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Changes in depth-transect redox conditions spanning the end-Permian mass extinction and their impact on the marine extinction: Evidence from biomarkers and sulfur isotopes

Kunio Kaiho [a,*], Masahiro Oba [a], Yoshihiko Fukuda [a], Kosuke Ito [a], Shun Ariyoshi [a], Paul Gorjan [b], Yuqing Riu [a], Satoshi Takahashi [a], Zhong-Qiang Chen [c], Jinnan Tong [c], Satoshi Yamakita [d]

[a] Institute of Geology and Paleontology, Tohoku University, Sendai 980-8578, Japan
[b] Department of Earth and Planetary Science, Washington University, St. Louis, MO 63130, USA
[c] State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, Wuhan 430074, China
[d] Department of Earth Science, Faculty of Education and Culture, Miyazaki University, Miyazaki 889-2192, Japan

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ABSTRACT

Changes in redox conditions during the Changhsingian to Griesbachian spanning the end-Permian mass extinction were recently reported based on analyses of organic molecules. We provide more precise organic-molecular data, that detail redox conditions spanning the end-Permian mass extinction at different palaeowater depths in the neritic Palaeotethys (estimated water depths: 10, 40, 100, and 200 m; Bulla, Huangzhishan, Meishan, and Chaohu sections, respectively) during this period. Here we propose that a change from occasional euxinia to anoxia in the shallow Palaeotethys occurred at the time of the mass extinction intercalated with oxic pulses. The second extinction at 0.7 myr after the main extinction was also caused by anoxia. New and published sulfur-isotope ratios ($^{34}S/^{32}S$) measured in carbonate-associated sulfate from the neritic Palaeotethys and in sulfide from pelagic central Panthalassa sediments show high values during the Changhsingian, consistent with the development of euxinia. The mass extinction coincided with a global fall in $\delta^{34}S$ values, as well as a shift in $\delta^{13}C$ values, indicating a global oxidation of H_2S. This organic and isotopic geochemistry implies that accumulation of hydrogen sulfide in intermediate and deep waters followed by oxidation of hydrogen sulfide led to dissolved oxygen consumption, surface-water anoxia, and acidification, resulting in the end-Permian mass extinction in the seas.

1. Introduction

The largest mass extinction in the Earth's history occurred at the end of the Permian. The end-Permian mass extinction has been tied to the development of anoxic or euxinic (sulfide-bearing) waters (Wignall and Twitchett, 1996, 2002; Isozaki, 1997; Grice et al., 2005; Kaiho et al., 2006; Gorjan et al., 2007; Cao et al., 2009; Algeo et al., 2011b), which accumulated in the warming late Permian Palaeotethys Ocean, as implied by the increased concentrations of aryl isoprenoid and isorenieratane, indicating photic zone euxinia, in South China (Grice et al., 2005; Cao et al., 2009), and low pristane/phytane ratio in South China (Cao et al., 2009) in ~100 m water depths in the low-latitude eastern Palaeotethys Ocean ~1 myr before the mass extinction. A positive shift in $\delta^{34}S_{CAS}$ during the Changhsingian was also attributed to the increased production of euxinic waters before the mass extinction (Kaiho et al., 2002; Newton et al., 2004). However, anoxic or euxinic waters also occurred during the mass extinction in the low-latitude Panthalassic Ocean based on the deep-sea pyrite framboid morphology (e.g., Wignall et al., 1998; Wignall et al., 2010; Algeo et al., 2010, 2011b) and concentrations of Mo, V, and U (Algeo et al., 2011b). In high-latitude Panthalassic shallow seas, photic zone euxinia coincided with the end-Permian extinction in Western Canada (Hays et al., 2007) and a decrease in the pristane/phytane ratio (from 1.5 to 1.1) occurred spanning the extinction horizon in Spitsbergen (Nabbefeld et al., 2010b). There is no consensus on the correlation of anoxia and euxinia development between the Palaeotethys and Panthalassic Oceans. Development of euxinia may have occurred earlier in the Palaeotethys Ocean than the Panthalassic Ocean. This paper clarifies the timing and water-depth distribution of euxinia and anoxia in the Palaeotethys Ocean and identifies differences between the Palaeotethys Ocean and the Panthalassic Ocean.

