An extensive anoxic event in the Triassic of the South China Block: a pyrite framboid study from Dajiang and its implications for the cause(s) of oxygen depletion

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Abstract

Water column oxygen deficiency has been considered as a potent driver of the extinction of marine benthos, and is a main feature of marine environments in the aftermath of the end-Permian mass extinction. The record of Permian-Triassic anoxia is more complex than previously thought, and is seen to vary between different palaeogeographic settings, but a full understanding is hindered by a paucity of evidence. During the Permian-Triassic interval the South China Block was located equatorially with Palaeotethys to the north and western Panthalassa to the south. This specific configuration provides a unique opportunity to compare the extent and duration of oxygen deficiency in Palaeotethys and Panthalassa under broadly similar climatic conditions. Sedimentary facies and pyrite framboid size-frequency distributions suggest that the oxygen-poor conditions became widespread across the
shallow-marine carbonate platform of the South China Block immediately above the Permian-Triassic boundary and mass extinction level. Oxygen deficiency was most intense at the southern margin of the block where it met Panthalassa. Proposed drivers of the expansion of oxygen minimum zones into platform settings include enhanced terrigenous input and/or ocean stratification, or alternatively the upwelling of nutrient-rich deep ocean water. The former mechanisms are theoretically more likely to have operated in the relatively restricted Palaeotethys which was surrounded by ancient lands. In contrast, Panthalassa would likely have experienced stronger oceanic circulation and therefore be more susceptible to the effects of upwelling. Although variations in the record of the South China Block anoxic event might reflect local factors, the greater intensity of oxygen deficiency and a concomitant larger negative shift in carbonate carbon isotopes on its Panthalassan margin point to a key role for upwelling. This mechanism was likely a major driver of the Permian-Triassic global oceanic anoxic event, which itself was at least partly responsible for the ongoing inhospitable conditions and delayed recovery following the end-Permian extinction.

Keywords: Permian-Triassic; microbialite; anoxia; upwelling; mass extinction

1. Introduction

Globally widespread ocean anoxia has been considered as a potent kill mechanism in the marine end-Permian mass extinction scenario (e.g. Wignall and Hallam, 1992; Wignall and Twitchett, 1996; Isozaki, 1997; Grice et al., 2005). However, there is growing evidence that the duration and intensity of the anoxic event are heterogeneous complex (Bond and Wignall., 2010; Liao et al., 2010; He et al., 2013; Li et al., 2016; Shen et al., 2016; Xiang et al., 2016). The variability in redox conditions between different sections may be a function of palaeogeography. Thus, in western Palaeotethys, the size distributions of pyrite frambooids indicate that oxygen depletion extended into turbulent, shallow water environments characterised by oolite deposition above the mass extinction boundary (MEB, corresponding to the bottom of
the Bed 25 in the Meishan global Stratotype (Yin et al., 2001) in the well-known Bulla section (Bond and Wignall, 2010). To the south, in Neotethys, anoxia persisted throughout the Late Permian and Early Triassic, at least in deep water settings (Bond and Wignall, 2010). Elsewhere, Wignall et al. (2016) demonstrated that anoxia developed in ‘ultra-shallow’ settings in the Early Triassic of Spitsbergen, far away on the northern margin of Pangaea. In contrast, δ^{98/95}Mo compositions and trace fossil assemblages from the nearby Sverdrup Basin of Arctic Canada record persistent well-oxygenated conditions on the sub-storm wave base deep-shelf and in shallower environments across the MEB (Beatty et al., 2008; Proemse et al., 2013). In the modern ocean, oxygen-poor conditions often appear in estuarine environments with high nutrient fluxes (Diaz, 2001; Diaz and Rosenberg, 2008; Levin et al., 2009; Rabalais and Gilbert, 2009) and in poorly-circulated water bodies such as the Black Sea (Friedrich et al., 2014). Modern manifestations of anoxia are of geographically limited extent, the like of which could not have been responsible for Permian-Triassic marine losses. Instead that interval saw a unique episode of the Phanerozoic during which oxygen-restricted conditions became exceptionally widespread in shallow-marine platform environments where they almost certainly had a causal role in the mass extinction and/or the subsequent delayed recovery. However, this link remains controversial and requires further elucidation from additional palaeogeographic settings.

