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Key Points:

- We provide new evidence for manganous-ferruginous and nitrogenous water conditions in early Cambrian oceans
- We found progressive water-column oxygenation at Silikou section during early Cambrian and possible mechanisms were proposed
- Our results suggest highly complex redox conditions and strong water-column stratification in early Cambrian oceans

Supporting Information:

- Supporting Information S1
- Table S1
- Table S2

Correspondence to:

C. Li, chaoli@cug.edu.cn

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Evidence for Highly Complex Redox Conditions and Strong Water-Column Stratification in an Early Cambrian Continental-Margin Sea

Zihu Zhang^{1,2}, Chao Li¹, Meng Cheng¹, Thomas J. Algeo^{1,3,4}, Chengsheng Jin⁵, Feng Tang⁶, and Junhua Huang³

¹State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan, China, ²School of Earth Sciences, China University of Geosciences, Wuhan, China, ³State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences, Wuhan, China, ⁴Department of Geology, University of Cincinnati, Cincinnati, OH, USA, ⁵Yunnan Key Laboratory for Palaeobiology, Yunnan University, Kunming, China, ⁶Institute of Geology, Chinae Academy of Geological Sciences, Beijing, China

Abstract Although oxic surface, ferruginous deep, and euxinic intermediate waters have been documented, the redox heterogeneity of early Cambrian oceans remains largely unclear, precluding our understanding of the relationship between marine redox evolution and early animal diversification. In this study, we analyzed iron species, redox-sensitive trace elements, and S-N-C isotopes of deepwater black shales in the Silikou section in the continental-margin Nanhua Basin (South China), which represent extensive clastic input mainly from the Cathaysia Block during the early Cambrian (~541–509 Ma). Integrated data reveal a continuous shift in bottom-water redox conditions at Silikou from euxinic in the lowermost black-shale interval (BS1, 0–37.4 m) to oxic in the uppermost black-shale interval (BS4, 296–372.9 m) accompanying a progressive movement of the O₂/H₂S redoxcline into the sediment. In between, most importantly, the BS2 interval (91–154 m) accumulated under manganous-ferruginous conditions (i.e., Fe-Mn reduction zone) characterized by an active Fe-Mn particulate shuttle, and the BS3 interval (204-260 m) under nitrogenous conditions (i.e., nitrate reduction zone) characterized by strong denitrification processes, suggesting highly complex redox conditions in early Cambrian oceans. The observed sequence of redox conditions supports a strong lateral and depth-related redox stratification in the early Cambrian ocean, including (from surface to deep and from nearshore to offshore) oxic, nitrate reduction, Fe-Mn reduction, and euxinic zones, which were sequentially recorded at Silikou likely due to secular expansion of the oxic surface layer and/or long-term relative sea level fall. Our study highlights the need for continued paleo-redox studies to explore the redox heterogeneity of early Cambrian oceans.

1. Introduction

The early Cambrian (~541-509 Ma) was a key period in Earth's history during which the majority of marine invertebrate phyla first appeared (i.e., the Cambrian Explosion; Erwin et al., 2011; Knoll & Carroll, 1999; Shu et al., 2014). Due to the physiological requirements of animals for oxygen and their inability to tolerate toxic H₂S, tracking oceanic redox evolution is crucial to understanding this biological event (Butterfield, 2009; Mills & Canfield, 2014; Sperling et al., 2013; Zhang et al., 2014). However, the nature of oceanic redox evolution during the early Cambrian is still under debate. For example, some studies have argued that strong oceanic oxygenation occurred in the early Cambrian (e.g., Chen et al., 2015; Li et al., 2017), whereas others have inferred only limited oxygenation during the same interval (e.g., Sperling et al., 2015; Xiang et al., 2017). Spatial heterogeneity of early Cambrian oceanic redox conditions was recently hypothesized to reconcile these conflicting views, with redox stratification in the form of an oxic surface layer, a euxinic intermediate layer, and a ferruginous deep layer (e.g., Feng et al., 2014; Jin et al., 2016; Zhang et al., 2017). In this scenario, oxygenation of the ocean would have led to an expansion of the oxic ocean-surface layer at the expense of the euxinic intermediate layer with limited effects on the anoxic deep ocean (Jin et al., 2016; Li et al., 2017; Tostevin et al., 2016; Wen et al., 2015). This process would have broadened the range of habitats open to early animals, possibly leading to feedback in metazoan evolution (Li et al., 2018). Therefore, a better understanding of marine redox heterogeneity is important for understanding the coevolution of marine redox conditions and animal life during the early Cambrian.

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Figure 1. Geological setting of Silikou section. (a) Paleo-locations of South China Block from ~635 to ~510 Ma (modified from Zhang et al., 2015). (b) Paleogeography of the Nanhua Basin in the early Cambrian (~541–509 Ma; modified from Goldberg et al., 2007). (c) Cross section of Nanhua Basin in the early Cambrian (modified from Wang et al., 2010). The Xiaotan section is shown in (b) and (c) for comparison to the study section (Silikou).

Although the complex three-redox-layer model has been documented (see above), the details of spatial variation in redox conditions of early Cambrian oceans remain largely unclear. In modern restricted anoxic basins, an oxic surface layer is separated from a euxinic deep layer by a relatively thin suboxic zone (i.e., O_2/H_2S redoxcline) in which Fe-Mn and nitrate reduction take place—for example, it reaches a maximum thickness of ~40 m in the >2,000-m-deep Black Sea (Algeo & Lyons, 2006; Murray et al., 2005). A theoretical model of similar spatial chemical zonation for early Cambrian and Proterozoic oceans was proposed by Li, Cheng, et al. (2015), in which the distribution of multiple redox zones conforms to the energy-yield sequence from oxygen, nitrate, Mn^{4+} , Fe^{3+} , and sulfate reductions during the remineralization of organic matter. If these redox zones all existed in early Cambrian oceans, the marine redox heterogeneity must have been more complex than the three redox layers presented in earlier studies (e.g., Feng et al., 2014; Jin et al., 2016; Zhang et al., 2017).

