Marine Mo biogeochemistry in the context of dynamically euxinic mid-depth waters: A case study of the lower Cambrian Niutitang shales, South China

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Abstract

Molybdenum (Mo) concentrations and Mo isotopes have been widely used as proxies for local and global redox conditions in early oceans (>520 Ma) that were stratified and characterized by dynamically euxinic mid-depth waters. However, the nature of the Mo cycle and accompanying isotopic fractionations in such oceans remain poorly known. To fill this gap, we conducted an integrated study of Mo isotopes and redox-sensitive trace element (RSTE) abundances in the Lower Cambrian Niutitang Formation at Yangjiaping, South China. This section accumulated on the northern shelf margin of the Nanhua Basin, a failed intracontinental rift basin with a good connection to the open ocean during the early Cambrian. The Niutitang Formation contains a ~18-m-thick lower black shale member, and a ~56-m-thick upper gray silty shale member. The lower member (LM) is moderately to strongly enriched in Mo, U and V, and heterogeneous in Mo isotopic composition ($\delta^{98}\text{Mo} = -0.65\text{‰}$ to $+2.14\text{‰}$), indicative of dominantly euxinic depositional conditions punctuated by ferruginous episodes (as shown by previously reported Fe speciation data). The upper member (UM) shows lesser enrichment of Mo, U and V, higher Mo/U ratios, and intermediate and more uniform Mo-isotopic compositions ($\delta^{98}\text{Mo} = +1.16\text{‰}$ to $+1.71\text{‰}$), indicative of weakly oxic to anoxic-euxinic depositional conditions. Geochemical profiles suggest that the LM-to-UM transition reflects a shift of the $\text{O}_2/\text{H}_2\text{S}$ chemocline from the water column to the sediment. Large $\delta^{98}\text{Mo}$ fluctuations in the LM may record variations of H_2S concentrations in the mid-depth euxinic waters. The intermediate and relatively uniform $\delta^{98}\text{Mo}$ values of the UM are attributed to the effects of a local Fe-Mn particulate shuttle.

In light of the observations at Yangjiaping and other contemporaneous sections in the Nanhua Basin, we propose a new marine Mo biogeochemical model for the early Cambrian ocean. In this model, an Fe-Mn reduction zone may have developed above mid-depth euxinic waters in nearshore areas of the Nanhua Basin due to relatively high availability of fluvial Fe-Mn oxides and their subsequent reduction below the chemocline. Within this redox framework, large sedimentary $\delta^{98}\text{Mo}$ variations observed for the Niutitang shales can be explained through the combined effects of Mo isotopic fractionation associated with adsorption onto Fe-Mn-oxides and spatially variable H_2S concentrations in the euxinic watermass. By compiling published data, we found that the large sedimentary $\delta^{98}\text{Mo}$ variations previously observed in the early Cambrian

Nanhua Basin and in other Neoproterozoic-Cambrian marine basins can be similarly explained. Our model provides a novel interpretation of the Mo biogeochemistry of early Earth oceans, within the framework of which Mo isotopes may serve to further our understanding of the oxygenation history of the Earth-surface system.

Keywords: Mo isotope; Nanhua Basin; Fe-Mn shuttle; Niutitang Formation; early Cambrian

1. INTRODUCTION

Recent studies of ancient seawater redox conditions have shown that anoxic, stratified oceans were dominant prior to and during the early Cambrian (hereafter termed “early oceans”) (Li et al., 2010; Poulton et al., 2010; Planavsky et al., 2011; Feng et al., 2014). In these oceans, the surface and deep layers were characterized by oxic and ferruginous conditions, respectively, whereas a fluctuating, dynamically maintained “euxinic wedge” generally developed at mid-depths (Li et al., 2010; Li et al., 2015). The secular redox evolution of early oceans is reflected in variations between these three redox environments (Canfield et al., 2008; Poulton and Canfield, 2011; Guilbaud et al., 2015). Molybdenum (Mo) isotopes in organic-rich mudstones have been extensively utilized as a proxy to track the oxygenation state of ancient seawater at both a local and global scale (Arnold et al., 2004; Kendall et al., 2009; Dahl et al., 2010; Dahl et al., 2011; Kendall et al., 2011; Chen et al., 2015; Cheng et al., 2015). The interpretation of Mo isotopes as a global-scale redox proxy depends on the quantitative uptake of seawater Mo by the sediment under strongly euxinic conditions, thus reducing isotopic fractionation to near zero, versus large fractionations for Mo accumulating in oxic sediments. However, we still know relatively little about the Mo biogeochemical cycle of stratified early oceans.

The Nanhua Basin, a failed intracratonic rift basin in South China (Fig. 1A) that contains a continuous stratigraphic succession from the Cryogenian to the middle Cambrian, is an exceptional field area for the study of biological and geochemical processes in early oceans. The Cambrian strata in the Nanhua Basin record a rapid radiation of animals and the first appearance of many invertebrate phyla, i.e., the “Cambrian Explosion” (Knoll and Carroll, 1999; Erwin et al.,

2011). Studies have shown that the stratified structure characteristic of Neoproterozoic oceans extended into early Cambrian (Feng et al., 2014; Wen et al., 2014; Fu et al., 2016; Jin et al., 2016). To date, a number of Mo isotope studies have been undertaken on Cambrian strata of the Nanhua Basin (Lehmann et al., 2007; Wen et al., 2011; Xu et al., 2012; Chen et al., 2015; Wen et al., 2015), yielding results that seem contrary to observations from modern marine systems, for example, fluctuating isotopic compositions for euxinic sediments and relatively high $\delta^{98}\text{Mo}$ values for oxic sediments. These unusual features may have been due to the unique redox structure of the early Cambrian ocean, as discussed herein.

The earliest Cambrian Niutitang Formation at Yangjiaping, which was located at the shelf margin of the Nanhua Basin (Fig. 1B), records a distinctive stratigraphic succession (Fig. 1C) that reflects basinward movement of the euxinic wedge (Feng et al., 2014). Thus, this section provides an excellent opportunity to investigate changes in the Mo isotope composition of the sediment associated with the redox transition from euxinic to weakly oxic waters within a stratified ocean. In this study, we aim to explore the effect of the mid-depth euxinic wedge on the oceanic Mo biogeochemical cycle and to develop an integrated paleoceanic model for the early Cambrian Nanhua Basin. Furthermore, an improved understanding of Mo cycling within early oceans will help to better define the potential and limits of Mo isotopes as a proxy for reconstruction of paleocean redox conditions and the history of oceanic oxygenation.

