

# Enhanced nitrogen fixation in the immediate aftermath of the latest Permian marine mass extinction

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## ABSTRACT

The carbon ( $\delta^{13}\text{C}_{\text{org}}$ ) and nitrogen ( $\delta^{15}\text{N}$ ) isotopic compositions of bulk organic matter were analyzed in two high-resolution Permian-Triassic transitional sections containing microbialite in south China. The results from these shallow-marine sections show that an abrupt negative shift in  $\delta^{15}\text{N}$ , from  $\sim +3\text{‰}$  to  $\sim 0\text{‰}$ , occurred immediately after the latest Permian mass extinction (LPE) in both sections, concurrent with a distinct negative shift in  $\delta^{13}\text{C}_{\text{org}}$ . The persistently low values of  $\delta^{15}\text{N}$  suggest that, following the LPE, microbial nitrogen fixation became the main source of biologically available nitrogen in the Nanpanjiang Basin and perhaps over a broader region of the eastern Paleotethys Ocean. Enhanced N fixation is probably indicative of the prevalence of stratified anoxic water masses characterized by intense denitrification and/or anaerobic ammonium oxidation at the time. Perturbation of the marine nitrogen cycle might have contributed to high temperatures following the main marine mass extinction through the release of the greenhouse gas  $\text{N}_2\text{O}$ . The sharp declines in  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{org}}$  may be ascribed to an abrupt change in shallow-water microbial communities, which differed in composition from contemporaneous deep-water communities.

## INTRODUCTION

The largest mass extinction of the Phanerozoic occurred at the end of the Permian, and eliminated  $>90\%$  of species in the ocean and  $\sim 70\%$  of vertebrate families on land (Erwin, 2006). Whole-ocean superanoxia has been implicated as the direct mechanism of this extinction (Grice et al., 2005; Riccardi et al., 2006). However, details of the timing, geographic extent, and intensity of oceanic anoxia during the Permian-Triassic (P-Tr) transition are still being resolved (Algeo et al., 2010). Paleoredox proxies such as S/C ratios and seawater sulfate and sulfide S isotope compositions show high variability during the P-Tr transition (Gorjan et al., 2007; Luo et al., 2010; Riccardi et al., 2006), suggesting large and frequent fluctuations in paleoredox conditions. Furthermore, isorenieratane records indicate that ephemeral photic-zone euxinia began at least 1.5 m.y. before the end-Permian mass extinction (without any immediate effects on marine biotas) and continued throughout the P-Tr crisis interval (Cao et al., 2009).

Mass extinction events are generally defined on the basis of the metazoan fossil record. Microbes are rarely preserved as fossils and, consequently, we know considerably less about their composition, spatial distribution, and response to environmental stresses during such events. One characteristic of the latest Permian mass extinction (LPE) is that skeletal limestones

are directly overlain by microbialites in many shallow-water settings around the world (Baud et al., 2007; Lehrmann et al., 2003). Microbialites, which were globally abundant during the Precambrian but declined greatly in early Paleozoic oceans (Riding and Liang, 2005), made a resurgence in the immediate aftermath of the LPE. These microbialites were inferred to contain cyanobacteria (Wang et al., 2005; Xie et al., 2010), although the microbial communities contributing to their formation have only recently been investigated in any detail (Yang et al., 2011; Chen et al., 2011). Here we present high-resolution  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$  profiles from two P-Tr sections containing microbialite in south China, the Taiping and Zuodeng sections, to explore changes in microbial ecosystems, marine biogeochemical cycles, and seawater chemistry during the P-Tr crisis interval.

