Water mass denitrification during the latest Permian extinction in the Sverdrup Basin, Arctic Canada

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ABSTRACT

Late Permian–Early Triassic bulk sedimentary nitrogen isotope ($\delta^{15}\text{N}$) and biomarker data have been generated from the northwest margin of Pangea. Sediments from the Buchanan Lake section, Arctic Canada, deposited prior to the latest Permian extinction (LPE) event are characterized by positive $\delta^{15}\text{N}$ values of $\sim 9\text{‰}$ associated with the presence of lycopane, implying upwelling of denitrified waters from an expanded oxygen minimum zone. The data show that anoxic bottom-water conditions were not developed in northeastern Panthalassa during the Late Permian. Promoted by dispersing coal ash from Siberian Traps volcanics, as marked by an abrupt rise in C/N ratios (>20) prior to the LPE event, euxinic conditions first developed at the LPE. Pronounced differences in the nitrogen inventory across the LPE event, however, suggest that while unfavorable conditions prevailed for aerobiosis in the paleo-Tethys, persistent upwelling of deoxygenated (denitrified) waters occurred in the Sverdrup Basin across the LPE, excluding the prevalence of photic zone euxinia along the northwest margin of Pangea.

INTRODUCTION

The latest Permian extinction (LPE) event, ~ 252 m.y. ago, resulted in the disappearance of $>90\%$ of marine and terrestrial species (Erwin, 2006). Possible explanations invoke Siberian Trap volcanism (Wignall and Twitchett, 1996), oceanic anoxia (Isozaki, 1997), H_2S poisoning, and drawdown of bioessential elements (Grasby and Beauchamp 2009), or a combination of these. Observations of coal ash deposition prior to the LPE (Grasby et al., 2011), along with mercury anomalies (Sanei et al., 2012), suggest that toxic conditions developed. While the existence of euxinic marine conditions in the Tethyan region across the LPE is widely accepted (Grice et al., 2005), inferences on the redox and environmental conditions of the Panthalassic Ocean are more equivocal (Algeo et al., 2010; Wignall et al., 2010). Indications of photic zone euxinia exist in marginal areas of Panthalassa (Algeo et al., 2012). In open-ocean settings, however, low oxygen conditions may have been restricted to the oxygen minimum zone (OMZ) across the LPE, rather than extending through to the photic zone or to the seafloor (Algeo et al., 2010).

Here we report the $\delta^{15}\text{N}$ record in Late Permian–Early Triassic sediments from the Sverdrup Basin, northwest Pangea (Fig. 1). Deep-water marine sedimentation in the basin, connected to Panthalassa via a western seaway, allows us to make inferences about the nitrogen cycling across the LPE. We demonstrate that expansion of low oxygen conditions in the northeastern Panthalassic Ocean began prior to that of the paleo-Tethys Ocean. The corresponding relationship between changes in denitrification, nitrate utilization, and nitrogen fixation

across the LPE in both oceans indicates rapid reorganization of the global marine ecosystem in response to changes in nutrient inventories, probably mediated through eruption of the Siberian Traps.

GEOLOGICAL SETTING

We sampled the Buchanan Lake section (located on Axel Heiberg Island, Nunavut, Canadian High Arctic; Fig. 1), which records sedimentation in the rapidly subsiding Sverdrup Basin. The section contains an uninterrupted, deep-water (maximum 1–2 km), shale-dominated marine record deposited under oxygen-depleted conditions across the LPE event (Grasby and Beauchamp, 2009). The extinction boundary is marked by a distinctive 1 cm pyrite layer associated with a pyrite rain-out event (sensu Grasby and Beauchamp, 2009) at the LPE boundary that also marks the change from Black Stripe Formation shale (below) to Blind Fiord Formation shale (above) (Fig. 2). Below the boundary, three prominent high-organic-carbon layers are associated with coal fly ash deposits, thought to represent fall out from organic combustion by Siberian Trap volcanism (Fig. 2) (Grasby et al., 2011).

Figure 1. Late Permian paleogeography (after Sanei et al., 2012). Asterisks mark location of Buchanan Lake (Arctic Canada) and Meishan (south China) (Cao et al., 2009). PTO—paleo-Tethys Ocean; NTO—neo-Tethys Ocean.