2. BACKGROUND: THE OCEANIC Mo CYCLE AND Fe-Mn SHUTTLES

Mo is present in modern seawater mainly as the molybdate anion (MoO_4^{2-}), which is conservative and highly soluble, resulting in a relatively high concentration (~104 nM) and a long residence time (0.44 Myr) in seawater (Miller et al., 2011). As the residence time of Mo is much longer than the ocean mixing time (1-2 ky) (Collier, 1985), seawater has a nearly uniform Mo isotopic composition ($\delta^{98}\text{Mo} = +2.3\text{‰}$) (Siebert et al., 2003). Mo removal to the sediment varies as a function of watermass redox conditions. In oxic waters, Mo is removed slowly through adsorption to manganese oxides (Mn_{ox}), yielding a light Mo isotopic composition ($\delta^{98}\text{Mo} = -0.7\text{‰}$) in the adsorbed fraction (Barling and Anbar, 2004). Mo adsorption to iron oxides/oxyhydroxides

(Fe_{ox}) under weakly oxic conditions results in a variable fractionation ($\Delta^{98}\text{Mo} = \delta^{98}\text{Mo}_{\text{seawater}} - \delta^{98}\text{Mo}_{\text{Fe-ox}} = 0.83\text{‰}$ to 2.19‰) (Goldberg et al., 2009). In euxinic waters, aqueous H₂S can effectively break the Mo=O bond, transforming MoO₄²⁻ into oxythiomolybdate species (MoO_{4-x}S_x²⁻, x = 1-4) (Helz et al., 1996). Under these conditions, Mo is actively scavenged into sediments at a rate that can be 100- to 1000-fold greater than that in oxic environments (Scott et al., 2008). Below a certain concentration of aqueous H₂S (~11 μM) (Erickson and Helz, 2000), the Mo isotopic composition of the sediment is controlled by redox-related fractionation (Neubert et al., 2008). Above this [H₂S]_{aq} threshold, almost all molybdate is converted to tetrathiomolybdate (MoS₄²⁻) and transferred quantitatively to the sediment via adsorption onto organic matter or incorporation into Fe-S-Mo nanoparticles (Algeo and Lyons, 2006; Helz et al., 2011), yielding a sediment Mo isotopic composition equal to that of the seawater source.

MoO₄²⁻ shows an affinity for Fe-Mn oxyhydroxides (Fe-Mn_{ox}) possible via forming polynuclear Mo oxides (Wasylenki et al., 2011), onto which it readily adsorbs and which can lead to accelerated removal of Mo to the sediment. As a result, ferromanganese sediments (i.e. nodules, crusts and red clays etc.) on the abyssal seafloor show Mo enrichments to 100s of ppm (Morford and Emerson, 1999), accounting for ~35-50% of the modern seawater Mo sink flux (Scott et al., 2008; Kendall et al., 2009). MoO₄²⁻ also readily adsorbs onto Fe-Mn_{ox} particulates that originate as fluvial sediment or that form at the oxic/anoxic chemocline in redox-stratified water bodies through oxidation of upward diffusing Fe²⁺_(aq) and Mn²⁺_(aq) (Algeo and Tribovillard, 2009; Scholz et al., 2013). The sinking Fe-Mn particulates transfer adsorbed Mo into anoxic waters below the chemocline, creating a “Fe-Mn shuttle”. Mo is subsequently released through reductive dissolution, leading either to an aqueous Mo maximum just below the chemocline (Shimmield and Price, 1986) or to elevated Mo concentrations in sediment porewaters if Fe-Mn particulates reach the sediment-water interface before dissolving (Morford et al., 2005). In the latter case, part of the released Mo may diffuse back into the overlying water column, but also a fraction is generally taken up by the sulfidic sediment (Morford and Emerson, 1999; Scott and Lyons, 2012; Dahl et al., 2013). The degree of redox variability of a given environment and the vertical stability of the chemocline strongly influence the operation of an Fe-Mn shuttle (Algeo and Tribovillard, 2009).

3. GEOLOGICAL SETTING

The Nanhua Basin formed through rifting at ~820 Ma, or possibly earlier, during breakup of the Rodinia supercontinent (Wang and Li, 2003; Peng et al., 2012), and it evolved into a failed intracratonic rift basin by the Ediacaran (Fig. 1A) (Jiang et al., 2003; Li et al., 2008). Paleogeographic reconstructions for the early Cambrian show shallow platform, slope, and basin environments along a northwest-southeast transect based on lithological change from shallow carbonates to basinal black shales or mudstones during the Fortunian (Fig. 1B) (Goldberg et al., 2007). Widely deposited black shales of the basal Niutitang Formation may record a global transgression in the early Cambrian (Wang et al., 1998; Zhu et al., 2003; Miller et al., 2006).

The Yangjiaping section is located in Yangjiaping village, Shimen County, northwestern Hunan Province. At Yangjiaping, the Niutitang Formation comprises, in ascending order: (1) basal beds including ~2.25 m of carbonaceous shale, <1 m of phosphatic sediment, and ~7 m of silty shale (not included in the present study); (2) a ~18-m-thick black shale (lower member; LM); and (3) a ≥ 56 -m-thick gray silty shale (upper member; UM) (Fig. 1C). The lithological change in UM relative to LM apparently suggests a following marine regression in the basin. The Ni-Mo polymetallic layer at the base of the LM (not exposed at Yangjiaping) is an important marker horizon for stratigraphic correlation across the Nanhua Basin (Och et al., 2013). SHRIMP zircon U-Pb dating of an ash bed below the Ni-Mo layer yielded ages of 532.3 ± 0.7 Ma (Zunyi section, Guizhou Province; Jiang et al., 2009), 536.3 ± 5.5 Ma (Ganziping section, Hunan Province; Chen et al., 2009), and 526.4 ± 5.4 Ma (Three Gorges section, Hubei Province; Okada et al., 2014) (Fig. 1C). Re-Os isotopic dating of the Ni-Mo polymetallic layer gave an age of 521 ± 5 Ma (Dazhuliushui and Maluhe sections in Guizhou Province and Sancha section in Hunan Province; Xu et al., 2011). The base of the LM of the Niutitang Formation thus dates to >521 Ma.

The Meishucunian Stage of the lower Cambrian in South China (equivalent to the Fortunian Stage and Stage 2 of the global Terreneuvian Series) is characterized by the appearance of four small shelly fossil assemblages (SSF 1-4), which can serve as important regional and intercontinental marker beds (Xiao et al., 2005; Steiner et al., 2007). SSF1, whose occurrence defines the Neoproterozoic-Cambrian boundary (Zhu et al., 2001), has been found within the

~2.25-m-thick carbonaceous shale of the basal beds at Yangjiaping (Fig. 1B) (Steiner et al., 2004). Higher in the Yangjiaping section, silty shales at ~110 m yielded fragments of trilobites such as *Hunanocephalus* sp. that first appeared at ~521-514 Ma, during the Qiongzhusian Stage of the lower Cambrian in South China (equivalent to Stage 3 of the global Series 2; Fig. 1C) (Yin et al., 1999), constraining the age of the upper part of the UM of the Niutitang Formation. In combination with the radiometric ages above, the study interval (i.e., the LM and UM of the Niutitang Formation at Yangjiaping) can most likely be assigned to global Cambrian stages 2-3 (529-514 Ma; Fig. 1C) (Cohen et al., 2013; updated).

