The Cenomanian-Turonian Anoxic Event in Southern Tibet: A Study of Organic Geochemistry

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Abstract: The Cenomanian-Turonian oceanic anoxic event (C/T OAE) is developed in southern Tibet. Organic geochemical study of the Cenomanian-Turonian sediments from the Gamba and Tingri areas shows that the mid-Cretaceous black shales in southern Tibet are enriched in organic carbon. The molecular analyses of organic matter indicate marine organic matter was derived from algae and bacteria. In the Gamba area, the organic matter is characterized by abundant tricyclic terpanes and pregane, which are predominant in 191 and 217 mass chromatograms, respectively. Pristane/phytane (Pr/Ph) ratios in the C/T OAE sediments are less than 1, demonstrating the domination of phytane. The presence of carotane can be regarded as a special biomarker indicating oxygen depletion in the C/T OAE sediments in the Tethyan Himalayas. In anoxic sediments, β-carotane and γ-carotane are very abundant. The β- and γ-carotane ratios relative to nC_{17} in the Cenomanian-Turonian anoxic sediments vary from 32.28 ~ 42.87 and 5.10 ~ 11.01.

Key words: Cenomanian-Turonian; oceanic anoxic event; organic geochemistry; southern Tibet

Introduction

Organic-rich black shales were widespread in Cretaceous (Berriasian-Turonian) marine sedimentary deposits of the Tethys. Their occurrence has been mostly explained by deposition in a poorly oxygenated environment. Several Cretaceous organic rich intervals are worldwide distributed and are known as "Oceanic Anoxic Events" (OAEs) (Schlanger and Jenkyns, 1976; Jenkyns, 1980). They are associated with positive $\delta^{13}C$ anomalies (Arthur et al., 1988) and marine biotic extinction (Raup and Sepkoski, 1984).

In southern Tibet, the mid-Cretaceous organic-rich black shales occur in both Gamba and Tingri areas (Yu and Wang, 1990). Sedimentological study supported by element geochemistry and micropaleontology data of the black shales indicates that the C/T OAE was developed in southern Tibet. The mid-Cretaceous black shales in southern Tibet were interpreted as anoxic deposits (Tao Ran, 1990; Wang et al., 2001).

Organic geochemical analysis of the mid-Cretaceous black shales in southern Tibet provides data on organic matter input, sedimentary environment of anoxic deposits, and relationship between special biomarkers and anoxic event. In addition, we briefly discussed the similarities and differences in C/T OAE between eastern and western Tethys.

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Experimental Samples and Methods

Samples

We had analyzed the mid-Cretaceous samples collected from the Tingri Gongzha and Gamba Zongshan sections. All samples were taken from the Earth's surface in the field.

Methods

Organic carbon contents of the samples from the Gamba Zongshan section were analyzed by direct combustion at the National Laboratory of Oil/Gas Geology and Exploration, Chengdu University of Technology. Powdered sediments (typically 100 g) were exhaustively extracted by Soxhlet apparatus (dichloro-methame/methanol; 3:1 v/v; 250 ml), using activated copper in the Soxhlet flash to remove elemental sulfur. The total organic extract was fractioned by Thin Layer Chromatography (TLC; Silica gel G; 0.4 mm; hexane) into saturates, aromatics, and polar fractions. Gas chromatography (GC) was carried out on HP6890 in the Guangzhou Institute of Geochemistry, Chinese Academy of Science. For analyses of aromatic and aliphatic hydrocarbons a HP5 column (25 m × 0.32 mm × 0.17 μm) was used, with helium as carrier gas at the following temperature program: 60℃ (5 min) to 290℃ for 40 min at 4℃/min. The FID temperature is 300℃.

The saturates were analyzed by Gas Chromatography-Mass Spectrometry (GC-MS) in the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences. The GC-MS ion source temperature was 180 ℃, ionizing voltage 70 eV. Temperature of the silica capillary column (HP5, 50 m × 0.32 mm × 0.17 μm) rised from 80 ℃ at 8 ℃/min to 120 ℃ and from 120 ℃ to 300 ℃ at 2 ℃/min and then was held at 300 ℃ for 21 minutes.

