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Depositional Environments Revealed From Biomarkers in Sediments Deposited During the Mid-Cretaceous Oceanic Anoxic Events (OAEs) in the Vocontian Basin (SE France)

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ABSTRACT

Biomarker and total sulfur (TS) analyses were carried out on laminated black shales and massive marls collected from Goguel level (OAE1a) and the Kilian and the Paquier levels (OAE1b) in the Vocontian Basin in southeast France. Total sulfur content and concentrations of thiophenes are abundant in the Goguel level, whereas furans and retene, which are originated from terrestrial plants, are predominant in the Kilian and the Paquier levels. These results suggests the expansion of intense anoxic waters to deep ocean during the deposition of Goguel level rather than during the periods covered by the Kilian and the Paquier levels. In contrast, the Kilian and the Paquier sediments are characterized by a large amount of terrestrial input. Therefore, it is inferred that OAE1a was associated with supplying a large amount of sulfur to the ocean, possibly by active volcanisms, whereas OAE1b was caused by a large amount of terrestrial matter and fresh water input.

Keywords: OAE, Thiophene, Sulfur content, Redox condition, Terrestrial input

INTRODUCTION

The mid-Cretaceous is generally referred to a greenhouse period characterized by exceedingly warm climate, small equator-to-pole temperature gradient, a lack of ice sheets and high sea level, and elevated tectonism and volcanism [1]. Oceanic Anoxic Events (OAEs) occasionally occurred during the mid-Cretaceous, and caused expansion of extremely oxygen-poor water in the ocean. These episodic events resulted in mass extinction of benthic fauna. Microfossil and organic geochemical records indicate drastic change in marine organisms during OAEs [2–5]. The mass extinction was probably closely related to anoxia (oxygen-poor condition),

i.e. reduced condition, of water column in ocean. The redox condition of water column has been reconstructed by using microfossil assemblages [3]. A few organic geochemical studies suggest that the anoxia reached photic zones of ocean [6]. Although intensive erosion of terrestrial soil has been inferred during OAE at the Permian - Triassic boundary [7], there are no data on activation of terrestrial soil erosion during the mid-Cretaceous OAEs. However, there exist a few studies on the linkages between oceanic anoxia, and terrestrial vegetation and/or transport of terrigenous matter from land to ocean from the Aptian to the Albian of Cretaceous (OAE1a and OAE1b) [8–9]. In this study, we evaluate the variation of anoxic condition and terrestrial input

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during the mid-Cretaceous OAE1a and OAE1b using biomarker compositions in the OAE-related sediments of the Vocontian Basin.

MATERIAL AND METHOD

Materials

Sedimentary rocks were collected from outcrops in the Vocontian Basin in the southeast France. During the Cretaceous, the Vocontian Basin was located at a paleolatitude of 25–30°N at the northern margin of the western Tethys, and it represented the hemipelagic part of a basin. Paleoenvironmental and paleohydrological conditions such as paleo-water depth in the basin are still under discussion. The layers of the OAE1a (Goguel) and the OAE1b (Kilian and Paquier) belong to the Marnes Bleues Formation, which mainly consists of monotonously dark marls and frequently black laminated shales [2, 10]. Samples collected from the field from these layers were kept in a clean room at a room temperature in the laboratory prior to geochemical analyses. For organic geochemical analysis, the samples were crushed to a fine powder in an agate mortar.

Total sulfur content

A portion of each sediment sample was vacuum-dried and analyzed for total sulfur (TS) content by a Dionex DX-500 (ion chromatography) at the Center for Instrumental Analysis, Hokkaido University.

Biomarker analysis

Extraction and separation were performed as described in Ref. 11. Lipids were extracted from the sediment samples with dichloromethane (DCM) and DCM / methanol (MeOH) (1/1 v/v). d_{62} -Triacotane were added prior to analysis as an internal standard. The extract was dried in a rotary evaporator and then re-dissolved in hexane. The lipid-containing hexane extract was passed through a silica gel column (95% activated), and polycyclic aromatic hydrocarbon (PAH) fractions was eluted with hexane / toluene (3/1 v/v). This fraction was analyzed by gas chromatography - mass spectrometry.

