Changes in marine nitrogen fixation and denitrification rates during the end-Devonian mass extinction

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Abstract

The end-Devonian was a critical interval in Earth history recording the transition from the Early Paleozoic greenhouse climate to the Late Paleozoic icehouse climate. A mass extinction at this time (the Hangenberg extinction) eliminated ~21% of genera and ~16% of families of marine invertebrates, although its causes remain poorly understood. The marine nitrogen cycle is intimately related to the nutrient status of seawater, microbial community composition, and the redox condition of the oceans, and, thus, it may provide insights into the mechanism(s) of the end-Devonian mass extinction and climate change. Here, we analyzed high-stratigraphic-resolution bulk-sediment nitrogen isotope variation ($\delta^{15}\text{N}_{\text{bulk}}$) in three sections from South China: (1) Long'an, an isolated carbonate platform section, (2) Qilinzhai, a shallow-water carbonate platform section between the Yangtze Oldland and the Youjiang Trough, and (3) Malanbian, a shallow-water carbonate platform section between the Yangtze and Cathaysia oldlands and distant from deep-water areas. Our $\delta^{15}\text{N}_{\text{bulk}}$ records show a major perturbation to the marine nitrogen cycle in the Middle *Si. praesulcata* Zone, which is marked by a decline in $\delta^{15}\text{N}_{\text{bulk}}$ from +4‰ to 0‰

at Long'an and from +4.5‰ to +2.5‰ at Malanbian. This perturbation coincided with the main end-Devonian mass extinction as well as with a negative shift in carbonate carbon isotopes ($\delta^{13}\text{C}_{\text{carb}}$). The shift to lower $\delta^{15}\text{N}$ values suggests locally enhanced nitrogen fixation, possibly as a consequence of increased denitrification in response to globally expanded marine anoxia. Thus, these $\delta^{15}\text{N}_{\text{bulk}}$ data are consistent with the hypothesis that intense anoxia was the immediate cause of the end-Devonian mass extinction. The $\delta^{15}\text{N}_{\text{bulk}}$ records generated in this study suggest that there was significant spatial and temporal variation in the nitrogen isotope composition of seawater nitrate in the Yangtze marginal sea during the latest Devonian. This variation may have been related to the complex paleogeography of the South China Craton, which contained numerous isolated and continent-attached platforms and deep-water basins that influenced watermass circulation, nutrient inventories and primary productivity levels, and watermass ventilation and redox conditions.

Keywords: late Devonian; mass extinction; Hangenberg Event; nitrogen cycle; paleogeography; South China

1. Introduction

The Devonian-Carboniferous (D-C) transition was a period of major biotic and paleoenvironmental change (Walliser, 1996; Sandberg et al., 2002). Several extinctions smaller than the major extinction at the Frasnian-Famennian boundary took place during a short interval (~1 million years) around the D-C boundary (~359 Ma), e.g., the Annulata, Dasberg, and Hangenberg events (Gradstein et al., 2012, and references therein). These extinctions, which

53 eliminated >45% of marine invertebrate genera (Sepkoski, 1996), affected all parts of the
54 biosphere, including shallow and deep benthic, nektonic, and planktonic marine communities as
55 well as terrestrial life (Walleriser, 1984). Although the extinctions during the D-C transition have
56 been investigated in a number of studies (Caplan and Bustin, 1999; Kaiser et al., 2006, 2008, 2011;
57 Marynowski and Filipiak, 2007; Marynowski et al., 2012; Qie et al., 2015), their causes remain
58 under debate, limiting our understanding of the co-evolution of the biosphere and environment
59 during this critical interval.

60 The most important of the D-C transition extinction events was the Hangenberg Event,
61 named for the Hangenberg black shale (HBS) of the Rheinisches Schiefergebirge in Germany
62 (Walleriser, 1984). This extinction strongly affected ammonoids, trilobites, conodonts, pelagic
63 ostracods, corals and bivalves (Becker, 1996; Olempska, 1997). Conodont biostratigraphic
64 investigations have constrained this extinction to the Middle *Siphonodella praesulcata* Zone,
65 about 0.3 to 0.8 Myr prior to the D-C boundary, which is defined by the first appearance datum
66 (FAD) of the conodont *Si. sulcata* (Caplan and Bustin, 1999, and references therein). The causes
67 of this extinction are debated and multiple hypotheses have been proposed, including
68 anoxic/euxinic marine environments (Algeo et al., 1995; Caplan and Bustin, 1999; Marynowski
69 and Filipiak, 2007; Marynowski et al., 2012), transient global cooling (Brand et al., 2004),
70 seawater acidification (Marynowski et al., 2012), eustatic effects (Bless, 1992), wildfire
71 (Marynowski and Filipiak, 2007), and asteroid impacts (Bai and Ning, 1988). Algeo et al. (1995)
72 specifically hypothesized that, although marine anoxia was the likely immediate cause of the mass
73 extinction, the ultimate trigger was the rapid spread of seed plants. Seed plants spread rapidly
74 during the latest Devonian (Chaloner et al., 1977; Scheckler, 1986; Meyer-Berthaud et al., 1999;

Cressler, 2006) and are likely to have caused a transient increase in continental weathering rates (Algeo and Scheckler, 2010), thus shedding nutrients into marine systems that stimulated higher marine productivity and anoxic/euxinic conditions.

The Hangenberg extinction was accompanied by significant perturbations to the global carbon cycle as recorded by widespread shifts in carbonate and organic carbon isotopes (Brand et al., 2004; Kaiser et al., 2006, 2008; Qie et al., 2015). These shifts, which are mainly positive, are inferred to have been caused by an increase in the fraction of organic carbon burial, possibly related to large-scale burial of organic matter in the HBS and correlative units in North America, Russia, and elsewhere. However, recent high-resolution chemostratigraphic studies of carbonate carbon isotopes suggest a more complex pattern, in which negative shifts are found in the Middle *Si. praesulcata* and at the D-C boundary in addition to a positive shift in the lower part of the Upper *Si. praesulcata* Zone (Kaiser et al., 2008; Qie et al., 2015).