Results

Total organic carbon (TOC) and its source

It is well established that TOC shows a positive correlation with dissolved oxygen content in the bottom water (Farrimond et al., 1990). In anoxic condition, TOC is relatively high (Farrimond et al., 1990). TOC in the Gamba Zongshan section varies mainly from 0.4% to 1.1% in weight, averaging 0.6% (67 samples). The maximum of TOC in black shales in this section is 1.7%. The sedimentology data indicate that TOC variations are recognizable in the field with its color and sedimentary structure. Rhythmicity in the sequence consists of intercalation of organic-rich laminated black shales and organic-poor bedded marls, or shales (Table 1, Fig. 1). Five anoxic periods can be recognized during the Cenomanian-Turonian in the Zongshan section based on lithology and TOC contents. These do not correlate with the global events. The so-called oceanic anoxic event does not mean that the global oceans experienced a continuous anoxic event all the time. For example, Kaiho and Hasegawa (1994) pointed out there were two anoxic periods during the Cenomanian-Turonian anoxic event in central Hokkaido, Japan. One period lasted 50 ka, from 0.15 Ma to 0.10 Ma before the C/T boundary; the other is from 0.03 Ma before the C/T boundary to 0.15 Ma after the C/T boundary. Estimated by sedimentation rates, these five periods of the C/T OAE in the Gamba area lasted 0.9 Ma, 2.1 Ma, 1.1 Ma, 2.3 Ma, and 1.4 Ma, respectively. Period 3 is the so-called Cenomanian-Turonian Boundary OAE, which lasted 0.7~1.0 Ma in other parts of the world (Schlanger et al., 1987). Among these five periods, TOC in Periods 1 and 3 is higher than that in Periods 4 and 5 while Period 2 has the lowest TOC

(Table 1).

Table 1. TOC of the sediments during the Cenomanian-Turonian event in the Gamba area, southern Tibet

Fm.	Epoch	Bed No.	Thickness (m)	Colour and lithology	Period No.	Lamination	TOC (%)
Xiuwuchubo	Turonian	50	13	Fresh gray limestone with shale		Massive	0.44(1)
		48 - 49	41	Light black shale	5	Regular laminated	0.52(6)
		44 - 47	32	Yellow-green limestone with shale		Non-regular laminated	0.40(7)
		42 - 43	70	Light black shale	4	Laminated	0.54(7)
		41	45	Yellow-green shale		Massive	0.59(4)
Lengqingre	Cenomanian	37 - 40	33.5	Black shale with limestone	3	Laminated	0.90(6)
		35 - 36	20.5	Fresh gray marlstone with shale		Massive	0.49(14)
		33 - 34	54.5	Black shale with limestone	2	Laminated	0.58(9)
		32	26	Fresh gray shale interbedded with marlstone		Massive	0.56(5)
		28 - 31	27.1	Black shale with limestone lens	1	Laminated	1.03(6)
		22 - 27	74.1	Gray siltstone with limestone		-	0.29(2)

Note: the number in bracket is the total number of analyzed samples.

The distribution of regular n-alkanes indicates that the dominant alkane is nC_{18} in reconstructed ion chromatograms (RIC) of mid-Cretaceous samples from southern Tibet (Fig. 2, Table 2). Near the C/T boundary, there are two peaks, nC_{18} and nC_{22} or nC_{25}. Their occurrence indicated that all the black shale samples appear to be dominated by marine (algal/bacterial) organic matter (Brassell et al., 1978).

All Cretaceous samples from southern Tibet lack biomarkers which can be regarded as higher plant sources such as lupane ($C_{30}H_{52}$) and oleanane ($C_{30}H_{52}$). Sterane series is dominated by C_{29}-sterane, which is considered to be the result of higher algal input (Grantham, 1986). The ratios of $\sum C_{27}$-sterane/$\sum C_{29}$-sterane and $\sum C_{28}$-sterane/$\sum C_{29}$-sterane are averaged 0.26 and 0.64 on average, respectively (Table 2).

