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Neotethys seawater chemistry and temperature at the dawn of the end Permian mass extinction

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ABSTRACT

The end of the Permian was a time of great death and massive upheaval in the biosphere, atmosphere and hydrosphere. Over the last decades, many causes have been suggested to be responsible for that catastrophe such as global warming, anoxia and acidification. The Gyanyima limestone block was an open ocean seamount in the southern Neotethys at subtropical latitude, and it affords us insight into open-ocean oceanographic changes during the end of the Permian. After careful screening using multiple tests, we reconstructed carbonate/seawater curves from the geochemical data stored in pristine brachiopod shell archives from the shallow water limestone of the Changhsingian Gyanyima Formation of Tibet. The reconstructed strontium isotope curve and data for the late Changhsingian are relatively invariant about 0.707013, but in the upper part of the succession the values become more radiogenic climaxing at about 0.707244. The $^{87}Sr/^{86}Sr$ curve and trend are similar to those observed for the Upper Permian succession in northern Italy, but dissimilar (less radiogenic) to whole rock results from Austria, Iran, China and Spitsbergen. The Ce/Ce* anomaly results ranging from 0.310 to 0.577 for the brachiopods and from 0.237 to 0.655 for the coeval whole rock before the event, and of 0.276 for whole rock during the extinction event, suggest normal redox conditions. These Ce* values are typical of normal open-ocean oxic water quality conditions observed in modern and other ancient counterparts. The biota and Ce* information clearly discounts global anoxia as a primary cause for the end-Permian biotic crisis. Carbon isotopes from brachiopod shells and whole rock are relatively invariant for most of the latest Permian interval, which is in stark contrast to the distinct negative carbon isotope excursion observed near and about the event. Estimates of seawater temperature at shallow depth fluctuated from 22.2 to 29.0 °C up to unit 8–2, and then gradually rise from 29.7 °C in unit 8–13 to values exceeding 35 °C at a stratigraphic level about 120 ky before the Permian–Triassic boundary, and just before the onset of the extinction interval. This dramatic increase in seawater temperature has been observed in global successions from tropical to mid latitude and from restricted to open ocean localities (e.g., northern Italy, Iran). The brachiopod archive and its geochemical proxies from Tibet support the paradigm that global warming must have been an important factor of the biotic crisis for the terrestrial and marine faunas and floras of the late Paleozoic world.

1. Introduction

The Permian was the theater of major global changes in the Earth's geodynamics, climate, and seawater/atmosphere geochemistry. In that changing world, the biotic response to flood basalt volcanism, high pCO_2 and associated rapid warming was dramatic (Retallack, 2013; Burgess et al., 2014). Facilitated by anoxia (Isozaki, 1997; table 2, Brand et al., 2012a) and/or ocean acidification (Clarkson et al., 2015), it culminated in the end Permian mass extinction (e.g., Erwin, 2006; Shen et al., 2011; Brand et al., 2012a).

Notwithstanding the plethora of studies focusing on the end Permian–Early Triassic time interval and trying to determine the causes of the extinction, so far no single cause has been identified as the leading one. However, global warming is considered by some authors as the leading cause for the biotic crisis at the end of the Permian (Kearsey et al., 2009; Brand et al., 2012a; Chen et al., 2013; Retallack, 2013; Burgess et al., 2014).

Here, we provide new information on the end Permian mass extinction from a different perspective, focusing on a biogenic archive

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covering the pre-extinction interval, and coming from a subtropical and open-ocean setting, which may be compared to the present-day Bermuda. In this perspective, after extensive screening, the biogenic archive was chosen to extract paleoenvironment information of fundamental importance in obtaining a pristine geochemical signal of the end Permian Neotethys seawater. This is why we selected brachiopods among the inhabitants of Paleozoic shallow-water benthic communities, because they were sensitive to global changes in the oceans during this extreme event. Also, their potential for storing pristine archival information is high, since they precipitate a low-Mg calcite shell that resists diagenesis and are found to be low metabolic and physiologically unbuffered organisms (Payne and Clapham, 2012). Furthermore, brachiopods are also known to precipitate their shell (secondary–tertiary layers) in isotopic equilibrium with ambient seawater (e.g., Lowenstam, 1961; Carpenter and Lohmann;, 1995; Brand et al., 2003; Parkinson et al., 2005; Brand et al., 2011, 2013). Thus, they are deemed one of the best carriers of primary proxies (trace elements, $\delta^{13}C$, $\delta^{18}O$, $^{87}Sr/^{86}Sr$, ΣREE and Ce*) able to unravel the seawater/atmosphere geochemistry and temperature during the Late Permian (e.g., Veizer et al, 1999; Brand et al., 2003; Korte et al., 2005; Zaky et al., 2015).

A limitation of the brachiopod archive is its discontinuous record due to the Signor–Lipps effect (Signor and Lipps, 1982) and to lithofacies change, thus resulting in an absence or scarcity of specimens in some sediments of the uppermost Permian succession (e.g., Angiolini et al., 2010). To overcome this difficulty, we selected the Gyanyima section in southwestern Tibet (Shen et al., 2010; Wang et al., 2010), which is characterized by high and continuous sedimentation during the latest Permian and by biostratigraphically constrained and well-preserved brachiopods up to a few meters below the Permian–Triassic boundary.

This leads us to the second focus of our research: the latest Permian interval or what we call the dawn of the extinction, which may have lasted hundreds to tens of thousands of years (Shen et al., 2011; Brand et al., 2012a; Burgess et al., 2014), to infer what seawater conditions were like immediately prior to the extinction and the implications about the causal mechanism(s) and the timing of the extinctions itself. In particular, among the parameters that may have changed dramatically, we are mostly interested to investigate the temperature rise and the oxygenation state of seawater leading up to this most important event. Finally, the third focus concerns the settings of end Permian sequences. Many studies have described the end Permian crisis in equatorial settings such as South China, Iran and northern Italy (e.g., Shen et al., 2011; Brand et al., 2012a; Schobben et al., 2014 and references therein), but few describe in any detail what happened at higher latitudes (Shen et al., 2006).

