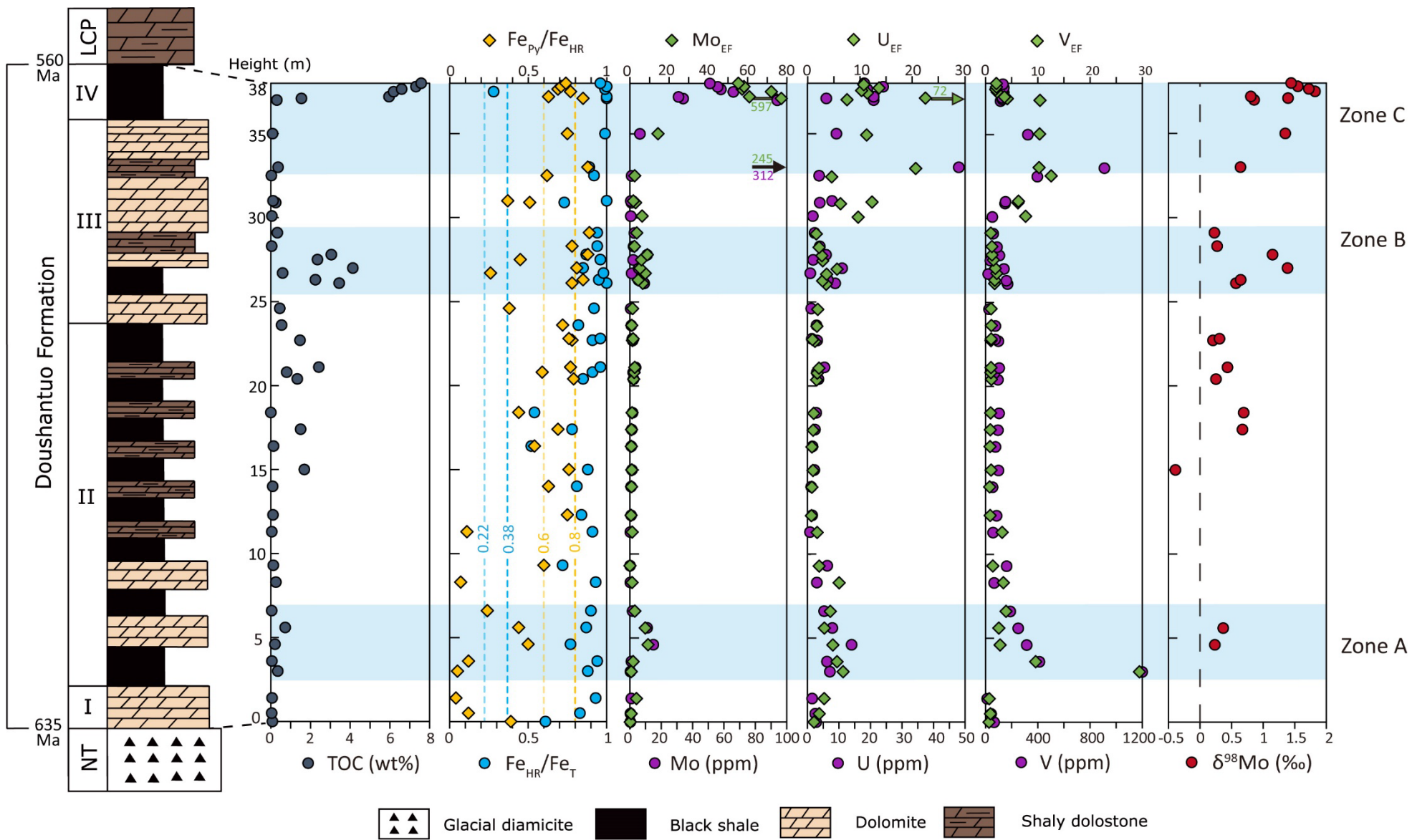


Fig. 2. Geochemical profiles for the XJMW section (Table 1), together with the stratigraphic column. The blue intervals signify high RSE enrichments, Mo isotopic compositions and TOC contents (Zone A, B and C).

5. Discussion

5.1. Three oceanic oxygenation events

Based on our data, three potential oxygenation intervals in the XJMW section (Fig. 2; Zone A: basal Member II, ~630 Ma, Zone B: mid Member III, ~580 Ma, and Zone C: Member IV ~570 Ma) are identified, based on elevated RSE concentrations and enrichment factors, TOC concentrations and $\delta^{98}\text{Mo}$ values. As mentioned above, the accumulation rates of RSE in reducing environments exceed those in oxic environments (Sahoo, et al., 2012), and with a greater extent of global oxygenation, greater enrichment of RSEs will occur in fewer locally anoxic settings. Therefore, the RSE enrichments of these three episodes suggest widespread OOE within the investigated late Ediacaran interval. We estimate that each OOE spanned an approximate maximum interval of ~8–10 million years (Table 1), and that dynamic redox variability through the stratigraphy likely regulated sedimentary RSE concentrations. The RSE concentrations shift to lower values between OOE, which most likely suggests a switch back to more reducing oceanic conditions, in agreement with the interpretation for the Wuhe section by Sahoo et al. (2012, 2016). In general, the timing of these three OOE generally concurs with that found in previous studies from other slope sections (see Sahoo et al., 2012, 2016; Kendall et al., 2015; Ostrander et al., 2019; Xu et al., 2022).

The Fe speciation data indicate that most samples from the Doushantuo Formation at the XJMW section were deposited under anoxic conditions, which in detail was mostly ferruginous with episodic euxinia. Since Mo, U and V exhibit their own different characteristic responses to redox conditions encountered in the water column and during early diagenesis (Morford et al., 2005), changes in their concentrations during any particular OOE may not necessarily covary (Fig. 2). In Zone A, a slight [Mo] and [U] increase is observed, despite Fe speciation evidence for ferruginous conditions (Fig. 2). This may reflect changes in the local depositional environment, including openness of the paleo-basin (Algeo and Lyons, 2006) and bulk sedimentation rate (Hardisty et al., 2018). Vanadium shows the highest value at the base of Zone A, while U is only moderately enriched, and Mo is lower than the average upper crustal value. Vanadium enrichment begins under higher Eh conditions (Nielsen, 2021) than U and Mo, and shows high affinity with organic matter, which is consistent with the relatively low $\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}}$ and high TOC. In Zone B, $\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}}$ ratios suggest that redox conditions fluctuated between ferruginous and euxinic conditions, which is consistent with slightly elevated RSE concentrations (Fig. 2). Molybdenum concentrations are less than 11 ppm (Fig. 2), and such concentrations only occur in modern sulphidic environments where sulphide is restricted to the porewaters (Scott et al., 2012), which may indicate less availability of Mo sourced from a less oxygenated open ocean. In Zone C, $\text{Fe}_{\text{Py}}/\text{Fe}_{\text{HR}}$ data strongly indicate euxinic conditions (Fig. 2), which is similar to Zone B. However, significantly higher RSE concentrations and high TOC contents (>7.5 wt%), with values comparable to those found in Phanerozoic euxinic shales deposited during, or following, periods of global ocean oxygenation (Och and Shields-Zhou, 2012), highlights the potential magnitude of this particular global OOE.

Samples between OOE have low Mo_{EF} and U_{EF} values (Fig. 3a), which is consistent with low concentrations of Mo and U in a predominantly anoxic ocean (Algeo and Tribovillard, 2009). The Mo and U enrichment factors observed in Zones A and B plot close to, or below, the modern seawater value, but in Zone C range between those for modern open seawater and those for euxinic basins in good connection with the open ocean (Fig. 3a). Ostrander et al. (2019) suggest that the high enrichment of RSEs in Doushantuo Member IV (Zone C) could have been caused by a local Fe-Mn oxide shuttle and a global-scale OOE.

Furthermore, Algeo and Lyons (2006) proposed that changes in the degree of connection with the open ocean also affects Mo abundance in basinal seawater and sediments. Due to basin restriction, the modern Black Sea has low deep-water Mo concentrations (~7 nM; Nägler et al., 2011), compared with the modern open ocean (~110 nM; Ho et al., 2018). By analogy, Och et al. (2016) interpreted low RSE concentrations from Ediacaran successions in the Yangtze Gorges area to indicate basin restriction, as the Yangtze Gorges sections were deposited in a proximal intrashelf lagoon (Jiang et al., 2011). The low RSE concentrations (close to crustal values) between OOE can only be inferred to be due to a less well-oxygenated global ocean if strong basin restriction can be ruled out. In this context, the XJMW section was located in a distal slope setting which may have been better connected to the open ocean before deposition of Doushantuo Member IV. Therefore, our data may potentially be explained by some combination of ocean oxygenation and basin restriction (see section 5.3). Below we constrain the extent of oxygenation further by exploring Mo isotope systematics.

5.2. Mo isotopes and Mo concentration systematics

The Mo isotope composition of marine sediments has the potential to record the global extent of euxinia when sequestration of the aqueous molybdate anion, following conversion of molybdate to thiomolybdate species, is near-quantitative, which requires relatively high $[H_2S]_{aq}$, low pH (Helz, 2021), and possibly basin restriction (Algeo and Lyons, 2006). Such a combination of conditions may not commonly occur, therefore it has been assumed that $\delta^{98}Mo$ values of organic rich sediments ($\delta^{98}Mo_{ORS}$) from anoxic basins (e.g., Nanhua Basin) represent a lower estimate for $\delta^{98}Mo_{OSW}$ (Arnold et al., 2004; Neubert et al., 2008). In general, a high, minimal $\delta^{98}Mo_{ORS}$ value is taken to reflect a well-oxygenated ocean, while conversely, a low value implies extensive ocean anoxia, especially for sediments deposited under euxinic conditions (Arnold et al., 2004; Kendall et al., 2017). However, $\delta^{98}Mo_{ORS}$ values lighter than the crustal composition (~+0.35—+0.6‰; Willbold and Elliot, 2017) cannot record the $\delta^{98}Mo_{OSW}$ value, and so require an alternative explanation. Lower $\delta^{98/95}Mo_{ORS}$ values than coeval $\delta^{98}Mo_{OSW}$ could be driven by two processes: Fe-Mn (oxyhydr)oxide shuttling (Scholz et al., 2013, 2017) or non-quantitative removal of Mo as thiomolybdate species under weakly sulphidic conditions (Tossell, 2005; Kerl et al., 2017; Hlohowskyj et al., 2021). In this study, the lower $\delta^{98}Mo_{ORS}$ values likely record non-quantitative drawdown of molybdate from the water column, which is supported by lower Fe_{Py}/Fe_{HR} ratios for these samples (Table 1).

