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Paleosalinity significance of occurrence and distribution of methyltrimethyltridecyl chromans in the Upper Cretaceous Nenjiang Formation, Songliao Basin, China

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ABSTRACT

A group of methyltrimethyltridecyl chromans (MTTCs) was found in core samples of Member 1 (K_2n^1) and Member 2 (K_2n^2) of the Nenjiang Formation (Upper Cretaceous) from the SK-I southern borehole (Songliao Basin, China). They are assigned for the first time in sediments older than the Tertiary in China. Their composition and distribution are indicative mainly of the redox and salinity conditions in the depositional environment. The δ-MTTC isomer is in relatively higher abundance in samples from enhanced salinity and reducing conditions, but was not detected in samples from aerobic and low salinity environments, while α-MTTC appears to be present in samples from environments with a broad range of salinity and redox conditions. The α-MTTC/γ-MTTC (α/γ) ratio has a similar indication as that of the α/δ ratio and could be used as a corroborative ratio of paleosalinity. A combination of biomarker parameters suggests that the massive lacustrine petroleum-prone source rocks associated with the K_2n^1 interval were likely developed under a stratified water column with enhanced salinity and an anoxic bottom water layer, associated with a much less saline (fresh to brackish) upper water layer.

1. Introduction

Methyltrimethyltridecyl chromans (MTTCs) are structurally similar to tocopherols (vitamin E) but with a hydrogen replacing an OH at C-6 (R_2; Fig. 1). According to the combination of functional groups at the R_1, R_3 and R_4 positions, MTTCs are termed α-MTTC, β-MTTC, γ-MTTC, δ-MTTC, ζ-MTTC and η-MTTC, although η-MTTC has never been found in a geological sample. In addition, MTTCs are classified as trimethyl-MTTC (α-MTTC), dimethyl-MTTC (β-, γ- and ζ-MTTC) and methyl-MTTC (δ-MTTC). Since the initial identification of α- and γ-MTTC in bituminous limestone from a gypsum sedimentary region (Goossens et al., 1984; Sinninghe Damsté et al., 1987), MTTCs have been reported from various modern and ancient sediments and crude oils. Sinninghe Damsté et al. (1989) indicated that δ- and γ-MTTC are dominant in hypersaline environments, while α-MTTC is the most abundant member in non-hypersaline environments associated with an absence or trace of δ-MTTC and γ-MTTC. In addition, β-MTTC is often present in both hypersaline and non-hypersaline environments, without a clear preference (Sinninghe Damsté et al., 1989). Furthermore, the α/δ MTTC ratio has been proposed as a marker for paleosalinity (Sinninghe Damsté et al., 1993; Grice et al., 1998), while a combination of Pr/Ph and MTTCI (MTTCI = α-MTTC/total MTTCs) values have been used to distinguish hypersaline, meso-saline and normal marine environments (Schwark et al., 1998; Peters et al., 2005). MTTCs have also been detected in sediments and crude oils from a wide range of depositional environments in China (Bao et al., 1987; Sheng et al., 1987; Fan and Fu, 1988; Jiang et al., 1990, 2004; Zhang and Huang, 1990; Huang, 2006). The isomers detected include δ-MTTC, α-MTTC, β-MTTC, γ-MTTC, 6-MTTC and ζ-MTTC, and these are found mainly in Tertiary and younger sediments and crude oils (Zhu et al., 2003, 2005); they have not been reported from pre-Tertiary sediments in China. The oldest reported occurrence globally was in Phosphoria retort shales of Permian age from the northwestern part of Montana (USA; Sinninghe Damsté et al., 1987).

Despite their wide occurrence, the origin and precursors of MTTCs are not clear and are still debated (Peters et al., 2005). Sinninghe Damsté and co-workers proposed a biological origin, possibly from eubacteria or archaea (Sinninghe Damsté et al., 1987; de Leeuw and Sinninghe Damsté, 1990; Kenig et al., 1995), while other studies suggest that they may be formed abiotically from biological precursors during diagenesis (Li et al., 1995; Lu et al., 2007). Consequently, the use of MTTCs as indicators of paleosalinity is ambiguous.

The finding of MTTCs in Upper Cretaceous sediments from a continuous core of the SK-1 southern borehole in the Songliao Basin of China provides an excellent opportunity for studying their source and significance in a lacustrine environment, including

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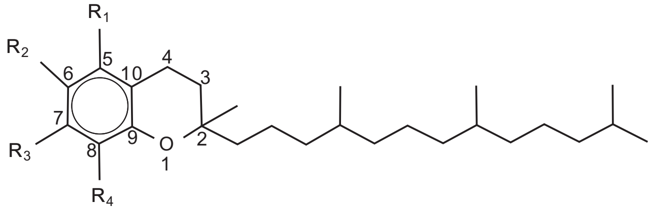

Tocopherols

	α	β	γ	δ	ζ	η
R_1	$-CH_3$	$-CH_3$	$-H$	$-H$	$-CH_3$	$-H$
R_2	$-OH$	$-OH$	$-OH$	$-OH$	$-OH$	$-OH$
R_3	$-CH_3$	$-H$	$-CH_3$	$-H$	$-CH_3$	$-CH_3$
R_4	$-CH_3$	$-CH_3$	$-CH_3$	$-CH_3$	$-H$	$-H$

Chromans

	α	β	γ	δ	ζ	η
R_1	$-CH_3$	$-CH_3$	$-H$	$-H$	$-CH_3$	$-H$
R_2	$-H$	$-H$	$-H$	$-H$	$-H$	$-H$
R_3	$-CH_3$	$-H$	$-CH_3$	$-H$	$-CH_3$	$-CH_3$
R_4	$-CH_3$	$-CH_3$	$-CH_3$	$-CH_3$	$-H$	$-H$

Fig. 1. Structures of tocopherols and chromans.

