

## Original Article

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# The Ediacaran ‘Miaohe Member’ of South China: new insights from palaeoredox proxies and stable isotope data

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**Abstract**

Throughout the Ediacaran Period, variable water-column redox conditions persisted along productive ocean margins due to a complex interplay between nutrient supply and oceanographic restriction. These changing conditions are considered to have influenced early faunal evolution, with marine anoxia potentially inhibiting the development of the ecological niches necessary for aerobic life forms. To understand this link between oxygenation and evolution, the combined geochemical and palaeontological study of marine sediments is preferable. Located in the Yangtze Gorges region of southern China, lagoonal black shales at Miaohe preserve alga and putative metazoans, including *Eoandromeda*, a candidate total-group ctenophore, thereby providing one example of where integrated study is possible. We present a multi-proxy investigation into water-column redox variability during deposition of these shales (c. 560–551 Ma). For this interval, reactive iron partitioning indicates persistent water-column anoxia, while trace metal enrichments and other geochemical data suggest temporal fluctuations between ferruginous, euxinic and rare suboxic conditions. Although trace metal and total organic carbon values imply extensive basin restriction, sustained trace metal enrichment and  $\delta^{15}\text{N}_{\text{sed}}$  data indicate periodic access to open-ocean inventories across a shallow-marine sill. Lastly,  $\delta^{13}\text{C}_{\text{org}}$  values of between  $-35\text{‰}$  and  $-40\text{‰}$  allow at least partial correlation of the shales at Miaohe with Member IV of the Doushantuo Formation. This study provides evidence for fluctuating redox conditions in the lagoonal area of the Yangtze platform during late Ediacaran time. If these low-oxygen environments were regionally characteristic, then the restriction of aerobic fauna to isolated environments can be inferred.

**1. Introduction**

The Neoproterozoic Era was characterized by intense environmental and biological change and, as such, marked a turning point in the development of the modern Earth system. Towards the end of this time (c. 575 Ma) came the emergence of the Ediacara Biota, representing the first large, structurally complex organisms (e.g. Narbonne & Gehling, 2003). This diversification of phyla has been hypothesized to be a result of increasing atmospheric and/or oceanic oxygen availability (e.g. Fike *et al.* 2006; Canfield *et al.* 2007). Termed the Neoproterozoic Oxygenation Event (NOE), the timing and extent of this environmental change has proved difficult to constrain (Shields-Zhou & Och, 2011). Moreover, recent studies (e.g. Canfield *et al.* 2008; Butterfield, 2009) indicate that oxygenation was more complex, with oceanic anoxia also common during late Neoproterozoic time, particularly along productive and restricted ocean margins (Sahoo *et al.* 2016; Tostevin *et al.* 2019). Alongside fluctuating oxygen levels, the Ediacaran Period was also characterized by events such as the Gaskiers glaciation and the global Shuram–Wonoka  $\delta^{13}\text{C}$  negative anomaly (e.g. Condon *et al.* 2005), with the latter considered to represent oceanic oxygenation (Fike *et al.* 2006; Shields *et al.* 2019). To understand these events and the relationship between evolution and oxygenation during late Neoproterozoic time, it is important to focus on deposits containing both Ediacaran fauna and a lithology suited to geochemical analysis.

The ‘Miaohe Member’ shales at Miaohe (c. 560–551 Ma) in South China represent one lithological unit where combined geochemical and palaeontological study is possible. Because of this, several studies have been published examining the redox geochemistry and/or stratigraphy of these rocks (An *et al.* 2015; Li *et al.* 2015; Xiao *et al.* 2017). Contained within the shales at the Miaohe site is an assemblage comprising colonial prokaryotes, benthic multicellular algae and several putative metazoans (e.g. *Calyptrina* and *Jiuqunaoella*). These early organisms are preserved as carbonaceous compressions and collectively termed the ‘Miaohe Biota’ (Zhu & Chen,

1984; Chen & Xiao, 1992; Xiao *et al.* 2002). Importantly, this assemblage is believed to have been benthic (Xiao *et al.* 2002); redox data obtained from the Miaohe Member shales should therefore reflect changes in oxygenation at the potentially inhabitable sediment–water interface. Combining trace metal, Fe speciation and pyrite framboid data, Li *et al.* (2015) report that the Miaohe-Biota-associated black shales were deposited in a predominantly anoxic environment, with the remaining Miaohe Member shales deposited under euxinic (anoxic and sulphidic) conditions. Additional redox data are available from studies of the Doushantuo Formation Member IV (DST IV), a unit conventionally correlated with the Miaohe Member (Zhu *et al.* 2013; Xiao *et al.* 2017; Zhou *et al.* 2017). Deposited between *c.* 635 Ma and *c.* 551 Ma, the Doushantuo Formation is of particular interest due to its widespread occurrence over much of South China and its variation in facies from deep marine to shallow marine shelf/lagoon (Zhu *et al.* 2003).

Geochemical proxies indicate a complicated redox environment during deposition of DST IV. Pyrite framboid analyses and  $Fe_{py}/Fe_{HR}$  and  $Fe_{HR}/Fe_T$  values (where  $Fe_{py}$ ,  $Fe_{HR}$  and  $Fe_T$  represent pyrite-bound, highly reactive and total iron, respectively) from multiple Yangtze platform sites record dominantly euxinic conditions (Li *et al.* 2010, 2015; Och *et al.* 2016; Sahoo *et al.* 2016). Enrichments of trace metals at multiple sites also suggest that DST IV deposition occurred under dominantly anoxic to euxinic bottom-water conditions (Li *et al.* 2010, 2015; Och *et al.* 2016; Zhu *et al.* 2018). Despite this, several studies provide evidence for global oceanic oxygenation during deposition of DST IV (Scott *et al.* 2008; Kendall *et al.* 2015; Chen *et al.* 2015; Och *et al.* 2016; Sahoo *et al.* 2016; Shi *et al.* 2018; Ostrander *et al.* 2019). Observed Mo and V concentrations in DST IV indicate access to a large trace metal (oxyanion complex) inventory and globally extensive oxic seas (Scott *et al.* 2008; Och *et al.* 2016; Sahoo *et al.* 2016). Similarly, studies of  $\delta^{34}S_{py}$ ,  $\delta^{98}Mo$  and  $\delta^{238}U$  data suggest that oceans were widely oxygenated at this time, and that oxyanion inventories remained high or even increased throughout the interval of DST IV deposition (McFadden *et al.* 2008; Kendall *et al.* 2015; Chen *et al.* 2015; Sahoo *et al.* 2016; Och *et al.* 2016; Shi *et al.* 2018; Ostrander *et al.* 2019). To explain the observed redox data, palaeoenvironmental reconstructions typically include the presence of a metastable euxinic zone that controlled local redox conditions during deposition of DST IV (Li *et al.* 2010). A second major feature of the DST IV redox landscape is the occurrence of intra-shelf basins. In these shallow, lagoonal settings, positive  $\delta^{34}S_{py}$  values,  $\delta^{15}N$  data (Och *et al.* 2016) and infrequent Mo enrichment (Li *et al.* 2015) indicate a partially restricted environment, disconnected from global redox patterns (Och *et al.* 2016). To link this complex palaeoenvironmental reconstruction with DST IV redox data from multiple sites across the Yangtze platform, a number of studies have examined the similarity of  $\delta^{13}C$  data from different locations (Jiang *et al.* 2007; Li *et al.* 2010, 2017; Zhu *et al.* 2013; An *et al.* 2015; Xiao *et al.* 2017; Zhou *et al.* 2017).

To understand water-column redox conditions contemporaneous to the deposition of the Miaohe Member facies, a multi-proxy approach is fundamental. In this study, Fe speciation, trace element (Mo, U, V and Cr) and  $\delta^{14}N$  data are used to investigate water-column redox conditions and associated controlling factors during deposition of the Miaohe Member shales. An attempt is also made to integrate palaeoredox proxy data with  $\delta^{13}C$  data, thereby enabling the results of this study to be placed within a regional stratigraphic framework, while addressing recent uncertainties around the regional correlation of DST IV and the Miaohe Member (cf. Zhu

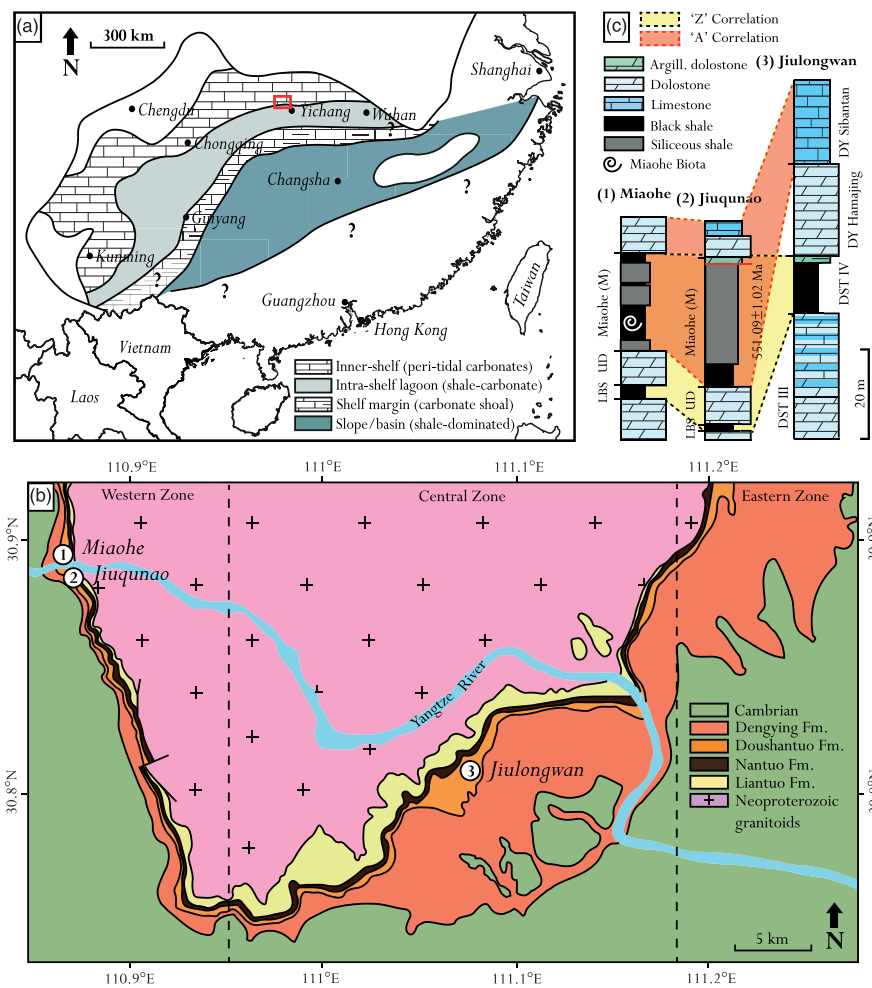
*et al.* 2013; An *et al.* 2015; Xiao *et al.* 2017; Zhou *et al.* 2017). Additionally, while the potential impact of weathering on surface outcrop sample redox proxy data is well documented (e.g. Raiswell *et al.* 2018), we specifically address this issue by providing an example of secondarily altered Fe speciation proxy data.