During the Permian-Triassic transition, the South China Block (SCB) was located near the equator with shelves at its margins extending into Palaeotethys to the north and western Panthalassa to the south (Fig. 1). Several studies document the development of oxygen-poor conditions above the MEB on the carbonate platform in the northern part of the SCB (Wignall and Hallam, 1996; Liao et al., 2010; Wang et al., 2016). In contrast, there are few studies of depositional redox conditions on the isolated carbonate platform in the southern part of the SCB. Ostracod assemblages in the Dajiang section from the Nanpangjiang Basin, which connected the SCB to Panthalassa, indicate well-oxygenated conditions across the MEB on a shallow-water, isolated carbonate platform (Forel et al., 2009). The validity of this ostracod-redox
proxy has recently been questioned (Brandão and Horne, 2009; Horne et al., 2011; Forel, 2013), and an independent test of depositional conditions above the MEB at Dajiang is needed. Pyrite framboid analysis is a well-established technique for assessing bottom-water dissolved oxygen levels, first calibrated in modern environments (Wilkin et al., 1996, 1997; Wilkin and Barnes, 1997; Suits and Wilkin, 1998), and since developed into a palaeo-redox indicator, supported by diverse independent geochemical and palaeocological proxies (Wignall and Newton, 1998; Wilkin and Arthur, 2001; Bond et al., 2004; Racki et al., 2004; Wignall et al., 2010).

Here, we present size-frequency distributions of pyrite framboids across the Permian-Triassic transition at Dajiang to re-evaluate depositional redox on this shallow-water, isolated carbonate platform. This permits a comparison of the duration and intensity of oxygen deficiency in shallow-marine environments on the Panthalassan and Palaeotethyan margins of the SCB. Contrasting manifestations of the Permian-Triassic anoxic event in these locations sheds light on its potential drivers.

2. Geological setting

The SCB was a small tectonic plate that broke from Gondwana during the Silurian and existed in isolation until it collided with North China, and became part of Pangaea during the Triassic. According to the previous palaeogeographic reconstruction (Golonka, 2002), and the radiolarian fauna biopalaeogeography of the SCB (He et al., 2005, 2008, 2011), in the Permian-Triassic interval the northern part of the SCB lay in Palaeotethys, whilst the Nanpanjiang Basin to the south opened into western Panthalassa (Fig. 1) (Kershaw et al., 2007). The Great Bank of Guizhou is a large, isolated shallow-marine carbonate platform within the Nanpanjiang Basin (Fig. 1; Lehrmann et al., 1998). Numerous outcrops of Permian-Triassic sediments have led to the Great Bank of Guizhou becoming a key region for study of environmental changes during the end-Permian mass extinction. These have focused on sedimentology (Lehrmann et al., 2001, 2003; Liu et al., 2007; Payne et al., 2007;
Collin et al., 2009), conodont biostratigraphy (Lehrmann et al., 2003; Liu et al., 2007; Ezaki et al., 2008; Jiang et al., 2014), and microfossil (foraminifera and ostracod) assemblages (Song et al., 2009; Forel et al., 2009). Carbon, sulphur and calcium isotopes studies in this area also have been used to constrain the paleoenvironment changes and their connections to the end-Permian mass extinction (Payne et al., 2004, 2010; Meyer et al., 2011; H.Y. Song et al., 2013, 2014a).