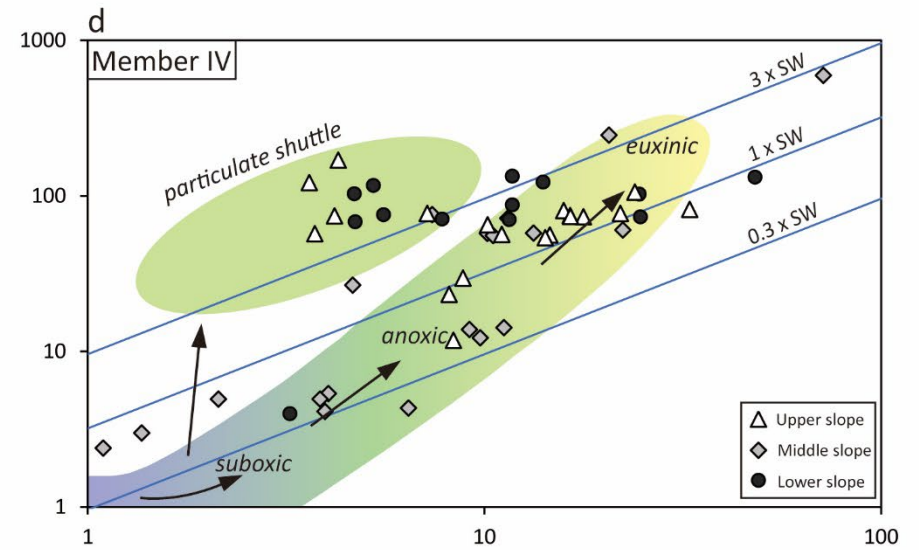
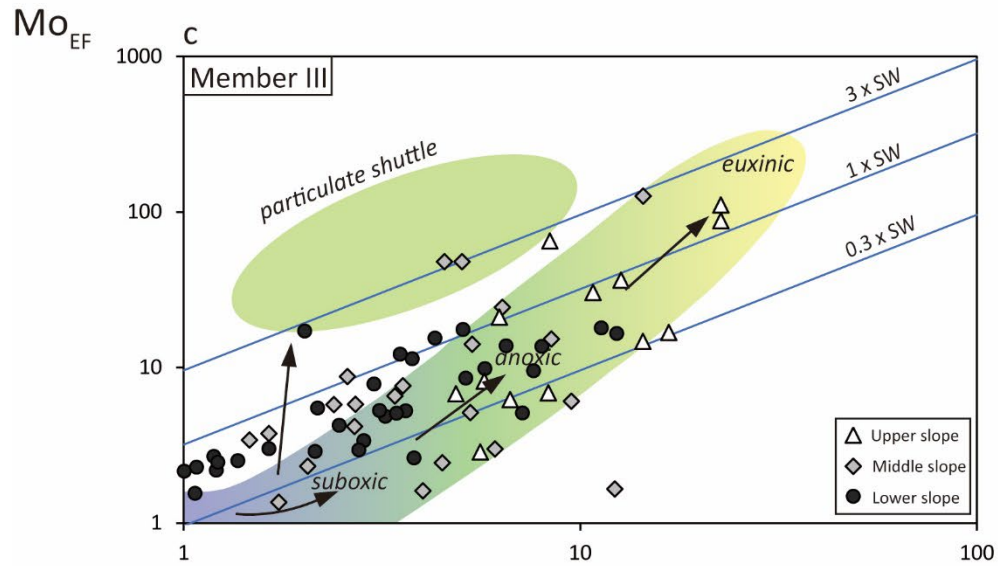
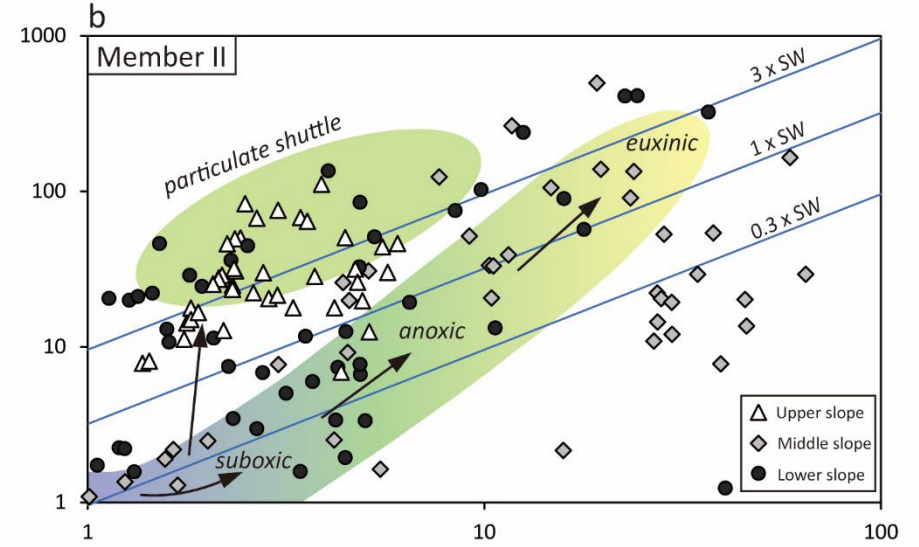
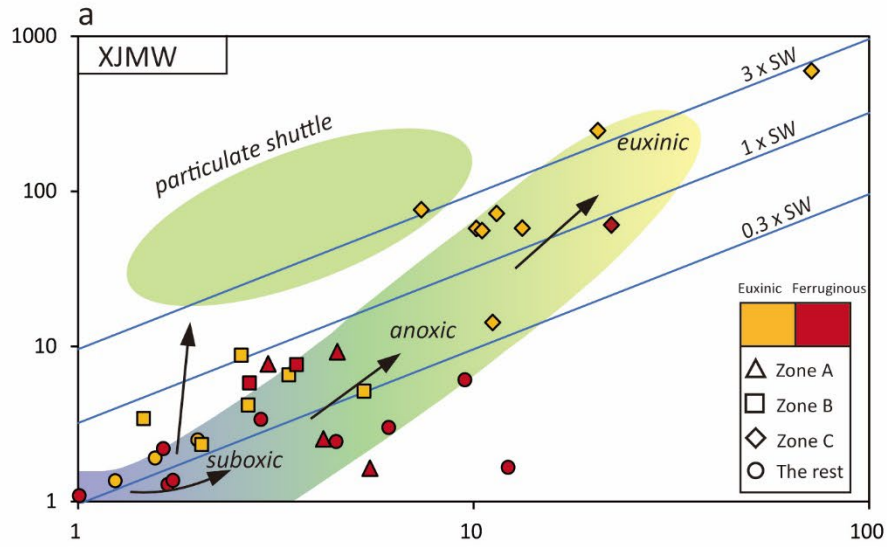
In the modern ocean, an Fe-Mn oxide shuttle for Mo drawdown has been proposed to operate in open-marine upwelling margins (e.g., California continental borderland, Peruvian margin and Namibian margin) and semi-restricted basins (e.g., Cariaco Basin, Baltic Sea Deep, and multiple fjords), raising sedimentary Mo_{EF}/U_{EF} ratios above those of seawater (Algeo and Tribovillard, 2009; Goldberg et al., 2012; Scholz et al., 2013, 2017; see Fig. 3). Bulk $\delta^{98}Mo_{ORS}$ values may therefore be controlled by the relative degree to which Fe-Mn (oxyhydr)oxides preferentially adsorb isotopically

light Mo (Goldberg et al., 2009, 2012).

When the bottom waters are more reducing, or when organic burial and microbial sulphate reduction (MSR) rates are higher, the generation of dissolved sulphide results in conversion of molybdate to thiomolybdate species. Both theoretical calculations (Tossell, 2005) and experimental observations (Kerl et al., 2017; Hlohowskyj et al., 2021) indicate large isotopic fractionations between thiomolybdate species ($\text{MoO}_x\text{S}_{4-x}^{2-}$). The products of higher degrees of thiolation tend to prefer lighter Mo isotopes and are more susceptible to scavenging by solid phases (Erickson and Helz 2000). Therefore, incomplete removal of more sulphidised thiomolybdate species from seawater to the sediments can cause low $\delta^{98}\text{Mo}_{\text{ORS}}$ values. The $\delta^{98}\text{Mo}_{\text{ORS}}$ value approaches $\delta^{98}\text{Mo}_{\text{OSW}}$ when H_2S increases and removal of thiomolybdates becomes more quantitative.

At the XJMW section, overall low $\delta^{98}\text{Mo}_{\text{ORS}}$ values occur between the OOE for samples where Fe speciation data are in the equivocal zone ($\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}}$ of 0.6–0.8), but Mo concentrations are low, suggesting a widespread anoxic ocean (Fig. 2). The low $\delta^{98}\text{Mo}_{\text{ORS}}$ values for the two ferruginous samples in Zone A, lowermost Member II, can only be regarded as lower estimates of $\delta^{98}\text{Mo}_{\text{OSW}}$, due to probable incomplete conversion of molybdate to tetrathiomolybdate (Goldberg et al., 2009; Brüske et al., 2020). In Zone B, some euxinic samples have higher $\delta^{98}\text{Mo}$ values but low Mo concentrations (Table 1 and Fig. 2). This may imply relatively expanded ocean oxygenation. Shoaling of the chemocline or regression may have promoted quantitative removal of Mo and minimum Mo isotope fractionation as more sediments were exposed to euxinic conditions.

The highest $\delta^{98}\text{Mo}$ values (up to +1.8‰) occur in Zone C, Member IV, suggesting widespread ocean oxygenation prior to 560 Ma (Fig. 2). These high $\delta^{98}\text{Mo}$ values generally co-occur with high RSE concentrations, which is consistent with deposition in a locally euxinic basin connected to an oxygenated global ocean. Interestingly, the sample with the highest Mo and U, and with very high V concentrations at the base of Zone C, has a relatively low $\delta^{98}\text{Mo}$ value. This could potentially suggest a sudden rise in the size of RSE reservoirs and non-quantitative removal of Mo from coeval seawater as the basin was transitioning to a euxinic state, as shown by the $\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}}$ data (Fig. 2). After that, all the RSE contents decline dramatically before increasing again as $\delta^{98}\text{Mo}$ gradually reaches its peak (>+1.8‰), after which $\delta^{98}\text{Mo}$ remains high (~+1.5‰).



U_{EF}

Fig. 3. (a) Mo_{EF} versus U_{EF} for samples from the XJMW section. (b) (c) (d) Compiled Mo_{EF}/U_{EF} ratios from Doushantuo Members II, III and IV, in slope parts of the Nanhua Basin. Upper slope data include the Rongxi section from Ostrander et al. (2019) and the Daotuo section from Ye et al. (2020). Middle slope data comprise the Taoying section from Ostrander et al. (2019) and the Xiajiaomeng West section from this study. Lower slope data involve the Wuhe and the Yuanjia sections from Ostrander et al. (2019). Solid blue lines are equivalent to multiples of the Mo/U molar ratio of modern seawater ($\times 0.3$, $\times 1$, and $\times 3$). Different redox and particulate shuttle fields are modified from Algeo and Tribovillard (2009). The “particulate shuttle” is linked to Fe-Mn redox cycling within the water column.

