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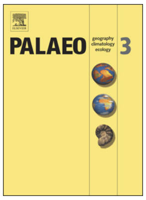

Expansion of photic-zone euxinia during the Permian–Triassic biotic crisis and its causes: Microbial biomarker records

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ABSTRACT

The incursion of euxinic waters into the ocean-surface layer is hypothesized to have been an important killing agent during the end-Permian mass extinction. However, both the causes and extent of oceanic euxinia during this crisis remain poorly known, making assessment of its role in the mass extinction difficult. Here, we document the distribution of aryl isoprenoids (AIs), which are biomarkers of obligate anaerobic green sulfur bacteria (Chlorobiaceae) that are indicative of photic-zone euxinia, in 12 Permian-Triassic Boundary (PTB) sections with a wide distribution globally. Profiles of AI abundance for the 12 study sections show significant spatio-temporal variation. No AIs were identified in the shallowest sections, but AIs are present both prior to and following the mass extinction in intermediate-depth sections and following the mass extinction in deep-water sections. This pattern suggests a combination of upward and oceanward expansion of photic-zone euxinia during the PTB crisis, possibly fueled by elevated riverine nutrient fluxes as a consequence of climatic warming, terrestrial ecosystem destruction, and enhanced erosion. This hypothesis is supported by the close association of AIs with elevated abundances of moretanes and dibenzofuran (DBF), which are biomarkers for terrestrial erosion. Expansion of oceanic euxinia at intermediate water depths may have established a long-term reservoir that fed episodic incursions of H_2S-bearing waters into shallow-marine environments, delaying the recovery of marine ecosystems during the Early Triassic. The biomarker records of the present study thus provide significant evidence of terrestrial-marine linkage during the PTB crisis.

1. Introduction

The end-Permian mass extinction (EPME) was the most severe biotic crisis in the Phanerozoic, killing over 90% of marine invertebrate species (Erwin et al., 2002). The eruption of the Siberian Traps Large Igneous Province is widely regarded as the ultimate cause of this biocrisis (Campbell et al., 1992; Kamo et al., 2003; Reichow et al., 2009; Svensen et al., 2009; Korte et al., 2010), but the direct killing mechanism remains controversial, with hypotheses invoking marine anoxia (Wignall and Twitchett, 1996; Isozaki, 1997), hypercapnia (Knoll et al., 2007), global cooling (Joachimski et al., 2012; Romano et al., 2013), and ocean acidification (Hinojosa et al., 2012; Clarkson et al., 2015), among other possibilities. Although early claims of whole-ocean anoxia (e.g., Wignall and Twitchett, 1996; Isozaki, 1997) have been disproven (e.g., Algeo et al., 2011a), more recent studies have shown that the Permian-Triassic boundary (PTB) interval was widely associated with a shift toward more reducing marine environmental conditions (Grice et al., 2005a; Kump et al., 2005; Kaiho et al., 2006; Hays et al., 2007; Riccardi et al., 2007; Gorjan et al., 2007; Algeo et al., 2007, 2008; Meyer and Kump, 2008; Takahashi et al., 2014). However, spatial patterns of marine redox variation (i.e., related to proximality and water depths) have been addressed to only a limited degree in a few studies (e.g., Feng and Algeo, 2014).

Among the various types of geochemical proxies used in paleoredox studies, biomarkers are important for their ability to discern photic-zone euxinia (PZE), i.e., sulfidic conditions within the surface layer of the ocean (Grice et al., 2005a; Xie et al., 2005, 2007; Chen et al., 2015). Certain photosynthetic microbes are obligate anaerobes, requiring both sunlight and H_2S, e.g., green sulfur bacteria (GSB) and purple sulfur bacteria (PSB) (Whiteside and Grice, 2016). GSB produce isorenieratane and chlorobactane, as well as aryl isoprenoids (AIs) as diagenetic breakdown products, and PSB produce okenane, all of which are

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characteristic indicators of PZE (Summons and Powell, 1986, 1987; Grice et al., 1996; Whiteside and Grice, 2016).

GSB biomarkers have been reported from a number of PTB sections (e.g., Grice et al., 2005a; Xie et al., 2005, 2007; Hays et al., 2007, 2012; Algeo et al., 2012), which indicates that at least portions of the global ocean were euxinic during the end-Permian crisis. However, the spatio-temporal distribution of GSB biomarkers in PTB sections has not been investigated in detail, leaving the relationship between oceanic euxinia and the end-Permian mass extinction unclear. Here, we present biomolecular records from multiple locales representing a range of water depths in order to investigate the spatial and temporal distributions of PZE during the end-Permian crisis. Additionally, we examine the relationship of PZE to changes in terrestrial weathering fluxes and tropical sea-surface temperatures (SSTs) in order to gain insights regarding the factors controlling the development of PZE during this crisis. The present study includes new biomarker data for five PTB sections (Bulla in northern Italy, and Laolongdong, Cili, Shangsi, and Chaohu in South China) as well as published biomarker data for seven other PTB sections with a broad global distribution.