The extinction appears to have occurred rapidly just before the Permian/Triassic (P/Tr) boundary (Jin et al., 2000; Kaiho et al., 2006, 2009). This extinction has been hypothesized to be the result of H_2S release from deeper waters to oxic shallow waters, where most marine organisms live, and/or the atmosphere, which coincides with a sharp

* Corresponding author.
E-mail address: kaiho@m.tohoku.ac.jp (K. Kaiho).

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drop in $\delta^{34}S_{CAS}$ (Newton et al., 2004; Kump et al., 2005; Kaiho et al., 2006; Gorjan et al., 2007. Clapham and Payne (2011) and Payne and Clapham (2012) hypothesized that the extinction was driven by ocean acidification. A second extinction occurs in the earliest Triassic 0.7 myr after the main extinction (Huang et al., 2011).

Here we reveal the relationships between the input of euxinic waters into shallow shelf waters, $\delta^{34}S$ values, and the two-step extinctions by a depth-transect study.

2. Studied sections and stratigraphic settings

We sampled from the P/Tr boundary sections at Chaohu (by Kaiho with Chen and Tong), Meishan (by Kaiho with Chen and Song), Huangzhishan (by Kaiho, Oba, and Takahashi with Song), Bulla (by Kaiho with Chen), and Ubara (by Kaiho and Yamakita; Fig. 1). During the Late Permian to Early Triassic, the Chaohu, Meishan, and Huangzhishan areas were located in the South China Block, which was situated in low-latitudes, in the eastern Palaeotethys Ocean (Ziegler et al., 1998; Fig. 1). Bulla was located in the low-latitude western Palaeotethys Ocean and Ubara was in the central Panthalassic Ocean (Ziegler et al., 1998). Palaeowater depths of these sections were estimated at 10 m for Bulla, because of the presence of oolites, 40 m for Huangzhishan, 100 m for Meishan, and 200 m for Chaohu. The palaeowater depths for the latter three sections were inferred based on palaeogeographic reconstructions by Chen et al. (2010, 2011).

The P/Tr succession in the Meishan section was deposited on a carbonate ramp (Zhang et al., 1996). The lithology is composed of Upper Permian bioclastic limestone, a white claystone bed (ash layer; extinction horizon), gray claystone, marlstones bearing the P/Tr boundary in its middle part, mudstones, alternation of mudstone and limestone (1.2 myr after the extinction), and limestone of Griesbachian age in ascending order (Chen et al., 2002, 2007). The base of the white clay (bed 25) is taken as the 0-m point in the measured section for this study (Fig. 2b).

The P/Tr boundary successions are exposed in the North Pindingshan and West Pindingshan sections of the Chaohu area, Anhui Province, China. Lithologically, the Changhsingian sequence is composed of dark gray mudstone overlain by a white clay and gray marl bed similar to the P/Tr boundary beds of the GSSP in the Meishan section, which are overlain by alternating mudstones and limestones of the Griesbachian (Fig. 2). Correlation of P/Tr boundary beds between Chaohu and Meishan is strengthened by the common presence of conodont zones in both sections (Tong et al., 2004, 2005). The base of the white clay just above the mass extinction horizon is taken as the 0-m point in the logged section for this study.