5.3. Implications for Basin Restriction

Some previous studies have debated whether the Nanhua Basin maintained a continuous connection with the open ocean during the Ediacaran Period (Sahoo et al., 2012, 2016; Wu et al., 2021; Jin et al., 2021). Ostrander et al. (2019) summarised the use of RSE concentrations and $\delta^{98}Mo$ values as indicators of a non-restricted or restricted basin.

In the modern day, low Mo contents but high $\delta^{98}Mo$ values occur in the Black Sea (Neubert et al., 2008) and euxinic basins of Kyllaren fjord (Noordmann et al., 2015), and Lake Rogoznica (Bura-Nakić et al., 2018). These basins capture the coeval $\delta^{98}Mo_{OSW}$, as minimized exchange of Mo from the ocean into these settings promotes near-quantitative removal of Mo to the sediments. As discussed previously, our data from the XJMW section show that the Nanhua Basin was more likely connected to the open ocean at the time of Member IV deposition, when two major transitions may have occurred. Firstly, the immediate increase in [Mo], [U] and [V] at the start of Member IV deposition may have been caused by transgression or shoaling of the chemocline. Transgression has been proposed by Och et al. (2016), during which a sulphidic wedge was postulated to extend over the platform due to sea-level rise. Secondly, redox conditions in the water column at XJMW changed from equivocal ($Fe_{PY}/Fe_{HR} = 0.62$) to more demonstrably euxinic ($Fe_{PY}/Fe_{HR} = 0.88$) (Table 1) at the start of Zone C (prior to the Member III/Member IV boundary), suggesting the probable progressive development of more intense euxinia. This would explain the initial rapid quantitative removal of RSEs from the water column, leading to an initial rise in the size of RSE reservoirs in sample XJMW37 (Table 1). However, this sample has a low $\delta^{98}Mo$ value (+0.64‰) suggesting incomplete Mo drawdown from the water column. Immediately above this sample, [Mo] decreases while $\delta^{98}Mo$ increases (Fig. 2), suggesting sustained highly euxinic conditions with limited connectivity to the global ocean. This is similar to the modern Black Sea deep water-mass scenario (the “basin reservoir effect”; Tribovillard et al., 2008). Increased and stable [Mo] and [U] at and after sample XJMW39, coupled with high $\delta^{98}Mo$, suggests that at least some connection was regained with the open ocean.

Fig. 3 shows data for slope sections, consisting of our data and published data, interpreted using the Mo_{EF}/U_{EF} model proposed by Algeo and Tribovillard (2009). In general, the consistent covariation in Mo and U enrichment factors between OOE likely indicates the occurrence of regionally euxinic bottom waters and unrestricted exchange between the local environment and the open ocean during each OOE (Fig. 3a). Member II (Fig. 3b) data show the greatest scatter, with data from the upper slope commonly falling into the particulate shuttle area, consistent with ferruginous conditions. Apart from a cluster of data from some middle-slope sections that indicate some level of possible restriction (some Mo_{EF}/U_{EF} values below $0.3 \times SW$ in the Taoying section), most other sections appear to have

been connected to the open ocean, with evidence for euxinia in some of the middle and lower slope sections. Member III (Fig. 3c) data show that a sulphidic wedge moved upslope, appearing in the upper and middle slope sections, with most samples falling in the unrestricted-marine area. For Member IV (Fig. 3d), the majority of data indicate open ocean conditions, with most of the Mo_{EF}/U_{EF} ratios consistently close to or exceeding the $1 \times SW$ line. This is also consistent with the $Mo_{EF}-U_{EF}$ data from intrashelf sections (Kendall et al., 2015), and points to locally euxinic bottom waters and unrestricted exchange between the local basin and the open ocean (Algeo and Tribovillard, 2009).

By contrast, some studies propose that the basin became semi-restricted because of the seaward presence of a submerged upland during this stage (Yeasmin et al., 2017). However, Kendall et al. (2015) compared the average Mo/TOC value (23 ppm/wt%) of Member IV ORM to those (25 ppm/wt%) for the weakly restricted Cariaco Basin (Algeo and Lyons 2006), and with high Mo_{EF}/U_{EF} , proposed that water exchange between the local (the intrashelf basin) and open ocean was not severely restricted. However, Mo/TOC data from Member IV at the XJMW section shows that high $\delta^{98}Mo$ values only occur when Mo/TOC values are relatively low, indicating that the local basin became progressively restricted after the deposition of sample XJMW 37 (~570 Ma; Table 1).

5.4. The spatial distribution of Mo data across the Nanhua Basin

The Mo_{EF}/U_{EF} compilation data for slope settings suggest episodic expansion and movement of a euxinic wedge across the slope of the Nanhua Basin. To investigate the spatial extent of redox conditions further, we next present a $\delta^{98}Mo$ and $[Mo]$ compilation across the Nanhua Basin. Six sections are placed in a proposed basinal reconstruction of the Nanhua Basin after Lu et al. (2013) in Fig. 4, of which the Jiulongwan section is an intra-shelf section, located in the Yangtze Gorges area (Fig. 1), and the other 5 sections are slope sections discussed above.

Member II (with Zone A at its base) data from the middle-to-lower slope sections (Taoying, Wuhe, and Yuanjia) correlate well (Fig. 4), as these sections were all deposited on the SE-facing slopes of the Nanhua Basin. All three sections evidence greater drawdown of Mo (up to ~180 ppm), indicating euxinic bottom waters. By contrast, the upper and middle slope sections (Rongxi and XJMW) have only slightly elevated $[Mo]$. Similarly, published Mo concentrations for Doushantuo Member II on the Yangtze platform are not particularly high (Och et al. 2016; Zhu et al. 2018). The Fe speciation data for slope sections show variations between oxic, anoxic and euxinic bottom waters (Sahoo et al., 2012, 2016; Ostrander et al., 2019), with upper slope sections showing less redox variability than deeper sections. A few samples at the Yuanjia section have high $\delta^{98}Mo$ values and $[Mo]$, which may be due to highly sulphidic conditions in this area. Negative $\delta^{98}Mo$ excursions with high Mo concentrations found in these deeper sections may have been the result of a deepening of the local chemocline, resulting in the establishment of an Fe-Mn oxide shuttle and drawdown of Mo to the sediments (Ostrander et al., 2019). This may also explain the preferential accumulation of Mo over U (Fig. 3), as Mo is more effectively scavenged (Algeo and Tribovillard, 2009). Similar negative $\delta^{98}Mo$ values have been observed in other sections, not only at the same stratigraphic level, but also in Member III (Taoying and Wuhe, sections) and Member IV (Jiulongwan, Rongxi, and Wuhe sections) (Fig. 4), making a post-depositional diagenetic explanation less likely. This effect, being particularly pronounced during OOE, suggests fluctuations between oxic and euxinic bottom waters (Ostrander et al., 2019). However, the most negative $\delta^{98}Mo$ values in Member II at the Taoying section co-occur with low $[Mo]$, which may be due to a large negative Mo isotope fractionation under weakly sulphidic

conditions.

For Member III (Zone B), only limited data exist for these sections, likely due to its carbonate lithology. A similar pattern of $\delta^{98}\text{Mo}$ evolution is observed in the middle slope XJMW and Taoying sections, but the possibly deeper Wuhe section has more negative $\delta^{98}\text{Mo}$ values. High $\delta^{98}\text{Mo}$ values (XJMW section: up to $\sim+1.4\text{‰}$) and high Mo concentrations (Taoying section: up to 76 ppm) are found in the middle slope of the basin. However, as carbonate is a relatively untested and potentially ambiguous material for Mo isotope study (Kendall, et al., 2017), alternative proxies are needed. The $\delta^{238}\text{U}$ data (around -0.2‰) of carbonate from different cratons, including the South China craton, suggest a global oceanic oxygenation event (Zhang et al., 2019).

For Member IV (Zone C), the Jiulongwan, Rongxi and Wuhe sections start with negative $\delta^{98}\text{Mo}$ values and high Mo concentrations in the lower part, but near modern seawater $\delta^{98}\text{Mo}$ values higher in the section. The XJMW section does not exhibit negative $\delta^{98}\text{Mo}$ values, but follows a similar trend to those sections. The Taoying section has very low [Mo] and only one reported $\delta^{98}\text{Mo}$ value, as samples were all deposited under ferruginous conditions. At Wuhe section, the samples with high Mo concentrations mostly have negative $\delta^{98}\text{Mo}$ values. Li et al. (2015) and Och et al. (2016) both proposed that the late Ediacaran marine redox state was highly heterogeneous, accompanied by negative $\delta^{98}\text{Mo}$ values and substantial enrichment in Mo at the Yangtze Gorges sections (Kendall et al., 2015). We suggest that the bottom waters in the intrashelf basin at the start of Member IV deposition (Jiulongwan: [Mo] = 663 ppm) were euxinic, and that a euxinic wedge extended to the outer slopes (Rongxi: [Mo] = 95 ppm and XJMW: [Mo] = 312 ppm). As the rapid increase of [Mo] occurs at the base of Member IV in intra shelf, upper, middle and lower slope portions of the basin, transgression (maximum flooding of the Shuram transgression; Busch et al., 2022) likely occurred at the beginning of Doushantuo Member IV deposition (~ 570 Ma). The accompanied deepening of the chemocline may have supplied an extra source of light Mo isotopes through reductive dissolution of Fe-Mn oxides (Ostrander et al., 2019).

At the top of Member IV, the Jiulongwan section on the Yangtze platform retains relatively high Mo concentrations (>100 ppm), and $\delta^{98}\text{Mo}$ exceeds 2‰ (Fig. 4). A peak in $\delta^{98}\text{Mo}$ values can be correlated with the upper slope sections, Rongxi ($\sim+1.3\text{‰}$) and XJMW ($\sim+1.8\text{‰}$), with all [Mo] higher than 20 ppm (Zone C; Fig. 4). The $\text{Fe}_{\text{PY}}/\text{Fe}_{\text{HR}}$ ratios of Jiulongwan Member IV are all above 0.8 (Kendall et al., 2015), while ratios fluctuate at Rongxi and XJMW. This suggests that the Jiulongwan section records $\delta^{98}\text{Mo}$ closest to that of the late Ediacaran open ocean. The maximum value for this section ($+2\text{‰}$) is close to modern seawater ($\sim+2.34\text{‰}$), indicating widespread global ocean oxygenation, which is also supported by the mean $\delta^{238}\text{U}$ of $0.24 \pm 0.16\text{‰}$ of the ORM from Member IV in the Yangtze Gorges region (Kendall et al. 2015).

Overall, our data and the compiled data suggest that the redox evolution of the Nanhua Basin can be summarized as follows: Zone A in Member II portrays a partially restricted basin with euxinic bottom water and RSE enrichments, indicating global oceanic oxygenation; Zone B in Member III presents a euxinic wedge on the mid-slope, with higher $\delta^{98}\text{Mo}$ ($\sim+1.4\text{‰}$) at XJMW and $\delta^{238}\text{U}$ values indicating oxygenation; Member IV (Zone C) is characterized by euxinic bottom waters in the intrashelf basin, fluctuating euxinia on upper to mid-slopes, with later peak $\delta^{98}\text{Mo}$ ($\sim+2\text{‰}$) and $\delta^{238}\text{U}$ values indicating global oceanic oxygenation close to modern ocean level.