4. SAMPLES AND METHODS

A total of 45 samples from the LM (20 samples) and UM (25 samples) of the Niutitang Formation in the Yangjiaping section, which were previously analyzed for sedimentary Fe speciation, Mo abundance, total organic matter (TOC), and pyrite S isotopes by Feng et al. (2014), were used in this study for further geochemical analyses. These samples were collected from the freshest rock exposures and samples that contain readily visible pyrite nodules or bands were discarded prior to crushing to minimize the inclusion of materials impacted most severely by later diagenesis (Feng et al., 2014). Sample powders were first ashed for ~8 h at 600°C in a muffle furnace to remove organic matter. Of the 45 samples, 16 that were inferred to have been deposited in a euxinic environment were selected for analysis of Mo isotopes and trace element (U, V) abundances.

For trace-element analysis, 50 mg of ashed powder were weighed into a Teflon beaker and dissolved using a standard HF-HNO₃-HCl protocol at a high temperature (190°C). All trace elements were analyzed by inductivity coupled plasma mass spectrometry (ICP-MS) (Agilent 7700) at the State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences (Wuhan). Internal reference standards BHVO-2 and BCR-2 were analyzed simultaneously to monitor data quality. Accuracy is better than 10% and the analytical precision is ~0.5% of reported values. Enrichment factors (EFs) for trace elements were calculated as:

$$X_{EF} = (X/Al)_{\text{sample}} / (X/Al)_{\text{AUCC}} \quad (1)$$

where X is the element of interest (e.g., Mo), and AUCC is average upper continental crust (McLennan, 2001). For correlative sections without published Al concentration data, Zr, Ti or Sc was used for normalization instead.

A procedure similar to that described in Zhou et al. (2015) was used for Mo isotope analysis. Depending on the Mo concentration of a sample, from 10 to 50 mg of powder was weighed out. A ^{97}Mo - ^{100}Mo double spike, which was calculated based on the Mo concentration and sample mass, was added to the sample, which was then digested using the same procedure as for trace-element analysis. The Mo content of the sample was purified in two steps: the anion resin GPM-1M (Bio-Rad) was first used to separate Mo and most Fe from the matrix, and the cation exchange resin AG50W-X8 (Bio-Rad) was then used to separate Mo from the remaining Fe and Zr. Mo isotope measurements were performed using a Neptune plus MC-ICP-MS instrument (Thermo Fisher Scientific) at the State Key Laboratory of Geological Process and Mineral Resources, China University of Geosciences (Wuhan). Results are reported using δ notation in per mil relative to the Johnson Matthey Company (JMC) Specpure Mo plasma standard (lot 602332B):

$$\delta^{98}\text{Mo} = ((^{98}\text{Mo}/^{95}\text{Mo})_{\text{sample}} / (^{98}\text{Mo}/^{95}\text{Mo})_{\text{JMC}} - 1) \times 1000\text{‰} \quad (2)$$

Relative to JMC standard, NIST SRM 3134, which is appealed as the international standard, has a value of $+0.27 \pm 0.06\text{‰}$ (Goldberg et al., 2013; Nägler et al., 2013). Using the JMC standard, the Mo isotopic compositions of modern seawater and the international standard SDO-1 (Devonian Ohio Shale) are $+2.3\text{‰}$ and $+1.10\text{‰}$, respectively. The reproducibility of the measured $\delta^{98}\text{Mo}$ ratios is better than 0.07‰ . The long-term external reproducibility for the replicate measurements of the standard reference materials is better than 0.05‰ .

To correct for minor amounts of terrigenously sourced Mo, the isotopic composition of the authigenic Mo fraction ($\delta^{98}\text{Mo}_{\text{auth}}$) was calculated using Mo = 1.5 ppm, Al = 8.04%, and $\delta^{98}\text{Mo} = +0.36\text{‰}$ as the parameters for the AUCC endmember (McLennan, 2001; Dahl et al., 2011). Calculated $\delta^{98}\text{Mo}_{\text{auth}}$ values are close to measured $\delta^{98}\text{Mo}$ values ($\delta^{98}\text{Mo}_{\text{auth}} = 1.0138 \times \delta^{98}\text{Mo} + 0.016$; $R^2 = 0.995$; $n = 16$, $p(\alpha) < 0.001$) because terrigenous Mo comprises only a small fraction of total Mo in most samples ($3.6 \pm 4.0\%$). Only the $\delta^{98}\text{Mo}_{\text{auth}}$ results are discussed below, and henceforth $\delta^{98}\text{Mo}$ refers to $\delta^{98}\text{Mo}_{\text{auth}}$.

5. RESULTS

The $\delta^{98}\text{Mo}$ results and other geochemical data for the study are given in Appendix Table A and shown in Figure 2. The black shales of the LM show fluctuating $\delta^{98}\text{Mo}$ values between -0.65‰ and $+2.14\text{‰}$, whereas the gray silty shales of the UM yield more uniform $\delta^{98}\text{Mo}$ values of $+1.16\text{‰}$ to $+1.71\text{‰}$ (Fig. 2). The Mo isotopic data from the Yangjiaping section are scattered over almost the entire range of reported $\delta^{98}\text{Mo}$ values from modern sediments (ca. -0.7‰ to $+2.3\text{‰}$), and they show no relationship to Mo concentrations ($R^2 = 0.00$, not shown). However, most samples (11 of 16) yield $\delta^{98}\text{Mo}$ values between $+1.0\text{‰}$ and $+1.7\text{‰}$, with only one sample $>2.0\text{‰}$ and two samples $<0\text{‰}$.

RSTEs are enriched throughout the study section, although the degree of enrichment is greater in the LM ($\text{Mo}_{\text{EF}} = 74\text{-}526$, $\text{U}_{\text{EF}} = 16\text{-}68$, and $\text{V}_{\text{EF}} = 6\text{-}76$) than in the UM ($\text{Mo}_{\text{EF}} = 8\text{-}44$, $\text{U}_{\text{EF}} = 2\text{-}8$, and $\text{V}_{\text{EF}} = 1\text{-}7$) (Fig. 2). Mn enrichments contrast with those of Mo, U and V, showing higher values in the UM than in the LM (Fig. 2).

6. DISCUSSION

Sedimentary $\delta^{98}\text{Mo}$ is controlled by local watermass redox conditions, basinal restriction, and mean global oceanic oxygenation status. Below, we will discuss each of these mechanisms separately to explore possible cause(s) for patterns of $\delta^{98}\text{Mo}$ variation in the Yangjiaping section and for the early Cambrian Nanhua Basin as a whole.