The Dajiang section in Guizhou Province, South China, preserves a detailed record of depositional conditions on a shallow-marine carbonate platform in the southern SCB during the Permian-Triassic. The section exposes one of several isolated shallow-marine carbonate platforms that together comprise the Great Bank of Guizhou (Lehrmann et al., 1998). The Upper Permian part mainly comprises skeletal packstones belonging to the Wuchiaping Formation, which yields diverse fusulinid and non-fusulinid foraminifers, corals, sponges, bryozoans, gastropods, brachiopods and calcareous algae (Lehrmann et al., 2003; Song et al., 2009; Lehrmann et al., 2015). This assemblage suggests that well-oxygenated, warm, tropical shallow-marine conditions persisted in the run-up to the mass extinction. The top surface of the packstone unit is marked by hollows filled by a wackestone that yields the basal Triassic conodont *Hindeodus parvus* (Jiang et al., 2014). This irregular surface has been ascribed to erosion and karstification (Liu et al., 2007; Collin et al., 2009; Wignall et al., 2009) or alternatively to submarine dissolution (Payne et al., 2007; Lehrmann et al., 2015). The Wuchiaping Formation is overlain by ~14 m of microbialites belonging to Daye Formation that rests directly on the packstones, or in places on the hollow-filling wackestones of the Wuchiaping Formation. The MEB is placed at this formational contact. The Daye Formation microbialite is dominated by calcified cyanobacteria, but it also contains foraminifera, ostracods, microconchids, thin-shelled bivalves and microgastropods that record the survival of a simple ecosystem on shallow-marine carbonate platforms following the end-Permian mass extinction (Wang et al., 2005; Yang et al., 2011). Several layers of molluscan grainstone, comprising small thin-shelled bivalves, gastropods, and ostracods occur in and on the top of the microbialite. The grainy texture and fragmentary nature of the
fossils within these intercalated layers indicate a shallow-marine environment subjected to episodic currents during deposition (Lehrmann et al., 2003, 2015). Above the microbialite and molluscan grainstones lies thin-bedded, poorly bioturbated muddy limestone. The first occurrence of the basal Triassic conodont *Hindeodus parvus* at Dajiang is coincident with the MEB (Jiang et al., 2014), suggesting there may have been a short, latest Permian hiatus or stratigraphic gap equivalent to Beds 25-27b at the Meishan global Stratotype (where Bed 25 is the MEB and Bed 27c is the first appearance datum of *H. parvus* (Yin et al., 2001)). The onset of microbialite deposition at Dajiang likely corresponds to the base of Meishan Bed 27c.

3. Methods

Pyrite framboid analysis has become a widely-used technique for predicting ancient marine benthic redox conditions. In modern environments pyrite framboids form as iron monosulphide aggregates in the narrow iron-reduction zone at the redox boundary. Framboids cease growing in the more intensely anoxic conditions of the underlying sulphate-reduction zone where crystalline and amorphous pyrite forms (Wilkin et al., 1996; Wilkin and Barnes, 1997; Suits and Wilkin, 1998). When bottom waters are euxinic, framboids develop in the water column but are unable to achieve diameters much larger than 5-6 μm before they sink below the iron reduction zone and cease to grow (Wilkin et al., 1996). Euxinic conditions produce populations of tiny framboids with a narrow size range in modern environments, and this signature is preserved in ancient sediments. In contrast, in dysoxic environments, seafloor conditions are weakly oxygenated and framboids form in the surficial sediments where their size is governed by the local availability of reactants, with the result that they are more variable and generally larger in size (Wilkin et al., 1996).

The size-frequency distribution of pyrite framboids has been widely employed in studies of marine redox across the Permian-Triassic transition (Wignall et al., 2005; Shen et al., 2007; Algeo et al., 2010; Bond and Wignall, 2010; Liao et al., 2010; He et al., 2013; Chen et al., 2015; Li et al., 2016). However, it is generally considered
difficult to apply this technique to microbialites, in which tiny framboids may be bioinduced products that perhaps do not reflect the depositional environment (Cavalazzi et al., 2007). Fortunately, the Dajiang section benefits from numerous molluscan grainstones intercalated with the microbialite above the MEB. These molluscan grainstones provide an opportunity to study benthic oxygenation on the shallow-marine carbonate platform in the aftermath of the end-Permian mass extinction without the need to disentangle the influence of the microbial metabolic effects on framboid formation.