In order to explore the redox heterogeneity of early Cambrian oceans, we carried out an integrated high-resolution paleo-redox study of the lower Cambrian Silikou section (Nanhua Basin, South China) using iron speciation, redox-sensitive trace elements (RSTEs), and C-N-S isotopes. This section received extensive siliciclastic inputs mainly from the Cathaysia Block, resulting in a stratigraphically expanded succession well suited for identification of small-scale redox zones, if present, within early Cambrian oceans. We aim to prove the existence of the Fe-Mn and nitrate reduction zones predicted for early Cambrian oceans and to provide new insights into water-column redox stratification patterns, which are important to further understanding of contemporaneous life-environment coevolutionary patterns.

2. Geological Setting and Stratigraphy

The South China Block, which consists of the Yangtze and Cathaysia Blocks, was an isolated microcontinent from ~750 to ~510 Ma that gradually moved from a midlatitude position (~30°N) at ~635 Ma to the paleo-equator at ~510 Ma (Figure 1a; Zhang et al., 2015). The Nanhua Basin, which is located between the Yangtze and Cathaysia Blocks, was a failed intracratonic rift basin whose formation was initiated by





Figure 2. General correlation framework of Silikou section (a Yangtze-Cathaysia transitional site) with the previously well-studied inner-shelf Xiaotan section on the Yangtze Block. Also shown are outcrop and sample photographs of the Silikou section. Correlations are based on available sequence stratigraphic data (Wang et al., 2014 for South China; this study for Silikou; see text for details). The Xiaotan data are from Cremonese et al. (2013) and Li et al. (2013). The sea level curve is from Peng et al. (2012). DY = Dengying Formation; LB = Laobao Formation.

breakup of the Rodinia supercontinent beginning at ~820 Ma (Wang & Li, 2003). It evolved into a passive continental-margin basin during the Ediacaran and Cambrian (Figure 1b; Wang & Li, 2003) that was probably well connected to the open ocean at both its northeastern and southwestern ends (Figure 1c; Jiang et al., 2003; note that all orientations are modern except as noted).

In the early Cambrian, the Yangtze Block exhibited parallel shelf-slope-basinal belts extending from the northwest to the southeast with the Nanhua Basin located to the southeast. Typical facies were carbonates on the inner shelf, interbedded shales and carbonates on the outer shelf, and shale/mudstone deposits in basinal areas (Figure 1b; Zhu et al., 2003; Steiner et al., 2007). In contrast, the Cathaysia Block accumulated mainly siliciclastics, including shale, siltstone, arkosic sandstone, quartz sandstone, and gravelly sandstone (Figures 1b and 1c; Yao et al., 2014). Deepwater deposits within the Nanhua Basin were much thicker on its southeastern margin (few hundreds of meters; cf. Yao et al., 2014) than its northwestern margin (few tens of meters; cf. Jin et al., 2016) owing to rapid accumulation of siliciclastics mainly from the Cathaysia Block.

The Silikou section is located in Silikou village of Sanjiang Dong Autonomous County, northern Guangxi Zhuang Autonomous Province, South China (25°44′36.4″N, 109°30′38.0″E). It was located in transitional facies of the Nanhua Basin between the Yangtze and Cathaysia Blocks (but closer to the latter) during the early Cambrian (Figure 1c). In this area, the lower Cambrian succession is conformable and consists of the Laobao Formation (equivalent to the Liuchapo Formation, and containing the Precambrian/Cambrian boundary) and the Qingxi Formation (Figure 2). The Qingxi Formation can be divided into three units of variable thickness: (1) an ~500-m-thick lower unit consisting of organic-rich black shales (average total organic carbon [TOC] = 3.7%) alternating with whitish-yellow organic-lean mudstones (TOC <0.1%), (2) an ~600-m-thick middle unit consisting of interbeds of quartz sandstone and shale, and (3) an ~200-m-thick upper unit consisting of limestone/dolostone. In this study, only the black shale intervals of the lower unit of the Qingxi Formation were analyzed, and the interval from ~50 to 80 m was not collected owing to dense vegetative cover (Figure 2).

A lack of age-diagnostic fossils at Silikou (where only sponges are present) precludes high-resolution biostratigraphic correlations to Yangtze Block sections (Figure 2). However, the general lithologic changes in Qingxi Formation at Silikou can be correlated to the lower Cambrian successions of the Yangtze Block (e.g., Xiaotan in Yunnan Province), which show changes from fine-grained, organic-rich black shale of Cambrian Stage 2 to mudstones, siltstones, and sandstones of Stage 3 and to carbonates at or close to the Stage 4/5 boundary, recording a basin-scale marine regression in South China (Figure 2; Zhu et al., 2003; Steiner et al., 2007; Peng et al., 2012; Wang et al., 2014). Within this correlation framework, general age constraints for the Silikou section are provided by radiometric dating of the Yangtze Block. The maximum age of the black shales of the lower Qingxi Formation is constrained by a zircon U-Pb date of 536 \pm 5 Ma for a K-bentonite layer at the top of the Liuchapo Formation in the Pingyin section (Guizhou Province; Zhou et al., 2013), which can be correlated to dated tuffs of the Liuchapo Formation (536.5 \pm 5.5 Ma) in the Ganziping section (Hunan Province; Chen et al., 2009) and of the Zhongyicun Member (535.2 \pm 1.7 Ma) in the Meishucun section (Yunnan Province; Zhu et al., 2009). Given the persistence of highstand conditions indicated by the studied black shale succession at Silikou, the depositional age of the lower Qingxi Formation must be older than the lowstand of Stage 4, whose minimum age is ~509 Ma (Peng et al., 2012). For these reasons, the maximum depositional interval of the studied black shales is ~27 Myr (i.e., ~536-509 Ma), which yields a minimum average sedimentation rate for the 370-m-thick study section of ~14 m/Myr.

