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What is main marine primary producer during the Cretaceous OAEs?: Evidences from marine kerogens.

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The mid-Cretaceous oceanic anoxic events (OAEs) are important to understand extremely greenhouse world. It is thought that enhanced marine productivity caused the global anoxia, although coccolithophorid and dinoflagellate productivity were diminished during the OAEs. Distinct algal biomarkers such as 2-methyl hopanoid and isorenieratane in the OAE levels indicate high activities of cyanobacteria and green sulfur bacteria, although detection of these biomarkers was limited. Amorphous organic matter (AOM) and very small palynomorph such as acritarchs are main components of OM in black shale but they were removed at the time of palynomorph analysis with size fractionation. In the present study, we analyzed kerogen including AOM and small acritarchs by fluorescent microscope and pyrolysis/thermochemolysis method to reconstruct variation in primary producers during OAEs.

Black shales were collected from the Goguel (OAE1a), Jacob, Kilian, Paquier (OAE1b), Breistroffer (OAE1d) and Thomel (OAE2) levels in SE France. These crushed samples were extracted with ultrasonication and their residues were sequentially treated by acids in a water bath shaker (Sawada et al., 2012). AOM classified into NFA (non-fluorescent AOM; wood origin), WFA (weakly fluorescent AOM; marine plankton origin) and FA (fluorescent AOM; cuticle or palynomorph origin), and acritarchs divided into five groups (sphaeromorph, pteromorph, acanthomorph, netromorph, polygonomorph). We analyzed pyrolysis and thermochemolysis of kerogen by using GC-MS equipped a Curie-point pyrolyzer.

Kerogens in the Goguel (OAE1a) samples are mainly comprised of WFA, and percentages of WFA (WFA%) are slightly higher in black shale samples. Green algal phycoma-like acritarchs, sphaeromorph, are abundant in the Goguel level, especially acme phase of OAE1a. Anoxia during the OAE1a might be related to high production of green algae. Terrestrial NFA are main components in all OAE1b samples, although WFA are higher in black shale samples of the Kilian and Paquier levels. These data show both enhanced marine production and excess terrestrial input led anoxia during the OAE1b. Sphaeromorph are also observed from black shales samples of OAE1b level s. In addition, percentages of long-spine type acanthomorph are higher in the Paquier level. The WFA% values are remarkably higher in the OAE1d and 2 samples, especially black shales of OAE2 (80-90%), which suggest that enhanced productivity during the OAE1d and OAE2. Netromorph, which has each spine in bipolar, is observed in only OAE1d samples. Sphaeromorph decrease but acanthomorph increase with decreasing WFA% values in the Trough interval (cooling phase) of the OAE2 level. 2-methyl hopane and a large amount of branched alkanes are detected by pyrolysis/thermochemolysis analysis from the OAE1a and OAE1b samples, respectively. These pyrolysis results are consistent with those of free biomarkers. Branched alkanes were characteristically detected as pyrolysate of WFA in accumulated layers of the Paquier level, and the relative abundances of these compounds correlated with free tail-to-tail isoprenoid concentration. These tail-to-tail isoprenoids are presumably derived from lycopanoid skeleton of marine phytoplankton such as green algae, which is supported by the results of kerogen.

Keywords: Oceanic Anoxic Events (OAEs), kerogen, acritarch, palynofacies, pyrolysis, thermochemolysis