In fact, the microbialite comprises two components: sparitic “thrombus” and intervening matrix. The matrix contains small foraminifers, ostracods, microconchids, thin-shelled bivalves and microgastropods and likely formed in open water rather than in an isolated microenvironment within the microbial mats. We have therefore sampled this matrix material in addition to the molluscan grainstones to build up our palaeo-redox history. Seventeen samples spanning the MEB at Dajiang were selected for pyrite framboid analysis. Three samples were taken from the skeletal packstones below the MEB, 8 are from the microbialite, 3 are from intercalated molluscan limestones and 3 are from the muddy limestone that lies on top of the microbialite. A polished block (approximately $2 \text{ cm} \times 2 \text{ cm}$) of each sample was examined for pyrite framboids using an FEI Quanta 200 scanning electron microscope (SEM) in the State Key Laboratory of Geological Processes and Mineral Resources, China University of Geosciences (Wuhan). The spatial resolution of the secondary electron image of the SEM is better than $3.5 \text{ nm}$. In backscattered electron mode, pyrite framboids are easily distinguished by their shape and structure. The diameter of individual framboids was measured directly on the SEM screen to the nearest $0.1 \mu\text{m}$. Where possible, at least 100 framboids were counted per sample.

4. Results

The skeletal packstone of the Wuchiaping Formation lacks pyrite framboids and contains only rare crystalline pyrite. In contrast, the Daye Formation, lying above the
MEB, is rich in pyrite framboids (Fig. 2). These are present in the microbialite, molluscan grainstone and muddy limestone facies. Individual microcrysts that build the framboids are clearly discernible and each has approximately the same diameter of less than 1 μm (Fig. 2). SEM observations reveal that the pyrite framboids are dispersed through the intervening matrix rather than in the sparitic “thrombus” of the microbialite facies – a preservation pattern clearly different from one recording framboid formation during later diagenesis.

In total, 1764 pyrite framboids measured in 14 samples from Dajiang, ranging from n = 81 to n = 246 framboids per sample (Fig. 3). Most pyrite framboids measured are smaller than 15 μm although a few samples exhibited a “tail” of slightly larger framboids. The mean framboid diameter across all samples is between 5.3 μm and 8.3 μm, whilst the minimum diameter of measured framboids is between 1 μm and 2 μm. Mean framboid diameter in the microbialite above the MEB ranges from 5.9 μm to 8.3 μm. Similar sized framboids are present in the molluscan grainstone layers (Figs. 3G, 3I, 3K and Figs. 4G, 4I, 4K) that mainly formed by mechanical sedimentation of episodic currents, where mean diameters range from 5.3 μm to 7.2 μm. Above the youngest molluscan grainstone, three samples of thin-bedded muddy limestone yielded abundant pyrite framboids with the mean diameters between 6.0 μm and 6.8 μm.

5. Discussion

5.1. Redox history at Dajiang

Pyrite framboid populations in the Dajiang section record a remarkable change in benthic oxygenation across the MEB on the Great Bank of Guizhou (Fig. 4). The absence of framboids in the pre-extinction skeletal packstones suggests that the water column was persistently well-oxygenated in shallow-marine settings in the run-up to the mass extinction. Under such conditions the platform was able to support a diverse community of fusulinid and nonfusulinid foraminifers, corals, sponges, bryozoans, gastropods, brachiopods, and calcareous algae (Lehrmann et al., 2003; Song et al., 2009; Lehrmann et al., 2015). Immediately above the MEB, the sudden appearance of