3. Background: Fe, Mo-U, S, and N Proxies

In order to investigate marine redox conditions in the Silikou section, we used a combination of paleoredox proxies in this study. Iron speciation and RSTEs have been widely used as proxies for reconstruction of local and, given certain caveats, global oceanic redox conditions (e.g., Canfield et al., 2008; Li et al., 2010; Jin et al., 2016; Scott et al., 2008; Sperling et al., 2015). The ratios of highly reactive iron (Fe_{HR}, including iron in oxides [Fe_{ox}], carbonates [Fe_{carb}], magnetite [Fe_{mag}], and pyrite [Fe_{py}]) to total iron (Fe_T) and of Fe_{py} to Fe_{HR} are the two main proxies employed in iron speciation studies. Generally, Fe_{HR}/Fe_T values <0.22 and >0.38 are indicative of oxic and anoxic conditions, respectively (Poulton & Canfield, 2011). Furthermore, if anoxia is indicated, Fe_{py}/Fe_{HR} values of <0.7–0.8 and >0.7–0.8 are indicative of ferruginous and euxinic conditions, respectively (Poulton & Canfield, 2011). Empirically, modern samples with Fe_T < 0.5% commonly yield elevated Fe_{HR}/Fe_T ratios implying anoxic conditions that are inconsistent with known bottom-water redox conditions (Clarkson et al., 2014). For this reason, a minimum Fe_T value of 0.5% is required in order to obtain robust iron speciation results.

Aqueous Mo and U are conservative under oxic conditions but reactive under anoxic conditions, although the uptake of Mo by sediments requires the presence of H_2S (Cheng et al., 2015; Tribovillard et al., 2006). Thus, strong authigenic enrichment of Mo in addition to U indicates euxinic conditions, whereas enrichment of U but not Mo signals a ferruginous environment (Algeo & Tribovillard, 2009).

During organic matter decay by microbial sulfate reduction (MSR), the generated H₂S is variably enriched in ³²S relative to its sulfate source (Habicht et al., 2002). Subsequent fixation of H₂S in the form of pyrite entails negligible sulfur isotopic fractionation (Böttcher et al., 1998; Mossmann et al., 1991; Price & Shieh, 1979; Wilkin & Barnes, 1996). Therefore, sulfur isotopic fractionation during MSR (Δ^{34} S) can be proxied by the difference between sulfate and pyrite sulfur isotopic values ($\delta^{34}S_{sulfate}$ and $\delta^{34}S_{py}$; $\Delta^{34}S = \delta^{34}S_{sulfate} - \delta^{34}S_{py}$). The $\Delta^{34}S$ during MSR is controlled mainly by the availability of sulfate and the rate of sulfate reduction (i.e., availability of organic substrate; Algeo et al., 2015; Gomes & Hurtgen, 2015; Leavitt et al., 2013). The former is particularly important at sulfate concentrations of <5 mM, when $\Delta^{34}S$ values exhibit a positive correlation with sulfate concentrations (Gomes & Hurtgen, 2015).

Nitrogen is an essential nutrient for eukaryotes that is biologically available only in the form of nitrate and ammonium (Algeo et al., 2014; Canfield et al., 2010). Conversion from atmospheric N₂ to a biologically available form (*nitrogen fixation*) is accompanied by a small fractionation, typically yielding a δ^{15} N value for fixed nitrogen of -3 to +1% (see reviews in Stüeken et al., 2016, and Zerkle et al., 2017, and references therein). On the other hand, a large fractionation (10–20‰) is generated by water-column denitrification and anammox processes, leaving the residual nitrate enriched in ¹⁵N after consumption of isotopically light nitrogen (see reviews in Ader et al., 2016 and Zerkle et al., 2017, and references therein). Therefore, the δ^{15} N



of local seawater is the result of the balance between nitrogen fixation and loss, which is closely related to water mass redox conditions.

4. Samples and Methods

A total of 70 fresh black shale samples were collected from a newly exposed roadcut (Figure 2). Each sample was collected as an ~1 kg block in the field. Subsequently, all potentially weathered surfaces, postdepositional veins, and visible pyrite crystals were removed and only the freshest ~50–100 g of material were taken from each sample, reduced to powder using a tungsten carbide crusher (Retsch, RS 200), and analyzed geochemically. TOC, iron speciation, major and trace elements, and S isotopes were analyzed in the State Key Laboratory of Biogeology and Environmental Geology at China University of Geosciences in Wuhan (CUG-Wuhan), and C-N isotopes were analyzed in the State Key Laboratory of Geological Processes and Mineral Resources at CUG-Wuhan.

For TOC concentrations, ~ 2 g of sample powder were acidified with 50% HCl to remove inorganic carbon, then neutralized to pH = 7, dried, and analyzed with a Jena multi-EA 4000 C-S analyzer. The analytical precision was better than 0.1%.

A sequential extraction method was used to quantify the iron fractions of each sample (Poulton & Canfield, 2005). The extracts containing Fe_{ox} , Fe_{carb} , and Fe_{mag} were then measured using atomic adsorption spectroscopy (Beijing Purkinje General Instrument Corporation Limited, TAS-990) with an RSD of less than 5%. Although there are no international standards for iron speciation analysis to date, data quality was monitored by reanalysis of samples (CUG-2 and CUG-3) previously analyzed in the Lyons biogeochemistry laboratory at the University of California, Riverside (UCR; Li, Planavsky, et al., 2015). Duplicate analyses of CUG-2 yielded a Fe_{carb} value of 0.13 \pm 0.02% (mean \pm 1 σ , n = 11, UCR value = 0.11%), a Fe_{ox} value of 0.20 \pm 0.01% (n = 11, UCR value = 0.20%), and a Fe_{mag} value of 0.10 \pm 0.01% (n = 11, UCR value = 0.10%). Duplicate analyses of CUG-3 yielded a Fe_{carb} value of 1.22 \pm 0.20% (mean \pm SD, n = 8, UCR value = 1.26%), a Fe_{ox} value of 0.20 \pm 0.01% (n = 8, UCR value = 0.20%), and a Fe_{mag} value of 0.54 \pm 0.09% (n = 8, UCR value = 0.64%). Fe_{py} was extracted using the chromium reduction method, in which pyrite S in samples was converted to H₂S by reaction with CrCl₂, subsequently recovered as Ag₂S in silver nitrate traps (Canfield et al., 1986).

