



Redox conditions across the G–L boundary in South China: Evidence from pyrite morphology and sulfur isotopic compositions

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ABSTRACT

The end-Guadalupian (middle Permian) mass extinction recorded the disappearance of shelf faunas such as fusulinids, small foraminifers, brachiopods, rugose corals which flourished in the warm shallow marine habitats after the late Pennsylvanian–early Permian glaciation. The causes for this mass extinction are still unclear. Marine anoxia, often as a cause for other mass extinctions, has been paid less attention in this extinction. Here we present a comprehensive study including pyrite morphology and sulfur isotopic compositions of pyrite across the Guadalupian–Lopingian (middle–upper Permian; G–L) boundary at Tianfengping in northern Yangtze Platform and at Penglitan in southern Yangtze Platform in South China. Our results show that the sulfur isotope ratios of pyrite mainly track the framboid size distributions in these two sections. Anoxia and intermittent euxinia occur at the G–L boundary evidenced by the coincidence between reduction of framboid size and the extremely negative sulfur isotope values of pyrite involving disproportionation, and corresponds to the main mass extinction of the end-Guadalupian, suggesting a causal link between them. Long-term dysoxic conditions during the middle Capitanian are evidenced by the relative small framboid size and lower sulfur isotope ratios of pyrite, and coincide with the first pulse of the end-Guadalupian mass extinction, also suggesting a causal link between them. The oxygen-depletion conditions in the Capitanian during the global sea level falling may be the main cause for the end-Guadalupian mass extinction.

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1. Introduction

The end-Guadalupian mass extinction (Shen and Shi, 1996; Wang and Sugiyama, 2001), also called mid-Capitanian mass extinction (Bond et al., 2010), is an independent mass extinction in the Permian (Jin et al., 1994; Stanley and Yang, 1994; Clapham et al., 2009). This bio-crisis is ranked fifth in terms of ecological severity (McGhee et al., 2013), and affected mainly the marine faunas including fusulinids (Jin et al., 2006), small foraminifers (Zhang et al., 2015a), corals (Wang and Sugiyama, 2001), brachiopods (Shen and Shi, 2002, 2009; Shen and Zhang, 2008), ammonoids (Shen et al., 2007) and conodonts (Mei et al., 1998). The proposed causes for this mass extinction are mainly volcanism (Wignall et al., 2009a; Isozaki, 2009; Wei et al., 2012a), global sea level fall (Chen et al., 2009; Wignall et al., 2009b; Qiu et al., 2014), cooling (Isozaki et al., 2007, 2011; Kofukuda et al., 2014) and marine anoxia (Isozaki, 1997; Saitoh et al., 2013a, 2014; Zhang et al., 2015b). However, the ultimate cause is still debated. Because of the limited

sections exhibiting continuous deposition across the Guadalupian–Lopingian (G–L) boundary (Jin et al., 2006), studies on the marine redox conditions across the G–L boundary are rare. Several studies had reported marine reducing conditions across the G–L boundary (Wignall et al., 2009b; Isozaki, 1997; Schoepfer et al., 2013; Zhang et al., 2015b), while Sheldon et al. (2014) reported a continental record of more oxidizing conditions during this mass extinction event. Thus, a thorough understanding of redox condition changes across the G–L boundary needs to be done by robust geochemical proxies.

Marine redox conditions in the bottom water column are mainly controlled by the diffusion of H₂S released by the bacterial sulfate reduction (BSR) if the oxygen supply from the surficial water or lateral water is constant. A comprehensive study including framboidal pyrite and $\delta^{34}\text{S}$ of pyrite ($\delta^{34}\text{S}_{\text{py}}$) can constrain the BSR process and offer a precise evaluation of marine redox conditions across the G–L boundary. Pyrite is formed by the reaction between H₂S produced by BSR in anoxic water column or porewater in sediments and reactive iron (Bernier and Raiswell, 1983). Although Butler and Rickard (2000) argued against the formation of framboidal pyrite via greigite precursor and suggested that the framboidal texture results from rapid nucleation when pyrite is strongly supersaturated in the absence of molecular O₂ and magnetic

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greigite intermediates, the formation of framboidal pyrite typically involves four stages (Wilkin and Barnes, 1996, 1997a): i) nucleation of iron monosulfide microcrystals; ii) reaction of microcrystals to greigite; iii) aggregation of the ferromagnetic greigite microcrystals into densely packed, spherical framboids; iv) conversion of greigite framboids to pyrite. Wilkin and Barnes (1997b) suggested that framboid size may be controlled by their residence time near the oxic-anoxic interface. Framboid growth times are expected to be shorter in euxinic environments than in oxic-dysoxic environments because of the hydrodynamic instability of pyrite particles in suspension. Thus, syngenetic framboids developed in euxinic conditions are generally small with a narrow size range while diagenetic framboids developed in sediments underlying oxic-dysoxic water column are larger with a wider size range (Wilkin et al., 1996; Wilkin and Arthur, 2001). Syngenetic and diagenetic pyrites yield variable morphologies associated with the progressive water column and/or pore water evolution (Raiswell, 1982), which is recorded by the pyritic sulfur isotopic composition (Calvert et al., 1996). The $\delta^{34}\text{S}_{\text{py}}$ can yield information about the degree of isotopic fractionation during BSR, the availability of sulfate, the location and timing of pyrite formation, rate of BSR, and redox conditions of water column (Gautier, 1986; Calvert et al., 1996; Lyons, 1997; McKay and Longstaffe, 2003). Therefore, the combination of pyrite morphology and $\delta^{34}\text{S}_{\text{py}}$ can precisely assess the redox conditions across the G–L boundary.