Compared with the carbon cycle, the marine nitrogen cycle during the D-C transition has received little study to date. Nitrogen (N) is an essential biotic nutrient and a main influence on marine primary productivity (Falkowski, 1997). Thus, any nitrogen cycle perturbations are likely to be intimately connected to the carbon cycle and to have implications for a common origin. Because the most important biogeochemical pathways in the marine nitrogen cycle have characteristic isotope fractionations (Sigman and Casciotti, 2001), analysis of the nitrogen isotope composition of organic matter in marine sediments can yield information about nutrient levels, redox conditions, and the composition of microbial communities in marine systems. In order to better understand the environmental and biological conditions of the Hangenberg mass extinction, we analyzed the nitrogen isotope composition of bulk nitrogen in three sections from South China

(Long'an, Qilinzhai, and Malanbian) (Fig. 1). Our results suggest that the marine nitrogen cycle underwent significant perturbations during the latest Devonian, and that the inferred controls on these perturbations were related to the underlying causes of the end-Devonian mass extinction.

2. The marine nitrogen cycle

Recent studies have provided a detailed understanding of the operation of the marine nitrogen cycle. In addition to the nitrogen fixed by lightning, microbial nitrogen fixation is the dominant source of bioavailable nitrogen (Gruber and Galloway, 2008). Cyanobacteria, such as *Trichodesmium*, are the most abundant diazotrophs in marine environments (Zehr et al., 2001, 2008; Zehr, 2011). The isotope fractionation of microbial nitrogen fixation processes is -1 to -3‰ relative to the atmospheric N_2 source ($\delta^{15}\text{N}_{\text{air}} \sim 0\text{‰}$) (Brandes and Devol, 2002; Gruber, 2008). However, Fe concentrations may affect this fractionation by a few per mille, with larger fractionations at higher Fe concentrations (Zerkle et al., 2008). Apart from assimilatory uptake and burial in organic matter, the major sinks for seawater fixed N are denitrification within the sediment or in the water column and the anammox process (Gruber and Galloway, 2008). Denitrification involves the bacterial use of nitrate as an electron acceptor in the respiration of organic matter with a maximum fractionation of ca. -27‰ (but commonly with an effective fractionation of $-20 \pm 3\text{‰}$), resulting in a strongly ^{15}N -enriched residual seawater nitrate pool. Denitrification in suboxic marine sediments typically yields much lower net fractionation (-1 to -3‰) owing to near-quantitative utilization of porewater nitrate (Sigman et al., 2003; Lehmann et al., 2004). The anammox reaction, in which ammonium and nitrate (or nitrite) are converted to N_2 , may eliminate more fixed N than denitrification in some marine environments (Kuypers et al.,

2005). The isotopic fractionation associated with this process is close to that of denitrification in the water column (Brunner et al., 2013).

The N-isotopic composition of marine sediment depends on the $\delta^{15}\text{N}$ of seawater fixed N, fractionation during assimilatory uptake, and subsequent alteration during decay in the water column and sediment (Robinson et al., 2012). Both ammonium and nitrate can be used as N sources in primary production, with fractionations of $-10(\pm 5)\text{‰}$ and $-3(\pm 2)\text{‰}$, respectively (Hoch et al., 1994; Waser et al., 1998). Nitrate is by far the more important source of N for eukaryotic marine algae, but ammonium is utilized by some modern microbial communities (Higgins et al., 2012) and may have been the main N substrate for eukaryotic algae during some OAEs (Altabet, 2001; Higgins et al., 2012). Assimilatory uptake enriches the residual fixed N pool in ^{15}N and can result in shifts in the $\delta^{15}\text{N}_{\text{NO}_3^-}$ of local watermasses (Hoch et al., 1994), but quantitative utilization of fixed N by marine autotrophs at annual timescales normally limits fractionation due to this process (Sigman et al., 2000; Somes et al., 2010). These processes determine the N isotopic composition of primary marine organic matter, before modification by diagenesis (see Section 5.1).

3. Geological background, materials and methods

3.1. Geological background

The three sections analyzed in this study are (1) the Long'an section, in Dujie village of Long'an County in Guangxi Zhuang Autonomous Region (N: $23^{\circ}10'34.8''$, E: $107^{\circ}27'48.0''$), (2) the Malanbian section, in Xinshao County in Hunan Province (N: $27^{\circ}22'48.8''$, E: $111^{\circ}34'2.4''$), and (3) the Qilinzhai section, in Dushan County in Guizhou Province (N: $25^{\circ}49'04''$, E: $107^{\circ}29'26''$)

(Fig. 1). During Late Devonian and Early Carboniferous, these areas were located in the eastern part of the South China Craton, which was situated close to the paleoequator and rotated $\sim 90^\circ$ counterclockwise relative to its present orientation (Fig. 1). The Yangtze Sea was a semi-restricted basin connected to the Paleo-Tethys Ocean on the east (note: all directions are in paleo-coordinates) and bordered by continents on the other three sides (Fig. 1). Due to coeval rift-related tectonism, the Yangtze Sea had a complex facies architecture with shallow-water carbonate platforms that were either isolated or attached to continents, separated by deep-water troughs (Fig. 1). Long'an was located on the isolated Nanning Platform, which was separated from landmasses by deep-water troughs; Malanbian was located on the continent-attached Xianggui Platform between the Yangtze and Cathaysia oldlands; and Qilinzhai was located on the margin of the mixed siliciclastic-carbonate Qiangui Platform close to the Youjiang Trough (Fig. 1). Sedimentary facies analysis suggests that the three sections were deposited around fair-weather wave base in water depths of a few tens of meters (Qie et al., 2015).

The litho- and biostratigraphy of the three study sections were described in detail in Qie et al. (2015) and are only briefly summarized here. The Long'an section is divided into Yonghsien and Long'an formations (Fig. 2). The Yonghsien Formation (-30 to 0 m) consists mainly of massive bioclastic wackestone, packstone and grainstone, while the Long'an Formation (0 to 8 m) is dominated by thin-bedded calcisphere wackestone and packstone. The D-C boundary, which is defined by the first appearance of the conodont *Si. sulcata*, is located at ~ 6 m above the base of the Long'an Formation, while the base of the Upper *Si. praesulcata* and Middle *Si. praesulcata* zones are located at ~ 2 m and ~ 5 m below the base of the Long'an Formation, respectively (Qie et al., 2015).

The Malanbian section contains the Menggong'ao and Malanbian formations (Fig. 3). The Menggong'ao Formation (below 0 m) consists of bioclastic lime mudstone to packstone with late Famennian miospore fossils (Qie et al., 2015). The uppermost part of the Menggong'ao Formation is characterized by an upward coarsening siliciclastic succession that may be correlative with the Hangenberg black shale-sandstone succession in Germany (Qie et al., 2015). The Malanbian Formation (0-42 m) contains massive intraclastic-peloidal packstone to grainstone with rare ostracods, echinoderms and calcispheres. The D-C boundary is ~28 m above the base of the Malanbian Formation (Fig. 3).