6.1. Marine redox conditions at Yangjiaping

Mo behavior and accompanying isotopic fractionations in the ocean are mainly controlled by marine redox conditions. Iron speciation and RSTE (Mo, U, V) enrichment are used here as proxies for local water-column redox conditions. Generally, a ratio of highly reactive iron to total iron ($\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$) of >0.38 indicates anoxic conditions, with pyrite-to-highly-reactive-iron ratios ($\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$) of <0.7 and >0.7 distinguishing between ferruginous and euxinic environments,

respectively (Raiswell and Canfield, 2012). Uranium behaves conservatively in oxic waters but is taken up rapidly by the sediment at Fe reducing conditions (Tribovillard et al., 2006). Vanadium is reduced in a stepwise manner, from V^{5+} to V^{4+} under mildly reducing conditions and to V^{3+} under euxinic conditions, resulting in significant enrichment in anoxic systems (Algeo and Maynard, 2004; Tribovillard et al., 2006). High enrichments of these RSTEs (see Section 2 for a description of Mo enrichment) indicate deposition of sediment in a persistently euxinic environment, i.e., with a stable chemocline within the water column.

The lower LM (LM-1, 0-8.8 m) yields low Fe_T (0.2-0.6%, average 0.4%), which is comparable to the analytical error of 0.2% in Fe speciation analysis, making redox interpretations based on iron ratios less secure (Clarkson et al., 2014). Fe_T concentrations show an abrupt increase to 4.4% at 9.3 m and a gradual decrease back to <1% upsection. In this interval (LM-2, 9.3-16.3 m), Fe_{HR} and Fe_T exhibit a good correlation ($R^2 = 0.99$, $p(\alpha) < 0.01$) with an average Fe_{HR}/Fe_T ratio of 0.75, indicating that total Fe is dominated by the highly reactive iron fraction. The Fe peak at 9.3 m may represent remobilized Fe from oxic shallow-shelf areas or inputs of Fe-bearing water from a deep ferruginous basin via a marine transgression or upwelling event (Raiswell and Canfield, 2012). The upsection decrease in Fe_T above 9.3 m was accompanied by an increase in Fe_{py}/Fe_{HR} from mostly <0.7 to >0.7, indicating a transition from ferruginous to euxinic conditions that was probably caused by decreased Fe inputs. The sample YB18 at 14.8 m contains almost no Fe_{py} but high Fe_{ox} which is explained by Feng et al. (2014) as a result of modern oxidative weathering of pyrite in this sample. Both LM-1 and LM-2 show high enrichments in Mo ($Mo_{EF} = 74-526$, average 222 for LM-1 and 133-215, average 165 for LM-2), U ($U_{EF} = 24-68$, average 42 for LM-1 and 16-30, average 23 for LM-2) and V ($V_{EF} = 11-198$, average 58 for LM-1 and 7-20, average 11 for LM-2), indicating strongly euxinic depositional conditions for most samples. LM-2 exhibits a weak decrease in RSTE enrichment relative to LM-1, which was possibly related to a transient shift from euxinic to ferruginous conditions due to the iron pulse that peaked at 9.3 m. In summary, LM-1 accumulated under persistently euxinic, Fe-limited conditions, whereas LM-2 records ferruginous conditions at its base caused by an Fe pulse, followed by a transition to euxinic conditions upsection.

The gray silty shales of the UM contain >1% Fe_T (1.2-4.1%, average 2.6%), allowing local

redox conditions to be evaluated on the basis of iron speciation data (Fig. 2). $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ranges from 0.08 to 0.58 with an average of 0.34 ± 0.14 , whereas $\text{Fe}_{\text{py}}/\text{Fe}_{\text{HR}}$ ranges from 0 to 0.91 with an average of 0.46 ± 0.35 . This combination of iron ratios suggests deposition under fluctuating, weakly oxic (where Mn oxides precipitate) to anoxic-ferruginous bottomwater conditions with occasional episodes of weak euxinia. RSTE concentrations for the UM support this interpretation. Mo removal under weakly oxic conditions is less efficient than under euxinic conditions (Scott and Lyons, 2012), and the modest enrichment of Mo in the UM ($\text{Mo}_{\text{EF}} = 6\text{--}76$, mean 25; Fig. 2) is consistent with the occasional presence of H_2S in bottom waters but excludes persistently euxinic conditions. Mo probably accumulated in the UM either through adsorption onto Mn- Fe_{ox} particulates in the water column (Dellwig et al., 2010) or through uptake from Mo-limited sulfidic sediment porewaters (Scott and Lyons, 2012). In addition, U and V show minimal enrichments ($\text{U}_{\text{EF}} = 4 \pm 2$; $\text{V}_{\text{EF}} = 3 \pm 2$), which are also consistent with weakly oxic to anoxic-ferruginous conditions of deposition. Redox fluctuations during deposition of the UM may reflect vertical movements of the $\text{O}_2/\text{H}_2\text{S}$ chemocline across the sediment-water interface.

The gradual decline in Mo, U and V enrichments upsection (Fig. 2) suggests that the average position of the $\text{O}_2/\text{H}_2\text{S}$ chemocline gradually shifted from within the water column during LM deposition to close to the sediment-water interface during deposition of the lower UM, and then downward into the sediment during deposition of the upper UM. For this reason, only the euxinic sediments in the LM offer a potential record of contemporaneous seawater $\delta^{98}\text{Mo}$, whereas local redox conditions were the dominant influence on $\delta^{98}\text{Mo}$ through the remainder of the section.

6.2. Restriction of early Cambrian Nanhua Basin?

Restriction of watermass exchange with the open ocean can limit Mo availability in cratonic basins and influence Mo isotopic fractionations during authigenic uptake by the sediment. Several lines of evidence indicate that the early Cambrian Nanhua Basin had good connection with open ocean. First, global paleogeographic reconstructions for the early Cambrian show South China as an isolated continent surrounded by the open ocean (Fig. 1A) (Li et al., 2008). Second, detailed regional stratigraphic studies have documented that water depths gradually increased to the

southeast from the Yangtze Platform into the deep Nanhua Basin (Fig. 1B) (Zhu et al., 2003; Jiang et al., 2011; Zhu et al., 2013; Jin et al., 2014). However, the amalgamation history between the Yangtze and Cathaysia blocks is still under debate (Li et al., 2009). Thus, the effect of the Cathaysia Block on restriction of the Nanhua Basin in the early Cambrian is impossible to evaluate with current information. Third, the same small shelly fossils (SSFs) found on the Yangtze Platform are present nearly worldwide (including the West Gondwana blocks, Siberia, Newfoundland, and Australia) (Steiner et al., 2007), which suggests unfettered movement of the shell producers among open-ocean sites. Finally, the carbonate carbon isotope profiles of lower Cambrian sections from the Yangtze Platform have been globally correlated (Komura and Watanabe, 2001; Jiang et al., 2007; Wang et al., 2012; Li et al., 2013; Guo et al., 2014), demonstrating a seawater carbonate chemistry similar to that of the global open ocean.

