

ASSESSMENT OF CYANOBACTERIAL INFLUENCE ON CRETACEOUS BIOPRODUCTIVITY

Björn KLEIN¹, Simon C. BRASSELL² and Jürgen RULLKÖTTER¹

1. Institute of Chemistry and Biology of the Marine Environment (ICBM), Carl von Ossietzky University of Oldenburg, PO Box 2503, D-26111 Oldenburg, Germany

2. Biogeochemical Laboratories, Department of Geological Sciences, Indiana University, Bloomington, IN 47405-1403, U.S.A.

Phytoplanktonic communities are an important source for sedimentary organic matter. Major members of these communities are cyanobacteria. Because of the lack of fossil remains, other than, e.g., for calcareous nannoplankton, an estimate of the contribution by cyanobacteria to the sedimentary organic matter is difficult. 2-Methylhopanoids are specific biomarkers for a number of cyanobacteria (Summons et al., 1999) and like the A-ring-desmethylated hopanoids readily detectable by standard analytical methods. The determination of the amount of 2-methylhopanoids either as free molecular biomarkers in the bitumen extractable from the sediment or as bound components which were preserved after incorporation into the insoluble kerogen is a possibility to assess the cyanobacterial contribution to the sedimentary organic matter.

The investigations were performed on a succession of sediment samples recovered during ODP Leg 198 on Shatsky Rise in the Pacific Ocean east of Japan. The sediments span an age range from the Cretaceous through the Palaeogene. During this time interval several abrupt and transient climate changes took place. These events were associated, among others, with drastic changes in primary production in ocean surface waters and in marine environmental conditions. In our study we focus on the events known as Oceanic Anoxic Events (OAE), especially the OAE1a, which is represented in the sediment cores recovered at Shatsky Rise.

Previous organic geochemical analyses of these sediments led to the assumption that a high phytoplanktonic productivity significantly contributed to the abundant sedimentary organic matter exceeding 30% C_{org} in certain intervals. The variety of detected 2-methylhopanoids points to a major contribution by cyanobacteria (Dumitrescu and Brassell, 2005).

Within this work the ratio of methylated and desmethylated hopanoids, expressed as the so-called 2-MeH index, was determined throughout the whole succession to cover the anoxic event as well as the over- and underlying sediment sections. For that purpose, pyrolysis-gas chromatography/mass spectrometry was employed to analyse the kerogen-

bound hopanoids and gas chromatography/mass spectrometry to investigate the free molecules in the bitumen fraction, respectively.

Pyrolysis was performed with the untreated sediment at 590°. The ratio of 22,29,30-*trinor*-hop-17(21)-ene to 2-methyl-22,29,30-*trinor*hop-17(21)-ene was obtained by integration of the peak areas in corresponding mass chromatograms (m/z 368 and m/z 382, respectively). The analysis of the free molecules in the bitumen was carried out on total extracts from the sediment after silylation of the polar derivatives. In the extracts, the 2-MeH index was calculated using the peak areas of saturated hopanoid and 2-methylhopanoid hydrocarbons and alcohols both present in varying concentrations.

In the pyrolysates hopanoids were only detected as unsaturated hydrocarbons, which leads to the assumption that these compounds were released from the kerogen *via* side chain cleavage. The resulting 2-MeH-index shows high values for time intervals with high C_{org} values (Fig. 1), but there are also time intervals with low indices at high organic carbon contents. A possible reason is a low significance of cyanobacteria at certain time intervals.

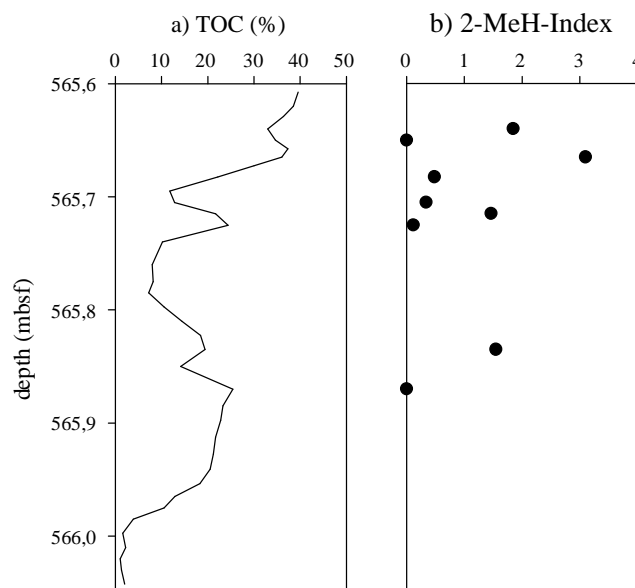


Figure 1. Profiles from ODP Site 1207B of a) total organic carbon (data by S.C. Brassell) and b) 2-methylhopanoid index from kerogen pyrolysis.

REFERENCES

- Dumitrescu, M. and Brassell, S.C. 2005 Biogeochemical assessment of sources of organic matter and paleoproductivity during the early Aptian Oceanic Anoxic Event at Shatsky Rise, ODP Leg 198. *Organic Geochemistry* 36, 1002-1022.
- Summons, R.E., Jahnke, L.L., Hope, J.M. and Logan, G.A. 1999 2-Methylhopanoids as biomarkers for cyanobacterial oxygenic photosynthesis. *Nature* 400, 554-557.