It should also be noted that both tricyclic terpanes and pregnane are abundant in the mid-Cretaceous black shales of the Zongshan section, which are predominated in 191 and 217 mass chromatograms (Fig 3). The ratios of C_{23}-tricyclic terpane/$C_{30}\alpha\beta$-hopane and C_{21}-pregrane/$C_{29}\alpha\beta\beta$-R-sterane in sample CTO4 from the Zongshan section are 2.01 and 3.97, respectively. The reason why the tricyclic terpane and pregnane are so highly concentrated in the mid Cretaceous black shales in the Gamba area is unclear.

Table 2. Selected biomarker parameters of the mid-Cretaceous samples from southern Tibet

Sample No.	Rock type	TOC%	Dominant n-alkane	HSI	30hop	23/30	SSI	sni-29	27/29st	28/29st	21/29	γ	Pr/Ph	Pr/17	Ph/18	β/17	γ/17
GPO1-29S4	Limestone	0.05	nC_{18}	0.57	6.82	0.31	0.42	0.54	0.08	0.17	0.15	0.48	0.25	0.50	0.18	0.93	0.26
GPO1-27S2	Limestone	0.07	nC_{18}	0.68	8.69	0.35	0.43	0.58	0.21	0.71	0.10	0.38	0.33	0.75	0.13	14.23	2.99
GPO1-27S1	Limestone	0.09	nC_{18}, nC_{25}	0.62	12.13	0.16	0.43	0.63	0.22	0.69	0.04	0.22	0.19	0.64	0.11	51.70	8.03
GPO1-24S1	Grayish-green shale	0.23	nC_{18}, nC_{22}	0.65	12.78	0.09	0.42	0.62	0.22	0.64	0.04	0.19	0.15	0.47	0.10	27.97	3.49
GPO1-23S1	Limestone	-	nC_{18}	0.56	8.96	0.39	0.42	0.56	0.35	0.79	0.19	0.35	0.19	0.40	0.14	0.64	0.19
GPO1-22S2	Limestone	0.10	nC_{18}	0.62	10.45	0.27	0.41	0.51	0.39	0.78	0.19	0.26	0.20	0.44	0.13	1.12	0.42
CT04	Black shale	0.20	nC_{18}	0.60	7.09	2.01	0.40	0.58	0.36	0.73	3.97	0.20	0.37	0.70	1.71	0.46	0.06

Note: 1. Ratio in height: HSI: $C_{31}\alpha\beta$-hopane [22S/(22S+22R)]; 30hop: $\alpha\beta-C_{30}$ hopane/$\beta\alpha$-C_{30} moretane; 23/30: C_{23}-tricyclic terpane/$C_{30}\alpha\beta$-hopane; SSI: C_{29}-$\alpha\alpha\alpha$-sterane [20S/(20S+20R)]; sni-29: C_{29} sterane [$\beta\beta$($\beta\beta$+$\alpha\alpha$)]; 27/29st: $\sum$27 sterane/$\sum$29 sterane; 28/29st: $\sum$28 sterane/$\sum$29 sterane; 21/29: C_{21}-pregrane/$C_{29}\alpha\beta\beta$-R-sterane; γ: gammacerane/C_{30}-$\alpha\beta$22S-hopane; Ratio in area: Pr/Ph: pristane/phytane; Pr/17: pristane/nC_{17}; Ph/18: phytane/nC_{18}; β/17: β-carotane/nC_{17}; γ/17: γ-carotane/nC_{17}2. Sample: GP01 is from the Tingri Gongzha section, CT is from the Gamba Zongshan section; 29 is the bed number; S4 is the 4th sample from the bottom upward.

Biomarkers and Oceanic Anoxic Event

Recent studies have shown that redox changes in sedimentary environment can be traced using special biomarkers. For example, black shales deposited in an anoxic setting have high contents of 28, 30-bisnorhopane (Farrimond et al., 1990), 25, 28, 30-trinorhopane (Grantham et al., 1979) and 17α, 21βC_{35}-hopane (Peters and Moldowan, 1991).

The pristane/phytane (Pr/Ph) ratio is often used to assess redox change. Pr/Ph ratios in the Gongzha section are very low, averaging 0.31. In the anoxic beds (samples GP01-24S1 and GP01-27S1), the minimum Pr/Ph ratio is 0.17. Above bed 27, the ratio rises to 0.29. The difference in Pr/Ph ratio between anoxic beds and surrounding beds could be probably attributed to the changes in redox conditions.

