

Organic geochemical implications of black shales related to the Permian/Triassic boundary, Tanba Belt, Southwest Japan

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Abstract: Outcrops containing the Permian/Triassic (P/T) boundary exposed in the Tanba Belt, Southwest Japan, have intercalated organic rich black shales. These black shales, related to the P/T boundary from the Ashimi section, Kyoto Prefecture, are examined to reveal their organic geochemical implications on the basis of their organic geochemical characteristics. Biomarker maturity parameters show that the black shales are matured to the post hydrocarbon generation stage before the major stage of hydrocarbon cracking. The measured TOC (total organic carbon) concentrations were in the range 2.2 to 5%. Considering their organic maturity levels, the initial TOC concentrations of the black shales at the time of deposition was evaluated to be at least more than 1.5 times. Visual kerogen analysis revealed that kerogen fractions do not contain any debris of higher plant origins, but are mostly composed of structureless amorphous kerogens. Little bioturbation, poor sedimentary structures, and dispersed nature of kerogen suggest that organic matter was transported vertically and deposited from suspension. The relative abundance of cholestanes derived from cholesterol is generally more than 50% in regular C₂₇ to C₂₉ series of steranes, showing the marked contribution of planktonic organic matter. The unresolved complex mixture shown on a gas chromatogram of saturated hydrocarbon fraction suggests the significant contribution of bacterial organic matter and/or organic matter related to bacterial activity.

Considering that anoxic-oxic conditions is not so important for the accumulation and preservation of organic matter in the open marine environment, oceanic anoxia cannot be responsible for the formation of these organic rich black shales. If the sedimentation rate is of a similar order to that of the present ocean floor, the black shales related to the P/T boundary show that the abnormally high primary production has taken place intermittently in the P/T transition time. The organic rich black shales show either a fertilized ocean due to the marked discharge of river-borne materials associated with a sea-level rise and/or the active ocean currents resulting in upwelling. Much dissolved oxygen is consumed due to prolific breeding of plankton. The abnormally high primary production in the P/T transition time can be related to the mass extinction of marine invertebrates and the evolution of marine plankton, especially in the upwelling region.

1. Introduction

The occurrence of the Permian-Triassic (P/T) boundary in bedded chert sequence in

Southwest Japan has been recently specified by Yamakita (1987) and Ishida *et al.* (1992). Many records related to the mass extinction and drastic change of the ocean are stored in sedimentary

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rocks of the P/T transition time. Among various lithologies of the P/T transition time, the organic rich black shales are of interest. The black shales are often formed in the P/T transition time and these also occur in the Lower Triassic siliceous rocks (Yamakita, 1987; Sano, 1988). These black shales have clues to understand the mass extinction and the change of oceanic environment in the P/T transition time.

Preservation of organic matter is controlled by several conditions such as the settling flux of organic matter, the oxic-anoxic conditions of ocean and sea floor, the dilution by inorganic sedimentary components, and the quality of organic matter. The abundance of organic matter in sedimentary rocks is often regarded to show anoxic condition of the ocean. However, the anoxic-oxic condition of the whole ocean must be distinguished from that of the bottom water-sediment interface. Organic matter consumes oxygen to form anoxic and reducing environment. The significant amount of organic matter, however, can be degraded through the process of sulphate reduction under the reducing environment (Foree and McCarty, 1970; Otsuki and Hanya, 1972). Calvert and Pedersen (1992) recently suggested that anoxic-oxic condition is not so important for the accumulation and preservation of organic matter in the open marine environment.

Marine organic rich sediments are generally formed under the high primary production zone in the marginal sea rich in nutrients supplied by upwelling (Bordovskiy, 1965; Romankevich, 1977). Ocean current systems influence the supply of nutrients, which in turn control the primary productivity in open marine environment. Whereas the ocean current supplies sea water rich in dissolved oxygen, which degrades organic matter during their settling. The formation of organic rich sediments is due to the interplay among the various controlling factors on production, accumulation and preservation of organic matter. The oceanic anoxia may be responsible for the formation of the P/T black shales (Ishida *et al.*, 1992; Yamashita *et al.*, 1992). However, the climatically and/or tectonically induced increases of upwelling can play an important role for the formation of organic rich sediments.

In the present paper, the black shales from Tanba Belt (Ishiga, 1985) related to P/T boundary are preliminary investigated to evaluate the pri-

mary productivity and oxic-anoxic condition of depositional environment. Their initial organic concentrations at the time of deposition are re-evaluated considering their organic maturity. The source of carbons is also examined based on visual kerogen analysis and biomarker compounds. These organic geochemical characteristics of the black shales related to P/T boundary are useful for understanding the geological significance of the formation of organic rich sediments in the P/T transition time.

2. Samples and experimental

Samples

The carbonaceous shales were collected from the Triassic bedded chert sequence embedded in Upper Jurassic melange of the Type I suite in the Tanba Belt (Ishiga, 1985). Location map and generalized stratigraphic column of the study area are shown in Figs. 1 and 2, respectively. The sequence comprises black bedded cherts and intercalating thin layers of gray siliceous claystone (so called Toishi type shale) and black carbonaceous shales. These rocks show rhythmic stratification and regular manner of single bed thickness of 1 to 2 cm. Lower part of the sequence of 3.6 m thick is indicated in Fig. 2. The black shales occasionally show lamination and graded upward into light gray siliceous claystones (Yamashita *et al.*, 1992), but are generally poor in visible sedimentary structures. Late Smithian to Spathian conodont *Neoapathodus homeri* occurs from the sequence indicated in columnar section (Fig. 2).