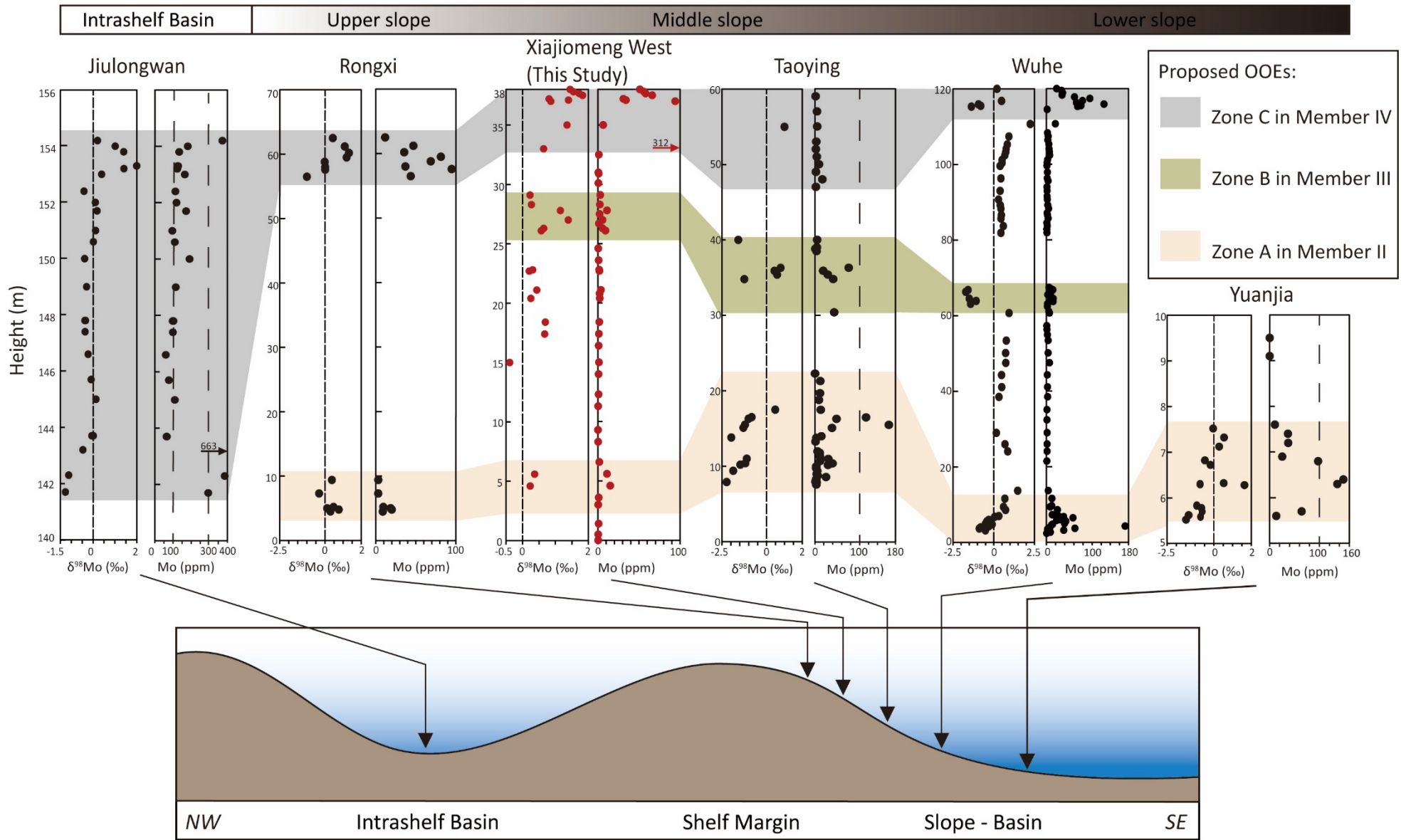


Fig. 4. The spatial distribution of Mo data across the Nanhua Basin. The bottom figure shows the paleogeographic reconstruction of the Yangtze Platform (cross-section view). The data for the Jiulongwan section are from Kendall et al. (2015). The XJMW section data are from this study. Rongxi, Taoying, Yuanjia and Wuhe section data are from Sahoo et al. (2012, 2016) and Ostrander et al. (2019). Different colour intervals indicate the proposed OOE's.

5.5. Temporal trends in ocean oxygenation: A molybdenum perspective

To place our data in a broader context, we compiled $\delta^{98}\text{Mo}$ and [Mo] data from the Ediacaran to early Cambrian, which includes data mainly from South China, Canada, and Czech Republic (Fig. 5). Between 635 Ma and ~620 Ma, Mo concentrations exhibit a spike (>170 ppm), with $\delta^{98}\text{Mo}$ values showing large variations (from -2.24 to +1.47‰). This may document the earliest widespread ocean oxygenation in the wake of the Marinoan glaciation (Sahoo et al., 2012). The negative $\delta^{98}\text{Mo}$ data are all from the lower Member II of the Doushantuo Formation at different sections (Ostrander et al., 2019). As explained above, the very negative $\delta^{98}\text{Mo}$ values with relatively high Mo concentrations may have been the result of changes in the position of the local chemocline and in global sea level (Ostrander et al., 2019). It is possible that during this time, ocean oxygenation was enhanced locally, stimulating operation of the Fe-Mn oxide Mo shuttle.

An interval of generally variable $\delta^{98}\text{Mo}$ and low Mo concentrations (close to crustal value, 2–4 ppm) between ~620 Ma and ~580 Ma possibly indicates a return to a small oceanic Mo reservoir, with most samples deposited under variable local redox conditions (mainly ferruginous), as indicated by published Fe speciation data (Johnston et al., 2013). As previously discussed for the OOE's in our section, at ~580 Ma (Zone B; Fig. 2), $\delta^{98}\text{Mo}$ values exceeded the river input value (+0.7‰), and Mo concentrations show modest enrichment, which is also consistent with Chen et al. (2015). Sahoo et al. (2016) compiled other RSE (U, V, Re and Cr) data that all show substantial enrichment at this time.

In the late Ediacaran, between ~570 Ma and ~560 Ma, $\delta^{98}\text{Mo}$ values reach >+2‰ (approaching modern seawater) for the first time in Earth's history, and Mo concentrations rise to the highest value (>600 ppm) (Fig. 5), as recorded in Member III/Member IV boundary at Wuhe section (Ostrander et al., 2019) and in the Member IV at the Jiulongwan section (Kendall et al., 2015). The sudden rise in [Mo] indicates that the Shuram excursion may have coincided with an increase in the size of oceanic Mo reservoir, which is also consistent with the rise in sulphate reservoir during this time (Shi et al., 2018). Our data from the XJMW section confirm the $\delta^{98}\text{Mo}$ spike in Member IV, and Mo enrichment is significant (>300 ppm) throughout Member IV, which indicates a pulse of ocean oxygenation close to modern levels in the late Ediacaran.

Canfield et al. (2007) linked the first appearance of the soft-bodied deep-water Ediacaran macrobiota in Newfoundland, now dated to between 574 and 564 Ma (Matthews et al., 2021), with a deep-ocean oxygenation event after ~580 Ma. The global OOE recorded by Doushantuo Member IV black shale is coincident with the appearance of the Wenghui biota, the Miaohe biota, and the White Sea assemblage between ~570 Ma and 550 Ma (Zhang et al., 2019; Rooney et al., 2020; Yang et al., 2021). The more diversified shallow-water Ediacaran assemblages, including the earliest bilaterians and calcifiers, appeared between 558 Ma and 539 Ma (Bengtson and Zhao, 1992; Narbonne et al., 2009; Johnston et al., 2012; Warren et al., 2012; Xiao et al., 2021). All of these Ediacaran biota appeared above Zone B, which is consistent with generally more expansive oxygenation indicated by the compiled Mo data. It is therefore likely that the OOE's played an important role in stimulating and

accelerating the diversification of metazoans, as more complex food webs and larger animals require higher oxygen levels (Knoll and Carroll, 1999).

However, this increase in Mo values was not unidirectional. A return to less oxygenated deep ocean conditions from ~550 Ma to ~530 Ma is marked by lower $\delta^{98}\text{Mo}$ values and Mo concentrations (Fig. 5), although the occurrence of OOE's became more frequent after the end of the Ediacaran Period, based on Mo enrichments (~540 Ma, ~530 Ma, and ~520 Ma). At ~521 Ma, $\delta^{98}\text{Mo}$ reached modern seawater values of ~+2.3‰ in multiple South China sections, corresponding to widespread ocean oxygenation, likely triggering radiations of aerobic bilaterians (Chen et al., 2015).