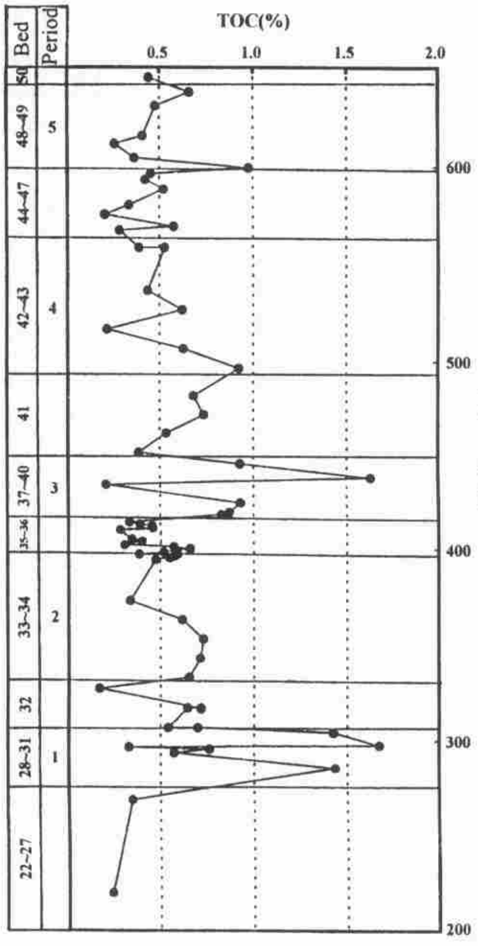

Fig. 1. Stratigraphic distribution of TOC in sediments from Cenomanian to Turonian in the Gamba Zongshan section.

The contents of β- and γ-carotanes are influenced by reducing and/or saline environments (Fu Jiamo et al., 1990). In comparison to the three worldwide anoxic beds (Late Jurassic Callovian, Early Cretaceous Aptian-Albian, and Middle Cretaceous Cenomanian-Turonian), the black shales in southern Tibet have very high β- and γ-carotanes. The β- and γ-carotane ratios relative to nC_{17}-nlkane in the Cenomanian-Turonian anoxic beds are 39.84 and 5.76, higher than those of both upper and lower beds. The two ratios in Callovian black shales vary within the ranges of 73.14 ~ 751.50 and 8.94 ~ 99.25, averaging 320.75 and 43.84, respectively, while they are only 5.30 ~ 10.68 and 1.81 ~ 2.20 in the upper and lower beds. The two ratios in Aptian-Albian black shales vary within the ranges of 32.28 ~ 42.87 and 5.10 ~ 11.01, averaging 37.58 and 8.06, respectively, which are much higher than those of 1.12 ~ 9.88 and 0.42 ~ 1.86 in the upper and lower beds. Therefore, the β- and γ-carotanes are sensitive monitors of redox changes in depositional environment in southern Tibet. Carotanes are relatively high in the black shales deposited in the reducing environment, while they are low in the oxic environment.

Discussion and Conclusions

Many papers are concerned with the organic geochemistry of the Cenomanian-Turonian OAE (Farrimond et al., 1990; Mello et al., 1989). But, most of them are restricted to western Tethys. This paper is the first one dealing with the organic geochemistry of the C/T OAE in east-

