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Oceanic pollution at the Permian-Triassic boundary in pelagic condition from carbon and sulfur stable isotopic excursion, Southwest Japan

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ISHIGA Hiroaki, ISHIDA Kotaro, SAMPEI Yoshikazu, MUSASHINO Makoto, YAMAKITA Satoshi, KAJIWARA Yoshimichi and MORIKIYO Toshiro (1993) Oceanic pollution at the Permian-Triassic boundary in pelagic condition from carbon and sulfur stable isotopic excursion, Southwest Japan. *Bull. Geol. Surv. Japan*, vol. 44(12), p. 721–726. 2fig.

Abstract: Non-carbonate organic $\delta^{13}C$ and sulfide $\delta^{34}S$ isotopic curves were examined in the Tenjin'maru section, Tokushima Prefecture and in the Sasayama section, Hyogo Prefecture, Southwest Japan. Both section show similar excursions. 1) Excursion of $\delta^{34}S$ indicates change of oceanic condition from Middle Permian oxic to Upper Permian and Lower Triassic anoxic condition. 2) But the value of $\delta^{34}S$ at the Permo-Triassic boundary represented by black organic mudstones, shows rather light value hitherto reported in the Tenjin'maru section and it has also proved in the Sasayama section. 3) Values of $\delta^{13}C$ in Middle Permian cherts vary, and those in the Upper Permian cherts show uniform, approximately -30. The $\delta^{13}C$ values at in the siliceous claystones below and above the boundary show negative excursion. 4) According to the excursion in the Tenjin'maru section, the $\delta^{13}C$ values in the black organic mudstones indicate positive excursion, which could be a probable methane fermentation at the bottom sediments in anoxic condition. Possible reactions are examined for decreasing of $\delta^{34}S$ value at this anoxic condition and for the inverse correlation of $\delta^{34}S$ and $\delta^{13}C$ recorded in the black organic mudstone.

1. Introduction

The Permian and Triassic (P–Tr) boundary was storaged in bedded cherts of Southwest Japan and successive records of change of oceanic condition are supposed to be in the sequences. This is because bedded cherts were deposited under pelagic condition where very low sedimentation (several mm per 1000 years) that reflects the global change (Hori and Maruyama, 1992). The P–Tr boundary is marked by black organic mudstones which consist of high content of silica (80%) and organic carbon (2%) in average (Yamakita, 1987; Ishida *et al.*, 1992). Although the tentatively fixed boundary by conodonts (Yamakita, 1993) involved inconsistency with radiolarian extinction (Ishiga, 1992), duration of the oceanic pollution of the Latest Permian to Smithian (Early Triassic) can be estimated at least 10 Ma (Isozaki, 1993).

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2. Section examined

The sequences examined here are Sasayama in Hyogo Prefecture and Tenjin'maru in Tokushima Prefecture. The former covers whole history of the Middle Permian to Smithian (Lower Triassic) (Ishida *et al.*, 1992), and the latter covers Uppermost Permian to Smithian (Yamakita, 1993). In both sections, the Upper Permian cherts drastically change into siliceous claystones which come up to meet the P–Tr boundary organic mudstones (or organic cherts in the Sasayama section) (Fig. 1). The organic mudstones again change into siliceous claystones and/or thinly alternated beds of cherts and claystones, then change upward into bedded cherts. Missing of cherts below and above the P–Tr boundary shows extinction of radiolarians. Color change clearly appeared in the Sasayama section from red cherts of the Middle Permian into grey to black cherts of the Upper Permian which indicates sedimentary environmental change from oxic to anoxic, and the anoxic condition lasted during deposition of Smithian grey claystones and cherts (Ishiga, 1992).

3. Organic geochemical feature of black organic mudstones

According to Ishida *et al.* (1993), the organic mudstones of the Tenjin'maru section contains no significant type III kerogen derived from higher plants and SEM observation clarified supposed existence of spherical bacterial organic materials less than 1 μm in diameter. Examined biomarkers indicate that weak peak of Pristane and Phytane was discriminated, and the ratio Pristane/Phytane shows under 0.2 (Ishida *et al.*, 1993). This points the organic mudstones were apparently formed under anoxic condition. The sterane ratio of 20S/(20S+20R) is 0.2 to 0.3 which suggests that these organic materials have not been suffered maturation which could correspond condition under 120–130°C.