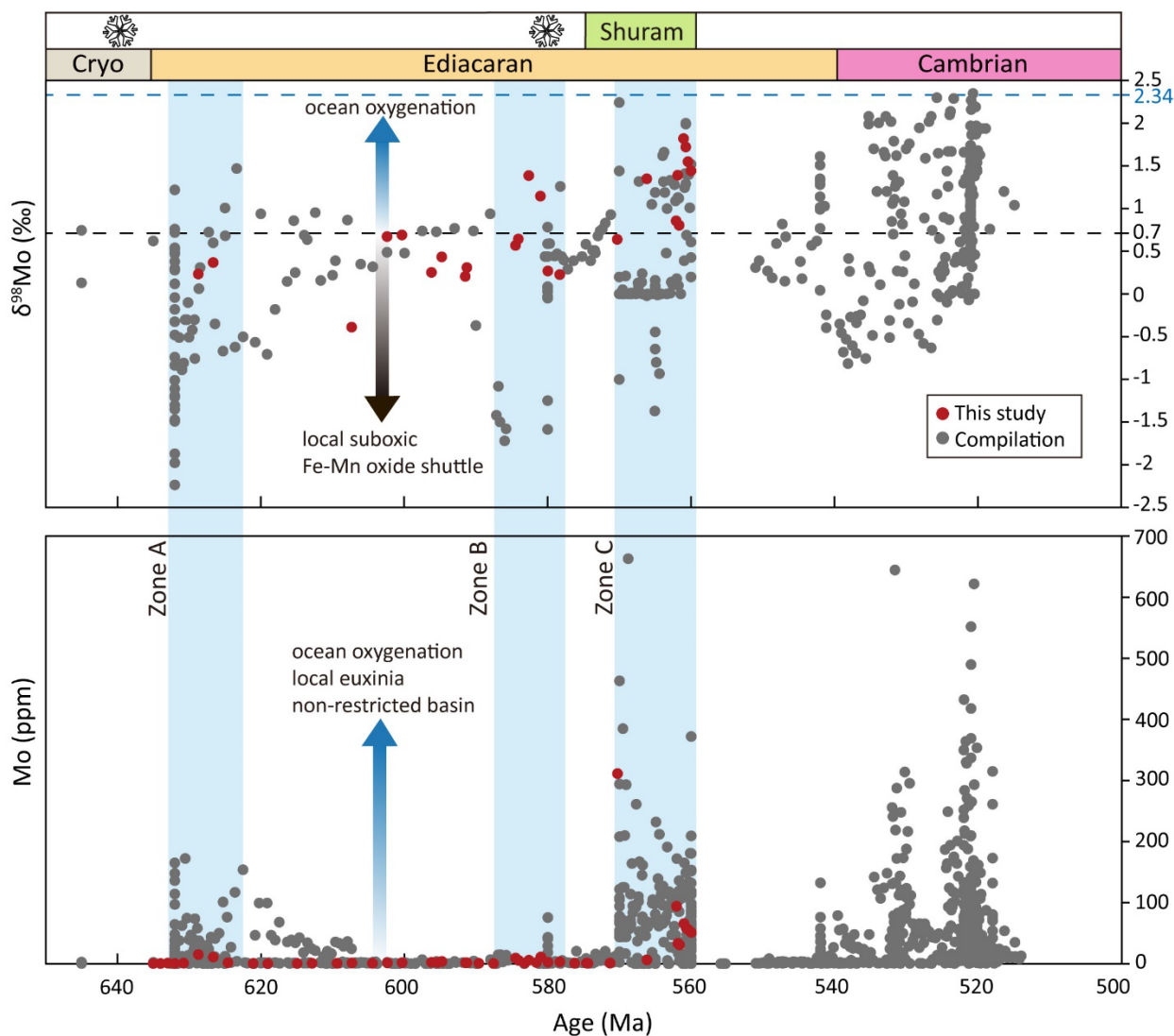


Fig. 5. A temporal record of $\delta^{98}\text{Mo}$ and $[\text{Mo}]$ based on this study and published data. Blue intervals indicate the three OOE that occurred during the Ediacaran period. In the time scale, the two snowflakes mark the major glaciations (Marinoan and Gaskiers). ‘This study’ indicates the newly obtained data from the XJMW section. ‘Compilation’ refers to updated Mo data compilation after Chen et al. (2015) and additional data source include Wen et al., 2015; Kendall et al., 2015; Kurzweil et al., 2015; Cheng et al., 2017; Sahoo et al., 2016; Zhu et al., 2018; Ostrander et al., 2019; Ye et al., 2020. The age model has been updated based Rooney et al. (2020), Yang et al. (2021), Bowyer et al. (2022) and a constant sedimentation rate model is used to calculate the ages of compiled data. Two dashed lines mark the average modern seawater $\delta^{98}\text{Mo}$ value (+2.34‰) and the riverine input (+0.7‰).

6. Conclusions

In order to explore oxygenation events and redox conditions in the Ediacaran ocean, we measured redox-sensitive element (RSE) abundances and Mo isotope compositions for the Doushantuo Formation at the Xiajiaomeng West (XJMW) section on the Nanhua Basin slope. By comparing these new data to previously published data, our main findings are as follows:

- 1) Our data from the newly discovered XJMW section shows that three OOE events occurred during the Ediacaran Period (~630 Ma, ~580 Ma and ~570 Ma), on the basis of high RSE concentrations paired with elevated $\delta^{98}\text{Mo}$ values. Importantly, the last OOE points to an extensively oxygenated ocean at ~570 Ma. The findings are generally consistent with other RSE studies (e.g., Scott et al., 2008; Sahoo et al., 2016), and is supported by U isotope data from South China, Siberia, USA (Zhang et al., 2019) and Namibia (Tostevin et al., 2019), and by Cr isotope data from the Wuhe section (Xu et al., 2022). The low RSE concentrations (close to crustal values) between OOE events indicate periodic re-development of extensive ocean anoxia.
- 2) The Nanhua Basin generally had a good connection to the open ocean. Two transgressions (Member I, and Member III to IV) are supported by our compiled data (Figs. 4 and 5). However, the Yangtze Gorges area may have gradually become more restricted, with limited connection to the open ocean, due to possible regression towards the end of Member IV deposition. This may explain a decrease in RSE concentrations coupled with higher $\delta^{98}\text{Mo}$ values. Additionally, shoaling of the chemocline could be another possible interpretation.
- 3) Fe speciation data indicate that almost all of the Doushantuo Formation was deposited under locally anoxic conditions, fluctuating between ferruginous and euxinic conditions. Most Member IV samples were deposited under euxinic conditions, with some indication of a transient episode of possibly oxic water column.
- 4) A compilation of $\delta^{98}\text{Mo}$ and [Mo] data reveals that ocean oxygenation waxed and waned during the late Neoproterozoic. Our new data and updated compilation show that $\delta^{98}\text{Mo}$ values approached the modern value at around ~570 Ma, pointing to a widespread oxygenated ocean at that time. The three proposed OOE events occurred in otherwise anoxic Ediacaran oceans, with dynamically shifting euxinic wedges on the slopes of the Nanhua Basin evidenced from a spatial comparison between different sections. The increased frequency of OOE events after the end of the Ediacaran Period (~540 Ma, ~530 Ma, and ~520 Ma) may have stimulated biotic innovations and radiations.

Acknowledgements

We are grateful to Gary Tarbuck (UCL), Andy Hobson (Leeds) and Stephen Reid (Leeds) for technical support in the labs. This study was financially supported by the joint NERC-NSFC Biosphere Evolution Transitions and Resilience (BETR) programme (NE/P01643/1, NSFC/41661134048), and the NERC project North China craton: A unique window into Earth's middle age (NE/R010129/1).

References

- Acquisti C., Kleffe J. and Collins S. (2006) Oxygen content of transmembrane proteins over macroevolutionary time scales. *Nature* 445, 47–52.
- Alcott L. J., Krause A. J., Hammarlund E. U., Bjerrum C. J., Scholz F., Xiong Y., Hobson A. J., Neve L., Mills B. J. W., März C., Schnetger B., Bekker A. and Poulton S. W. (2020) Development of Iron Speciation Reference Materials for Palaeoredox Analysis. *Geostand. Geoanal. Res.* 44, 581–591.
- Algeo T. J. and Lyons T. W. (2006) Mo–total organic carbon covariation in modern anoxic marine environments: Implications for analysis of paleoredox and paleohydrographic conditions. *Paleoceanography* 21, PA1016.
- Algeo T. J. and Maynard J. B. (2004) Trace-element behavior and redox facies in core shales of Upper Pennsylvanian Kansas-type cyclothems. *Chem. Geol.* 206, 289–318.
- Algeo T. J. and Tribouillard N. (2009) Environmental analysis of paleoceanographic systems based on molybdenum–uranium covariation. *Chem. Geol.* 268, 211–225.
- Anbar A. D. (2004) Molybdenum Stable Isotopes: Observations, Interpretations and Directions. *Rev. Mineral. Geochem.* 55, 429–454.
- Anderson T. F. and Raiswell R. (2004) Sources and mechanisms for the enrichment of highly reactive iron in euxinic Black Sea sediments. *Am. J. Sci.* 304, 203–233.
- Archer C. and Vance D. (2008) The isotopic signature of the global riverine molybdenum flux and anoxia in the ancient oceans. *Nature Geoscience* 1, 597–600.
- Arnold G. L., Anbar A. D., Barling J. and Lyons T. W. (2004) Molybdenum Isotope Evidence for Widespread Anoxia in Mid-Proterozoic Oceans. *Science* 304, 87–90.
- Barling J., Arnold G. L. and Anbar A. D. (2001) Natural mass-dependent variations in the isotopic composition of molybdenum. *Earth Planet. Sci. Lett.* 193, 447–457.
- Bengtson S. and Zhao Y. (1992) Predatorial Borings in Late Precambrian Mineralized Exoskeletons. *Science* 257, 367–369.
- Benkovitz A., Matthews A., Teutsch N., Poulton S. W., Bar-Matthews M. and Almogi-Labin A. (2020) Tracing water column euxinia in Eastern Mediterranean Sapropels S5 and S7. *Chem. Geol.* 545, 119627.
- Bowyer F. T., Zhuravlev A. Y., Wood R., Shields G. A., Zhou Y., Curtis A., Poulton S. W., Condon D. J., Yang C. and Zhu M. (2022) Calibrating the temporal and spatial dynamics of the Ediacaran - Cambrian radiation of animals. *Earth Sci. Rev.* 225, 103913.

Bowyer F., Wood R. A. and Poulton S. W. (2017) Controls on the evolution of Ediacaran metazoan ecosystems: A redox perspective. *Geobiology* 15, 516–551.

Breit G. N. and Wanty R. B. (1991) Vanadium accumulation in carbonaceous rocks: A review of geochemical controls during deposition and diagenesis. *Chem. Geol.* 91, 83–97.

Bristow T. F. and Kennedy M. J. (2008) Carbon isotope excursions and the oxidant budget of the Ediacaran atmosphere and ocean. *Geology* 36, 863–866.

Brucker R. L. P., McManus J., Severmann S. and Berelson W. M. (2009) Molybdenum behavior during early diagenesis: Insights from Mo isotopes. *Geochem. Geophys. Geosyst.* 10, Q06010.

Brüske A., Weyer S., Zhao M. Y., Planavsky N. J., Wegwerth A., Neubert N., Dellwig O., Lau K. v. and Lyons T. W. (2020) Correlated molybdenum and uranium isotope signatures in modern anoxic sediments: Implications for their use as paleo-redox proxy. *Geochim. Cosmochim. Acta* 270, 449–474.

Bura-Nakić E., Andersen M. B., Archer C., de Souza G. F., Marguš M. and Vance D. (2018) Coupled Mo-U abundances and isotopes in a small marine euxinic basin: Constraints on processes in euxinic basins. *Geochim. Cosmochim. Acta* 222, 212–229.

Busch J. F., Hodgkin E. B., Ahm A. S. C., Husson J. M., Macdonald F. A., Bergmann K. D., Higgins J. A. and Strauss J. v. (2022) Global and local drivers of the Ediacaran Shuram carbon isotope excursion. *Earth Planet. Sci. Lett.* 579, 117368.

Cai Y., Hua H., Xiao S., Schiffbauer J. D. and Li P. (2010) Biostratigraphy of the late Ediacaran pyritized Gaojiashan lagerstätte from southern Shaanxi, south China: importance of event deposits. *Palaios* 25, 487–506.

Calver C. R. (2000) Isotope stratigraphy of the Ediacarian (Neoproterozoic III) of the Adelaide Rift Complex, Australia, and the overprint of water column stratification. *Precambrian Res.* 100, 121–150.

Calver C. R., Crowley J. L., Wingate M. T. D., Evans D. A. D., Raub T. D. and Schmitz M. D. (2013) Globally synchronous Marinoan deglaciation indicated by U-Pb geochronology of the Cottons Breccia, Tasmania, Australia. *Geology* 41, 1127–1130.

Canfield, D.E. (2005) The early history of atmospheric oxygen: homage to Robert M. Garrels. *Annu. Rev. Earth Planet. Sci.* 33, 1–36.