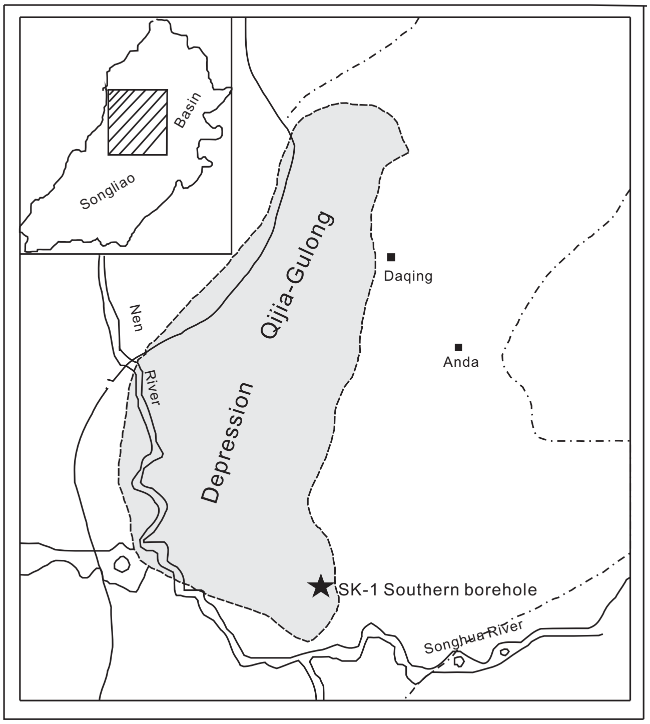

Fig. 2. Location of Songliao Basin and SK-1 southern borehole where the samples are from.

the implications for paleosalinity. In addition, we document new organic geochemical evidence for the paleoenvironmental conditions during deposition of massive lacustrine source rock formations of the Upper Cretaceous in the Songliao Basin.

2. Samples and experimental procedures

The Songliao Basin is in northeastern China and covers a vast area of 260,000 km^2, with a total thickness of 10 km of Cretaceous lacustrine sediments (Fig. 2). The SK-1 boreholes are situated on the Qijia-Gulong Depression, one of the major depositional centers in the basin. During the Upper Cretaceous, the basin developed two major sedimentary settings for organic rich source rocks, associated with the K_2q^{1+2} of the Qingshankou Formation and the K_2n^{1+2} of the Nenjiang Formation. The core samples were collected from a depth of 950–1300 m in the SK-1 southern borehole, covering the whole section of the K_2n^1 and the lower part of the K_2n^2. The lithology of this section is made up mainly of gray to dark mudstones (occasionally green) interbedded with oil shale intervals, and the depositional environment is regarded as mainly deep to shallow shore lacustrine facies (Wang et al., 2008).

The samples were crushed to pass 100 mesh and Soxhlet extracted using CH_2Cl_2/MeOH (9:1). After evaporative solvent removal, the extracts were dissolved in hexane to remove asphaltenes and the maltene fraction was separated into aliphatic, aromatic and polar fractions via alumina/silica gel column chromatography using hexane, hexane/CH_2Cl_2 (4:1) andCH_2Cl_2/MeOH (1:1), respectively.

A Thermo Finnigan Trace Ultra Gas Chromatograph with a flame ionization detector (FID) was used for gas chromatography (GC). A J&W DB-5 fused silica column (30 m × 0.25 mm i.d.; 0.25 μm film thickness) was used. The injector and detector temperatures were 290 °C and 300 °C, respectively. The samples were injected in splitless mode and N_2 was the carrier gas. The oven temperature was initially 80 °C (held 2 min) and was programmed at 4 °C /min to 290 °C (held 20 min).

GC–mass spectrometry (GC–MS) was performed with a HP 6890 series II GC instrument interfaced to an HP 5972 mass spectrometer (electron impact ion source, 70 eV). GC conditions were as above. The MS scan range was m/z 50–600. He was the carrier gas at 1.0 ml/min. The aromatic and aliphatic fractions were analysed for the occurrence of MTTCs and biomarkers. The MTTCs were detected by way of m/z 121 (δ-MTTC) + m/z 135 (β-MTTC, γ-MTTC and ζ-MTTC) + m/z 149 (α-MTTC) chromatograms. Relative quantification followed the methods described by Sinninghe Damsté et al. (1993). The gammacerane index was calculated from peak areas in m/z 191 chromatograms.

The total organic carbon (TOC) content was measured using Rock–Eval 6 (French Vinci Technologies) and was calculated as the combination of the CO_2 released below 400 °C and the discharged CO discharged below 570 °C.

Algal microfossils were identified using transmitted light microscopy and fluorescence microscopy. The surface of core samples was washed using distilled water before treatment with acid. After distilled water washing and drying, the treated samples (ca. 20–50 g) were crushed to 0.5 mm and dissolved in a mixture of HCl and HF. Subsequently, they were centrifuged in distilled water to concentrate the residue and remove clay and waste. The organic matter (OM) was floated using dense liquid (HI + KI + Zn, 2.0 g/ml). The residues were removed using filtration and the floated OM was collected and subjected to microscopy for identification and quantification of algal genera.

3. Results

Five MTTC isomers were found in the aromatic fractions (Fig. 3). Their occurrence and distribution in the core profile display clear changes coinciding with chronostratigraphic unit changes. Based on the MTTC distribution and the variation in related parameters such as α-MTTC/total-MTTC (MTTCI) and pristane/phytane (Pr/Ph), the profile could be divided into five sections (I–V). Fig. 3 shows the representative summed mass chromatograms for the MTTCs from each section. The details of each section are described below (from top to bottom).

