



# Geochemical evidence from bio-apatite for multiple oceanic anoxic events during Permian–Triassic transition and the link with end-Permian extinction and recovery

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## ARTICLE INFO

### Article history:

Received 21 October 2011

Received in revised form

20 June 2012

Accepted 4 July 2012

Editor: G. Henderson

Available online 4 September 2012

### Keywords:

conodont trace elements

oceanic anoxic event

end-Permian extinction

triassic biotic recovery

microbialite

carbon cycle

## ABSTRACT

A detailed, 20 myr redox history of Permian to Triassic oceans (Changhsingian to Carnian stages) has been constructed using Ce-anomaly ( $\Omega_{\text{Ce}}$ ) and Th/U ratios from conodont albid crown apatite material. The results show that the well-established phenomenon of intense ocean anoxia (coincident with the end-Permian mass extinction) is faithfully recorded in conodont  $\Omega_{\text{Ce}}$  and Th/U data. Extending this conodont redox record shows that end-Permian anoxia persisted possibly into the earliest Dienerian Stage and that two intense oceanic anoxic events also occurred later in the Early Triassic (earliest Smithian–earliest Spathian, and middle Spathian), followed by a weaker manifestation of anoxia in the Anisian Stage, seen in  $\Omega_{\text{Ce}}$  data. Marine benthic radiation, following the end-Permian mass extinction, began after the Smithian–earliest Spathian anoxic event suggesting a suppression of evolution prior to this due to these inimical conditions. The failure of the middle Spathian anoxic event to retard the evolutionary rebound implies shallow shelf seas remained well ventilated at this time even if the oceans did not. Other attributes of the Early Triassic record also closely coincide with redox fluctuations: phases of anoxia intensification saw the proliferation of microbial carbonates and major negative carbon isotope swings that can be attributed to chemocline shallowing causing alkalinity pulses and enrichment in light, remineralised carbon and/or indicate a trigger mechanism related to increased fluxes of light C from Siberian volcanic sources.

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## 1. Introduction

The long-delayed and highly variable recovery rates of marine invertebrates after the end-Permian mass extinction is one of the most intriguing facets in life's history. Although, nektonic groups, such as ammonoids and conodonts recovered rapidly (Brayard et al., 2009; Stanley, 2009), the majority of benthic groups did not re-diversify until either the Spathian or Anisian stages more than 5 million years later (Payne et al., 2011; Song et al., 2011). Early Triassic seafloors were characterised by the proliferation of anachronistic Precambrian-like facies, especially in equatorial carbonate locations where flat-pebble conglomerates and microbial reefs developed (Pruss et al., 2006; Wignall and Twitchett, 1999). Ocean anoxia has been widely implicated in the

end-Permian extinction, and it is suggested that prolongation of these conditions hindered radiation of seafloor communities (Hallam, 1991; Isozaki, 1997). This hypothesis may provide an explanation for the uniquely long Triassic recovery interval and it is investigated here using independent geochemical redox proxies derived from Triassic bio-apatite from equatorial carbonate localities in South China. Recent studies in this region have revealed the detailed timing of the recovery (Song et al., 2011), allowing potential cause-and-effect to be directly compared.

