



Bioessential element-depleted ocean following the euxinic maximum of the end-Permian mass extinction



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ABSTRACT

We describe variations in trace element compositions that occurred on the deep seafloor of palaeo-superocean Panthalassa during the end-Permian mass extinction based on samples of sedimentary rock from one of the most continuous Permian–Triassic boundary sections of the pelagic deep sea exposed in north-eastern Japan. Our measurements revealed low manganese (Mn) enrichment factor (normalised by the composition of the average upper continental crust) and high cerium anomaly values throughout the section, suggesting that a reducing condition already existed in the depositional environment in the Changhsingian (Late Permian). Other redox-sensitive trace-element (vanadium [V], chromium [Cr], molybdenum [Mo], and uranium [U]) enrichment factors provide a detailed redox history ranging from the upper Permian to the end of the Permian. A single V increase (representing the first reduction state of a two-step V reduction process) detected in uppermost Changhsingian chert beds suggests development into a mildly reducing deep-sea condition less than 1 million years before the end-Permian mass extinction. Subsequently, a more reducing condition, inferred from increases in Cr, V, and Mo, developed in overlying Changhsingian grey siliceous claystone beds. The most reducing sulphidic condition is recognised by the highest peaks of Mo and V (second reduction state) in the uppermost siliceous claystone and overlying lowermost black claystone beds, in accordance with the end-Permian mass extinction event. This significant increase in Mo in the upper Changhsingian led to a high Mo/U ratio, much larger than that of modern sulphidic ocean regions. This trend suggests that sulphidic water conditions developed both at the sediment–water interface and in the water column. Above the end-Permian mass extinction horizon, Mo, V and Cr decrease significantly. On this trend, we provide an interpretation of drawdown of these elements in seawater after the massive element precipitation event during the end-Permian maximum development of the reducing water column. A decrease in the Mo/U ratio despite enrichment of Mo and U also supports that of Mo. Calculations of the total amounts of these elements precipitated compared with the global seawater inventory suggest that when more than 6–10% of the global ocean became euxinic as much as the study section, most of the dissolved elements would precipitate into sediments, resulting in a global element-depleted seawater condition. Mo, V, and Cr act as bioessential elements for both primary producers and animals. The continuing reducing water column and the lack of bioessential elements could have had a considerable effect on primary producer turnover and marine life metabolism not only in the pelagic environment, but also in surrounding marine environments.

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1. Introduction

The largest biotic catastrophe, end-Permian mass extinction was associated with development of oceanic anoxia (e.g., [Wignall and](#)

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[Twitchett, 1996](#)). Recent research has demonstrated that many shallow-marine platforms of Late Permian and Early Triassic age experienced euxinic conditions, as evidenced by blooms of anaerobic green sulphur bacteria (e.g., [Grice et al., 2005](#); see [Fig. 1](#)) and enrichments of redox-sensitive elements (e.g. [Fio et al., 2010](#); [Fig. 1](#)). Among redox-sensitive elements, uranium increased in

