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Oceanic redox evolution across the end-Permian mass extinction at Shangsi, South China

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ABSTRACT

The end-Permian mass extinction (EPME) was the most severe extinction event of the Phanerozoic. To investigate oceanic redox conditions around the EPME, we conducted a series of geochemical analyses, including iron speciation, trace element geochemistry, total organic carbon (TOC), and nitrogen isotopes of kerogen ($\delta^{15}N_{kero}$), around the EPME at the Shangsi section, South China. Three intervals with different redox conditions can be distinguished based on iron speciation. During the first interval (early and middle Changhsingian), bottom waters were pervasively euxinic. In the second interval (late Changhsingian and the EPME), bottom water fluctuated between oxic and anoxic, but non-sulfidic conditions, with the oxic mode becoming increasingly predominant over time. During the third interval, following the EPME, bottom waters appeared to have been consistently anoxic, although again not pervasively euxinic. This redox history is supported by enrichments in the authigenic fraction of redox-sensitive elements. These relatively high $\delta^{15}N_{kero}$ values (>1.0‰) corresponding with Changhsingian euxinia suggest reducing bottom waters did not impinge on the photic zone. The shift to values near 0‰ within and above the EPME indicates an ecological expansion of diazotrophs. Stratigraphic trends of Ni_{xs}, Cd_{xs}, P_{xs}, and TOC indicate that primary productivity was highest in the first interval, coinciding with euxinic bottom water, then decreased during the lower part of Interval 2 and remained at low level through the remainder of the studied section. The temporal relationship between redox condition and primary productivity suggests that euxinia was supported by high productivity and carbon export in the early Changhsingian. The expansion of N_2 fixation coincides closely with the previously documented warming of the ocean surface at Shangsi and may be related to reduced oceanic circulation and suppressed vertical mixing. The temporal distribution of deepwater anoxia and euxinia suggests that they were not primary causes for the extinction of benthos at Shangsi.

1. Introduction

The end-Permian mass extinction (EPME) was the most severe extinction event of the Phanerozoic and has been estimated to have eliminated more than 90% of marine species across the Permian and Triassic boundary (PTB, Sepkoski, 1984, 2002). Many trigger and kill mechanisms have been proposed during the past few decades, such as an extraterrestrial impact (Becker et al., 2001; Basu et al., 2003), volcanism (Bowring et al., 1998; Courtillot and Renne, 2003; Kamo et al., 2003), rapid global warming (Brand et al., 2012; Joachimski et al., 2012), large-scale reorganization of carbon cycle (Berner, 2002), oceanic acidification (Payne et al., 2010; Beauchamp and Grasby, 2012; Hinojosa et al., 2012; Black et al., 2014; Clarkson et al., 2015), and oceanic anoxia/euxinia (Wignall and Twitchett, 1996; Isozaki, 1997; Grice et al., 2005; Cao et al., 2009; Algeo et al., 2011; Brennecka et al., 2011; Grasby et al., 2015).

Evidence for oceanic anoxia around the EPME has been recognized for nearly two decades (Wignall and Twitchett, 1996; Isozaki, 1997; Shen et al., 2011b). Several lines of evidence, including biomarkers and sulfur isotope composition, indicate that anoxic/sulfidic environments were widespread in slope-basin environments immediately prior to and during the EPME (Grice et al., 2005; Riccardi et al., 2006, 2007; Cao et al., 2009; Luo et al., 2010; Shen et al., 2011b). However, it remains unclear how the anoxic and euxinic conditions around the EPME were generated, with potential drivers including both enhanced organic matter (OM) biodegradation and reduced oceanic circulation (Hotinski et al., 2001; Zhang et al., 2001; Kiehl and Shields, 2005; Meyer et al., 2008; Winguth and Winguth, 2012). Maintaining anoxia via enhanced OM biodegradation is a dynamic process, relying on sufficient primary productivity in the water column to supply OM to the benthos. Primary productivity showed considerable spatial variability across the Permian ocean, and while it appears to have increased across

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the EPME in most parts of the world (Algeo et al., 2013), South China experienced a precipitous decline (Song et al., 2013b; Shen et al., 2015). Areas of the ocean receiving nutrients via western-boundary coastal upwelling may have been especially vulnerable to decreasing productivity (Beauchamp and Baud, 2002; Schoepfer et al., 2012, 2013; Knies et al., 2013; Proemse et al., 2013), and the location of Shangsi along the western margin of the South China craton means it may have been affected by this process.