The Huangzhishan section is located in the Huangzhishan town of Huzhou City, in northwestern Zhejiang Province, South China, 60 km southeast of the Meishan section. The latest Permian succession comprises bioclastic limestone of the Changhsing Formation. The overlying unit, the Huangzhishan Formation (Chen et al., 2009), is composed of dark gray mudstone, gray mudstone, and marlstone. The Yinkeng Formation comprises mudstone with a claystone bed in its basal part. The overlying Helongshan Formation is composed of limestone. Correlation of P/Tr boundary beds between Huangzhishan and Meishan is

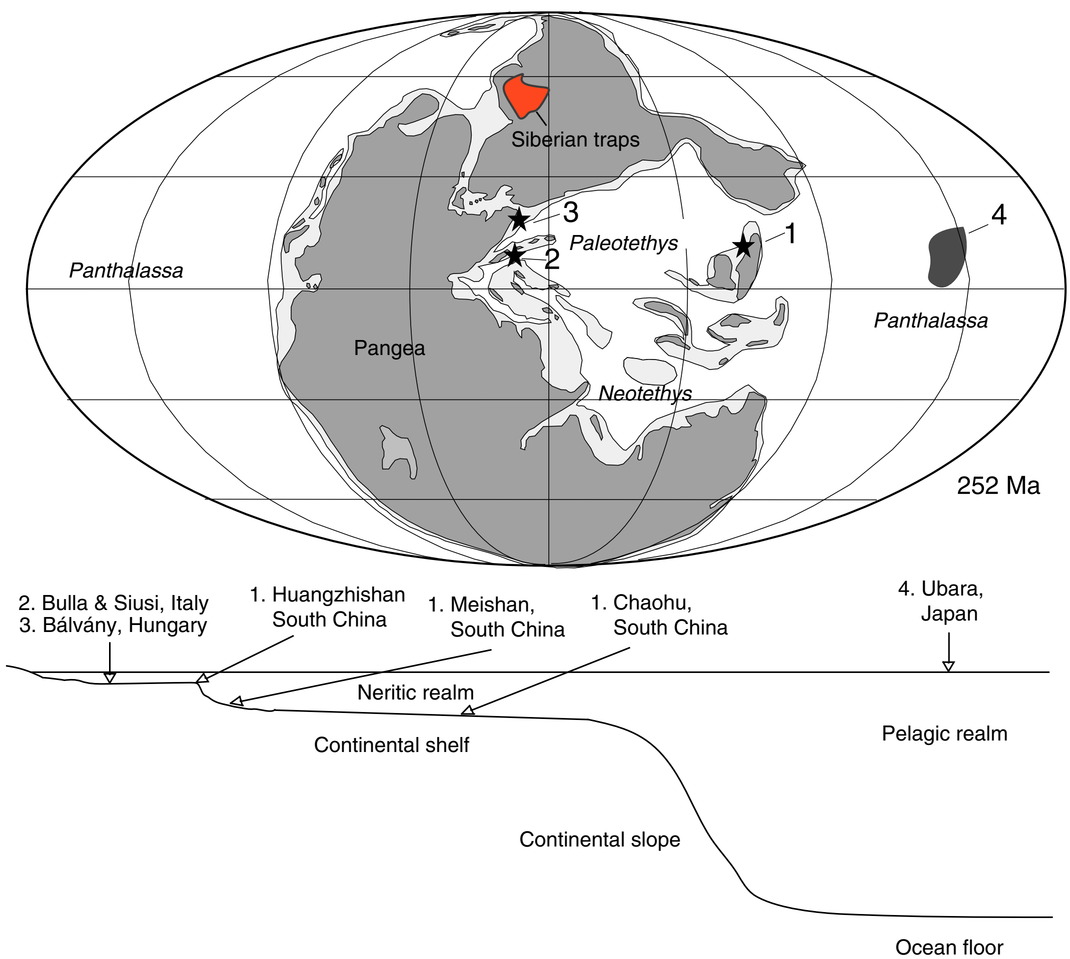

Fig. 1. Palaeogeographic map showing the study sites and reference sections [the Meishan and Huangzhishan sections in southern China (1), the Bulla and Siusi sections, Italy (2), Bálvány section, Hungary (3), and the Ubara section, Japan (4)], and the Siberian traps during the P/Tr transition [base map follows Ziegler et al., 1998]. Depositional depths of the sections are also shown.