Figure 2. Lithology of Buchanan Lake section (Arctic Canada). **A:** Plot of total organic carbon (TOC, wt%) analyzed by Rock Eval pyrolysis (RE) and LECO CS-444 (carbon and sulfur determinator), and zones with high concentrations of combusted coal (Grasby et al., 2011). **LPE**—latest Permian extinction. **B:** $\delta^{15}\text{N}$ ratios, $\delta^{15}\text{N}$ (‰) and lycopane concentrations ($\mu\text{g/g}$ sediment). **C:** Sulfur (wt%), Mo/Al ratio, and C/S ratios. Lithology: shaley chert (gray shading); siliceous shale (black shading); nonsiliceous shale with carbonate beds (green shading with black bars); siltstone, sandstone with minor shale (and some slumping) (yellow shading); pyrite layer (orange bars) (for details, see Grasby and Beauchamp, 2008).

METHODS

We studied 40 dried and homogenized samples from an interval of 86 m below and 34 m above the base of the Blind Fiord Formation, which coincides with the LPE boundary in the Buchanan section (Fig. 2). Total nitrogen and $\delta^{15}\text{N}$ were analyzed by elemental analyzer–isotope ratio mass spectrometry on an ANCA-GSL/20–20 system. A KBr-KOH-treated aliquot measures the amount of inorganic nitrogen (IN) and its isotopic signature ($\delta^{15}\text{N}_{\text{inorg}}$) (Schubert and Calvert, 2001). Approximately 20% of the samples were analyzed in duplicates with a mean standard deviation of 0.16‰. Results presented in Table DR1 in the GSA Data Repository¹ are standard δ values (in per mil; ‰ versus air). Original total organic carbon (TOC, wt%) measurements by Rock-Eval 6 pyrolysis (maximum 550°) and sulfur (S, wt%) contents were repeated on a LECO CS 444 analyzer. Approximately 2 g of sediment were extracted (methanol/dichloromethane 1:3) using a microwave system (Milestone MLS 1200 Mega). Extracts were run over a copper column to remove elemental sulfur. After saponification, the neutral extracts were desulfurized with Raney Nickel and subsequently hydrogenated (see the Data Repository). Identification and quantification were done by gas chromatography–mass spectrometry (Shimadzu QP-2010 Plus with an Optic3 [Atlas GL] injector).

PROXY DATA

The $\delta^{15}\text{N}$ signal produced in the photic zone depends on the isotopic composition of nitrate and the degree to which this inorganic nitrogen pool is utilized (Altabet and François, 1994). This relationship can be complicated in regions of significant denitrification (i.e., the reduction of nitrate/nitrite to N_2), which leaves subsurface waters highly enriched in ^{15}N , and/or by atmospheric nitrogen fixation, which produces organic matter highly depleted in ^{15}N . In modern productive and oxygen depleted settings, moderate to good preservation of sedimentary organic matter (OM) produces little diagenetic alteration of $\delta^{15}\text{N}$ values compared to sinking particles (Altabet et al., 1999a, 1999b), and there is little difference between the $\delta^{15}\text{N}$ of the original OM and diagenetically produced NH_4^+ (Williams et al., 1995). In addition, postdepositional temperature changes have negligible effect on sedimentary $\delta^{15}\text{N}$ (Ader et al., 1998). Given the low metamorphic grade of the Buchanan Lake section (below greenschist facies) (Grasby and Beauchamp, 2008), preferential $^{14}\text{NH}_4^+$ loss