Meanwhile, enhanced vertical stratification due to a rise in global surface temperatures could lead to anoxic conditions even in low-productivity environments. While rapid warming around the PTB has been documented (Joachimski et al., 2012; Sun et al., 2012; Chen et al., 2013), modeling studies have had difficulty generating pervasively anoxic conditions through warming alone (Hotinski et al., 2001; Winguth and Maier-Remier, 2005). Thus, further study is necessary to understand the roles of the primary productivity and climatic warming in the dynamics of oceanic redox conditions around the EPME.

The Shangsi PTB section was considered for the Global Stratotype Section and Point (GSSP) of the PTB (Yang et al., 1987; Li et al., 1989) and has been the subject of numerous studies including biostratigraphy, cyclostratigraphy, geochemistry, and geochronology (Mundil et al., 2004; Jiang et al., 2011; Shen et al., 2011a; Wu et al., 2013). Thus, it is an ideal section to study the pattern of oceanic redox evolution and its temporal relationship with the EPME in south China. In this study, we conducted a series of analyses on samples collected from the EPME interval of the Shangsi section, including measurements of iron speciation, total organic carbon (TOC), trace elements, and nitrogen isotope of kerogen ($\delta^{15}N_{kero}$). We used these proxies to explore the temporal evolution of redox conditions and primary productivity around the PTB at the Shangsi section, with the aim of better understanding the relative roles of organic matter degradation and oceanic circulation in generating and maintaining anoxia and euxinia around the EPME.

2. Geological setting

The Shangsi section is located near Guangyuan City of Sichuan Province (Fig. 1). The Permian sequence at the Changjianggou valley near Shangsi is very well exposed along a creek. The section represents deposition in a slope facies, on the margin of the intracratonic carbonate platform that made up the majority of the South China microcontinent in the Permian and earliest Triassic (Wang and Jin, 2000; Yin et al., 2014; Luo et al., 2014, Fig. 1). The South China microcontinent was located at subtropical latitudes, approximately 23–25°N, during the interval surrounding the PTB (Liu et al., 1999). Lithostratigraphically, the Permian–Triassic transitional sequence at the section is composed of the Talung Formation in the uppermost Permian and the Feixianguan Formation in the lowest Triassic. The exact location of the biostratigraphic PTB at the section is still unclear because the first occurrence of the index species *Hindeodus parvus* occurs relatively high, nearly 5 m above the lithological and geochemical transitions representing the EPME (Jiang et al., 2011; Yang et al., 2014).

The studied interval in this paper includes the uppermost 10.15 m of the Talung Formation, which is composed of dark grey siliceous limestone with centimeter-to-decimeter scale bedding, interbedded with siliceous shale and illite–montmorillonite claystone. Its top is marked by a 25-cm-thick limestone (Bed 26 of Li et al., 1989) containing abundant Changhsingian conodonts and ammonoids, which is overlain by three mudstone/ash beds (Bed 27a-c, 15 cm thick in total) of the Feixianguan Formation. The lowest part of the Feixianguan Formation is composed of yellow to yellowish green calcareous mudstone and argillaceous limestone interbedded with a few ash beds but shows increasing carbonate content upsection, ultimately grading into a light grey algal laminated limestone with centimeter-to-decimeter scale bedding at 102.84 m, which contains abundant conodonts including *H. parvus* (Li et al., 1989; Lai et al., 1996; Jiang et al., 2011; Yang et al., 2014; Fig. 2).

