Marine redox variations and nitrogen cycle of the early Cambrian southern margin of the Yangtze Platform, South China: Evidence from nitrogen and organic carbon isotopes

Dan Wang^{a,*}, Ulrich Struck^b, Hong-Fei Ling^a, Qing-Jun Guo^c, Graham A. Shields-Zhou^{d,e}, Mao-Yan Zhu^e, Su-Ping Yao^a

^a State Key Laboratory for Mineral Deposits Research, School of Earth Sciences and Engineering, Nanjing University, Nanjing 210023, China

^b Museum für Naturkunde, Leibniz Institute for Evolution and Biodiversity Science, Berlin 10115, Germany

^c Center for Environmental Remediation, Institute of Geographic Sciences and Natural Resources Research, Chinese Academy of Sciences, Beijing 100101, China

^d Department of Earth Sciences, University College London, Gower Street, London WC1E 6BT, UK

^e State Key Laboratory of Palaeobiology and Stratigraphy, Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences, Nanjing 210008, China

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ABSTRACT

The early Cambrian is a crucial interval, during which the marine environment encountered significant perturbations alongside key biological innovations. The nitrogen isotopic composition of ancient sediments has the potential to record co-variation between the marine ecosystem and environmental conditions. Here we report bulk nitrogen and organic carbon isotopic compositions accompanied by Mo concentration data (a proxy for redox conditions) for a shelf marginal drill core section (Sancha) and a deep basinal outcrop section (Yuanjia) in Hunan province, South China.

For the Cambrian Fortunian Stage, variable $\delta^{15}\text{N}_{\text{bulk}}$ values (-4 to $+2\text{‰}$) and low $\delta^{13}\text{C}_{\text{org}}$ values (-35‰ to -33‰) from the Yuanjia section indicate that anoxic waters shoaled into the photic zone, with ammonia assimilation competing with anammox in the basinal area. In the late Cambrian Stage 2, low $\delta^{15}\text{N}_{\text{bulk}}$ and $\delta^{13}\text{C}_{\text{org}}$ values, together with high Mo_{bulk} concentrations ($\delta^{15}\text{N}_{\text{bulk}} = -5$ to 0‰ ; $\delta^{13}\text{C}_{\text{org}} = -33.5$ to -31.0‰ ; >100 ppm Mo_{bulk} in Sancha section and $\delta^{15}\text{N}_{\text{bulk}} = \sim 0\text{‰}$; $\delta^{13}\text{C}_{\text{org}} = \sim -33\text{‰}$; >100 ppm Mo_{bulk} in Yuanjia section), reflect intense N_2 -fixation accompanied by intermittent ammonia assimilation under expanded euxinic condition with shoaling chemocline possibly into the photic zone. In the early Cambrian Stage 3, relatively high $\delta^{15}\text{N}_{\text{bulk}}$ values, alongside positive $\delta^{13}\text{C}_{\text{org}}$ excursions, at both sections indicate an increasing contribution from ^{15}N -enriched nitrate assimilation and hence more oxic conditions. Shelf margin sediments from the middle and late parts of Cambrian Stage 3 are characterized by low $\delta^{15}\text{N}_{\text{bulk}}$ values ($\sim 0\text{‰}$), being lowest in the basinal area (-3 to 0‰). In combination with high Mo_{bulk} concentration (>100 ppm) and high $\text{Mo}/\text{TOC}_{\text{bulk}}$ ratios (averaging ~ 18) in deep basinal sediments, these data suggest that the photic zone became anoxic again, but that sulfidic conditions occurred in the basinal area only. Compared with Stage 2, euxinia was less extensive during this interval, with photosynthetic biomass dominating over chemoautotrophic biomass at both localities.

Based on a combination of $\delta^{15}\text{N}$ data from this study and published data from studies on contemporaneous sections in Yunnan Province and the Three Gorges area, it is possible to reconstruct the spatial variability and temporal evolution of redox conditions in the various marine environments along the southern margin of the Yangtze platform. The basinal area appears to have been dominated by anoxia and intermittent euxinia in the photic zone during most of the early Cambrian (Fortunian Stage to Stage 3) with the exception of more oxic conditions during early Stage 3. On the platform, oxygenated shallow water prevailed with the exception of the notable Cambrian Stage 2 anoxic event. The outer shelf area experienced anoxia from Stage 2 to Stage 3 of the early Cambrian, although of possibly limited areal extent. The high Mo_{bulk} concentrations and $\text{Mo}/\text{TOC}_{\text{bulk}}$ ratios suggest that the South China basin was

* Corresponding author at: School of Earth Sciences and Engineering, Nanjing University, 163 Xianlin Road, Nanjing 210023, China. Tel.: +86 025 89680885; fax: +86 025 83686016.

E-mail address: njuwangdan@gmail.com (D. Wang).

well connected with the considerably oxygenated open ocean and that the mean low $\delta^{15}\text{N}_{\text{bulk}}$ values ($\sim +1.6\text{‰}$) from the basin may reflect generally lower $\delta^{15}\text{N}$ composition for seawater nitrate in the early Cambrian compared with modern value.

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1. Introduction

The early Cambrian is a key interval in the development of the Earth system with major chemical perturbations to the ocean and a significant bio-radiation ('Cambrian Explosion') co-occurring at this time. Revolutionary changes to marine ecosystems during the early Cambrian undoubtedly involved complex mutual interactions and co-evolution with environmental changes. Numerous geochemical data have been obtained to reconstruct changes in the marine environment during that time. Some geochemical studies suggest that ocean basins were well oxygenated by the late Ediacaran (Canfield et al., 2007; Fike et al., 2006; Scott et al., 2008). However, more researchers provide evidence for the persistence of ferruginous and/or intermittently euxinic deep waters into the early Cambrian, particularly over the Yangtze block of South China (Canfield et al., 2008; Goldberg et al., 2007; Li et al., 2010; Och et al., 2013; Poulton and Canfield, 2011; Wille et al., 2008; Xu et al., 2012). The widespread occurrence of oceanic anoxia apparently conflicts with the contemporaneous bio-radiation, necessitating more research into the details of early Cambrian ocean redox conditions.

A 'sandwich'-like model for Precambrian ocean margins has recently been proposed, with mid-depth euxinic waters in between oxic surface waters and ferruginous deep waters (Li et al., 2010, 2012a; Lyons et al., 2012; Poulton and Canfield, 2011; Poulton et al., 2010; Reinhard et al., 2009). Such a 'sandwich'-like redox structure may also have existed during the late Neoproterozoic in South China (Li et al., 2010, 2012a), where it likely persisted into the early Cambrian (Feng et al., 2014; Jin et al., 2014). Mid-depth euxinia over the margins of the Yangtze platform expanded greatly during a worldwide marine transgression in Cambrian Stage 2 (~early Tommotian) and then shrank gradually during the subsequent regression that was accompanied by widespread oxygenation of the shallower realms (Feng et al., 2014; Jin et al., 2014). Such spatial and temporal variations of the marine redox structure have probably played a key role in biological innovation during the contemporaneous Cambrian bio-radiation.

Given that the nitrogen cycle is not only closely related to marine environmental conditions and biological metabolism, but also reflects the ocean redox structure, an increasing number of studies have been conducted on the nitrogen isotope systematics of Ediacaran – early Cambrian marine sediments (Ader et al., 2014; Cremonese et al., 2013, 2014; Kikumoto et al., 2014; Wang et al., 2013). However, these studies mainly focused on the shallow platform realm. In order to better constrain the Early Cambrian N cycle, not only in the shallow platform waters but also in the distant basinal waters, as well as redox conditions along the southern margin of the Yangtze platform, we carried out a comprehensive study of bulk nitrogen and organic carbon isotopes, and Mo concentrations of sedimentary rock samples from a drill core at the shelf margin (Sancha section) and a deep basinal outcrop section (Yuanjia section) in Hunan Province, China (Fig. 1).

1.1. The marine nitrogen cycle

Nitrogen is essential for life because this element is an important constituent of amino acids, nucleic acids, pigments such as chlorophyll, and other biomolecules (Canfield et al., 2010; Godfrey and Glass, 2010). The biogeochemical nitrogen cycle is governed by biological functions that are closely coupled to oxygen and

carbon cycling. As a consequence, nitrogen isotope signals preserved in organic matter can reflect the redox state of the ocean as well as metabolic processes and pathways. Recently, a growing number of nitrogen isotope studies on marine sediments have demonstrated the potential of N isotope systematics in reconstructing the environmental and biogeochemical history of the oceans (Robinson et al., 2012; Tesdal et al., 2013).

In the modern ocean, biologically available nitrogen enters the marine system mainly through N_2 -fixation by aerobic or anaerobic autotrophs such as cyanobacteria with a negligible isotopic fractionation (Sigman et al., 2009). After the death of organisms, organic-N is converted to ammonium (NH_4^+) through ammonification with little fractionation ($\epsilon = \delta^{15}\text{N}_{\text{reactant}} - \delta^{15}\text{N}_{\text{product}} < 3\text{‰}$) (Prokopenko et al., 2006; Sigman et al., 2009). This ammonium is then rapidly oxidized to nitrite (NO_2^-) and subsequently to nitrate (NO_3^-) through nitrification with negligible fractionation under modern oxic conditions or with a significant fractionation under oxygen-deficient conditions (Sigman et al., 2009; Wang et al., 2013). The removal of fixed-N from the marine system takes place via denitrification and anaerobic ammonium oxidation (or anammox) in anoxic environments, if not retained in the sedimentary pile. During denitrification, oxidized N species (NO_3^- and NO_2^-) are reduced to gaseous forms of N such as nitrous oxide (N_2O) or N_2 with substantial isotopic fractionation (c. 20‰ to 30‰) in the water column, but with negligible fractionation in the sediments (Sigman et al., 2009). The anammox process is conducted by strictly anaerobic chemoautotrophic bacteria with ammonium (NH_4^+) being oxidized to N_2 by nitrite (NO_2^-) (Kuypers et al., 2003); isotopic fractionation during this process remains unclear but has been inferred to be $\sim 25\text{‰}$ (Prokopenko et al., 2006). During both water-column denitrification and anammox processes, $^{14}\text{NO}_3^-$ is preferentially used and so the heavier isotope ^{15}N will become relatively enriched in the nitrate pool (Sigman et al., 2009).

Today phototrophic organisms are able to utilize various forms of dissolved nitrogen species such as dinitrogen, nitrate, ammonia and urea to synthesize organic matter, which is then transported to the sediments and preserved through geological time (Sigman et al., 2009; Waser et al., 1998). However, organic particles are mostly produced in the euphotic zone, and they usually go through biotic alterations such as microbial digestion or deamination during sinking and deposition (Robinson et al., 2012). In modern oceans, suspended organic particles in surface waters have the lowest $\delta^{15}\text{N}$ due to N_2 fixation or assimilation of low- $\delta^{15}\text{N}$ ammonium released by heterotrophic organisms (ammonium recycling), but their $\delta^{15}\text{N}$ values increase below the euphotic zone (Altabet, 1988; Sigman et al., 2009). Particulate nitrogen, which is relatively enriched in ^{15}N , is preferentially exported as sinking particles. The $\delta^{15}\text{N}$ values of these particles do not change with depth in regions of high sediment accumulation such as continental margins, but show a slightly decreasing trend in regions of low organic N depositional flux (Altabet et al., 1991; Sigman et al., 2009).