## 2. Geological setting and study sites

The Miaohe shales examined in this study have been described before in detail (e.g. Ding *et al.* 1996; Wang *et al.* 1998; Xiao *et al.* 2002). Palaeogeographic reconstructions indicate that deposition of the Miaohe unit was along a carbonate-rich passive margin, in a shallow, shelf lagoon environment (Condon *et al.* 2005) (Fig. 1a). In this setting, redox variability would have been strongly controlled by the presence of a shelf margin complex that would have limited communication between the lagoon and deeper basin (Jiang *et al.* 2011). Conventionally, the Miaohe unit is considered to form the uppermost part of the Ediacaran Doushantuo Formation, which is today exposed in outcrop along the edge of the Huangling anticline in the Yangtze Gorges region of South China (Jiang *et al.* 2003). At this location, the Doushantuo Formation overlies the terminal Cryogenian Nantuo Formation, and is itself overlain by the upper Ediacaran Dengying Formation (Fig. 1b) (Xiao *et al.* 2017). Typically, the Doushantuo Formation in this area is considered to comprise a basal *c.* 5 m thick dolostone (Member I); an overlying interbedded mudstone and argillaceous dolostone unit of *c.* 70 m thickness (Member II); a *c.* 40 m thick dolostone that passes upwards into an interbedded limestone and argillaceous dolostone; and a final *c.* 20 m thick black shale unit (DST Member IV) (Jiang *et al.* 2006, 2011; Zhou & Xiao, 2007; McFadden *et al.* 2008).

Although the Doushantuo Formation can be broadly traced around the circumference of the Huangling anticline, incomplete exposure has resulted in uncertainty over the stratigraphic placement of DST IV between localities (An *et al.* 2015; Xiao *et al.* 2017; Zhou *et al.* 2017). In particular, the relationship between DST IV described at Jiulongwan (Fig. 1b) and the Miaohe Member examined in this study has proved difficult to reconcile. Due to subtle differences in the uppermost Doushantuo Formation between sections, Zhou *et al.* (2017) divided the Huangling study area into eastern, central and western zones (Fig. 1b). Notably, several locations in the western zone (e.g. Miaohe, Qinglinkou, Jiuqunao and Sixi) show distinct variations when compared with the central and eastern zones; instead of the *c.* 20 m thick black shale characteristic of Member IV at the Jiulongwan section, the rocks overlying Member III at these localities comprise two black shales separated by a dolostone unit (An *et al.* 2015; Xiao *et al.* 2017; Zhou *et al.* 2017). These three units have been termed the lower black shale (LBS), upper dolostone (UD) and Miaohe Member (M) (Zhou *et al.* 2017). However, disruption is apparent at these localities in the western zone, with regional-scale rotational sliding providing a likely mechanism for the observed repetition of the black shale and evident syn-sedimentary deformation within the upper dolostone (Vernhet *et al.* 2007; Zhu *et al.* 2013). Despite this, the original sequence of lithologies within Doushantuo Member IV remains controversial, with some studies partially correlating the Miaohe Member as described in the western zone (M) with Doushantuo Member IV (Xiao *et al.* 2017; Zhou *et al.* 2017), or partially with the younger Shibantan Member of the Dengying Formation (Fig. 1c) (An *et al.* 2015).

In this study, the Miaohe Member shales from the Miaohe site are examined and compared with potentially correlative black shale units from the neighbouring Jiuqunao section and the Jiulongwan



**Fig. 1.** (a) Palaeoenvironmental map of the Yangtze Platform region in South China during deposition of Doushantuo Member IV (DST IV), modified after Steiner *et al.* (2001) and Jiang *et al.* (2011). The red square indicates the location of (b). (b) Geological map of the southern portion of the Huangling anticline, modified after Xiao *et al.* (2017). The locations of sections examined in this study are: 1, Miaohe; 2, Jiuqunao; and 3, Jiulongwan. Vertical dashed lines divide the area into eastern, central and western zones as defined by Zhou *et al.* (2017). (c) Simplified stratigraphic columns for the Miaohe (this study; Li *et al.* 2015), Jiuqunao (Li *et al.* 2015) and Jiulongwan (Li *et al.* 2010) sections. Two stratigraphic correlations are proposed for the Miaohe, Jiuqunao and Jiulongwan sites: the 'Z' correlation (Xiao *et al.* 2017; Zhou *et al.* 2017) and the 'A' correlation (An *et al.* 2015). The location of the ash bed dated at  $551.09 \pm 1.02$  Ma by Schmitz (2012) is indicated, as is the location of the Miaohe Biota (Xiao *et al.* 2002).

section further to the east (Fig. 1b). The succession at Miaohe comprises a series of finely laminated organic-rich black and siliceous shales, with occasional carbonate concretions. Directly overlying the shales at Miaohe is an *c.* 80 cm thick argillaceous dolostone that directly underlies, and potentially transitions into the Ediacaran Dengying Formation (Zhu *et al.* 2007; An *et al.* 2015; Xiao *et al.* 2017). In addition to anomalously low  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  values (e.g.  $\delta^{13}\text{C}_{\text{org}}$  values of between  $-22\%$  and  $-40\%$ ; Xiao *et al.* 2017), the black shales at the Miaohe site are notable for containing the Miaohe Biota, a collection of colonial prokaryotes and algal macrofossils preserved as carbonaceous compressions (Zhu & Chen, 1984; Chen & Xiao, 1992; Xiao *et al.* 2002). The Miaohe Biota occur over a 2 m interval, approximately 5–7 m from the base of the Miaohe shales at the Miaohe site (Xiao *et al.* 2002).

### 3. Geochemical redox proxies

#### 3.a. Iron speciation

Iron geochemistry has been widely used as a method for discerning water-column redox conditions in both modern and ancient marine

environments (e.g. Raiswell & Canfield, 1998; Raiswell *et al.* 2001; Poulton & Raiswell, 2002; Shen *et al.* 2002, 2003; Poulton *et al.* 2004). Sedimentary iron typically comprises carbonate-associated Fe ( $\text{Fe}_{\text{carb}}$ ), ferric-oxides ( $\text{Fe}_{\text{ox}}$ ), magnetite Fe ( $\text{Fe}_{\text{mag}}$ ), pyrite Fe ( $\text{Fe}_{\text{py}}$ ) and other poorly reactive or non-reactive iron-silicate minerals (Canfield, 1989; Raiswell *et al.* 1994; Raiswell & Canfield, 1996, 1998; Poulton *et al.* 2004). Poulton & Canfield (2005) developed a sequential extraction scheme to quantify operationally defined Fe pools that broadly target these Fe phases, and this has been widely used to distinguish anoxic-ferruginous, euxinic and oxic water bodies (see Poulton & Canfield, 2011; Poulton, 2021). In this scheme,  $\text{Fe}_{\text{carb}}$ ,  $\text{Fe}_{\text{ox}}$ ,  $\text{Fe}_{\text{mag}}$  and  $\text{Fe}_{\text{py}}$  constitute the highly reactive iron pool ( $\text{Fe}_{\text{HR}}$ ), and  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  and  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  ratios are used together to define the redox state of the water-column.

Observations from both modern and Phanerozoic sediments indicate that an  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  threshold of 0.38 generally marks the upper limit for deposition of sediments in an oxic water-column, with values of  $> 0.38$  indicative of anoxia (Raiswell & Canfield, 1998; Poulton & Canfield, 2011). However, sediments deposited rapidly in an anoxic environment have been documented to record lower  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  ratios (Raiswell & Canfield, 1998), and caution

should be applied when interpreting ratios between 0.22 and 0.38 (Poulton & Canfield, 2011; Raiswell *et al.* 2018; Poulton, 2021). As defined empirically, an  $Fe_{py}/Fe_{HR}$  value of  $< 0.6$  – for samples with  $Fe_{HR}/Fe_T > 0.38$  – likely indicates ferruginous conditions (Benkovitz *et al.* 2020; Poulton, 2021), whereas a value of  $> 0.8$  suggests euxinia (Poulton *et al.* 2004; Canfield *et al.* 2008).  $Fe_{py}/Fe_{HR}$  values between 0.6 and 0.8 should be interpreted with caution (Poulton & Canfield, 2011; Poulton, 2021). Generally,  $Fe_{HR}/Fe_T$  and  $Fe_{py}/Fe_{HR}$  proxies should both be applied with consideration for the depositional environment (including rate of deposition, sediment composition, fluctuating redox conditions and biological/physical reworking),  $Fe_T$  content, post-depositional alteration and surface weathering of pyrite (Clarkson *et al.* 2014; Raiswell *et al.* 2018).

### 3.b. Redox-sensitive trace metals

The enrichment of redox-sensitive trace metals in organic-rich shales can also be used to decipher palaeoredox conditions. Due to changes in solubility, the burial fluxes of Mo, V, U and Cr are several orders of magnitude larger in reducing environments than in an oxidizing environment (Emerson & Husted, 1991). In a euxinic setting, amplification of Mn/Fe redox cycling and the availability of organic carbon substrates is increased, thereby influencing patterns of trace metal enrichment (Morse & Luther, 1999; Algeo & Maynard, 2004).

In seawater, molybdenum occurs as the molybdate oxyanion complex,  $MoO_4^{2-}$  (Broecker & Peng, 1982). Given reducing conditions, molybdate is readily sequestered by Mn-oxyhydroxides at the sediment–water interface and released to pore waters (Bertine & Turekian, 1973; Calvert & Pedersen, 1993; Crusius *et al.* 1996; Erickson & Helz, 2000; Zheng *et al.* 2000; Goldberg *et al.* 2012). In the presence of free  $H_2S$ , molybdate present in sediment pore water is able to react to form particle-reactive thiomolybdates ( $MoO_xS_{4-x}$ ) (Helz *et al.* 1996), which are easily scavenged by sulphur-rich organic molecules, metal-rich compounds (Tribovillard *et al.* 2004; Helz *et al.* 1996, 2011) and FeS (Vorlicek *et al.* 2004; Poulson Brucker *et al.* 2012). Although moderately enriched in sediments deposited in non-sulphidic anoxic conditions, Mo is more strongly enriched in sediments deposited in a euxinic environment (e.g. Tribovillard *et al.* 2006).