## CARBON AND NITROGEN ISOTOPE PROFILES

Isotopic profiles for the study sections reveal sharp negative shifts in  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$  at the level of the LPE horizon (Fig. 1). Pre-crisis skeletal limestones yield average  $\delta^{13}\text{C}_{\text{org}}$  values of  $-26.5\text{‰}$  and  $-24.0\text{‰}$  in the Taiping and Zuodeng sections, respectively. A distinct negative shift of  $>2\text{‰}$  occurs simultaneously with the transition from the skeletal limestone to the microbialite, producing a  $\delta^{13}\text{C}_{\text{org}}$  minimum in both sections at the base of the microbialite.  $\delta^{13}\text{C}_{\text{org}}$  remains relatively constant within

the microbialite interval at Taiping except for a small negative shift in the uppermost part, whereas  $\delta^{13}\text{C}_{\text{org}}$  increases gradually in the microbialite interval at Zuodeng (Fig. 1).

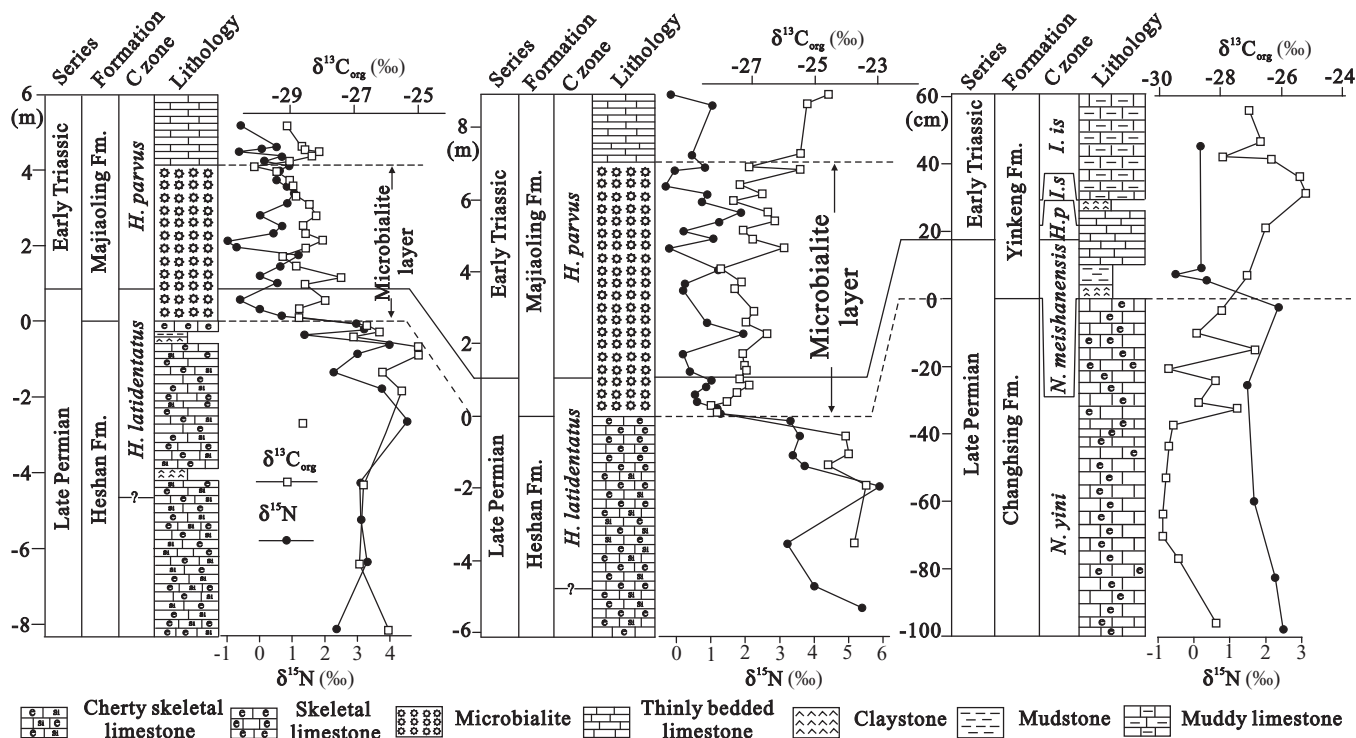
The  $\delta^{15}\text{N}$  values in the skeletal limestone at Taiping range from  $2.3\text{‰}$  to  $4.5\text{‰}$ , with an average of  $\sim 3\text{‰}$ , except for one black mudstone sample in the upper part of the skeletal limestone that yields a value of  $1.4\text{‰}$  (Fig. 1). An abrupt negative shift in  $\delta^{15}\text{N}$ , from  $+3\text{‰}$  to  $<+1\text{‰}$ , occurs at the transition from skeletal limestone to microbialite, concurrent with the decline in  $\delta^{13}\text{C}_{\text{org}}$ . In the microbialite interval,  $\delta^{15}\text{N}$  varies from  $-1\text{‰}$  to  $+1\text{‰}$  with minimum values near the base of the unit. The low  $\delta^{15}\text{N}$  values continue well into the overlying thinly bedded limestone. The Zuodeng section has a  $\delta^{15}\text{N}$  profile similar to that of the Taiping section (Fig. 1). A complete description of geological background, methods, and supporting data for this study can be found in the GSA Data Repository.<sup>1</sup>