It has been suggested that $\delta^{15}\text{N}$ alteration occurs mainly at the seafloor, and that there may be various changes in the $\delta^{15}\text{N}$ of bulk sediments such as increases or decreases during early burial in low-productivity regions, depending on oxic or anoxic conditions, respectively (Lehmann et al., 2003; Robinson et al., 2012). Diagenetic alteration under oxic conditions usually increases the $\delta^{15}\text{N}$ composition of organic matter (Gaye et al., 2009; Lehmann et al., 2002; Möbius et al., 2011; Nakanishi and Minagawa, 2003). This is

Fig. 1. Simplified geological map of the Yangtze block (after Jiang et al., 2012; Steiner et al., 2007; Zhu et al., 2007) and stratigraphic columns of Sancha and Yuanjia sections (after Li et al., 2012b and Guo et al., 2013).

because amino acids are much more easily degraded and therefore release more ^{14}N under oxic than anoxic conditions (Nguyen and Harvey, 1997). However, NH_4^+ generated beneath the seafloor can be captured by clay minerals, in which case $\delta^{15}\text{N}_{\text{bulk}}$ values may show little or no change (Freudenthal et al., 2001).

In the modern oxygenated oceans, the global mean $\delta^{15}\text{N}$ value of nitrate is $\sim +5\text{‰}$ (Sigman et al., 2009), and the average $\delta^{15}\text{N}$ value in sediments is $\sim +7\text{‰}$, which is close to the expected value following complete assimilation of seawater nitrate and minor modification at the seafloor (Pinti and Hashizume, 2011). By contrast, in some regions near zones of water column anoxia with high water-column denitrification and/or anammox rates and complete nitrate assimilation, the $\delta^{15}\text{N}$ values of seafloor sediments may be higher (Tesdal et al., 2013). In some modern stratified basins such as the Black Sea, where the $\text{O}_2/\text{H}_2\text{S}$ interface exists in the water column instead of in the sediment column, green or purple sulfur bacteria (GSB and PSB) that live principally near the chemocline in the presence of free H_2S in the photic zone (Ohkouchi et al., 2005) can either participate in N_2 -fixation or assimilate ammonia and/or nitrite with a large and variable fractionation depending on the seawater ammonia concentration (Ohkouchi et al., 2005; Pennock et al., 1996), producing very low $\delta^{15}\text{N}$ values. In these anoxic environments, microbial degradation is suggested to retain the initial $\delta^{15}\text{N}$ value or only slightly decrease the $\delta^{15}\text{N}$ value (Altabet et al., 1999; Higgins et al., 2010; Junium and Arthur, 2007; Möbius et al., 2010). Therefore, $\delta^{15}\text{N}$ values of sediments can directly reflect both the nitrogen biogeochemical cycle and the redox conditions in the marine

environment. However, an evaluation is needed to determine whether or not the original $\delta^{15}\text{N}$ values of sediments have been significantly modified during diagenesis, before they can be used as a biogeochemical tracer.

1.2. Molybdenum geochemistry

The trace element molybdenum, preserved in black shales, can be a useful redox proxy of the modern ocean (Algeo and Maynard, 2004; Dahl et al., 2011; Scott et al., 2008; Scott and Lyons, 2012; Tribouillard et al., 2006). In the modern oxygenated ocean, Mo is the most abundant transition metal ($\sim 105\text{ nM}$) (Collier, 1985; Lyons et al., 2009) and exists primarily as molybdate (MoO_4^{2-}), with a residence time of $\sim 0.8\text{ Myr}$ (Emerson and Husted, 1991; Morford and Emerson, 1999). The major source of Mo to the ocean is oxidative weathering of crustal sulfides and black shales (Bertine and Turekian, 1973). The largest modern oceanic sink for Mo is co-precipitation and adsorption with Mn-oxyhydroxides in oxic environments (Barling et al., 2001; McManus et al., 2006; Siebert et al., 2003). However, the behavior of Mo depends strongly on redox conditions. Under anoxic and non-sulphidic (ferruginous) conditions, dissolved Mo can be transported to the sediments via absorption to Fe (oxyhydr)oxides as has been observed in the modern ferruginous Matano Lake, Indonesia (Crowe et al., 2008a; Goldberg et al., 2009). In anoxic environments with minor amounts of dissolved sulfide, molybdate transported from the oxic environment is converted to a series of particle-reactive thiomolybdate

($\text{MoO}_4\text{S}_{4-x}^{2-}$) species (Helz et al., 1996). Furthermore, in euxinic seawater, in which aqueous hydrogen sulfide (H_2S) exceeds a threshold concentration of about $11\text{ }\mu\text{mol}$, tetrathiomolybdate (MoS_4^{2-}) forms and is rapidly scavenged by pyrite and organic matter, resulting in near-quantitative removal of Mo (Algeo and Lyons, 2006; Erickson and Helz, 2000; Helz et al., 1996, 2011; Huerta-Diaz and Morse, 1992; Tribouillard et al., 2004; Vorlíček and Helz, 2002; Vorlíček et al., 2004). This leads to significant Mo enrichment in the sediments as long as concentrations remain high in ambient seawater. Previous studies have concluded that minor Mo enrichments in black shales (between crustal average 2 ppm to 25 ppm) normally imply non-euxinic conditions, while large Mo enrichments ($>100\text{ ppm}$) represent permanently euxinic conditions in the depositional environment, and imply a good connection to the oxic open ocean (Algeo and Lyons, 2006; Scott and Lyons, 2012). Intermediate Mo enrichments (25–100 ppm) may reflect either intermittent euxinia or Mo depletion in the water column (Algeo and Lyons, 2006; Scott and Lyons, 2012).

Mo concentrations and TOC contents exhibit co-variation in modern euxinic marine sediments as well as in many ancient black shales (Algeo and Lyons, 2006; Algeo and Maynard, 2004; Holland, 1984; Robl and Barron, 1988). It has been demonstrated that sedimentary Mo/TOC ratios can be a useful paleohydrographic proxy to assess the degree of watermass restriction, but only under anoxic conditions (Algeo and Lyons, 2006; Algeo and Rowe, 2012). In sulfidic silled basins, aqueous Mo concentrations can be lowered as a result of sedimentary Mo uptake without adequate resupply through deep water renewal (Algeo and Lyons, 2006; Algeo and Rowe, 2012). As a result, sedimentary Mo concentrations and Mo/TOC ratios decrease as the redox conditions become increasingly sulfidic in silled basins, and it has been suggested that modern sedimentary Mo/TOC ratios with values of >35 , ~ 15 – 35 , and <15 indicate weak, moderate, and strong restriction, respectively (Algeo and Lyons, 2006; Algeo and Rowe, 2012).

By analyzing the nitrogen isotope compositions and Mo concentrations of bulk sedimentary samples, we hope to be able to reveal primary changes in nutrient cycling/sources to the ancient ocean, and to identify the dominant metabolic process (nitrogen fixation, or nitrification, or denitrification/anammox) involved in nitrogen cycling. Based on these data and results from previous studies of the neighboring, shallow marine environment, we further discuss changes in productivity, ecosystem evolution and chemical/redox stratification of the basin along the southern margin of the Yangtze platform during the early Cambrian.

2. Geological setting

Paleogeographic reconstruction shows that the late Ediacaran–early Cambrian succession overlying the Yangtze block of South China was deposited in various paleoenvironmental settings from large platformal areas with a transitional zone interpreted as outer shelf, into slope and then deeper more basinal areas (Jiang et al., 2012; Steiner et al., 2007; Zhu et al., 2007). The shelf regions of the Yangtze block were subaerially exposed and partially eroded during the earliest Cambrian, but a transgression during Cambrian Stage 2 (~early Tommotian) submerged the shelf margins and led to homogeneous deposition of fine-grained, frequently organic-rich sediments across the entire Yangtze block (Jiang et al., 2012; Steiner et al., 2007; Zhu et al., 2003). These ‘black shales’ are suggested to have been deposited under widespread anoxic, or even euxinic conditions based on numerous lines of geochemical evidence (Canfield et al., 2008; Goldberg et al., 2005, 2007; Guo et al., 2007a; Kimura and Watanabe, 2001; Lehmann et al., 2007; Och et al., 2013; Wang et al., 2012a; Wille et al., 2008; Xu et al., 2012). Presumably, because of the rapidity of

this sea level rise, lower Cambrian units across much of South China are condensed with only a few centimeters thickness in the deeper water realms (Goldberg et al., 2007; Schütter, 1998; Steiner et al., 2001, 2007). Related to this condensation, a polymetallic enrichment layer occurs sporadically in the lower portion of this transgressive black shale along a NE-striking 1600 km belt, which can be used as a correlation marker (Jiang et al., 2012; Och et al., 2013; Zhu et al., 2003), but mineable ore layer is usually less than half meters in thickness and exposed only within Guizhou and Hunan provinces (Jiang et al., 2006, 2007). The deposit formed under sulfidic depositional conditions although the origin of the metal enrichment has proven controversial (Jiang et al., 2006; Lehmann et al., 2007; Steiner et al., 2007).

Our two studied sections are both located in Hunan Province where the sedimentary facies dramatically changes from platform margin to slope and deep basinal facies (Vernhet, 2007). Drill core samples were obtained from the Sancha section in Zhangjiajie. The Sancha section is located at shelf margin area and consists of uppermost Dengying and Niutitang formations with a sedimentary hiatus between them. The uppermost Dengying Formation consists mainly of massive dolomite, while the overlying Niutitang Formation comprises black shales and siltstone with phosphatic nodules and a polymetallic rich layer at the base (Fig. 1). Pb–Pb ages of $521 \pm 54\text{ Ma}$ for sulfide ores from Sancha section outcrops in Hunan and of $531 \pm 24\text{ Ma}$ for the underlying black shales at Zunyi, Guizhou have been obtained (Jiang et al., 2006). These ages are consistent with the Re–Os isochron age of $521 \pm 5\text{ Ma}$ ($n = 14$) for the sulfide ore layer at the base of the Niutitang Formation sampled at three mine sites at the Sancha, Dazhuliushui and Maluhe sections (Xu et al., 2011) and also with the U–Pb age of $532 \pm 0.7\text{ Ma}$ for zircons from a volcanic ash bed beneath the Ni–Mo sulfide marker layer in the lowermost Niutitang Formation in Guizhou province (Jiang et al., 2009).