In an oxic water mass, vanadium occurs as vanadate oxyanions ( $HVO_4^{2-}$  and  $H_2VO_4^-$ ), which are readily adsorbed onto both Mn- and Fe-oxyhydroxides (Calvert & Piper, 1984; Wehrli & Stumm, 1989). In anoxic conditions, V(V) is readily reduced to V(IV), forming vanadyl ( $VO^{2+}$ ) and hydroxyl ( $VO(OH)_3^-$ ) species, in addition to insoluble hydroxides ( $VO(OH)_2$ ). The resulting ions can then be scavenged via organometallic ligand formation or surface adsorption (Emerson & Husted, 1991; Morford & Emerson, 1999). Given a more strongly reducing euxinic environment, V(V) is further reduced to V(III), which can be taken up by geoporphyrins, or precipitated as solid  $V_2O_3$  oxides or  $V(OH)_3$  hydroxides (Breit & Wanty, 1991; Wanty & Goldhaber, 1992). Unlike Mo, V is readily sequestered and enriched in sediments deposited in a reducing but non-sulphidic water-column (e.g. Algeo & Maynard, 2004; Tribovillard *et al.* 2006).

Uranium is mainly present in seawater as carbonate-bound uranyl ions,  $UO_2(CO_3)_3^{4-}$  (Anderson *et al.* 1989). In an anoxic environment, the reduction of U(VI) to U(IV) forms  $UO^{2+}$  uranyl ions or less soluble uranous fluoride compounds and occurs independently to Fe and Mn cycling. Because of this, U enrichment primarily takes place within the sediment (Anderson *et al.* 1989; Algeo

& Maynard, 2004; McManus *et al.* 2005). At this location, U accumulates due to adsorption by humic acid ligand complexes or the precipitation of uraninite ( $UO_2$ ),  $U_3O_7$  or  $U_3O_8$  (e.g. Klinkhammer & Palmer, 1991; Crusius *et al.* 1996; McManus *et al.* 2005). The presence of free  $H_2S$  and active sulphate reduction is thought to accelerate the latter process (Langmuir, 1978; Klinkhammer & Palmer, 1991). Typically, U is enriched in non-sulphidic anoxic facies and strongly enriched in euxinic facies, although vulnerable to remobilization and secondary depletion (e.g. Algeo & Maynard, 2004; Tribovillard *et al.* 2006).

In oxic seawater, Cr mainly occurs as the chromate oxyanion,  $CrO_4^{2-}$  (Cranston & Murray, 1978). In an anoxic setting, Cr(IV) is readily reduced to Cr(III), subsequently forming hydroxyl and aquahydroxyl cations (e.g.  $Cr(OH)_2^+$ ). These cations are able to react to form insoluble  $Cr(OH)_3$  and  $Cr_2O_3$ , or a complex with humic/fulvic acids to enable adsorption by Fe- and Mn-oxyhydroxides, thereby enabling transport of Cr to the sediment (Elderfield, 1970; Emerson *et al.* 1979; Breit & Wanty, 1991; Algeo & Maynard, 2004). In sulphidic conditions, structural and electronic incompatibilities limit uptake of Cr(III) by Fe-sulphides (Huerta-Diaz & Morse, 1992; Morse & Luther, 1999). As a result, Cr is typically enriched in anoxic sediments, with little change to the relative degree of anoxic enrichment under euxinic conditions (e.g. Algeo & Maynard, 2004).

The behaviour demonstrated by each of the redox-sensitive trace elements, Mo, U, V and Cr creates relative patterns of sedimentary enrichment. Firstly, strong Cr, V and/or U enrichment without strong Mo enrichment indicates anoxic but not euxinic conditions, while strong Mo, U or V enrichment without strong Cr enrichment indicates euxinia (Algeo & Maynard, 2004; Tribovillard *et al.* 2006). In a suboxic ( $O_2 < 5 \mu M$ ) water-column, Mo, U, V and Cr solubilities are all increased and sedimentary enrichment is therefore low (Algeo & Maynard, 2004). Commonly, trace metal enrichment or depletion is assessed by normalization to a reference shale (Wedepohl, 1971, 1991; McLennan, 2001; Tribovillard *et al.* 2006; Algeo & Tribovillard, 2009). In anoxic basins, the uptake of Mo, U and V is also closely linked to the availability of total organic carbon (TOC). This is because reduced metal species such as thiomolybdate and vanadyl ions are bound by organic particles (Lyons *et al.* 2009). Because of this, trace metal and TOC ratios can be used as palaeogeographic proxies for understanding the extent of basin restriction and deep-water renewal (Algeo & Lyons, 2006; Algeo & Rowe, 2012).

### 3.c. Nitrogen isotopes

The isotopic signature ( $\delta^{15}N_{sed}$ ) of nitrogen in marine sediments is linked to multiple biogeochemical processes, including nitrification, denitrification, nitrogen fixation and anammox. During denitrification,  $NO_3^-$  is reduced to  $N_2$  or  $N_2O$ , and the seawater nitrate reservoir is enriched in  $^{15}N$  relative to atmospheric nitrogen ( $\delta^{15}N = 0\%$ ) due to isotopic fractionation (Sigman *et al.* 2009; Kikumoto *et al.* 2014). Conversely, diazotrophic  $N_2$  fixation results in slightly negative  $\delta^{15}N_{sed}$  values (e.g. Ader *et al.* 2014; Zhang *et al.* 2014). Due to the near-complete ventilation of modern oceans, present-day  $\delta^{15}N_{sed}$  values have a mode of +5 to +6%, with an overall range of between +1% and +15% (Tesdal *et al.* 2013; Ader *et al.* 2014). This is due to nitrate limitation, whereby denitrification and/or assimilation exceed oceanic nitrate input and/or recycling (e.g. Kikumoto *et al.* 2014).

Because of the link between oxygenation and marine productivity,  $\delta^{15}N_{sed}$  values can be tentatively used as palaeoredox proxies (e.g.

Sigman *et al.* 2009). In a redox-stratified ocean, the oxic–anoxic interface is elevated in the water-column. In deeper, anoxic waters, the nitrogen generated by biological processes will be in the form of ammonium ( $\text{NH}_4^+$ ), while in oxygenated surface waters organic nitrogen will be converted to  $\text{NO}_3^-$ . In this scenario,  $\delta^{15}\text{N}_{\text{sed}}$  values strongly relate to both the depth of the redox transition zone and mixing (upwelling) between the deep ammonium pool and the shallow nitrate-rich pool. Although difficult to standardize, typical  $\delta^{15}\text{N}_{\text{sed}}$  values from primarily anoxic settings tend towards 0‰ (Quan & Falkowski, 2009; Ader *et al.* 2014). In a euxinic water-column,  $\text{N}_2$  fixation is favoured and occurs with a fractionation of between 0 and –2‰, further reducing  $\delta^{15}\text{N}_{\text{sed}}$  values (Cremonese *et al.* 2013). Because of the variability associated with  $\delta^{15}\text{N}_{\text{sed}}$  in modern marine settings,  $\delta^{15}\text{N}_{\text{sed}}$  should only be used for local palaeoredox reconstructions in conjunction with other established proxies (Quan *et al.* 2008).

#### 4. Materials and methods

The 20 surface outcrop samples used in this study were collected from the Miaohé Member black shales at Miaohé (Fig. 1b). Small portions were obtained from clean surface sections and powdered for geochemical analysis.

##### 4.a. Iron speciation

Several operationally defined Fe pools were measured during iron speciation analysis (Poulton & Canfield, 2005). These are carbonate-associated Fe ( $\text{Fe}_{\text{carb}}$ ), ferric-oxides ( $\text{Fe}_{\text{ox}}$ ), magnetite Fe ( $\text{Fe}_{\text{mag}}$ ) and pyrite Fe ( $\text{Fe}_{\text{py}}$ ). Total Fe was also measured ( $\text{Fe}_{\text{T}}$ ).

$\text{Fe}_{\text{py}}$  was measured using an adaptation of the method outlined by Canfield *et al.* (1986). Initially, 2–4 g of gravimetrically measured powdered sample was placed in a digestion flask, to which 8 mL of concentrated HCl was added. After heating under a constant flow of  $\text{N}_2$  to determine whether acid volatile sulphide (AVS) was present (no AVS was detected), 16 mL of acidified  $\text{CrCl}_2$  was added to the solution and heated to boiling for 2 hours, during which time any liberated  $\text{H}_2\text{S}$  was collected in a  $\text{AgNO}_3$  trap as  $\text{Ag}_2\text{S}$ . The concentration of  $\text{Fe}_{\text{py}}$  was then determined gravimetrically.

The remaining Fe pools ( $\text{Fe}_{\text{ox}}$ ,  $\text{Fe}_{\text{mag}}$  and  $\text{Fe}_{\text{carb}}$ ) were measured following the sequential extraction technique of Poulton & Canfield (2005). Between 50 and 100 mg of powdered sample was placed in a centrifuge tube. To each of the samples, 10 mL of 1 M sodium acetate (adjusted to a pH of 4.5 with acetic acid) was added and constantly agitated for 48 hours at a temperature of 50°C. After centrifugation and removal of the supernatant, 10 mL of 0.28 M sodium dithionite (adjusted to a pH of 4.8 with 0.2 M acetic acid and 0.3 M tri-sodium citrate) was added and shaken for 2 hours at ambient temperature. For the final step, 10 mL of 0.2 M ammonium oxalate (buffered with 0.17 M oxalic acid) was added and shaken for 6 hours at ambient temperature.

$\text{Fe}_{\text{T}}$  was measured via a multi-acid digestion. Initially, 100 mg of each sample was ashed at 450°C for 8 hours. Following this, 5 mL of concentrated  $\text{HNO}_3$ , 2 mL of HF and 2–3 drops of  $\text{HClO}_4$  were added. The solutions were then heated and left to dry, after which boric acid was added and evaporated to dryness. The samples were then re-dissolved in concentrated  $\text{HNO}_3$ .