The Qilinzhai section is divided into Gelaohe and Tangbagou formations (Fig. 4). The Gelaohe Formation (below 0 m) consists mainly of calcareous mudstone with thin- to medium-bedded lime mudstone and bioclastic wackestone and packstone and contains abundant Devonian brachiopods and corals. The main lithologies of the Tangbagou Formation (0 to 18 m) are bioclastic wackestone and packstone interbedded with lime mudstone. The conodont fauna indicates that the lowermost Tangbagou Formation (0-13 m) belongs to the Upper *Si. praesulcata* Zone. The precise position of the D-C boundary has not been established, but based on the presence of the conodont *Si. homosimplex*, it is probably around 13-14 m.

The Hangenberg event interval (Middle to Upper *Si. praesulcata* zones) was ~0.21-0.26 Myr in duration based on geochronological data from Gradstein et al. (2012) and Myrow et al. (2014). The main Hangenberg extinction horizon (i.e., the base of the Middle *Si. praesulcata* Zone) is located 11.6 m below the D-C boundary at Long'an and 30.8 m below the D-C boundary at Malanbian. In the Qilinzhai section, the Middle *Si. praesulcata* Zone which might be very thin according to the corresponding thickness at the Long'an and Malanbian section is absent and the

thickness of the Upper *Si. praesulcata* zone is ~13 m (Qie et al., 2015). The average sediment accumulation rates (after compaction) for the event intervals at Long'an, Malanbian, and Qilinzhai are thus 45-55, 118-147, and >50-62 m Myr⁻¹, respectively.

3.2. Materials and methods

Large and fresh hand specimens (~1 kg) were collected from fresh outcrops for geochemical analysis. In the lab, the hand specimens were cut into small chips and any weathered surfaces and veins were removed. The chips were ultrasonicated in deionized (DI) water for ~5 minutes and dried in oven at 60°C. The dried chips were ground to <100 mesh in a steel stainless puck mill. Because the bulk nitrogen contents of the samples were low, it was necessary to enrich nitrogen prior to isotopic analysis. For this purpose, all samples were decarbonated with 6 N HCl. The same or even higher concentrations of HCl have been used in a number of earlier nitrogen isotope studies (e.g., [Sælen et al., 2000](#); Luo et al., 2011, 2015; [Kikumoto et al., 2013](#); [Saitoh et al., 2014](#), [Yao et al., 2015](#)). The acid residues were cleaned to neutral pH with DI water and freeze-dried. As the samples analyzed here are rich in carbonate (>95%) and low in siliciclastic minerals, no HF treatment was carried out on the residues.

Total nitrogen content (TN), total organic carbon content (TOC) and nitrogen isotope composition ($\delta^{15}\text{N}_{\text{bulk}}$) of acid residue were analyzed by elemental analyzer-isotope ratio monitoring mass spectrometry (EA-IRMS, EA: Flash EA2000, IRMS: MAT253). About 20-30 mg of HCl residue was weighed into a tin cup and loaded into the auto-sampler connected to the Flash EA. Each sample was combusted at 960°C, and the produced CO₂ was removed using Carbo-Sorb, and water was trapped with anhydrous magnesium perchlorate. Every sample was

followed by a blank to test the combustion efficiency. Only the samples for which the following blank yielded no or a tiny nitrogen peak were used. The samples from the Long'an and Qilinzhai sections were analyzed in the State Key Laboratory of Geological Processes and Mineral Resources at the China University of Geosciences in Wuhan, whereas those from the Malanbian section were analyzed in the Nanjing Institute of Geology and Mineral Resources in Nanjing. Nitrogen isotope compositions are reported as per mille (‰) variation relative to atmospheric N₂. International standards IAEA-N-1 (TN: 21.1%; $\delta^{15}\text{N} = 0.4 \pm 0.2\text{‰}$) and USGS-34 (TN: 13.9%; $\delta^{15}\text{N} = -1.8 \pm 0.2\text{‰}$) and a lab standard urea (TN: 46.7%; $\delta^{15}\text{N} = -0.4 \pm 0.2\text{‰}$) were used to calibrated nitrogen isotope compositions. Analytical precision is better than $\pm 0.2\text{‰}$ (1 σ) based on multiple analyses of IAEA-N-1, and $\pm 0.4\text{‰}$ (1 σ) based on replicate analyses of study samples.

4. Results

All data reported here can be found in the supplementary materials.

4.1. Long'an section

The TOC content of the samples at Long'an section is generally <0.3%, while the carbonate content is mostly >90% with a mean of 98.5% (Fig. 2). The TN content is generally >10 ppm with a mean of ~40 ppm. The C_{org}/N_{bulk} molar ratios vary from ~5 to 126 with a mean of 48. Distinct variations in $\delta^{15}\text{N}_{\text{TN}}$ are present during the D-C transition in the Long'an section (Fig. 2). In the Lower *Si. praesulcata* Zone (–26 to –5 m), $\delta^{15}\text{N}_{\text{bulk}}$ varies around +4.0‰. Starting from the base of the Middle *Si. praesulcata* Zone, $\delta^{15}\text{N}_{\text{bulk}}$ decreases sharply to ~0‰ by the top of this conodont zone, after which a gradual recovery to ~+4‰ in the Upper *Si. praesulcata* Zone and lower part of

the *Si. sulcata* Zone is observed, except for a minor negative shift.

4.2. Malanbian section

The carbonate content of most samples is >95%, while the TOC content is <0.1% (Fig. 3). Bulk nitrogen contents vary from ~1.0 to 62 ppm with a mean of ~26 ppm. The C_{org}/N_{bulk} molar ratios range from ~9 to 64 with a mean of ~30. In the Lower *Si. praesulcata* Zone, $\delta^{15}N_{bulk}$ values fluctuate around +4‰ (Fig. 3). A significant negative shift in $\delta^{15}N_{bulk}$, from +4‰ to +2‰, is present in the Middle *Si. praesulcata* Zone. From the base of the Upper *Si. praesulcata* Zone to the lower part of *Si. sulcata*-*Si. duplicata* Zone, $\delta^{15}N_{bulk}$ is relatively constant, varying around +3‰. A slight negative shift is present in the upper *Si. sulcata*-*Si. duplicata* Zone, in which $\delta^{15}N_{bulk}$ declines from +3‰ to +2‰.