The Yuanjia section in Zhongfang County which is a basinal section (Jiang et al., 2011) consists of the upper part of the Liuchapo Formation and the overlying Niutitang Formation. The Liuchapo Formation is mainly composed of black cherts with phosphatic siliceous interlayers. The Niutitang Formation comprises mainly black shales with a phosphatic nodule layer and a polymetallic rich layer at the base and another phosphate nodule layer at a horizon 33–40 m from the base of the section (Fig. 1). The Precambrian–Cambrian boundary has been suggested to be placed within the upper Liuchapo Formation where there occurs a negative $\delta^{13}\text{C}_{\text{org}}$ excursion that could be correlated with the negative $\delta^{13}\text{C}_{\text{carb}}$ excursion in the Daibu Member of the Zhujiqing Formation at Xiaotan section (Guo et al., 2013; Li et al., 2013a; Zhou et al., 1997).

High organic H/C ratios (0.3–1.8) of the Liuchapo and Xiaoyanxi (equivalent to the Niutitang Formation) formations at the Yanwutan–Lijiatuo section, which is about 75 km away from Sancha section and only 4 km away from Yuanjia section in Hunan Province (Guo et al., 2007b), suggest that the studied area did not experienced greenschist facies metamorphism (Hayes et al., 1983). Observations on the petrography of sedimentary rocks at the studied sections and on the regional geology also show that the Ediacaran and early Cambrian strata in this region preserve original structures of the shales and mudstones, suggesting little metamorphism occurred to the strata.

3. Material and methods

The Sancha drill-core samples guarantee minimum secondary alteration due to surface weathering. For the Yuanjia outcrop section, only fresh samples were selected for chemical treatment and isotopic analyses. All selected samples were cut into pieces about

3–5 cm in diameter avoiding calcite or siliceous veining and ground into a homogeneous powder. Ground samples were oven-dried at a temperature of 40 °C, in preparation for carbon and nitrogen isotope analyses. Isotopic ratios for nitrogen and organic carbon were measured in the laboratories of the “Museum für Naturkunde” in Berlin using a Thermo Finnigan Elemental Delta V Mass Spectrometer coupled with a Thermo 1112 Flash Elemental Analyser via a Thermo ConFloIII Interface. Replicates of $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ sample analyses exhibited a standard deviation of less than $\pm 0.3\%$.

For carbon isotope analysis, about 20–30 mg of ground sample were weighed and digested in 2 mol/L hydrochloric acid (HCl) overnight to completely remove carbonate. Residues were washed with distilled water to remove chlorides and dried at 40 °C overnight. The decalcified sample powder was then wrapped into tin capsules for organic carbon isotope and total organic carbon ($\text{TOC}_{\text{decarb}}$) measurements. Carbon isotope values ($\delta^{13}\text{C}_{\text{org}}$) are reported in per mil relative to the international V-PDB standard value. Total nitrogen and organic carbon contents in decalcified samples ($\text{TN}_{\text{decarb}}$ and $\text{TOC}_{\text{decarb}}$) were measured at the Center of Modern Analysis Nanjing University, using Elementar Vario MICRO.

According to the organic matter content, approximately 30–150 mg of bulk material was weighed into tin capsules for nitrogen isotope and total nitrogen content (TN_{bulk}) measurements and a carbon-absorbing trap was used in the EA to avoid interferences during the nitrogen isotope analysis due to high carbon contents. Nitrogen isotope delta values ($\delta^{15}\text{N}_{\text{bulk}}$) are reported relative to air and $\delta^{15}\text{N}_{\text{bulk}}$ and TN_{bulk} data are calculated using a Peptone house-standard whose value is $\delta^{15}\text{N}_{\text{bulk}} = +7.6\%$, $\text{TN} = 12.1\%$. Samples with total nitrogen content (TN_{bulk}) higher than 0.012 mg are considered to yield reasonable $\delta^{15}\text{N}_{\text{bulk}}$ results. The reliability of nitrogen isotope analytical performance has been proven previously in extensive ‘Round Robin’ comparative testing (Bahlmann et al., 2010).

Trace element contents were measured at two laboratories: at the State Key Laboratory for Mineral Deposits Research, Nanjing University using a Bruker Aurora M90 ICP-MS, and at the laboratory of the Institute of Geographic Sciences and Natural Resources Research, using a PE Elan DRC-e ICP-MS. Bulk samples were leached with 2 mol/L HCl in order to remove carbonate and phosphate, after which the remains were fully dissolved in high pressure Teflon bombs using a conc. HF + conc. HNO_3 mixture with a volume ratio of 1:3. After evaporation, samples were re-dissolved in 3% HNO_3 for analysis. Analytical uncertainties for most elements were typically lower than 5%.

4. Results

The results for bulk nitrogen ($\delta^{15}\text{N}_{\text{bulk}}$) and organic carbon ($\delta^{13}\text{C}_{\text{org}}$) isotopes, total organic carbon contents in bulk and decarbonated samples (TOC_{bulk} and $\text{TOC}_{\text{decarb}}$), total nitrogen contents in bulk and decarbonated samples (TN_{bulk} and $\text{TN}_{\text{decarb}}$) and Mo concentrations in bulk samples (Mo_{bulk}) from the Sancha and Yuanjia sections are presented in Tables 1 and 2, together with C/N_{decarb} ratios (calculated from the measured $\text{TOC}_{\text{decarb}}$ and $\text{TN}_{\text{decarb}}$ contents on an atomic basis) and Mo/TOC_{bulk} ratios (calculated directly from the measured Mo_{bulk} concentration and TOC_{bulk} data, ppm/%). Depth profiles for $\delta^{15}\text{N}_{\text{bulk}}$, $\delta^{13}\text{C}_{\text{org}}$, TOC_{bulk} , TN_{bulk} , Mo_{bulk} concentrations and Mo/TOC_{bulk} for both sections are shown in Fig. 2.

4.1. Sancha section

For the phosphatic nodule and polymetallic rich unit in the lower Niutitang Formation (0–20 m), the $\delta^{13}\text{C}_{\text{org}}$ profile fluctuates between -33.5% and -31.0% , and exhibits a small negative shift.

The TOC_{bulk} contents are high, ranging from 1.1% to 19.0% with an average value of 9.4%. The $\delta^{15}\text{N}_{\text{bulk}}$ profile smoothly decreases from $+1.1\%$ to -1.0% , with the exception of a sharp negative shift to the lowest value -4.7% . TN_{bulk} contents lie between 0.025% and 0.134%, averaging 0.092%. Mo_{bulk} concentrations are high, ranging from 30 ppm to 1180 ppm, averaging 166 ppm. Correspondingly, Mo/TOC_{bulk} ratios are relatively high, averaging 27.6 (Fig. 2a).

For the black shales in the middle part of the Niutitang Formation (20–80 m), $\delta^{13}\text{C}_{\text{org}}$ values firstly increase to a high value of -29.3% , then decrease back to a low value of -31.2% , exhibiting a positive excursion in this interval. TOC_{bulk} contents decrease to 0.7–3.1%, averaging 1.8%. $\delta^{15}\text{N}_{\text{bulk}}$ values are relatively high, fluctuating between $+0.3\%$ and $+3.1\%$, accompanied by relatively stable TN_{bulk} contents (0.042% to 0.132%, with an average of 0.101%). Similarly, Mo_{bulk} concentrations decrease to 7–46 ppm with an average value of 23 ppm, while Mo/TOC_{bulk} ratios range from 7.8 to 20.5, averaging 13.4 (Fig. 2a).

For the black shales in the upper part of the Niutitang Formation (80–140 m), $\delta^{13}\text{C}_{\text{org}}$ values remain constant between -30.6% and -30.2% . TOC_{bulk} contents in this part are low, averaging 0.3%. The $\delta^{15}\text{N}_{\text{bulk}}$ curve continuously decreases to near zero, and TN_{bulk} contents do not show any apparent change (averaging 0.073%). Mo_{bulk} concentrations are low, averaging 3 ppm, while Mo/TOC_{bulk} ratios average 7.9 (Fig. 2a).

4.2. Yuanjia section

In the upper part of the Liuchapo Formation (0–18 m), $\delta^{13}\text{C}_{\text{org}}$ values are relatively low and exhibit a negative excursion, firstly decreasing from -33.9% to -34.8% , and then increasing back to -32.9% in the uppermost Liuchapo Formation. TOC_{bulk} contents range from 1.0% to 6.9%, averaging 2.9%. $\delta^{15}\text{N}_{\text{bulk}}$ values mainly fluctuate between -4.3% and $+1.4\%$. TN_{bulk} contents are relatively low, ranging between 0.013% and 0.047% with an average value of 0.024%. Mo_{bulk} concentrations are between 2.20 ppm and 30.2 ppm with an average value of 11.7 ppm. Correspondingly, Mo/TOC_{bulk} ratios are characterized by an average value of 4.1 (Fig. 2b).

For the phosphatic nodule and polymetallic rich unit in the lower Niutitang Formation (18–22 m), $\delta^{15}\text{N}_{\text{bulk}}$ values fluctuate around zero and $\delta^{13}\text{C}_{\text{org}}$ values are relatively constant around -32.5% . TOC_{bulk} contents sharply increase above 10% while TN_{bulk} contents gradually increase from 0.024% to 0.117%. Mo_{bulk} concentrations obtain their highest level here at 271 ppm with a highest Mo/TOC_{bulk} ratio of 13.9 (Fig. 2b).

For the black shales with phosphate nodules layer in the middle part of the Niutitang Formation (22–40 m), $\delta^{13}\text{C}_{\text{org}}$ values increase to -30.6% , and then decrease back to -33.6% at the top of the second phosphate nodule layer. TOC_{bulk} contents are high, ranging from 2.1% to 19.0% with an average value of 12.2%. However, TOC_{bulk} contents of three samples (Yuj-563, Yuj-565 and Yuj-568) are abnormally low. Although this might be attributed to the degradation of organic matter, the $\delta^{13}\text{C}_{\text{org}}$ positive excursion during this interval remains unaffected. $\delta^{15}\text{N}_{\text{bulk}}$ values exhibit a positive excursion (-1.63% to $+2.16\%$), accompanied by increasing TN_{bulk} contents (0.024–0.249%, averaging 0.136%). Mo_{bulk} concentrations range between 2.21 ppm and 100 ppm, averaging 44.3 ppm. The average value of Mo/TOC_{bulk} ratios is 3.5 (Fig. 2b).

For the black shales in the upper part of the Niutitang Formation (40–71 m), the $\delta^{13}\text{C}_{\text{org}}$ curve keeps increasing from -33.1% to -31.7% , while TOC_{bulk} contents are consistently high, averaging 12.1%. $\delta^{15}\text{N}_{\text{bulk}}$ values decrease smoothly from $+1.8\%$ to -3.0% . Meanwhile, the TN_{bulk} contents jaggedly decrease from approximately 0.25% to 0.05%. Notably, Mo_{bulk} concentrations dramatically increase to over hundreds of ppm, averaging 229 ppm.

Table 1Results of organic carbon and bulk nitrogen isotope analysis of Sancha section samples. The TOC_{bulk} contents and Mo_{bulk} concentrations are from Li et al. (2013b).

