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Organic geochemical characterization of Upper Cretaceous oxic oceanic sediments in Tibet, China: a preliminary study

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Abstract

Cretaceous strata, spanning the Berriasian to Maastrichtian, crop out widely in southern Tibet. The sedimentary sequence can be divided into the Gyabula, Chuangde and Zhongzuo formations. The Gyabula Formation, which is Berriasian–Coniacian in age, is composed mainly of black shales characterized by relatively high total organic carbon (TOC) levels and a positive organic carbon isotope excursion near the Cenomanian/Turonian boundary, which can be correlated to oceanic anoxic events (OAE2) or with the so-called Bonarelli Horizon in the western Tethys. The oceanic sediments of the Chuangde Formation are represented by red beds of Santonian–Campanian age, and are characterized by low TOC values, a negative organic carbon isotope excursion, and low nC_{17}/nC_{27} and nC_{17}/hopane ratios, which indicate that the primary production and burial of organic matter during this period was low. We suggest that the climate at the time was cool and the oceanic water oxygen-rich.

Keywords: Upper Cretaceous; Oxic environment; Oceanic red beds; Tibet

1. Introduction

Santonian–Campanian reddish coloured mudstones intercalated with limestones and marls crop out in the Tibetan Himalaya. These red beds were deposited in an oceanic environment that was characterized by having a high content of dissolved oxygen (Hu et al., 2001). By contrast, throughout the earlier Cretaceous (Berriasian–Turonian), deposition of organic-rich muds was widespread in this area. This has been attributed to deposition in a mostly anoxic environment (Wang et al., 2001). The late Cretaceous red beds and mid Cretaceous black shales in the Tibetan Himalaya that are a result of this deposition are similar to coeval successions known from the Alps, the Iberian Peninsula and the North Atlantic Ocean (Wilson and Norris, 2001; Hu et al., 2002). Even though many studies on oceanic anoxic events (OAEs) pertaining to Cretaceous black shales have been published since the pioneering work of Schlanger and Jenkyns (1976) (e.g., Arthur et al., 1988; Stein et al., 1989; Erbacher et al., 1996; Sinninghe Damaste and Koster, 1998; Jenkyns et al., 2001), publications on oxic oceanic sediments, and especially of their organic geochemistry, are scarce. In this paper we present results of an organic geochemical study of late Cretaceous red beds and black shales from the Tibetan Himalaya and discuss their possible climatic implications.

2. Geological setting

The study area is located along the southern Yarlung Zangbo Suture Zone in the Tethys Himalaya. Palaeogeographically it is located on the northern passive

