

**PALEOCEANOGRAPHIC CHANGES RECORDED BY BIOMARKERS IN
SEDIMENTS DEPOSITED DURING OCEANIC ANOXIC EVENT 1A AND 1B IN
SOUTHEAST FRANCE**

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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, enhanced by active tectonism (Takashima *et al.*, 2006). Oceanic Anoxic Events (OAEs) have occasionally occurred during mid-Cretaceous, and caused expansion of extremely oxygen-poor water in the ocean. It is known that these episodic events resulted in mass extinction of benthic fauna and well preservation of sedimentary organic matter, which linked reduction of atmospheric CO₂. Clearly laminated, black-colored and organic-rich black shales are typical sediments deposited during OAEs. In this study, biomarker analyses were conducted on laminated black shales corresponding to OAE1a (Goguel) and OAE1b (Kilian), and adjacent massive marls deposited in Vocontian Basin in southeast France in order to reconstruct paleoceanographic variations during OAEs.

Black shales and adjacent sediments were collected from the outcrops and cores in Vocontian Basin in southeast France. The sequence of Goguel is composed of six laminated black shale layers and adjacent massive marls. Kilian is composed of laminated black shales, several faintly laminated layers, and adjacent marls. The sediment samples were crushed to fine powder. Lipids were ultrasonically extracted from the powder samples with methanol and methanol / dichloromethane (1/1 v/v). The extracted lipids were separated by silicagel column chromatography to aliphatic and polycyclic aromatic hydrocarbons with hexane and hexane / toluene (3/1 v/v), respectively. These fractions were analysed by gas chromatography / mass spectrometer (GC/MS).

The n-alkane distributions of both Goguel and Kilian showed unimodal with a maximum at n-C₁₈ to n-C₂₀, although some samples of Kilian showed bimodal distributions centered at n-C₁₆ and n-C₁₉. All of samples were abundant in short chain n-alkanes originated from marine algae, and pristane (Pr) and phytane (Ph) were abundantly contained relative to n-C₁₇ and n-C₁₈. Pr/Ph ratios of Goguel were nearly constant in black shales and massive marls. In contrast, Pr/Ph ratios significantly varied during Kilian, and were lower in black shales than those of massive marls. Such variations were attributed to either variation of redox conditions or high contributions of archaea-derived phytanes. The ratios of C₃₂ hopanes

(22S/22S+22R) and C₂₉ steranes (20S/20S+20R) in Kilian and Goguel averaged to be 0.6 and 0.5, respectively, although C₂₉ sterane ratios of Kilian ranged from 0.28 to 0.53. Moreover, diasteroidal and triaromatic steroidal compounds were also identified in all samples. Thus, the maturity levels were ranged from late diagenesis to early catagenesis.

Several aromatic thiophenes and furans (*e.g.* dibenzothiophene and dibenzofuran) were abundantly detected in all samples. The concentrations of thiophenes and furans showed clearly difference between Goguel and Kilian. Goguel were characterized by abundant thiophenes and poor furans. In contrast, Kilian were characterised by abundant furans and poor thiophenes. The sedimentary thiophenes are thought to be formed by reaction between organic matter and sulfide such as H₂S under anoxic condition. Alternatively, furans are derived from terrestrial higher plants and lichens. Therefore, these results suggested that Goguel was characterized by more abundant sulfide water and less abundant transportation of terrestrial matter. Conversely, Kilian was characterized by poor sulfide water and abundant terrestrial matter.

Biomarkers derived from archaeal membrane lipids could be identified as 2,6,15,19-tetramethylcosane (TMI) and 2,6,10,15,19-pentamethylcosane (PMI) in Kilian, although not in Goguel. A large amount of PMI and TMI were detected in the black shale layers, in which the Pr/Ph ratios decreased described above. Phytane originates either from the phytol side chain of algal and cyanobacterial chlorophyll or archaeal membrane lipids. Kuypers *et al.* (2002) reported that a large amount of archaea-derived organic matter have contributed to those preserved in the black shales of OAE1b. Therefore, it is expected that archaeal biomass have expanded in the ocean during Kilian in the Vocontian Basin. On the other hand, no or small amount of archaea may have inhabited during OAE1a because of no detection of archaeal-derived biomarkers, although there is more recent report that archaea-derived biomarkers were identified in sediments of OAE1a (J. Thurow, pers. comm.). These results possibly suggested the linkage between OAEs and the evolution of microorganisms such as archaea.

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