Geochemical Analyses of hydrocarbons and kerogens

The samples were dried at room temperature, carefully cleaned by grinder and washed by benzene/methanol (9:1) to remove contamination. The solvent washed samples were then pulverized by a jaw crusher and a ball-mill to less than 200 mesh. The powdered samples were extracted in a soxhlet extraction apparatus with benzene/methanol (9:1) for 48 hrs. The extracts was evaporated and subjected to preparative thin layer chromatography on silicic acid (KISELGEL 60 PF254, MERK) with elution by *n*-hexane to isolate saturated and aromatic hydrocarbons.

The solvent extracted samples were demineralized with HCl(6N)/HF(55%) (1:1) and then

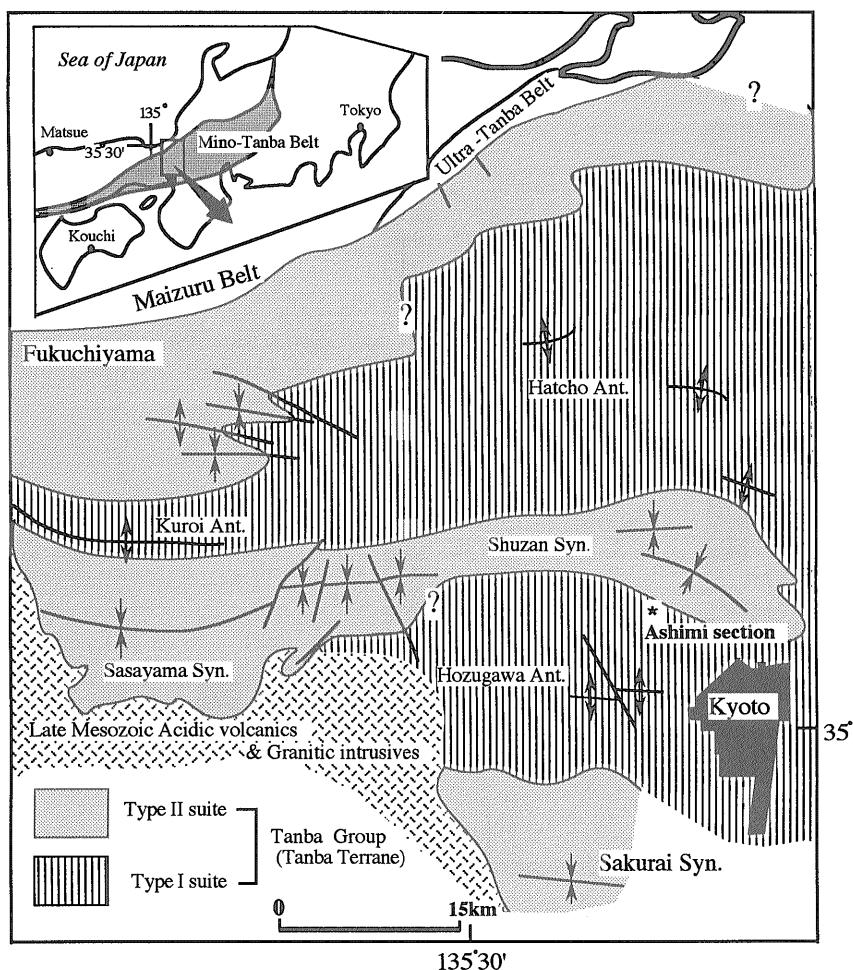


Fig. 1 Index map showing black shales related to the P/T boundary included to the Type I suite in the Tanba Belt (Ishiga, 1983), Southwest Japan.

washed with distilled water to *c.a.* pH 7. Kerogens for CHN elemental analysis were centrifuged and dried at 50°C. Kerogens for visual kerogen analysis were similarly recovered from the rock fragment samples of *c.a.* 5 mm in diameter.

Instrumental

All analyses for hydrocarbons were performed using a Shimadzu GC-14A or Shimadzu QP2000A Gas Chromatograph-Mass Spectrometer equipped with a 30 m × 0.25 mm i.d. fused silica capillary column coated with DB-5 (J & B). The oven was programmed from 40 to 300°C at 4°C/min. Samples were injected using splitless injection system. The mass spectrometer was oper-

ated at an electron energy of 70 eV, an ion source temperature of 250°C and a separator temperature of 250°C. The CHN elemental analyses were performed by using YANAKO CHN corder MT-3.

3. Results

Organic geochemical characteristics of the samples

The carbonaceous shales are visibly poor in primary sedimentary structures. The dispersed dark organic matter (kerogens) of 10 to 30 μm in diameter is distinctly observed in thin sections of the black shales. Abundant organic matter is