Dissolved iron concentrations were measured using atomic absorption spectroscopy (AAS). Replicate analyses of PACS-2, an international sediment standard, gave a relative standard deviation (RSD) of < 5% for all sequential extraction stages, and

an  $\text{Fe}_{\text{T}}$  accuracy of > 98%. Iron speciation analyses were performed in the Cohen Geochemistry Laboratory, University of Leeds.

##### 4.b. Redox-sensitive trace metals

The trace metal (Mo, U, V and Cr) content of each sample was measured via multi-acid digestion. Firstly, 3 mL of HF and 2 mL  $\text{HNO}_3$  were added to 60 mg of powdered sample and the mixture heated at 200°C for 16 hours. The resulting solution was left to cool and evaporate to dryness. A further 2 mL of HF, 1 mL of  $\text{HNO}_3$  and 2 mL of  $\text{HClO}_4$  were added and the solution was again heated at 200°C for 16 hours. This solution was left to cool and evaporate before 1 mL of  $\text{HNO}_3$  and 1 mL of  $\text{HClO}_4$  were added. Following a final phase of cooling and evaporation to dryness, 1 mL of  $\text{HNO}_3$  was added. Aliquots of 1 mL for each sample were then analysed using inductively coupled plasma mass spectrometry (ICP-MS) at the instrument laboratory of the London Geochemistry and Isotope Centre (LOGIC), University College London.

##### 4.c. Stable isotopes

Analyses were performed at the Bloomsbury Environmental Isotope Laboratories (BEIF) of University College London, using a Thermo-Finnigan elemental analyser mass spectrometer (continuous flow). Rock samples were first washed, cut into small chips and ground after removing altered and recrystallized fragments. An amount of rock powder between 10 mg and 200 mg was used for nitrogen isotope analyses, depending on the expected nitrogen concentration. The error associated with  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{org}}$  is  $\pm 0.50\%$ . Some samples needed to be analysed repeatedly in order to ensure a meaningful nitrogen isotope signal, although here we publish only the highest-fidelity values based on the signal background and peak intensity.  $\delta^{15}\text{N}$  values were calibrated during each session using the minor internal standard drift experienced by the elemental analyser.

##### 4.d. Total organic carbon

TOC values were determined after first adding 10 mL of 10% HCl to 1000 mg of sample. Samples were then centrifuged and the supernatant discarded, before being rinsed and dried at 50°C overnight. Carbon was then measured using a Leco C/S analyser (Leco Corporation, St Joseph, MI, USA) at the London Geochemistry and Isotope Centre (LOGIC), University College London.

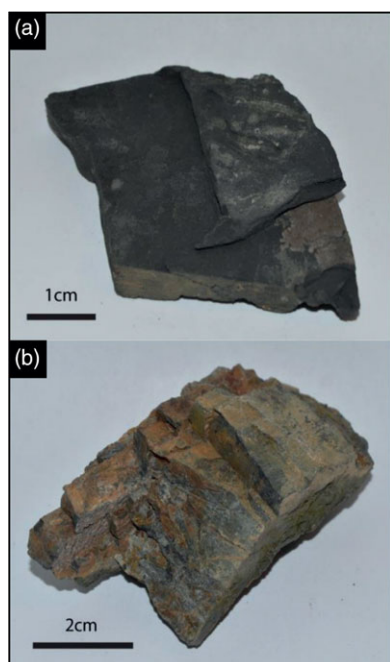
##### 4.e. Redox-sensitive trace metal enrichment factors

Trace metal concentrations are commonly normalized to the concentrations of detrital elements such as Al, Ti and Sc and presented as ‘enrichment factors’ (EFs; e.g. Tribouillard *et al.* 2006; Algeo & Tribouillard, 2009). In this study, Mo, V, U and Cr EFs were calculated using the equation:  $\text{EF}_x = ([X]/\text{Ti}_{\text{sample}})/([X]/\text{Ti}_{\text{upper continental crust}})$ . Average upper continental crust trace metal concentrations for normalization were obtained from McLennan (2001).

## 5. Results

### 5.a. Samples

Although several of the samples associated with the Miaohé Biota-bearing strata are dark shales, the majority of samples powdered for geochemical analysis were evidently silicified. Relatively immobile metals Ti, Sc, Th and REE all covary linearly (see online Supplementary Material, available at <http://journals.cambridge>.



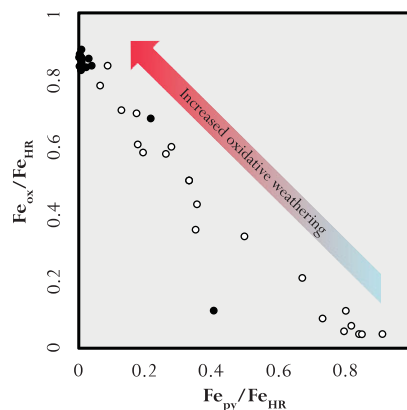
**Fig. 2.** Contrast between the (a) least visibly weathered sample, collected from the Miaohu Member at Miaohu at a stratigraphic height of 7.0 m, and (b) most visibly weathered sample, collected from the same section at 12.9 m.

org/geo) but are significantly depleted in all samples relative to upper continental crust (McLennan, 2001), indicating that Fe concentrations have been diluted by silica and/or other non-silicate minerals to varying extents. Because of this silicification, a minority of the samples analysed record  $Fe_T$  values below the 0.5 wt% threshold conventionally considered appropriate for Fe speciation analyses (Clarkson *et al.* 2014; Raiswell *et al.* 2018). Similar  $Fe_T$  values are recorded in equivalent Miaohu Member samples obtained by Li *et al.* (2015), and for the subset of samples from both studies that contain < 0.5 wt%  $Fe_T$ , Fe speciation analyses must be considered to be potentially ambiguous.

The hand specimens used in this study showed visible evidence of oxidative weathering, particularly along previously exposed surfaces (see online Supplementary Material; Fig. 2). As previously discussed, Fe speciation proxies should only be applied with consideration for the environment of deposition, potential post-depositional alteration and the impact of weathering (Clarkson *et al.* 2014; Raiswell *et al.* 2018). Equivalent samples obtained by Li *et al.* (2015) were excavated at depth, while those obtained for this study are surface outcrop samples; a comparison of the two studies therefore provides an opportunity to quantitatively assess the impact of clear visible surface weathering on Fe speciation data. Unlike the weathered samples evaluated in this study, and despite evidence of increased  $Fe_{ox}$  in some samples (Fig. 3), Li *et al.* (2015) argue that the presence of microscopic pyrite framboids means any significant impact due to oxidative weathering is unlikely for their excavated samples. These differences are demonstrated by the mean  $Fe_{py}/Fe_{HR}$  values of 0.04 and 0.46 recorded in this study and by Li *et al.* (2015), respectively.

### 5.b. Iron speciation

Although a study by Ahm *et al.* (2017) found a difference of up to 30% for  $Fe_{HR}/Fe_T$  data between outcrop and core samples from the Vinini Formation in Nevada, USA, it is likely that the  $Fe_{HR}/Fe_T$



**Fig. 3.**  $Fe_{py}/Fe_{HR}$  versus  $Fe_{ox}/Fe_{HR}$  cross-plot for samples from this study (solid black points) and Li *et al.* (2015) (white points). The high  $Fe_{ox}/Fe_{HR}$  and low  $Fe_{py}/Fe_{HR}$  values observed in samples from this study are indicative of modern weathering. Samples from Li *et al.* (2015) are more distributed, reflecting transient alteration.

proxy is mostly unaffected by modern oxidative weathering. Previously, a study of 231 carbonate samples (Sperling *et al.* 2013) found no statistical correlation between  $Fe_{py}/Fe_{HR}$  and  $Fe_{HR}/Fe_T$  data despite pyrite weathering, thereby implying that the  $Fe_{py}$  fraction is transformed into immobile iron (oxyhydr) oxides that are preserved in the vicinity of the original pyrite. This is consistent with the behaviour of Fe during chemical weathering (Poulton & Raiswell, 2002). Because of this, the  $Fe_{HR}/Fe_T$  proxy can be used despite evidence of secondary oxidative weathering. The Miaohu section shales record  $Fe_{HR}/Fe_T$  values of between 0.46 and 0.9 (Table 1; Fig. 4), suggesting that deposition occurred in a sustained anoxic setting. It is important to note that although several of the samples used in this study record  $Fe_T$  concentrations of < 0.5 wt%,  $Fe_{HR}/Fe_T$  ratios from all samples analysed consistently record anoxia. These values are also similar to the  $Fe_{HR}/Fe_T$  ratios obtained by Li *et al.* (2015).

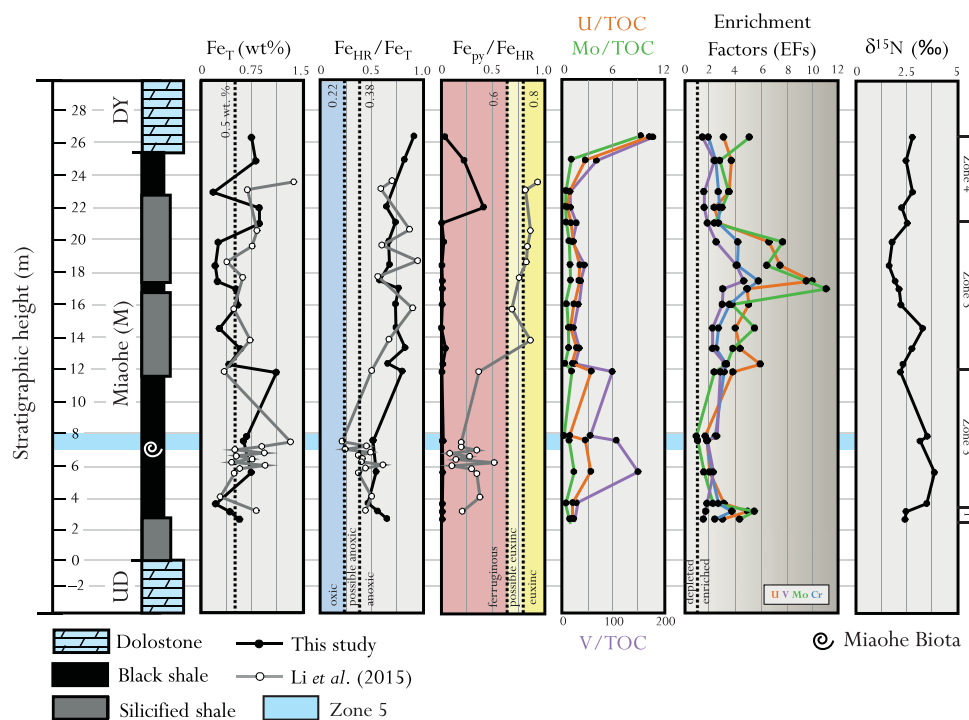
$Fe_{py}/Fe_{HR}$  values ( $0.00 \leq Fe_{py}/Fe_{HR} \leq 0.41$ ) appear to indicate anoxic-ferruginous conditions. However, as discussed in Section 5.a., evidence for pyrite weathering and  $Fe_{ox}$  enrichment (e.g. samples M0.5, M14 and M10; Table 1; Fig. 3) together imply that primary  $Fe_{py}/Fe_{HR}$  may have been diminished due to secondary alteration. Similar  $Fe_{py}/Fe_{HR}$  data from Li *et al.* (2015) ( $0.07 < Fe_{py}/Fe_{HR} < 0.92$ ) are likely more representative of water-column redox state, particularly in the uppermost, non-fossiliferous section where  $Fe_{py}/Fe_{HR}$  ratios suggest euxinia ( $0.74 \leq Fe_{py}/Fe_{HR} \leq 0.92$ , with one exception at 15.4 m).