Canfield D. E., Poulton S. W., Knoll A. H., Narbonne G. M., Ross G., Goldberg T. and Strauss H. (2008) Ferruginous conditions dominated later neoproterozoic deep-water chemistry. *Science* 321, 949–952.

Canfield D. E., Poulton S. W. and Narbonne G. M. (2007) Late-Neoproterozoic deep-ocean oxygenation and the rise of animal life. *Science* 315, 92–95.

- Canfield D. E., Raiswell R., Westrich J. T., Reaves C. M. and Berner R. A. (1986) The use of chromium reduction in the analysis of reduced inorganic sulfur in sediments and shales. *Chem. Geol.* 54, 149–155.
- Chen B., Hu C., Mills B. J. W., He T., Andersen M. B., Chen X., Liu P., Lu M., Newton R. J., Poulton S. W., Shields G. A. and Zhu M. (2022) A short-lived oxidation event during the early Ediacaran and delayed oxygenation of the Proterozoic ocean. *Earth Planet. Sci. Lett.* 577, 117274.
- Chen X., Ling H. F., Vance D., Shields-Zhou G. A., Zhu M., Poulton S. W., Och L. M., Jiang S. Y., Li D., Cremonese L. and Archer C. (2015) Rise to modern levels of ocean oxygenation coincided with the Cambrian radiation of animals. *Nature Communications* 6, 1–7.
- Chen Z., Zhou C., Xiao S., Wang W., Guan C., Hua H. and Yuan X. (2014) New Ediacara fossils preserved in marine limestone and their ecological implications. *Scientific Reports* 4, 1–10.
- Cheng M., Li C., Zhou L., Feng L. J., Algeo T. J., Zhang F. F., Romaniello S., Jin C. S., Ling H. F. and Jiang S. Y. (2017) Transient deep-water oxygenation in the early Cambrian Nanhua Basin, South China. *Geochim. Cosmochim. Acta* 210, 42–58.
- Clarkson M. O., Poulton S. W., Guilbaud R. and Wood R. A. (2014) Assessing the utility of Fe/Al and Fe-speciation to record water column redox conditions in carbonate-rich sediments. *Chem. Geol.* 382, 111–122.
- Cole D. B., Mills D. B., Erwin D. H., Sperling E. A., Porter S. M., Reinhard C. T. and Planavsky N. J. (2020) On the co-evolution of surface oxygen levels and animals. *Geobiology* 18, 260–281.
- Condon D., Zhu M., Bowring S., Wang W., Yang A. and Jin Y. (2005) U-Pb ages from the neoproterozoic Doushantuo Formation, China. *Science* 308, 95–98.
- Dahl T. W., Hammarlund E. U., Anbar A. D., Bond D. P. G., Gill B. C., Gordon G. W., Knoll A. H., Nielsen A. T., Schovsbo N. H. and Canfield D. E. (2010) Devonian rise in atmospheric oxygen correlated to the radiations of terrestrial plants and large predatory fish. *Proc. Natl. Acad. Sci.* 107, 17911–17915.
- Dickson A. J., Cohen A. S. and Coe A. L. (2012) Seawater oxygenation during the Paleocene-Eocene Thermal Maximum. *Geology* 40, 639–642.
- Dickson A. J., Jenkyns H. C., Idiz E., Sweere T. C., Murphy M. J., van den Boorn S. H. J. M., Ruhl M., Eldrett J. S. and Porcelli D. (2021) New Constraints on Global Geochemical Cycling During Oceanic Anoxic Event 2 (Late Cretaceous) From a 6-Million-year Long Molybdenum-Isotope Record. *Geochem. Geophys. Geosyst.* 22, e2020GC009246.
- Droser, M.L., Tarhan, L.G. and Gehling, J.G. (2017) The rise of animals in a changing environment: global ecological innovation in the late Ediacaran. *Annu. Rev. Earth Planet. Sci.* 45, 593-617.

Dunk R. M., Mills R. A. and Jenkins W. J. (2002) A reevaluation of the oceanic uranium budget for the Holocene. *Chem. Geol.* 190, 45–67.

Fike D. A., Grotzinger J. P., Pratt L. M. and Summons R. E. (2006) Oxidation of the Ediacaran Ocean. *Nature* 444, 744–747.

Frei R., Gaucher C., Poulton S. W. and Canfield D. E. (2009) Fluctuations in Precambrian atmospheric oxygenation recorded by chromium isotopes. *Nature* 461, 250–253.

Goldberg T., Archer C., Vance D. and Poulton S. W. (2009) Mo isotope fractionation during adsorption to Fe (oxyhydr)oxides. *Geochim. Cosmochim. Acta* 73, 6502–6516.

Goldberg T., Archer C., Vance D., Thamdrup B., McAnena A. and Poulton S. W. (2012) Controls on Mo isotope fractionations in a Mn-rich anoxic marine sediment, Gullmar Fjord, Sweden. *Chem. Geol.* 296–297, 73–82.

Goldberg T., Gordon G., Izon G., Archer C., Pearce C. R., McManus J., Anbar A. D. and Rehkämper M. (2013) Resolution of inter-laboratory discrepancies in Mo isotope data: an intercalibration. *J. Anal. At. Spectrom.* 28, 724–735.

Goldberg T., Poulton S. W., Wagner T., Kolonic S. F. and Rehkämper M. (2016) Molybdenum drawdown during Cretaceous Oceanic Anoxic Event 2. *Earth Planet. Sci. Lett.* 440, 81–91.

Hans Wedepohl K. (1995) The composition of the continental crust. *Geochim. Cosmochim. Acta* 59, 1217–1232.

Hardisty D. S., Lyons T. W., Riedinger N., Isson T. T., Owens J. D., Aller R. C., Rye D. M., Planavsky N. J., Reinhard C. T., Gill B. C., Masterson A. L., Asael D. and Johnston D. T. (2018) An evaluation of sedimentary molybdenum and iron as proxies for pore fluid paleoredox conditions. *Am. J. Sci.* 318, 527–556.

Helz, G.R. (2021) Dissolved molybdenum asymptotes in sulfidic waters. *Geochem. Perspect. Lett.* 19, 23–26.

Helz G. R., Miller C. v., Charnock J. M., Mosselmans J. F. W., Patrick R. A. D., Garner C. D. and Vaughan D. J. (1996) Mechanism of molybdenum removal from the sea and its concentration in black shales: EXAFS evidence. *Geochim. Cosmochim. Acta* 60, 3631–3642.

Hlohowskyj S. R., Chen X., Romaniello S. J., Vorlicek T. P., Anbar A. D., Lyons T. W. and Chappaz A. (2021) Quantifying Molybdenum Isotopic Speciation in Sulfidic Water: Implications for the Paleoredox Proxy. *ACS Earth Space Chem.* 5, 2891–2899.

Ho P., Lee J. M., Heller M. I., Lam P. J. and Shiller A. M. (2018) The distribution of dissolved and

- particulate Mo and V along the U.S. GEOTRACES East Pacific Zonal Transect (GP16): The roles of oxides and biogenic particles in their distributions in the oxygen deficient zone and the hydrothermal plume. *Mar. Chem.* 201, 242–255.
- Holland H. D. (2002) Volcanic gases, black smokers, and the great oxidation event. *Geochim. Cosmochim. Acta* 66, 3811–3826.
- Jiang G., Shi X., Zhang S., Wang Y. and Xiao S. (2011) Stratigraphy and paleogeography of the Ediacaran Doushantuo Formation (ca. 635–551 Ma) in South China. *Gondwana Res.* 19, 831–849.
- Jin C., Li C., Algeo T. J., Wang G., Shi W., Cheng M., Zhang Z., Wang H., Li N. and Wang W. (2021) Spatial heterogeneity of redox-sensitive trace metal enrichments in upper ediacaran anoxic black shales. *J. Geol. Soc. London* 178, jgs2020-234.
- Johnston D. T., Poulton S. W., Goldberg T., Sergeev V. N., Podkovyrov V., Vorob'eva N. G., Bekker A. and Knoll A. H. (2012) Late Ediacaran redox stability and metazoan evolution. *Earth Planet. Sci. Lett.* 335, 25–35.
- Johnston D. T., Poulton S. W., Tosca N. J., O'Brien T., Halverson G. P., Schrag D. P. and Macdonald F. A. (2013) Searching for an oxygenation event in the fossiliferous Ediacaran of northwestern Canada. *Chem. Geol.* 362, 273–286.
- Kaufman A. J., Jiang G., Christie-Blick N., Banerjee D. M. and Rai V. (2006) Stable isotope record of the terminal Neoproterozoic Krol platform in the Lesser Himalayas of northern India. *Precambrian Res.* 147, 156–185.
- Kendall B., Dahl T. W. and Anbar A. D. (2017) The stable isotope geochemistry of molybdenum. *Rev. Mineral. Geochem.* 82, 683–732.
- Kendall B., Komiya T., Lyons T. W., Bates S. M., Gordon G. W., Romaniello S. J., Jiang G., Creaser R. A., Xiao S., McFadden K., Sawaki Y., Tahata M., Shu D., Han J., Li Y., Chu X. and Anbar A. D. (2015) Uranium and molybdenum isotope evidence for an episode of widespread ocean oxygenation during the late Ediacaran Period. *Geochim. Cosmochim. Acta* 156, 173–193.
- Kerl C. F., Lohmayer R., Bura-Nakić E., Vance D. and Planer-Friedrich B. (2017) Experimental Confirmation of Isotope Fractionation in Thiomolybdates Using Ion Chromatographic Separation and Detection by Multicollector ICPMS. *Anal. Chem.* 89, 3123–3129.
- Knoll, A.H. (2011) The multiple origins of complex multicellularity. *Annu. Rev. Earth Planet. Sci.* 39, 217-239.
- Knoll A. H. and Carroll S. B. (1999) Early animal evolution: Emerging views from comparative biology and geology. *Science* 284, 2129–2137.