4. Analytical method

The δ^{34}S values of the sulfide sulfur from the rock samples were examined by the Kiba reagent method and analysed by the Finnigan Mat delta-E mass spectrometer at Tsukuba University. Detailed method was indicated in Kajiwara and Kaiho (1992). Organic carbon samples separated by disolution of rocks in 6N hydrochloric acid were used for the δ^{13}C examination. Analyses by the Nier-McKinney type mass spectrometer, Varian Mat 250 at Shinshu University were carried out. Isotopic compositions are given with respect to the international standard PDB for carbon and CDT for sulfur.

5. Excursion of δ^{34}S and δ^{13}C curves

The major excursion of δ^{34}S curve in the Sasayama section (Kajiwara *et al.*, in preparation, a) shows dramatic change from oxic to anoxic condition in the upper Permian, which apparently coincides with the color change of cherts. Sudden drop of these values in the P–Tr boundary organic mudstones is apparent in the Sasayama section and this record was also indicated in the Tenjin'maru section (Ishiga and Yamakita, 1993). This isotopic excursion simply indicating oxic condition (Kajiwara, 1992; Kajiwara *et al.*, in preparation, b) coincides to the rise of δ^{13}C values, but the supposed environment is opposed to that proved from the geochemical analysis of the mudstones (Ishida *et al.*, 1993) mentioned later.

The excursion of the δ^{13}C in the Sasayama section indicates periodic drop of values (less than −35‰) during Middle Permian and also shows gradual convergence to the values around −30‰ in the Upper Permian.

Sudden drop also occurred in siliceous claystones below the P–Tr boundary. Although the values change from −35 to −30‰ in both Upper Permian and Lower Triassic siliceous claystones in the Sasayama section, tendency of this drop is similar with that in the Tenjin'maru section. So, record of the δ^{13}C values of the Tenjin'maru section might make up lack of data of the boundary mudstones in the Sasayama section (Fig. 2), which indicate astonishing rise at this stage. Inverse correlation of excursion of δ^{34}S and δ^{13}C values in the P–Tr boundary suggests appearance of peculiar condition in bottom sediments, and discussion leading to a hypothesis for this phenomenon is required.