Gas chromatography / mass spectrometry (GC-MS)

Identification of the lipid fraction was carried out by GC-MS using a Hewlett Packard 6890 attached to a capillary GC (30 m x 0.25 mm i. d. DB-5HT column, J&W Scientific) directly coupled to a Hewlett Packard XL MSD quadrupole mass spectrometer (electron voltage, 70 eV; emission current,

350 μ A; mass range, m/z 50–550 in 2.91 s). The GC temperature was programmed as follows: 50°C for 4 min, 50–300°C at 4°C /min and 300°C for 20 min. Identification of the compounds was made from mass chromatographic responses (mass fragmentation pattern and molecular ion *etc.*) and relative retention times in comparison with library data (NIST05) and the literature.

RESULTS AND DISCUSSION

Total sulfur content

Total sulfur (TS) contents are generally high in the sediments which deposited under reduced condition such as the Mediterranean sapropels, the Black sea sediments and the Cretaceous black shales [12–13] due to precipitation of sulfides. In our study, the characters of the TS contents are clearly distinguished between OAE1a and OAE1b (Fig. 1A). These contents are much higher in the Goguel than the Kilian and the Paquier. The remarkably high TS contents are observed in laminated shale samples in the Goguel (over 1%) and the Kilian (over 0.5%), whereas, the maximum of these contents (1.72%) is observed in massive marl samples in the Goguel (Table 1).

Dibenzothiophene and these alkyl derivatives

Dibenzothiophene (DBT), the derivatives of methyl-dibenzothiophenes (MDBTs) and dimethyldibenzothiophenes (DMDBTs) are mainly identified as the sulfur-containing compounds (Fig. 2B). The major peaks of DBT, MDBTs, and DMDBTs are m/z 184, 198, and 212, respectively as shown in Fig. 2B. Previous studies [14] reported that the ratios of DBT and MDBT to phenanthrene (DBT/PHE, MDBT/PHE) were higher in the sediments in which the TS contents were higher, although the precursors of these compounds are unknown. Therefore, these compounds possibly indicate to anoxic conditions. In this study, the ratios of thiophenes (DBT plus MDBTs) to phenanthrene (THI/PHE) in the Paquier level are similar to that in the Goguel level, but higher than in the Kilian level. However, the TS contents in the Paquier level are clearly lower than the Goguel level (Fig. 1A).

Terrigenous biomarkers

Dibenzofuran (DBF), the derivatives of methyl-dibenzofurans (MDBFs) and dimethyldibenzofurans (DMDBFs) were identified as the oxygen-containing compounds (Fig. 2A). The major peaks of DBF, MDBFs, and DMDBFs are m/z 168, 182, and 196,

Table 1 Results of analyses on total sulfur content (TS), thiophene / phenanthrene (THI/PHE), furan / phenanthrene (F/PHE) and retene / phenanthrene (RET/PHE) ratios in samples from the Goguel (OAE1a), and the Kilian and Paquier (OAE1b) levels.

