High-resolution SIMS oxygen isotope analysis on conodont apatite from South China and implications for the end-Permian mass extinction

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Jun Chen [a,*], Shu-zhong Shen [b], Xian-hua Li [c], Yi-gang Xu [a], Michael M. Joachimski [d], Samuel A. Bowring [e], Douglas H. Erwin [f], Dong-xun Yuan [b], Bo Chen [b], Hua Zhang [b], Yue Wang [b], Chang-qun Cao [b], Quan-feng Zheng [g], Lin Mu [h]

[a] State Key Laboratory of Isotope Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, Guangzhou 510640, China
[b] State Key Laboratory of Palaeobiology and Stratigraphy, Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences, Nanjing 210008, China
[c] State Key Laboratory of Lithospheric Evolution, Institute of Geology and Geophysics, Chinese Academy of Sciences, Beijing 100029, China
[d] GeoZentrum Nordbayern, Universität Erlangen-Nürnberg, Schlossgarten 5, 91054 Erlangen, Germany
[e] Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, MA 02139, USA
[f] Department of Paleobiology, National Museum of Natural History, Smithsonian Institution, MRC-121, Washington, DC 20013-7012, USA
[g] Key Laboratory of Economic Stratigraphy and Palaeogeography, Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences, Nanjing 210008, China
[h] Department of Invertebrate Palaeontology, Nanjing Institute of Geology and Palaeontology, Chinese Academy of Sciences, Nanjing 210008, China

ARTICLE INFO

ABSTRACT

Understanding the interplay of climatic and biological events in deep time requires resolving the precise timing and pattern of paleotemperature changes and their temporal relationship with carbon cycle variations and biodiversity fluctuations. In situ oxygen isotope analyses of conodont apatite from South China enables us to reconstruct high-resolution seawater temperature records across the Permian–Triassic boundary (PTB) intervals in the upper slope (Meishan), lower slope (Shangsi), and carbonate platform (Daijiagou and Liangfengya) settings. Constrained by the latest high-precision geochronological dates and high-resolution conodont biozones, we can establish the temporal and spatial patterns of seawater temperature changes and assess their potential connections with the carbon cycle disruption and biodiversity decline. We find a rapid warming of ~10 °C during the latest Permian–earliest Triassic that postdated the onset of the negative shift in $\delta^{13}C_{carb}$ by ~81 kyr (thousand years), the abrupt decline in $\delta^{13}C_{carb}$ by ~32 kyr and the onset of mass extinction by ~23 kyr, which contradicts previous claims that the extreme temperature rise started immediately before or coincided with the onset of mass extinction. Our new evidence indicates that climate warming was most likely not a direct cause for the main pulse of the end-Permian mass extinction (EPME), but rather a later participant or a catalyst that increased the pace of the biodiversity decline. In addition, a prominent cooling is recorded in the earliest Changhsingian, with the main phase (a drop of ~8 °C in ~0.2 Ma) confined to the lower part of the *Clarkina wangi* zone and synchronous with the positive limb of the carbon isotope excursion (CIE) around the Wuchiapingian–Changhsingian boundary (WCB) in Meishan and Shangsi. Further long-term and high-resolution studies from other sections are needed to confirm the full contexts and underlying dynamics of the WCB "cooling event".

1. Introduction

The catastrophic EPME has long been recognized as the most severe crisis during the Phanerozoic, and marked a fundamental shift in Earth's ecological structure (Raup and Sepkoski, 1982). Numerous hypotheses have been proposed as the cause(s) of this cataclysm, including bolide impact, ocean anoxia, and flood basalt volcanism (Knoll et al., 2007; Payne and Clapham, 2012). Severe environmental perturbations related

to the Siberian Traps volcanism have been considered by many as one of the most plausible scenarios for the killing mechanism (Campbell et al., 1992; Renne et al., 1995; Kamo et al., 2003; Svensen et al., 2009; Black et al., 2012). This "favored" hypothesis has received strong support from recent high-precision geochronological dates from the Meishan stratotype section (Burgess et al., 2014) and the Siberian Traps (Burgess and Bowring, 2015). A new age model (Burgess and Bowring, 2015) of the Siberian Traps volcanism (explosive, effusive, and intrusive) demonstrated that pyroclastic and lava eruptions predated the onset of the EPME by 300 ± 126 kyr, supporting a causal connection. Furthermore, two-thirds of an estimated 4×10^6 km³ of magma were emplaced/erupted over this ~300-kyr interval, before and during the mass extinction interval. The bulk of intrusive activity

began within the mass extinction interval (within 61 ± 48 kyr; Burgess et al., 2014) and continued for at least 500 kyr after the cessation of mass extinction.