Sample	Lithology	Depth (m)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	TOC (%)		$\delta^{15}\text{N}_{\text{bulk}}$ (‰)	TN (%)		C/N (atom)	Mo _{bulk} (ppm)	Mo/TOC _{bulk} (ppm/%)
				decarb	bulk		decarb	bulk			
Niutitang Formation											
SC-001	P-nodules layer	0	−31	9.3	1.1		0.037		293.9	238	217.9
SC-003	P-nodules layer	1.7	−31.9	4.4	1.2	0.4	0.029	0.025	177.8	30	25.7
SC-004	P-nodules layer	2.4	−31.1	19.4	19.0	−0.1	0.240	0.085	94.5	67	3.5
SC-005	P-nodules layer	2.9	−33.5	25.6	17.9	1.1	0.344	0.134	86.7	32	1.8
SC-009	Ni–Mo layer	4.2	−32.3	19.1	16.2	−0.5	0.188	0.102	118.3	220	13.6
SC-011	Ni–Mo layer	5.7	−32.4	17.4	15.1	−0.1	0.181	0.105	111.8	1180	77.9
SC-013	Dolomitic black shales	7.7	−31.8	15.1	14.1	−0.2	0.168	0.099	105.0	120	8.5
SC-015	Dolomitic black shales	8.7	−31.9	15.3	12.0	−0.5	0.151	0.096	118.3	142	11.8
SC-016	Dolomitic black shales	9.1	−32	8.8	8.3	−0.5	0.154	0.094	66.9	129	15.5
SC-017	Dolomitic black shales	9.7	−31.8	3.6	1.8	−0.9	0.043	0.034	97.1	31	17.3
SC-019	Dolomitic black shales	10.7	−31.9	9.7	8.9	−0.6	0.144	0.088	78.5	119	13.4
SC-021	Dolomitic black shales	11.9	−31.8	7.0	6.6	−0.5	0.170	0.104	48.1	202	30.8
SC-023	Dolomitic black shales	12.9	−31.8	8.1	7.7	−4.7	0.123	0.118	76.6	99	12.9
SC-026	Dolomitic black shales	14.6	−32.4	5.2	4.8	−1	0.100	0.061	60.8	88	18.2
SC-028	Dolomitic black shales	15.6	−31.5	7.2	4.6	−0.8	0.134	0.060	62.7	96	20.6
SC-030	Dolomitic black shales	17.2	−31.6	13.4	12.6	0	0.155	0.091	101.2	205	16.3
SC-031	Dolomitic black shales	18.2	−31.5	8.9	7.5	0.5	0.143	0.110	72.2	42	5.6
SC-033	Dolomitic black shales	19.8	−32.9	11.4	10.1	0.8	0.169	0.123	78.7	63	6.3
SC-037	Dolomitic black shales	22.9	−31.1	9.7	8.9	0.7	0.167	0.125	67.7	60	6.8
SC-039	Black shales	24.5	−30.4	2.4	2.2	0.8	0.124	0.108	22.2	46	20.5
SC-042	Black shales	27	−30.1	2.3	2.1	1	0.107	0.105	24.9	32	14.9
SC-047	Black shales	31.1	−31.3	2.1	2.0	2.5	0.154	0.132	15.5	32	16.4
SC-050	Black shales	34.1	−30.1	2.1	2.0	2.2	0.132	0.108	18.2	30	15.0
SC-058	Black shales	39.6	−29.8	2.8	2.7	1.4	0.127	0.111	26.1	21	7.8
SC-064	Black shales	44.5	−29.6	2.4	2.3	2	0.146	0.114	18.9	19	8.3
SC-069	Black shales	49.4	−30	3.2	3.1	0.8	0.133	0.092	28.2	43	14.1
SC-070	Black shales	50.9	−29.3			0.7	0.089	0.094	0.0	12	
SC-073	Black shales	53.6	−29.9	2.2	1.9	1.8	0.124	0.101	20.7	22	11.3
SC-076	Black shales	56.7	−30.2	1.9	0.8	0.3	0.121	0.042	18.1	7	8.6
SC-081	Black shales	62.6	−29.9	0.9	0.8	2	0.127	0.098	7.8	13	16.0
SC-088	Black shales	74.3	−30.3	0.9	0.8	3.1	0.124	0.108	8.2	7	8.4
SC-092	Black shales	80.9	−31.2	0.7	0.7	1.2	0.130	0.100	6.3	13	19.5
SC-099	Black shales	92.5	−30.6	0.3	0.3	0.6	0.115	0.089	3.0	2	7.1
SC-107	Black shales	107.5	−30.2	0.4	0.4	0.5	0.068	0.054	7.5	5	12.5
SC-109	Black shales	111.7	−30.3	0.4	0.4	0.5	0.088	0.067	5.6	2	5.1
SC-122	Black shales	138.3	−30.6	0.3	0.3	0.2	0.100	0.080	3.7	2	6.9

Correspondingly, Mo/TOC_{bulk} ratios increase from 8.3 to 33.8, averaging 18.2 (Fig. 2b).

5. Discussion

5.1. Regional correlation

Stratigraphic correlation for deep water sections is difficult due to the lack of marker fossils. At Yuanjia section, the Precambrian–Cambrian boundary could be placed at the negative $\delta^{13}\text{C}_{\text{org}}$ excursion in the upper Liuchapo Formation (Guo et al., 2013) because this excursion may correlate with the $\delta^{13}\text{C}_{\text{carb}}$ and/or $\delta^{13}\text{C}_{\text{org}}$ negative excursions in the Daibu Member of the Zhujiqing Formation at Xiaotan section, Yunnan Province (Cremonese et al., 2013; Li et al., 2013a; Zhou et al., 1997) and in the lower part of the Yanjiahe Formation at Wuhe section, Three Gorges area (Cremonese et al., 2014; Ishikawa et al., 2008; Kikumoto et al., 2014) (Fig. 3b). The small shelly fossil (SSF) zones I and II were identified at Zhongyicun Member of the Zhujiqing Formation, Yunnan and lower Yanjiahe Formation, Three Gorges (Fig. 3a) (Guo et al., 2014; Li and Xiao, 2004; Yang et al., 2014). The combination of carbon isotope correlation and SSFs records suggests that the upper Liuchapo Formation belongs to the Cambrian Fortunian Stage (Fig. 3). Upward, the $\delta^{13}\text{C}_{\text{org}}$ curve exhibits positive excursions in the Dahai Member of the Zhujiqing Formation, Yunnan and in the upper Yanjiahe Formation, Three Gorges area (Cremonese et al., 2013, 2014; Kikumoto et al., 2014) (Fig. 3b), which are typical of early Cambrian Stage 2, consistent with the appearance of the third SSF biozone (Fig. 3a) (Guo et al., 2014; Li and Xiao, 2004; Yang et al., 2014).

Unfortunately, these high $\delta^{13}\text{C}_{\text{org}}$ values were not observed in our study (Fig. 3b), suggesting that deposits of early Stage 2 are missing at Sancha section on the elevated shelf margins due to erosion, and/or are highly condensed at the Yuanjia section due to the extremely low sedimentary rates in the deeper basinal realm (Jiang et al., 2012; Steiner et al., 2007; Zhu et al., 2003).

The early Cambrian Ni–Mo enrichment layers can be tracked at a 1600 km belt along the whole southern margin of the Yangtze Platform and can be used as a correlation marker throughout the region (Jiang et al., 2012; Och et al., 2013; Zhu et al., 2003). A Re–Os isochron age of 521 ± 5 Ma ($n = 14$) has been obtained for the sulfide ore layer near the base of the Niutitang Formation from three mining sites, including Sancha section (the other two sites are Dazhuliushui and Maluhe sections) (Xu et al., 2011) (Fig. 3a). This age is consistent with U–Pb SHRIMP ages of 522.7 ± 4.9 Ma for zircons from a volcanic ash bed approximately one meter below the Ni–Mo layer at Taoying section (Wang et al., 2012b) and of 532.3 ± 0.7 Ma for zircons from a volcanic ash bed about 5 m below the Ni–Mo layer at Zhongnancun section (Jiang et al., 2009), both at the base of the Niutitang Formation in Guizhou (Fig. 3a). The correlation between Ni–Mo enrichment layers of the basal Niutitang Formation in Hunan and Guizhou provinces and the upper Shiyantou Formation at Xiaotan section in Yunnan by Och et al. (2013) is supported by a U–Pb age of 526.5 ± 1.1 Ma for zircons from a volcanic ash bed within the lower part of the Shiyantou Formation at Meishucun section in Yunnan (Compston et al., 2008) (Fig. 3a). Sediments corresponding to the lower-middle Shiyantou Formation are missing at Sancha section due to the erosional event that started during early Stage 2 as mentioned above, and are highly

Table 2

Results of organic carbon and bulk nitrogen isotope analysis of Yuanjia section samples. $\delta^{13}\text{C}_{\text{org}}$ and TOC_{bulk} contents are from Guo et al. (2013), and Mo_{bulk} concentrations of the Niutitang Formation are from Guo et al. (2015).