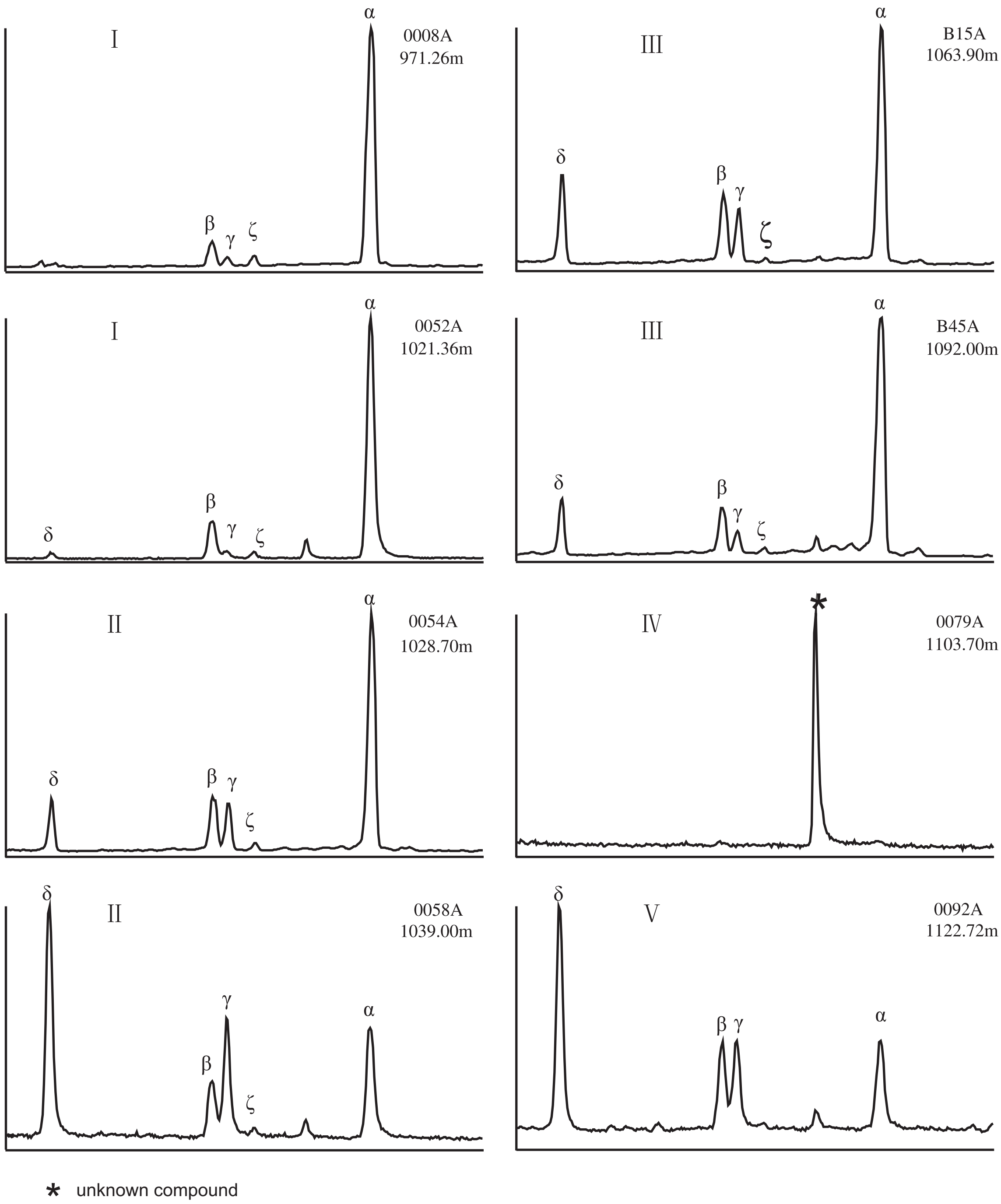

Fig. 3. Representative mass chromatograms (*m/z* 121 + 135 + 149) showing profile variation in MTTCs occurrence.

Section I ranges from 950 m up to 1026 m, covering the entire lower part of the K_2n^2 of the Nenjiang Formation. This section is characterized by the non-detection of δ-MTTC and a dominance of α-MTTC, while β-MTTC and γ-MTTC occur in relatively small amounts. A small peak at the same retention time as δ-MTTC in samples from this section lacks the characteristic *m/z* 121 and 161 ions, and has prominent ions at *m/z* 259 and 274, so is not due to α-MTTC (Fig. 3). The relative abundance of the isomers is $\alpha \gg \beta > \gamma \gg \delta$. The ratio of α/γ varies from 15 to 60, while the MTTCI ratio varies from 0.82 to 0.88. Because δ-MTTC was not detected in this section, the α/δ ratio can be assumed to be >100.

Section II represents the top part of the K_2n^1 of the Nenjiang Formation and covers an interval from 1026 m to 1046 m. This section is characterized largely by a dominance of δ-MTTC, associated with significant presence of γ-MTTC, except that near the top of section II the distribution is dominated by α-MTTC (e.g. 1028.7 m; Fig. 3). The relative abundance of the MTTCs is mostly in the order $\delta > \gamma > \alpha > \beta$, although is sometimes $\alpha > \delta > \beta > \gamma$). The MTTCI value varies from 0.16 to 0.64 and is the lowest of the whole profile. The α/δ and α/γ ratios are both <2, ranging from 0.28 to 0.82 and 0.83 to 1.9, respectively.

Section III contains the most important organic rich source rocks of the Nenjiang Formation and covers most of the middle to lower part of the K_2n^1 section, ranging from 1046 m to 1099 m. All the MTTC isomers occur (although ζ is only a trace component) and are dominated by α-MTTC (Fig. 3). The relative abundance is in the order $\alpha > \delta > \beta \gg \gamma$. MTTCI varies from 0.51 to 1.0, while α-MTTC/δ-MTTC and α-MTTC/γ-MTTC are in the range 1.4–33.7 and 3.6–21.9, respectively.

Section IV covers the interval 1099–1116 m of the K_2n^1 member and is characterized by the virtual absence of MTTC isomers (Fig. 3). The TOC content (0.24–0.84%) is the lowest in the profile. Coincidently, the section also lacks gammacerane. The low TOC content is connected with a sedimentary faces dominated by siltstones or silty mudstones.

Section V is the bottom part of the K_2n^1 member from a depth of 1116–1126 m. It has a high TOC content (3.6–9.2%). All five MTTCs are present and are dominated mainly by δ-MTTC, although the very top sample of the section has α-MTTC dominance and ζ-MTTC as a trace component. The α-MTTC/δ-MTTC is 0.49–1.0, while the sample at the very top of the section does not contain δ-MTTC and seems to be a transitional sample to section IV. The relative abundance of β-MTTC in section V ranges from much higher to slightly higher than that of γ-MTTC.