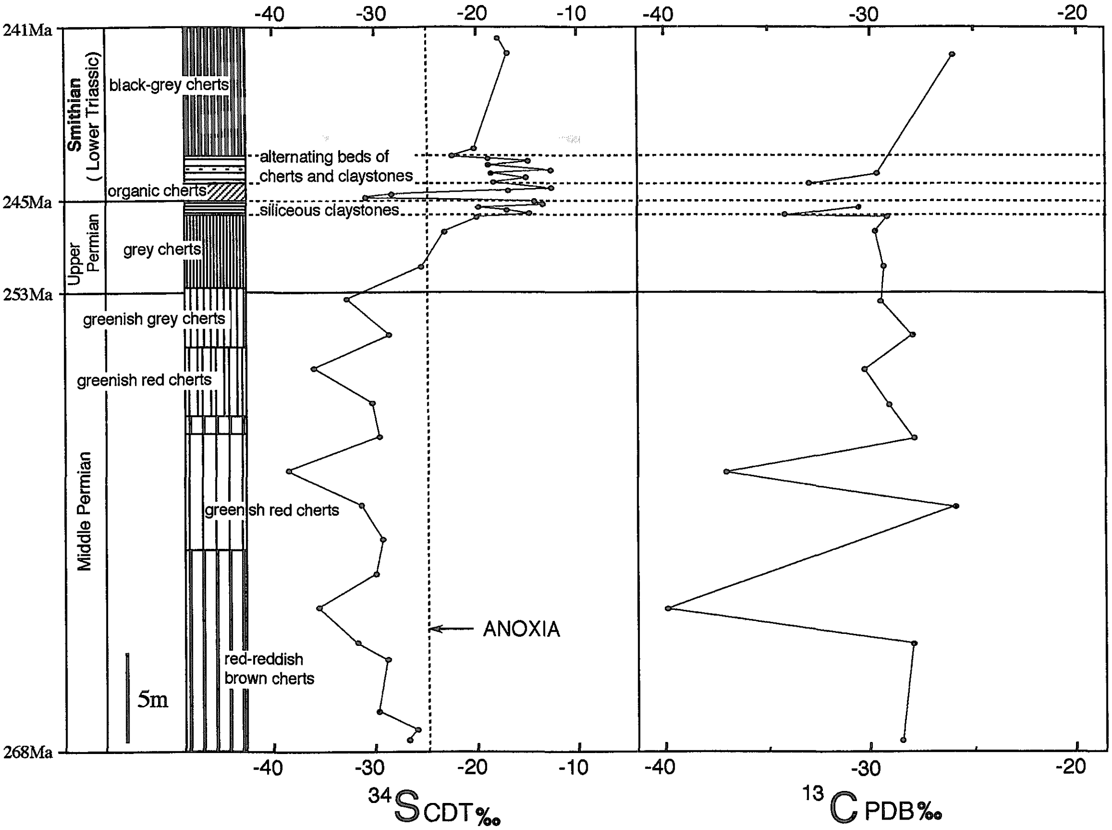

Fig. 1 $\delta^{34}S$ and $\delta^{13}C$ isopopic curves in the Middle Permian to Smithian (Lower Triassic) bedded chert sequence in Sasayama section (Ishida *et al.*, 1992), Hyogo Prefecture, Southwest Japan.

6. Discussion

The peculiar condition represented by the geochemical analysis to the excursion of $\delta^{34}S$ values needs explanation of organic reaction in anoxic ocean or interface between the bottom sediments and ocean. If sedimentation rate was very low in the boundary organic mudstones, then the organic materials supplied at the P–Tr boundary might have occasional exposure to decomposition. And the reduction of organic carbon as CO_2 and CH_4 can be inspired, because the unresolved complex mixture of the organic mudstones are mainly composed of bacterial origin (Ishida *et al.*, 1993). Supposed reaction of methane fermentation is below after Jeris and McCarty (1965).

$CH_3COOH = CH_4 + CO_2$

$CO_2 + H_2O = H^+ + HCO_3^-$

The rise of the $\delta^{13}C$ values could be caused by commencement of bacterial methan fermentation which produces a marked carbon isotopic fractionation, which is known to give light CH_4 $\delta^{13}C$ values of between -50 to -100% and, leaving carbon enriched in the heavy isotope (Bowen, 1988; Dimitrakopoulos and Muehlenbachs, 1987). This geochemical change played an important role in formation of the organic mudstones to explain sharp drop of $\delta^{34}S$ values in the anoxic box. Then in the anoxic, H_2S–rich floor, the following reactions are supposed (Kimoto and Fujinaga, 1990) which produce sulphur and sulphur compounds.

$H_2CO_3 + H_2S = HCOOH + S + H_2O$

$HCOOH + H_2S = H_2CO + S + H_2O$

And a successive second order cycle of sulphur or sulfate reduction giving light $\delta^{34}S$ values in the P–Tr boundary. This is supposed mechan-