## MARINE SOURCE OF ISOTOPE SIGNALS

Multiple lines of evidence suggest that the isotopic shifts at the LPE are not related to an increase in the proportion of terrestrial organic matter in the analyzed samples. First, the study sections were located in the interior of isolated high-relief carbonate platforms in a large marine basin (the Nanpanjiang Basin; Fig. DR1 in the Data Repository). The carbonate content of analyzed samples remains consistently high ( $>95\%$ ) during the transition from skeletal limestone to microbialite, documenting no increase in terrigenous siliciclastic flux (see the Data Repository). It is unlikely that much terrestrial organic matter was transported to the study sites. Second, the strong positive correlation between the  $\delta^{13}\text{C}_{\text{carb}}$  and  $\delta^{13}\text{C}_{\text{org}}$  (see the Data Repository) in these two sections implies a dominant fraction of marine organic matter. Third, the  $\delta^{13}\text{C}_{\text{org}}$  profiles of the study sections exhibit negative shifts

<sup>1</sup>GSA Data Repository item 2011203, geological background, methods, and molecular data, is available online at [www.geosociety.org/pubs/ft2011.htm](http://www.geosociety.org/pubs/ft2011.htm), or on request from [editing@geosociety.org](mailto:editing@geosociety.org) or Documents Secretary, GSA, P.O. Box 9140, Boulder, CO 80301, USA.

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**Figure 1.** Profiles showing  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$  variations during Permian-Triassic transition in sections at Taiping (left), Zuodeng (middle), and Meishan (right). Base of microbialite represents latest Permian marine mass extinction horizon. Conodont biostratigraphy is from Lehmann et al. (2003). The  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{org}}$  data in Meishan section were replotted from Cao et al. (2009) and Riccardi et al. (2007), respectively. Conodont zone (C zone) in Meishan section is according to Jiang et al. (2007). *H.p.*—*Hindeodus parvus* zone; *I.s.*—*Isarcicella staeschei* zone; *I.is.*—*I. isarcica* zone; *N.*—*Neogondolella*.

in the microbialite, different from the  $\delta^{13}\text{C}_{\text{org}}$  profiles in sections that were contaminated by terrestrial organic matter (Cao et al., 2002). We infer that the  $\delta^{13}\text{C}_{\text{org}}$  and  $\delta^{15}\text{N}$  records presented here represent the isotopic composition of contemporaneous marine organic matter. Variation in burial temperatures is unlikely to account for isotopic shifts in the study units because the sections are only a few meters thick and all samples had similar thermal histories.