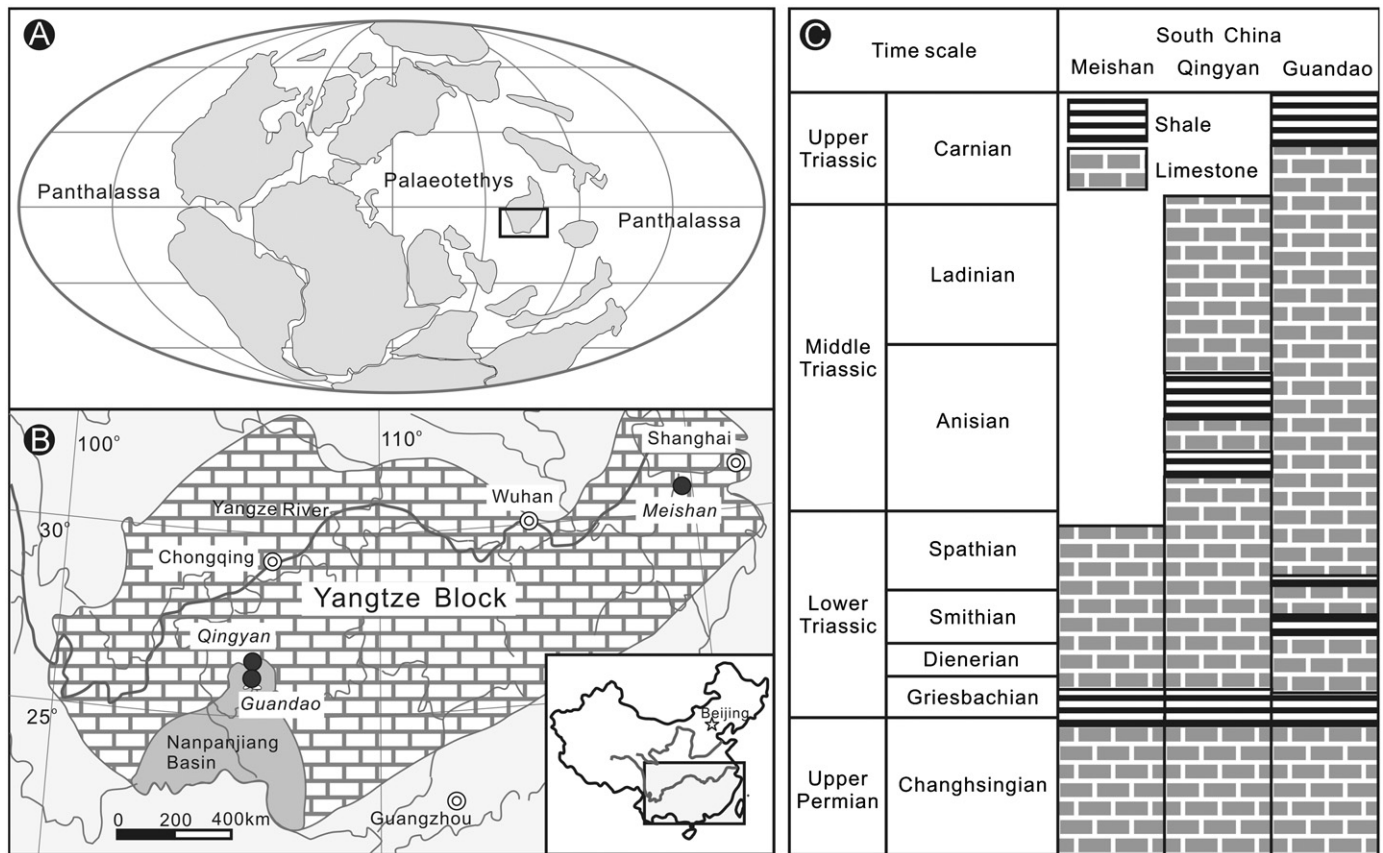
The Permian–Triassic (P–Tr) redox history of Panthalassa Ocean reveals major fluctuations in the intensity of anoxia after the onset of ocean euxinicity at the end of the Permian as shown by pyrite petrography (Wignall et al., 2010). However, comparable studies of shelf seas have only focused on the P–Tr boundary interval (Algeo et al., 2008; Cao et al., 2009; Fenton et al., 2007; Grice et al., 2005; Liao et al., 2010; Riccardi et al., 2006; Wignall and Hallam, 1992; Wignall and Twitchett, 2002). In this study we have examined the 20 million year record of redox conditions spanning the Late Permian to Late Triassic based on conodont apatite geochemical data from three

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**Fig. 1.** Schematic maps of the study areas. (A) Palaeogeographic map illustrating the position of South China during the end-Permian extinction. Modified from (Erwin, 2006). (B) Map showing the studying sites. Modified from (Lehrmann et al., 1998). (C) Simplified chrono- and lithostratigraphy of South China during the P–Tr interval.