Although ζ-MTTC was detected in trace amount in all samples except those from section IV, it is rarely reported in studies of Chinese samples; its geochemical significance is not clear and needs further investigation.

4. Discussion

To enable a better understanding and discussion of the significance of the occurrence and distribution of MTTCs and their related ratios, more detailed information for all 42 samples is provided in Table 1, including burial depth, TOC content, hydrogen index (HI), MTTC ratios, gammacerane index and the assembly of algae microfossils and lithology. The related Figs. 4–6 are plotted according to

Table 1
Depth, Rock–Eval, MTTC, biomarker ratio, algal fossil and lithology data.

Sample	Organo facies	Depth (m)	TOC (%)	HI (mg/g)	α/δ	α/γ	MTTCI	Pr/Ph	Ga/C_{31}R	Lithology and assembly of algae fossils and salinity implications
1	I	955.40	0.96	184	–	12.4	0.82	1.97	–	Gray silt-containing mudstone interbedded with gray mudstone. *Granodiscus* and *Leiosphaeridia* (occasional *Sigmopollis*) dominant, *Botryococcus braunii* significant, and occasional *dinoflagellates*. Interpretation: fresh to brackish water
2		957.00	1.03	176	–	16.5	0.86	1.15	0.36	
3		962.00	0.88	186	–	18.3	0.87	1.74	–	
4		971.26	1.67	181	–	25.0	0.87	1.72	–	
5		978.16	1.89	249	–	29.6	0.88	1.96	–	
6		983.92	2.27	356	–	31.4	0.86	1.98	–	
7		989.92	1.60	260	–	36.7	0.87	1.75	–	
8		1001.37	2.34	422	–	43.7	0.83	2.24	–	
9		1007.17	2.13	455	–	45.0	0.86	2.92	–	
10		1012.61	3.66	623	–	32.3	0.83	2.49	–	
11		1016.80	4.15	727	–	15.5	0.79	0.92	0.78	
12		1021.36	4.34	715	–	59.6	0.90	1.05	–	
13	II	1028.70	1.36	475	3.00	5.2	0.64	0.65	0.79	Gray mudstone. *Sigmopollis* dominant, *Leiosphaeridia* and *Botryococcus braunii* in moderate abundance. Interpretation: fresh to brackish water
14		1034.00	2.14	491	0.16	0.7	0.16	0.66	2.39	
15		1039.00	2.98	603	0.34	1.0	0.24	0.74	0.78	
16		1045.24	3.98	718	0.46	1.7	0.33	0.70	1.58	
17	III	1051.04	4.45	680	–	69.1	0.91	0.76	0.96	Gray and dark mudstone and shales. *Botryococcus braunii* dominant *Granodiscus* and *Leiosphaeridia* occasionally in abundant, occasional *dinoflagellata*. Interpretation: fresh to slightly brackish water
18		1058.04	1.57	440	–	7.6	0.61	0.72	1.62	
19		1061.10	2.58	599	4.53	7.8	0.69	0.81	0.53	
20		1063.90	4.07	711	1.54	4.5	0.56	0.96	0.53	
21		1066.70	3.09	652	3.37	6.4	0.64	0.75	0.75	
22		1069.60	5.72	762	19.39	17.7	0.76	0.90	0.42	
23		1072.40	3.71	688	1.47	3.5	0.51	0.64	1.20	
24		1075.20	4.14	712	2.88	5.8	0.63	0.76	0.75	
25		1078.00	3.45	677	1.95	4.8	0.59	0.64	1.08	
26		1080.60	3.10	704	2.16	6.0	0.62	0.56	2.08	
27		1083.30	6.43	647	0.73	2.9	0.44	0.59	0.95	
28		1086.00	2.22	477	2.97	8.9	0.67	0.73	3.96	
29		1092.00	5.70	812	3.48	11.6	0.70	0.46	1.66	
30		1094.50	12.00	806	1.60	5.4	0.58	0.62	0.21	
31		1097.50	2.79	544	2.28	13.1	0.66	0.60	0.93	
32	IV	1099.50	0.24	75	–	–	1.00	1.24	–	Siltstone or silty mudstone. No algal fossils identified
33		1100.50	0.19	111	–	–	1.00	1.03	–	
34		1103.70	0.36	144	–	–	1.00	1.60	–	
35		1107.14	0.53	164	–	–	1.00	1.85	–	
36		1110.90	0.84	455	–	–	1.00	1.30	0.86	
37	V	1116.92	4.05	566	6.64	21.0	0.64	1.39	0.29	Silty mudstone. *Botryococcus braunii* dominant, but occasionally *Leiosphaeridia* dominant, occasional *Granodiscus* or *Pediastrum boryanum* in moderate abundance. Interpretation: fresh to brackish water
38		1118.40	0.16	–	7.46	11.7	0.65	2.78	0.21	
39		1121.40	5.45	587	3.07	6.3	0.47	2.36	0.25	
40		1122.72	4.35	649	0.32	1.0	0.21	0.88	2.09	
41		1123.20	7.01	766	1.00	3.5	0.34	1.05	0.53	
42		1124.3	7.97	737	0.74	2.7	0.31	0.8	0.76	