### 5.c. Redox-sensitive trace metals

Although most samples studied record Mo, U, V and Cr enrichment relative to average shale values (McLennan, 2001), four discrete ‘intervals’ of trace metal enrichment can be identified (Fig. 4). The first interval occurs at a stratigraphic height of 2–3 m and records moderate trace metal enrichment (e.g. Mo EFs: 4.29–5.46; U EFs: 2.96–4.92; Cr EFs: 2.35–3.68). For this interval, Mo EFs are increased relative to Cr. Mo/TOC, U/TOC and V/TOC values are low, at 0.91, 1.16 and 21.71 respectively. At a stratigraphic height of 3–12 m, trace metal enrichment is generally reduced and Mo is depleted relative to Cr (Mo EFs: 0.89–3.26; Cr EFs: 1.73–3.23). Although increased, trace metal/TOC values remain low over this interval (Mo/TOC: 0.35–1.40; U/TOC: 0.90–3.46; V/TOC: 24.04–149.22). A third

**Table 1.** Geochemical data for the studied Miaohu Member samples from the Miaohu Section, South China. TOC – total organic carbon; TN – total nitrogen; EF – enrichment factor (normalized using upper continental crust values from McLennan, 2001).

Sample	Height (m)	TOC (wt%)	TN (wt %)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	$\delta^{15}\text{N}$ (‰)	Mo EF	V EF	U EF	Cr EF	Mo/TOC (ppm/wt%)	V/TOC (ppm/wt %)	U/TOC (ppm/wt %)	Fe <sub>carb</sub> (wt%)	Fe <sub>ox</sub> (wt %)	Fe <sub>mag</sub> (wt%)	Fe <sub>py</sub> (wt%)	Fe <sub>HR</sub> (wt%)	Fe <sub>T</sub> (wt %)	Fe <sub>HR</sub> /Fe <sub>T</sub>	Fe <sub>py</sub> /Fe <sub>HR</sub>
MR2	2	0.85	0.009	-38.19	2.41	4.29	1.44	2.96	2.35	0.91	21.71	1.16	0.01	0.32	0.04	0.003	0.37	0.57	0.65	0.009
MR2.5	2.5	-	0.016	-38.28	2.46	5.46	1.63	4.92	3.68	-	-	-	0.01	0.20	0.03	0.002	0.24	0.43	0.55	0.008
MR3	3	1.42	0.019	-38.07	3.47	2.20	1.73	3.07	2.62	0.48	26.94	1.25	0.01	0.09	0.01	0.001	0.10	0.22	0.46	0.009
MR5	5	0.89	0.039	-37.59	3.85	1.49	2.22	1.92	2.05	1.40	149.22	3.38	0.01	0.35	0.04	0.004	0.40	0.74	0.54	0.011
MR7	7	1.34	0.046	-37.89	3.15	1.00	1.76	1.73	1.73	0.84	105.90	2.73	0.01	0.28	0.03	0.003	0.32	0.63	0.51	0.009
MR7 FS	7.3	2.51	0.057	-37.89	3.50	0.89	2.50	1.58	2.39	0.27	54.27	0.90	0.03	0.29	0.02	0.006	0.35	0.68	0.51	0.016
M0.5	11.4	0.65	0.025	-36.93	2.19	2.30	2.77	3.75	3.07	1.14	97.83	3.46	0.02	0.77	0.09	0.003	0.88	1.11	0.79	0.003
M1	11.9	2.10	0.035	-37.52	2.32	3.26	3.16	5.92	3.23	0.35	24.04	1.18	0.01	0.23	0.03	0.004	0.27	0.42	0.65	0.013
M2	12.9	0.89	0.019	-37.40	2.76	3.76	2.16	4.31	2.43	0.79	32.29	1.69	0.04	0.41	0.02	0.019	0.48	0.59	0.82	0.039
M3.3	14.2	0.57	0.009	-37.21	3.28	5.47	2.16	3.95	2.63	0.75	21.21	1.02	0.02	0.17	0.01	0.000	0.21	0.28	0.73	0.000
M4.8	15.7	1.62	0.030	-37.37	2.21	3.69	2.93	5.00	3.48	0.54	30.78	1.38	0.01	0.35	0.04	0.002	0.40	0.55	0.73	0.006
MR5.8	16.7	-	-	-36.86	2.12	11.09	2.97	4.87	4.90	-	-	-	0.02	0.34	0.04	0.003	0.40	0.52	0.76	0.008
M6.3	17.2	0.67	0.008	-37.24	1.93	9.52	4.62	9.97	5.76	1.01	35.18	1.99	0.00	0.13	0.01	0.001	0.14	0.25	0.57	0.009
M7.3	18.2	0.49	0.008	-37.40	1.64	6.42	4.04	7.46	4.10	0.96	43.02	2.08	0.01	0.12	0.02	0.000	0.14	0.21	0.67	0.003
M8.8	19.7	0.46	0.006	-37.49	1.78	7.66	2.45	6.59	4.16	0.83	18.85	1.33	0.01	0.14	0.01	0.004	0.17	0.26	0.66	0.023
M10	20.9	1.26	0.022	-37.49	2.53	2.32	1.77	2.64	2.61	0.49	26.78	1.05	0.02	0.55	0.06	0.001	0.63	0.86	0.73	0.002
M11	21.9	2.69	0.043	-37.71	2.25	2.91	1.50	2.30	2.68	0.41	15.16	0.61	0.26	0.06	0.01	0.225	0.55	0.86	0.64	0.407
M12	22.9	2.33	0.034	-37.54	2.78	3.43	1.49	3.46	2.62	0.47	14.52	0.88	0.01	0.10	0.01	-	0.12	0.19	-	-
M14	24.9	0.57	0.013	-36.72	2.46	2.72	2.30	3.64	2.39	1.11	66.65	2.75	0.00	0.64	0.08	0.033	0.75	0.81	0.81	0.217
M15.5	26.4	0.10	0.010	-34.82	2.77	5.06	1.38	3.03	1.83	9.20	178.50	10.30	0.02	0.43	0.05	0.023	0.52	0.75	0.91	0.031



**Fig. 4.** Iron speciation, trace metal and  $\delta^{15}\text{N}$  data from the Miaohé Member (M) section at Miaohé.  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  values of  $< 0.22$  indicate deposition in an anoxic environment, while values of  $> 0.38$  suggest anoxia.  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  values of  $0.22\text{--}0.38$  represent possible anoxia and should be interpreted with caution.  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  values of  $< 0.6$  indicate deposition was in an anoxic-ferruginous setting, while values of  $> 0.8$  indicate euxinic conditions.  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  values of  $0.6\text{--}0.8$  record possible euxinia and should be interpreted with caution. Abbreviations:  $\text{Fe}_{\text{T}}$  – total iron;  $\text{Fe}_{\text{HR}}$  – highly reactive iron;  $\text{Fe}_{\text{py}}$  – iron pyrite; TOC – total organic carbon; DY – Dengying Formation; UD – Upper Dolostone. The location of the Miaohé Biota is indicated (Xiao *et al.* 2002).

interval occurs at a stratigraphic height of 12–21 m and is characterized by increased trace metal enrichment (Mo EFs: 2.32–11.09; V EFs: 1.77–4.62; U EFs: 2.64–9.97; Cr EFs: 2.43–5.76). Mo EFs are greater than Cr EFs, and low trace metal/TOC values similar to the first interval are also recorded (Mo/TOC: 0.49–1.01; U/TOC: 1.02–2.08; V/TOC: 18.85–43.02). Lastly, a interval of reduced trace metal enrichment is recorded at a stratigraphic height of 21–26.4 m (Mo EFs: 2.91–5.06; U EFs: 2.30–3.64; Cr EFs: 1.83–2.68). Patterns of trace metal enrichment are not observed and there is no clear relationship between Cr and Mo. V does not show enrichment, with recorded V EFs of 0.84–1.26, typical of average continental crust values. Although initially low, Mo/TOC, U/TOC and V/TOC values rapidly increase with increasing stratigraphic height (e.g. Mo/TOC values of 0.47, 1.11 and 9.20 at 22.9, 24.9 and 26.4 m, respectively).

As discussed previously, the samples used in Li *et al.* (2015) are less weathered than those used in this study (Fig. 3), providing an opportunity to investigate the potential effects of weathering on the distribution of redox-sensitive trace metals. The mean concentrations of Mo, V and Cr in our weathered samples are lower (online Supplementary Material) and statistically different (*t*-test, *P*-values  $< 0.05$ ) to those from Li *et al.* (2015). The mean enrichment factors are statistically different for Cr and V (*t*-test, *P*-values  $< 0.05$ ) but statistically indistinguishable for Mo (*t*-test, *P*-values  $> 0.05$ ) (online Supplementary Material). This suggests that the recorded enrichments of redox-sensitive trace metals may have been altered by weathering to some extent. Despite the discrepancy in enrichment factor values, the stratigraphic trends are broadly consistent and the impact on palaeoredox interpretation is limited.