4.3. Qilinzhai section

The Qilinzhai samples are characterized by high carbonate content (mostly 90% with a mean of 98%) and low TOC content (mostly <0.2%) (Fig. 4). The bulk nitrogen content varies from ~12 to 86 ppm with a mean of ~26 ppm. The C_{org}/N_{bulk} molar ratios range from ~11 to 81 with a mean of ~48. In the lowermost Upper *Si. praesulcata* Zone, $\delta^{15}N_{bulk}$ varies around +6‰ (Fig. 4). Two negative shifts in the lower and middle parts of the Upper *Si. praesulcata* Zone result in a decrease in $\delta^{15}N_{bulk}$ to ~+3.5‰, a value that persists in the upper part of this conodont zone and into the lower *Si. sulcata* Zone (Fig. 3).

5. Discussion

5.1. Diagenetic evaluation of $\delta^{15}\text{N}_{\text{bulk}}$

The study samples are characterized by high carbonate content (mostly >96%) and correspondingly low siliciclastic content (see supplementary materials). Thus, the main source of nitrogen was organic matter, which is supported by a positive correlation between TOC and TN for each study section (Fig. 5). The positive TN intercept can be ascribed to absorption of NH_4^+ by clay minerals during organic matter remineralization (Haendel et al., 1986), a process that does not induce significant nitrogen isotope fractionation (Williams et al., 1995).

The effects of diagenesis on $\delta^{15}\text{N}_{\text{bulk}}$ have been intensively studied (Freudenthal et al., 2001; Lehmann et al., 2002; Jia and Kerrich, 2004; Junium and Arthur, 2007; Higgins et al., 2012; Robinson et al., 2012). During early diagenesis, certain labile nitrogen-rich compounds such as amino acids undergo decay, which may affect the $\delta^{15}\text{N}$ of remaining organic matter (Freudenthal et al., 2001; Lehmann et al., 2002). However, the absence of significant correlation between $\delta^{15}\text{N}_{\text{bulk}}$ and $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ (Fig. 5) suggests that diagenetic alteration has not systematically altered the primary organic nitrogen isotope compositions. Furthermore, no significant changes in TN concentrations and $\text{C}_{\text{org}}/\text{N}_{\text{bulk}}$ molar ratios accompany shifts in $\delta^{15}\text{N}_{\text{bulk}}$ (Fig. 2-4). A recent study has shown that differences in $\delta^{15}\text{N}$ between sinking organic particles and sedimentary organic matter may be related to water depth (Robinson et al., 2012). Specifically, diagenetic alteration is evident along continental slopes, where sinking organic matter undergoes substantial alteration within the water column, and the $\delta^{15}\text{N}$ of sedimentary organic matter is greater than that of the sinking flux. In contrast, sedimentary organic matter generally has a $\delta^{15}\text{N}$ composition similar to that of sinking organic particles on continental shelves with high sediment accumulation rates and organic matter content (Robinson et al., 2012). The three sections in this study were all located on

shallow carbonate platforms with potentially high sedimentation rates. Therefore, we suggest that alteration of organic matter in the water column did not significantly affect the nitrogen isotope composition of deposited organic matter. Thermal alteration in deep burial settings can produce modest N isotope fractionations (Busigny et al., 2003; Jia and Kerrich, 2004; Rivera et al., 2015). The conodont alteration index (CAI) was used to assess the general thermal history of the study successions. At Malanbian and Qilinzhai, most CAI values range from 1.5 to 3.0, indicating burial temperatures of 50-200°C. CAI values of ~4 have been recorded at Long'an, corresponding to a maximum burial temperature of 300°C. The absence of evidence of hydrothermal alteration, together with the well-preserved carbonate rock fabric, suggests that the nitrogen isotope composition of sedimentary organic matter in the study samples was not significantly affected by burial fluids.

5.2. Spatial variation in $\delta^{15}N_{bulk}$ during the D-C transition

The residence time of fixed N in seawater, ca. ~1.5 to 3.0 kyr, is relatively short (Gruber and Sarmiento, 1997). For this reason, the $\delta^{15}N$ of seawater fixed N has the potential to show distinct spatial and temporal variation. For example, regional variation in seawater nitrate $\delta^{15}N$ of the surface and thermocline layers of the modern ocean is as large as 18‰ (i.e., from +2‰ to +20‰), although nitrate in the deep ocean exhibits a much narrower $\delta^{15}N$ range, ca. +4.8(±0.2)‰ (Sigman et al., 2000). Variation in nitrate $\delta^{15}N$ in the surface ocean is mainly controlled by regional differences in N fixation, nutrient utilization, and denitrification rates (which are related to organic matter sinking fluxes and watermass redox conditions) (Altabet and Francois, 1994; Sigman et al., 1999; Sigman and Casciotti, 2001). Based on sediment $\delta^{15}N_{bulk}$, we infer that significant spatial

heterogeneity in the $\delta^{15}\text{N}$ of seawater fixed nitrogen existed in the Yangtze Sea during the D-C transition (see below).

The degree of variation in $\delta^{15}\text{N}_{\text{bulk}}$ in the Lower and Middle *Si. praesulcata* zones is unclear due to absence of strata of this age at Qilinzhai and only a single sample from the Middle *Si. praesulcata* Zone at Malanbian. However, the extant samples all yield similar $\delta^{15}\text{N}_{\text{bulk}}$ values, varying around +4.0‰ (Figs. 2, 3), thus providing no evidence for spatial variability during this interval. On the other hand, significant spatial and temporal variation is evident in the Upper *Si. praesulcata* Zone, in which $\delta^{15}\text{N}_{\text{bulk}}$ ranges from +1‰ to +3‰ at Long'an (Fig. 2), from +3‰ to +6‰ at Qilinzhai (Fig. 4), and remains relatively constant around +3‰ at Malanbian (Fig. 3). In addition, the secular trends within this interval differ among the study sections: at Qilinzhai two negative shifts resulted in a stepwise decrease in $\delta^{15}\text{N}_{\text{bulk}}$ from +6‰ to +4.5‰ and then to +3‰, whereas at Long'an $\delta^{15}\text{N}_{\text{bulk}}$ underwent a gradual positive shift from +1.5‰ to +3‰. However, all three study sections show similar $\delta^{15}\text{N}_{\text{bulk}}$ values ($\sim$ +3‰) during the D-C transition (Figs. 2-4). The reasons for the different $\delta^{15}\text{N}_{\text{bulk}}$ trends at Malanbian versus Long'an are not clear and will require further investigation.