Sample	Lithology	Depth (m)	$\delta^{13}\text{C}_{\text{org}}$ (‰)	TOC (%)		$\delta^{15}\text{N}_{\text{bulk}}$ (‰)	TN (%)		C/N (atom)	Mo _{bulk} (ppm)	Mo/TOC _{bulk} (ppm/%)
				decarb	bulk		decarb	bulk			
Liuchapo Formation											
Yuj-503	Chert	0	−33.9								
Yuj-508	Chert	3.5	−34	2.0	1.7	1.4	0.024	0.025	95.5		
Yuj-511	Chert	6	−34.1	0.7		−1.8	0.023	0.017	36.1	4.10	
Yuj-516	Chert	9.5	−34.4	1.1	1.0	−1.7	0.026	0.019	49.0	4.70	4.7
Yuj-520	Chert	13	−34.8	1.2	1.2	1.4	0.040	0.028	35.8		
Yuj-522	Chert	14	−34.4	1.3	1.3	−2.1	0.027	0.017	57.4	2.20	1.8
Yuj-524	Chert	15	−33.1	3.5	3.6	0.3	0.047	0.030	87.9		
Yuj-526	Chert	16	−32.8	1.9	1.8	−3	0.027	0.017	83.4	8.70	4.8
Yuj-527	Chert	16.5	−33	2.8	2.7	−4.3	0.027	0.013	120.0	15.6	5.7
Yuj-529	Shaly chert	17.5	−32.9	7.2	6.9	−2.1	0.069	0.024	122.2	16.6	2.4
Yuj-531	Cherty black shale	18.15	−32.3	6.6	6.1	−0.5	0.071	0.047	108.5	30.2	5.0
Niutitang Formation											
Yuj-532	Phosphoritic black shale	18.2	−32.8	6.5	6.3	0.7	0.063	0.055	121.1	33.0	5.2
Yuj-533	Black shale	18.45	−32.9	5.8	5.7	1	0.061	0.056	110.0	28.5	5.0
Yuj-534	Black shale	18.65	−32.9	3.6	3.4	−1.6	0.034	0.024	123.0	15.0	4.4
Yuj-535	Black shale	19	−32.4	6.3	5.8	0	0.069	0.037	106.2		
Yuj-536	Black shale	19.3	−32.9	17.5	19.5	−0.6	0.161	0.068	126.6	271	13.9
Yuj-537	Black shale	19.6	−32.4	25.8	16.9	1.6	0.311	0.117	96.9		
Yuj-543	Black shale	21.2	−32	12.8	12.6	−0.5	0.135	0.074	110.3	17.1	1.4
Yuj-545	Black shale	21.6	−32	14.9	14.9	0	0.170	0.089	101.9		
Yuj-549	Stone coal	22.5	−32	15.8	16.9	1.3	0.223	0.121	82.7	19.6	1.2
Yuj-554	Black shale	23.7	−31.8	14.4	16.7	2	0.227	0.152	73.8		
Yuj-557	Black shale	24.5	−31.7	17.5	13.2	1.4	0.195	0.091	104.8	50.9	3.9
Yuj-559	Black shale	26.5	−31.4	18.8	19.0	2.2	0.256	0.183	85.7		
Yuj-563	Black shale	28.5	−31.3	5.9	4.7					2.21	0.5
Yuj-565	Black shale	29.5	−30.6	2.2	2.1					2.93	1.4
Yuj-568	Black shale	30.5	−31.5	10.0	9.8					17.7	1.8
Yuj-570	Black shale	31.5	−32	13.1	12.5	1.6	0.334	0.236	45.9		
Yuj-571	Black shale	32.5	−32.3	14.8	14.5	1.6	0.303	0.202	56.9	100	6.9
Yuj-573	Black shale	33.2	−32.5	12.4	12.4	1.3	0.269	0.182	53.7	92.0	7.4
Yuj-575	Black shale	34.1	−33.6	9.4	9.2	1.2	0.216	0.147	50.9	11.0	1.2
Yuj-579	Black shale	36	−32.3	14.6	14.8	0.1	0.297	0.189	57.2	65.4	4.4
Yuj-580	Black shale	37.05	−32.7	17.8		0.9	0.307	0.208	67.7		
Yuj-581	Black shale	38.3	−33.4	16.5	12.4	0.4	0.430	0.238	44.9		
Yuj-583	Black shale	39.7	−33.3	12.9	12.2	1.6	0.333	0.249	45.1	81.6	6.7
Yuj-584	Black shale	40.5	−33.1	12.8	12.3	1.5	0.324	0.242	45.9		
Yuj-586	Black shale	42.5	−32.9	15.4	14.6	0.7	0.277	0.187	64.8		
Yuj-587	Black shale	43.85	−32.6	16.5	14.6	1.3	0.312	0.201	61.5	143	9.8
Yuj-588	Black shale	44.5	−32.8	14.7	13.6	1.8	0.417	0.307	41.3		
Yuj-589	Black shale	45.5	−32.9	12.4	11.9	1	0.235	0.170	61.6		
Yuj-591	Black shale	46.5	−33.2	12.8	12.1	1.4	0.306	0.227	48.7		
Yuj-592	Black shale	49	−32.9	12.1	11.1	0.6	0.309	0.218	45.9		
Yuj-593	Black shale	51.5	−32.2	12.1	11.9	−0.8	0.106	0.050	133.5		
Yuj-594	Black shale	53.5	−32	12.3	11.3	1	0.266	0.190	54.0		
Yuj-595	Black shale	56.5	−31.9	13.2	12.1	0.5	0.270	0.175	57.2	254	21.0
Yuj-596	Black shale	58.5	−31.3	26.3	22.5	−0.2	0.300	0.141	102.4		
Yuj-597	Black shale	61	−31.7	14.8	13.4	−0.6	0.252	0.157	68.7	453	33.8
Yuj-598	Black shale	63.5	−31.6	9.6	7.3	−2.4	0.188	0.099	59.9		
Yuj-599	Black shale	65.5	−31.7	6.5	6.6	−2.2	0.100	0.061	76.1		
Yuj-601	Black shale	69.5	−31.7	8.6	7.9	−1.2	0.161	0.123	62.2	65.3	8.3
Yuj-602	Black shale	70.7	−31.5	10.6	10.4	−3	0.151	0.053	81.8		

condensed at Yuanjia section due to extremely low sedimentary rates in the deep water realm (Jiang et al., 2012; Steiner et al., 2007; Zhu et al., 2003). Thus, the Ni–Mo enrichment layer at the base of Niutitang Formation in our study likely belongs to the later portion of Cambrian Stage 2 (Fig. 3).

The early Cambrian deep basinal sediments of the Niutitang Formation in Hunan are poor in fossils compared with equivalent shallow water successions. Based on the similar increasing trend in $\delta^{13}\text{C}_{\text{org}}$ in this study and at Xiaotan section (Cremonese et al., 2013), the lower-middle part of the Niutitang Formation in Hunan could be approximately correlated with the basal Yu'an-shan Formation in northeastern Yunnan (Fig. 3b). The Yu'an-shan Formation belongs to Stage 3 and the middle and upper part of this formation in eastern Yunnan contains the famous Chengjiang fauna (Zhang and Hou, 1985). According to studies of sponges and SSF fragments

at the Sancha section, the upper part of the Niutitang Formation may be approximately correlated with the middle-upper part of the Yu'an-shan Formation in Yunnan (Steiner et al., 2005, 2007) (Fig. 3a). In addition, the lower Shuijingtuo Formation in Hubei province contains the *Rhombocorniculum cancellatum* taxon-range Zone as well as trilobites and so already belongs to Stage 3 (Qiongzhusian Stage) (Guo et al., 2014; Steiner et al., 2007) (Fig. 3a). Therefore, we correlate the upper Niutitang Formation at Sancha and Yuanjia sections with the Shuijingtuo Formation in the Three Gorges area and the middle-upper part of the Yu'an-shan Formation in Yunnan (Fig. 3).

5.2. Evaluation of nitrogen isotope data

Microbial degradation of organic matter during early diagenesis and thermal maturation during burial may have modified nitrogen

Fig. 2. Nitrogen and organic carbon isotopic profiles and C, N and Mo concentrations in bulk samples for Sancha and Yuanjia sections. The TOC_{bulk} contents and Mo_{bulk} concentrations of Sancha section are from Li et al. (2013b). $\delta^{13}C_{org}$ and TOC_{bulk} contents of Yuanjia section are from Guo et al. (2013) and Mo_{bulk} concentrations in the Niutitang Formation of Yuanjia section are from Guo et al. (2015).

contents and possibly their isotopic compositions as well. To make sure whether our nitrogen isotopic data are reliable and record the primary marine signals, we will first discuss the TOC_{decarb} , TN_{decarb} contents, C/N_{decarb} (atom) ratios and their relationships with nitrogen isotopic compositions.

For Sancha and Yuanjia sections, plots of TN_{decarb} – TOC_{decarb} show rough linear correlations (Fig. 4a and d), indicating that the nitrogen mainly originated from primary organic matter (Calvert, 2004). The intercepts on the TN axis reflect inorganic clay-bound nitrogen components (Fig. 4a and d), which were mostly derived from the digestion of organic matter by microorganisms (Macko et al., 1986).

Normal marine mean C/N ratio of organic matter in modern oceans is ~6.6 (Redfield, 1963). Loss of N may lead to high C/N ratios and result in the alteration of N isotopic records. The C/N_{decarb}

ratios range from 3.0 to 293.9 with a mean value of 61.5 in the Sancha section and from 35.8 to 133.5 with a mean value of 76.7 in the Yuanjia section, similar to other typically high Precambrian C/N ratios (>100) (Beaumont and Robert, 1999; Garvin et al., 2009; Papineau et al., 2009). In Sancha section, the C/N_{decarb} ratios exhibit a strong linear correlation with TOC_{decarb} contents, except for the lowermost phosphorus-nodules layer (Fig. 4b). For the Yuanjia section, there is linear correlation between C/N_{decarb} ratios and TOC_{decarb} contents in the upper Liuchapo Formation (Fig. 4e), and significant co-variation between N/C_{decarb} ratios and TN_{decarb} contents for the black shales in the Niutitang Formation (Fig. 4f). These linear correlations imply preferential loss of organic N from the sediments during diagenesis and/or thermal metamorphism. Fortunately, plots of $\delta^{15}N_{bulk}$ – TOC_{decarb} , $\delta^{15}N_{bulk}$ – TN_{decarb} and $\delta^{15}N_{bulk}$ – C/N_{decarb} exhibit no linear correlation for the

Xiaotan section, Yunnan

Fig. 3. Latest Ediacaran to early Cambrian stratigraphic correlation on Yangtze block. (a) Lithological columns, fossil records and radiometric ages. Fossil records are mainly from Guo et al. (2014), Li and Xiao (2004), Steiner et al. (2005, 2007) and Yang et al. (2014). U–Pb ages are from Wang et al. (2012b), Compston et al. (2008) and Jiang et al. (2009). Pb–Pb ages are from Jiang et al. (2006). Re–Os age is from Xu et al. (2011); (b) Organic carbon isotope profiles of Xiaotan section, Yunnan (shallow platform, Cremonese et al., 2013), Wuhe section, Three Gorges (outer shelf, Cremonese et al., 2014; Kikumoto et al., 2014), Sancha section, Hunan (shelf margin, this study) and Yuanjia section, Hunan (deep basin, this study).

Fig. 4. Analyses of total nitrogen (TN_{decarb}), total organic carbon (TOC_{decarb}) and C/N_{decarb} data in the decarbonated samples for Sancha and Yuanjia sections. (a, d) Cross plots of TN_{decarb} versus TOC_{decarb} . (b, e) Cross plots of C/N_{decarb} versus TOC_{decarb} . (c, f) Cross plots of N/C_{decarb} versus TN_{decarb} .

Fig. 5. Analyses of $\delta^{15}N_{\text{bulk}}$ data in the bulk samples and total nitrogen (TN_{decarb}), total organic carbon (TOC_{decarb}), C/N_{decarb} data in the decarbonated samples for Sancha and Yuanjia sections. (a, d) Cross plots of $\delta^{15}N_{\text{bulk}}$ versus TOC_{decarb} . (b, e) Cross plots of $\delta^{15}N_{\text{bulk}}$ versus TN_{decarb} . (c, f) Cross plots of $\delta^{15}N_{\text{bulk}}$ versus C/N_{decarb} .