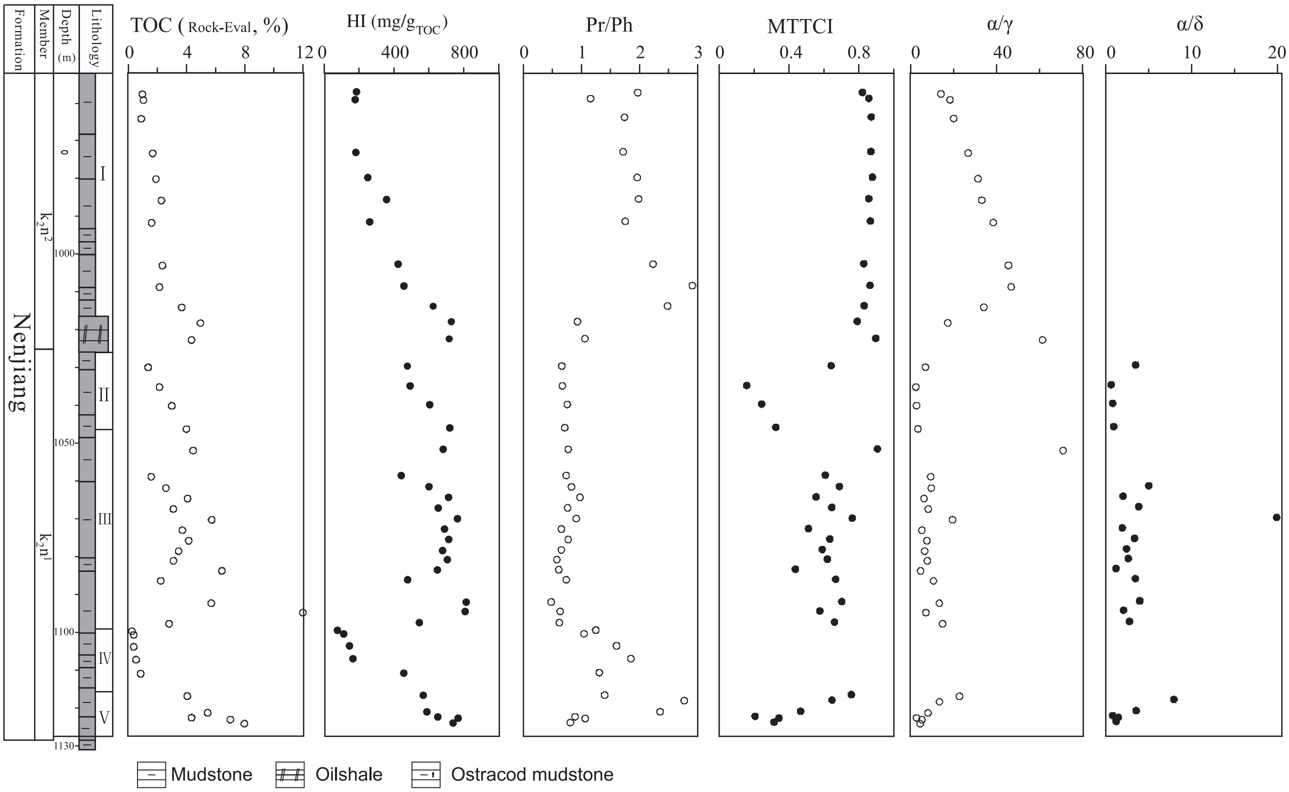

Fig. 4. Depth variation in TOC, HI, Pr/Ph and MTTC ratios for the Nenjiang Formation.

the data in Table 1, which shows that the five sections are clearly distinguished from each other according to these parameters.

4.1. Factors correlating with the occurrence of MTTCs

The depth variations in the occurrence and distribution of MTTCs are not random, but show some correlation with the changes in other organic geochemical indices (Fig. 4).

The K_2n^2 member (interval of section I) generally has a lower TOC content of 0.96–4.34% (mostly <3%). The HI ranges from 180 mg/g to 600 mg/g, with most samples <300 mg/g, indicating Type II and III OM dominance. This coincides with the dominance of α-MTTC and an assumed α/δ value of >100, as δ-MTTC was not detected.

The occurrence and distribution of MTTCs in the K_2n^1 section is more complicated and shows irregular periodical changes, as this stratum is divided into four sections as described above. The MTTCs are not uniformly distributed through the section, as α-MTTC and δ-MTTC dominance displays irregular changes. It is evident that the TOC content and OM type (as suggested from HI) are not the factors controlling the occurrence of MTTCs. We analysed the MTTC distributions in samples from the K_2q^{2-3} member of the Qingshankou Formation from a nearby borehole and the results show a similar pattern to that of K_2n^2 of the Nenjiang Formation. The K_2q^{2-3} member is an older and more mature Upper Cretaceous sequence than K_2n^{1-2}, which is a low TOC section and the MTTCs are characterized by α-MTTC dominance and the absence of δ-MTTC. So, this demonstrates that MTTC distribution is not controlled by maturity.

The variation in the occurrence of MTTCs and related ratios in the profile displays some changes consistent with the variation in Pr/Ph (Fig. 4). The non-detection of δ-MTTC in section I of K_2n^2 and the completed lack of MTTCs in section IV of K_2n^1 from a depth of 1099–1116 m, coincides with Pr/Ph values >1, while the major part of K_2n^1 displays Pr/Ph < 1. The variation in Pr/Ph shows some correlation with the changes of α/γ and MTTCI (Figs. 4 and 5c). For example, a Pr/Ph value >1 coincides with high values of α/γ and MTTCI, while the sections with Pr/Ph < 1 have low values of α/γ and MTTCI. Furthermore, although there is no clear linear relationship between Pr/Ph and MTTCI, Fig. 6 shows that the samples from sections III and IV of K_2n^1 and section I of K_2n^2 have MTTCs that are clearly grouped differently from the five samples from section V.

Coincidently, the absence of δ-MTTC from section I of K_2n^2 and lack of MTTCs from 1099 m to 1116 m also coincides with the absence of gammacerane (occasionally present in trace abundance), while the occurrence of all five MTTC isomers is associated with the presence of gammacerane through sections II, III and V of K_2n^1. The absence of δ-MTTC from Chinese peat and swamp environments has been reported by Zhang and Huang (1990).

The microfossil analysis shows that, although the major genera of algae vary greatly in the different sections, the majority are fresh to brackish water types. The sedimentary facies analysis also indicates that the K_2n^1 section was developed mainly under deep water interrupted with short periods of shallow or coastal lacustrine environments, while the K_2n^2 section was deposited under shallow to moderately deep water (Gao et al., 2010; Zhang et al., 2010).

4.2. Paleoenvironmental significance and origin of MTTCs

The occurrence and distribution of MTTCs are correlated with the profile variation in Pr/Ph ratio, gammacerane index and algal fossil information, thereby providing a basis for discussing the environmental significance and origin of the MTTCs.