The degree of restriction of modern marine watermasses can be assessed based on bottomwater aqueous Mo concentrations ($[\text{Mo}]_{\text{aq}}$), which are generally more depleted in silled basins. Algeo and Lyons (2006) demonstrated a range of sediment Mo/TOC ratios in modern silled marine basins, ranging from ~4.5 ppm/wt% for the Black Sea ($[\text{Mo}]_{\text{aq}} = \sim 3\text{-}5 \text{ nM}$) to ~45 ppm/wt% for Saanich Inlet ($[\text{Mo}]_{\text{aq}} = \sim 90\text{-}110 \text{ nM}$) (Fig. 3). These values correlate strongly with the degree of deepwater restriction as a consequence of basin-scale drawdown of aqueous Mo and other RSTEs through removal to the sediment with limited resupply. At Yangjiaping, the LM exhibits mean Mo/TOC ratios of $13 \pm 6 \text{ ppm/wt\%}$, whereas the UM exhibits mean Mo/TOC ratios of $17 \pm 5 \text{ ppm/wt\%}$. Assuming modern oceanic boundary conditions, Mo/TOC ratios of ~13-17 ppm/wt%, as observed at Yangjiaping, would be equivalent to a moderate to strong degree of deepwater restriction (i.e., similar to the Cariaco Basin or Framvaren Fjord). However, this conjecture is at odds with our inference of free watermass exchange between the Nanhua Basin and the open ocean (see above).

This apparent contradiction can be resolved if global seawater Mo concentrations were lower during the early Cambrian than in modern seawater (Algeo, 2004). Similar or lower sediment Mo/TOC ratios have been reported from lower Cambrian strata in Oman ($5\text{-}22 \text{ ppm/wt\%}$, average $11 \pm 6 \text{ ppm/wt\%}$) (Wille et al., 2008) and the Tarim Basin of China ($1\text{-}17 \text{ ppm/wt\%}$, average $5 \pm 5 \text{ ppm/wt\%}$) (Yu et al., 2009), suggesting that such values are representative of the early Cambrian

global ocean in general, instead of a restricted-basin watermass. Sedimentary Mo/TOC ratios of ~13-17 ppm/wt% at Yangjiaping are roughly equivalent to an aqueous Mo concentration of ~30-45 nM (Algeo and Rowe, 2012, their figure 3A), which, if representative of the early Cambrian global ocean, indicates that contemporaneous seawater Mo concentrations were less than half of their modern level. However, this estimate represents a minimum value based on the inference of full watermass exchange between the Nanhua Basin and early Cambrian global ocean, whereas an assumption of partial restriction of the Nanhua Basin (which potentially is possible) would yield seawater Mo estimates between the ~30-45 nM minimum and the 104 nM modern seawater Mo concentration. It should be noted that, even at the minimum concentration, the residence time of Mo in the early Cambrian ocean would have been much longer (>100 kyr) than the seawater mixing time, yielding a homogeneous seawater Mo isotope composition in the global ocean.

We should note that the difference between the mean Mo/TOC ratios of the LM (13 ± 6 ppm/wt%) and UM (17 ± 5 ppm/wt%) is not statistically significant. Compilation of data for stratigraphic equivalents of the Niutitang Formation representing a range of paleo-water depths in the Nanhua Basin shows only limited variation in Mo/TOC ratios, with an average of 11 (6-19) ppm/wt% ($n = 238$) [i.e., median (16th-84th percentile range)] (Fig. 3), implying that aqueous Mo concentrations were relatively uniform throughout the basin. The similarity of Mo/TOC ratios for Yangjiaping and other lower Cambrian sections of the Nanhua Basin suggests that no significant topographic barriers existed within the basin. At the same time, due to the good connection between the Nanhua Basin and the open ocean, basin restriction would have had very limited effect on the Mo isotopic compositions in the Nanhua Basin watermass.

6.3. Interpretation of Mo isotopic records at Yangjiaping

6.3.1. LM: fluctuating H₂S concentrations

Two LM samples with intermediate $\delta^{98}\text{Mo}$ values (+0.89‰ for YB11 and +1.34‰ for YB14) were deposited in ferruginous waters, possibly reflecting a fractionation caused by Mo adsorption onto Fe-Mn_{ox}. This interpretation is supported by the higher Fe_{ox} concentrations of these samples

(1.0-1.6‰) than in other LM samples (<0.4‰, except YB-18 which was altered by modern pyrite oxidation; Feng et al., 2014). The remaining LM samples (n = 8), which represent euxinic sediments, have Mo isotopic compositions ranging from -0.65‰ to +2.14‰. Several considerations argue against these values being a record of contemporaneous seawater $\delta^{98}\text{Mo}$. First, because no known process removes Mo to the sediment that is isotopically heavier than seawater Mo, the $\delta^{98}\text{Mo}$ of seawater cannot be lower than that of its source (Wille et al., 2008). For this reason, the negative values of -0.65‰ and -0.27‰ in the LM cannot represent seawater $\delta^{98}\text{Mo}$ because they are lower than the isotopic composition of the upper continental crust (0‰-+0.4‰, Dahl et al., 2011; Voegelin et al., 2014) and modern rivers (+0.7‰, Archer and Vance, 2008). Secondly, variation in seawater $\delta^{98}\text{Mo}$ will accompany changes in the Mo reservoir size (Wille et al., 2008; Dahl et al., 2010). The observation that Mo and other RSTEs show high and relatively stable concentrations in the LM implies no significant changes in the global seawater Mo reservoir size or the basin-ocean connection (see Section 6.2) and, thus, little or no change in contemporaneous seawater $\delta^{98}\text{Mo}$. Therefore, the wide range in $\delta^{98}\text{Mo}$ of LM samples (-0.65‰ to +2.14‰) is unlikely to represent variations in seawater $\delta^{98}\text{Mo}$.

The most likely control on $\delta^{98}\text{Mo}$ of the LM at Yangjiaping was local watermass redox conditions, specifically, aqueous H_2S concentrations. Under euxinic conditions, high $[\text{H}_2\text{S}]_{\text{aq}}$ (>11 μM) leads to quantitative conversion of MoO_4^{2-} to MoS_4^{2-} without significant isotopic fractionation, but low $[\text{H}_2\text{S}]_{\text{aq}}$ (<11 μM) leads to only partial, transient (on a scale of years, depending on the pH) conversion to MoS_4^{2-} with variable Mo isotope fractionations (Helz et al., 1996; Erickson and Helz, 2000; Poulson et al., 2006). In the latter circumstance, a positive linear relation exists in the modern Black Sea between $[\text{H}_2\text{S}]_{\text{aq}}$ and sediment $\delta^{98}\text{Mo}$, making the latter a possible proxy for the former in ancient seawater (Arnold et al., 2012). Given continuously euxinic conditions during deposition of LM-1 (see Section 6.1), we infer that the wide range of $\delta^{98}\text{Mo}$ values (Fig. 2) reflects low (<11 μM) and variable $[\text{H}_2\text{S}]_{\text{aq}}$ during their deposition. For these samples, the highest $\delta^{98}\text{Mo}$ value represents the largest $[\text{H}_2\text{S}]_{\text{aq}}$ (i.e., approaching 11 μM) and the minimum Mo-isotope fractionation (i.e., approaching 0‰), whereas the lowest $\delta^{98}\text{Mo}$ value represents the smallest $[\text{H}_2\text{S}]_{\text{aq}}$ and maximum Mo-isotope fractionation relative to contemporaneous seawater.