The Shangsi section has been the subject of extensive palaeontological study, with the stratigraphic distribution of ammonoids, brachiopods, foraminifers, conodonts, bivalves, radiolarians, and gastropods all having been published (Yang et al., 1987, 2014; Li et al., 1989; Wignall et al., 1995; Lai et al., 1996; Jiang et al., 2011; Shen et al., 2011a; Song et al., 2013a), allowing for excellent biostratigraphic age control. The recent geochronological study (Shen et al., 2011a, Fig. 2) indicates that the ash bed immediately below Bed 26 is 252.28 ± 0.13 Ma, geochronological ages of three other ash beds, respectively at 0.3 m (252.37 ± 0.08 Ma), 1.0 m (252.68 ± 0.12 Ma), and 2.9 m (253.10 ± 0.12 Ma) below the top of Bed 26, are also available), and an ash bed 0.5 m above the top of Bed 26 is 252.16 ± 0.09 Ma, basically equivalent to the PTB at Meishan.

The onset of the EPME occurred at top of Bed 26. Only 10 out of 47 species survived into Bed 27 (Yang et al., 1987; Li et al., 1989; Wignall et al., 1995; Huang et al., 2011). The disappearance of surviving Permian fauna after the EPME event was limited to the basal part of Bed 28. Thus, the whole EPME interval at the Shangsi section includes beds 27a-c and the basal part of Bed 28, which is much less than 1 m of strata, with duration of less than 120,000 years (Shen et al., 2011a; Wu et al., 2013).

3. Sampling and methods

A total of 42 samples collected from the Shangsi section within a 16.35-m interval were analyzed for this study. Our sampling started 10 m below the top of Bed 26 and ended 6.35 m above the top of Bed 26, thus spanning the complete EPME and PTB interval. These samples were broken into pieces (diameter ~2 mm) by hammer. Pieces of the crushed samples were then chosen for pulverizing, avoiding veins and cavities. The selected material (>50 g) was then further powdered using a SPEX 8515 Shatterbox with a ceramic puck.

For ICP-MS analyses, the samples were treated by multi-acid digestion (HNO_3–HF–HCl) techniques (Kendall et al., 2010; Li et al., 2010): about 0.5 g powdered sample splits were ashed at 550 °C overnight. The mass lost on ignition was calculated by the mass difference between pre- and post-combustion and used later for correction of the elemental abundances. In order to remove Ca^{2+} (primarily from carbonates and mixed siliciclastic–carbonate rocks), aliquots of ~50 mg of each sample were first treated with ~2 mL concentrated HNO_3 and heated at 200 °C for 2 h within sealed Teflon bombs. The sample was then spun at 3500 r.p.m. for 8 min. The supernatant was transferred quantitatively into a 15-mL polyethylene bottle, and the undigested residue was retained. For carbonate-replete samples, this step was repeated two to three times. The residual sample was further treated with ~3 mL concentrated HNO_3/HF (1:2 mixture) and heated at 200 °C for 72 h in a sealed Teflon bomb. The bomb was subsequently opened and dried down on a hot plate at 120 °C. During the last digestion step, the sample was heated at 200 °C for 5 h with ~1 mL concentrated HCl in a sealed Teflon bomb. As a result of variations in sample composition, an additional round of digestion was sometimes necessary to achieve complete dissolution. After complete digestion, we returned the HNO_3 supernatant to the Teflon bomb. Following an evaporation step to remove concentrated acid, the final sample residue was mixed with 1 mL 500 ppb indium (In) as an internal standard, and then diluted to 50 mL using 1% HNO_3. Trace and major elements were analyzed for the target elements on a quadrupole inductively coupled plasma mass spectrometer (ICP-MS) at the Beijing Research Institute of Uranium Geology, China National Nuclear Corporation. The analytical precision monitored by GSR-1, GSR-2, and GSR-3 is better than 5%.

Trace element excess (X_{xs}; Tribovillard et al., 2006), representing the authigenic component of any given element after the terrigenous contribution is subtracted, was calculated for each measured trace element as follows:

$$X_{xs} = X_{sample} - Al_{sample} \times (X_{AUCC}/Al_{AUCC}) \quad (2)$$