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abundant pyrite framboids in microbialite facies suggests an abrupt depletion of water-column oxygen. Using criteria developed by Bond and Wignall (2010) and Wignall et al. (2010), the continuous occurrences of abundant pyrite framboids in the microbialite, molluscan grainstone and muddy limestone with mean values of 5.3-8.3 μm supports the onset of persistent lower dysoxic conditions in the water column at or immediately above the MEB. The tight connection between the oxygen deficiency in water column and the faunal mass extinction in this section further confirms the hypothesis that widespread oceanic anoxia acts as a killer for marine benthos in the Permian-Triassic transition (e.g. Wignall and Twitchett, 1996; Isozaki, 1997; Grice et al., 2005).

Multiple palaeoredox proxies have been applied for the Permian-Triassic transition globally, including pyrite framboids (Bond and Wignall, 2010; Liao et al., 2010; He et al., 2013; Li et al., 2016; Wang et al., 2016), Th/U ratios (Wignall and Twitchett, 1996, 2002), Ce anomalies (Kakuwa and Matsumoto, 2006; Fio et al., 2010; Song et al., 2012; Loope et al., 2013), uranium content and its isotopic composition (Brennecka et al., 2011; Lau et al., 2016), molecular biomarkers (Grice et al., 2005; Xie et al., 2007; Cao et al., 2009; Luo et al., 2013), and ostracod and trace fossil assemblages (Crasquin-Soleau and Kershaw, 2005; Beatty et al., 2008; Forel et al., 2009; Chen et al., 2015). Comparison and validation of different proxies is an important part of evaluating redox conditions across the MEB. Previous studies of the Dajiang section suggested that because its ostracod assemblages were dominated by deposit-feeding taxa, well-oxygenated conditions must have prevailed across the MEB (Forel et al., 2009). However, the validity of this interpretation based on ostracod assemblages has been questioned (Brandão and Horne, 2009; Horne et al., 2011), and the interpretation of persistently oxic conditions requires reassessment. Forel (2013) recognised that the small carapace size of the Dajiang ostracods, and their high intraspecific variabilities, was likely evidence of dysoxic conditions in the aftermath of the mass extinction. This conclusion is clearly consistent with our pyrite framboid data, in which all post-MEB samples preserve framboid populations typical of dysoxic conditions. Besides the ostracods, other biotic indicators of stressed or
post-extinction environments proliferated in the microbialite above the MEB. This facies is characterised by a low diversity and high abundance of small body-size “opportunists” or “disaster” species, such as some foraminifers (Earlandia sp. and Rectocornuspira kalhori) (Ezaki et al., 2003; Galfetti et al., 2008; Song et al., 2009; Yang et al., 2011), microconchids (Helicoconchus aff. Elongates, Microconchus aff. Aberrans and Microconchus aff. utahensis) (Yang et al., 2015a, b), and small gastropods and bivalves (Wang et al., 2005; Yang et al., 2011). This unusual microbialite ecosystem can be interpreted as a result of oxygen deficiency in the bottom water. Modern oxygen-stressed marine ecosystems are dominated by small body-size opportunists that have rapid growth and short life cycles (Nilsson and Rosenberg, 2000; Levin, 2003; Gutiérrez et al., 2008).

Other published geochemical proxies are in broad consensus with our framboi-d-based interpretation of the redox history at Dajiang. $S_{\text{pyrite}}/\text{TOC}$ ratios and degree of pyritization values from Dajiang indicate dysoxic-anoxic condition in bottom water above the MEB (H.Y. Song et al., 2014b). The concentration of uranium and its isotopic composition from Dajiang and Guandao sections of South China and the Taşkent section in Turkey suggest a hundred-fold increase in the extent of seafloor anoxia above the MEB (Lau et al., 2016). The covariation of pyrite S and carbonate carbon isotopic compositions from the Nhi Tao section of Vietnam record recurrent upwelling of anoxic deep-ocean waters to the shallow carbonate platform in the Nanpanjiang Basin after the mass extinction event (Algeo et al., 2007, 2008). The interpretation of each of these studies is consistent with our pyrite framboi-d data and indicates the expansion of oxygen-poor water to the shallow-marine carbonate environment immediately above the MEB.