#### 5.d. Nitrogen isotopes

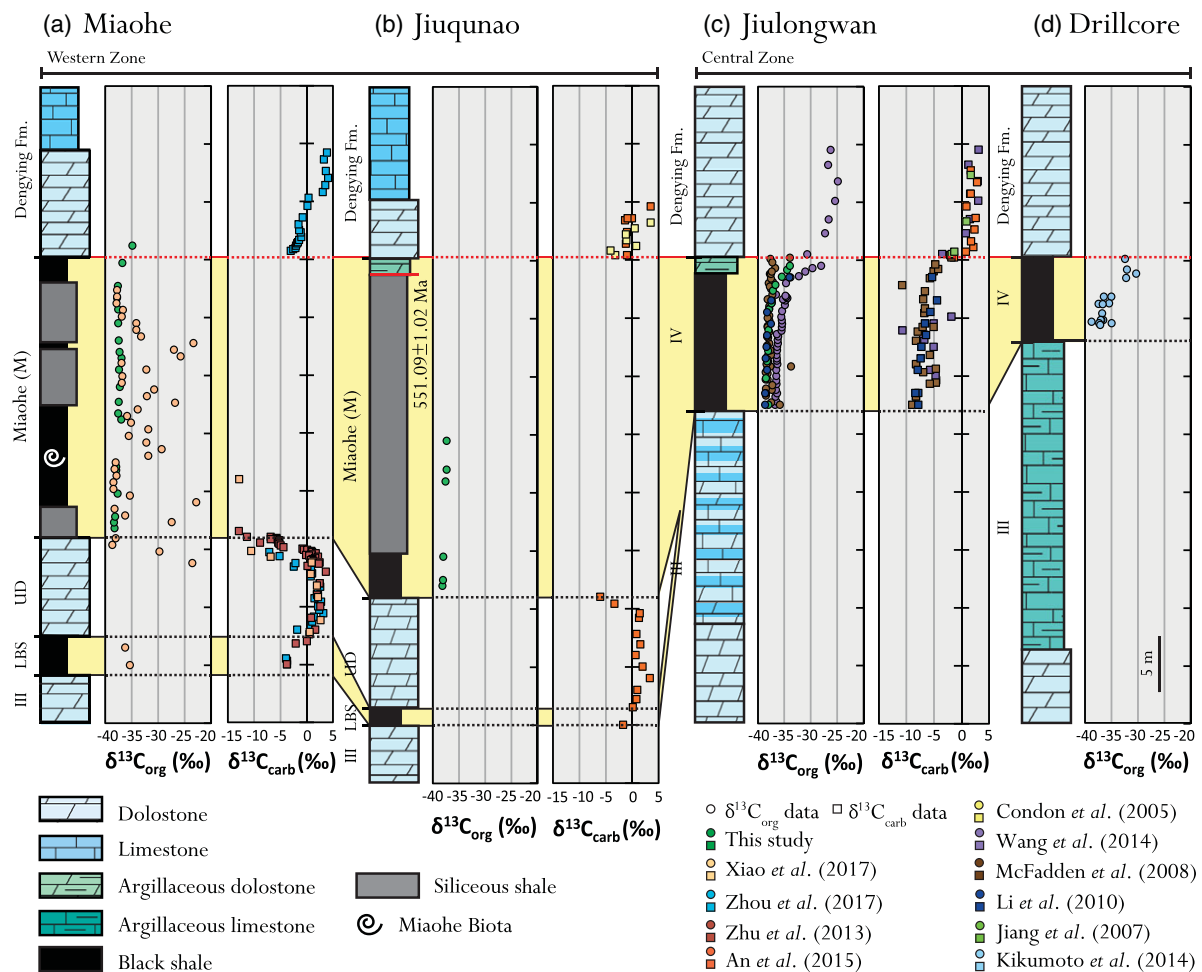
Sedimentary total nitrogen (TN) values for the Miaohé section samples range from 0.006 to 0.057 wt% (mean of 0.024 wt%).  $\delta^{15}\text{N}$  data are generally consistent, ranging from 3.85‰ at 5 m stratigraphic height to 1.64‰ at 18.2 m stratigraphic height (Table 1; Fig. 4). Generally,  $\delta^{15}\text{N}$  data show a steady decrease with increasing stratigraphic height upwards through the Miaohé section.

Although it is possible that clay-bound nitrogen may have influenced nitrogen isotope values, the strong positive covariation between TN and TOC ( $R^2 = 0.64$ ; online Supplementary Material) together with a near-zero intercept for Miaohé Member shales suggests that any contribution from allochthonous clay-bound N is limited. In addition, thermal nitrogen volatilization preferentially removes  $^{14}\text{N}$  during thermal maturation. There is no obvious covariation between  $\delta^{15}\text{N}$  and TN values for the Miaohé Member shales (online Supplementary Material), indicating limited impact on  $\delta^{15}\text{N}$  values.

#### 5.e. Carbon isotopes

Sedimentary TOC values for the Miaohé section samples range from 0.10 to 2.69 wt% (mean of 1.19 wt%) (Table 1). With the exception of a calcareous sample at 26.4 m stratigraphic height,  $\delta^{13}\text{C}_{\text{org}}$  values range from  $-36.7$  to  $-38.3$ ‰ (Table 1; Fig. 5) and therefore occur within the DST IV domain (McFadden *et al.* 2008; Li *et al.* 2010; Wang *et al.* 2014; Xiao *et al.* 2017). Generally, a subtle *c.* 3‰ increase in  $\delta^{13}\text{C}_{\text{org}}$  values with increasing stratigraphic height is observed. At Jiuqunao, TOC values for the upper black shale range from 0.55 to 5.63 wt% (mean of 2.80 wt%). Similar to at Miaohé,  $\delta^{13}\text{C}_{\text{org}}$  values at Jiuqunao are between  $-37.3$





**Fig. 5.** Lithostratigraphy,  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  profiles for Miaohé, Jiūqunāo (Western Zone), Jiūlóngwān and the drillcore site (Central Zone). The yellow zone indicates the correlation proposed in this study. UD – Upper Dolomite; LBS – Lower Black Shale; III – Doushantuo Member III; IV – Doushantuo Member IV. The location of the ash bed dated at  $551.09 \pm 1.02$  Ma by Schmitz (2012) is indicated, as is the location of the Miaohé Biota (Xiao *et al.* 2002).

and  $-38.1\text{‰}$  and therefore consistently within the DST IV domain (Fig. 5). A slight increase in  $\delta^{13}\text{C}_{\text{org}}$  values with increasing stratigraphic height is also observed. The  $\delta^{13}\text{C}_{\text{org}}$  values at Jiulongwan range from  $-33.9$  to  $-38.4\text{‰}$  (Fig. 5). A trend of increasing  $\delta^{13}\text{C}_{\text{org}}$  values upwards is observed, with the lower 10 samples recording values of less than  $-35\text{‰}$ , and the highest values occurring close to the boundary with the overlying Dengying Formation.

In general, thermal maturation during catagenesis and/or metamorphism would lead to preferential removal of  $^{12}\text{C}$  and loss of organic matter, thereby creating a diagnostic negative correlation between TOC and  $\delta^{13}\text{C}_{\text{org}}$  values. In the Miaohé section, only a very weak covariation between TOC and  $\delta^{13}\text{C}_{\text{org}}$  values is observed (online Supplementary Material). This suggests that the organic carbon isotopes have not been significantly influenced by thermal maturation.

## 6. Discussion

### 6.a. Carbon isotopes: chemostratigraphy and regional placement

Constraining the link between the Miaohé Biota and  $\delta^{13}\text{C}$  data at Miaohé, relative to  $\delta^{13}\text{C}$  data at adjacent sites, is necessary to ensure that a stratigraphic framework is developed for the Doushantuo

Formation that allows broader Ediacaran correlation. Recorded  $\delta^{13}\text{C}_{\text{org}}$  data for the Shibantan Member and DST IV at Jiulongwan are discrete; typically, Shibantan Member  $\delta^{13}\text{C}_{\text{org}}$  values are  $-25$  to  $-30\text{‰}$  (Wang *et al.* 2014), while DST IV  $\delta^{13}\text{C}_{\text{org}}$  values are constrained to  $-35$  to  $-40\text{‰}$  (McFadden *et al.* 2008; Li *et al.* 2010; Wang *et al.* 2014; Xiao *et al.* 2017). With the exception of a single calcareous sample at the Doushantuo–Dengying boundary, the  $\delta^{13}\text{C}_{\text{org}}$  data obtained from the Miaohé Member at Miaohé in this study are remarkably similar to  $\delta^{13}\text{C}_{\text{org}}$  data (this study; McFadden *et al.* 2008; Li *et al.* 2010; Wang *et al.* 2014) from DST IV at Jiulongwan (Fig. 5). It is therefore simple to infer at least partial correlation between the Miaohé Member and DST IV, and reject the inferred partial correlation with the younger Shibantan Member as proposed by An *et al.* (2015). In Xiao *et al.* (2017), the main objection to this correlation (referred to as the ‘Z’ correlation) was that several samples from the Miaohé Member at Miaohé record  $\delta^{13}\text{C}_{\text{org}}$  values within the ‘Shibantan Domain’. Interestingly,  $\delta^{13}\text{C}_{\text{org}}$  values from the same section in this study are significantly less variable, conforming to recorded values from DST IV at Jiulongwan (McFadden *et al.* 2008; Li *et al.* 2010; Wang *et al.* 2014; this study) and Jiūqunāo (this study).

Patterns of  $\delta^{13}\text{C}_{\text{org}}$  data also provide support for correlation of the Miaohé Member with DST IV (Fig. 5). At Jiulongwan, Jiūqunāo, Miaohé and the drillcore site described by Kikumoto

*et al.* (2014),  $\delta^{13}\text{C}_{\text{org}}$  data for the Miaohé Member (Miaohé, Jiulongwan) and DST IV (Jiulongwan, drillcore) behave similarly, with  $\delta^{13}\text{C}_{\text{org}}$  values for all sites and from all datasets increasing. Below the contact with the overlying Dengying Formation, several datasets also show an abrupt increase in  $\delta^{13}\text{C}_{\text{org}}$  values (Jiulongwan: this study; Li *et al.* 2010; Kikumoto *et al.* 2014; Wang *et al.* 2014). Although the increase at Miaohé is less pronounced, the uppermost sample from this study records a  $\delta^{13}\text{C}_{\text{org}}$  value of  $-34.82\%$ , a significant increase from  $-36.72\%$  recorded 1.5 m deeper in the section. Interestingly, this sample is calcareous and, although originally interpreted as part of the basal Hamajing Member, may have been collected from a minor argillaceous carbonate bed, similar to those observed at Jiulongwan (An *et al.* 2015; Xiao *et al.* 2017) and Jiulongwan (Condon *et al.* 2005; Zhu *et al.* 2007; Lu *et al.* 2013; An *et al.* 2015; Xiao *et al.* 2017). Although considered in this study to form part of the upper Doushantuo Formation, placement of this > 1 m thick carbonate unit has proved difficult; at Jiulongwan, it has been variously regarded as part of the basal Dengying Formation (Lu *et al.* 2013) or upper Doushantuo Formation (Condon *et al.* 2005; Zhu *et al.* 2007; An *et al.* 2015; Xiao *et al.* 2017). In addition to uncertainty over placement of this minor carbonate unit, it should be noted that the Dengying–Doushantuo contact is transitional, with variable expression depending on locality. It is therefore unlikely that the Dengying–Doushantuo contact has been consistently interpreted between sites. At Jiulongwan, an ash bed found underlying the minor argillaceous carbonate unit is used to date the uppermost Miaohé Member ( $550.55 \pm 0.75$  Ma, Condon *et al.* 2005;  $551.09 \pm 1.02$  Ma, Schmitz, 2012) and the placement of the minor carbonate bed has implications for constraining the timing of deposition of the Miaohé Member.