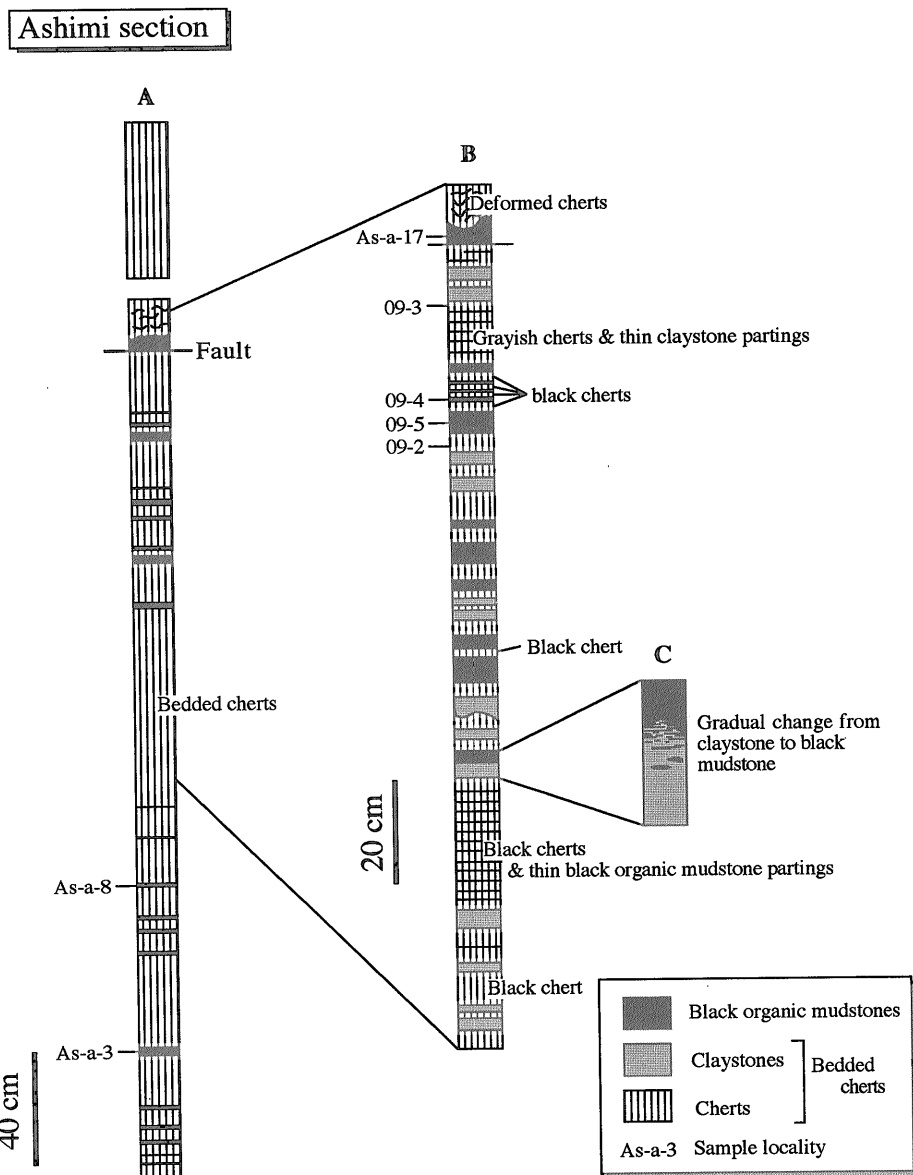


Fig. 2 Columnar section including the black shales at the Asimi section (Yamashita *et al.*, 1992). As-a-3, As-a-8, As-a-17, 09-4, 09-5 are the sample names and their stratigraphic horizons. *Neospathodus homeri* of the Lower to Middle Triassic conodonts has been found in the samples 09-2 and 09-3 (Yamashita *et al.*, 1992).

slightly orientated along secondary structures possibly due to the compaction and clay mineral transformations. The occurrence of organic matter is different from those in non-marine oil shales, since kerogens in oil shales are generally interlaminated with thin primary laminae. One of

transmitted-light photomicrographs of kerogen fractions extracted from the carbonaceous shales is shown in Fig. 3. Black colored structureless kerogens are commonly observed in five samples. Any structured kerogens with possible organic tissues were not observed in all samples, suggesting

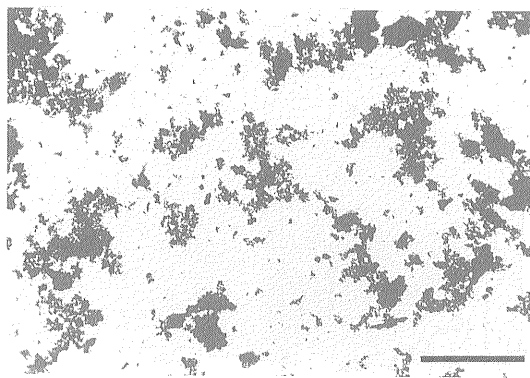


Fig. 3 Typical photomicrograph showing kero-gen extracted from the black shale (sam-ple 09-5). Note most kero-gens are struc-tureless amorphous kero-gens. Black color shows its relatively high maturity level.

that the black shales were poor in kero-gens of higher plant origins.

The TOC (Total organic carbon) concentra-tions of the black shales are in the range of 2.2 to 5.3% (Table 1). These values are less than those of most non-marine oil shales and nearly the same as those of organic rich Cretaceous marine black shales (*e.g.* Stein *et al.*, 1986). The black shales are evidently richer in TOC than Neogene marine black shales (generally less than 2%) from Japanese oil fields. The C/N (carbon to nitrogen ratio) of carbonaceous shales ranging from 19.4 to 30.4 are similar to or less than those of Mio-cene marine black shales (Taguchi, 1968), show-ing that the organic matter of black shales is com-paratively rich in nitrogen compounds. This is consistent with that kero-gens visually lacks higher plant debris which is poor in nitrogen.

The typical gas chromatograms of saturated hydrocarbon fractions from the black shales are shown in Fig. 4. The saturated hydrocarbon distri-bution is characterized by the unresolved com-plex mixture (UCM), which appears in the reten-tion time ranging from 45 to 65 min. Normal alkane distribution is unimodal with a maximum peak at n -C₂₀ or C₂₄. An odd/even-carbon num-ber predominance is significantly observed in the higher molecular weight n -alkanes ranging from C₂₄ to C₃₄. Pristane and phytane, typical acyclic isoprenoid hydrocarbons of sedimentary rocks, are not detected in saturated hydrocarbon frac-tion of all samples. These acyclic isoprenoid

Table 1 Total organic carbon (TOC) concentra-tions and carbon to nitrogen ratios (C/N) of the black shales from Ashimi sec-tion in the Tanba Belt, Southwest Japan.