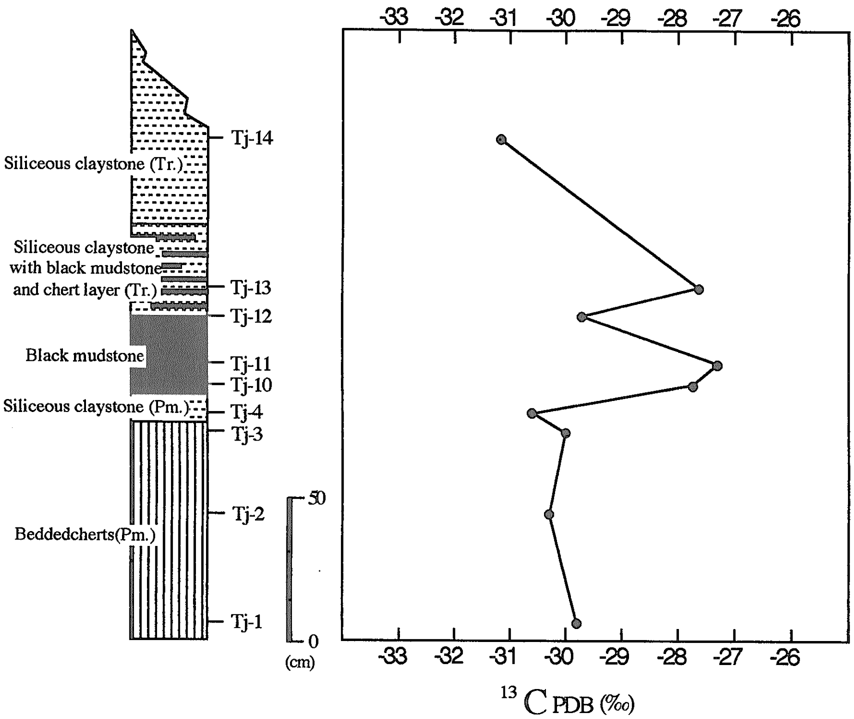

Fig. 2 δ^{13}C isopopic curves in the Upper Permian (Pm) to Lower Triassic (Tr) bedded chert sequence in the Tenjin'maru section (Yamakita, 1987), Tokushima Prefecture, Southwest Japan.

ism of the inverse excursion between δ^{34}S and δ^{13}C stable isotopes during the deposition of the P–Tr boundary organic mudstones with very low sedimentation rate.

In conclusion, lithologic and color change and curves of δ^{34}S and δ^{13}C isotopes in the Middle to Upper Permian cherts reveals gradual change in oceanic condition from oxic to anoxic occurred at horizon below the P–Tr boundary. The P–Tr boundary is represented by organic black mudstones and where methan fermentation occurred and second order sulfate reduction were induced. The P–Tr boundary deterioration was a long termed pollution event caused by amalgamation of continents to form longitudinally elongated Pangea Super Continent (Van Andel, 1985) and this continents could put a barrier for latitudinal ocean circulation of the Panthalassa.

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炭素および硫黄安定同位体からみたペルム－トリアス紀境界における遠洋域の海洋汚染

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要　旨

徳島県木沢村天神丸および兵庫県篠山町におけるペルム－トリアス系境界を含む層状チャート層において non-carbonate organic matter の $\delta^{13}C$ の変化を測定した．また兵庫県篠山町のセクションについては筆者らの一人梶原ほかによって報告予定である sulfide の $\delta^{34}S$ 測定結果についてもあわせて報告し，ペルム－トリアス系境界における環境の変遷を考察した．両セクションともに類似の変化を示し，1)$\delta^{34}S$ の変化から，ペルム系中部では酸化環境にあったが，ペルム系上部の黒色チャートからトリアス系下部の灰色チャートまでは還元環境に変化したと推定される．2)しかし，ペルム－トリアス系境界の黒色有機質泥岩では $\delta^{34}S$ は逆に軽くなる．3)$\delta^{13}C$ は，ペルム系中部は変化に富むが，ペルム系上部では一定して－30を示す．ペルム－トリアス系境界前後の珪質粘土岩では変化に富むものの，やや軽くなる．4)天神丸では黒色有機質泥岩において逆に $\delta^{13}C$ は重くなる傾向を示し，$\delta^{34}S$ とは逆の変化を示す．$\delta^{13}C$ が重くなることは，底質が強還元状態となりメタン発酵が行われた可能性を示唆する．記録された $\delta^{34}S$ と $\delta^{13}C$ の逆の相関について，可能な反応を併せて示した．

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