sample No.	depth (m)	lithology	TS%	THI/PHE	F/PHE	RET/PHE
<i>Goguel (OAE1a)</i>						
GO-12	0.00	massive marl	0.25	0.16	n. d.	0.07
GO-11	0.28	massive marl	0.31	0.16	0.07	0.04
GO-f	0.42	faintly laminated black shale	1.44	0.11	0.21	0.02
GO-e	0.71	massive marl	0.59	0.16	0.17	0.02
GO-d	0.89	clearly laminated black shale	0.79	0.16	0.23	0.01
GO-c	1.00	massive marl	0.45	0.17	0.22	0.03
GO-b	1.14	clearly laminated black shale	0.77	0.21	0.24	0.02
GO-a	1.32	massive marl	0.80	0.15	0.15	0.02
GO-L2	1.51	clearly laminated black shale	0.67	0.23	n. d.	0.01
GO-9	1.71	massive marl	0.82	0.21	0.12	0.03
GO-8	2.00	clearly laminated black shale	1.01	0.15	0.24	0.01
GO-7	2.07	massive marl	0.31	0.11	0.20	0.04
GO-6	2.71	clearly laminated black shale	0.88	0.21	0.24	0.03
GO-5	3.16	massive marl	1.72	0.18	0.13	0.04
GO-4	3.35	clearly laminated black shale	0.58	0.25	0.26	0.04
GO-3	4.03	massive marl	0.71	0.13	0.13	0.04
GO-2	4.53	clearly laminated black shale	1.43	0.21	0.22	0.06
GO-1	5.00	massive marl	0.76	0.14	n. d.	0.05
<i>Kilian (OAE1b)</i>						
Ki-8	0.00	massive marl	0.47	0.02	0.03	0.01
Ki-7	0.03	massive marl	0.32	0.16	0.44	0.09
Ki-6	0.05	massive marl	0.40	0.08	0.62	0.09
Ki-12	0.81	clearly laminated black shale	0.74	0.10	n. d.	n. d.
Ki-11	1.33	clearly laminated black shale	0.59	0.10	0.38	0.21
Ki-4	1.57	massive marl	0.40	0.18	0.40	0.10
Ki-3	1.64	massive marl	0.40	0.17	0.31	0.11
Ki-2	2.11	massive marl	0.43	0.19	0.35	0.08
Ki-1	2.35	massive marl	0.37	0.05	0.46	0.08
<i>Paquier (OAE1b)</i>						
MR870	0	clearly laminated black shale	0.3	0.13	0.42	0.10
MR8	0.07	faintly laminated black shale	0.2	0.11	0.44	0.09
MR7225	0.22	clearly laminated black shale	0.66	0.18	0.44	0.12
MR7150	0.29	faintly laminated black shale	0.19	0.16	0.41	0.13
MR6167	0.4	clearly laminated black shale	0.32	0.30	0.32	0.29
MR6151	0.42	clearly laminated black shale	0.3	0.21	0.38	0.22
MR6130	0.24	clearly laminated black shale	0.22	0.28	0.34	0.32
MR6100	0.27	faintly laminated black shale	0.38	0.17	0.45	0.13
MR667	0.51	clearly laminated black shale	0.26	0.32	0.40	0.29
MR647	0.52	faintly laminated black shale	0.26	0.25	0.46	0.20
MR69	0.56	clearly laminated black shale	0.61	0.16	0.33	0.17
MR420	0.75	clearly laminated black shale	0.3	0.17	0.45	0.09
MR320	0.87	faintly laminated black shale	0.33	0.18	0.43	0.12
MR1	1.21	clearly laminated black shale	0.4	0.20	0.32	0.15

TS: Total Sulfur, THI/PHE: Σ (dibenzothiophene + methyldibenzothiophene)/phenanthrene, F/PHE: Σ (dibenzofuran + methyl dibenzofuran)/phenanthrene, RET/PHE: retene/phenanthrene