Sample	TOC(%)	C/N
As-a-3	2.19	19.4
As-a-8	3.02	23.7
09-4	2.42	25.4
09-5	4.04	29.3
As-a-17	5.29	30.4

hydrocarbons might have been evaporated, since relatively lower molecular weight hydrocarbons ($<C_{17}$) are very poor in the samples.

M/z 217 and m/z 191 mass fragmentograms (Fig. 5) show that steroidal and triterpenoidal alkanes are significantly present in all samples, although they are poor compared to n -alkanes as shown in Fig. 4. Steranes with 27 carbons are the most abundant in all samples. Identifications of steranes in the m/z 217 fragmentogram and triter-panes in the m/z 191 fragmentogram are based on Peters and Moldowan (1993), and the results are shown in Tables 2 and 3, respectively.

4. Discussion

Organic maturity of the P/T black shales

The organic maturity of the black shales can be evaluated by several biomarker maturity parameters (Table 3). The 20S/(20S+20R) ra-tio of C₂₉ steranes are generally more than 0.5 which are nearly at the equilibrium value of the isomer ratio. The $\beta\beta/(\alpha\alpha+\beta\beta)$ ratio of C₂₉ ster-anes is measured to be about 0.7, showing high maturity level of the samples. The abundant lower molecular C₂₁ and C₂₂ steranes (L/(L+H) ra-tio in Table 4) shows that the thermal cracking of C₂₇ to C₂₉ regular steranes has proceeded sig-nificantly. However, we could not detect any C₂₁ and C₂₂ steranes in the samples As-a-3 and As-a-17. The ratio of Ts/(Ts+Tm) is generally about 0.6. These maturity parameters show that the or-ganic maturity of the black shales is at the post oil generation stage before the major stage of oil cracking (*e.g.* Peters and Moldowan, 1993). This maturity level corresponds to the maximum tem-perature of 100 to 120°C in the Mesozoic Paris ba-sin (apparent heating rate is *c.a.* 1°C/m.y.)

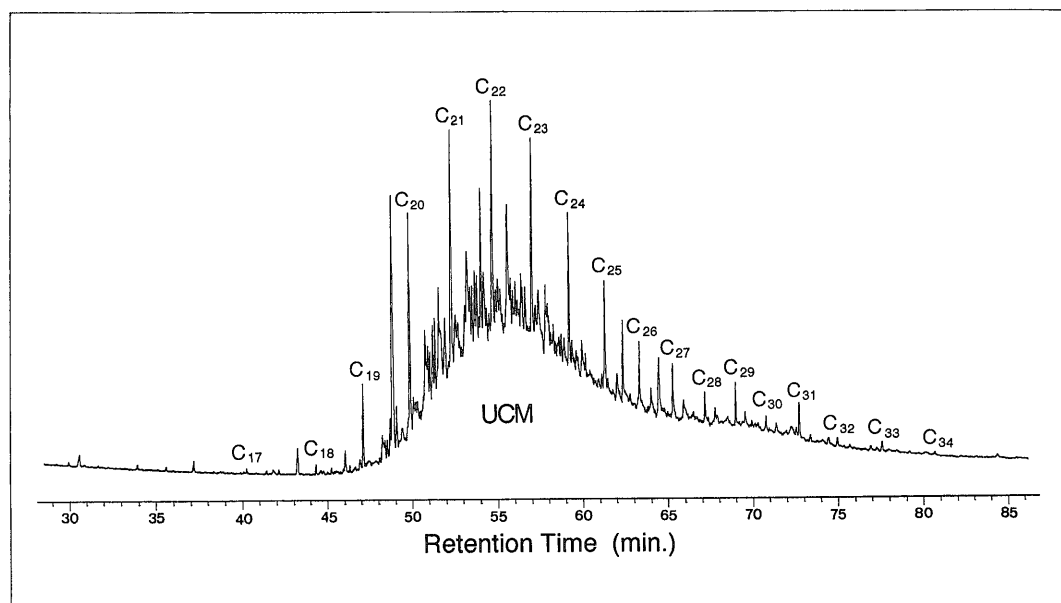


Fig. 4 Gas chromatogram of the saturated hydrocarbon fraction from the sample 09-5. C₁₇ to C₃₄ are *n*-alkanes with corresponding carbon numbers. Note gas chromatogram is characterized by the UCM (unresolved complex mixture).

(Mackenzie and McKenzie, 1983), and corresponds to the maximum temperature of 140 to 160°C in the young active Niigata basin (apparent heating rate is *c.a.* 10 to 100°C/m.y.) (Suzuki *et al.*, 1987; Suzuki, 1990). Considering the geologic age of the black shales, the maximum temperature of the sample can be estimated to be about 140°C at most.

Source of carbons

Gas chromatogram of saturated hydrocarbon fraction is characterized by the UCM. The UCM is a complex mixture of branched and cyclic alkanes, and is often found in biodegraded petroleum (Blumer *et al.*, 1973). It is recently suggested that the UCM in biodegraded petroleum mainly comprises one ring cycloalkyl compounds (Killops and Al-Juboori, 1990). In non-biodegraded petroleum, the UCM is not observed in the GC determination of *n*-alkane distributions. The gas chromatogram of saturated hydrocarbon fraction from the black shales is, however, different from those of biodegraded petroleum, since the black shales is rich in *n*-alkanes which can be easily biodegraded, and poor in biomarker compounds such as steroidal and triterpenoidal alkanes which are relatively stable against biodegradation (Alex-

ander *et al.*, 1983). The significant UCM of the black shales suggests that a part of their organic compounds is of microbial origin or that their initial organic matter at the time of deposition is slightly biodegraded.