For $\delta^{34}S_{py}$, excess V_2O_5 was mixed with the extracted Ag_2S and measured on a Thermo-Fisher Scientific Delta V Plus isotope-ratio mass spectrometer (IRMS) coupled with a Flash elemental analyzer (EA). The $\delta^{34}S_{py}$ values were reported in δ -notation relative to the international standard of Vienna Cañon Diablo Troilite (VCDT) in the form of $\delta^{34}S_{py} = ([^{32/34}S_{sample}]/[^{32/34}S_{VCDT}] - 1) \times 1,000$. Three IAEA standards, S1 ($\delta^{34}S = -0.3\%$), S2 ($\delta^{34}S = +22.7\%$), and S3 ($\delta^{34}S = -32.3\%$), were used to monitor and calibrate analytical results during S-isotope analysis, yielding a precision better than 0.2‰ (1 σ).

For bulk organic carbon ($\delta^{13}C_{org}$) and bulk nitrogen isotopes ($\delta^{15}N_{bulk}$), all samples were acidified with 6-N HCl to remove carbonates. The acidified residues were rinsed to neutral pH and dried prior to analysis. For organic nitrogen isotopes ($\delta^{15}N_{org}$), the HCl-acidified sample residues were further treated with 50% HF to remove siliciclastic minerals. Total nitrogen (TN) content and $\delta^{15}N_{bulk}$ and $\delta^{15}N_{org}$ were analyzed online by EA-IRMS (EA: Flash EA2000, IRMS: MAT253). International standards IAEA-N-1 (TN: 21.1%; $\delta^{15}N = +0.4 \pm 0.2\%$) and USGS-34 (TN: 13.9%; $\delta^{15}N = -1.8 \pm 0.2\%$) and a laboratory standard (TN: 46.7%; $\delta^{15}N = -0.4 \pm 0.2\%$) were used for N-isotope calibration and data quality monitoring. Nitrogen isotopic results are reported in the standard delta notation as per mille variation relative to the atmospheric N₂ standard in the form of $\delta^{15}N = ([^{15}N/^{14}N]_{sample}/[^{15}N/^{14}N]_{standard} - 1) \times 1,000$. Analytical precision was better than 0.2‰ (1 σ) based on multiple analyses of IAEA-N-1, and 0.4‰ (1 σ) based on replicate analyses of study samples. China national standards GBW04407 ($\delta^{13}C = -22.4\%$) and GBW04408 ($\delta^{13}C = -36.9\%$) were used for C-isotope calibrations and data quality monitoring. Results are given in the standard delta notation as per mille variation relative to the other of $\delta^{13}C_{org} = ([^{13}C/^{12}C]_{sample}/[^{13}C/^{12}C]_{standard} - 1) \times 1,000$. Analytical precision was generally better than 0.2‰ (1 σ).

For trace element concentrations, 50 mg of sample powder were weighed into a Teflon beaker, mixed with HF and HNO₃, and heated to 190 $^{\circ}$ C for 48 hr. Then the solution was dried, mixed with HCl and heated to



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Figure 3. Integrated chemostratigraphy of total organic carbon (TOC), Fe species, redox-sensitive trace elements, and S-N-C isotopes at Silikou section. BS1 to BS4 are the four black shale intervals with specific redox conditions based on our integrated data set (see section 6.1). The vertical line(s) in each box represents key threshold value(s) of Fe speciation and redox-sensitive trace element proxies discussed in the text. LB = Laobao Formation. Lithologic legend as in Figure 2.

120 °C for 12 hr. Additional rounds of digestion were performed if the rock powders were not completely digested after this treatment. After complete digestion, the solution was diluted to ~100 g by 2% HNO₃ and measured on inductively coupled plasma mass spectrometry (Agilent, 7700). The international standards BHVO-2 and BCR-2 were used to monitor data quality. Analytical precision was better than 5% for the elements analyzed in this study.

Enrichment factors (EFs) relative to upper continental crust (UCC) were calculated as $X_{EF} = (X/AI)_{sample}/(X/AI)_{UCC}$, where X represents the element of interest (Tribovillard et al., 2006), and UCC elemental concentrations (AI = 8.04%, Mo = 1.5 ppm, and U = 2.8 ppm) were taken from Table 5 of McLennan (2001).

5. Results

All analytical results, including TOC, iron speciation, trace elements, and C-N-S isotopes, are summarized in Tables S1 and S2, and the key geochemical data are illustrated in Figures 3 and 4. Based on the different redox conditions implied by the integrated data set (see section 6.1), we divided the Silikou black shale succession into four units, from the base to the top: BS1 (0–37.4 m), BS2 (91–154 m), BS3 (204–260 m), and BS4



Figure 4. Crossplot of Mo_{EF} versus U_{EF} of Silikou section. The trend lines are modified from Algeo and Tribovillard (2009). SW = seawater. See Figure 3 for BS1 to BS4.

(296–372.9 m; where BS signifies *black shale*). Whitish-yellow organic-lean mudstones are present between the four units (i.e., at 37.4–91 m, 154–204 m, and 260–296 m) and, to a minor degree, within the units (e.g., the upper parts of BS1 [35.6 m] and BS2 [145.7–146.7 m]), but by definition they are not considered to be part of the BS units.

Almost all analyzed geochemical proxies exhibit clear stratigraphic trends at Silikou (Figure 3). TOC concentrations are variable but generally high in BS1 (2.0–18.1%, average 8.5%), moderate in BS2 (1.4–7.7%, average 3.4%) and BS3 (0.5–3.1%, average 2.0%), and low in BS4 (0.1–1.0%, average 0.4%). Fe_T concentrations show the opposite trend, with low values (<1%) for most samples in BS1, moderate in BS2 (0.6–2.8%, average 1.6%) and BS3 (1.4–5.2%, average 2.6%), and high (mostly >3%) in BS4. The ratios of both Fe_{HR}/Fe_T and Fe_{py}/Fe_{HR} decrease upsection, with Fe_{HR}/Fe_T mostly >0.38 in BS1-BS3 but <0.38 in BS4, and Fe_{py}/Fe_{HR} >0.7 in BS1 but mostly <0.7 in BS2-BS4. Mo_{EF}, U_{EF}, and V_{EF} exhibit the highest values in BS1, moderate enrichments in BS2 and BS3, and negligible enrichment (i.e., close to upper-crustal values) in BS4.