Heretofore, marine redox conditions across the G–L boundary have been investigated via sulfur isotope compositions (Yan et al., 2013; Saitoh et al., 2014; Zhang et al., 2015b), elemental ratios (Shi et al., 2016) and limited pyrite morphology data (10 samples) (Wignall et

al., 2009b). Their studies showed dysoxic to anoxic conditions (Wignall et al., 2009a, 2009b; Yan et al., 2013; Shi et al., 2016) or persistent sulfidic conditions at the G–L boundary (Saitoh et al., 2014; Zhang et al., 2015b). Here, we present a comprehensive analysis including pyrite morphology and pyritic sulfur isotope compositions at the Penglaitan GSSP section in Guangxi Province in southern Yangtze Platform and Tianfengping section in Hubei Province in northern Yangtze Platform, both of which had been studied for conodont biostratigraphy (Mei et al., 1998; Xia et al., 2006; Zhang et al., 2008). Our work displays a more detailed pattern of redox condition changes across the G–L boundary in South China.

1.1. Geological setting

The studied Tianfengping section ($30^{\circ}19'37''\text{N}$, $109^{\circ}18'52''\text{E}$) is located at an abandoned pyrite mine site, 100 m west of No. 108 highway near the Tianfengping village about 18 km northwest of Enshi city in South China (Fig. 1). The Penglaitan GSSP (for the base of the Wuchiapingian stage) section ($23^{\circ}41'43''\text{N}$, $109^{\circ}19'16''\text{E}$) is located at the southern bank of the Hongshuihe River near a rocky Penglaitan islet about 12 km southeast of Laibin city in South China (Fig. 1). The Penglaitan section is about 740 km south of the Tianfengping section.

During the Capitanian (end of Guadalupian, middle Permian), the South China block was located in the eastern side of Pangea and in the tropical zone. The South China block was composed of the Yangtze platform in the west and the Cathaysia Platform in the east, separated by the Jiangnan (JN) Basin in the middle (Fig. 1). A famous long-term basin,

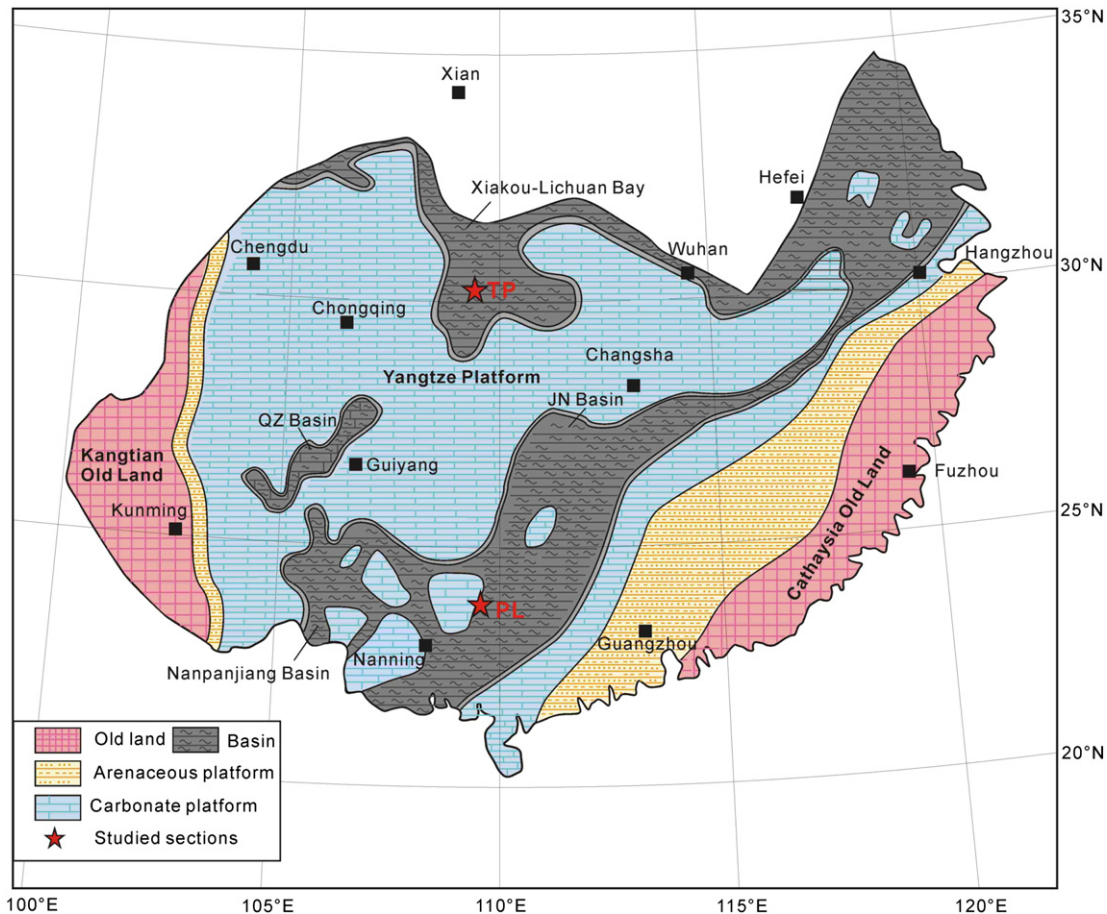


Fig. 1. Capitanian paleogeography of South China (modified from Zhu (1989); Wang and Jin (2000); Chen et al. (2003) and Du et al. (2015)) and the locations of studied sections. PL: Penglaitan section; TP: Tianfengping section. QZ Basin: Qianzhong intrashelf basin; JN Basin: Jiangnan basin.

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