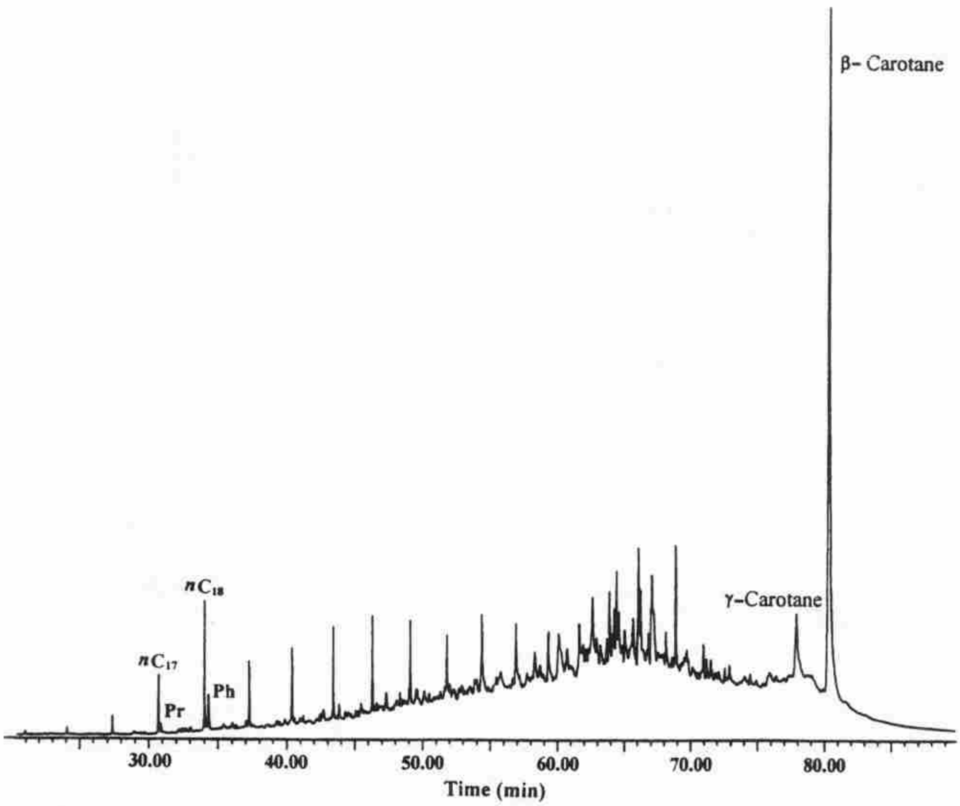

Fig. 2. Reconstructed ion chromatograms (RIC) of sample GP01-24S1 from the Cenomanian/Turonian anoxic sediments in the Tingri area, southern Tibet, showing very low Pr/Ph ratio and abundant carotane compound.

ern Tethys realm.

The TOC of mid-Cretaceous black shales in southern Tibet (averaging 0.58%) is lower than in other regions. In Europe, the TOC of C/T black shales is greater than 10%, within the range of 1.3% - 31.2% (Farrimond at al. 1990), 10 - 30 times greater than in Tibet. TOC in the Santos Basin of Brazil also accounts for 2% ~ 5% (Mello et al., 1989). The low values in southern Tibet may be attributed to several factors. TOC contents are lower as a result of weathering during the Cenozoic when the Qinghai-Tibet Plateau was deformed. Or, southern Tibet experienced a different mid-Cretaceous climate and marine environment, which resulted in a lower supply and preservation of organic carbon.

The organic matter inputs were dominated by marine organic matter (algae and bacteria) during the mid-Cretaceous in southern Tibet. The Type-Ⅱ karogen is dominant, similar to that in western Tethys.

A high ratio of gammacerane/C_{30}-hopane is a specific indicator of a hypersaline depositional environment (Fu Jiamo et al., 1990). The average gammacerane/ C_{30}-hopane in Cenomanian-