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Figure 5. Schematic representations of progressive water-column oxygenation, gradual bottom-water redox transition, and persistent downward movement of O₂/H₂S redoxcline observed at Silikou section with (a) single bottom-water redox condition, (b) multiple bottom-water redox conditions distributed from shallow nearshore to deep offshore regions (Li, Cheng, et al., 2015), and (c) multiple bottom-water redox conditions distributed vertically during the deposition of studied black shales at Silikou. Both persistent expansion of the oxic surface layer and sea level fall are considered possible drivers of the progressive water-column oxygenation trend observed at Silikou. Lithologic legend as in Figure 2, and BS1 to BS4 as in Figure 4. Note that redox zones are not to scale.

The $\delta^{13}C_{org}$ profile shows the lowest values in BS1 (mostly -32% to -30%) and a gradual increase from the base of BS2 (~ -30%) to the highest values in BS4 (~ -25%). $\delta^{34}S_{py}$, which ranges broadly from -15 to +45‰, shows lower values in BS1 and variable but higher values in BS2-BS4. The most significant change in the $\delta^{34}S_{py}$ profile is a large increase in the middle of BS2: BS1 (average = -1.7%) and the lower half of BS2 (average = -5.7%) exhibit similar values that are statistically distinct from those of the upper half of BS2 (average = +12.2%), BS3 (average = +13.2%), and BS4 (average = +10.6%).

Both $\delta^{15}N_{\text{bulk}}$ and $\delta^{15}N_{\text{org}}$ show almost uniformly low values in BS1 (-0.6 to +1.0‰), a weak increase in BS2 (-0.3 to +2.5‰), an abrupt increase to +4.7‰ at the base of BS3 followed by a gradual decrease to +2.4‰ at the top of this unit, and relatively uniform values of +2.2 to +3.9‰ in BS4. Amino acids are easily degraded during diagenesis, releasing isotopically light NH⁴⁺ that can be captured by clay minerals and driving the residual $\delta^{15}N_{\text{org}}$ to higher values (Freudenthal et al., 2001; Nguyen & Harvey, 1997). Owing to this fractionation of N-isotopes between sedimentary components, $\delta^{15}N_{\text{bulk}}$ theoretically is more reliable than $\delta^{15}N_{\text{org}}$ as an estimate of original marine nitrate $\delta^{15}N$. However, the Silikou samples yielded similar $\delta^{15}N_{\text{org}}$ and $\delta^{15}N_{\text{org}}$ (Freudenthal et al., 2002; Zerkle et al., 2017). This inference is supported by a moderate positive correlation between total N (TN) and TOC ($R^2 = 0.52$, p < 0.01, not shown), which indicates that most nitrogen at Silikou is resident in organic components.

6. Discussion

6.1. Marine Redox Variations at Silikou 6.1.1. BS1: Euxinic Condition

Owing to low Fe_T concentrations (<0.5%), redox interpretations for the BS1 interval are based mainly on RSTE data. All samples show large enrichments of Mo (EF = 11–237, average 64) and U (EF = 1.7–25, average 9.5), to as much as 2 orders of magnitude above the crustal level (Figure 3), indicating euxinic bottom-water conditions during their deposition (Figure 5). For the subset of samples containing sufficient Fe_T (>0.5%), iron

speciation analysis yielded $Fe_{HR}/Fe_T > 0.38$ and $Fe_{py}/Fe_{HR} > 0.7$ (Figure 3), consistent with the inference from RSTEs of euxinic bottom-water conditions.

Unit BS1 exhibits low $\delta^{34}S_{py}$ values with limited variability ($-1.7 \pm 3.2\%$; mean $\pm 1\sigma$; Figure 3). The small isotopic variability is consistent with sulfidic conditions under which MSR occurred mainly in the water column, where sulfate availability was not hydrologically limited relative to sedimentary porewaters (cf. Sageman & Lyons, 2004). Although we were not able to generate carbonate-associated-sulfate $\delta^{34}S$ data for the study units, the S-isotopic composition of contemporaneous seawater sulfate was likely approximately +30‰ as suggested by previous studies (Algeo et al., 2015; Kampschulte & Strauss, 2004), which implies an average isotopic fractionation ($\Delta^{34}S$) of ~32‰ for MSR during BS1. This relatively large fractionation implies an ample sulfate supply and, thus, MSR in the water column rather than in sedimentary porewaters (Canfield & Des Marais, 1991; Sageman & Lyons, 2004). However, this fractionation is still smaller than the maximum of ~48‰ for single-step MSR reported by Habicht et al. (2002), which may reflect either an early Cambrian marine sulfate reservoir smaller than that of the modern ocean (cf. Algeo et al., 2015; Feng et al., 2014; Loyd et al., 2012) or higher MSR rates due to the abundance (average 8.0% in BS1) and high lability of early Cambrian organic matter (see section 4).

Bioavailable N for primary production, particularly in the euphotic zone, generally has two sources: newly fixed N from atmosphere N₂ and recycled N from remineralized organic matter (Ader et al., 2014). Nitrate and nitrite are generally lacking in euxinic environments owing to their quantitative reduction (see review in Stüeken et al., 2016). Owing to the link between euxinia and water-column stratification, recycling of remineralized N from euxinic deep waters is generally slow, and under these conditions bioavailable N in the euphotic zone is mainly supplied by N-fixing diazotrophic cyanobacteria (Higgins et al., 2012; Kuypers et al., 2004; Stüeken et al., 2016). The N-fixation process is known to yield a small N-isotope fractionation (approximately -3 to +1%) relative to the source nitrogen (i.e., atmospheric N₂ with $\delta^{15}N = 0\%$; Stüeken et al., 2016). At Silikou, the observed $\delta^{15}N_{bulk}$ values of BS1 (-0.2% to +0.9%, average +0.4%) are thus close to those of atmospheric N₂, which is consistent with newly fixed N as the main source of bioavailable nitrogen in the euxinic bottom waters of Silikou.