Low $[\text{H}_2\text{S}]_{\text{aq}}$ may have been prevalent in euxinic waters throughout the early Cambrian Nanhua Basin. To test this hypothesis, we compiled all published $\delta^{98}\text{Mo}$ data from lower Cambrian units (roughly 529-514 Ma) of the Nanhua Basin ($n = 155$, representing 5 sections). We focused our analysis on a subset of 118 samples of fine-grained siliciclastic rocks having Fe speciation and Mo concentration data, permitting assessment of local depositional redox conditions. Of these 118 samples, 52 have $\text{Fe}_{\text{HR}}/\text{Fe}_{\text{T}}$ ratios and Mo concentrations indicative of euxinic depositional conditions. The $\delta^{98}\text{Mo}$ of this subset ranges from -0.7‰ to $+2.3\text{‰}$. Persistently high $\delta^{98}\text{Mo}$ values of ca. $+2.3\text{‰}$ in euxinic shales of the Yu'an-shan member at Meishucun (Wen et al., 2011; Wen et al., 2015), which is a secondary stratotype section correlative with Yangjiaping (Zhu et al., 2003; Jin et al., 2014; Jin et al., 2016), have been argued to represent early Cambrian seawater $\delta^{98}\text{Mo}$ (Chen et al., 2015). If so, then most samples of the LM in the Yangjiaping section must have been deposited in bottomwaters with $[\text{H}_2\text{S}]_{\text{aq}} < 11 \mu\text{M}$. Furthermore, only $\sim 3.8\%$ (2 of 52) of all the euxinic samples in our Nanhua Basin compilation dataset have $\delta^{98}\text{Mo}$ higher than $+2.0\text{‰}$ (Fig. 4) and, thus, potentially record the contemporaneous seawater $\delta^{98}\text{Mo}$ signal. This observation suggests that euxinic waters within the early Cambrian Nanhua Basin were generally characterized by low $[\text{H}_2\text{S}]_{\text{aq}}$ (i.e., $< 11 \mu\text{M}$). Seawater H_2S concentrations are controlled by sulfate reservoir size, and sulfate concentrations in early Cambrian oceans may have been $\sim 2 \text{ mM}$ or less, i.e., much lower than in the modern ocean (28 mM) (Lloyd et al., 2012; Feng et al., 2014; Algeo et al., 2015). Low seawater sulfate concentrations, with given iron fluxes and marine productivity, were probably key factors in sustaining $[\text{H}_2\text{S}]_{\text{aq}}$ below $11 \mu\text{M}$ in the early Cambrian Nanhua Basin.

6.3.2. UM: Fe-Mn shuttle effects

Manganese behavior in the LM versus the UM of the Niutitang Formation is markedly different. Although all samples show $\text{Mn}_{\text{EF}} < 1.0$ (Fig. 2), indicating a Mn deficit relative to the upper continental crust, Mn concentrations are less depleted in the UM relative to the LM (see Appendix Table A), and a good linear relationship is observed between Mn and Fe concentrations in the UM ($R^2 = 0.83$, $p(\alpha) < 0.01$) but not in the LM ($R^2 = 0.19$) (Fig. 5A). These patterns are

consistent with Mn-Fe behavior in modern stratified basins such as the Black Sea, Baltic Sea, and Oslo Fjord, in which reduction of Mn(IV) to Mn(II) and Fe(III) to Fe(II) around the O_2/Mn^{2+} - Fe^{2+} chemocline can result in remobilization of these elements from the sediment (Trouwborst et al., 2006). Further, dissolved Fe/Mn ratios in these systems are constant in oxic and weakly oxic waters due to their similar behaviors but decrease significantly in euxinic environments due to sequestration of Fe in pyrite (Pakhomova and Yakushev, 2011). These processes can account for (1) the deficit of Mn in both the LM and UM relative to the upper continental crust due to its reduction, (2) the greater depletion of the LM relative to the UM, owing to the more reducing conditions of the former, and (3) the linear relationship between Mn and Fe concentrations in the UM but not the LM, owing to variable sequestration of Fe in pyrite of the latter. The observed Mn-Fe concentration patterns are consistent with our inference that the O_2/H_2S chemocline shifted from the water column to the sediment-water interface during the transition from the LM to the UM of the Niutitang Formation.

Precipitation and reduction of Fe-Mn_{ox} may have significantly influenced levels of authigenic Mo enrichment due to the strong adsorption of Mo onto Fe-Mn_{ox}. As adsorption of U onto Fe-Mn_{ox} is limited, authigenic Mo enrichment can substantially exceed that of U when a local Fe-Mn_{ox} particulate shuttle is active in the water column or at the sediment-water interface (Algeo and Tribovillard, 2009). At Yangjiaping, LM samples exhibit large Mo_{EF} and U_{EF} as well as Mo/U ratios of 1-3 times that of modern seawater, reflecting sediment uptake of RSTEs from a euxinic water column (Fig. 5B; see Section 6.1). In contrast, the UM exhibits only modest enrichments of RSTEs, with lower concentrations of Mo and, especially, U, consistent with less reducing watermass conditions than for the LM. UM samples also show elevated Mo/U ratios relative to the open-marine trend (Fig. 5B) (Algeo and Tribovillard, 2009), which suggests operation of a local Fe-Mn_{ox} particulate shuttle. Fe-Mn_{ox} particulate shuttles are generally found only in stratified basins in modern oceans due to the need for a redox gradient, and they are most effective at transferring Mo to the sediment in systems with fluctuating O_2/H_2S chemoclines, as in the modern Baltic Sea (Dellwig et al., 2010; Scholz et al., 2013) and Saanich Inlet (Berrang and Grill, 1974; Francois, 1988).