- Kurzweil F., Drost K., Pašava J., Wille M., Taubald H., Schoeckle D. and Schoenberg R. (2015) Coupled sulfur, iron and molybdenum isotope data from black shales of the Teplá-Barrandian unit argue against deep ocean oxygenation during the Ediacaran. *Geochim. Cosmochim. Acta* 171, 121–142.
- Laakso T. A. and Schrag D. P. (2020) The role of authigenic carbonate in Neoproterozoic carbon isotope excursions. *Earth Planet. Sci. Lett.* 549, 116534.
- Lenton T. M., Boyle R. A., Poulton S. W., Shields-Zhou G. A. and Butterfield N. J. (2014) Co-evolution of eukaryotes and ocean oxygenation in the Neoproterozoic era. *Nature Geoscience* 7, 257–265.
- Lenton T. M., Daines S. J. and Mills B. J. W. (2018) COPSE reloaded: An improved model of biogeochemical cycling over Phanerozoic time. *Earth Sci. Rev.* 178, 1–28.
- Li C., Love G. D., Lyons T. W., Fike D. A., Sessions A. L. and Chu X. (2010) A stratified redox model for the ediacaran ocean. *Science* 328, 80–83.
- Li C., Planavsky N. J., Shi W., Zhang Z., Zhou C., Cheng M., Tarhan L. G., Luo G. and Xie S. (2015) Ediacaran Marine Redox Heterogeneity and Early Animal Ecosystems. *Scientific Reports* 5, 1–8.
- Li J., Liang X. R., Zhong L. F., Wang X. C., Ren Z. Y., Sun S. L., Zhang Z. F. and Xu J. F. (2014) Measurement of the Isotopic Composition of Molybdenum in Geological Samples by MC-ICP-MS using a Novel Chromatographic Extraction Technique. *Geostand. Geoanal. Res.* 38, 345–354.
- Lu M., Zhu M., Zhang J., Shields-Zhou G., Li G., Zhao F., Zhao X. and Zhao M. (2013) The DOUNCE event at the top of the Ediacaran Doushantuo Formation, South China: Broad stratigraphic occurrence and non-diagenetic origin. *Precambrian Res.* 225, 86–109.
- Lyons, T.W., Anbar, A.D., Severmann, S., Scott, C. and Gill, B.C. (2009) Tracking euxinia in the ancient ocean: a multiproxy perspective and Proterozoic case study. *Annu. Rev. Earth Planet. Sci.* 37, 507–534.
- Lyons T. W., Reinhard C. T. and Planavsky N. J. (2014) The rise of oxygen in Earth's early ocean and atmosphere. *Nature* 506, 307–315.
- Lyons T. W. and Severmann S. (2006) A critical look at iron paleoredox proxies: New insights from modern euxinic marine basins. *Geochim Cosmochim Acta* 70, 5698–5722.
- März C., Poulton S. W., Beckmann B., Küster K., Wagner T. and Kasten S. (2008) Redox sensitivity of P cycling during marine black shale formation: Dynamics of sulfidic and anoxic, non-sulfidic bottom waters. *Geochim. Cosmochim. Acta* 72, 3703–3717.
- Massey M. S., Lezama-Pacheco J. S., Jones M. E., Ilton E. S., Cerrato J. M., Bargar J. R. and Fendorf S. (2014) Competing retention pathways of uranium upon reaction with Fe(II). *Geochim. Cosmochim. Acta* 142, 166–185.
- Matthews J. J., Liu A. G., Yang C., McIlroy D., Levell B. and Condon D. J. (2021) A Chronostratigraphic

Framework for the Rise of the Ediacaran Macrobiota: New Constraints from Mistaken Point Ecological Reserve, Newfoundland. *GSA Bulletin* 133, 612–624.

McFadden K. A., Huang J., Chu X., Jiang G., Kaufman A. J., Zhou C., Yuan X. and Xiao S. (2008) Pulsed oxidation and biological evolution in the Ediacaran Doushantuo Formation. *Proc. Natl. Acad. Sci.* 105, 3197–3202.

McLennan S. M. (2001) Relationships between the trace element composition of sedimentary rocks and upper continental crust. *Geochem. Geophys. Geosyst.* 2, 2000GC000109.

Miller A. J., Strauss J. v., Halverson G. P., Macdonald F. A., Johnston D. T. and Sperling E. A. (2017) Tracking the onset of Phanerozoic-style redox-sensitive trace metal enrichments: New results from basal Ediacaran post-glacial strata in NW Canada. *Chem. Geol.* 457, 24–37.

Miller C. A., Peucker-Ehrenbrink B., Walker B. D. and Marcantonio F. (2011) Re-assessing the surface cycling of molybdenum and rhenium. *Geochim. Cosmochim. Acta* 75, 7146–7179.

Morford J. L., Emerson S. R., Breckel E. J. and Kim S. H. (2005) Diagenesis of oxyanions (V, U, Re, and Mo) in pore waters and sediments from a continental margin. *Geochim. Cosmochim. Acta* 69, 5021–5032.

Nägler T. F., Anbar A. D., Archer C., Goldberg T., Gordon G. W., Greber N. D., Siebert C., Sohrin Y. and Vance D. (2014) Proposal for an International Molybdenum Isotope Measurement Standard and Data Representation. *Geostand. Geoanal. Res.* 38, 149–151.

Nägler T. F., Neubert N., Böttcher M. E., Dellwig O. and Schnetger B. (2011) Molybdenum isotope fractionation in pelagic euxinia: Evidence from the modern Black and Baltic Seas. *Chem. Geol.* 289, 1–11.

Nakagawa Y., Takano S., Firdaus M. L., Norisuye K., Hirata T., Vance D. and Sohrin Y. (2012) The molybdenum isotopic composition of the modern ocean. *Geochem. J.* 46, 131–141.

Narbonne G. M. (2004) Modular construction of early Ediacaran complex life forms. *Science* 305, 1141–1144.

Narbonne G. M. (2005) The Ediacara biota: Neoproterozoic origin of animals and their ecosystems. *Annu. Rev. Earth Planet. Sci.* 33, 421–463.

Narbonne, G.M., Laflamme, M., Greentree, C. and Trusler, P. (2009) Reconstructing a lost world: Ediacaran rangeomorphs from Spaniard's Bay, Newfoundland. *J. Paleontol.* 83, 503–523.

Neubert N., Nægler T. F. and Böttcher M. E. (2008) Sulfidity controls molybdenum isotope fractionation into euxinic sediments: Evidence from the modern Black Sea. *Geology* 36, 775–778.

Nielsen S. G. (2020) Vanadium Isotopes: A Proxy for Ocean Oxygen Variations (Elements in Geochemical Tracers in Earth System Science). Cambridge University Press.

Noordmann J., Weyer S., Montoya-Pino C., Dellwig O., Neubert N., Eckert S., Paetzel M. and Böttcher M. E. (2015) Uranium and molybdenum isotope systematics in modern euxinic basins: Case studies from the central Baltic Sea and the Kyllaren fjord (Norway). *Chem. Geol.* 396, 182–195.

Och L. M., Cremonese L., Shields-Zhou G. A., Poulton S. W., Struck U., Ling H., Li D., Chen X., Manning C., Thirlwall M., Strauss H. and Zhu M. (2016) Palaeoceanographic controls on spatial redox distribution over the Yangtze Platform during the Ediacaran–Cambrian transition. *Sedimentology* 63, 378–410.

Och L. M. and Shields-Zhou G. A. (2012) The Neoproterozoic oxygenation event: Environmental perturbations and biogeochemical cycling. *Earth Sci. Rev.* 110, 26–57.

Ostrander C. M., Sahoo S. K., Kendall B., Jiang G., Planavsky N. J., Lyons T. W., Nielsen S. G., Owens J. D., Gordon G. W., Romaniello S. J. and Anbar A. D. (2019) Multiple negative molybdenum isotope excursions in the Doushantuo Formation (South China) fingerprint complex redox-related processes in the Ediacaran Nanhua Basin. *Geochim. Cosmochim. Acta* 261, 191–209.

Ouyang Q., Zhou C., Xiao S., Chen Z. and Shao Y. (2019) Acanthomorphic acritarchs from the Ediacaran Doushantuo Formation at Zhangcunping in South China, with implications for the evolution of early Ediacaran eukaryotes. *Precambrian Res.* 320, 171–192.

Poulton S. W. (2021) The Iron Speciation Paleoredox Proxy. (Elements in Geochemical Tracers in Earth System Science). Cambridge University Press.

Poulton S. W. and Canfield D. E. (2011) Ferruginous Conditions: A Dominant Feature of the Ocean through Earth's History. *Elements* 7, 107–112.

Poulton S. W. and Canfield D. E. (2005) Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. *Chem. Geol.* 214, 209–221.

Poulton S. W., Fralick P. W. and Canfield D. E. (2004) The transition to a sulphidic ocean ~ 1.84 billion years ago. *Nature* 431, 173–177.

Poulton S. W. and Raiswell R. (2002) The low-temperature geochemical cycle of iron: From continental fluxes to marine sediment deposition. *Am. J. Sci.* 302, 774–805.

Prave A. R., Condon D. J., Hoffmann K. H., Tapster S. and Fallick A. E. (2016) Duration and nature of the end-Cryogenian (Marinoan) glaciation. *Geology* 44, 631–634.

Qu Y., Zhu S., Whitehouse M., Engdahl A. and McLoughlin N. (2018) Carbonaceous biosignatures of the earliest putative macroscopic multicellular eukaryotes from 1630 Ma Tuanshanzi Formation,

north China. *Precambrian Res.* 304, 99–109.

Raiswell R. and Canfield D. E. (1998) Sources of iron for pyrite formation in marine sediments. *Am. J. Sci.* 298, 219–245.

Raiswell R., Newton R. and Wignall P. B. (2001) An Indicator of Water-Column Anoxia: Resolution of Biofacies Variations in the Kimmeridge Clay (Upper Jurassic, U.K.). *J. Sediment. Res.* 71, 286–294.

Rooney A. D., Cantine M. D., Bergmann K. D., Gómez-Pérez I., Baloushi B. al, Boag T. H., Busch J. F., Sperling E. A. and Strauss J. v. (2020) Calibrating the coevolution of Ediacaran life and environment. *Proc. Natl. Acad. Sci.* 117, 16824–16830.

Rooney A. D., Strauss J. v., Brandon A. D. and Macdonald F. A. (2015) A Cryogenian chronology: Two long-lasting synchronous Neoproterozoic glaciations. *Geology* 43, 459–462.

Rothman D. H., Hayes J. M. and Summons R. E. (2003) Dynamics of the Neoproterozoic carbon cycle. *Proc. Natl. Acad. Sci.* 100, 8124–8129.

Rudnick, R.L. and Gao, S. (2003) Composition of the continental crust. *The Crust* 3, 1–64.

Sahoo S. K., Planavsky N. J., Jiang G., Kendall B., Owens J. D., Wang X., Shi X., Anbar A. D. and Lyons T. W. (2016) Oceanic oxygenation events in the anoxic Ediacaran ocean. *Geobiology* 14, 457–468.

Sahoo S. K., Planavsky N. J., Kendall B., Wang X., Shi X., Scott C., Anbar A. D., Lyons T. W. and Jiang G. (2012) Ocean oxygenation in the wake of the Marinoan glaciation. *Nature* 489, 546–549.

Scholz F., McManus J. and Sommer S. (2013) The manganese and iron shuttle in a modern euxinic basin and implications for molybdenum cycling at euxinic ocean margins. *Chem. Geol.* 355, 56–68.

Scholz F., Siebert C., Dale A. W. and Frank M. (2017) Intense molybdenum accumulation in sediments underneath a nitrogenous water column and implications for the reconstruction of paleo-redox conditions based on molybdenum isotopes. *Geochim. Cosmochim. Acta* 213, 400–417.

Schrag D. P., Higgins J. A., Macdonald F. A. and Johnston D. T. (2013) Authigenic carbonate and the history of the global carbon cycle. *Science* 339, 540–543.

Scott C. and Lyons T. W. (2012) Contrasting molybdenum cycling and isotopic properties in euxinic versus non-euxinic sediments and sedimentary rocks: Refining the paleoproxies. *Chem. Geol.* 324–325, 19–27.