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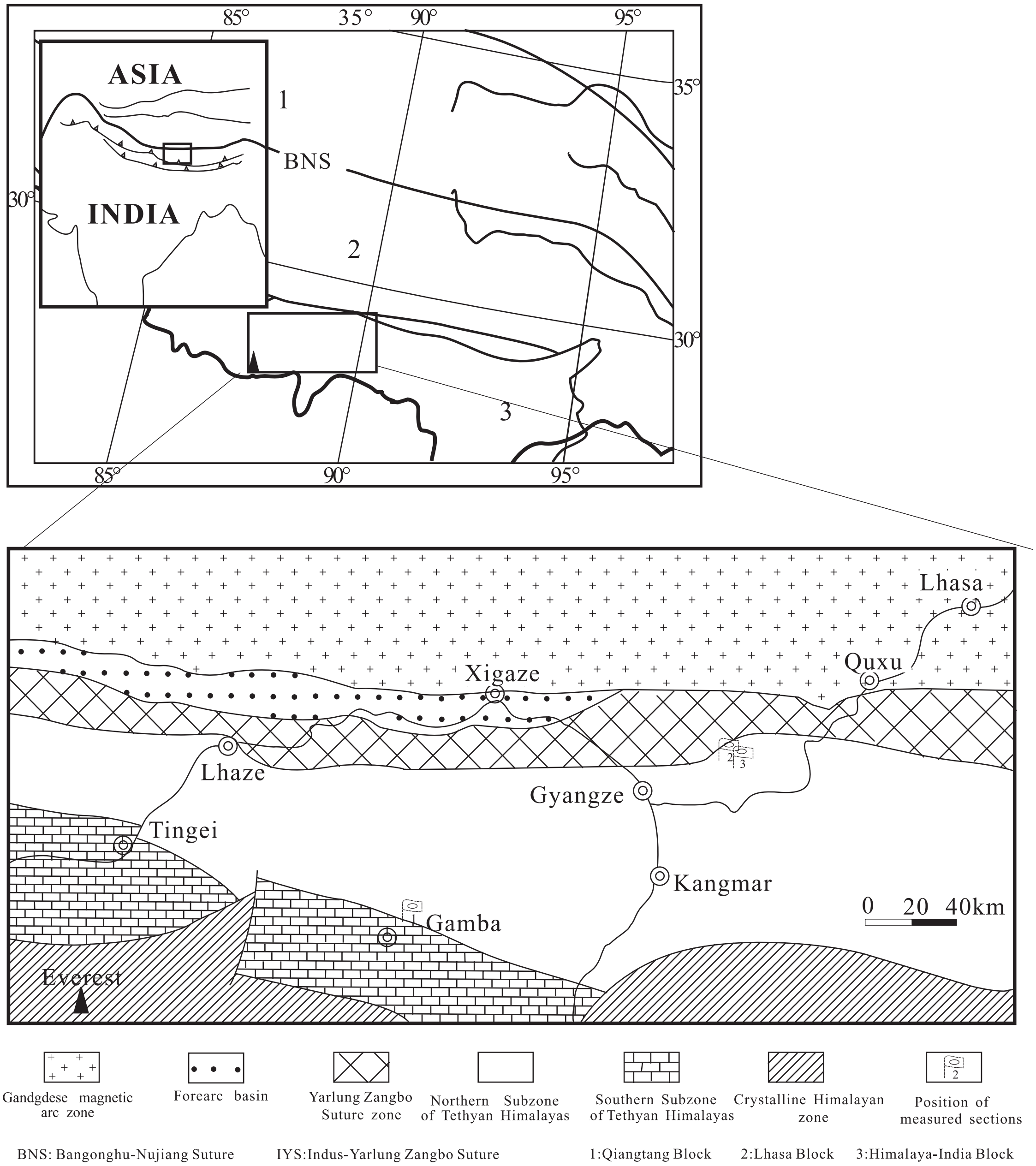

Fig. 1. Generalised geological map of the central part of southern Tibet showing the locations of the sections studied. 1, Gamba; 2, Chuangde; 3, Gyabula.

continental margin of the Indian Plate (Fig. 1). Three Cretaceous sections, Chuangde, Gyabula and Gyamba, were studied in detail because they represent different depositional settings (Willems and Zhang, 1993; Wang et al., 2001).

During the mid Cretaceous the study area was at a latitude of ca. 21 °S (Patzelt et al., 1996) and surrounded by an ocean connected eastward to the Pacific Ocean and westward to the Mediterranean Tethys (Wang et al., 2001). The early and mid Cretaceous sedimentary deposits consist of intercalated fine-grained quartzose and calcareous sandstones, black shales/mudstones and hemipelagic limestones, which reflect deposition on a deepening shelf and its upper slope. The succession has been subdivided into, in ascending order, the Dongshan, Chaquela, Lengqingre, Xiawuchubo, Jiubao and Zhongshan formations, and has been described in detail by Wen (1974) and Wan (1992).