Pr/Ph has been widely used as an indicator of depositional redox conditions (Powell and McKirdy, 1973; Barbe et al., 1990), with Pr/Ph > 3 indicative of oxic to suboxic depositional conditions, while Pr/Ph < 0.8 indicates saline to hypersaline and/or anoxic conditions. The ratio has also been considered to be indicative of enhanced salinity when <0.5 (Schwark et al., 1998). However, due

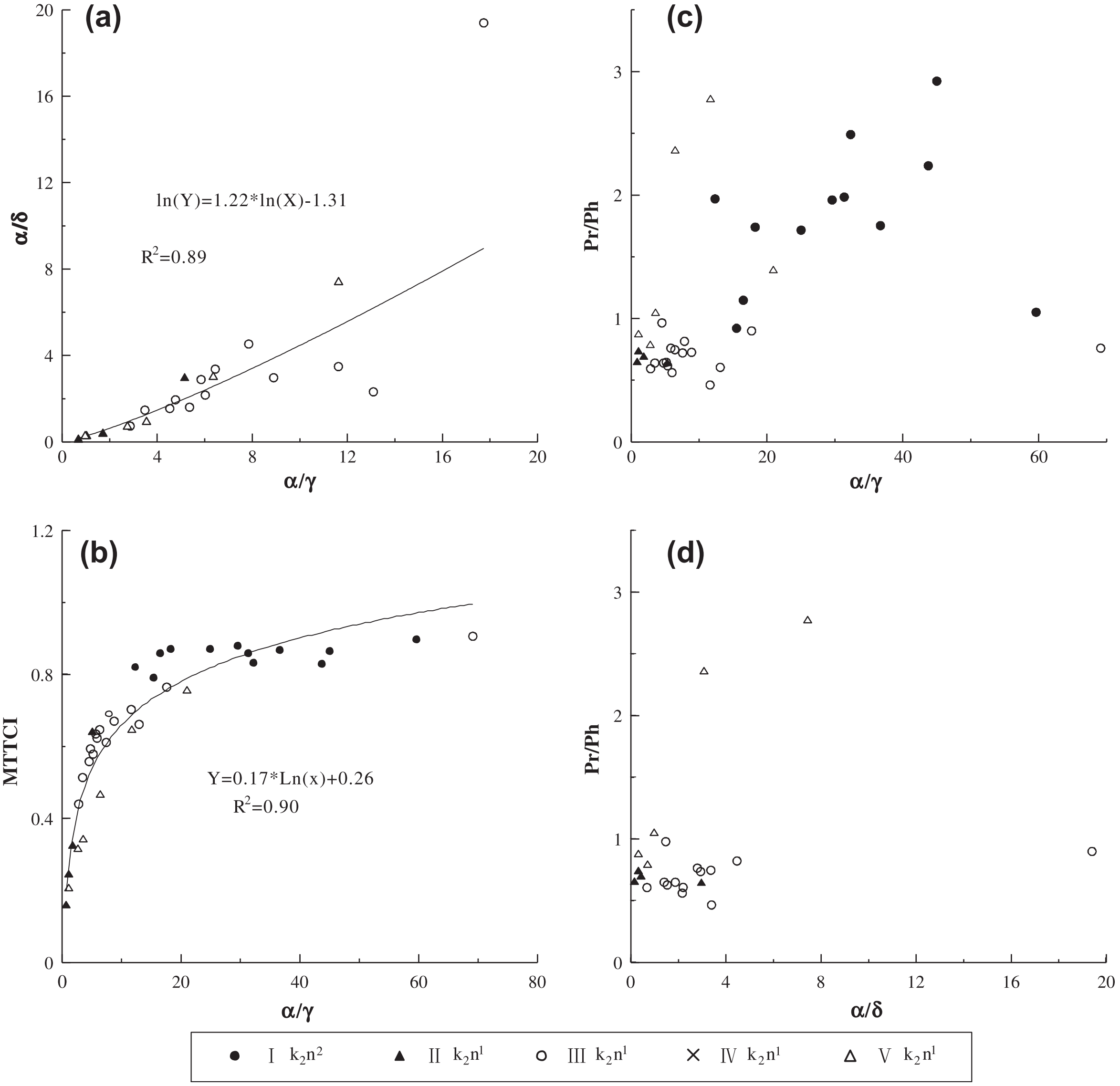

Fig. 5. Cross-correlation of α/γ vs. α/δ, Pr/Ph and MTTCI, and α/γ vs. Pr/Ph.

to other potential origins of both Pr (e.g. Rontani et al., 2010) and Ph, Pr/Ph values in the range of 0.8–3.0 are not recommended for indicating depositional redox conditions without corroborating evidence (Peters et al., 2005). Because only some samples in the dataset have a Pr/Ph value <0.8, the Pr/Ph ratio in this study is taken as suggestive of redox conditions.

Gammacerane is widely regarded as an empirical indicator of paleosalinity, and possibly a marker for photic zone anoxia (ten Haven et al., 1985, 1988; Moldowan et al., 1985; Sinninghe Damsté et al., 1995; Schwark et al., 1998), as it is considered to originate from tetrahymanol in bacterivorous ciliates living at the boundary of an enhanced salinity water layer, with an upper layer of less saline water. Salinity stratification implies circulation restriction and possibly temperature stratification, which in turn causes an enhancement of redox stratification in the water body. Therefore, significant amounts of gammacerane are generally suggestive of either an effect of salinity or anoxicity, or a combination of both. Where the gammacerane/22R C_{31} hopane ($Ga/C_{31}R$) ratio is high in the dataset, anoxic conditions, as suggested from low Pr/Ph values, are corroborated.