Sancha section (Fig. 5a–c), implying that the primary nitrogen isotope compositions were not modified significantly during diagenesis. However, for the Yuanjia section, $\delta^{15}\text{N}_{\text{bulk}}$ values do show weak positive correlations with $\text{TN}_{\text{decarb}}$ contents in the lower Niutitang Formation and a stronger positive correlation in the upper Niutitang Formation (Fig. 5e). These positive correlations cannot be explained either by post-depositional remineralization or by thermal metamorphism, since $\delta^{15}\text{N}_{\text{bulk}}$ values in sediments normally increase with decreasing $\text{TN}_{\text{decarb}}$ content due to the preferential loss of ^{14}N during alteration, thus causing negative correlations (Möbius, 2013; Pinti et al., 2007; Thomazo et al., 2011). Instead, the positive correlation between $\delta^{15}\text{N}_{\text{bulk}}$ and $\text{TN}_{\text{decarb}}$ contents could reflect two end-members of nitrogen source in the bulk sediments under varying redox conditions. Ammonium or atmospheric N_2 with low $\delta^{15}\text{N}$ values contributed as the main nitrogen source under anoxic conditions, while ^{15}N -enriched nitrate was the dominant source under oxic conditions. Thus the observed $\text{TN}_{\text{decarb}}$ – $\delta^{15}\text{N}_{\text{bulk}}$ trend recorded by the Yuanjia section could probably result from the redox conditions in the photic zone shifting between anoxic and oxic during different time periods.

Based on published Fe speciation data (Canfield et al., 2008; Chen et al., 2015; Feng et al., 2014; Jin et al., 2014; Och, 2011; Och et al., 2013; Wang et al., 2012a), the Liuchapo and Niutitang formations (and correlative formations) were mostly deposited under anoxic conditions. Anaerobic degradation of organic matter during early diagenesis retains the initial $\delta^{15}\text{N}$ value or decreases $\delta^{15}\text{N}$ only to a slight extent (less than 2‰) (Freudenthal et al., 2001; Möbius et al., 2010; Robinson et al., 2012). On the other hand, although thermal metamorphism can increase C/N ratios to hundreds and even thousands, $\delta^{15}\text{N}$ values might only increase to a small extent, depending on metamorphic grade, with increases of ~1–2‰ at greenschist facies and of ~3–4‰ at amphibolite facies (Bebout and Fogel, 1992; Jia, 2006; Mingram and Bräuer, 2001). As the $\delta^{15}\text{N}_{\text{bulk}}$ values from our studied successions are unlikely to have been modified significantly by post-depositional thermal alteration because of high H/C ratio values having been measured at the nearby coeval Yanwutan–Lijiatuo section (Guo et al., 2007b), nitrogen isotopic shifts if any caused by thermal alteration should be expressed consistently through the section in such a limited stratigraphic interval.

Based on the discussion above, although the preferential loss of nitrogen during depositional and post-depositional processes may have modified $\delta^{15}\text{N}_{\text{bulk}}$ values of the studied samples, such modifications would have been only of minor import. Thus, our $\delta^{15}\text{N}$ data have the potential to record the primary signals for the early Cambrian ocean along the southern margin of the Yangtze platform.

5.3. Paleoenvironmental implications of $\delta^{15}\text{N}_{\text{bulk}}$ and $\delta^{13}\text{C}_{\text{org}}$ variations

Based on the stratigraphic correlations above in Section 5.1, the paleoenvironmental implications of the $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ variations during different intervals are discussed and explored below and a plausible N cycle model for the early Cambrian basin along the southern margin of the Yangtze platform is then proposed.

5.3.1. Cambrian Fortunian Stage

Currently available Fe speciation data indicate that euxinic waters were not widespread during the latest Ediacaran – the earliest Cambrian interval and that the water column was stratified with an oxygenated upper layer overlying a ferruginous deep-water column in the basin of South China (Canfield et al., 2008; Chen et al., 2015; Feng et al., 2014; Goldberg et al., 2007; Och, 2011; Och et al., 2013; Wang et al., 2012a) (Fig. 6a). Low Mo_{bulk} concentrations and Mo/TOC_{bulk} ratios at the upper Liuchapo Formation in Yuanjia section are consistent with this speculation

(Fig. 2b). In such a stratified basin, ammonia could accumulate to a high concentration in anoxic deep waters, while nitrate would be present in oxygenated surface water, analogous to the modern Matano Lake in Indonesia (Crowe et al., 2011). In this interval, $\delta^{15}\text{N}_{\text{bulk}}$ values vary greatly from –4.3‰ to +2‰ in the Yuanjia section (Fig. 2b), implying an unstable redox transition zone in the surface mixed layer, which broadly corresponds to the photic zone (Ader et al., 2014) (Fig. 6a). In this case, the nitrate reservoir is likely to have been small, and was either reduced to ammonia by mixed Fe(II)/(III) oxy(hydr)oxide species through abiotic processes (Hansen et al., 1996), or converted to $\text{NO}_2^-/\text{N}_2/\text{NH}_4^+$ mediated by anaerobic nitrate-dependent Fe(II)-oxidizing microorganisms under dominantly ferruginous conditions (Busigny et al., 2013; Shen et al., 2013; Straub et al., 1996; Weber et al., 2006a,b) (Fig. 6a), although nitrogen isotopic fractionation effects associated with these processes are still unclear. Ammonia would have been competitively assimilated by organisms and converted to N_2 through anammox (Ader et al., 2014) (Fig. 6a). According to such a scenario, low $\delta^{15}\text{N}_{\text{bulk}}$ values (–4‰ to –2‰) may result from partial assimilation of ammonia with a large isotopic fractionation effect (Crowe et al., 2008b; Higgins et al., 2012; Kappler et al., 2005), while high $\delta^{15}\text{N}_{\text{bulk}}$ values around +2‰ would mainly be due to the assimilation of ^{15}N -enriched ammonia by anaerobic organisms such as green and purple bacteria (Crowe et al., 2008b; Kappler et al., 2005). Thus, $\delta^{15}\text{N}_{\text{bulk}}$ fluctuations may thus be explained by competition between ammonia assimilation and anammox metabolisms under anoxic conditions.

$\delta^{13}\text{C}_{\text{org}}$ values are low (–35‰ to –33‰) and exhibit a negative shift (Fig. 2b) that could result from the assimilation of ^{12}C -enriched inorganic carbon by anaerobic organisms (Küspert, 1982; Schouten et al., 2000; Struck et al., 2001) (Fig. 6a). This suggests that an isotopically light dissolved inorganic carbon (DIC) pool impinged on the photic zone, consistent with the scenario of a shoaling chemocline (separating ferruginous deep waters from oxygenated surface waters) within the surface mixed layer as implied by $\delta^{15}\text{N}_{\text{bulk}}$ data above.

5.3.2. Cambrian Stage 2

It has been postulated that a mid-depth zone of euxinic water sandwiched between oxic surface waters and ferruginous deep waters developed in the early Cambrian due to an increasing sulfate supply from weathering, which then greatly expanded during worldwide transgression in Cambrian Stage 2 (Feng et al., 2014; Jin et al., 2014). This expansion was developed widely from the shelf margin to the slope-basin areas of the South China basin as evidenced by iron speciation and Mo chemistry data (Canfield et al., 2008; Chen et al., 2015; Feng et al., 2014; Guo et al., 2007a; Och, 2011; Och et al., 2013) (Fig. 6b). A Ni–Mo enrichment layer along the transitional zone between the platform and basin was deposited under these euxinic conditions (Lehmann et al., 2007; Steiner et al., 2001). Previous studies argued that the Ni–Mo enrichments in the sediments could originate from hydrothermal input (Lott et al., 1999; Steiner et al., 2001), enrichment from seawater (Lehmann et al., 2007; Mao et al., 2002), or more likely the combination of both processes (Pašava et al., 2008). Recent studies demonstrated that the Ni–Mo sulfide ore layer, which is usually less than half meters in thickness (Jiang et al., 2006), has relatively lower $\delta^{98}\text{Mo}$ values (<1.6‰) (Lehmann et al., 2007; Xu et al., 2012) (low-temperature hydrothermal fluids $\delta^{98}\text{Mo}$ = +0.8‰, McManus et al., 2002), while black shales above and below this Ni–Mo ore layer have high $\delta^{98}\text{Mo}$ values (~1.9–2.4‰) (Chen et al., 2015) (modern seawater $\delta^{98}\text{Mo}$ = +2.34‰, Goldberg et al., 2013), suggesting that hydrothermal input of Mo may have contributed only to the Ni–Mo ore layer, but not to the adjacent black shales (Chen et al., 2015). Thus Mo enrichment in the black shales resulted from redox processes and could provide information about the

Fig. 6. Schematic scenarios for biogeochemical cycling of the early Cambrian ocean along the southern margin of the Yangtze platform during the four separated phases: (a) Cambrian Fortunian Stage, the chemocline which separates ferruginous deep waters from oxygenated surface waters shoaled into the photic zone and the dominate process of N cycle shifted between ammonia assimilation and anammox; (b) Late Cambrian Stage 2, upwelling anoxic deep water bring nutrient phosphorus, free H_2S and ^{12}C -enriched inorganic carbon to the shallow water during the transgression, so that expanded euxinia with shoaling chemocline possibly into the photic zone widely spread along the southern margin of the Yangtze platform; (c) Early Cambrian Stage 3, as the chemocline deepened, nitrate assimilation become to play an important role, indicating a larger nitrate pool; (d) Middle and late parts of Cambrian Stage 3, the chemocline shoaled into the photic zone again, but sulfidic conditions occur only in the basinal area and had not influenced the shelf margin yet.

ocean Mo reservoir. In this study, high Mo_{bulk} concentrations (>100 ppm) in the black shales at both Sancha and Yuanjia section (Fig. 2) lend support for widespread euxinic conditions of the basin during this time interval (Scott et al., 2008; Scott and Lyons, 2012) (Fig. 6b). The lower $\text{Mo}/\text{TOC}_{\text{bulk}}$ (~1–14) in the Yuanjia section than that (averaging ~27) in the Sancha section (Fig. 2) could result from the aqueous Mo depletion in the hydrographically restricted deeper watermass (Algeo and Lyons, 2006; Algeo and Rowe, 2012). Deepwater restriction could probably due to the existence of submersed Cathaysia block southeast to the Yangtze block (Li et al., 1996; Wang and Li, 2003), limiting deep water exchange between the basin and the open ocean, although the exact location of Cathaysia block are still unclear.