As Fe-Mn_{ox} adsorption preferentially takes up isotopically light Mo, the operation of an

Fe-Mn_{ox} shuttle will shift authigenic Mo toward lower Mo isotopic compositions. In the modern Cariaco Basin, which is characterized by weakly euxinic waters and an active Fe-Mn_{ox} shuttle, bulk sediment $\delta^{98}\text{Mo}$ is $\sim 0.5\text{‰}$ lighter than seawater $\delta^{98}\text{Mo}$ (Arnold et al., 2004). Similarly, the UM at Yangjiaping shows intermediate $\delta^{98}\text{Mo}$ values (from +1.16‰ to +1.71‰, mean +1.52‰; Fig. 2) that are similarly lower than the inferred Mo isotopic composition of contemporaneous seawater. Fractionation caused by Mn_{ox} adsorption is constant while that related to Fe_{ox} adsorption depends on mineralogy (Barling and Anbar, 2004; Goldberg et al., 2009). The linear relationship between the Mn and Fe concentrations in the UM (Fig. 5A) indicates relatively constant Mn/Fe ratio and Fe mineralogical composition in water columns, which may explain the relatively uniform $\delta^{98}\text{Mo}$ values of the UM.

Whether an Fe-Mn_{ox} particulate shuttle operated broadly within the early Cambrian Nanhua Basin has important implications for Mo biogeochemical cycling. Existing redox models for the basin invoke a dynamically maintained euxinic wedge at intermediate depths (Feng et al., 2014; Jin et al., 2016), on the margins of which an Fe-Mn_{ox} shuttle is likely to have operated, leading to significant Mo enrichments. The basinwide importance of Fe-Mn_{ox} shuttles can be assessed based on Mo_{EF}-U_{EF} data ($n > 200$) compiled for multiple lower Cambrian sections (Fig. 5B). Although the absolute Mo_{EF}-U_{EF} values of modern marine systems (Algeo and Tribovillard, 2009) may not match those of the early Cambrian owing to the possibility of reduced seawater Mo mass in the latter, the general trends should be similar. The majority of data from the Nanhua Basin conform to the pattern of the modern open ocean, which is mainly controlled by bottom-water redox variation over a continuum from oxic to euxinic conditions (red arrow in Fig. 5B). This pattern is consistent with a dominant local redox control on Mo and U enrichment in the Yangjiaping shales. However, a large subset of samples shows higher Mo_{EF}/U_{EF}, indicating local development of Fe-Mn_{ox} shuttles within the redox-stratified Nanhua Basin (Fig. 5B).

6.4. Synthesis: Mo biogeochemistry in the early Cambrian Nanhua Basin and its broader implications

Mo biogeochemical cycling in the early Cambrian Nanhua Basin took place in the context of

a stratified oceanic redox structure, in which euxinia existed dynamically at intermediate depths, separating oxic shallow waters from ferruginous deep waters (Fig. 6; Li et al., 2010; Feng et al., 2014; Jin et al., 2016). Based on our interpretation of $\delta^{98}\text{Mo}$ data at Yangjiaping and other sections, we propose that an Fe-Mn_{ox} reduction zone, similar to modern oxic/anoxic chemocline, may have developed just above the euxinic wedge due to sinking of Fe-Mn_{ox} particulates from the surface oxic waters (Li et al., 2015). This Fe-Mn_{ox} reduction zone would have gradually attenuated distally because of decreasing fluvial Fe-Mn_{ox} availability (Pakhomova and Yakushev, 2011; Li et al., 2015). H₂S concentrations ($[\text{H}_2\text{S}]_{\text{aq}}$) in the euxinic watermass, which were controlled by the relative availabilities of sulfate, reactive iron, and organic matter (Li et al., 2015), reached a peak within the euxinic wedge and decreased both shoreward and basinward (Fig. 6).

Within this model framework, all of the existing Mo isotopic data from lower Cambrian units of the Nanhua Basin can be explained. An Fe-Mn_{ox} shuttle is likely to have operated in the nearshore Fe-Mn_{ox} reduction zone. There, isotopically light Mo was adsorbed in oxic surface waters and released in the Fe-Mn_{ox} reduction zone, after which it was rapidly scavenged by either sulfidic porewaters (“A” in Fig. 6) or a euxinic lower water column (“B” in Fig. 6) into the sediment, resulting in higher Mo_{EF} relative to U_{EF}. Scenario A applies to the UM at Yangjiaping, which was deposited under mainly weakly oxic to anoxic-ferruginous conditions with only occasional episodes of weak euxinia (see Section 6.1) and exhibits a moderate Mo-isotopic fractionation ($\geq 0.62\text{‰}$). It should be noted that Mo behavior and isotopic fractionation in sediment porewaters remain poorly known (Scott and Lyons, 2012), which can potentially result in much more complicated Mo isotopic compositions. Furthermore, given ferruginous conditions in the deep basin, an Fe-Mn_{ox} shuttle also may have likely operated at the boundary between distal oxic surface waters and ferruginous deep waters (“D” in Fig. 6). However, this Fe-Mn_{ox} shuttle may not have contributed much authigenic Mo to the sediment given the absence of sulfidic waters nearby.

Our model predicts strong spatial variation in sediment $\delta^{98}\text{Mo}$ values. Because of the compounded effects of Mo isotopic fractionation associated with low $[\text{H}_2\text{S}]_{\text{aq}}$ and Fe-Mn_{ox} adsorption, the most negative sediment $\delta^{98}\text{Mo}$ values are expected close to the boundary between the Fe-Mn_{ox} reduction zone and the euxinic wedge, where sediments can record $\delta^{98}\text{Mo}$ with a fractionation of $>3\text{‰}$ due to both the Fe-Mn_{ox} adsorption and the lowest $[\text{H}_2\text{S}]_{\text{aq}}$ in euxinic

bottomwaters (Fig. 6). With increasing $[H_2S]_{aq}$ in deeper waters offshore, the Mo-isotopic fractionation associated with low $[H_2S]_{aq}$ will gradually diminish. Because the isotopic effect of Fe-Mn_{ox} adsorption will also diminish offshore due to decreasing fluvial Fe-Mn_{ox} availability, the highest sediment $\delta^{98}Mo$ values—those closest to the $\delta^{98}Mo$ composition of contemporaneous seawater—are expected in the area of maximum $[H_2S]_{aq}$ within the euxinic wedge (“C” in Fig. 6). Beyond this point to the basinward boundary of the euxinic wedge, sediment $\delta^{98}Mo$ values are predicted to decrease again owing to less-than-quantitative conversion to thiomolybdates and uptake of aqueous Mo under weakening euxinic conditions. However, negative Mo-isotopic fractionations as large as those in the nearshore Fe-Mn_{ox} reduction zone will not be achieved owing to decreasing Fe-Mn_{ox} availability and the weak isotopic effects of Fe-Mn_{ox} adsorption in the deep basin. The highly variable $\delta^{98}Mo$ values of LM black shales at Yangjiaping, as well as those from other euxinic facies in the late Neoproterozoic and early Cambrian Nanhua Basin (Lehmann et al., 2007; Wille et al., 2008; Xu et al., 2012; i.e., Kendall et al., 2015; Wen et al., 2015), conform well to the scenarios associated with a euxinic wedge (Fig. 6).