Although the temporal overlap between the Siberian Traps volcanism and the EPME links the two events, many questions remain unresolved about the nature of the connection. For example, which pulse of the Siberian Traps volcanism is responsible for the EPME? What is the underlying dynamic behind such disparity between the volcanism and biotic crisis? Resolving such questions requires establishing a precise timeline between the environmental deterioration and biodiversity decline, since most large igneous province eruptions (Wignall, 2001; Bond and Wignall, 2014) are expected to impact the Earth's climate via carbon cycle disruption, short-term cooling followed by long-term warming, and ocean acidification. The negative shift of $\delta^{18}O$ in whole rock carbonates from the Carnic Alps of Austria initially suggested climate warming of ~5–6 °C around the PTB, although the possible influences from salinity and/or diagenesis cannot be excluded (Holser et al., 1989), which makes such whole rock $\delta^{18}O$ record unreliable. Conodont apatite is preferred to whole rock carbonates and brachiopod calcites due to its resistance to diagenesis (Luz et al., 1984; Wenzel et al., 2000). Thus the $\delta^{18}O$ signature of conodonts is widely regarded as an applicable proxy for reconstruction of seawater temperatures in the Paleozoic and Triassic (Trotter et al., 2008, 2015; Joachimski et al., 2012; Sun et al., 2012; Romano et al., 2013). Using this methodology, climate change around the EPME was demonstrated on the basis of $\delta^{18}O$ data derived from conodont apatite in South China and Iran. These results indicated that the major seawater temperature increase started immediately before (Joachimski et al., 2012) or at the mass extinction horizon (Schobben et al., 2014) and suggested climate warming as one of the causes of the EPME.

Owing to the absence of oxygen isotope data from Bed 25 in Meishan, the base of which corresponding to the onset of the EMPE (Jin et al., 2000; Shen et al., 2011; Wang et al., 2014), it was ambiguous whether the increase of temperatures predates, coincides with, or postdates the onset of mass extinction. Also, available $\delta^{18}O$ data across the EPME (Joachimski et al., 2012; Schobben et al., 2014) were all derived from the conventional isotope ratio mass spectrometry (IRMS) method, which requires large sample size (>0.5 mg, or 10–50 specimens depending on the size/weight of individuals) and analyzes on "bulk" materials. Since conodonts near the PTB are mostly small in size and of low abundance, particularly within the EPME interval and above, low-yielding conodont samples were excluded from the IRMS analyses, thus reducing the much needed temporal resolution.

Understanding the interplay between climatic and biological events around the EPME requires resolving the precise timing and pattern of paleotemperature changes and their temporal relationship with carbon cycle variations and biodiversity fluctuations, which is the aim of this contribution, undertaken through the combination of analytical method, materials selection, and updated temporal framework:

(1) In situ SIMS method. We overcome the limitation of conventional IRMS analyses (i.e., sample size) by measuring oxygen isotope compositions of individual conodont elements using the in situ secondary ion mass spectrometry (SIMS) method. To eliminate as many diagenetic and preservation artifacts as possibly we followed strict analytical procedures (see Supplementary material for details) and applied with considerable caution on the $\delta^{18}O$ variability (Wheeley et al., 2012; Zigaite and Whitehouse, 2014). This technique has been proven to have considerable potential for reconstructing paleoclimate and paleoceanography (Trotter et al., 2008, 2015; Rigo et al., 2012; Wheeley et al., 2012), and can significantly increase the spatial and temporal resolutions based on samples with low-yielding conodont elements.