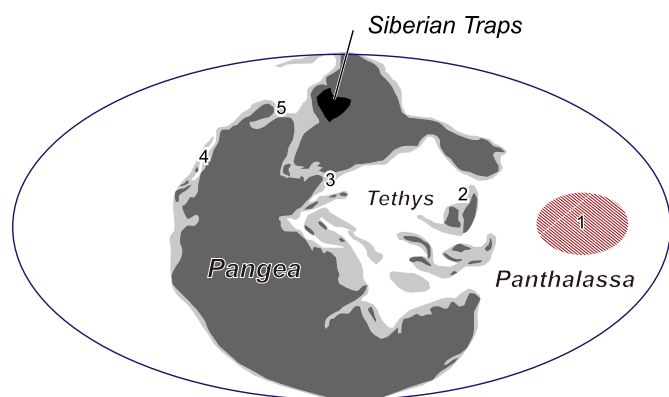


Fig. 1. Palaeogeographic map showing the location of the study sections. Akkamori section of Japan (1), Meishan section of South China (2), Velebit Mountain section, Croatia (3), Peace River Basin section, Canada (4) and Sverdrup Basin section, Canada (5). The base map is after Ziegler et al. (1998). Organic geochemical evidences of anaerobic green sulphur bacterial bloom have been reported from the eastern and southern shallow Tethys (2; Grice et al., 2005) and eastern margin of Panthalassa (4; Hays et al., 2007) for examples. Enrichments of redox-sensitive elements also have been reported from western shallow Tethys (3; Fio et al., 2010) and western Pangean shallow shelf (5; Grasby and Beauchamp, 2009; Grasby et al., 2011; Algeo et al., 2012).

sediments and this ultimately resulted in uranium drawdown, suggested by a decrease in the sedimentary uranium isotope ratio ($^{238}\text{U}/^{235}\text{U}$) and an increase in the thorium/uranium (Th/U) ratio from shallow marine carbonates (Brennecke et al., 2011).

The environmental conditions existing in Permian–Triassic low-latitude pelagic Panthalassa are recorded in pelagic sedimentary rocks within the accretionary complexes of Japan (Fig. 1; Matsuda and Isozaki, 1991). Their lithological sequence consists of upper Permian bedded chert, uppermost Permian siliceous claystone and uppermost Permian to lowermost Triassic carbonaceous black claystone (Yamakita, 1987; Isozaki, 1994, 1997; Yamakita et al., 1999; Takahashi et al., 2009, 2010). Recent biostratigraphic and carbon isotope studies suggest that the widely occurring mass-extinction event boundary and the biostratigraphic Permian–Triassic boundary (PTB) occur at the base of the black claystone and within the black claystone, respectively (Fig. 2; Takahashi et al., 2009, 2010; Sano et al., 2012). The upper Permian grey-coloured chert and overlying claystones have been interpreted to have formed under anoxic water conditions (Isozaki, 1997). Moreover, geochemical studies have clarified some details of the deep-sea redox conditions. Low manganese (Mn) concentrations (Kato et al., 2002) and the existence of reduced iron (Fe; Matsuo et al., 2003) in the upper Permian to lower Triassic sedimentary rocks (Ubara and Tenjinmaru sections) indicate somewhat reducing bottom water conditions. Algeo et al. (2011) suggested that the depositional environment did not reach euxinia, but was suboxic, based on analytic results of low redox-sensitive element concentrations (vanadium [V], molybdenum [Mo] and uranium [U]) in latest Permian to earliest Triassic sedimentary rocks from the Ubara and Gujo-Hachiman sections. However, the detailed processes of the redox variations remain uncertain, partly because most of the previously studied PTB sections have some problems of lithological continuity, such as a lack of Induan Age fossil occurrences and small faults (see data compiled in Takahashi et al., 2009 and Sano et al., 2012). This paper describes variations in the compositions of trace elements from a continuous deep-sea PTB section, considering biostratigraphic, lithostratigraphic, and chemostratigraphic evidence (Akkamori section 2 [Am-2]; Takahashi et al., 2009, 2010, 2013), and its environmental records during the end-Permian mass extinction and its aftermath. Geological setting and analytical methods were provided in the Supplementary Online Material (SOM).