Mo absorbed by Fe-Mn_{ox} particulates can be reductively released and diffused back into the water column in the modern ocean (Morford et al., 2009). However, in a stratified early ocean with active Fe-Mn_{ox} shuttles, the burial flux of isotopically light Mo is likely to have been larger because (1) most of the Mo released by nearshore Fe-Mn_{ox} cycling would have been effectively taken up either in underlying sulfidic porewaters or the nearby euxinic wedge watermass (i.e., scenarios A and B in Fig. 6), and (2) the efficiency of Fe-Mn_{ox} cycling may have been higher owing to a more pronounced redox gradient. For these reasons, the rate of authigenic Mo uptake may have been higher in early stratified oceans than in the modern. At the same time, most Mo removed to the sediment under euxinic conditions would have a $\delta^{98}Mo$ lower than that of contemporaneous seawater due to widely low H_2S concentrations. In theory, these two mechanisms might likely cause unusually heavy seawater $\delta^{98}Mo$ of the early oceans. Although quantitative estimation of the effects of these mechanisms is difficult, they should be considered in applying Mo-isotopic records to reconstruction of the redox state of early oceans. Furthermore, given that the stratified nature of early oceans has been widely recognized (see the review in Lyons et al., 2014), we suggest that the new Mo biogeochemical model proposed in this study for

the early Cambrian Nanhua Basin may have broader applicability to basins of other locations and ages.

7. CONCLUSIONS

To explore the Mo biogeochemical cycle within a redox-stratified early ocean, we carried out a detailed Mo-isotopic study on shales of the lower Cambrian (~529-514 Ma) Niutitang Formation in the shelf-margin Yangjiaping section, South China. Our key findings are:

- (1) Black shales of the lower member (LM) of the Niutitang Formation were deposited under mainly euxinic conditions with episodes of ferruginous conditions due to pulsed inputs of reactive Fe. In contrast, gray silty shales of the upper member (UM) were deposited under conditions fluctuating from suboxia to weak euxinia.
- (2) The LM shows $\delta^{98}\text{Mo}$ values ranging from -0.65‰ to $+2.14\text{‰}$. This variation mainly reflects low ($<11\text{ }\mu\text{M}$), fluctuating $[\text{H}_2\text{S}]_{\text{aq}}$ in contemporaneous seawater. By compiling published $\delta^{98}\text{Mo}$ data from many age-roughly-equivalent sedimentary units in the early Cambrian Nanhua Basin, we found that only a small subset of euxinic samples recorded the Mo isotopic composition of contemporaneous seawater, indicating that seawater $[\text{H}_2\text{S}]_{\text{aq}}$ was generally low ($<11\text{ }\mu\text{M}$) during this period.
- (3) An Fe-Mn shuttle operated vigorously during deposition of the UM but only weakly or not at all during deposition of the LM at Yangjiaping. Limited $\delta^{98}\text{Mo}$ variation in the UM (from $+1.16\text{‰}$ to $+1.71\text{‰}$) and elevated Mo/U ratios reflect the combined effects of Mo adsorption onto Fe-Mn particulates and sulfidic porewaters.
- (4) Variation of sediment $\delta^{98}\text{Mo}$ in lower Cambrian units of the Nanhua Basin can be explained by a new Mo biogeochemical model in which a nearshore Fe-Mn reduction zone developed between oxic surface waters and the mid-depth euxinic wedge. In this model, highly variable sediment $\delta^{98}\text{Mo}$ can be explained by combined fractionations associated with low $[\text{H}_2\text{S}]_{\text{aq}}$ and strong Mo adsorption onto Fe-Mn_{ox} associated with active Fe-Mn cycling. This model highlights the potential for compounded fractionation effects on sedimentary $\delta^{98}\text{Mo}$ records, and it may have broader implications for other

early oceans possessing a similar stratified redox structure.

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FIGURE CAPTIONS

Figure 1. Geological setting of the Yangjiaping section. (A) Global paleogeography in the early Cambrian (adapted from Li et al., 2008). (B) Simplified tectonic-lithofacies map of South China during the Fortunian (modified from Goldberg et al., 2007). (C) Generalized stratigraphy of the Yangjiaping section (modified from Feng et al., 2014). Ed = Ediacaran, Ft = Fortunian, St = Stage, MSC = Meishucunian, DY = Dengying Formation, LM = lower member (black shale interval) and UM = upper member (silty shale interval). Biostratigraphic data are from Steiner et al. (2004) and Yin et al. (1999). The radiometric age of 526.4 ± 5.4 Ma is from the adjacent Three Gorges section Okada et al. (2014).

Figure 2. Chemostratigraphy of the LM and UM of the Niutitang Formation at Yangjiaping. The Mo-isotope and Mn, U, and V abundance data are original to this study; the remaining data were compiled from Feng et al. (2014). The vertical dashed lines in boxes denote key values of geochemical proxies as discussed in text. LM = lower member and UM = upper member.

Figure 3. Crossplot of Mo versus TOC. The data shown are for the LM and UM of the Niutitang Formation at Yangjiaping and correlative units from multiple other sections of the Yangtze Block, including the inner-shelf sections at Xiaotan (Och et al., 2013) and Shatan (Goldberg et al., 2007), the outer shelf to shelf margin sections at Dingtai (Xu et al., 2011) and Yangjiaping (Feng et al., 2014 and this study), and the upper-slope sections at Songtao (Guo et al., 2007) and Zhitang (Zhang, 2014). The dashed green trend lines (numbers are given as $\text{mean} \pm 1\sigma$) were adopted from Algeo and Lyons (2006), and the solid blue trend line is the average [number is given as median (16^{th} - 84^{th} percentile range) to remove several over-scattering data] for all lower Cambrian units of the Yangtze Block. LM = lower member and UM = upper member.

Figure 4. A histogram of sample frequencies of $\delta^{98}\text{Mo}$ values. The data shown are for the study Niutitang shales at Yangjiaping (this study) and correlative units from multiple other sections of

the Yangtze Block, including Meishucun (Wen et al., 2015), Zunyi (Xu et al., 2012; Wen et al., 2015), Longbizui (Chen et al., 2015), Jijiawan (Chen et al., 2015), and Huangjiawan (Lehmann et al., 2007).

Figure 5. Crossplots of (A) Mn versus Fe_T , and (B) Mo_{EF} versus U_{EF} . The data shown are for the study Niutitang shales (LM and UM) at Yangjiaping and (in B) correlative units from multiple other sections of the Yangtze Block (as given in the Fig. 3 caption). The trend lines in B are modified from Algeo and Tribovillard (2009). LM = lower member and UM = upper member.

Figure 6. Schematic representation of the Mo cycle in the early Cambrian ocean within the framework of a modified “euxinic wedge model”. SWI = sediment-water interface, aq = aqueous, SW = seawater, PW = porewater. See text for detailed explanation.

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