5.2. Comparison with wider redox record

Whilst the Dajiang section testifies to the expansion of dysoxic waters onto the shallow-marine carbonate platform immediately above the MEB in the southern SCB, pyrite framboi-ds of the Laolongdong and Cili sections suggest a similar event also occurred on the block’s northern margins (Liao et al., 2010; He, 2013; Wang et al.,
Oxygen-poor conditions were widespread across shallow-marine carbonate platforms of the equatorial SCB (Fig. 5). Further afield, in the Bulla section of western Palaeotethys, the shallow-water, post-MEB Tesero Oolite also contains abundant pyrite frambooids indicative of dysoxic conditions in that region (Bond and Wignall, 2010). Tiny frambooids are also abundant in the Early Triassic of Spitsbergen, which was located in a north-facing Boreal seaway, where they indicate the development of ultra-shallow marine anoxia on a clastic ramp (Wignall et al., 2016). The co-occurrence of oxygen-poor conditions in shallow-marine environments in diverse palaeogeographic locations shows the global significance of this anoxic event in the Permian-Triassic transition. Nevertheless, the extent of oxygen deficiency varied between locations. Even with the SCB, pyrite frambooid populations from Dajiang (mean values, 5.3-8.3 μm) are clearly smaller than those from the Cili (mean values, 7.3-11.1 μm) and Laolongdong (mean values, 7.6-9.5 μm) (Fig. 6). According to the redox continuum laid out by Bond and Wignall (2010), the variation in pyrite frambooid sizes across the SCB indicates a greater intensity of oxygen deficiency at its southern, Panthalassan margin than in its northern, Palaeotethyan areas. The anoxic event may therefore have originated in Panthalassa. Pyrite frambooid size distributions, and by inference redox, are relatively stable above the MEB at Laolongdong and Cili, whereas they appear to be more variable at Dajiang, where there are modest fluctuations between populations typical of lower dysoxic, and anoxic depositional conditions. This may be a consequence of recurrent upwelling of anoxic deep-ocean waters in Panthalassa (Algeo et al., 2007, 2008). By the time this water reached Palaeotethys and the northern part of the SCB, its chemistry was likely somewhat more homogenised, hence the more stable redox record from Cili and Laolongdong.

5.3. Causes of the anoxic event

Although the Permian-Triassic marine anoxic event has left evidence far and wide, as a variety of proxies in multiple locations testifies, its cause remains controversial. The anoxic event has been attributed to gas hydrate leaks (Heydari and Hassanzadeh, 2003), but there is still insufficient evidence to support this hypothesis.
More plausibly, the widespread anoxia above the MEB has been posited to be the result of a rapid increase in sea surface temperature (Joachimski et al., 2012; Sun et al., 2012; Chen et al., 2015); warm ocean waters have reduced dissolved oxygen carrying capacity. The elevated sea surface temperatures may have been responsible for the development of marine anoxia, but the contemporaneous major negative δ¹³C_carb excursion across the Permian-Triassic transition suggests that other, globally significant factors were also at play. Increased terrigenous influx to the oceans has been proposed as a causal mechanism in the marine anoxic event (Algeo and Twitchett, 2010) and this may have fuelled a cyanobacterial bloom (Xie et al., 2007; Wu et al., 2014) which would have enhanced the consumption of dissolved oxygen via degradation of organic matter produced by the cyanobacteria. The volume of terrigenous influx to a marine environment is generally related to the spatial pattern of the ancient lands that lie nearby, and in theory it should take a long time for terrigenous input to cause anoxia over an entire ocean basin. A relatively slow mechanism for the development of widespread anoxic conditions is inconsistent with a globally isochronous and relatively sudden faunal mass extinction, if indeed anoxia was the (primary) kill mechanism. If terrigenous input were the primary driver of anoxia, one would expect to see the most intense oxygen depletion in areas such as Palaeotethys, which was surrounded and enclosed by ancient lands during the Permian-Triassic interval (Fig. 1). In such a runoff-anoxia scenario, the vast swathes of Panthalassa ought to be less affected by runoff due to its enormous water body and its long distance from the source of terrigenous material. Pyrite framboïd analysis indicates that oxygen deficiency was more intense on the Panthalassan margin of the SCB (Dajiang section) than at its northern, Palaeotethyan margin (Laolongdong and Cili sections). This is inconsistent with a terrigenous driver of oxygen depletion. Instead, we invoke an upwelling model.