At Jiulongwan, Jiulongwan and Miaohé,  $\delta^{13}\text{C}_{\text{carb}}$  data further support correlation of the Miaohé Member with DST IV. For each site, multiple datasets record the same trend: an increase from negative  $\delta^{13}\text{C}_{\text{carb}}$  values at the Dengying–Doushantuo contact, to positive values further up the section (Jiang *et al.* 2007; Wang *et al.* 2014; An *et al.* 2015; Xiao *et al.* 2017; Zhou *et al.* 2017) (Fig. 5). This similarity between not only  $\delta^{13}\text{C}_{\text{org}}$  data, but  $\delta^{13}\text{C}_{\text{carb}}$  data for Miaohé, Jiulongwan, Jiulongwan and the drillcore site is unlikely to be coincidental, and a potential third correlation – that the Miaohé Member cannot be correlated with either the Shibantan Member or DST IV as tentatively discussed in Xiao *et al.* (2017) – can be rejected.

The DST IV  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{13}\text{C}_{\text{carb}}$  data from Baiguoyuan, a site located along the northern flank of the Huangling anticline (Qian *et al.* 1995; Zhuang *et al.* 1999; Wallis, 2006; Zhu *et al.* 2013; Och *et al.* 2016), provides further support for correlation of DST IV with the Miaohé Member at Miaohé. For this section, the same upwards recovery of  $\delta^{13}\text{C}_{\text{carb}}$  data (from  $-7.42\%$  to  $+4.86\%$ ) is recorded across the Dengying–Doushantuo contact, while  $\delta^{13}\text{C}_{\text{org}}$  data for DST IV remains within the ‘DST IV domain’ (see Xiao *et al.* 2017) and shows a consistency similar to  $\delta^{13}\text{C}_{\text{org}}$  data from DST IV at Jiulongwan (this study; McFadden *et al.* 2008; Li *et al.* 2010; Wang *et al.* 2014) and the Miaohé Member at Jiulongwan and Miaohé (this study).

Although  $\delta^{13}\text{C}$  data provide evidence for correlation of the Miaohé Member at Jiulongwan and Miaohé with DST IV, placement of the LBS unit is less clear. An *et al.* (2015) correlate the LBS with DST IV, while Zhou *et al.* (2017) and Xiao *et al.* (2017) consider the sum of the LBS, intermediate dolostone and Miaohé Member to correlate with DST IV. Zhou *et al.* (2017) suggest that, in the latter scenario, an eastwards facies change would result in the

disappearance of the intermediate dolostone in the Central Zone (Fig. 1b). Considering that basinal-scale rotational sliding occurred during deposition of the overlying lower Dengying/Liuchapo Formation (e.g. Vernhet *et al.* 2007; Zhu *et al.* 2013), and the recognition that such a slide is present at Miaohé (Zhu *et al.* 2013), we consider it more likely that the LBS, when present, represents a portion of DST IV that has acted as a slip surface, carrying deformed dolostones of the Hamajing Member (the intermediate dolostone with positive  $\delta^{13}\text{C}_{\text{carb}}$  values). This interpretation appears the most parsimonious explanation for the lack of such units, or related isotopic complexity at the relatively undisturbed Jiulongwan section in the east.

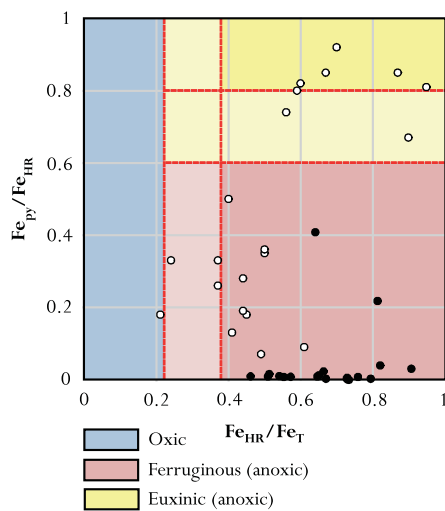
### 6.b. Palaeoredox proxies

Several studies indicate that the oceanic redox environment of southern China during the Ediacaran was spatially complex (e.g. Li *et al.* 2010, 2015; Och *et al.* 2016; Sahoo *et al.* 2016; Zhu *et al.* 2018). Previous Fe speciation, trace metal and pyrite framboid analyses from the Miaohé Member at Miaohé indicate that deposition of the lower, Miaohé Biota-associated shales was in a suboxic to anoxic but non-sulphidic environment, while the uppermost shales were deposited under euxinic conditions (Li *et al.* 2015). At the adjacent Jiulongwan and Jiulongwan sites, Fe speciation, trace metal and pyrite framboid data provide evidence for deposition in dominantly euxinic conditions (Li *et al.* 2010, 2015). New Fe speciation, trace metal and  $\delta^{15}\text{N}$  data are discussed below, providing additional redox information for the period of deposition of the Miaohé Member at Miaohé.

#### 6.b.1. Iron speciation and redox-sensitive trace metals

In this study,  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  values are all > 0.46 and therefore suggest persistent anoxia during deposition of the Miaohé Member (Fig. 4). Although Li *et al.* (2015) mainly record  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  values greater than the anoxic threshold (0.38) for the same section, several values at 4.9–6.9 m occur within the ‘possibly anoxic’ and ‘oxic’ domains, roughly the same stratigraphic height as the preserved Miaohé Biota (Fig. 4). It should be noted, however, that Li *et al.* (2015) record a greater number of data points over the fossiliferous section, and that the  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  data with the lowest values from this study occur over roughly the same interval.

Although most of the Miaohé Member at Miaohé was likely deposited in an anoxic water-column, distinguishing euxinic and anoxic-ferruginous conditions is more complex. The  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  ratios obtained in this study ( $0.00 \leq \text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}} \leq 0.41$ ) cannot be relied upon due to secondary pyrite weathering (see Section 5.a.; Figs 2, 3, 6).  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  data obtained from rocks of the same site and stratigraphic setting by Li *et al.* (2015) are consistently higher ( $0.07 \leq \text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}} \leq 0.92$ ) and, in the uppermost c. 10 m, indicative of euxinia (Fig. 4). In this current study, patterns of trace metal enrichment also support at least periodic euxinia, particularly in the uppermost Miaohé Member. For clarity, five discrete zones can be discerned using trace metals (Fig. 4): (1) euxinia at 2–3 m as indicated by moderate overall trace metal enrichment and an increased enrichment of Mo relative to Cr; (2) anoxic, non-sulphidic conditions between 3–6.5 m and 7.5–12 m, as indicated by an overall decrease in trace metal enrichment and the increased enrichment of Cr relative to Mo; (3) persistent euxinia at 12–21 m as indicated by a relatively rapid increase in trace metal enrichment, and an increased enrichment of Mo relative to Cr; (4) an anoxic, but not necessarily sulphidic environment, as indicated by decreasing trace metal concentrations and similar enrichments



**Fig. 6.**  $Fe_{HR}/Fe_T$  versus  $Fe_{py}/Fe_{HR}$  for this study (solid black points) and Li *et al.* (2015) (white points). Dotted red lines indicate thresholds: first, an  $Fe_{HR}/Fe_T$  value of  $> 0.38$  indicates anoxia, while a value of  $> 0.22$  indicates possible anoxia; and second, an  $Fe_{py}/Fe_{HR}$  value of  $> 0.8$  indicates euxinia, a value of  $> 0.6$  indicates possible euxinia and a value of  $< 0.6$  indicates ferruginous conditions.

of Mo and Cr at 21–26.4 m; and (5) an anoxic to suboxic setting during deposition of the shales at 7–8 m, whereby enrichments in U and V are minor and Mo is depleted (Fig. 3). Trace metal data for the same section from Li *et al.* (2015) are indicative of suboxic to anoxic, but non-sulphidic conditions; notably, Mo concentrations are  $< 3$  ppm and therefore close to crustal values. The  $Fe_{py}/Fe_{HR}$  ratios from Li *et al.* (2015) for the lower Miaohé Biota-associated shales mostly fall within the ferruginous domain (Figs 4, 6), although it is important to note that the proportion of  $Fe_{ox}$  found in some of these samples (e.g. MH-5 and MH-9; Li *et al.* 2015) could indicate secondary pyrite weathering (Fig. 3). Li *et al.* (2015) suggest that any impact of weathering on their samples was limited; however, it remains possible that the ferruginous signal recorded by the lowermost shales is inaccurate.