The significant steroidal hydrocarbons suggests that a part of organic matter in the black shales is derived from eukaryotic organisms, although they have been thermally degraded slightly. The C₂₇ steranes are generally the most abundant among regular C₂₇ to C₂₉ steranes, showing the significant contribution of zoo- and phytoplankton to the preserved organic matter (Huang and Meinschein, 1979; Suzuki and Shimada, 1982) (Fig. 5 and Table 4).

Relatively long chain *n*-alkanes ranging from C₁₇ to C₃₃ with a peak at C₂₀ or C₂₁ can not be interpreted by prokaryotic organisms, even though the *n*-alkane distribution has been modified by the thermal cracking. Cyanobacteria does not produce abundant lipid and long chain hydrocarbons (Oren *et al.*, 1985). Eukaryotic algae often contain abundant lipid and long chain fatty acids, and can be a source of long chain hydrocarbons. Pristane and phytane, which are believed to be derived primarily from the phytol

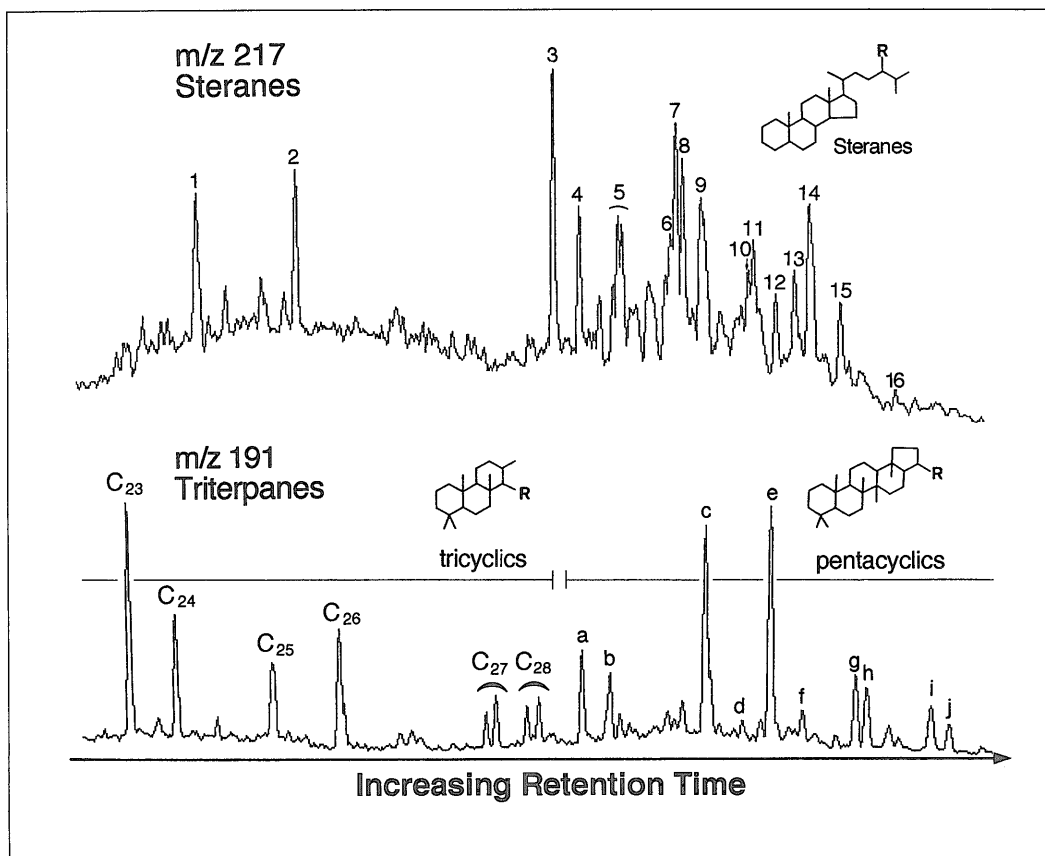


Fig. 5 Mass fragmentograms m/z 217 and m/z 191 of the saturated hydrocarbon fraction from the sample 09-5. See Tables 2 and 3 for compound identifications.

moiety in chlorophyll, are not detected in the black shales. They might have evaporated considering that *n*-alkanes with carbon numbers less than 18 are similarly very poor in GC trace of the saturated hydrocarbons.

The black shale related to the P/T boundary has few visible sedimentary structures. Kerogens are not concentrated in the laminae but occur as dispersed organic matter in the sediments. This occurrence of the kerogen suggests that organic matter is transported vertically and deposited from suspension. The Lower Triassic black shales mainly comprise organic matter derived from plankton with the additional organic matter related to bacterial activity.

Geological significance of the P/T black shales

In the case of matured samples, we have to consider the decomposition and the expulsion of

organic matter during early to late diagenesis. The weight loss of marine kerogen during diagenesis and metamorphism is generally in the range of 30 to 50% (*e.g.* Tissot *et al.*, 1987). Considering that the P/T black shales are at the post oil generation stage, the initial TOC concentration at the time of deposition can be evaluated to be about 1.5 times higher at least than those measured (Table 1). The initial TOC values estimated to be *c.a.* 4 to 8% are abnormally high compared to those of present marine sediments.