By the latest Permian, Panthalassa spanned a vast area between northern and southern poles (Fig. 1). The variety of water temperatures in this huge ocean (in comparison with e.g. Palaeotethys) might have been a driving factor in the emplacement of deep-ocean waters into shallow-marine environments (Rahmstorf et
In the end-Permian palaeogeography, the southern part of the SCB is the border where it met the western Panthalassa. Previous oceanic modelling results favored a ventilation in most parts of the Panthalassa, upwelling in the peri-equatorial western Panthalassa (Winguth et al., 2002; Kidder and Worsley, 2004; Winguth and Maier-Reimer, 2005; Winguth and Winguth, 2012, 2013). This fits with the data presented here: although local anoxia can be caused by several factors, the greater intensity of carbonate platform oxygen deficiency on the Panthalassan margin of the SCB suggests that upwelling of deep-ocean water may have been the key driver of Permian-Triassic anoxia. This hypothesis is supported by evidence from Nhi Tao in Vietnam, which also faced Panthalassa, and records recurrent upwelling of anoxic deep-ocean waters to the shallow carbonate platform above the MEB (Algeo et al., 2007, 2008). In modern ocean, upwelling of oxygen deficient deep water onto the inner shelf resulted in the development of severe hypoxia in the open coast, with the shallowest reaches to the 30-m isobath in the northeast Pacific (Grantham et al., 2004; Bograd et al., 2008; Chan et al., 2008). Moreover, it has been suggested that upwelling of highly alkaline deep waters into shallow-water environments may lead to the formation of great thickness of anachronistic limestones within relatively short time interval (Deng et al., in press). Such a model may fit the Daye Formation.

The well-known, globally widespread negative shift in δ¹³C_carb during the Permian-Triassic transition has also been ascribed to numerous causes (for a review see Korte and Kozur, 2010) including volcanogenic CO₂ emission (Payne and Kump, 2007; Xie et al., 2007; Luo et al., 2011; Shen et al., 2012), gas hydrates release (Erwin, 1993; Krull et al., 2004), and the upwelling of anoxic deep-ocean waters (Grotzinger and Knoll, 1995; Knoll et al., 1996; Algeo et al., 2007, 2008). During the Late Permian, black shales (e.g. the Dalong Formation) are widespread in the deep basins of Palaeotethys, and these may have provided the material base for gas hydrates accumulation. Away from platform margin areas, the lack of black shale in the much of Panthalassa would have inhibited the accumulation of gas hydrates in that ocean. If the negative δ¹³C_carb excursion was generated by gas hydrates release, it is predicted to have been of greater magnitude in Palaeotethys than in Panthalassa. In fact, a more
marked $\delta^{13}$C$_{\text{carb}}$ shift is recorded at Dajiang than at Laolongdong or Cili (Fig. 6). Interestingly, the intensities of the $\delta^{13}$C$_{\text{carb}}$ shift correlate positively with the intensity of oxygen deficiency on the SCB carbonate platform (Fig. 6). Thus, the intensity of each increases from Laolongdong to Cili, and reaches a peak at Dajiang (Fig. 6). Whilst volcanogenic CO$_2$ emissions were probably the major driver of the negative $\delta^{13}$C$_{\text{carb}}$ excursion, one would expect its effects to be homogeneous over a wide area. Shifts of different magnitude observed on the SCB implicate another factor: the coupling between the intensities of the $\delta^{13}$C$_{\text{carb}}$ shift and water-column oxygen deficiency was probably a result of differing degrees of upwelling of anoxic deep-ocean waters in different palaeogeographic settings in the region.