during high-temperature devolatilization would have had only minor influence on $\delta^{15}\text{N}$ preservation (Bebout and Fogel, 1992). Because total N is completely bound as IN, which is mainly NH_4^+ fixed within the clay lattice, in Late Permian–Early Triassic deposits (Table DR1; $R^2 = 0.97$), and the fact that NH_3 and NH_4^+ are derived from associated marine OM during diagenesis (Rau et al., 1987), $\delta^{15}\text{N}_{\text{tot}}$ would reflect the original OM. The argument for this is twofold: (1) we observe nearly identical $\delta^{15}\text{N}$ - NH_4^+ (mean 8.67‰) and $\delta^{15}\text{N}_{\text{tot}}$ (mean 8.85‰) values, and (2) a covariance between TOC and TOC/IN ratio (hereafter: C/N ratio) of 0.96 suggests an organic origin for the IN (Fig. DR1; see the Data Repository). C/N ratios of <10 correlate with intervals of predominantly thermally altered marine OM (Grasby et al., 2011), while C/N ratios >15 coincide with zones of abundant combustion-derived char (Fig. 2), justifying the use of C/N ratios as an OM source indicator. The C/N decrease (<5) above the LPE occurs in intervals of lower TOC (<0.8 wt%) and may be the result of increased adsorption of diagenetically produced NH_4^+ onto clay minerals. The lack of covariation between $\delta^{15}\text{N}$ - NH_4^+ and the C/N ratio ($R^2 = 0.2$) indicates no significant alteration of the $\delta^{15}\text{N}$ signal (Table DR1). The presence of lycopane in ancient, organic-rich sediments indicates anoxic depositional environments characterized by photic zone euxinia, well-developed OMZ, or anoxic lakes (Sinninghe Damsté et al., 2003). In addition, sulfur content (wt%), C/S ratios, and previously published redox sensitive proxies (Mo/Al ratios) are used to infer environmental conditions along the northwest Pangea margin (Fig. 2).

RESULTS AND DISCUSSION

Late Permian Denitrification Record in Panthalassa

The Late Permian $\delta^{15}\text{N}$ record from Buchanan Lake is characterized by moderately high and relatively uniform values of $\sim 9.2\text{‰} \pm 0.3\text{‰}$ (Fig. 2). TOC is primarily of marine origin (C/N 5–12), and has values between 0.5% and 4.0%. Three distinct TOC maxima characterized by enhanced C/N values (>15) are associated with high concentrations of combusted coal reported by Grasby et al. (2011) (Fig. 2). As other mechanisms for $\delta^{15}\text{N}$ enrichment, such as progressive drawdown of the nitrate pool, are not reported for oxygen-depleted environments (Schubert and Calvert, 2001), the heavy $\delta^{15}\text{N}$ values suggest upwelling of a denitrified, and thus ^{15}N -rich, water mass into the photic zone where residual nitrate could be utilized by plankton. Denitrification requires suboxic conditions, and occurs today in organic-rich continental margin sediments and in intermediate waters within an intense OMZ. Thus, $\delta^{15}\text{N}$ values >9‰ in the Black Stripe Formation indicate develop-

ment of an intense OMZ along the northwest Pangea margin prior to the LPE. This is further supported by the persistent occurrence of lycopane (Fig. 2), a biomarker reported in modern and ancient organic-rich sediments deposited within OMZs (Sinninghe Damsté et al., 2003). This contrasts with observations of rather weak dysoxic conditions in central Panthalassa during much of the Late Permian (Wignall et al., 2010; Algeo et al., 2010); however, it corroborates inferences of productive cold-water upwelling systems and intense OMZ elsewhere along the northwest Pangea margin (Schoepfer et al., 2012). High $\delta^{15}\text{N}$ values (average 9.2‰), in conjunction with enhanced lycopane concentrations (Fig. 2), occur 10–5 m below the LPE boundary, indicating progressive intensification of water-column denitrification through expansion of the OMZ. This agrees with data-model observations by Algeo et al. (2010) and Winguth and Winguth (2012) that large regions of the Panthalassic Ocean underwent only limited redox changes, with oxygen-depleted conditions concentrated within the OMZ.

Superimposed on the long-term trend of oxygen depletion prior to the LPE, global loading of fly ash derived from coal and/or shale combustion due to Siberian flood basalts (Fig. 2) may have fostered the development of euxinia at the LPE boundary (Grasby et al., 2011). Fly ash is a source of readily available macronutrients and micronutrients (Jala and Goyal, 2006), and this additional nutrient input would have further stimulated biologic productivity, leading to greater oxygen demand. The development of euxinic conditions is supported by redox-sensitive proxies (Grasby and Beauchamp, 2009) such as low C/S ratios (<1) coupled with high sulfur content (6 wt%), high Mo/Al values (>10), as well as pyrite rain-out events (Fig. 2) immediately following the third coal-ash loading event (Fig. 2). However, there is an absence of isorenieratane and its alteration products, derived from the carotenoid pigments of green sulfur bacteria (Chlorobiaceae) (Sinninghe Damsté et al., 1993), throughout the sediment sequence, suggesting that euxinia did not reach the photic zone in the Sverdrup Basin.