The preservation of organic matter in marine sediments is controlled by (1) oxic-anoxic condition at the time of deposition, (2) river-borne and air-borne contribution of the stable terrestrial organic matter, (3) the primary productivity, and (4) sedimentation rate of inorganic materials. In the deep ocean, the influence of terrestrial organic matter is generally minor (Hedges and Parker,

Table 2 Identification of steranes in the m/z 217 fragmentogram (Fig. 5).

Peak No.	Compounds	Carbon Number
1	Pregnane	21
2	Methylpregnane	22
3	13 β (H),17 α (H)-Diacholestane (20S)	27
4	13 β (H),17 α (H)-Diacholestane (20R)	27
5	13 β (H),17 β (H)-Diacholestane + 13 β (H),17 α (H)-Methyldiacholestane (20S)	27 28
6	5 α (H),14 α (H),17 α (H)-Cholestane (20S)	27
7	5 α (H),14 β (H),17 β (H)-Cholestane (20R)	27
8	5 α (H),14 α (H),17 β (H)-Cholestane (20S)	27
9	5 α (H),14 α (H),17 α (H)-Cholestane (20R) + 13 α (H),18 α (H)-24-Ethyldiacholestane + 13 α (H),17 α (H)-24-Ethyldiacholestane	27 29 29
10	5 α (H),14 β (H),17 β (H)-24-Methylcholestane (20R)	28
11	5 α (H),14 β (H),17 β (H)-24-Methylcholestane (20S)	28
12	5 α (H),14 α (H),17 α (H)-24-Methylcholestane (20R)	28
13	5 α (H),14 α (H),17 α (H)-24-Ethylcholestane (20S)	29
14	5 α (H),14 β (H),17 β (H)-24-Ethylcholestane (20R)	29
15	+ 5 α (H),14 β (H),17 β (H)-24-Ethylcholestane (20S)	29
15	5 α (H),14 α (H),17 α (H)-24-Ethylcholestane (20R)	29
16	5 α (H),14 α (H),17 α (H)-24-n-Propylcholestane (20R)	30

Table 3 Identification of triterpanes in the m/z 191 fragmentogram (Fig. 5).

Peak No.	Compounds	Carbon Number
a	18 α (H)-22,29,30-Trisnorneohopane (Ts)	27
b	17 α (H)-22,29,30-Trisnorhopane (Tm)	27
c	17 α (H),21 β (H)-30-Norhopane	29
d	17 β (H),21 α (H)-30-Norhopane	29
e	17 α (H),21 β (H)-Hopane	30
f	17 β (H),21 α (H)-Hopane (Moretane)	30
g	17 α (H),21 β (H)-29-Homohopane (22S)	31
h	17 α (H),21 β (H)-29-Homohopane (22R)	31
i	17 α (H),21 β (H)-29-Bishomohopane (22S)	32
j	17 α (H),21 β (H)-29-Bishomohopane (22R)	32

1976). The absence of higher vascular plant debris and higher waxy hydrocarbons from higher land plants in the P/T black shale is consistent well with their deep marine depositional environment. Considering that the black shales are rich in clay minerals compared to stratigraphically upper and lower radiolarian cherts (Fig. 2), the sedimentation rate of black shale could be slower than that of radiolarian chert. According to Ishida *et al.* (1992), the clayey strata of *c.a.* 3 m thick with the black shales at and above P/T boundary has accumulated within 3 m.y. at most in Sasayama section of the Tanba Belt. The mean rate of

the sedimentation can be estimated to be 1 mm/kyr. Considering the compaction during diagenesis, the sedimentation rate more than 2 mm/kyr, which is similar to that of the present ocean floor, can be expected. However, we have poor information on the sedimentation rate of the black shales from Ashimi section in the present paper. If we can assume that the sedimentation rates of the black shales are nearly in the similar order to that of the present ocean floor, the marked increase of primary productivity and/or the abnormally anoxic depositional environment can be the crucial conditions to form the organic rich black shales.

Table 4 Maturity and source parameters from sterane and triterpane biomarker compositions. Overlapped compounds are manually divided for calculations.

Sample	Maturity Parameters				Source Parameters* ⁵		
	S/(S+R) ^{*1}	L/(L+H) ^{*2}	$\beta\beta/(\beta\beta+\alpha\alpha)$ ^{*3}	Ts/(Ts+Tm) ^{*4}	%C ₂₇	%C ₂₈	%C ₂₉
As-a-3	0.51	0.0	0.67	0.57	52	24	24
As-a-8	0.45	0.74	0.68	0.58	60	17	23
09-4	0.54	0.38	0.70	0.60	52	22	26
09-5	0.52	0.52	0.67	0.61	50	25	25
As-a-17	0.52	0.0	0.70	0.48	52	22	26

*¹ 20S/(20S + 20R) $\alpha\alpha\alpha$ -C₂₉ sterane (sterane isomer ratio); The ratio of peaks 13/(13+15) in the m/z 217 fragmentogram.

*² (C₂₁+C₂₂)/(C₂₁+C₂₂+C₂₇+C₂₈+C₂₉)- $\alpha\alpha\alpha$ -sterane (sterane side chain cleavage). The ratio of peaks (1+2)/(1+2+9+12+15) in the m/z 217 fragmentogram.

*³ $\alpha\beta\beta/(\alpha\beta\beta+\alpha\alpha\alpha)$ -C₂₉ sterane (sterane isomer ratio). The ratio of peaks 14/(13+14+15) in the m/z 217 fragmentogram.

*⁴ The ratio of 18 α -22,29,30-Trisnorneohopane (Ts) and 17 α -22,29,30-Trisnorhopane (Tm). The ratio of peaks a/(a+b) in the m/z 191 fragmentogram.