6. Conclusions

The size distribution of pyrite frambooids from the Dajiang section, located on the Panthalassan margin of the southern South China Block, indicates that oxygen-poor, dysoxic water invaded the shallow-marine carbonate platform environment immediately above the MEB, and further demonstrates its killer role in the Permian-Triassic mass extinction event. Comparison with data from the Laolongdong and Cili sections from the Palaeotethyan margin of the northern SCB reveals that mean frambooid diameters are smaller at Dajiang. Thus, the Panthalassan margin of the SCB experienced a greater intensity of oxygen deficiency than the Palaeotethyan margin.

The intensity of oxygen depletion on the SCB is closely coupled to that of the well-known Permian-Triassic $\delta^{13}$C$_{\text{carb}}$ negative shift. At Dajiang, both are of greater magnitude than at Laolongdong and Cili. The close correlation between the intensities of the negative $\delta^{13}$C$_{\text{carb}}$ shift and oxygen deficiency during the Permian-Triassic transition of the SCB suggests that the anoxic events on the shallow-marine carbonate platform were mainly caused by the upwelling of anoxic deep-ocean waters from Panthalassa. We therefore invoke upwelling as a key factor in the spread of marine anoxia and the major changes in the carbon isotope record across the Permian-Triassic
boundary.

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References


Algeo, T.J., Twitchett, R.J., 2010. Anomalous Early Triassic sediment fluxes due to elevated weathering rates and their biological consequences. Geology 38,


Forel, M.B., Crasquin, S., Kershaw, S., Feng, Q., Collin, P.Y., 2009. Ostracods (Crustacea) and water oxygenation in the earliest Triassic of South China:
implications for oceanic events at the end-Permian mass extinction. Australian

Friedrich, J., and 38 coauthors, 2014. Investigating hypoxia in aquatic environments:
diverse approaches to addressing a complex phenomenon. Biogeosciences 11,
1215-1259.

Galfetti, T., Bucher, H., Martini, R., Hochuli, P.A., Weisssert, H., Crasquin-Soleau, S.,
Brayard, A., Goudeaud, N., Brühwiler, T., Guodun, K., 2008. Evolution of
Early Triassic outer platform paleoenvironments in the Nanpanjiang Basin
(South China) and their significance for the biotic recovery. Sedimentary
Geology 204, 36-60.

Golonka, J., 2002. Plate-tectonic maps of the Phanerozoic. In: Kiessling, W., Flügel,
E., Golonka, J. (Eds.), Phanerozoic Reef Patterns, 72. SEPM Spec Publ, pp.
21-76.

Grantham, Brian A., Chan, F., Nielsen, K.J., Fox, D.S., Barth, J.A., Huyer, A.,
ecosystem and oceanographic changes in the northeast Pacific. Nature 429,
749-754.

Grice, K., Cao, C.Q., Love, G.D., Böttcher, M.E., Twitchett, R.J., Grosjean, E.,

Grotzinger, J.P., Knoll, A.H., 1995. Anomalous carbonate precipitates: is the
Precambrian the key to the Permian? Palaios 10, 578-596.


Palaeoecology 203, 207-237.


the Nanpanjiang Basin, South China: implications for oceanic conditions associated with the end-Permian extinction and its aftermath. Palaios 18, 138-152.

Lehrmann, D.J., and 16 coauthors, 2015. Environmental controls on the genesis of marine microbialites and dissolution surface associated with the end-Permian mass extinction: new sections and observations from the Nanpanjiang basin, South China. Palaios 30, 529-552.