At the Sancha section, $\delta^{15}\text{N}_{\text{bulk}}$ values are close to zero with a lowest value of -4.7‰ , and $\delta^{13}\text{C}_{\text{org}}$ values are also low, at -33.5 to -31.0‰ (Fig. 2a). At the Yuanjia section, the analyzed data exhibit a similar pattern ($\delta^{15}\text{N}_{\text{bulk}}$ values near zero with low $\delta^{13}\text{C}_{\text{org}}$ values around -32.5‰) (Fig. 2b), but these data may have not fully recorded the biogeochemical signature of the deep water realm because of the extremely condensed nature of sedimentary deposition due to a rapid rise in sea level (Goldberg et al., 2007; Schütter, 1998; Steiner et al., 2001, 2007). The $\delta^{15}\text{N}_{\text{bulk}}$ signature which is close to the $\delta^{15}\text{N}$ value of air (0‰) indicates that biologically available nitrogen mainly came from N_2 -fixation by diazotrophic cyanobacteria accompanied by little or no isotopic fractionation (Sigman et al., 2009). Owing to the high energy demand of breaking the molecular nitrogen bond, N_2 -fixation can only occur when fixed-N (nitrate and ammonia) concentrations are low, and nutrient phosphorus is in excess supply (Tyrrell, 1999). This means that fixed-N (nitrate and ammonia) in the surface water most likely had been consumed by intense denitrification and/or anammox processes (Junium and Arthur, 2007; Luo et al., 2011) while phosphorus was efficiently recycled under anoxic conditions (Ingall et al., 1993; Van Cappellen and Ingall, 1994). In the early Cambrian, increasing weathering sulfate flux into the ocean (Feng et al., 2014; Jin et al., 2014) and high TOC (Fig. 2) stimulated intensive microbial sulfate reduction (MSR). When

heterotrophic organisms such as sulfate reducing microbes (BSM) decompose the organic matter sinking into the stratified anoxic deep water, an isotopically light DIC repository forms (Fry et al., 1991; Velinsky and Fogel, 1999), and at the same time ammonia, free H_2S and phosphorus are released as well [sulfate reduction: $(\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}\text{H}_3\text{PO}_4 + 53\text{SO}_4^{2-} = 106\text{CO}_2 + 54\text{S}^{2-} + 16\text{NH}_3 + 106\text{H}_2\text{O} + \text{H}_3\text{PO}_4$] (Jenkyns et al., 2001) (Fig. 6b). During the transgression at this interval, upwelling anoxic deep waters brought nutrient phosphorus, free H_2S and ^{12}C -enriched inorganic carbon to the shallow water realm (Fig. 6b). Nutrient phosphorus boosted marine productivity, enhancing deep-water anoxia, which in turn encouraged benthic phosphorus regeneration in a process of positive feedback (Calvert et al., 1996; Ingall and Jahnke, 1994; Ingall and Van Cappellen, 1990; Murphy et al., 2000) (Fig. 7). The key to this positive loop is the transfer of phosphorus from deep anoxic waters to the photic zone (Calvert et al., 1996; Ingall and Jahnke, 1994) (Fig. 6b), which is demonstrated by the widespread phosphorite layers and nodules across the Yangtze Platform produced by upwelling P-replete water interacting with oxygenated surface waters (Wille et al., 2008). Enhanced marine productivity has been suggested by very high TOC_{bulk} contents in this interval (Fig. 2). Low $\delta^{13}\text{C}_{\text{org}}$ values are consistent with the assimilation of the ^{12}C -enriched inorganic carbon brought up to the photic zone by upwelling (Fig. 6b). The extremely low $\delta^{15}\text{N}_{\text{bulk}}$ value of -4.7‰ at Sancha section may have been produced by green or purple sulfur bacteria participating in ammonia assimilation with a large fractionation (Ohkouchi et al., 2005; Pennock et al., 1996) when upwelling currents were vigorous enough for some ammonia to reach the surface water before being converted to N_2 (Ader et al., 2014) (Fig. 6b). Therefore, the $\delta^{15}\text{N}_{\text{bulk}}$ and $\delta^{13}\text{C}_{\text{org}}$ variations suggest enhanced oceanic anoxia and a rise of the chemocline separating sulfidic deep waters from oxygenated surface waters, possibly into the photic zone (Fig. 6b). In addition, the presence of free H_2S requires nitrate depletion due to the redox potential $\text{O}_2 > \text{NO}_3^- > \text{SO}_4^{2-}$ (Boyle et al., 2013), which means that instead of denitrification, anammox could have been the dominant process by which fixed-N was removed from the oceanic system,

Fig. 7. Schematic depiction for a positive feedback loop between anoxia, phosphorus supply and productivity in our studied area, after Calvert et al. (1996), Ingall and Jahnke (1994), Ingall and Van Cappellen (1990) and Murphy et al. (2000).

using nitrite as the electron acceptor ($\text{NH}_4^+ + \text{NO}_2^- = \text{N}_2 + 2\text{H}_2\text{O}$) (Kuypers et al., 2003).

5.3.3. Early Cambrian Stage 3

During the early Cambrian Stage 3, less anoxic environments have been supported by Fe speciation data from the middle part of the Niutitang (Jiumenchong) Formation in Zhongnan section, Guizhou (Och et al., 2013), Yangjiaping section, Hunan (Feng et al., 2014), Songtao section, Guizhou (Canfield et al., 2008), and Longbizui section, Hunan (Wang et al., 2012a), suggesting dominantly ferruginous conditions, with mid-depth euxinic conditions retreating from the shelf margin to the slope areas, and even occasionally oxic bottom waters in the shelf margin and upper-slope area (Feng et al., 2014; Jin et al., 2014) (Fig. 6c). In Sancha section, moderate Mo_{bulk} concentrations and $\text{Mo}/\text{TOC}_{\text{bulk}}$ ratios ($[\text{Mo}]_{\text{bulk}} = 7\text{--}46$ ppm, $\text{Mo}/\text{TOC}_{\text{bulk}} = 8\text{--}21$) (Fig. 2) indicate non-euxinic to intermittently euxinic environment (Scott and Lyons, 2012), reflecting fluctuated chemocline around the water-sediment interface at the Sancha section (Fig. 6c). For the deep-basinal Yuanjia section, Mo_{bulk} concentrations range from 2 to 100 ppm with an average value of 44 ppm (Fig. 2), suggesting at least intermittently euxinic bottom waters (Scott and Lyons, 2012) (Fig. 6c). Low $\text{Mo}/\text{TOC}_{\text{bulk}}$ ratios ($\sim 1\text{--}7$) in the deep-basinal Yuanjia section probably reflect a high degree of deepwater restriction (Algeo and Lyons, 2006; Algeo and Rowe, 2012). During this interval both positive $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ excursions occur at the Sancha and Yuanjia sections (Fig. 2). Heavier $\delta^{13}\text{C}_{\text{org}}$ values than before are consistent with the deepening of the chemocline and organic synthesis by oxygenic photosynthesis using CO_2 in the atmosphere as the dominant process for carbon cycling (Goldberg et al., 2007) (Fig. 6c).

As the chemocline deepened, ammonia would have been quantitatively oxidized to nitrate through nitrification (Fig. 6c). In this case, water-column denitrification and anammox would have resulted in a positive fractionation and a ^{15}N -enriched nitrate pool (Cline and Kaplan, 1975; Liu and Kaplan, 1988) (Fig. 6c). Organisms would have assimilated ^{15}N -enriched nitrate as a bioavailable nitrogen source, leading to the preservation of relatively high $\delta^{15}\text{N}_{\text{bulk}}$ signals (0–2‰) in the sediments (Fig. 2). However, the $\delta^{15}\text{N}_{\text{bulk}}$ values (0–2‰) are lower than the average $\delta^{15}\text{N}_{\text{nitrate}}$ value of modern seawater (+5‰) (Sigman et al., 2009). One possible explanation for this is that the nitrate reservoir of the local basin was small, probably because of intensive loss of nitrate through denitrification, anammox, and reduction by Fe^{2+} at the redox boundary (Busigny et al., 2013; Hansen et al., 1996; Shen et al., 2013; Straub et al., 1996; Weber et al., 2006a,b) (Fig. 6c), driving N_2 -fixation as compensation to lower the $\delta^{15}\text{N}_{\text{bulk}}$ values toward 0‰ (Ader et al., 2014). Another possible explanation is that instead of locally intense N_2 -fixation, the $\delta^{15}\text{N}_{\text{bulk}}$ compositions from Sancha and Yuanjia sections at this period could record the $\delta^{15}\text{N}$ value of the global nitrate reservoir, which was lower than that of the modern ocean. A systematic long-term variation in marine sedimentary

$\delta^{15}\text{N}$ values has been proposed (Algeo et al., 2014), suggesting ^{15}N -depleted isotopic compositions in the Cambrian ocean (Algeo et al., 2014). Low marine sedimentary $\delta^{15}\text{N}$ values are likely to have been due to enhanced sedimentary denitrification without nitrogen isotopic fractionation effects during greenhouse highstands (Algeo et al., 2014). At the end of this interval, both $\delta^{13}\text{C}_{\text{org}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ decrease back to low values, indicating that the chemocline rose again, along with the reestablishment of anoxia in the basin. One possible reason for the apparent rise of the chemocline could be regression, following the earlier transgression evidenced from the Niutitang (Jiumenchong or Guojiaba) Formation in Yangjiaping section, Hunan, Songtao section, Guizhou, and Shatan section, Sichuan (Feng et al., 2014; Jin et al., 2014). Also the high degree of deepwater restriction was probably controlled by the lower sea level during the regression (Algeo and Rowe, 2012).

5.3.4. Middle and late Cambrian Stage 3

In the middle and late parts of Cambrian Stage 3, Mo_{bulk} concentrations and $\text{Mo}/\text{TOC}_{\text{bulk}}$ ratios are high (averaging 229 ppm and 18, respectively) in the Yuanjia section (Fig. 2b), suggesting euxinic environment and more aqueous Mo repletion in the deep watermass than the earlier periods (Algeo and Lyons, 2006; Algeo and Rowe, 2012; Scott and Lyons, 2012) (Fig. 6d). Furthermore, the higher $\text{Mo}/\text{TOC}_{\text{bulk}}$ ratios than those ($\sim 1\text{--}14$) of the Stage 2 transgression imply a larger global Mo reservoir (Algeo and Rowe, 2012; Sahoo et al., 2012; Scott et al., 2008), which could probably mainly be due to more oxygenated open ocean, although enhanced weathering during the Stage 3 regression may also have made contributions. Meanwhile, low Mo_{bulk} concentrations and $\text{Mo}/\text{TOC}_{\text{bulk}}$ ratios (averaging 3 ppm and ~ 8 , respectively) at Sancha section indicate that euxinic conditions did not spread to the shelf marginal regions (Scott and Lyons, 2012) (Fig. 6d). During this time, the $\delta^{15}\text{N}_{\text{bulk}}$ curve decreases to near 0‰ in Sancha section with relatively constant $\delta^{13}\text{C}_{\text{org}}$ values (around -30.5‰), while the $\delta^{15}\text{N}_{\text{bulk}}$ profile gradually decreases to -3‰ with an increasing trend for the $\delta^{13}\text{C}_{\text{org}}$ curve (from -33.0‰ to -31.5‰) at Yuanjia section (Fig. 2). The low $\delta^{15}\text{N}_{\text{bulk}}$ values (-3‰) could have resulted from ammonia assimilation, representing a shoaling chemocline and euxinic conditions in the photic zone (Fig. 6d). $\delta^{15}\text{N}_{\text{bulk}}$ values near 0‰ at Sancha section indicate that the expanded non-sulfidic anoxia enhanced denitrification and anammox within the redox transition zone, and led to the complete consumption of the bioavailable nitrogen (nitrate and ammonia) in the surface water, making N_2 -fixation the dominant process (Fig. 6d).