n. d.: not detected

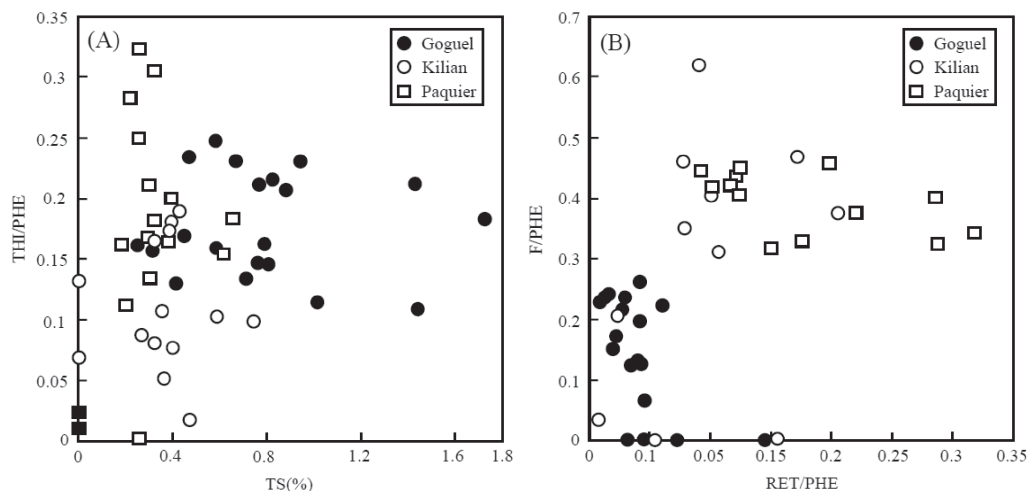


Fig. 1 Relationship between (A) thiophene / phenanthrene ratio (THI/PHE) and total sulfur content (TS), and (B) furan / phenanthrene (F/PHE) and retene / phenanthrene (RET/PHE) ratios among the three OAE levels (Goguel: OAE1a; Kilian and Paquier: OAE1b). thiophene: Σ (dibenzothiophene + methylbenzothiophene), furan: Σ (dibenzofuran + methylbenzofuran)

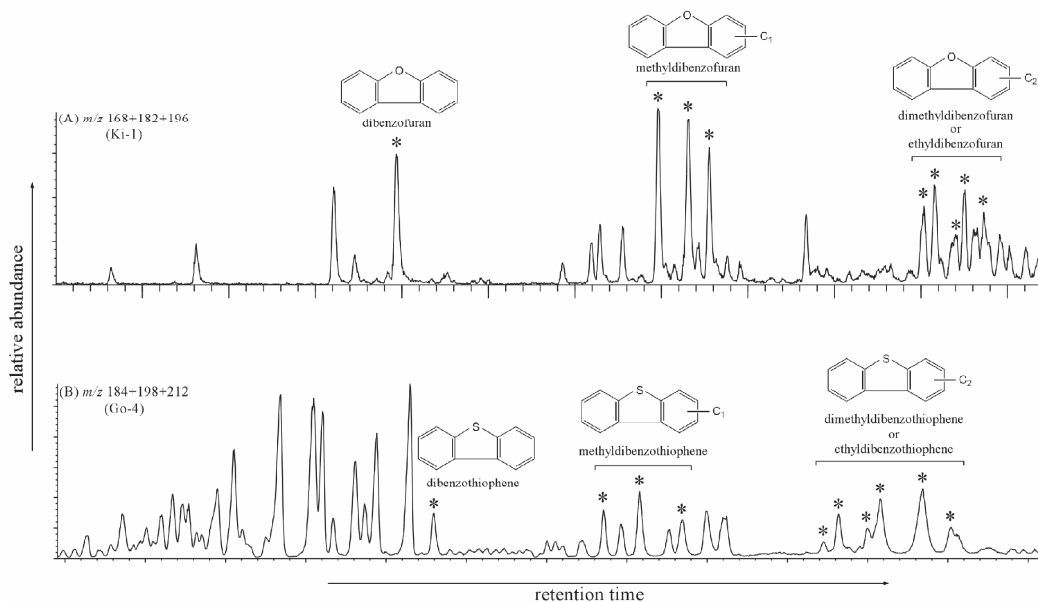


Fig. 2 Mass fragmentograms of (A) m/z 168 + 182 + 196 of the Kilian (Ki-1), and (B) m/z 184 + 198 + 212 of the Goguel (Go-4).

respectively (Fig. 2A). In general, DBF is derived from the lower plants such as lichen and/or polysaccharide in terrestrial soil [7, 15]. These compounds are normalized by the phenanthrene as well as DBT. Furans (DBF + MDBFs) to phenanthrene (F/PHE) are clearly higher in sediments of the Kilian and Paquier levels than those from the Goguel level.