2. Results

Selected results of the EDXRF and ICP-MS analyses are shown in Fig. 2, Fig. 3, and SOM. In all of the samples from the study section, SiO_2 is the major component (75.20–95.11%) and Al_2O_3 (2.19–6.31%) is the second highest component. These two components vary inversely (Figs. 2 and 3; correlation coefficient $R = -0.92$). Manganese oxide (MnO) and the enrichment factor of Mn (Mn_{EF} ; this normalisation is described in SOM) have small values of 0.0038–0.0281% and 0.18–0.73, respectively (Fig. 3). Similar vertical variation (coefficient = 0.86) ranging from 0.12–4.47% was seen in iron oxide (Fe_2O_3) and the enrichment factor of Fe (Fe_{EF}) was 0.12–1.59 (Fig. 2). The U and the enrichment factor of U (U_{EF}) increase from the basal bed (Bed 3) of the study section to the top of the siliceous claystone (Bed 29; 1.32–13.29 ppm and 1.57–10.46, respectively). Above Bed 29, U and U_{EF} have high values of 6.32–19.12 ppm and 4.35–11.03, respectively, within the black claystone beds (Beds 30–32). The V and the enrichment factor of V (V_{EF}) increase within the chert beds (Beds 6–14), with peak values in Bed 12 (2045.8 ppm, 91.47). After decreasing, V and V_{EF} again rise from Bed 20 and peak at the base of the black claystone (basal 0–1 cm of Bed 30; 1366.13 ppm, 28.69). These values then decrease again and become low within the black claystone (Beds 30–32). The chromium (Cr) and enrichment factor of Cr (Cr_{EF}) generally rise from Bed 15 (12.60 ppm, 0.49) to Bed 29 (239.58 ppm, 6.36) with a trough at Beds 24–26. They decrease drastically at the base of the black claystone and then remain low (20.92–74.14 ppm, 0.57–2.01) throughout the black claystone (Beds 30–32). The Mo and the enrichment factor of Mo (Mo_{EF}) values constantly increase upward through the basal chert beds (Beds 3–14; 2.73–114.22 ppm, 6.06–256.80, respectively). The values increase farther from the grey siliceous claystone of Bed 20, with a trough at Beds 28–29 (38.43 ppm, 56.43), and peak at the base of the black claystone (0–1 cm of Bed 30; 5074.42 ppm, 7602.35). Mo and Mo_{EF} then decrease into the black claystone horizon at ~30 cm above its base (41.50 ppm, 58.95) and have values within 20.79–84.10 ppm and 23.67–106.76 in the overlying black claystone strata (to Bed 32). The Ce anomaly (Ce/Ce^*) varies between 0.77 and 1.16 throughout the section (Fig. 3). The sulphide sulphur (S_{Sulphide}) contents were normalised by total organic carbon (TOC; C_{Org} ; Takahashi et al., 2009) into $S_{\text{Sulphide}}/\text{C}_{\text{Org}}$ ratio (Fig. 2). The ratio was relatively higher within Beds 3–28 (3.11–56.51), relatively lower (0.52–1.46) in Bed 29 and the basal 20 cm of Bed 30, and then increased toward Bed 31 (11.93).

3. Discussion

3.1. Redox evaluations

3.1.1. Sulphur/carbon ratio

The $S_{\text{Sulphide}}/\text{C}_{\text{Org}}$ ratio of normal marine sediment is around 0.4 in organic-carbon-limited sulphate-reduction systems, whereas the values of euxinic and anoxic marine sediment (e.g., Black Sea) exceed 0.4, except in the case of a low reactive iron supply that creates pyrite minerals (Berner and Raisewell, 1983; Berner, 1984; Raisewell, 1986; Raiswell and Berner, 1985). Considering these criteria, the $S_{\text{Sulphide}}/\text{C}_{\text{Org}}$ ratios in the Am-2 section are high in Beds 3–29, the basal 20 cm of Bed 30, and the 63–100 cm horizon of the black claystone (Beds 30–32), suggesting anoxic–euxinic bottom water conditions (Fig. 2). The significantly low S_{Sulphide} in the 30 cm horizon and low $S_{\text{Sulphide}}/\text{C}_{\text{Org}}$ in the 32–57 cm horizon of Bed 30 have two possible interpretations: 1) an oxic–suboxic depositional environment, or 2) reactive iron (as the main host material of S) was depleted in the deep-sea. Considering coinstantaneous geochemical data, the latter is plausible. Because these horizons have a low Fe_{EF} (Fig. 2), there is anoxic evidence in the high TOC

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