*⁵ Relative abundance among regular $\alpha\alpha\alpha$ -C₂₇, C₂₈ and C₂₉ steranes (peaks 9, 12, 15 in the m/z 217 fragmentogram).

Anoxic depositional condition can be defined as those environments where the water contains free hydrogen sulphide. European fjords, Cariaco Trench and the Black Sea are well known as typical anoxic depositional environment, where the abundant organic matter are actually preserved. However, the view that oxidation of organic matter does not occur, or is greatly retarded, in the absence of oxygen does not necessarily be supported by recent works. Oxidation of organic matter by sulphate reduction often occurs more efficiently than that under oxygenated condition (Foree and McCarty, 1970, Otsuki and Hanya, 1972). In addition, Mackin and Swider (1989) showed that the maximum contribution of O₂ to total organic matter decomposition in a coastal mud flat was clearly less than that by sulphate reduction. It is also pointed out that the oxidation rates of organic matter under an oxic and an anoxic basin are not so much different (Henrichs and Farrington, 1987). Calvert and Pedersen (1992), consequently concluded that the anoxia in the marine environment is not essential for the formation of organic rich sediments.

The TOC concentrations of present deep ocean sediments are generally less than 0.5% (Bordovskiy, 1965; Romankevich, 1977, Premuzic *et al.*, 1982). While the initial TOC concentrations of the P/T black shale were evaluated to be 4 to

8%. These initial TOC concentrations are significantly higher than those (1 to 4%) of immature Cretaceous black shales from the Atlantic Ocean (Stein *et al.*, 1986). The formation of organic rich sediments in the P/T transition time can not easily be interpreted only by the oceanic anoxia, since the decomposition of organic matter can proceed significantly under an anoxic condition. The abnormally increased primary productivity in the P/T transition time should be considered as one of the essential causes for the formation of the organic rich black shales in the P/T transition time.

The relative abundance of cholestane (C₂₇ sterane) among regular C₂₇ to C₂₉ steranes is more than 50% (Table 3). Diatomaceous siliceous rocks of the Onnagawa Formation were widely deposited in northeast Japan in Middle to Late Miocene. The average TOC concentration of the Onnagawa sediments is the highest compared to those from stratigraphically lower and upper formations such as Nishikurosawa Formation and Funakawa Formation (Japan Natural Gas Association, 1992). The invasion of nutrients rich sea water from the north to the expanding Japan Sea can be considered as one of major reasons for the marked increase of primary production which formed abundant siliceous sediments. The steroidal hydrocarbon compositions of the

Onnagawa siliceous rocks and crude oils possibly derived from the Onnagawa source rocks have been reported by many authors (Suzuki and Shimada, 1982; Taguchi *et al.*, 1986; Sakata *et al.*, 1988; Hirai, 1988; Hirai *et al.*, 1990; Yamamoto and Watanabe, submitted), and it is known that cholestane is the most abundant sterane among regular steranes. Cholestane in the black shales related to the P/T boundary are comparatively more abundant than those in the Onnagawa siliceous rocks as shown in Fig. 6. The black shales are characterized by the very high abundance of cholestane which are derived from planktonic organic matter, supporting the high primary productivity at the time of black shale deposition.

Regional stratigraphic studies recently showed a distinct pattern of regression-transgression in the P/T transition time (Holser and Magaritz; 1987; Hallam, 1992; Wignall and Hallam, 1993). Several third-order eustatic sea-level cycles during the Triassic have been recognized,

and the regional sea-level rises with the greatest magnitude occurred in earliest Griesbachian, early Anisian, earliest Carnian, earliest Norian, and earliest Jurassic (Embry, 1988). These rapid sea-level rises can be related to the formation of organic rich black shales. In the open marine environment, the sufficient supply of nutrients is an important factor for the increase of primary productivity. Nutrients in the ocean can be derived from river-borne terrestrial materials. As argued for the Cretaceous black shales by Pedersen and Calvert (1990), the increased supply of terrestrial materials through rivers associated with a sea-level rise can fertilize the ocean. On the other hand, according to Hallam (1978) and Embry (1988), sea-level cycles in the Triassic can be interpreted as tectono-eustatic in origin, reflecting changes in the volume of the ocean basins due to sea floor spreading and oceanic volcanism. The drastic change of topography of sea floor due to tectonics can also affect the ocean current systems. Tectonically controlled ocean currents can