6.1.2. BS2: Ferruginous-Manganous Conditions

In unit BS2, most samples exhibit a combination of $Fe_{HR}/Fe_T > 0.38$ and $Fe_{py}/Fe_{HR} < 0.7$, apparently indicating anoxic and ferruginous conditions for the bottom waters during its deposition (Figure 3). RSTEs show only weak to moderate enrichments (Figure 3), consistent with ferruginous conditions (Tribovillard et al., 2006). Furthermore, the much greater enrichments of Mo relative to U suggest strong operation of a Fe-Mn particulate shuttle (Figure 4), which readily conveys Mo but not U to the sediments through Fe-Mn-oxide adsorption and subsequent release by Fe-Mn-particle reduction in anoxic bottom waters (Algeo & Tribovillard, 2009). In modern silled basins, Fe-Mn shuttles are most active when the O_2/H_2S redoxcline is close to the sediment-water interface (SWI; Algeo & Tribovillard, 2009). Therefore, we infer ferruginous-manganous conditions (i.e., Fe-Mn reduction) for the bottom waters of BS2, with the O_2/H_2S redoxcline located above but close to the SWI at that time (Figure 5).

The $\delta^{34}S_{py}$ shows a large increase from an average of -5.7% in the lower part of BS2 (91–135 m) to an average of +12.3‰ in its upper part (135–154 m; Figure 3). Because the availability of sulfate in sediment porewaters is limited by the rate of downward diffusion of sulfate from the overlying water column, porewaters tend to represent (semi)closed systems in which the produced H₂S becomes progressively more enriched in ³⁴S with time (Algeo et al., 2015; Canfield & Des Marais, 1991). The sharp rise in $\delta^{34}S_{py}$ in the middle of BS2 thus likely records a transition of pyrite formation from sulfate-unlimited conditions (i.e., mainly in the water column) to sulfate-limited conditions (i.e., mainly within the sediment column), reflecting a shift of the O₂/H₂S redoxcline downward into (or partially within) the sediment.

The higher $\delta^{15}N_{\text{bulk}}$ values of BS2 (-0.3‰ to +2.5‰, average +1.1‰) relative to those in BS1 might reflect partial conversion of nitrate to N₂ through denitrification under ferruginous-manganous conditions, as seen in modern ferruginous lakes where ~60% of NO₃⁻ is reduced by denitrification (Michiels et al., 2017). Incomplete denitrification may have led to heavier $\delta^{15}N$ of the residual nitrate that, following bioassimilation, yielded heavier $\delta^{15}N_{\text{org}}$ and $\delta^{15}N_{\text{bulk}}$ values. The parallel increases of $\delta^{15}N_{\text{bulk}}$ and $\delta^{34}S_{\text{py}}$ from the lower to the upper part of BS2 (Figure 3) possibly indicate that nitrate reduction increased within the water column at the same time that sulfate reduction was constrained to below the SWI.



6.1.3. BS3: Nitrogenous Condition

In unit BS3, most samples yield $Fe_{HR}/Fe_T > 0.38$ and $Fe_{py}/Fe_{HR} < 0.7$, apparently indicating ferruginous bottom-water conditions (Figure 3). Relative to BS2, the level of RSTE enrichment is reduced (Figure 3), consistent with weakly reduced bottom water conditions, while the pattern of Mo_{EF} -vs-U_{EF} covariation is still consistent with operation of a weak Fe-Mn particulate shuttle (Figure 4).

As with BS2, the high but variable $\delta^{34}S_{py}$ values of BS3 (+12.5 ± 13.5‰) are consistent with a restricted sulfate supply and, thus, with MSR occurring in sediment porewaters. $\delta^{15}N_{bulk}$ values show a maximum of +4.7‰ at the base of BS3, followed by a gradual decrease to +2.4‰ near the top of this unit (Figure 3). The peak $\delta^{15}N_{bulk}$ values are consistent with enhanced ¹⁴N-loss via denitrification (i.e., nitrate reduction) and/or anamox (Lam et al., 2009), both of which lead to higher $\delta^{15}N$ in the residual fixed N pool. We interpret the $\delta^{15}N_{bulk}$ maximum at the base of BS3 to record the transition from a low-Eh condition that supported Fe-Mn reduction to a high-Eh condition that restricted Fe-Mn reduction. This transition coincided with the O₂/H₂S redoxcline moving mostly into the sediment at Silikou (Figure 5). The slow decline in $\delta^{15}N_{bulk}$ upward within unit BS3 is consistent with a gradual shift from partial denitrification in the water column to more quantitative denitrification in sediment porewaters as the O₂/H₂S redoxcline receded deeper below the SWI. Thus, we suggest a nitrogenous condition for the bottom waters during the deposition of BS3.

6.1.4. BS4: Oxic Condition

In unit BS4, the Fe_{HR}/Fe_T ratios of all samples except two are <0.38, indicating dominantly oxic depositional conditions during its deposition (Figure 3). In agreement with the iron speciation results, RSTEs show mainly crustal concentrations, and there is no evidence for operation of a Fe-Mn particulate shuttle (Figures 3 and 4). The uniformly high $\delta^{34}S_{py}$ values are consistent with oxic conditions, as indicated by iron speciation and RSTE data, because MSR was completely limited to sediment porewaters, and the resulting S-isotopic fractionations were small under oxic conditions (see above). BS4 exhibits lower and more uniform $\delta^{15}N_{bulk}$ values (2.5 ± 0.23‰) than BS3, which is consistent with quantitative denitrification in sediment porewaters following permanent movement of the O₂/H₂S redoxcline below the SWI (see above and cf. Zerkle et al., 2017; Figure 5).

