

LIPID BIOMARKERS AS INDICATORS OF THE ORGANIC MATTER SOURCES IN EASTERN MEDITERRANEAN SAPROPELS

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Abstract

A series of Pleistocene-Pliocene sapropels from ODP Site 969, located on the Mediterranean Ridge, were investigated for their extractable lipid components. The organic carbon contents in sapropels of Pleistocene age showed a typical range of values, up to 7.4%, whereas the Pliocene sapropels were extraordinary organic-carbon rich with values reaching 32.2%. The molecular composition of extractable lipids was dominated by alkyl diols and ketols, alkenones and sterols with less important amounts of n-alkanes and n-alcohols. The molecular data indicate that organic matter in sapropels is predominantly derived from marine algal sources. Nevertheless, the distribution of terrestrial lipids indicates a significant rise of land-derived influx during sapropel formation. Additionally, stanol/stenol ratios suggest that anoxic conditions prevailed during the formation of highly organic-rich sapropels.

Key-words : *geochemistry, deep sea sediments, carbon*

Introduction

One of the focus of the ODP Leg 160 was upon the origin and paleoceanographic significance of Mediterranean sapropels [1]. These are dark-colored layers rich in organic carbon which occur in young (less than 5 millions year) sequences, intercalated with oxidized, organic-carbon-poor hemipelagic sediments. Their deposition is thought to occur as a response to major climatic, hydrological and biogeochemical changes. Since their first discovery in the 60's, the Mediterranean sapropels (mainly those of late Pleistocene to Holocene age) have received much attention, and several hypotheses on their origin and significance have been proposed.

According to one hypothesis sapropels are the result of the establishment of anoxia in the Mediterranean bottom waters which leads to enhanced organic carbon preservation. This hypothesis was strongly supported by isotopic anomalies observed in sapropels [2] and by faunal studies indicating a stable density stratification of the water column [3]. Increased fresh-water inputs would have provoked this stratification and such inputs have been considered to originate either from floods of the Nile river [4] or from increased precipitation in the northern borderlands of the eastern Mediterranean [5].

An alternative hypothesis postulates that enhanced marine productivity and concurrent increased rise of the organic carbon flux to the seafloor would be responsible for the formation of sapropels [6]. Anoxic conditions alone could not have been responsible for the accumulation of organic carbon reaching values of 20%. The formation of such organic rich layers requires that primary productivity exceeds 500 gC/cm²/yr, a value in the range of those encountered in modern upwelling systems. The postulated increase in productivity is thought to be triggered by riverine nutrient supply [7]. Other authors have argued that the very high organic carbon contents observed in several sapropels reflect both increased export production and decreased oxygen advection in deep waters. Whatever mechanism exerted the primary control on the formation of sapropels (basin-wide anoxia or increased export productivity) its operation appears to be triggered by an external forcing, since the occurrence of sapropels closely correlates with minima in the Earth's orbital precession cycle [8].

Bulk organic geochemical characteristics of sapropels

ODP Site 969 is located on the Mediterranean Ridge (33°50.40'N and 24°53.06'E) at 2200 m of water depth. Over 80 sapropel beds recovered from the lower Pliocene through Holocene section occurring in distinct bundles and separated by intervals of oxidized, yellowish brown sediment.

The upper group of sapropel beds comprises the typical Holocene-upper Pleistocene sequence with S1, S3, S4, S5, S6, and S7 all present, showing organic carbon contents up to 7%. In the uppermost Pliocene to lower Pleistocene sequence, sapropels have maximum organic carbon content of 17.6% with a more usual range of 2% to 10% [9]. Two distinctive groups of predominantly black sapropel beds occurred in a gray colored interval of middle Pliocene age. These sapropels are extraordinary organic-carbon rich with a maximum of 30.5% which, to our knowledge, is the highest organic carbon content ever measured in a Mediterranean sapropel.

Corg/N ratios for almost all sapropels exceeded the value of 12 with an average of 17 and a maximum of 23. The surprisingly high values of Corg/N ratios could suggest a predominance of terrestrial organic matter which however is not in accordance with the indications provi-

ded by the Rock Eval parameters [9]. These high Corg/N ratios in the sapropels are tentatively interpreted as representing an effective removal of nitrogen compounds from the marine organic matter during diagenesis; however, it cannot be ruled out that the primary marine organic matter was already poor in nitrogen-bearing constituents.

Results of Rock-Eval pyrolysis showed hydrogen indices for many samples to exceed 300 mg hc/g Corg, with a maximum value slightly above 450 mg hc/g Corg [9]. The hydrogen index values indicate partial oxidation of the primary marine organic matter and/or an admixture of terrigenous organic matter. Consistent with the relationship between organic matter type and elemental composition, oxygen indices show an opposite trend to the hydrogen indices. A general tendency for higher hydrogen indices with increasing content of organic matter is observed. Sulfur contents were high in all sapropels, especially for those of middle Pliocene age, where a maximum of 13.2% was encountered, and their downhole profile roughly paralleled that of organic carbon.

This paper deals with the study of major extractable (free) lipid constituents in selected Pleistocene and Pliocene sapropels. The data are used to assess the origin of the organic matter (marine versus terrestrial) as well as the dominant specific biological sources.

Experimental

Two types of sapropel samples have been examined here. First, a series of samples taken from Pleistocene sapropels S5, S6 and S7. Second, a series of closely spaced samples from within two middle Pliocene sapropel layers and in sediments above and below these layers. These middle Pliocene sapropels are located just below the last common occurrence (LCO) of *Discoaster tamalis*. The detailed experimental methodology has been reported in detail elsewhere [10]. Lipids were solvent extracted and separated by flash chromatography on silica gel. Non-aromatic hydrocarbons and long chain alkenones were analyzed directly by gas chromatography whereas hydroxyl-bearing compounds were firstly derivatized to their trimethylsilyl ethers. Structural confirmations were obtained by Gas chromatography-Mass spectrometry and quantitation was done using internal standard methods.

Lipid composition and origin

- **n-Alkanes:** The series of n-alkanes ranged from n-C15 to n-C37 and their distributions are dominated by long chain homologues. Total concentrations were from 5.03 to 11.4 µg/g in Pleistocene sapropels and higher, up to 38.20 µg/g, in Pliocene ones, while they remained low, less than 1 µg/g d.w., in non-sapropel sediments. The predominant long chain n-alkanes showed a strong odd-over-even chain length predominance, which is characteristic of terrestrial higher plants and can be thus used to trace inputs of terrigenous organic matter. Consequently the n-alkane series indicate a significant terrigenous contribution to the organic matter [10].

- **n-Alcohols:** n-alkan-1-ols ranged from C16 to C32 and were dominated by components higher than C20. Their concentrations vary from 4.46 to 16.84 µg/g in Pleistocene sapropels, and from 4.54 to 70.43 µg/g in Pliocene ones. Levels were very low in non-sapropel samples. The n-alcohol composition is characteristic of terrigenous higher plants inputs.

- **diols, ketols:** Long chain alkyl diols and ketols were among the most abundant lipid constituents identified in sapropels [10]. Their concentrations varied from 4.8 to 103.4 µg/g in Pleistocene sapropels and