Spatial variation in $\delta^{15}\text{N}_{\text{bulk}}$ of the Upper *Si. praesulcata* Zone is unlikely to have been caused by section-specific differences in thermal maturity or nitrate consumption. Although the thermal maturity of the three study sections varies somewhat, all of them are unmetamorphosed, and moderate variation in thermal maturity is unlikely to have generated the observed section-specific differences in nitrogen isotope compositions (cf. Rivera et al., 2015). As there is a large isotope fractionation associated with biotic assimilation of seawater nitrate, with preferential uptake of $^{14}\text{NO}_3^-$ (Wada and Hattori, 1991), incomplete consumption of seawater nitrate can generate

differences in phytoplankton $\delta^{15}\text{N}$. However, this situation most commonly develops in high-nutrient low-chlorophyll (HNLC) regions of the open ocean that are deficient in iron (Ganeshram et al., 2000), such as the modern subarctic Pacific Ocean (Sigman and Casciotti, 2001). This condition is not known to exist in modern epicontinental seas and was unlikely to have existed within the Late Devonian Yangtze Sea.

We infer that regional paleoceanographic factors were responsible for spatial heterogeneity in mean $\delta^{15}\text{N}_{\text{bulk}}$ values and in secular trends among the study sections. The Qilinzhai section was located on the Qiangui Platform margin, which was close to the deep Youjiang Trough (Fig. 1). The higher $\delta^{15}\text{N}_{\text{bulk}}$ values at Qilinzhai may have been the result of upwelling of ^{15}N -enriched nitrate generated through denitrification in the thermocline region of the Youjiang Trough (see below). This inference is supported by the higher $\delta^{13}\text{C}_{\text{carb}}$ values at Qilinzhai relative to the other two sections (Qie et al., 2015). The Malanbian section was located on the proximal part of the Xianggui Platform in close proximity to the Yangtze and Cathaysia oldlands (Fig. 1). For this reason, nutrients at Malanbian might have been supplied by fluvial systems, resulting in relatively invariant $\delta^{15}\text{N}_{\text{bulk}}$ values. Alternatively, uniformly low rates of marine productivity in this inner-shelf setting may have had the same effect. The Long'an section, which was located on the isolated Nanning Platform close to the open ocean, did not receive nutrients from terrestrial sources and may not have been influenced by upwelling, resulting in a relative dearth of nutrients that may have promoted greater nitrogen fixation. These hypotheses will require further testing, however.

5.3. Secular perturbations of marine nitrogen cycle during the D-C transition

At Long'an and Malanbian, $\delta^{15}\text{N}_{\text{bulk}}$ values in the Lower *Si. praesulcata* Zone are similar to the modern open-ocean nitrate $\delta^{15}\text{N}$ of $\sim +5\text{‰}$ (Sigman and Casciotti, 2001), suggesting that oceanic environments at that time might have been close to the modern ocean. The sharp negative shift in $\delta^{15}\text{N}_{\text{bulk}}$ in the Middle *Si. praesulcata* Zone at Long'an and, possibly, Malanbian suggests that the marine nitrogen cycle underwent a significant perturbation at that time. This negative shift in $\delta^{15}\text{N}_{\text{bulk}}$ correlates with a slight negative shift in $\delta^{13}\text{C}_{\text{carb}}$ (Figs. 2, 3) (Qie et al., 2015).

The $\delta^{15}\text{N}_{\text{bulk}}$ values in the upper part of the Middle *Si. praesulcata* Zone vary around 0‰ at Long'an (Fig. 2). These values are similar to the N-isotopic composition of atmospheric dinitrogen (N_2). Several potential explanations can be ascribed for the low $\delta^{15}\text{N}_{\text{bulk}}$ values at the Long'an section. Since incomplete utilization of seawater nitrate was unlikely in the epicontinental Yangtze Sea (see above), the more likely explanation is strong microbial nitrogen fixation (i.e., by diazotrophic cyanobacteria). This process has a small isotope fractionation, ca. -2‰ to 0‰ , yielding seawater fixed nitrogen (NH_4^+) that is characterized by low $\delta^{15}\text{N}$ values (Minagawa and Wada, 1986; Carpenter et al., 1997). Thus, marine sediment $\delta^{15}\text{N}_{\text{bulk}}$ values are likely to decrease to $\sim 0\text{‰}$ when microbial nitrogen fixation is the main source of biologically available nitrogen. This phenomenon has been observed in several geological intervals with of strong activity by nitrogen-fixing microbes (Jenkyns et al., 2001; Kuypers et al., 2004; Junium and Arthur, 2007; Luo et al., 2011). The higher $\delta^{15}\text{N}_{\text{bulk}}$ values in the upper part of the Middle *Si. praesulcata* Zone at Malanbian suggest a smaller fraction of microbially fixed nitrogen, which is consistent with greater influence by terrigenous nitrogen inputs in a section located close to a continent (cf. Sigman and Casciotti, 2001; Tuite and Macko, 2013).

Due to the high energy required to cleavage the triple bonds of N_2 , microbial nitrogen

fixation is prevalent only when bioavailable nitrogen is deficient (Tyrrell, 1999). The main pathways for loss of seawater fixed nitrogen are denitrification and anaerobic ammonium oxidation (anammox) (Kuypers et al., 2003; Byrne et al., 2009; Ward et al., 2009; Murray, 2005). The denitrification process, which converts nitrate to N_2 in several steps, occurs mainly in suboxic/anoxic environments and has a large isotope fractionation ($\sim 20\%$) when it occurs in the water column (Sigman and Casciotti, 2001; Brandes and Devol, 2002). The residual nitrate in seawater thus becomes enriched in ^{15}N , as in the eastern tropical North Pacific where seawater nitrate $\delta^{15}N$ reaches $+15\%$ (Sigman and Casciotti, 2001). The anammox process, in which coupled reactions simultaneously reduce nitrite and oxidize NH_4^+ to N_2 , is found mainly just below O_2 - H_2S chemoclines (Mulder et al., 1995). The nitrogen isotope fractionation associated with the anammox process is $\sim 23\%$ to 29% (Brunner et al., 2013). For both denitrification and anammox, the residual fixed nitrogen reservoir becomes progressively isotopically heavier as the remaining fraction of fixed nitrogen becomes smaller. If the residual fixed nitrogen reservoir is sufficiently large, it may contribute to a positive $\delta^{15}N$ anomaly in the sediment (e.g., Kienast et al., 2002; Algeo et al., 2008). On the other hand, if it is fully consumed (or nearly so), then other processes, such as nitrogen fixation, will control the nitrogen isotopic composition of the sediment. In the present study units, $\delta^{15}N_{bulk}$ values of $\sim 0\%$ in the upper part of the Middle *Si. praesulcata* Zone suggest that denitrification and/or anammox reduced nearly all seawater nitrate in the latest Devonian Yangtze Sea to N_2 , resulting in a $\delta^{15}N$ signature dominated by nitrogen fixation.