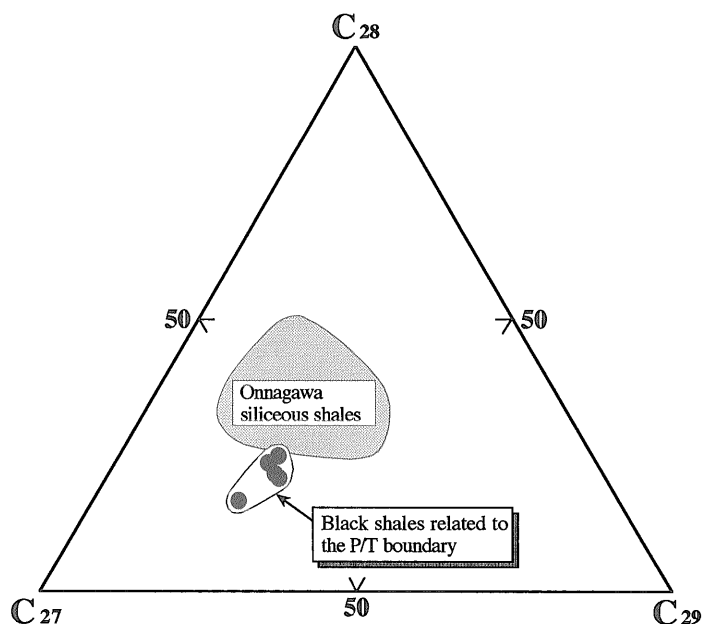


Fig. 6 Ternary diagram showing the relative abundances of C_{27} , C_{28} , and C_{29} -regular 20R- $\alpha\alpha\alpha$ -steranes (Peaks 7, 12, 15). Note Triassic black shales are significantly rich in C_{27} sterane compared to Miocene Onnagawa siliceous rocks. Data of Onnagawa shales are from Suzuki and Shimada (1982), Yamamoto and Watanabe (submitted) and unpublished data. The sterane ternary plots of Crude oils from Neogene Tertiary Akita basin (Sakata *et al.*, 1988; Hirai, 1988; Hirai *et al.*, 1990) are within the range of Onnagawa siliceous shales.

form upwelling to transport nutrients. Organic rich black shales commonly observed in the P/T transition time show the fertilized ocean and/or the active ocean currents to form upwelling. Prolific breeding of plankton by the abnormally high primary productivity consumes much dissolved oxygen, and can affect the ecological system, especially in upwelling regions. The abnormally high primary production can be responsible for the mass extinction of marine invertebrates and the evolution of marine plankton in the P/T transition time.

5. Conclusion

The black shales related to the P/T boundary from Tanba Belt are rich in organic carbon, of which the initial concentrations were evaluated in the range 4 to 8% considering their organic maturity. Poor visible sedimentary structures and dispersed structureless kerogen (amorphous kerogen) suggest that major organic matter has been vertically transported or deposited from suspension. These black shales are characterized by the very high relative abundance of C₂₇ steranes (cholestanes) derived from plankton. The black shales comprise organic matter mainly derived from plankton although their organic composition is slightly modified by bacterial activity. The abundant organic matter can consume dissolved oxygen to maintain a highly anoxic condition of bottom-sediment interface. However, the occurrence of the organic rich black shales can not be easily interpreted by the oceanic anoxia. Recent works strongly suggest that decomposition rates of marine organic matter under an oxic and an anoxic condition are not so different. If the sedimentation rate is nearly in the similar order to that of present ocean, the black shales show that abnormally high primary production has taken place intermittently in the P/T transition time. The fertilized ocean due to the marked discharge of river-borne materials associated with a climatically induced rapid sea-level rise and/or the significant circulation of ocean current to form upwelling can be responsible for the formation of organic rich black shales. The abnormally high primary production in the P/T transition time can be related to the mass extinction of marine invertebrates and the evolution of marine plankton in the upwelling regions.

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西南日本丹波帯のペルム紀、トリアス紀境界付近に見られる
黒色頁岩の有機地球化学的意味

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要 旨

西南日本内帯の丹波帯に露出しているペルム紀/トリアス紀の境界部付近には有機物に富む黒色頁岩がしばしば挟在している。このような有機質黒色頁岩が持つ意味を明らかにするため、丹波帯声見地域より黒色頁岩を採取しその有機物組成について検討した。これらの黒色頁岩には分子化石であるバイオマーカー化合物が有意に保存されている。バイオマーカー成熟指標から判断して、黒色頁岩は石油生成帯を過ぎ炭化水素の熱クラッキングが進行しつつある成熟段階にあることがわかる。全炭素濃度は2.2~5.3%の間にあるが、成熟度を考慮すると、堆積時の初期濃度は少なくともそれらの1.5倍以上あったものと考えられ、海成堆積物としては異常に高い初期有機炭素濃度によって特徴づけられている。ビジュアルケロジェン法による観察ではこれらのケロジェンには高等植物に由来する碎屑片が全く含まれず、特定の構造を持たない無定型のケロジェンよりなる。また、生物攪乱作用が認められないこと、堆積構造に乏しいこと、ケロジェンは分散して存在していることから、有機物は主として鉛直輸送され堆積したことがわかる。堆積岩に通常認められるステロイド炭化水素の中では、コレステロールに由来するコレスタン類が全体の50%以上を占めるという顕著な特徴を持っている。以上のことは黒色頁岩の有機物が主にプランクトン類に由来していることを示している。ただし、飽和炭化水素のガストマトグラムにはさまざまなアルキル環状飽和炭化水素からなる未分離複合混合物(unresolved complex mixture)が共通して認められ、バクテリア由来、または、バクテリアの活動に由来する有機物も関与している。

溶存酸素濃度や酸化還元性が堆積物有機物の保存を大きく左右しないことを考えると、いわゆる海洋無酸素現象が有機物を保存し有機質黒色頁岩の形成を促したという説明は適切でない。有機質黒色頁岩形成時の無機物質の堆積速度が現在の外洋域のそれと同程度であるものとする、ペルム紀/トリアス紀境界部に産する黒色頁岩は、当時の海洋にしばしば異常に高い基礎生産性が出現したことを示している。海水準の上昇にともない河川由来の多量の栄養塩類が海洋にもたらされ当時の海洋がしばしば肥沃になったこと、活動的な海流が湧昇流を形成しやすかったことなどが当時の海洋に高い基礎生産性を出現させたものと考えられる。異常に高い基礎生産により繁殖したプランクトン類は溶存酸素を大量に消費する。ペルム紀/トリアス紀移行期における異常な基礎生産性が特に大陸周辺の湧昇域における海洋生物の大量絶滅や海洋プランクトン類の進化と密接に関係していることも考えられる。

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