#### MARINE NITROGEN CYCLE DURING THE P-TR TRANSITION

Distinct negative shifts in  $\delta^{15}\text{N}$  in the study sections suggest large changes in the marine nitrogen cycle during the P-Tr transition (Fig. 1). One potential explanation for these shifts is incomplete utilization of bioavailable N by photosynthesizers. However, incomplete nitrate utilization as a function of iron limitation occurs mainly in high-nutrient low-chlorophyll regions of the open ocean (Ganeshram et al., 2000) rather than in pericratonic carbonate platform settings such as those in which the units studied accumulated. Widespread development of shallow-marine anoxia in the Early Triassic (Cao et al., 2009; Grice et al., 2005) would have favored recycling of mineral-associated and organic phosphorus from the sediment to the water column, enhancing nitrate utiliza-

tion. Enhanced continental weathering in the aftermath of the end-Permian crisis also would have increased the supply of phosphate and iron delivered to the ocean (Sephton et al., 2005; Xie et al., 2007). Therefore, it is unlikely that incomplete nitrate utilization was responsible for the sharp decline in  $\delta^{15}\text{N}$  observed in the study sections. Chemoautotrophic bacterial activity generally produces larger negative fractionations (to  $-14\text{‰}$ ; Möbius et al., 2010) than those observed in the study sections (Fig. 1).

A more likely mechanism to account for the negative shifts in  $\delta^{15}\text{N}$  at the LPE in the study sections is enhanced N fixation. The N isotopic composition of the microbialite ( $-1\text{‰}$  to  $+1\text{‰}$ ) is similar to that of atmospheric  $\text{N}_2$  ( $0\text{‰}$ ), consistent with the limited fractionation associated with diazotrophic (N fixing) marine cyanobacteria (Carpenter et al., 1997). Owing to the high energy demand of N fixation, this process occurs only when nutrient nitrogen concentrations are extremely low (Tyrrell, 1999). Strong N fixation in the Late Permian Nanpanjiang Basin implies a deficit of bioavailable N in contemporaneous seawater, which is commonly the result of enhanced loss of nitrate under oxygen-poor conditions. The main pathways for nutrient nitrogen loss are through denitrification, anaerobic ammonia oxidation, and/or burial of organic matter (Murray et al., 2005). Therefore, the  $\delta^{15}\text{N}$

records of the study sections suggest an expansion of anoxic water masses following the LPE.

At a minimum, such N-depleted conditions existed across the South China craton, as evidenced by low  $\delta^{15}\text{N}$  values in the correlative (non-microbialite bearing) beds at Meishan, located in the northeastern part of the South China block (Fig. 1; Cao et al., 2009). A negative N isotope excursion (to  $-2\text{‰}$ ) is also found immediately above the latest Permian extinction horizon at Guryul Ravine, a P-Tr section in northern India (Algeo et al., 2007), suggesting that N fixation may have been prevalent throughout the Tethyan Ocean region. Furthermore, a small but sustained negative shift in  $\delta^{15}\text{N}$  (from  $\sim+6\text{‰}$  to  $+5\text{‰}$ ) begins at the LPE in the West Blind Fiord section from the northern Pangean margin (T. Algeo's unpublished data), suggesting that the nitrate N isotopic composition of Panthalassic seawater also evolved during the latest Permian. Thus, the pronounced negative N isotopic excursions seen at Taiping and Zuodeng may be indicative of a broader, potentially global perturbation of the marine nitrogen cycle during the P-Tr transition, although more data are needed to test this hypothesis. The duration of this episode of depletion of bioavailable N may have been at least several hundred thousand years, as shown by the persistence of light  $\delta^{15}\text{N}$  values to the tops of the study sections (Fig. 1).

Although not precisely dated, the microbialite facies proliferated from the *Neogondolella meishanensis* zone to the *Isarcicella staeschei* zone (Yang et al., 2011).

Changes in the marine nitrogen cycle following the LPE may have had significant climate consequences. Trace metals are essential components of many enzymes, and their stripping from a euxinic water column through rapid removal to the sediment as metal sulfides may have affected the rates of certain biogeochemical processes (Saito et al., 2003). For example, copper is an essential component of the enzyme NOS (nitric oxide synthase), the only known catalyst of the terminal step that converts  $\text{N}_2\text{O}$  to  $\text{N}_2$  in the denitrification pathway (Buick, 2007). If strongly reducing conditions following the LPE (Grice et al., 2005; Riccardi et al., 2006) caused a reduction in copper in global seawater, then more  $\text{N}_2\text{O}$  may have been released to the atmosphere, contributing to greenhouse warming due to the strong radiative forcing of  $\text{N}_2\text{O}$ , which is  $\sim 1000$  times greater than that of  $\text{CO}_2$ .