### 6.b.2. Nitrogen isotopes

Nitrogen isotope ( $\delta^{15}N_{sed}$ ) values from Miaohé Member samples are generally stable between 1.5 and 4‰, with the highest  $\delta^{15}N_{sed}$  values found in the lower half of the section (Fig. 4). Together with iron speciation and trace metal data, these  $\delta^{15}N_{sed}$  values imply redox stratification during deposition of the Miaohé Member. In a stratified water-column, nitrate is depleted by assimilation in the upper mixed layer and subsequently denitrified at the redox transition zone, below which ammonia accumulates and is quantitatively converted to  $N_2$  or  $N_2O$  by coupled nitrification, denitrification and anammox (Ader *et al.* 2014). Because of the different processes operating vertically in a stratified water mass, sedimentary nitrogen isotope values relate to the positioning of the intermediate redox transition zone. Typically,  $\delta^{15}N_{sed}$  values of  $c. 0$ ‰ can be expected in this setting due to nitrate limitation and productivity fuelled by  $N_2$ -fixation (Quan & Falkowski, 2009). Instead,  $\delta^{15}N_{sed}$  values of between 1.5 and 4‰ are recorded, implying partial nitrate availability and normal productivity. Additionally, a source of nitrate is necessary to sustain euxinia, and inferred nitrate availability during deposition of the Miaohé Member at Miaohé is consistent with the Fe speciation data from Li *et al.* (2015) and trace metal enrichments observed in this study. At Miaohé, it is possible that surface water carried nitrate from the open ocean across the sill of the

otherwise restricted basin, thereby reducing the influence of  $N_2$ -fixation on  $\delta^{15}N_{sed}$  values. Regardless, basin restriction would still have resulted in a nitrate-limited environment, with loss due to denitrification and assimilation. This is largely consistent with the hypothesis put forward by Kikumoto *et al.* (2014), where steadily decreasing  $\delta^{15}N_{sed}$  values upwards through the Doushantuo Formation are thought to be the result of oxygenation of the global ocean, oxidation of a dissolved organic carbon pool and a gradual increase in the nitrate reservoir. Evidence for this is also provided in the form of Mo and V concentrations (Scott *et al.* 2008; Och *et al.* 2016; Sahoo *et al.* 2016) and  $\delta^{34}S_{py}$ ,  $\delta^{98}Mo$  and  $\delta^{238}U$  data (McFadden *et al.* 2008; Chen *et al.* 2015; Kendall *et al.* 2015; Och *et al.* 2016; Sahoo *et al.* 2016; Shi *et al.* 2018; Ostrander *et al.* 2019).

Nitrogen isotope data are also available for the Jiuqunao, Jiulongwan and the drillcore correlative sites (Kikumoto *et al.* 2014; Och *et al.* 2016). For DST IV,  $\delta^{15}N_{sed}$  values at Jiulongwan are stable at  $c. 4$ ‰, while those at the drillcore site are broadly similar to  $\delta^{15}N_{sed}$  data from Miaohé ( $2.3$ ‰  $< \delta^{15}N_{sed} < 4.2$ ‰). A similar depositional setting to Miaohé can therefore be inferred, characterized by water-column stratification, partial nitrate availability and normal productivity. Lower values are found at Jiuqunao ( $0.5$ ‰  $< \delta^{15}N_{sed} < 2.5$ ‰), implying nitrate limitation and productivity fuelled by nitrogen fixation. Because of the close proximity of these sites, the different  $\delta^{15}N_{sed}$  values indicate a structurally complex depositional basin, with isotopic nitrogen values relating to (1) sill depth and (2) access to the open ocean and dissolved nitrate inventory.

### 6.c. Palaeogeographic control on local redox conditions

As previously mentioned, the Miaohé Member at Miaohé and Jiuqunao, and DST IV at Jiulongwan are thought to have been deposited in an intra-shelf lagoon environment (Vernhet & Reijmer, 2010; Jiang *et al.* 2011; Zhu *et al.* 2013). In this setting, intra-basinal water-column redox conditions would have related strongly to sill depth and communication with the open ocean. The trace metal/TOC proxy data examined in this study can be compared with data from modern anoxic systems to provide an insight into basin restriction and the palaeogeographic controls on redox conditions. For the Black Sea, typical renewal times and Mo/TOC values are  $c. 400$ – $800$  years and  $c. 4.5$ , respectively, while those for the Framvaren Fjord are  $c. 100$ – $125$  years and  $c. 9$ , respectively (Algeo & Rowe, 2012). Trace metal/TOC proxy values for the Miaohé Member are lower than those of the Black Sea, therefore implying basin restriction and limited communication generally during deposition. However, two discrete trace metal/TOC zones can also be discerned (Fig. 4): (1) a period of moderate restriction at stratigraphic height 2–12 m (e.g.  $0.27 < Mo/TOC < 1.40$ ;  $0.90 < U/TOC < 3.46$ ); and (2) a period of extensive restriction at stratigraphic height 12–23 m (e.g.  $0.35 < Mo/TOC < 1.01$ ;  $0.61 < U/TOC < 2.08$ ). The section of the Miaohé Member from 12 to 23 m also records high  $Fe_{py}/Fe_{HR}$  values and strong Mo, U, V and Cr enrichment, indicating that deposition of this unit occurred in a restricted basin characterized by poor ventilation, euxinia and extended water renewal times. Lastly, an abrupt increase in Mo/TOC, U/TOC and V/TOC values coincident with a lithological change from shale to dolostone occurs at stratigraphic height 23–25 m (Fig. 4).

Isotope data, including  $\delta^{34}S_{py}$ ,  $\delta^{98}Mo$  and  $\delta^{238}U$ , indicate widespread oxygenation during late Ediacaran time (McFadden *et al.* 2008; Chen *et al.* 2015; Kendall *et al.* 2015; Och *et al.* 2016; Sahoo *et al.* 2016; Shi *et al.* 2018; Ostrander *et al.* 2019). Redox conditions during deposition of the Miaohé Member and DST IV can

therefore be attributed to local basin configuration and restriction as indicated by trace metal/TOC proxy data. Several authors (e.g. Li *et al.* 2015; Och *et al.* 2016; Bowyer *et al.* 2017) discuss the importance of partially conflicting redox data despite the acute geographical proximity of several of the intra-basinal study sites. Building on the ‘sulphidic-wedge’ model proposed by Li *et al.* (2010), Och *et al.* (2016) and Bowyer *et al.* (2017) propose a scenario where local redox conditions would have related to the movement of a stratified euxinic wedge over subsequent silled basins due to eustatic sea-level change. In this setting, the sustained trace metal enrichment and  $\delta^{15}\text{N}_{\text{sed}}$  levels at Miaohe can be explained by surface water flow across the sill from the open ocean, where redox-sensitive trace metals were likely abundant. Communication with a largely oxygenated open ocean would have also provided a mechanism for infiltration by the low-diversity Miaohe Biota assemblage, the preservation of which at *c.* 7 m stratigraphic height implies sporadic oxygenation and eustatic change, albeit in a generally oxygen stressed environment. Although sedimentary trace metal enrichments and sustained euxinia at Jiulongwan (Li *et al.* 2010) similarly indicate access to the open ocean, low Mo enrichments (Li *et al.* 2015; Och *et al.* 2016) and lower  $\delta^{15}\text{N}_{\text{sed}}$  values (Och *et al.* 2016) at Jiuqunao imply sustained restriction and limited access to the open-ocean nitrate and redox-sensitive trace metal inventories. Because of the close proximity of these sites, considerable basin complexity can be inferred.

To summarize, eustatic sea-level change would have controlled communication between the structurally complex intra-shelf basin and the open ocean. During a period of eustatic sea-level rise, increased nitrate availability would have fuelled productivity, enabling the development of euxinic bottom water. In this setting, trace metals from the open ocean would have been easily scavenged and sequestered by Miaohe Member sediments. At more proximal locations, access to the open ocean was reduced, euxinia was inhibited and trace metals were not easily scavenged.

#### 6.d. Palaeoredox and evolution of the Miaohe Biota

Molecular evidence points to the emergence of complex metazoans, including crown-group demosponges and cnidarians prior to deposition of the Miaohe Member (Erwin *et al.* 2011). Despite this, the Miaohe Biota comprises a simple, low-diversity assemblage. This lack of complexity is likely the result of quasi-continuous anoxic-stress within the intra-shelf lagoon environment; however, nutrient availability, water energy and temperature fluctuations could have also contributed (Li *et al.* 2015). In this restricted setting, periodic access to the open ocean could have provided partial relief from these stresses, enabling simple metazoan communities to persist. This is consistent with their occurrence during a period of inferred eustatic sea-level rise. As previously noted by Li *et al.* (2015), the Miaohe Biota colonization is linked to spatially variable redox patterns. At Jiulongwan and in the overlying Miaohe Member at Miaohe, euxinia and toxic stress would have inhibited metazoan colonization, while the absence of the Miaohe Biota at Jiuqunao is likely due to isolation from the open ocean. If continental margins at other locations globally were similarly redox-stressed, then the suppression of evolution can be inferred for the late Ediacaran.

## 7. Conclusions

The Miaohe Member has previously been partially correlated with DST IV (Xiao *et al.* 2017; Zhou *et al.* 2017) or with the younger Shibantan Member of the Dengying Formation (An *et al.* 2015).

New Miaohe Member  $\delta^{13}\text{C}$  data from Miaohe and Jiuqunao are remarkably similar to  $\delta^{13}\text{C}$  data from DST IV at Jiulongwan, and partial correlation with DST IV at Jiulongwan can therefore be inferred. Although Zhou *et al.* (2017) and Xiao *et al.* (2017) consider the sum of the LBS, intermediate dolostone and Miaohe Member to correlate with DST IV, it is likely that the LBS represents a portion of the Miaohe Member that has acted as a slip surface, carrying deformed dolostones of the Hamajing Member (the intermediate dolostone). This interpretation appears to be the most parsimonious explanation for the lack of such units, or related isotopic complexity at the relatively undisturbed Jiulongwan section in the east.

New  $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$  data from the Miaohe Member at Miaohe is indicative of sustained anoxia, while patterns of redox-sensitive trace metal enrichment imply water-column euxinia during deposition of the uppermost Miaohe Member shales. Miaohe Biota-associated and over- and underlying shales record limited relative Mo enrichment and were likely deposited in a predominantly anoxic but non-euxinic setting. These conclusions are largely supported by  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  data from Li *et al.* (2015). Secondary oxidative weathering and  $\text{Fe}_{\text{py}}$  depletion is recorded by the samples obtained for this study, and  $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$  ratios therefore cannot be interpreted.

Trace metal/TOC proxy values indicate that the Miaohe Member at Miaohe was deposited in a water-column characterized by restriction and limited renewal. Despite this, sustained trace metal concentrations and  $\delta^{15}\text{N}_{\text{sed}}$  values imply at least partial access to open-ocean inventories. As discussed in Och *et al.* (2016) and Bowyer *et al.* (2017), it is likely that communication with the open ocean at Miaohe, Jiuqunao, Jiulongwan and other intra-shelf basin sites was controlled by a sill; during periods of eustatic sea-level rise, nitrate and trace metal inventories would have been replenished, thereby facilitating the development of euxinic bottom water. The intra-shelf basin was also likely characterized by significant structural complexity, with limited communication between sites. At more proximal locations such as Jiuqunao, access to the open ocean would have been reduced, inhibiting water-column euxinia. This environmental stress could have influenced Ediacaran metazoan development in southern China and other similar sites globally.

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