The late Cretaceous (especially Santonian–Campanian) reddish coloured mudstones in Gyangze area, which are intercalated with marls and limestone beds, overlie the mid Cretaceous “black shales”. This marine sequence was recently redefined and described by Li et al. (1999) and Wang et al. (2001), and was subdivided

Table 1
Stratigraphic framework, planktonic foraminiferal zones, and the relationship between the three sections examined

Gyabula and Chuangde sections		Stage	Gamba section	
Formation	Zone		Zone	Formation
Zhongzuo		Maastrichtian		
	G. stuartiformis		*G. stuartiformis*	Zhongshan
Chuangde	*G. ventricosa*	Campanian	*G. ventricosa*	
	G. elevata		*G. elevata*	
	D. asymetrica	Santonian	*D. asymetrica*	
Gyabula		Coniacian	*D. concavata*	Jiubao
			D. primitiva	
			M. renzi	Xiawuchubo
		Turonian	*H. Helvetica*	
	W. archaeocretacea		*W. archaeocretacea*	
			R. cushmani	Lengqingre
		Cenomanian	*R. reicheli*	
			R. brotzeni	
		Albian | Berrasian		

into the Gyabula, Chuangde and Zhongzuo formations. The subdivision of stages and detailed descriptions have been carried out by Wan (1992), Willems and Zhang (1993), Wang et al. (2001) and Zhao and Wan (2003). The stratigraphic framework and planktonic foraminiferal zones are summarized in Table 1, which also includes correlations of the three sections examined.

3. Material and methods

"Anoxic" sediment samples were collected from the Gyabula Formation at Gyabula, and from the Lengqingre, Xiawuchubo and Jiubao formations at Gamba. Red-bed samples were collected from the Chuangde Formation at Chuangde. During sampling the weathered sediments were first removed from the surface of the section. Samples weighing about 1 kg were collected from the black shales of the Gyabula and Gamba sections, whereas samples weighing at least 2 kg were taken from the red beds of the Chuangde Formation.

The analytical procedures used in this study are standard (Durand and Nicais, 1980) in organic geochemistry. Briefly, rock samples were selected through handpicking and any contaminated matter was removed. They were then washed in distilled water and 0.1 M HCl, dried at 40 °C, then ground and sieved through a 125-μm mesh sieve. The powdered samples were used for total organic carbon (TOC) analysis using a LECO TOC analyzer and for solvent extraction. Soluble organic matter was obtained by chloroform extraction using a Soxhlet apparatus. During extraction the samples and blanks were analyzed in order to monitor whether any samples were contaminated during this procedure.

Extracted soluble organic matter (SOM) was concentrated using a Rotavapor and separated by column chromatography. The fraction of saturated hydrocarbons was subjected to GC-MS analysis for the identification of compounds. The residue after Soxhlet extraction was processed with HCl and HF to isolate kerogen (insoluble organic matter). The kerogen concentrate was washed with distilled water and dried at

Table 2
TOC and $\delta^{13}C$ values for the samples examined from Gyabula and Chuangde sections

Sample	TOC (wt %)	$\delta^{13}C$[a] (‰ vs. PDB)
CD235	0.02	−25.28
CD210	0.02	−24.80
CD195	0.04	−25.83
CD36W3	0.03	n.d.
CD35W2	0.03	−25.96
CD180	0.03	−26.07
CD150	0.02	−26.49
CD110	0.03	−25.86
CD094	0.06	−26.14
CD045	0.04	−26.46
CD025	0.09	−25.60
CD005	0.12	−25.78
CD31C1	0.13	n.d.
CD29C3	0.19	n.d.
CD29C2	0.22	n.d.
CD28C3	0.24	n.d.
CD28C1	0.17	−25.36
CD27W3	0.15	−25.50
CD27W1	0.15	−25.42
CD26S1	0.24	−25.85
CD25-2	n.d.	−25.02
CD25W1	0.20	−24.37
CD25C1	0.22	n.d.
CD24W1	0.50	−24.82
CD24C3	0.33	−24.32
CD23C1	0.12	−25.91
CD22C1	0.13	−25.76

n.d., not detected/measured.
[a] Average value of the two measurements with an error < 0.3‰ (PDB).