Retene is also identified as a terrigenous organic compound. It is known to be a biomarker originated

from gymnosperms such as conifer [16]. Retene to phenanthrene (RET/PHE) ratios are also higher in the Kilian and Paquier samples compared to the Goguel, and this agrees well with the results from F/PHE ratios.

Differences in depositional environments

In this study, it is found that the Goguel (OAE1a) sediments are characterized by high sulfur contents

(TS and thiophenes) but a small amount of terrigenous input (furans and retene). According to Ref. 17, OAE1a occurred during the transgressive interval due to spreading ocean ridge associated with active volcanisms. The excessive CO₂ was released to the atmosphere by volcanoes, and this phenomenon resulted in enhanced global warming and decrease of oxygen solubility resulting in anoxic water masses. Moreover, these volcanoes supplied extra sulfur and phosphorus to the ocean as nutrient for marine organisms [18]. It is known that the organic matter preserved in OAE1a sediments predominantly consists of type II kerogen, which are mainly produced by marine plankton [19]. Our findings of high sulfur content are in agreement with the results of previous studies, which suggested that intense anoxic condition (high S) prevailed by active volcanisms and sedimentary organic matter was mainly originated from marine organisms during the Goguel level.

The Kilian and Paquier levels are characterized by intervals of increasing riverine runoff [20], and the Paquier represents a maximum flooding surface [2]. In our results, both Kilian and Paquier samples have low sulfur (although thiophene concentrations are high in the Paquier) and a large amount of terrigenous matter. The Jacob level, which represents another sub-event of OAE1b and is stratigraphically positioned lower than the Kilian, is characterized by high terrigenous input [2, 9]. The OAE type such as the Jacob is so-called 'detritic oceanic anoxic event (D-OAE)', while the type such as the Goguel is so-called 'productivity oceanic anoxic event (P-OAE)'. Our results suggest that the Kilian and the Paquier are of the same type, which is D-OAE. The high terrigenous input in the Paquier and the Kilian intervals are presumably attributed to the regression, which is similar to the Jacob. Hence, the OAE1b levels were possibly induced not by active volcanisms, as was the case for OAE1a, but by increased riverine runoff (freshwater), which induced dilution of surface water and salinity stratification. In addition, surface ocean productivity probably increased because of utilizable nutrient were exported from land area. The formation of black shales during OAE1b occurred under a depositional environment that was characterized by high terrigenous input and surface ocean productivity.

CONCLUSIONS

Results of analyses of the laminated black shales and massive marl samples deposited during the Aptian to Albian mid-Cretaceous Oceanic Anoxic

Events (OAEs) for thiophene, furan, and retene as well as total sulfur content lead the following conclusions.

1. The sediments corresponding to the Goguel level (OAE1a) contain abundant sulfur and organic sulfur compounds, whereas the concentrations of terrigenous organic matter such as furan and retene are relatively low. This suggests that intense anoxic waters, characterized by enhanced sulfide precipitations expanded in the Vocontian Basin, and the transport of terrigenous matter decreased under transgressive stages. The OAE1a was possibly caused by active volcanisms that supplied extra sulfur or phosphorus to the ocean.

2. The sediments corresponding to the Kilian and Paquier levels (OAE1b) exhibit similar characteristics in terms of biomarker compositions. These sediments contain abundant terrigenous organic compounds, but low total sulfur content and thiophene concentrations. We suggest that a large amount of terrigenous matter was transported to the Vocontian Basin during OAE1b, and the anoxic conditions were less intense than during OAE1a. Hence, OAE1b was possibly caused by intensified salinity stratification resulting from freshwater runoff and also the high surface productivity due to supply of nutrient from the surrounding lands.

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