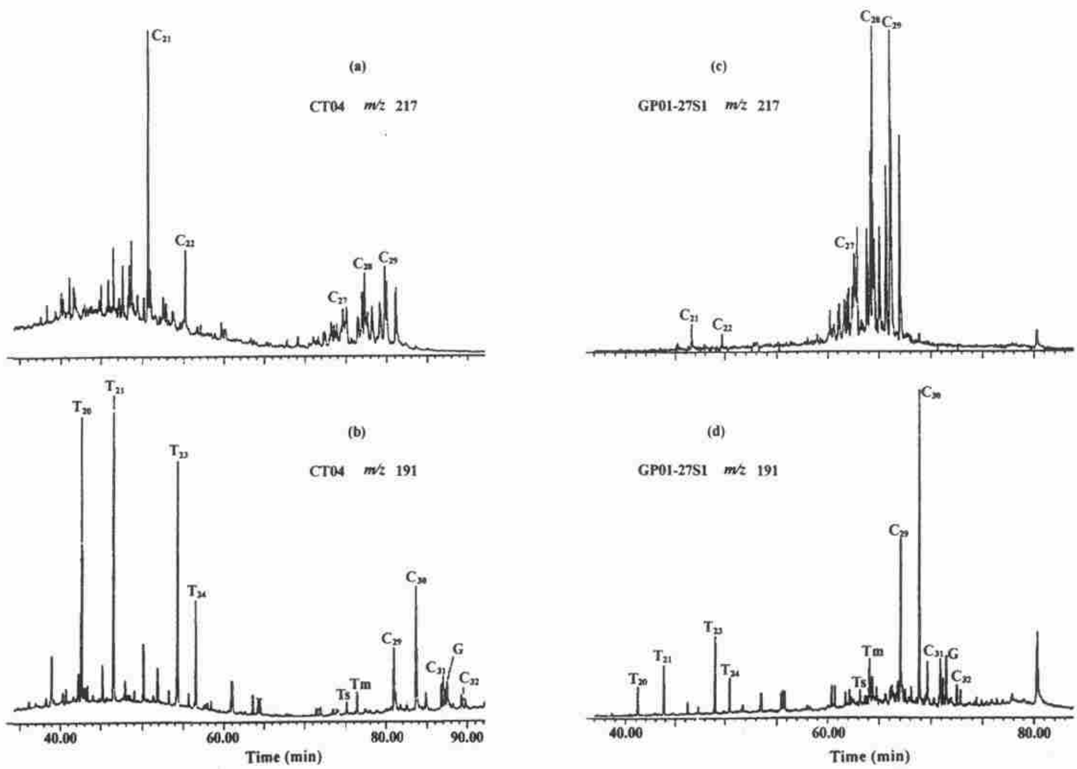

Fig. 3. Representative m/z 191 (hopane) and m/z 217 (terpane) mass fragmentograms of the Cenomanian-Turonian anoxic sediments in southern Tibet. a, b. Black shale sample CT04 from the Gamba area; c, d. marl sample GP01-27 S1 from the Tingri area. The selected tricyclic terpanes are labeled with "T", followed by carbon number and hopanes are labeled with "C", followed by carbon number. G. gammacerane; steranes are labeled according to their carbon numbers.

Turonian samples is 0.14, suggesting a low salinity (γ column in Table 2) and a kind of low saline environment. It also means that the Cenomanian-Turonian anoxic beds in southern Tibet resulted from dissolved-oxygen-low anoxic environment in the open ocean, instead of a closing hypersaline depositional environment.

Despite an extensive, multidisciplinary study of Cenomanian/Turonian black shales, the precise controls over the onset and cessation of widespread organic-rich sedimentation are still unclear. Nevertheless, the present organic geochemical investigation has greatly enriched the data regarding the C/T OAE, with the following conclusions.

1) During the Cenomanian-Turonian periods in southern Tibet, rhythmic sequence consists of intercalated organic-rich laminated black shales and organic-poor marls or shales, showing periodic redox change. The TOC of the black shales (averaged 0.58%) is lower than in other parts of the world.

2) Organic inputs are dominated by marine organic matter (algae and bacteria) with a minor terrestrial input in the mid-Cretaceous in southern Tibet. The karogen type is mainly Type Ⅱ, similar to that in western Tethys. There are abundant tricyclic terpanes and pregnane, which are predominant in 191 and 217 mass chromatograms in the black shales of the Gamba area.

3) The difference in Pr/Ph ratio between the anoxic beds and other beds could be attributed to changes in redox conditions. Pr/Ph ratios in the Gongzha section are very low, averaging 0.31. The β- and γ-carotanes are sensitive monitors of redox change in depositional environment in southern Tibet. In the black shales, carotanes are relatively high; in the oxic beds, carotanes are low. Corresponding to the three global anoxic events (Late Jurassic Callovian, Early Cretaceous Aptian-Albian, and Middle Cretaceous Cenomanian-Turonian), the black shales in southern Tibet have very high β- and γ-carotanes.

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