The gradual positive shift in $\delta^{15}N_{bulk}$ in the Upper *Si. praesulcata* Zone at Long'an suggests that microbial nitrogen fixation became less significant during this time (Fig. 2). This can be ascribed to reduced nitrogen loss through denitrification and/or anammox, indicating amelioration

of marine redox conditions. Due to weaker denitrification, the enrichment in ^{15}N of seawater nitrate in upwelling zones would have decreased, which is consistent with the decrease in $\delta^{15}\text{N}_{\text{bulk}}$ from +6‰ to +3‰ at Qilinzhai, a section that was affected by upwelling (see Section 3.1).

5.4. Relationship to carbon cycle perturbations

The carbon cycle experienced significant perturbations during the D-C transition, as recorded in variation of $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{13}\text{C}_{\text{org}}$ (Caplan and Bustin, 1999; Brand et al., 2004; Kaiser et al., 2006, 2008; Buggisch et al., 2008; Qie et al., 2015). The causes of these perturbations remain poorly known (Kaiser et al., 2008; Qie et al., 2015). The Middle *Si. praesulcata* Zone is characterized by simultaneous negative shifts in $\delta^{13}\text{C}_{\text{carb}}$ and $\delta^{15}\text{N}_{\text{bulk}}$ (Fig. 2-4). The $\delta^{15}\text{N}_{\text{bulk}}$ records suggest that nutrient nitrogen was deficient and anoxic environments were extensive at that time. Therefore, we infer that the concurrent negative shift in $\delta^{13}\text{C}_{\text{carb}}$ can be due to reduced primary productivity, related to a general decline in marine ecosystems during the end-Devonian mass extinction and/or to a regional deficiency of seawater nutrients (Kump, 1991).

A positive shift of $\delta^{13}\text{C}_{\text{carb}}$ in the lower part of the Upper *Si. praesulcata* Zone was coincident with a positive shift in $\delta^{15}\text{N}_{\text{bulk}}$ at Long'an and a negative shift in $\delta^{15}\text{N}_{\text{bulk}}$ at Qilinzhai (Fig. 2, 4). As discussed above, these $\delta^{15}\text{N}_{\text{bulk}}$ records suggest weakened denitrification and diminished seawater anoxia during the lower part of the Upper *Si. praesulcata* Zone. This pattern may record a spatially variable response of the marine nitrogen cycle to the recovery of primary productivity and increased organic carbon burial following the HBS mass extinction. In the upper part of the Upper *Si. praesulcata* and the lower *Si. sulcata* zones, $\delta^{13}\text{C}_{\text{carb}}$ declines in all three study sections (Fig. 2-4) (Qie et al., 2015), which is similar to $\delta^{13}\text{C}_{\text{carb}}$ patterns in D-C boundary

sections globally (Kaiser et al., 2008). This negative shift has been attributed to a decline in primary productivity and/or a decrease in the fraction of organic carbon burial (Kaiser et al., 2006, 2008; Qie et al., 2015). Our $\delta^{15}\text{N}_{\text{bulk}}$ data suggest that marine nitrogen cycle was characterized by a continued decline in nitrogen fixation rates, allowing $\delta^{15}\text{N}_{\text{bulk}}$ to return to background values characteristic of contemporaneous open-ocean fixed nitrogen. The marine nitrogen and carbon cycles may have been linked at that time through a reduced loss of fixed nitrogen to denitrification, along with a concurrent decline in organic matter remineralization in contracted oxygen-minimum zones, owing to reduced primary productivity and organic carbon sinking fluxes. A decline in marine primary productivity during the earliest Carboniferous may have been caused by a decrease in fluvial nutrients due to weaker continental weathering, which is supported by a negative shift in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ ratios (Brand et al., 2004).

5.5. Implications for the end-Devonian mass extinction

Several mechanisms have been proposed for the Hangenberg mass extinction (see Section 1), among which expansion of marine anoxia/euxinia has the most supporting evidence (Algeo et al., 1995; Caplan and Bustin, 1999; Marynowski and Filipiak, 2007; Marynowski et al., 2012). Apart from widespread deposition of organic-rich black shales (Algeo et al., 1995; Caplan and Bustin, 1999), expansion of marine anoxia into the photic zone has been documented by biomarker evidence of green sulfur bacteria, i.e., isorenieratane and its derivatives (Marynowski and Filipiak, 2007; Marynowski et al., 2012). In South China, the stratigraphic interval corresponding to the HBS contains little or no black shale, which is also undeveloped in some European sections (see Matyja et al., 2015, and references therein). This seems to be a common situation in

shallow-marine settings, whereas expanded anoxia is characteristic of intermediate to deep-water sections.

Our nitrogen isotope data suggest that redox conditions underwent significant changes during the D-C transition with the development of strongly reducing conditions during the Middle *Si. praesulcata* Zone. A shift to $\delta^{15}\text{N}_{\text{bulk}}$ values of $\sim 0\%$ at Long'an documents intense denitrification and/or anammox destruction of biologically available nitrogen and its replacement by new microbially fixed nitrogen. Widespread denitrification and/or anammox indicates the existence of suboxic or anoxic conditions, probably in the deeper parts of the Yangtze Sea and/or surrounding open-ocean areas. The coincidence between the Hangenberg anoxic event and the end-Devonian mass extinction suggests that expansion of marine anoxia was the immediate cause of the biocrisis, lending support to previous hypotheses of this type (Algeo et al., 1995; Marynowski and Filipiak, 2007; Marynowski et al., 2012).