40 °C, then treated with chloroform to remove solvent-soluble organic matter. Elemental analysis of the kerogen was performed using a Heraeus CHN-O-Rapid analyzer, and stable carbon isotope ratio analysis was carried out using a Delta Plus XL. An ''Indiana'' standard was used for IRMS calibration and the calibrated CO_2 was used as test gas to calibrate the isotope ratios of the samples measured. The precision of the Delta Plus XL is $<0.3‰$ (PDB) for IRMS.

4. Results

A total of 27 samples from the Gyabula and Chuangde sections and seven from the Gamba section were collected. Twenty-six TOC measurements and 21 stable carbon isotope values for solid organic matter (kerogen) were obtained by elemental analysis and IRMS, respectively. The TOC and stable carbon isotope data are given in Table 2. Both sets of values were measured for the majority of samples from the Gyabula and Chuangde sections. Not surprisingly it was found that the TOC values are very low and the stable carbon isotope compositions of the kerogen are very light in the red beds. The TOC and stable carbon isotope composition of solid organic matter from the Gamba section were not measured in this study. Previous work has shown that the TOC range for the black shales in the section is 0.2–1.7 wt% (Hu et al., 2001).

GC-MS analysis was carried out on 20 samples from Gyabula and Chuangde sections, and again seven samples from Gamba section. A high content of nC_{17} hydrocarbon and a low amount of nC_{27} hydrocarbon and hopane were indicated for the black shales. In contrast, the red beds have a generally low content of nC_{17} hydrocarbon and a high content of nC_{27} hydrocarbon and hopane.

5. Discussion

Our results show that the black shales are comparatively rich in organic matter (TOC always higher than 0.2%) by comparison with the red beds (TOC generally less than 0.1%) (Fig. 2), the TOC decreasing gradually