Although Feng et al. (2014) and Jin et al. (2014) have proposed that widespread mid-depth euxinia gradually shrank after the Stage 2 transgression, more details on the marine redox structure evolution during Cambrian Stage 3 are still not clear. Our data suggest that seawater was clearly less anoxic at the beginning of Cambrian Stage 3 than during the transgression, then anoxia expanded again and euxinic conditions were reestablished in the

Fig. 8. Nitrogen and organic carbon isotope chemostratigraphy of (a) Xiaotan section in Yunnan (Cremonese et al., 2013), (b) Wuhe section in Three Gorges area (Cremonese et al., 2014; Kikumoto et al., 2014), and (c) Sancha, (d) Yuanjia sections in Hunan, South China.

slope-basin areas without reaching the shelf margin area in the middle and late Cambrian Stage 3 (Fig. 6b–d). The reduction of euxinic waters in the middle and late Cambrian Stage 3 could be attributed to a decrease in sulfate concentrations induced by previous intensive MSR and pyrite formation. However, the increasing exposure of pyrite-rich sediments during regression would have increased the sulfate flux through weathering into the ocean, enhancing seawater sulfate concentrations (Feng et al., 2014; Jin et al., 2014), and so the reduction of euxinic waters was possibly controlled by organic matter supply. Low TOC_{bulk} contents of this interval in Sancha section are consistent with this hypothesis. Primary productivity was possibly limited due to the lack of upwelling currents, which caused phosphorus retention in deep anoxic waters. $\delta^{13}\text{C}_{\text{org}}$ values at this time are higher than those from Cambrian Stage 2 (Fig. 2), despite evidence for chemocline shoaling into the photic zone during both periods (Fig. 6b and d). If this ^{13}C -enrichment resulted from a relatively higher proportion of photosynthetic versus chemoautotrophic biomass exporting into the sediments, this could mean that the chemocline was deeper in the photic zone during this interval than during the transgression in the Cambrian Stage 2, although the exact depths are unknown.

5.4. Paleoenvironment along the southern margin of the Yangtze platform

The evolution of life in the early Cambrian is closely linked with the ocean chemistry and marine redox structure. To further reconstruct the spatiotemporal variability of marine redox conditions along the southern margin of the Yangtze platform, we correlate $\delta^{15}\text{N}$ data from this study and published data from Xiaotan section in Yunnan Province (Cremonese et al., 2013) and Wuhe section in the Three Gorges area (Cremonese et al., 2014; Kikumoto et al., 2014), which are located in the shallow platform and transitional zone, respectively (Fig. 8). Stratigraphic correlation is based on the discussion above in Section 5.1.

The Fortunian Stage $\delta^{15}\text{N}_{\text{bulk}}$ values ranged between +2‰ and +6‰ at Xiaotan section (Fig. 8a), indicating relatively normal marine productivity conditions on the shallow platform (Cremonese et al., 2013), which could have benefited the bloom of small shelly fossils (SSFs) there. However, in the Three Gorges area, lower $\delta^{15}\text{N}_{\text{bulk}}$ values between 0‰ and +3‰ could reflect a stronger contribution from N_2 -fixation, and that waters in the outer-shelf area were less oxitic than the shallow platform during this time interval (Cremonese et al., 2014; Kikumoto et al., 2014) (Fig. 8b). By comparison, the basinal area where Yuanjia strata were deposited was more anoxic with the chemocline in the photic zone, evidenced by variable $\delta^{15}\text{N}_{\text{bulk}}$ values between −4.3‰ and +2‰ (Fig. 8d).

During early Stage 2, $\delta^{15}\text{N}_{\text{bulk}}$ values fluctuated largely between −1‰ and +6‰ at Xiaotan and Wuhe sections (Fig. 8a and b), indicating changes in the N cycle between nitrogen fixation and water-column denitrification and/or anammox, which reflects chemocline fluctuations in both the shallow platform and outer-shelf area (Cremonese et al., 2013, 2014; Kikumoto et al., 2014). For the early Cambrian Stage 2, the $\delta^{15}\text{N}_{\text{bulk}}$ signal from the shelf margin and basinal areas are not available, owing to the sedimentary hiatus at the Sancha section and very condensed strata in the Yuanjia section, respectively (Jiang et al., 2012; Steiner et al., 2007; Zhu et al., 2003).

During late Stage 2, geographically wide distribution of low $\delta^{15}\text{N}_{\text{bulk}}$ (Fig. 8) implies that upwelling sulfidic waters led to widespread seawater anoxia in most parts of the basin along the southern margin of the Yangtze Platform, which is consistent with the previous study (Och et al., 2013). This major anoxic event may have resulted in the extinction of many SSF-secreting organisms (Zhu et al., 2006). However, we infer that this was a local anoxic event occurring in this basin while the open ocean was oxygenated to modern-like levels, evidenced by high $\delta^{98}\text{Mo}$ values ($\sim +2.4\%$) (Chen et al., 2015). Mo_{bulk} concentrations and $\text{Mo}/\text{TOC}_{\text{bulk}}$ ratios in the studied sections of this stage are high ($[\text{Mo}]_{\text{bulk}} > 100 \text{ ppm}$, mean $\text{Mo}/\text{TOC}_{\text{bulk}} = \sim 23$). These high concentrations and ratios

Fig. 9. Nitrogen isotope distributions of modern surface sediments and early Cambrian basin of South China. Modern sediment $\delta^{15}\text{N}_{\text{bulk}}$ data are from Tesdal et al. (2013), shallow platform $\delta^{15}\text{N}_{\text{bulk}}$ data are from Cremonese et al. (2013) and outer shelf $\delta^{15}\text{N}_{\text{bulk}}$ data are from Cremonese et al. (2014) and Kikumoto et al. (2014).

indicate that the shallow waters of the basin were well connected with the oxygenated open ocean and that the open ocean had a large Mo reservoir that could continuously provide abundant Mo into the restricted basin where Mo was efficiently trapped in black shales deposited under euxinic conditions.

In the earliest part of Stage 3, $\delta^{15}\text{N}_{\text{bulk}}$ values in Yunnan and Hunan provinces show positive shifts (2–3‰) (Fig. 8), which suggest seawater oxygenation along most of the whole Yangtze Platform, possibly heralding the explosion of Chengjiang-type fauna. Then combining the low $\delta^{15}\text{N}_{\text{bulk}}$ (<0‰) in deep waters and relatively high $\delta^{15}\text{N}_{\text{bulk}}$ (~2–3‰) in shallow waters into an integrated isotopic and biostratigraphic framework, it is suggested that another anoxic event occurred during middle and late parts of Cambrian Stage 3. However, sulfidic conditions were presented in basinal realms without reaching the shelf margin, while the shallow platform became more oxygenated, accommodating the Chengjiang-type faunas. By this time, the South China basin was well connected with oxygenated open ocean, characterized by a large Mo reservoir as evidenced by high Mo_{bulk} concentrations and $\text{Mo}/\text{TOC}_{\text{bulk}}$ ratios ($[\text{Mo}]_{\text{bulk}} > 100 \text{ ppm}$, mean $\text{Mo}/\text{TOC}_{\text{bulk}} = \sim 18$) from the Yuanjia section.

On the basis of high Mo_{bulk} concentrations and $\text{Mo}/\text{TOC}_{\text{bulk}}$ ratios in the euxinic black shale from this and previous studies (Feng et al., 2014; Guo et al., 2007a), the South China basin was well connected with the open ocean and Mo could be effectively transported into the basin (Algeo and Lyons, 2006; Algeo and Rowe, 2012; Scott and Lyons, 2012). Similarly, nitrate could also be supplied to the basin through surface currents from the open ocean. Therefore, the distribution of $\delta^{15}\text{N}_{\text{bulk}}$ values from the basin of South China could be representative of the global nitrate reservoir, although N-cycling processes may have modified this locally. The frequency distribution of $\delta^{15}\text{N}_{\text{bulk}}$ values in the basin was similar to that of the modern ocean (Fig. 9), excepting that most $\delta^{15}\text{N}_{\text{bulk}}$ values range around 1–3‰ and average only +1.6‰, compared with a modern

mean seawater $\delta^{15}\text{N}_{\text{nitrate}}$ value of +5‰ (Sigman et al., 2009) (Fig. 9). In particular, $\delta^{15}\text{N}_{\text{bulk}}$ data from shallow platform Xiaotan section where the seawater was presumably well oxygenated, mainly range around +3‰ with a lower mean value of +2.4‰ as well (Fig. 9). These results are consistent with the proposal of a globally ^{15}N -depleted nitrate pool during the Cambrian, resulting from intensive sedimentary denitrification during the greenhouse climates and high sea-levels that were characteristic of this period (Algeo et al., 2014). The negative tail of the distribution (−5 ~ 0‰) records the local signal of ammonium assimilation and/or N_2 -fixation when anoxia expanded into the photic zone (Ader et al., 2014) (Fig. 9).

6. Summary and conclusions

The nitrogen isotope composition preserved in sedimentary rocks can record and reflect interactions between the environmental, ecological and biological evolution of the marine paleoenvironment. $\delta^{13}\text{C}_{\text{org}}$, $\delta^{15}\text{N}_{\text{bulk}}$, Mo_{bulk} concentrations and $\text{Mo}/\text{TOC}_{\text{bulk}}$ data were recovered for the early Cambrian shelf margin and deep basin sediments at the southern margin of the Yangtze Platform. Based on these data, a comprehensive understanding of N cycling and redox evolution in the shelf and basin environment during the early Cambrian has been obtained.

The basinal area adjacent to the Yangtze platform was anoxic during the Cambrian Fortunian Stage, and characterized by a shoaling chemocline that impinged upon the photic zone. The dominant process within the N cycle shifted at this time between ammonia assimilation and anammox. In the late Cambrian Stage 2, N_2 -fixation became the dominant process under expanded euxinic condition along with shoaling chemocline possibly into the photic zone in both shelf margin and basinal areas. During the early Cambrian Stage 3, nitrate assimilation came to play an important role, indicating that water stratification was weaker, the nitrate pool was larger, and oxic shallow waters more expanded than before. During the middle and late parts of Cambrian Stage 3, the photic zone became anoxic again, but sulfidic conditions were present only in the basinal area without approaching shelf margin area.

Combining data from this study on sections from the shelf margin to basinal area with data from previous studies of shallow platform sections provides a comprehensive perspective on the spatial variation and temporal evolution of redox conditions in these various marine environments along the southern margin of the Yangtze Platform. Anoxia with intermittent euxinia in the photic zone of the basinal area dominated the interval from the Cambrian Fortunian Stage to Cambrian Stage 3, with the exception of early Stage 3 when an oxygenation event occurred. On the platform, generally oxygenated shallow water was affected only by a major anoxic event during Cambrian Stage 2. The outer shelf area experienced anoxia from Stage 2 to Stage 3 of the early Cambrian. However, this anoxic event, found only in the South China basin, may have been limited in extent and took place against the backdrop of a global ocean that was highly oxygenated. The South China basin was well connected with the open ocean and so mean low $\delta^{15}\text{N}_{\text{bulk}}$ values (~+1.6‰) probably recorded the ^{15}N -depleted isotopic composition of the global nitrate reservoir in the early Cambrian ocean.

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