Therefore, sections II and III of the K_2n^1 member associated with Pr/Ph < 0.8 and the occurrence of significant gammacerane ($Ga/C_{31}R > 0.4$; avg. 0.23) might suggest that a salinity-stratified water column and anoxic depositional conditions prevailed during the deposition of these sections. On the other hand, sections I and IV with Pr/Ph 0.92–2.92 and an absence of gammacerane may be indicative of an oxic or suboxic depositional conditions and non-stratified water body. It should be pointed out that a low Pr/Ph value and the presence of gammacerane also occurs at the bottom of the section I (samples 11 and 12; Table 1), and these can be taken as a transition period from section II, with brief changes in the lacustrine depositional environments. Section V displays a higher and varying Pr/Ph ratio of 0.80–2.78 and significant amounts of gammacerane ($Ga/C_{31}R$ 0.21–2.08). So, the Pr/Ph ratio may be suggestive of a wide range of redox conditions for section V but the occurrence of gammacerane suggests that this section may have been deposited under an enhanced salinity environment. Therefore, the lack of δ-MTTC, as well as the complete absence of MTTCs associated with Pr/Ph > 1, may be indicative of an oxic to suboxic depositional environment, while α-MTTC dominance, often associated with Pr/Ph < 1, is likely indicative of a reducing depositional environment.

Gammacerane occurs mainly in most parts of K_2n^1 and is associated with α-MTTC or δ-MTTC dominance. This suggests that a

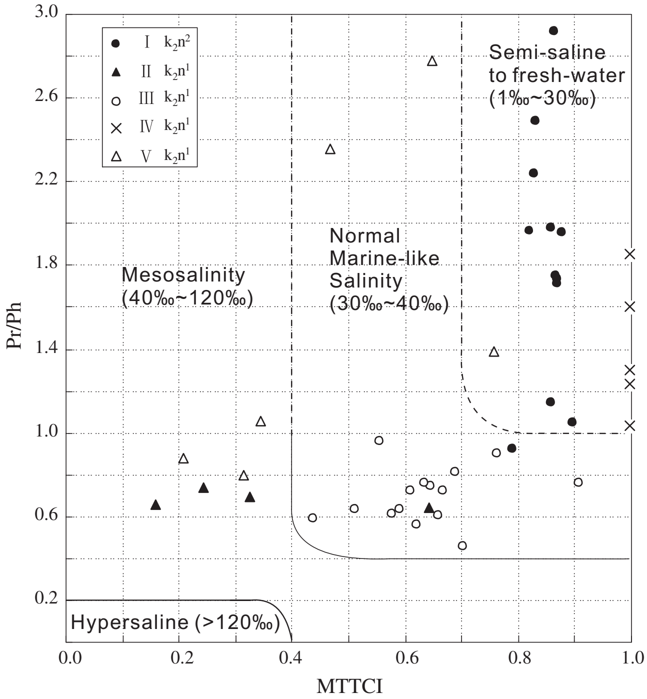

Fig. 6. Proposed revision of salinity inferences from MTTCI vs. Pr/Ph for the Nenjiang Formation (after Schwark et al., 1998).

salinity stratified water column existed during the deposition of sections II, III and V of K_2n, with the bottom water layer having high salinity. The complete absence of gammacerane from the entire K_2n^2 section and interval IV of K_2n^1, which is associated with α-MTTC dominance and δ-MTTC deficiency or a complete lack of MTTC isomers, respectively, is indicative of a non-stratified water column.

Accordingly, a δ-MTTC dominance associated with Pr/Ph < 1 is indicative of anoxicity and hypersaline conditions in the water body, an α-MTTC dominance associated with Pr/Ph < 1 is indicative of enhanced salinity stratified and reducing conditions in the bottom water layer, while an α-MTTC dominance associated with an trace of δ-MTTC or a complete absence of MTTCs with Pr/Ph > 1 is suggestive of oxic or suboxic fresh to brackish water conditions.

The algal fossils also provide important evidence for the salinity conditions. Because they are largely fresh water to brackish genera over the whole profile, this suggests that the sections associated with low Pr/Ph values <1, the presence of gammacerane and the dominance of α-MTTC or δ-MTTC were deposited under stratified conditions with anoxic bottom waters, while sections I and IV, associated with the non-detection of δ-MTTC, undetectable gammacerane and lack of algal fossils, as well as high Pr/Ph values >1, were likely deposited under oxic and non-stratified fresh to brackish water conditions.

Although the MTTC ratios are widely used as indicators of paleosalinity, the reason for the correlation is unknown because the origin of MTTCs is not clear (Peters et al., 2005).

The co-existence and/or co-absence of MTTCs and algal fossils from the Songliao Basin imply that the MTTCs or their precursors likely originated from algal OM input. However, discrepancies in the occurrence of MTTCs and in the variation of algal species further suggests that algae are likely one of the input sources of MTTC precursor compounds; in other words, the MTTCs are abiotically formed from the precursors derived from algae during sedimentation and early diagenesis. Anyhow, there are also possibilities that MTTCs may be formed physicochemically by way of reactions under certain depositional conditions or biochemically from bacterial communities. Consequently, the occurrence of MTTCs is controlled by the depositional and early burial redox and salinity conditions of the water layer beneath the upper water column.

Sinninghe Damsté et al. (1989) proposed using the α/δ MTTC ratio as a paleosalinity indicator: a value >100 is indicative of non-hypersaline conditions, while a value <2 is indicative of hypersaline environments (Sinninghe Damsté et al., 1993; Grice et al., 1998). Because a high value of α/δ MTTC can be assumed due to the non-detection of δ MTTC in section I, this ratio is largely applicable to most parts (sections I, II, III and V) of the profile except section IV of K_2n^1 where MTTCs are completely absent. Furthermore, Schwark et al. (1998) suggested using Pr/Ph vs. MTTCI to distinguish a hypersaline from a normal marine salinity environment. Pr/Ph < 0.2 and MTTCI < 0.5 were assigned to hypersaline conditions, Pr/Ph > 0.2 and MTTCI < 0.4 were considered to represent a mesosaline environment, while Pr/Ph > 0.4 and MTTCI > 0.4 were regarded as representing a normal marine saline environment (Schwark et al., 1998). So, both α/δ and MTTCI ratios can be applied through most of the profile of the K_2n^1 and K_2n^2 sections, except the interval in K_2n^1 where there is an absence of MTTCs. However, these two proposals do not address brackish to fresh water environments although MTTCs are found in such depositional settings, as demonstrated in this and other studies in China (Fan and Fu, 1988; Zhu et al., 2005). Therefore, with reference to the occurrence of MTTCs and the related ratios in the K_2n^2 section, it is now suggested that MTTCI > 0.7 and Pr/Ph > 1 associated with a lack of δ-MTTC are indicative of fresh water to brackish and oxidizing environments.