The ultimate cause of expansion of marine anoxia during the D-C transition remains in debate, although certain observations place important constraints on the range of viable mechanisms. Intensification of marine anoxia is most commonly associated with global climatic warming and stronger oceanic stratification, as at the Permian-Triassic boundary (Sun et al., 2012; Song et al., 2013), the Triassic-Jurassic boundary (McElwain et al., 1999; Hesselbo et al., 2002), the Toarcian OAE (Svensen et al., 2007; McArthur et al., 2008), and the mid-Cretaceous OAEs (Wilson and Norris, 2001; Turgeon and Creaser, 2008). In each case, the trigger for these changes was massive release of greenhouse gases to the atmosphere from volcanic or magmatic sources. In contrast, the D-C transition is characterized by global climatic cooling and expanded continental glaciation (Brezinski et al., 2008; Isaacson et al., 2008; Brezinski et al., 2010), and there is no

evidence of contemporaneous large-scale volcanic/magmatic activity such as the Siberian Traps during the P-Tr transition and the Deccan Traps at the end-Cretaceous. This pattern suggests that climate changes were the effect, rather than the cause, of marine anoxia. Specifically, cooling during the D-C transition was a response to massive burial of organic matter in marine shales, which significantly reduced atmospheric CO₂ levels (Algeo et al., 1995; Berner, 2006). One possible cause of enhanced organic carbon burial is higher marine productivity, which may have been stimulated by increased riverine nutrient fluxes driven by expansion of terrestrial ecosystems and enhanced continental weathering (Algeo et al., 1995; Martin, 1996; Algeo and Scheckler, 1998; Peterhänsel and Pratt, 2001; Tuite and Macko, 2013). Higher terrestrial nutrient fluxes around the D-C boundary are indicated by multiple lines of evidence, including a peak in seawater ⁸⁷Sr/⁸⁶Sr, increased smectite and kaolinite in marine clay-mineral assemblages, and blooms of marine algae and N-isotope gradients in epicontinental sea settings (Algeo et al., 1995; Jaminski et al., 1998; Algeo et al., 2001; Tuite and Macko, 2013). The specific event driving organic carbon burial at this time was probably a rapid spread of seed plants, a clade that appeared during the Late Devonian and that contributed to a rapid increase in terrestrial floral biomass—and, thus, pedic weathering potential—as it expanded into drier upland habitats (Algeo and Scheckler, 1998; Algeo and Scheckler, 2010). The observation of increases in polycyclic aromatic compounds (PAHs), which are indicative of more frequent wildfire, around the D-C boundary (Marynowski and Filipiak, 2007; Matyja et al., 2015) is readily accounted for in this scenario, as wildfires became more common due to (1) increased terrestrial floral biomass, especially in drier upland areas prone to wildfires, and (2) atmospheric O₂ levels increased rapidly owing to organic carbon burial (Algeo and Ingall, 2007).

The intensity of marine anoxia gradually diminished in the Upper *Si. praesulcata* Zone, as suggested by our $\delta^{15}\text{N}_{\text{bulk}}$ data (Fig. 2-4). This is consistent with the initial global recovery of marine benthos and nekton after the Hangenberg mass extinction (Kaiser et al., 2008). This interval is also one of eustatic transgression (Johnson et al., 1985; Haq and Schutter, 2008). Conventionally, transgressions are associated with more reducing conditions (Wignall, 1991; Hallam and Wignall, 1999), but this pattern is the product of climatic warming driving enhanced organic carbon burial, as during the Permian-Triassic boundary, Triassic-Jurassic boundary, Toarcian, and mid-Cretaceous events (see above). In contrast, organic carbon burial drove climate cooling during the Late Devonian (Algeo et al., 1995), so that, as organic carbon burial rates declined around the D-C boundary, climatic warming produced eustatic transgression in combination with generally less reducing conditions. However, further study, including other redox proxies, will be required to fully document redox variation during the D-C transition.

5.6. Long-term (latest Devonian to Tournaisian) evolution of nitrogen cycle

A recent compilation of marine $\delta^{15}\text{N}_{\text{bulk}}$ data for the past 660 Myr found that greenhouse climate intervals were characterized by low $\delta^{15}\text{N}$ values (-2‰ to $+2\text{‰}$), while icehouse climate intervals generally featured higher $\delta^{15}\text{N}$ values ($+4\text{‰}$ to $+8\text{‰}$) (Algeo et al., 2014). One of the key transitions occurred during the Late Devonian to Early Carboniferous (Algeo et al., 2014, their figure 1), although its timing was not narrowly constrained owing to the low resolution of this Phanerozoic dataset. However, this nitrogen isotope record is consistent with other geologic evidence, including oxygen isotopes (Joachimski and Buggisch, 2002; Brand et al., 2004) and eustatic elevations (Isaacson et al., 2008; Kaiser et al., 2011), that the Late Devonian to Early

Carboniferous was a critical interval in the transition from the Early Paleozoic greenhouse to the Late Paleozoic icehouse.

High-resolution nitrogen isotope studies of Upper Devonian-Lower Carboniferous successions provide more detailed information concerning this greenhouse-to-icehouse transition. Late Devonian marine formations in various North American basins yield $\delta^{15}\text{N}$ values mostly of +1‰ to +4‰ (Calvert et al., 1996; Caplan and Bustin, 1998; Levman and Bitter, 2002; Tuite and Macko, 2013; Rooney et al., 2015). The present study sections in South China yield slightly higher, relatively invariant background $\delta^{15}\text{N}_{\text{bulk}}$ values of +3.5‰ to +4.5‰ (Figs. 2-4). Compilation of N-isotope data suggest that the transition from Early Paleozoic greenhouse climate to Late Paleozoic icehouse climate coincided with two positive shifts in marine N-isotope values. The first episode occurred during the Famennian, when $\delta^{15}\text{N}$ increased from ~1‰ in Middle and early Late Devonian units (Algeo et al., 2014 and references therein) to ~4‰ at the D-C transition (this study; Fig. 6). The second episode began in the lower *Si. isosticha* Zone of the middle Tournaisian (Early Carboniferous), when $\delta^{15}\text{N}_{\text{bulk}}$ values begin to increase in conjunction with a positive excursion in $\delta^{13}\text{C}_{\text{carb}}$ (Fig. 6; Yao et al., 2015, their figure 2). During this interval, $\delta^{15}\text{N}_{\text{bulk}}$ rises from +3/+4‰ to +6/+7‰ at Long'an and from +2/+3‰ to +4/+5‰ at Malanbian. Unlike the $\delta^{13}\text{C}_{\text{carb}}$ excursions, which return to background values within the *Si. isosticha* Zone (for a total excursion duration of ~2-3 Myr), $\delta^{15}\text{N}_{\text{bulk}}$ values continue to rise to the top of each section within the *Gnathodus typicus* Zone of the late Tournaisian (Yao et al., 2015). This pattern is consistent with a long-term shift in $\delta^{15}\text{N}_{\text{bulk}}$ values, as proposed by Algeo et al. (2014), whose Phanerozoic curve (their figure 1) shows high $\delta^{15}\text{N}_{\text{bulk}}$ values through the Late Carboniferous (for a total excursion duration of >50 Myr).