LPE Event

The Latest Permian Extinction event horizon at Buchanan Lake records the peak of euxinic conditions (Grasby and Beauchamp, 2009). The horizon is marked by a rapid excursion to lighter $\delta^{15}\text{N}$ values (8.3‰) (Fig. 2), followed by gradually lighter $\delta^{15}\text{N}$ values ($\sim 8\text{‰}$) into the Early Triassic; the latter is not due to dilution by terrestrial OM supply, because OM is predominantly of marine origin (C/N ~ 5). The negative shift could not be caused by ventilation of the thermocline driven by lower sea-surface temperature and higher oxygen solubility lessening the spatial extent of denitrification

¹GSA Data Repository item 2013041, raw geochemical data, technical details on biomarker analyses, and a cross plot of C/N ratio versus inorganic nitrogen, is available online at www.geosociety.org/pubs/ft2013.htm, or on request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

during greenhouse-hothouse conditions that occurred across the LPE boundary (Kidder and Worsley, 2010). Incomplete nitrate utilization may also be ruled out because anoxia would have promoted recycling of sedimentary phosphorus into the water column, further stimulating nitrate utilization. The most likely cause of the decline in $\delta^{15}\text{N}$ values after the LPE is a change in the balance between denitrification and nitrogen fixation (as known from the late Quaternary), which controls the abundance and isotopic composition of nitrate in the ocean (Ganeshram et al., 2000). Deutsch et al. (2007) suggested that rates of N_2 fixation are associated, both geographically and temporally, with marine nitrogen removal, implying a close coupling of nitrogen fixation to nitrogen-deficient water in denitrification zones. Thus, in response to reduced N supply from anoxic deep waters (caused by intense denitrification) to the photic zone, diazotrophs would have increased N fixation after the LPE. The input of the diazotrophs biomass ($\sim 0\%$; Carpenter et al., 1997) would lead to significantly reduced values of $\delta^{15}\text{N}$ of the particulate OM sediment record. The concurrent presence of lycopane and enhanced Mo/Al ratio along with disseminated pyrite layers and undisturbed laminae (Grasby and Beauchamp, 2009) indicate that oxygen-depleted conditions prevailed during that time. Schoepfer et al. (2012) argued, based on a negative $\delta^{15}\text{N}$ shift (6‰) at Opal Creek (northwest Pangea), for a collapse of the coastal upwelling system and enhanced N fixation in response to bottom-water anoxia at the Permian-Triassic boundary. The latter corroborates distinct changes in phytoplankton community at the same time as inferred from $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ records from the Sverdrup Basin (Algeo et al., 2012). However, at Buchanan Lake, the prevalence of high $\delta^{15}\text{N}$ ($>8\%$) above the LPE does not suggest complete denitrification, or a transition to lower productivity conditions as suggested by Schoepfer et al. (2012). Rather, the negative $\delta^{15}\text{N}$ trend beginning 7 m below the LPE is more likely due to added biomass of diazotrophs to the planktonic population, which dilutes the dominant signals of upwelling and recycling of nutrients, high organic productivity, and partial denitrification in oxygen-depleted waters.

Cao et al. (2009) reported a distinct shift to negative $\delta^{15}\text{N}$ values at the extinction level (top of bed 24) at Meishan, south China (Fig. 3), that was contemporary with the decline in $\delta^{15}\text{N}$ value in northeastern Panthalassa. Furthermore, Luo et al. (2011) reported enhanced nitrogen fixation following the LPE in the eastern paleo-Tethys Ocean. This indicates the episodic loss of N cycling through nitrate, and the prevalence of N_2 -fixing cyanobacteria as a consequence of photic zone euxinic conditions (Grice et al., 2005). The decline in $\delta^{15}\text{N}$ in both oceans following the boundary event (Fig. 3) is attributed