By comparing the variations in MTTCI, α/γ and α/δ ratios (Fig. 4), it is clear that all three ratios display high values in section I (where the α/δ is taken as >100; see Table 1), while α/γ shows a steady increase with depth, but reduces quickly at the bottom of section I. Fig. 5a and b also shows that α/γ has a positive relationship with α/δ and MTTCI. This suggests that the α/γ MTTC ratio has similar paleosalinity significance as the α/δ and MTTCI ratios. With reference to the paleosalinity significance of the MTTCI ratio (Schwark et al., 1998), a mesosaline environment is suggested when α/γ MTTC is <2, and a fresh water to brackish environment when α/γ MTTC is >15, while normal marine salinity is suggested by α/γ MTTC in the range of 2–15.

In addition, the changes in the relative abundance of β-MTTC vs. γ-MTTC on the profile may bear some implications for environmental change. In K_2n^2, the relative abundance of β-MTTC is similar to that of γ-MTTC and is associated with high α/γ MTTC values >15. In section II of K_2n^1, the relative abundance of β-MTTC is less than that of γ-MTTC, which is associated with α/γ and α/δ MTTC values <2, while in sections III and V of K_2n^1, the relative abundance of β-MTTC is greater than that of γ-MTTC, with a α/γ MTTC value ranging from 4–15. It seems that the relative abundance of β-MTTC vs. γ-MTTC is indicative of salinity; for example, β-MTTC > γ-MTTC is indicative of a non-hypersaline environment, while β-MTTC < γ-MTTC suggests a hypersaline environment.

4.3. Redox and paleosalinity conditions changes during deposition of Nenjiang Formation

By referring to the variation of Pr/Ph vs. MTTCI and the salinity region division proposed by Schwark et al. (1998), an amended salinity zonation is proposed, based on the core samples from the Upper Cretaceous of the Songliao Basin (Fig. 6). There are four salinity regions, defined as hypersaline, mesosaline, normal marine saline and brackish to fresh water. The Nenjiang Formation samples are mainly distributed within the latter three regions. The brackish to fresh water region is newly proposed here and separated from the normal marine salinity region defined by Schwark et al. (1998), and is based on two considerations. First, the division on the initial correlation figure (Schwark et al., 1998) did not encompass brackish to fresh water environments, although MTTCs are associated with a broad range of salinity from fresh water to hypersaline. Secondly, the low salinity samples in this region are mainly from the K_2n^2 section, which is characterized by a lack of δ-MTTC and gammacerane and a fossil algal assemblage dominated by fresh water to brackish water genera.

Duo to the lack of MTTCs, some of the samples from section IV (1099–1116 m) in K_2n^1 do not allow MTTCI to be calculated. Therefore, these samples are all assigned a nominal MTTCI value of 1 in Fig. 6, so that they can be plotted and distributed in the brackish to fresh water region. These samples are also deficient in gammacerane and algal fossils. However, the siltstone lithology and high Pr/Ph values (1.03–1.85) indicate that this section interval was likely developed under much shallower and more dynamic, as well as probably more oxic, fresh to brackish water depositional conditions. The uppermost two samples from section V display a transitional character, with MTTCI increased from 0.65 to 0.76 and associated with Pr/Ph 1.39, and these two samples plot in the marine salinity and brackish to fresh water regions (Fig. 6), respectively. Therefore, this distribution suggests a transitional trend toward much less saline conditions from section V to section IV. Furthermore, the δ-MTTC dominance in some of the samples from sections II and V is comparable with that of MTTCs in the Tertiary source rocks of the Jianghan Basin (Grice et al., 1998; Bao et al., 2008) and this similarity may suggest that similar hypersaline conditions might have existed during the deposition of these two sections. However, the significant difference is the occurrence of 6-MTTC in the Jianghan Basin, which is rare and not seen in the Songliao Basin and other sedimentary rocks (Sheng et al., 1987; Fan and Fu, 1988; Zhu et al., 2003, 2005). The reason for the occurrence of 6-MTTC may be due to the lower maturity of source rocks in the Jianghan Basin.

A stratified water column with a high salinity and an anoxic bottom water layer and a much fresher top water layer is important for the formation of thick petroleum-prone source rocks in lacustrine environments. The much fresher top layer provided excellent conditions for certain algae to flourish, providing high primary productivity, while reducing and highly salinity bottom water conditions provided excellent conditions for the deposition and preservation of the detrital algal OM. The combination of these favorable conditions in a vast lacustrine environment therefore led to the massive formation of petroleum-prone source rocks in the Songliao Basin.

5. Conclusions

(i) The occurrence of MTTCs in core samples from the Upper Cretaceous Nenjiang Formation of the Songliao Basin in China is geochemically significant in indicating the redox and salinity conditions of paleo-depositional environments.

(ii) The absence of MTTCs and the lack of detectable algal fossils in section IV of the K_2n^1 interval may be supportive of an algal origin for MTTCs or their precursors.

(iii) The δ-MTTC isomer seems to be more sensitive to redox conditions as it is often absent from oxic and low salinity depositional environments, but is enriched in reduced and enhanced salinity environments.

(iv) The distribution and comparison of the α/γ MTTC ratio with the α/δ MTTC ratio suggest that the two contain similar salinity information, and α/γ MTTC has the advantage that it is more widely applicable due to the frequent absence of δ-MTTC from samples deposited under oxic and low salinity conditions. When α/γ MTTC is <2, $2 < \alpha/\gamma < 15$, and $\alpha/\gamma > 15$, this is indicative of mesosalinity, normal marine salinity and semi-saline to fresh water environments, respectively.

(v) The massive lacustrine petroleum-prone source rocks in the Nenjiang Formation were formed under a stratified water column, with the top layer of much lower salinity providing the primary input of OM, while the higher salinity bottom layer water provided reducing conditions effective for OM preservation.

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