The aim of our study is to investigate the geochemistry (trace elements, $\delta^{13}C$, $\delta^{18}O$, $^{87}Sr/^{86}Sr$, ΣREE and Ce*) of brachiopod shells from the Gyanyma section located at subtropical latitude in the southern Neotethys, to 1) interpret their biochemical response before and at the onset of the latest Permian event, 2) evaluate and constrain in time the temperature rise and seawater redox, and 3) garner a better understanding of how Neotethys seawater and/or Late Permian atmosphere may have changed before and during the Earth's greatest biotic crisis.

2. Geological setting

The Gyanyima section (30°43′13.5″N and 80°41′42.4″E) was studied by a number of authors (Wang and Xu, 1988; Guo et al., 1991; Shen et al., 2001, 2003, 2010; Crasquin-Soleau et al., 2007; Wang et al., 2010). It is located in Burang County, Ngari Region in southwestern Tibet, China, and is about 50 km northwest of the Town of Burang (Fig. 1). The section consists of 350 m of Lopingian–Lower Triassic reefal and bioclastic limestones, which outcrops 30–50 km south of the Indus-Tsangbo (= Yarlung–Zangbo) Suture Zone that separates the Lhasa Block from the Himalaya Tethys Zone to the south. Based on its reefal carbonates and interbedded thick basalts, the large block that contains the Gyanyima section has been interpreted as a carbonate platform on a Neotethyan seamount (Shen et al., 2001, 2003, 2010).

The investigated section (Fig. 2) comprises the Lopingian Gyanyima Formation that is rich in foraminifers, corals, brachiopods and ostracods, and the overlying Triassic Lanchengquxia Formation. The Gyanyima Formation is subdivided into 10 units for a total thickness of about 310 m (Fig. 2); units 1, 6, 9 and 10 are dominated by reefal limestone (bafflestone and framestone) with rare bioclastic limestone (packstone and grainstone). Unit 2 contains micritic limestone; units 3 and 4 consist of bioclastic limestone; unit 5 consists of submarine basalt; unit 7 comprises micritic limestone, with shale and reefal limestone; unit 8 and part of unit 9 contain cherty limestone. In particular, the limestone from unit 9 (sample T-9-33) to the base of the overlying Lanchengquxia Formation (unit 11; Y-11-1) consists of bioclastic packstones and grainstones with brachiopods, gastropods, echinoderms, bryozoans, foraminifers, green algae, and *Tubiphytes*, and alternating boundstone dominated by corals and sponges. These biofacies suggest infralittoral shallow to open subtidal environments around fair-weather wave base, and well oxygenated and normal salinity seawater during deposition of the Gyanyima sediments (see supplementary Fig. 2). The Triassic samples from unit 11 (Y-11-2 to Y-11-4) consist of fine-grained grainstone with crinoids, bivalves, ostracods, calcispheres, and widespread Fe-oxide covering the bioclasts, the matrix, and the syntaxial cements and locally concentrated along hardground/firmground thin horizons. These observations and the biogenic allochems record a deepening trend below fair-weather wave base, a crisis in the carbonate factory and lower sedimentation rates at the Permian-Triassic boundary in the Tibetan seamount. All samples from units 9 to 11 (sample 11-4) show the same marine early diagenetic paragenesis with nonluminescent scalenohedral to equant calcite cement. Above level Y-11-34, the sediments are pervasively dolomitized (equidimensional mosaics of zoned, Fe-rich dolomitic crystals), with microbialites. In fact, Shen et al. (2010, p. 4) reported thrombolites and stromatolite-like structures that possibly suggest restricted peritidal environments. However, due to the pervasive dolomitization, it is difficult to evaluate the original depositional depth of unit 11.

Except for the first meter of unit 11, we confirm that the overall succession was deposited in a normal marine, subtidal environment as suggested by Shen et al. (2010) and Wang et al. (2010). Wang et al. (2010) described a rich foraminiferal fauna from the Gyanyima Formation and subdivided it into two biozones: (1) a lower *Colaniella parva* Biozone, and (2) an upper *C. parva–Dilatofusulina orthogonios–Urushtenella* Biozone. The upper biozone is late Changhsingian (Wang et al., 2010), and consequently that infers a lower Changhsingian age for the lower biozone. In fact, a recent discussion (Vachard, 2014) on the distribution of *C. parva* underscores the fact that it has not been found in rocks older than late Changhsingian. This suggests that the sediments of the Gyanyima Formation may be limited to the upper Changhsingian, as *C. parva* occurs in its basal unit. However, in the absence of other biostratigraphic data, we prefer to maintain a conservative approach, and follow Wang et al. (2010) who considered the 310 m sequence belonging to the Changhsingian.

Conodonts are rare in the Permian part of the Tibetan succession possibly due to the reefal environment (Shen et al., 2010), but they become abundant in the Triassic Lanchengquxia Formation. More specifically, the abundance of the Griesbachian (Induan) conodonts *Clarkina carinata* and *Clarkina tulongensis* 1.3 m above the base of the Lanchengquxia Formation allows us to tentatively constrain the Permian–Triassic boundary at the Gyanyima section between horizons Y-11-1 and Y-11-2 (Shen et al., 2010, fig. 6; Appendix 3).

3. Materials

Rhynchonelliformea brachiopods and host limestone samples were collected from a number of horizons (Appendix 1B and 2) of the