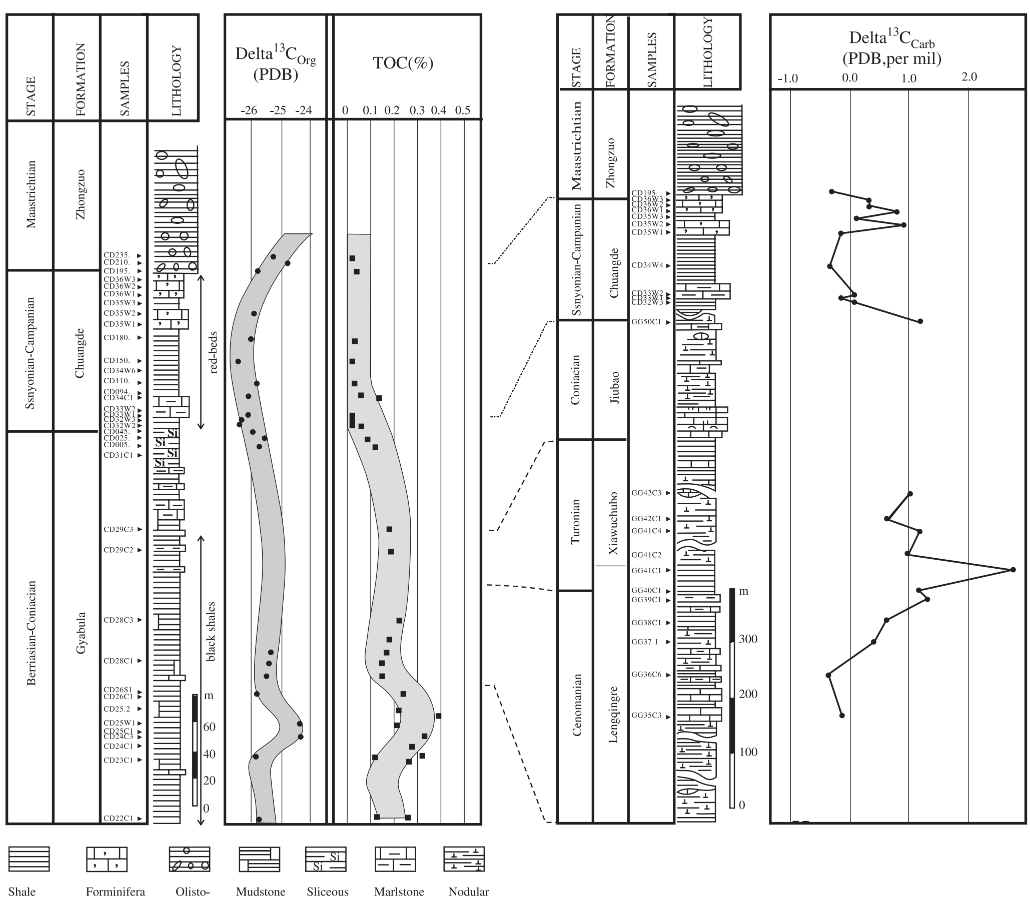

Fig. 2. Variation in TOC (%), carbon isotope composition of organic carbon ($\delta^{13}C_{org}$, per mil relative to PDB standard) and carbon isotope composition of carbonate rock ($\delta^{13}C_{carb}$, per mil relative to PDB standard). Samples from the Chuangde and Gyabula formations are from the Chuangde and Gyabula sections (left), respectively; those from the Lengqingre and Xiawuchubo formations are from the Gamba section (right). Data for the Jiubao Formation are not shown. Correlation of the sections is based on microfossil zones (Wang et al., 2001).

from the mid to the late Cretaceous deposits. The stable carbon isotope composition of the kerogen shows that the red beds have more negative values than the black shales (Fig. 2).

Although the TOC values for the mid Cretaceous black shales are relatively high, pyrite concretions and an abundance of the bottom-feeding trace fossil *Chondrites* indicate dysoxic rather than anoxic bottom-water conditions. This is consistent with previously determined TOC values for black shales in southern Tibet, which are lower than those in the western Tethys (Farrimond et al., 1990); in Europe the TOC in mid Cretaceous black shales is typically higher than 10%, and falls within range of 1.3–31.2% (Farrimond et al., 1990). The lower values in southern Tibet may be attributed to either reduced preservation of organic carbon (Wang et al., 2001) or lower primary productivity, although the positive $\delta^{13}C_{carb}$ excursion recorded in southern Tibet sections might indicate an increase in bioproductivity near the Cretaceous/Palaeogene boundary.

Several compounds were identified in the soluble organic matter (SOM) that was analyzed using GC-MS. The precursors of nC_{17} and nC_{27} indicate origins in algae and terrestrial organic matter, respectively. The presence of hopane implies that some of the organic matter is of bacterial origin. Both the nC_{17}/nC_{27} and nC_{17}/hopane ratios for the red beds are lower than those of the black shales. Generally, the nC_{17}/nC_{27} ratios are greater than 0.2 in the latter but <0.1 in the red beds; most nC_{17}/hopane ratios are greater than 10.0 in the black shales and usually less than 10.0 in the red beds. A high nC_{17}/nC_{27} ratio indicates less terrestrial input, whereas a high nC_{17}/hopane ratio usually suggests that the algal input and/or preservation was higher than that of bacterial origin in the sedimentary organic matter. The higher nC_{17}/nC_{27} and nC_{17}/hopane ratios for the black shales, by comparison with the red-bed ratios, indicate that algal remains dominate the organic matter in the mid-Cretaceous black shales (Fig. 3). The low nC_{17}/nC_{27} and nC_{17}/hopane ratios for the red beds suggest that a mixture of bacteria and terrestrial remains is preserved