Permian and Triassic shallow-water sections in South China, (i.e. Meishan, Qingyan, Guandao, Fig. 1).

In comparisons to other sources of bio-apatite, such as ichthyoliths, conodont albid crown has been shown to provide a record of water column cerium anomalies ( $\Omega\text{Ce}$ ) and thorium/uranium ratios ( $\text{Th}/\text{U}$ ), little affected by diagenetic issues (Trotter and Eggins, 2006; Wright et al., 1987). Both  $\Omega\text{Ce}$  and the ratios of  $\text{Th}/\text{U}$  provide valuable indices for estimating past redox conditions in seawater. In oxic conditions, soluble  $\text{Ce}^{3+}$  is oxidized to precipitates of  $\text{CeO}_2$ , whilst other lanthanides are trivalent and unaffected by redox states (Liu et al., 1988). This results in negative  $\Omega\text{Ce}$  values in oxic oceans whilst anoxic oceans have zero or positive values (de Baar et al., 1988; Wright et al., 1987). Uranium has two different redox states: in oxic conditions  $\text{U}^{6+}$  is stable and highly soluble but it converts to the insoluble  $\text{U}^{4+}$  in anoxic waters whilst the solubility of  $\text{Th}$  is unaffected by redox changes. This results in an increase of  $\text{Th}/\text{U}$  ratios in anoxic facies (Wignall and Myers, 1988). If the extent of ocean anoxia becomes substantial, as suggested for the Early Triassic (Brenneke et al., 2011), then the ocean U reservoir will become depleted (Ehrenberg et al., 2008) leading to an increase in  $\text{Th}/\text{U}$  ratios.

## 2. Geological setting and studied sections

During the P–Tr transition, the South China Block was located near the equator in the eastern Palaeotethys Ocean (Fig. 1A). The intensively studied Meishan section crops out in the county of Changxing, about 300 km west of Shanghai city, eastern China (Fig. 1B). The Global Stratotype Section and Point (GSSP) of the P–Tr boundary is placed at the base of Bed 27c (Yin et al., 2001).

Abundant conodont species in the Changhsingian and Griesbachian stages enable correlation with sections elsewhere in South China (Jiang et al., 2007; Tong and Yang, 1998; Zhang et al., 2007).

The Qingyan section is located in the Huaxi District, 30 km south of Guiyang, capital city of the Guizhou Province, South China (Fig. 1B). During the Early–Middle Triassic, Qingyan was situated at the transition between Yangtze Platform in the north and Nanpanjiang Basin in the south (Feng et al., 1997; Mei and Zhou, 1992). The boundary zone was a long but narrow slope, about 400 km long and 25–70 km wide, and lay as an S-shaped belt from northeast to southwest and separated a shallow carbonate platform from a deep basin of mixed carbonate and clastic facies in southern Guizhou (Feng et al., 1997; Mei and Zhou, 1992; Wang, 1986). The uppermost Permian to Middle Triassic succession is exposed continuously at Qingyan (Fig. 1C, Chen et al., 2010). The Upper Permian sequence contains massive bioclastic limestone and cherty limestone (with cherty mudstone in the topmost part) that yield abundant fossils of corals, sponges, brachiopods and foraminifers. The Lower and Middle Triassic sequence is dominated mainly by thin to medium-bedded limestone and yellowish mudstone, yielding abundant conodonts and foraminifers (Ji et al., 2011; Song et al., 2011).

The Guandao section is situated in Bianyang town, 120 km south of Guiyang, South China (Fig. 1B). The Upper Permian to Upper Triassic sequence, carbon isotopic data, and fossil assemblage such as conodonts and foraminifers have been well documented (Lehrmann et al., 1998; Payne et al., 2006b; Payne et al., 2004; Payne et al., 2011; Song et al., 2011; Tong et al., 2007), and therefore, is addressed only briefly here. Guandao was located at the basin margin near the Great Bank of Guizhou, comprising two sections: the Lower Guandao section exposes Late Permian–Anisian (Middle Triassic) strata, and the Upper Guandao section

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