6.1.5. Redox Shifts Evidenced by $\delta^{13}C_{org}$

In addition to the evidence for progressive redox shifts provided by integrated Fe-Mo-U-S-N data, the $\delta^{13}C_{org}$ profile of the Silikou section shows a pronounced secular pattern that can be related to its redox evolution (Figure 3). The $\delta^{13}C_{org}$ profile exhibits uniformly low values (-32 to -30‰) in BS1, a steady upsection shift from -30 to -25‰ through BS2 and BS3, and uniformly high values (-26 to -24‰) in BS4. Although it is possible to envision an external driver of such a $\delta^{13}C_{org}$ trend, for example, falling atmospheric pCO_2 causing reduced photosynthetic fractionation (e.g., Hinga et al., 1994; Rau, 1994), the observation that the shift in $\delta^{13}C_{org}$ at Silikou is confined to the transitional redox interval (i.e., units BS2-BS3) suggests that it was most likely tied to the local evolution of water mass redox conditions. A reasonable explanation is organic matter derivation mainly from strongly ¹³C-depleted anaerobic chemoautotrophs in the euxinic unit BS1, from a mixture of anaerobic chemoautotrophic and eukaryotic algae in the oxic unit BS4 (cf. Jiang et al., 2012). The relative smoothness of the $\delta^{13}C_{org}$ shift through units BS2 and BS3 is thus interpreted to be the result of a gradual change in the amounts of organic matter sourced from these two autotrophic communities in conjunction with the progressive shift from euxinic to oxic conditions at Silikou.

6.2. Primary Nature of the Marine Redox Shifts at Silikou

It is unlikely that the redox patterns documented above were a product of modern weathering of the study section based on several lines of evidence. First, our samples were collected from a new roadcut, and we carefully screened for weathering effects, selecting only fresh rock pieces for geochemical analysis (see section 4 and Figure 2). Second, modern weathering usually has a strong effect on RSTE concentrations and Fe_{py}, which is oxidized to Fe_{ox}. This process generates higher Fe_{ox} and lower Fe_{py}/Fe_{HR} ratios and RSTE concentrations, but Fe_{HR}/Fe_T ratios will remain high if the sample was originally deposited under anoxic conditions. In fact, we observe not only elevated Fe_{ox}, low Fe_{py}/Fe_{HR} values, and upper-crustal RSTE concentrations but also low Fe_{HR}/Fe_T (mostly <0.38) in Unit BS4 (Figure 3 and Table S1), values that are more consistent with originally oxic bottom-water conditions. As to anoxic Units BS1–BS3, it is not possible that modern weathering could have generated higher Fe ratios and RSTE enrichments if they were originally



deposited under oxic conditions. Third, because the bottom-water redox shifts inferred here for the Silikou section are based on an integrated data set of multiple redox proxies (i.e., Fe-Mo-U-S-N-C), it is difficult to imagine that modern oxidative weathering could have altered all of these proxies in a coordinated manner. Collectively, these considerations lead us to conclude that the progressive upsection bottom-water redox shifts at Silikou reported in this study represent a primary redox signal largely unaltered by modern weathering.

6.3. Mechanisms for Progressive Water-Column Oxygenation at Silikou

Our integrated Fe-Mo-U-S-N-C data set suggests a gradual transition in bottom-water redox conditions at Silikou during the early Cambrian, from sulfate reduction to Fe-Mn reduction, to nitrate reduction, and finally to oxic conditions (Figure 5). At the same time, the O_2/H_2S redoxcline, which was originally located in the water column, migrated into the sediment, first to shallow depths and eventually to deeper depths that caused the bottom waters to transition to permanently oxic conditions. One explanation for this pattern of progressive water-column oxygenation at Silikou is a protracted, local, or basin-wide relative fall of sea level, which would have caused shallowing of the depositional environment and downward movement of the $O_2/$ H₂S redoxcline (Figure 5). For example, rapid Cathaysia-clastic filling of the Nanhua Basin and a consequent decline in accommodation space (see section 2) could have caused a relative sea level fall at Silikou. Another mechanism, a global sea level fall, has been inferred for Stages 2 to 5 of the early Cambrian (Peng et al., 2012), and this event is recorded in the Nanhua Basin as a basin-scale transition from black shales to carbonates (see section 2 and Figure 2; Miller et al., 2006; Wang et al., 2014; Zhu et al., 2003). However, we note that the studied black shale succession at Silikou is lithologically uniform and shows no evidence of significant sea level falls during its deposition. Therefore, it was probably deposited entirely during the highstand interval of early Cambrian Stages 2-3, with overlying sandstone/carbonate deposits representing the eustatic regression of Stages 4–5 (see section 2 and Figure 2).

Another mechanism to account for progressive water-column oxygenation at Silikou is secular expansion of the oxygenated surface layer of early Cambrian oceans (Figure 5). There are multiple lines of evidence in support of water-column oxygenation of marine shelves/basins during the early Cambrian, particularly on the Yangtze Block of South China (e.g., Fe speciation and RSTEs: Cheng et al., 2017, Jin et al., 2016; Li et al., 2017; and Mo-U isotope: Chen et al., 2015, Cheng et al., 2017; Dahl et al., 2017), although the deep ocean is likely to have remained anoxic at that time (Sperling et al., 2015; Stolper & Keller, 2018). Early Cambrian surface-ocean oxygenation is likely to have been driven by rising atmospheric O_2 levels (Li et al., 2017, 2018). Long-term expansion of the oxygenated ocean-surface layer would have caused a downward movement of the O_2/H_2S redoxcline and progressive water-column oxygenation, as recorded by intermediate-depth sections such as Silikou. However, uncertainties in correlations between Silikou and Yangtze Block sections (see section 2) prevent a detailed comparative assessment of the timing of oxygenation events in these two areas at present.

Although our geochemical data set for Silikou provides highly detailed information regarding bottom-water redox conditions within the early Cambrian Nanhua Basin, a single study site is insufficient for complete evaluation of these alternative mechanisms for long-term redox changes (i.e., regional or global sea level fall versus secular oxygenation of the oceans). At present, we cannot determine which was the more important mechanism, and further work on coeval lower Cambrian sections, in both South China and globally, will be needed to resolve this issue.