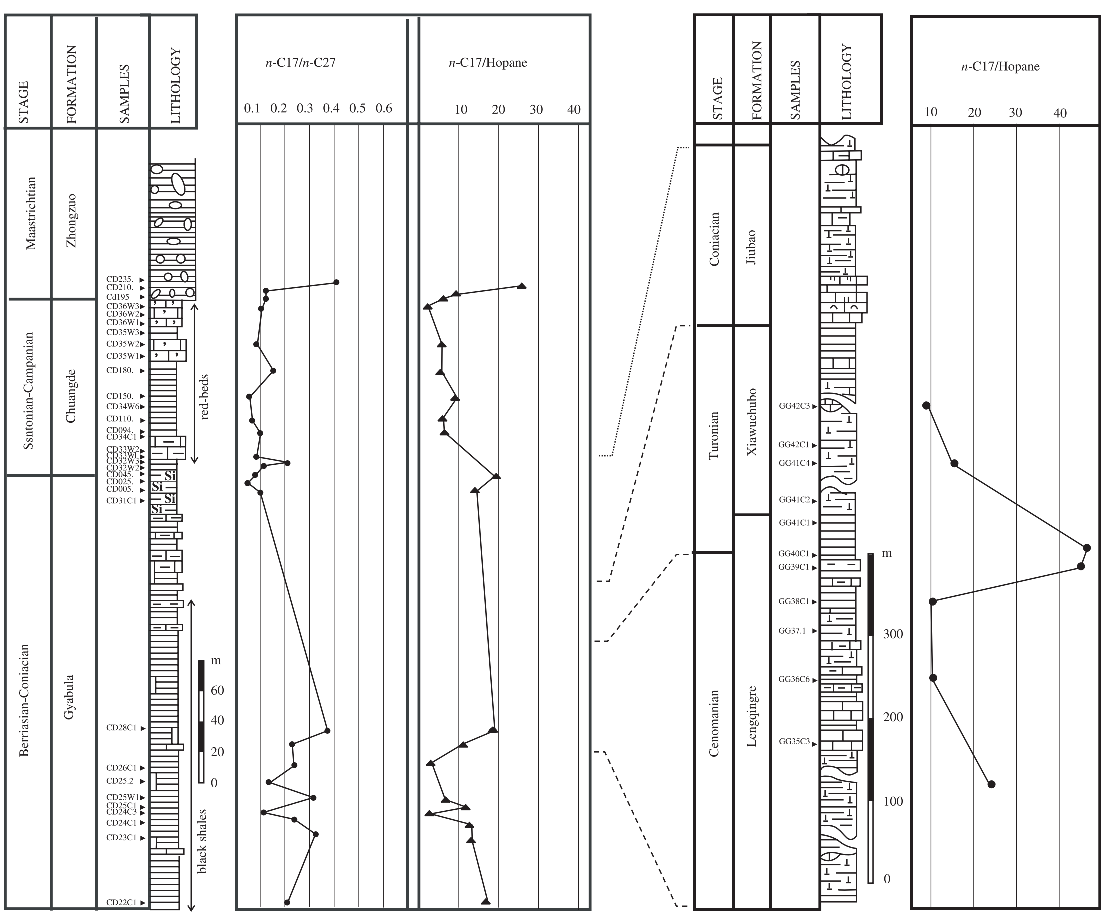

Fig. 3. Variation in nC_{17}/nC_{27} and nC_{17}/hopane ratios during the mid and late Cretaceous. Samples from the Chuangde and Gyabula formations are from the Chuangde and Gyabula sections (left), respectively; those from the Lengqingre and Xiawuchubo formations are from the Gamba section (right). Ratios of nC_{17}/nC_{27} were in total ion current (RIC) of GC-MS. Ratios of nC_{17}/hopane were calculated in RIC and m/z 191 mass chromatogram by area, respectively. For key to lithologies, see Fig. 2.

in these beds. In addition, the positive $\delta^{13}C_{carb}$ excursion that occurs in the mid Cretaceous deposits (Yin and Wang, 1998; Wang et al., 2001) and the negative $\delta^{13}C_{carb}$ excursion in the red beds (Hu et al., 2001) reflects the fact that burial of organic carbon in the red beds was less than in the black shales.

The results of our chemical analysis of major elements show that in the red beds the Ba/Al ratio, as an indicator of marine primary productivity (Thompson and Schmitz, 1997), is lower than that in the black shale (Fig. 4). This suggests that primary productivity in the ocean was low during red-bed deposition, which is in agreement with negative $\delta^{13}C_{org}$ and low nC_{17}/nC_{27} ratios in the red beds.