### GLOBAL CARBON CYCLE DURING THE P-TR TRANSITION

Shifts in  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{org}}$  in the study sections lagged behind that of the marine carbonate  $\delta^{13}\text{C}_{\text{carb}}$  record (Fig. 2; Luo et al., 2011). Fluctuations in  $\delta^{13}\text{C}_{\text{carb}}$  during the Late Permian–Early Triassic are known to be globally correlatable, indicating that they reflect changes in the C isotopic composition of dissolved inorganic carbon in seawater (Korte and Kozur, 2010). A large (3‰–6‰) negative shift in  $\delta^{13}\text{C}_{\text{carb}}$  reflecting a major perturbation of the global carbon cycle, began in the mid-Changhsingian, i.e., well

before the LPE (Korte and Kozur, 2010; Xie et al., 2007). Luo et al. (2011) demonstrated that this shift occurred in two steps in both of the sections studied, the first  $>5$  m below the LPE, and the second beginning  $\sim 0.5$ – $1.0$  m below the LPE (within the skeletal limestone) and continuing to  $\sim 1$ – $2$  m above the LPE (within the microbialite). These differences in timing suggest that variations in organic  $\delta^{13}\text{C}$  and  $\delta^{15}\text{N}$  at Taiping and Zuodeng had fundamentally different causes from the global shifts in carbonate  $\delta^{13}\text{C}$ .

The negative shifts in  $\delta^{15}\text{N}$  and  $\delta^{13}\text{C}_{\text{org}}$  occurred simultaneously at the level of the LPE in both study sections (Fig. 1), indicating that both are a response to environmental changes associated with the extinction event. The difference in organic and carbonate C isotopes  $\Delta^{13}\text{C}$  ( $\delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$ ) is related to photosynthetic fractionation and can be used to assess changes in the primary producer community. Riccardi et al. (2007) documented little change in  $\delta^{13}\text{C}_{\text{org}}$  and a large reduction in  $\Delta^{13}\text{C}$  at the LPE in the Meishan and Shangsi sections, which they attributed to a larger fraction of organic matter derived from green sulfur bacteria, an anaerobic photosynthetic organism that fractionates to a lesser degree than eukaryotic marine algae. In contrast, the negative  $\delta^{13}\text{C}_{\text{org}}$  shifts in the study sections are larger (3‰–4‰) than the concurrent negative shifts in  $\delta^{13}\text{C}_{\text{carb}}$  ( $\sim 2$ ‰), yielding larger  $\Delta^{13}\text{C}$  values in the microbialite than in the underlying limestone (Fig. 2). The higher  $\Delta^{13}\text{C}$  values of the study sections (relative to Meishan and Shangsi) may result from the absence of green sulfur bacteria in shallow-water environments, consistent with the absence of biomarkers for green sulfur bacteria in the microbialite

facies (Chen et al., 2011). These observations support the hypothesis that there were different microbial communities in shallow- and deep-water environments after the LPE.

### NATURE OF MICROBIALITE COMMUNITY

Biomarkers such as 2-methylhopanes associated with  $\delta^{15}\text{N}$  records have documented the presence of diazotrophic cyanobacteria in P-Tr environments in deep-water facies (Xie et al., 2005; Cao et al., 2009). Some microfossils present in the microbialite have been interpreted as cyanobacteria (Xie et al., 2010; also see the Data Repository). However, we found no or extremely low abundance of 2-methylhopanes in the microbialite (see the Data Repository). Prevalent nitrogen fixation in the microbialite shown here indicates that diazotrophic cyanobacteria in the shallow-water microbialite might differ from the deep-water planktonic cyanobacterial community (Stal et al., 1984; Zehr et al., 1995) or some noncyanobacteria microbes might contribute, partly, to the  $\text{N}_2$  fixation in the earliest Triassic microbialite. Zehr et al. (1995) found a high diversity of anaerobic heterotrophic nitrogen-fixing organisms in modern marine cyanobacterial mats. Our records, presented here, indicate that these diazotrophs might have flourished in the shallow water of ca. 252 Ma, and different  $\text{N}_2$  fixing microbial communities existed in shallow- and deep-water environments after the LPE.