2. Study sections

We examined 12 PTB marine sections from all major Permian-Triassic oceans, including the Panthalassa, Paleo-Tethys, and Neo-Tethys oceans (Table 1; Fig. 1C). These sections can be catalogued into three types according to sedimentary water depths: (1) shallow platform sections above fair-weather wave base (i.e., water depths <50 m, and commonly <20 m; cf. Brett et al., 1993), including Bulla in northern Italy and Laolongdong and Cili in South China, (2) intermediate shelf/ramp sections located between fair-weather wave base and storm wave base (i.e., ~50–200 m water depth), including Huangzhishan (Kaiho et al., 2012) and Meishan in South China (Grice et al., 2005a; Cao et al., 2009), the Perth Basin of Western Australia (Thomas et al., 2004; Grice et al., 2005a), Kap Stosch in Greenland (Hays et al., 2012), Spitsbergen (Nabbefeld et al., 2010b), and the Peace River Basin (Hays et al., 2007) and West Blind Fiord in Canada (Algeo et al., 2012), and (3) deep shelf/ramp sections (>200 m water depth), including Shangsi and Chaohu in South China (Fig. 1C). Background details for each section are given below.

2.1. Shallow platform sections

The Bulla section (Southern Alps, northern Italy) was located in the western Paleo-Tethys during the Permian-Triassic transition (Fig. 1). PTB strata belong to the uppermost Bellerophon Formation (Bulla Member) and lower Werfen Formation (Tesero Member). The former consists of gray and dark-gray fossiliferous limestone and dolostone interbedded with siltstone, sandstone and gypsum, whereas the latter comprises oolitic grainstone (Farabegoli et al., 2007). These facies accumulated on a shallow carbonate platform (ca. < 10 m water depth) (cf. Hine, 1977). The EPME, which is marked by sharp declines in fossil abundance and biodiversity and the appearance of small ooids, is located at the base of the Tesero Member (Gorjan et al., 2007). The extinction horizon consists of mixed terrigenous-calcareous material and exhibits hummocky cross-bedding and wave ripples, pointing to high-energy storm sedimentation in an area proximal to sources of terrigenous clastics. The PTB is located 1.30 m above the base of the Tesero Member based on the first occurrence of the conodont *Hindeodus parvus* (Perri, 1991).

The Laolongdong section (Chongqing Province, China) was located on the paleo-western margin of the Yangtze Platform (South China Craton), facing the Paleo-Tethys Ocean (Liao et al., 2010; Fig. 1). The Upper Permian consists of skeletal limestone of the Changxing Formation that is sharply overlain by microbialite, with the contact between these two units corresponding to the EPME horizon (Ezaki et al., 2003; Kershaw et al., 2012). The occurrence of microbialite implies

Table 1
Paleogeographic and paleoenvironmental characteristics of the 12 study sections.

Sections	Paleogeographic settings	Lithology of the PTB beds (*C. yini-I. isarcia* zones)	Water depth change up section	Environmental interpretation	Estimated water depth	Principal references
Bulla, northern Italy	Western Tethys	Thick bedded bioclastic limestone to thin bedded oolitic limestone beds	Shallowing	Near the FWWB	~20–30 m	Gorjan et al. (2007), Farabegoli et al. (2007)
Cili, South China	Eastern Tethys	Massive reef like bioclastic limestone to massive microbialites and oolites	Deepening	Near the FWWB	~20–40 m	Wang et al. (2009), Luo et al. (2013)
Laolongdong, South China	Eastern Tethys	Thick bedded to massive bioclastic limestone to massive microbialites	Deepening	Near the FWWB	~20–40 m	Wu et al. (2006), Liao et al. (2010)
Huangzhishan, South China	Eastern Tethys	Medium-thick bedded bioclastic limestone to thin-medium bedded muddy limestone with claystone and mudstone	Deepening	Upper part of FWWB-SWB zone	~40–80 m	Chen et al. (2009)
Hovea-1, Perth Basin, Australia	Northern margin of Gondwana	Mudstone, sandy siltstone and shelly storm beds to finely laminated mudstone and thin bedded limestone	Deepening	Lower part of FWWB-SWB	~20–50 m	Thomas et al. (2004)
Spitsbergen, Norway	Shelf sea in Boreal Ocean	Sandstone with few mudstone to mudstone with sandstone, and thin bedded limestone	Deepening	Near the SWB	~ 60–80 m	Mørk et al. (1999), Nabbefeld et al. (2010a, 2010b)
Peace River Basin, Arctic Canada	Northwestern margins of Pangea	Silty mudstone to sandstone	Shallowing	Near the SWB	~80–100 m	Hays et al. (2007)
Kap Stosch	Margin of Boreal Ocean (Greenland)	Shale and siltstone to sandstone	Shallowing	Near the SWB	~80–100 m	Hays et al. (2012)
Meishan, South China	Eastern Tethys	Medium-thick bedded bioclastic limestone to thin bedded clay beds; thin bedded mudstone/shale; medium bedded limestone	Deepening	FWWB-SWB zone	~80–100 m	Zhang et al. (1996), Chen et al. (2007, 2015), Tian et al. (2014)
West Blind Fjord, Arctic Canada	Boreal Ocean basin	Chert to sandstone and siltstone	Shallowing	Below the SWB	~100–200 m	Algeo et al. (2012)
Shangsi, South China	Eastern Tethys	Thin bedded siliceous limestone to clay beds and thin bedded carbonaceous mudstone	Shallowing	Inner shelf basin	~200–300 m	Wignall et al. (1995), Song et al. (2012), Lei et al. (2012)
Chaohu, South China	Eastern Tethys	Thin bedded siliceous Mudstone to medium bedded carbonaceous limestone and claystone	Shallowing	Inner shelf basin	~200–400 m	Chen et al. (2011), Song et al. (2013)

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