During the early Cretaceous, a carbonate platform developed along the margin of north Tethys (van de Schootbrugge et al., 2000) and the Tethyan Himalaya (Jadoul et al., 1998). In Tibet, the sedimentary record indicates that the maximum transgression occurred towards the end of the Cenomanian (Wan, 1992), which is in agreement with the reconstruction by Sliter (1976) of global sea-level changes through this period. At the same time, the climate was warmest and the atmospheric level of CO_2 probably highest (Scholle and Arthur, 1980; Barnes, 1999). The increase in CO_2 was linked by Fisher (1984) to volcanism and by Larson (1991) to a mantle superplume. With the increase in atmospheric CO_2 and temperature, the sea level gradually rose during the late Cretaceous and the climate became warm and humid. As a result, increased primary productivity led to the deposition and burial of relatively more organic matter in oceanic sediments, as indicated by their relatively high TOC content.

Because much organic carbon was generated and buried during the mid Cretaceous, CO_2 in the atmosphere gradually decreased and oxygen increased toward the end of Cretaceous. This would have induced significant cooling of the climate, increased levels of O_2 in the oxygen reservoir (Arthur et al., 1988), and led to a lowering of sea level (Stoll and Schrag, 2000). Associated with the cooling was aridity, a decrease in nutrient levels in the ocean and, hence, a reduction in primary productivity (Fig. 4). As both the atmosphere and the ocean were rich in oxygen, most of the organic matter in oceanic sediments was oxidized, with the result that only small quantities of marine and terrestrial origin were preserved (Figs. 2, 3).

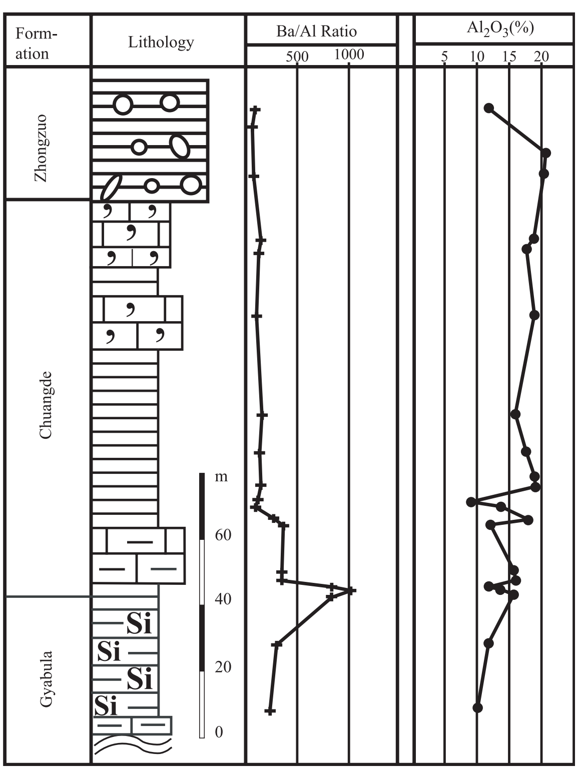

Fig. 4. Ba/Al ratios and Al_2O_3 content variation in the late Cretaceous red beds. Low ratios of Ba/Al indicate a low supply of nutrients in the ocean. The limited variation in percentage of Al_2O_3 in the sediments suggests that the dilution of terrestrial organic matter was fairly constant. The samples are from Chuangde (Zhongzuo and Chuangde formations) and Gyabula (Gyabula formation) sections, respectively. For key to lithologies, see Fig. 2.

6. Conclusions

The late Cretaceous oceanic red beds in Tibet are characterized by their low organic carbon content, a negative carbon isotope excursion, and lower ratios of both nC_{17}/nC_{27} and nC_{17}/hopane. These data suggest that the climate was cool and arid, and the oceanic water was well-oxygenated and poor in nutrients.

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