6.4. Water-Column Redox Stratification at Silikou

Early Cambrian oceans are thought to have been redox stratified, with an oxic surface layer, a ferruginous deep layer, and a middepth euxinic wedge (Feng et al., 2014; Jin et al., 2016; Zhang et al., 2017). Our integrated Fe-Mo-U-S-N-C data set from Silikou can further refine this redox model. The geochemical signals observed in BS2 (Fe_{HR}/Fe_T > 0.38, Fe_{py}/Fe_{HR} < 0.7, moderate RSTE enrichment with Mo > U, and intermediate $\delta^{34}S_{py}$ values) are indicative of a ferruginous-manganous zone, in which Fe-Mn reduction took place, and the signals observed in BS3 (Fe_{HR}/Fe_T > 0.38, Fe_{py}/Fe_{HR} < 0.7, weak RSTE enrichment, higher and more variable $\delta^{34}S_{py}$ values, and higher but upward decreasing $\delta^{15}N_{bulk}$ values) are indicative of a nitrogenous zone, in which nitrate reduction was a dominant process. The Fe-Mn and nitrate reduction zones together correspond to what is sometimes referred to as the suboxic zone in modern sediment porewater

studies, which is typically quite thin (a few millimeters to tens of millimeters; Canfield & Thamdrup, 2009). In studies of modern water masses, the Fe-Mn and nitrate reduction zones have been documented from only a few stably stratified, anoxic deep basins such as the Black Sea, in which they span an ~40-m-thick zone located between the oxic surface layer and the euxinic deep layer (Murray et al., 2005). Given the known redox stratification of the early Cambrian ocean in the Nanhua Basin (Feng et al., 2014; Jin et al., 2016; Zhang et al., 2017), the gradual redox transitions recorded by the Silikou section (see section 6.1) most likely recorded the presence of manganous-ferruginous and nitrogenous zones between the oxic surface layer and the euxinic deep layer (Figures 5b and 5c) rather than consecutive occurrence of single redox condition in the bottom waters at Silikou (Figure 5a). The existence of these redox zones in early Cambrian oceans is supported by other evidence as well: a Fe-Mn reduction zone was proposed to explain large sedimentary δ^{98} Mo variations in lower Cambrian Niutitang Formation shales (Cheng et al., 2016), and a nitrate reduction zone was implicated in the preservation of the early Cambrian Chengjiang Biota (Hammarlund et al., 2017).

Geochemical evidence for manganous-ferruginous and nitrogenous zones in early Cambrian oceans provides empirical support for predictions of the multiple chemical zonation model of Li, Cheng, et al. (2015). This model proposed that Proterozoic and early Cambrian oceans were characterized by redox gradients from shallow nearshore to deep offshore regions, conforming to the energy-yield sequence of oxygen, nitrate, Mn^{4+} , Fe³⁺, and sulfate reductions during the remineralization of organic matter (Figure 5b). However, a solely vertical distribution of these redox zones can also explain the gradual bottom-water redox transition and downward movement of O₂-to-H₂S redoxcline at Silikou (Figure 5c). Because the early Cambrian deep ocean most likely remained anoxic (cf. Sperling et al., 2015; Stolper & Keller, 2018), the spatial distribution of redox zones on continental shelves would have depended on the sources and fluxes of oxidants to the ocean. Given that Mn-Fe oxides and sulfate were sourced mainly through subaerial weathering and riverine delivery, the manganous-ferruginous and euxinic zones would have developed relatively close to land, that is, in midshelf settings, which is consistent with the known spatial distribution of the euxinic wedge in the Nanhua Basin (Feng et al., 2014; Jin et al., 2016; Zhang et al., 2017). Nitrate and nitrite in modern oceans derive mainly from riverine input, eolian dust, and microbial decomposition of marine organic matter, which usually is abundant on eutrophic continental margins (Libes, 2009). Therefore, the nitrogenous zone is predicted to have developed close to land areas also. Based on these considerations and ample clastic input from the Cathysia Block (see section 2), it was most likely that a lateral and depth-related redox gradient existed within the early Cambrian Nanhua Basin sea (i.e., Figure 5b). However, redox variation in a single section such as Silikou cannot directly demonstrate the existence of the lateral and depth-related redox gradient predicted by Li, Cheng, et al. (2015), the key test of which must be a redox analysis of multiple sections along a proximality trend within a tightly constrained stratigraphic correlation framework.

7. Conclusions

In order to explore the redox conditions and water-column stratification of early Cambrian oceans, we carried out an integrated study of iron speciation, trace element concentrations, and S-N-C isotopes on lower Cambrian black shales in the Silikou section (>509 Ma; Nanhua Basin, South China). Our integrated Fe-Mo-U-S-N-C data set demonstrates progressive water-column oxygenation through time along with a downward migration of the O₂/H₂S redoxcline into the sediment. Bottom-water redox conditions at Silikou evolved gradually through the sulfate reduction (i.e., euxinic), Fe-Mn reduction (i.e., ferruginous-manganous), nitrate reduction (i.e., nitrogenous), and oxic zones. Multiple considerations prove that this redox pattern is a primary signal and not related to modern weathering. Our study thus provides the first systematic evidence for the existence of manganous-ferruginous and nitrogenous conditions and suggests highly complex redox conditions in early Cambrian oceans. The pattern of progressive water-column oxygenation at Silikou can be explained by secular expansion of the oxic surface layer of the ocean and/or by regional or global sea level falls. The pattern of secular bottom-water redox variation at Silikou is permissive of the existence of a strong lateral and depth-related redox stratification in the early Cambrian sea of the Nanhua Basin, as predicted by the multiple chemical zonation model of Li, Cheng, et al. (2015), although confirmation of this hypothesis will require a redox analysis of multiple sections along a proximality trend within a tightly constrained stratigraphic correlation framework. Our study highlights the need for further analysis of redox conditions and water-column stratification in early Cambrian oceans, an understanding of which is essential for evaluation of contemporaneous life-environment coevolutionary patterns.



Acknowledgments

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