This long-term shift in $\delta^{15}\text{N}_{\text{bulk}}$ values was attributed to two potential mechanisms, either or both of which might have operated concurrently: (1) a eustatic fall related to increased continental ice mass, reducing the amount of denitrification that occurred within shelf sediments, and shifting denitrification into continental slope oxygen-minimum zones, where N-isotope fractionation effects would have been much larger; and (2) changes in global-ocean circulation patterns that intensified upwelling on continental margins, leading to expanded oxygen-minimum zones and, thus, relatively more water-column denitrification (Algeo et al., 2014; Yao et al., 2015). Thus, the compiled $\delta^{15}\text{N}$ data suggest that the climate transition from Early Paleozoic greenhouse to Late Paleozoic icehouse was stepwise, occurring in several phases from the Famennian to at least the mid-Tournaisian. Further research will be needed to document the duration, global extent, and origin of marine nitrogen cycle perturbations during the late Early and Late Carboniferous.

The long-term shift toward higher $\delta^{15}\text{N}_{\text{bulk}}$ values during the Late Devonian-Early Carboniferous was interrupted by two negative N-isotope excursions: (1) the ‘FINE event’ (Famennian nitrogen isotope excursion) in the Middle *Si. praesulcata* Zone of the Famennian stage of the Late Devonian, and (2) the ‘TINE event’ (Tournaisian nitrogen isotope excursion) in the lower *Si. isosticha* Zone of the mid-Tournaisian stage of the Early Carboniferous (Fig. 6). These excursions were transient events (~100 kyr in duration, based on average sedimentation rates; see Section 3.1). It may be significant that, following each negative excursion, $\delta^{15}\text{N}_{\text{bulk}}$ returned to values almost identical to pre-excursion $\delta^{15}\text{N}_{\text{bulk}}$ values. This pattern is seen most clearly at Long’an, whereas at Malanbian the interval of stable $\delta^{15}\text{N}_{\text{bulk}}$ values between the negative excursions is relatively condensed (Fig. 6). These excursions are interpreted to represent short-term increases in microbial nitrogen fixation rates, probably in response to nitrogen

limitation of primary productivity, with a post-perturbation return to a stable N cycle equilibrium characterized by $\delta^{15}\text{N}_{\text{bulk}}$ values reflecting the N-isotopic composition of contemporaneous open-ocean seawater nitrate (ca. +3.5 to +4.5‰).

6. Conclusions

High-resolution bulk-sediment $\delta^{15}\text{N}$ records during the Devonian-Carboniferous transition are reported from three sections in South China (Long'an, Malanbian, and Qilinzhai). These records document major perturbations to the marine nitrogen cycle in the Middle *Si. praesulcata* Zone, in which $\delta^{15}\text{N}_{\text{bulk}}$ declines from $\sim +4\text{‰}$ to 0‰ at Long'an and from $+4.5\text{‰}$ to $+2.5\text{‰}$ at Malanbian. This perturbation coincided with the main end-Devonian (Hangenberg) mass extinction as well as with a negative shift in carbonate carbon isotopes. The shift to low $\delta^{15}\text{N}$ values ($\sim 0\text{‰}$) suggests local enhancement of microbial nitrogen fixation, possibly as a consequence of increased denitrification in response to globally expanded areas of marine anoxia. Thus, our $\delta^{15}\text{N}$ data are consistent with the hypothesis that intense anoxia was the immediate cause of the end-Devonian mass extinction. The $\delta^{15}\text{N}_{\text{bulk}}$ records presented in this study suggest that there was significant spatial and temporal variation in the nitrogen isotope composition of seawater fixed nitrogen within the latest Devonian Yangtze Sea. This variation may have been related to the complex paleogeography of the South China Craton, which contained numerous isolated and continent-attached platforms and deep-water basins that influenced watermass circulation, nutrient inventories and primary productivity levels, and watermass ventilation and redox conditions.

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Figure captions

Figure 1. Paleogeographic reconstructions of the world (A) and South China Craton (B) during the D-C transition. The global paleogeographic reconstruction was modified from Scotese and McKerrow (1990), whereas the regional reconstruction was based on Qie et al. (2015) and references therein. The stars represent the sections in this study. LA: Long'an, QLZ: Qilinzhai, MLB: Malanbian, S. China: South China.

Figure 2. Litho- and biostratigraphy of the Long'an section, including profiles of TOC, TN, C_{org}/N_{bulk} molar ratio, $\delta^{13}C_{carb}$ and $\delta^{15}N_{bulk}$. The $\delta^{13}C_{carb}$ data were replotted from Qie et al. (2015). The coarse grey lines represent a three-point moving average. Fm.: Formation; C Zone: conodont zone, Lithol.: Lithology. Note vertical scale change within the Yonghsien Formation.

Figure 3. Litho- and biostratigraphy of the Malanbian section, including profiles of TOC, TN, C_{org}/N_{bulk} molar ratio, $\delta^{13}C_{carb}$ and $\delta^{15}N_{bulk}$. The $\delta^{13}C_{carb}$ data were replotted from Qie et al. (2015). The coarse grey lines represent a three-point moving average. Fm.: Formation; C Zone: conodont zone, Lithol.: Lithology.

Figure 4. Litho- and biostratigraphy of the Qilinzhai section, including profiles of TOC, TN, C_{org}/N_{bulk} molar ratio, $\delta^{13}C_{carb}$ and $\delta^{15}N_{bulk}$. The $\delta^{13}C_{carb}$ data were replotted from Qie et al. (2015). The coarse grey lines represent a three-point moving average. Fm.: Formation; C Zone: conodont zone, Lithol.: Lithology. I and II represent negative shifts in $\delta^{15}N_{bulk}$.

Figure 5. Crossplots of TN vs TOC (A-C), $\delta^{15}N_{bulk}$ vs TN (D-F), and $\delta^{15}N_{bulk}$ vs C_{org}/N_{bulk} molar ratio (G-I). A-C show significant ($p(\alpha) < 0.01$) positive correlations, suggesting that organic matter was the main source of bulk nitrogen. D-F and G-I show no significant correlations.

Figure 6. Compiled $\delta^{15}N_{bulk}$ data from the D-C boundary to the mid-Tournaisian for (A) Long'an and (B) Malanbian. The $\delta^{15}N$ data are from this study and Yao et al. (2015). FINE: Famennian nitrogen isotope event; TINE: Tournaisian nitrogen isotope event.

Figure 1

FIGURES

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