Figure 3. $\delta^{15}\text{N}$ records from Buchanan Lake (Arctic Canada) and Meishan (south China) (Cao et al., 2009). Latest Permian extinction (LPE) event horizon is correlated between Meishan (beds 24–25 contact) and Buchanan Lake (Black Stripe Formation–Blind Fiord Formation contact). Approximate Wuchiapingian–Changhsingian contact at Buchanan Lake is 90–110 m below LPE (Grasby and Beauchamp, 2009).

to a disruption of the N cycle and consequent increase in atmospheric N_2 fixation in the paleo-Tethys, with this low $\delta^{15}\text{N}$ signal diluting the effect of denitrification in Panthalassa. This follows Holocene to recent observations from the eastern tropical North Pacific, where the denitrification signal may be diluted by advected isotopically light nitrate from subtropical oligotrophic regions (Thunell and Kepple, 2004). For the Late Permian–Early Triassic, it suggests a tight coupling of the oceanic N reservoir with a circulation pattern that exports surface waters from the paleo-Tethys, as proposed by Meyer et al. (2008). It further implies that the increased loss of nitrogen from Panthalassa suboxic zones was countered by comparably large changes in paleo-Tethys N_2 fixation, maintaining some biological productivity in the ocean (Algeo et al., 2010); the likely photoautotrophic source of lycopane (Sinninghe Damsté et al., 2003), which is abundant across the LPE boundary, provides additional support for this.

IMPLICATIONS

The $\delta^{15}\text{N}$ records from Panthalassa and paleo-Tethys confirm data-model results (Wignall et al., 2010; Winguth and Maier-Reimer, 2005) that widespread Panthalassic dysoxia started prior to development of anoxia in the paleo-Tethys Ocean. While positive values of $\delta^{15}\text{N}$ ($\sim 3\%$ – 4%) in the Lungtan Formation and/or early Changxing Formation reflect open-ocean, normal N cycling through nitrate in the paleo-Tethys (Cao et al., 2009), $\delta^{15}\text{N}$ of $\sim 9\%$ and the presence of lycopane in the Black Stripe Formation indicate denitrification and N loss in an oxygen-depleted, suboxic water mass in the Sverdrup Basin along the northeastern Panthalassa margin (Fig. 3). The latter agrees with Kidder and Worsley's (2010) "Greenhouse state"

characterized by gradually weaker thermal mode ocean circulation and expansion of the OMZ, but still-sufficient ventilation of the deep ocean. Intense upwelling along the northeastern Panthalassa margin, associated with enhanced productivity, may have intensified the OMZ and thus partial denitrification (Schoepfer et al., 2012), similar to modern marginal areas such as the Arabian Sea. Although diluted by advected light nitrate, persistent evidence of water-mass denitrification across the LPE suggests that changes in oxygenation are largely controlled by upwelling, recycling of nutrients, and high organic productivity, consistent with the high-productivity scenario for Early Triassic oceanic anoxia (Meyer et al., 2011). Atmospheric release of nitrous oxides produced through denitrification within the OMZ may have amplified the transition from a greenhouse into a hothouse state (Kidder and Worsley, 2010). In the paleo-Tethys, sulfidic waters reached the photic zone and provided a source for H_2S -rich waters as much as 1.5 m.y. prior to the main extinction event (Cao et al., 2009). In contrast, the absence of green sulfur bacteria-derived biomarkers at Buchanan Lake suggests that the continuous upwelling of deoxygenated and/or denitrified waters across the LPE, and euxinia in Panthalassa, was restricted to the OMZ rather than in the photic zone. These data are consistent with empirical data (Algeo et al., 2010) and modeling results (Winguth and Winguth, 2012) implying that oxygen depletion expanded within the OMZ in northeastern Panthalassa rather than at abyssal depths. The significant change in the oceanic nitrogen inventories across the LPE event suggests that while unfavorable conditions prevailed for aerobiosis in the paleo-Tethys, persistent upwelling of deoxygenated (denitrified) waters occurred in the Sverdrup Basin across

the LPE, excluding the prevalence of photic zone euxinia in the Panthalassic Ocean.

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