Scott C., Lyons T. W., Bekker A., Shen Y., Poulton S. W., Chu X. and Anbar A. D. (2008) Tracing the stepwise oxygenation of the Proterozoic ocean. *Nature* 452, 456–459.

Scott C., Slack J. F. and Kelley K. D. (2017) The hyper-enrichment of V and Zn in black shales of the Late

Devonian-Early Mississippian Bakken Formation (USA). *Chem. Geol.* 452, 24–33.

Shi W., Li C., Luo G., Huang J., Algeo T. J., Jin C., Zhang Z. and Cheng M. (2018) Sulfur isotope evidence for transient marine-shelf oxidation during the Ediacaran Shuram Excursion. *Geology* 46, 267–270.

Shields G. A., Mills B. J. W., Zhu M., Raub T. D., Daines S. J. and Lenton T. M. (2019) Unique Neoproterozoic carbon isotope excursions sustained by coupled evaporite dissolution and pyrite burial. *Nature Geoscience* 12, 823–827.

Sperling E. A., Frieder C. A., Raman A. v., Girguis P. R., Levin L. A. and Knoll A. H. (2013) Oxygen, ecology, and the Cambrian radiation of animals. *Proc. Natl. Acad. Sci.* 110, 13446–13451.

Sperling E. A., Wolock C. J., Morgan A. S., Gill B. C., Kunzmann M., Halverson G. P., Macdonald F. A., Knoll A. H. and Johnston D. T. (2015) Statistical analysis of iron geochemical data suggests limited late Proterozoic oxygenation. *Nature* 523, 451–454.

Summons R. E., Bradley A. S., Jahnke L. L. and Waldbauer J. R. (2006) Steroids, triterpenoids and molecular oxygen. *Philosophical Transactions of the Royal Society B: Biological Sciences* 361, 951–968.

Tossell J. A. (2005) Calculating the partitioning of the isotopes of Mo between oxidic and sulfidic species in aqueous solution. *Geochim. Cosmochim. Acta* 69, 2981–2993.

Tostevin R., Clarkson M. O., Gangl S., Shields G. A., Wood R. A., Bowyer F., Penny A. M. and Stirling C. H. (2019) Uranium isotope evidence for an expansion of anoxia in terminal Ediacaran oceans. *Earth Planet. Sci. Lett.* 506, 104–112.

Tostevin R. and Mills B. J. W. (2020) Reconciling proxy records and models of Earth's oxygenation during the Neoproterozoic and Palaeozoic. *Interface Focus* 10. 20190137

Tribovillard N., Algeo T. J., Baudin F. and Riboulleau A. (2012) Analysis of marine environmental conditions based on molybdenum–uranium covariation—Applications to Mesozoic paleoceanography. *Chem. Geol.* 324–325, 46–58.

Tribovillard N., Algeo T. J., Lyons T. and Riboulleau A. (2006) Trace metals as paleoredox and paleoproductivity proxies: An update. *Chem. Geol.* 232, 12–32.

Tribovillard N., Bout-Roumazielles V., Algeo T., Lyons T. W., Sionneau T., Montero-Serrano J. C., Riboulleau A. and Baudin F. (2008) Paleodepositional conditions in the Orca Basin as inferred from organic matter and trace metal contents. *Mar. Geol.* 254, 62–72.

Vance D. and Thirlwall M. (2002) An assessment of mass discrimination in MC-ICPMS using Nd isotopes. *Chem. Geol.* 185, 227–240.

Wang J. and Li Z. X. (2003) History of Neoproterozoic rift basins in South China: implications for

Rodinia break-up. *Precambrian Res.* 122, 141–158.

Wanty R. B. and Goldhaber M. B. (1992) Thermodynamics and kinetics of reactions involving vanadium in natural systems: Accumulation of vanadium in sedimentary rocks. *Geochim. Cosmochim. Acta* 56, 1471–1483.

Warren L. v., Pacheco M. L. A. F., Fairchild T. R., Simões M. G., Riccomini C., Boggiani P. C. and Cáceres A. A. (2012) The dawn of animal skeletogenesis: Ultrastructural analysis of the Ediacaran metazoan *Corumbella weneri*. *Geology* 40, 691–694.

Wasylenki L. E., Rolfe B. A., Weeks C. L., Spiro T. G. and Anbar A. D. (2008) Experimental investigation of the effects of temperature and ionic strength on Mo isotope fractionation during adsorption to manganese oxides. *Geochim. Cosmochim. Acta* 72, 5997–6005.

Wei G. Y., Planavsky N. J., He T., Zhang F., Stockey R. G., Cole D. B., Lin Y. B. and Ling H. F. (2021) Global marine redox evolution from the late Neoproterozoic to the early Paleozoic constrained by the integration of Mo and U isotope records. *Earth Sci. Rev.* 214, 103506.

Wen H., Fan H., Zhang Y., Cloquet C. and Carignan J. (2015) Reconstruction of early Cambrian ocean chemistry from Mo isotopes. *Geochim Cosmochim Acta* 164, 1–16.

Willbold M. and Elliott T. (2017) Molybdenum isotope variations in magmatic rocks. *Chem. Geol.* 449, 253–268.

Wood R. A., Poulton S. W., Prave A. R., Hoffmann K. H., Clarkson M. O., Guilbaud R., Lyne J. W., Tostevin R., Bowyer F., Penny A. M., Curtis A. and Kasemann S. A. (2015) Dynamic redox conditions control late Ediacaran metazoan ecosystems in the Nama Group, Namibia. *Precambrian Res.* 261, 252–271.

Wu Y., Tian H., Li J., Li T. and Ji S. (2021) Reconstruction of oceanic redox structures during the Ediacaran-Cambrian transition in the Yangtze Block of South China: Implications from Mo isotopes and trace elements. *Precambrian Res.* 359, 106181.

Xiao S., Chen Z., Pang K., Zhou C. and Yuan X. (2021) The shibantan lagerstätte: Insights into the proterozoic– phanerozoic transition. *J. Geol. Soc. London* 178, jgs2020-135.

Xiao S., Knoll A. H., Yuan X. and Poeschel C. M. (2004) Phosphatized multicellular algae in the Neoproterozoic Doushantuo Formation, China, and the early evolution of florideophyte red algae. *Am. J. Bot.* 91, 214–227.

Xiao S. and Laflamme M. (2009) On the eve of animal radiation: phylogeny, ecology and evolution of the Ediacara biota. *Trends Ecol. Evol.* 24, 31–40.

Xiao S., Shen B., Zhou C., Xie G. and Yuan X. (2005) A uniquely preserved Ediacaran fossil with direct evidence for a quilted bodyplan. *Proc. Natl. Acad. Sci.* 102, 10227–10232.

- Xiao S., Zhou C., Liu P., Wang D. and Yuan X. (2014) Phosphatized Acanthomorphic Acritarchs and Related Microfossils from the Ediacaran Doushantuo Formation at Weng'an (South China) and their Implications for Biostratigraphic Correlation. *J. Paleontol.* 88, 1–67.
- Xiong Y., Guilbaud R., Peacock C. L., Cox R. P., Canfield D. E., Krom M. D. and Poulton S. W. (2019) Phosphorus cycling in Lake Cadagno, Switzerland: A low sulfate euxinic ocean analogue. *Geochim. Cosmochim. Acta* 251, 116–135.
- Xu D., Wang Xinqiang, Zhu J. M., Jiang G., Shi X., Wang Xiangli and Sahoo S. K. (2022) Chromium isotope evidence for oxygenation events in the Ediacaran ocean. *Geochim. Cosmochim. Acta* 323, 258–275.
- Yang C., Rooney A. D., Condon D. J., Li X. H., Grazhdankin D. v., Bowyer F. T., Hu C., Macdonald F. A. and Zhu M. (2021) The tempo of Ediacaran evolution. *Sci. Adv.* 7, eabi9643.
- Ye Q., Tong J., An Z., Hu J., Tian L., Guan K. and Xiao S. (2017) A systematic description of new microfossil material from the upper Ediacaran Miaohu Member in South China. *J. Syst. Palaeontol.* 17, 183–238.
- Ye Y., Wang H., Wang X., Zhai L., Wu C., Canfield D. E. and Zhang S. (2020) Tracking the evolution of seawater Mo isotopes through the Ediacaran–Cambrian transition. *Precambrian Res.* 350, 105929.
- Yeasmin R., Chen D., Fu Y., Wang J., Guo Z. and Guo C. (2017) Climatic–oceanic forcing on the organic accumulation across the shelf during the Early Cambrian (Age 2 through 3) in the mid-upper Yangtze Block, NE Guizhou, South China. *J. Asian Earth Sci.* 134, 365–386.
- Yuan X., Chen Z., Xiao S., Zhou C. and Hua H. (2011) An early Ediacaran assemblage of macroscopic and morphologically differentiated eukaryotes. *Nature* 470, 390–393.
- Zhang F., Xiao S., Kendall B., Romaniello S. J., Cui H., Meyer M., Gilleaudeau G. J., Kaufman A. J. and Anbar A. D. (2018) Extensive marine anoxia during the terminal ediacaran period. *Sci. Adv.* 4, eaan8983.
- Zhang F., Xiao S., Romaniello S. J., Hardisty D., Li C., Melezhik V., Pokrovsky B., Cheng M., Shi W., Lenton T. M. and Anbar A. D. (2019) Global marine redox changes drove the rise and fall of the Ediacara biota. *Geobiology* 17, 594–610.
- Zhang S., Jiang G., Zhang J., Song B., Kennedy M. J. and Christie-Blick N. (2005) U–Pb sensitive high-resolution ion microprobe ages from the Doushantuo Formation in south China: Constraints on late Neoproterozoic glaciations. *Geology* 33, 473–476.
- Zhang Y., Wen H., Zhu C., Fan H., Xiao J. and Wen J. (2021) Molybdenum isotopic evidence for anoxic marine conditions during the end-Permian mass extinction. *Chem. Geol.* 575, 120259.

Zhou C., Huyskens M. H., Lang X., Xiao S. and Yin Q. Z. (2019) Calibrating the terminations of Cryogenian global glaciations. *Geology* 47, 251–254.

Zhu B., Jiang S., Pi D., Ge L. and Yang J. (2018) Trace Elements Characteristics of Black Shales from the Ediacaran Doushantuo Formation, Hubei Province, South China: Implications for Redox and Open vs. Restricted Basin Conditions. *J. Earth Sci.* 29, 342–352.

Zhu M., Zhang J., Steiner M., Yang A., Li G. and Erdtmann B. (2003) Sinian-Cambrian stratigraphic framework for shallow- to deep-water environments of the Yangtze Platform: an integrated approach. *Prog. Nat. Sci.* 13, 951–960.

Zhu, M., Zhao, F., Yin, Z., Zeng, H. and Li, G. (2019) The Cambrian explosion: Advances and perspectives from China. *Sci. China Earth Sci.* 49, 1455-1490.