It is interesting to note that the  $\delta^{15}\text{N}$  values of the samples from the overlying thinly bedded limestone are similar to those from the microbialite layer, i.e., ranging from  $-1$ ‰ to  $+1$ ‰

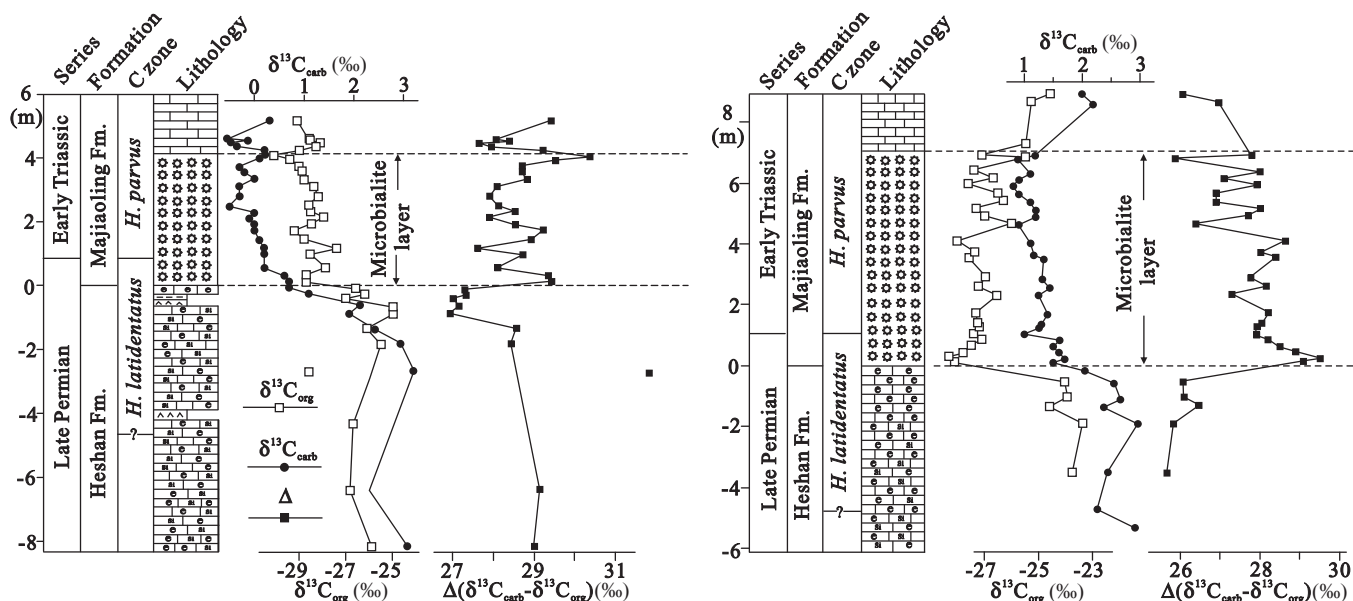


Figure 2. Variation of carbonate and organic carbon isotopic composition and carbon isotope fractionation ( $\Delta = \delta^{13}\text{C}_{\text{carb}} - \delta^{13}\text{C}_{\text{org}}$ ) during Permian-Triassic transition in Taiping section (left) and Zuodeng section (right). C zone—conodont zone; *H.*—*Hindeodus*.



(Fig. 1). This suggests that nitrogen fixation was still vigorous, irrespective of the change in lithofacies. The disappearance of the microbialite might have been caused by changes in composition of nitrogen fixers (such as from cyanobacteria to others) or water depth as microbialite was restricted to shallow shelf environments (Kershaw et al., 2007).

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