(2) Multiple stratigraphic sections. To resolve the temporal and spatial pattern of paleotemperature changes across the EPME interval, we generated high-resolution in situ oxygen isotope data

from four sections in South China (Meishan, Shangsi, Daijiagou and Liangfengya). We selected the condensed Meishan and Shangsi sections, since extensive studies from both sections have produced integrated, high-resolution geochronological dates (Shen et al., 2011; Burgess et al., 2014), carbon isotopes (Shen et al., 2013), and conodont biostratigraphy (Shen et al., 2013; Yuan et al., 2014). Published IRMS data from both sections (Joachimski et al., 2012; Chen et al., 2013) were also available for comparison with our new SIMS records. Samples from the well-studied Daijiagou (Yuan et al., 2015) and Liangfengya (Yuan and Shen, 2011) sections were also analyzed; both sections were deposited on a shallow carbonate platform during the Permian–Triassic transition, in contrast to Meishan (upper slope) and Shangsi (lower slope) and thus can be used for spatial comparison.

(3) Uniform temporal framework. To constrain the timing and rate of paleotemperature changes, the stratigraphic depth of all samples are adjusted to a uniform timescale, mainly based on the latest U–Pb ages (Shen et al., 2011; Burgess et al., 2014) and conodont zones (Yuan et al., 2014) from Meishan to correlate with other sections. This results in a high-resolution, time dependent record for the latest Permian–earliest Triassic interval.

2. Studied sections and materials

Conodont samples used in this study were collected from four sections in South China (Fig. 1), which were located at a paleolatitude of ~25 N° on the Yangtze carbonate platform and its northern marginal basin in the eastern Palaeotethys Ocean during the Late Permian–Early Triassic (Stampfli and Borel, 2004). Sequence stratigraphy and facies analysis (Shen and He, 1991; Shen and Shi, 1995; Wignall and Hallam, 1996; Yin et al., 2001; Song et al., 2013) indicated that the studied sections were deposited in different environmental settings around the PTB, including the upper slope (Meishan), lower slope (Shangsi), and carbonate platform (Daijiagou and Liangfengya). Details on studied sections (Fig. 2) and materials can be found in the Supplementary material.

3. Biostratigraphic correlation and temporal framework

High-resolution Late Permian–Early Triassic conodont biostratigraphy (Shen and Mei, 2010; Shen et al., 2010), lithostratigraphy (Cao and Zheng, 2007; Yin et al., 2014), and $\delta^{13}C_{carb}$ chemostratigraphy (Shen et al., 2013) allowed us to correlate the sections with the newly revised conodont-based integrated records from the Meishan stratotype section (Yuan et al., 2014) serving as the standard. After thorough evaluation, the published conodont zones from Shangsi (Jiang et al., 2011; Shen et al., 2011, 2013), Daijiagou (Yuan et al., 2015), and Liangfengya (Yuan and Shen, 2011) were directly applied or accordingly modified as biostratigraphic constraints for intra-regional correlations (Supplementary Tables S1–4).

Several baselines for correlation were first established: (1) The PTB is at 42.11 m in Meishan, 100.4 m in Shangsi, 0.58 m in Daijiagou, and 0 m in Liangfengya, defined by the first appearances of *Hindeodus parvus*, except for Shangsi where the first occurrence of *H. parvus* was proven to be younger than many other occurrences including the FAD (First Appearance Datum) (Nicoll et al., 2002; Henderson, 2006; Jiang et al., 2011). *Hindeodus eurypyge* was regarded as an alternative index for our definition of the PTB in Shangsi (Shen et al., 2011, 2013), that is at the same level as in the restudy of Jiang et al. (2011) where the first occurrences of *Clarkina taylorae* and *Hindeodus changxingensis* defined the PTB. (2) The onset of the EPME is defined at the base of Bed 25 (41.93 m) at Meishan (Jin et al., 2000; Shen et al., 2011; Wang et al., 2014), corresponding to the base of Bed 27 (100.1 m) at Shangsi (Shen et al., 2011, 2013), the base of "boundary clay" (0 m) at Daijiagou (Shen and Shi, 1995), and the base of Bed 29 (−0.51 m) at Liangfengya