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LATE QUATERNARY MEDITERRANEAN SAPROPELS II. Organic Geochemistry and Palynology of S₁ Sapropels and Associated Sediments

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Abstract

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Six S₁ sapropel samples from the eastern Mediterranean were investigated organic geochemically to study the lateral variation within this organic-rich layer. Five of these samples were also analyzed palynologically. In addition, some sediment samples from below and overlying the sapropel intervals were investigated for their organic geochemical characteristics.

Organic matter of S₁ sapropels is of a mixed marine, terrigenous and bacterial origin. A trend of relatively increasing amounts of continentally derived organic matter towards more seaward and deeper realms can be observed from both palynological and organic geochemical data. This trend is supported to some extent by $\delta^{13}\text{C}$ -values of the organic matter.

The sapropelic intervals deposited on the Nile Cone are characterized by expanded thicknesses and a “diluted” organic carbon content due to a higher sedimentation rate. The environmental conditions (in terms of preservation) during sapropel formation over the eastern Mediterranean were probably not uniform. At site 29 the conditions were favourable for the deposition of sapropel with a higher organic carbon content than at the other locations. This might have been caused by better preservation conditions.

An increasing discharge from the river Nile seems to be the driving force for formation of the S₁ sapropels. Based on this assumption a model for sapropel formation is proposed. Although not all the data could be explained properly by this model, most phenomena can be explained.

1. Introduction

Black organic-rich layers, so-called sapropels, are widely distributed over the eastern

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Mediterranean. Sapropel layers in the Mediterranean are defined as those containing > 2% organic carbon and having a thickness of > 1 cm (Kidd et al., 1978). Therefore, not all reported organic-rich layers are true sapropels, as sometimes the organic carbon content is < 2%. Layers, containing 0.5–2% org. C are

defined as sapropelic layer (Kidd et al., 1978). In the Late Quaternary the occurrence of at least twelve sapropels has been recorded (Cita and Grignani, 1982). The youngest one (S_1) has been dated by the ^{14}C method at 7000–9000 yr. B.P. (e.g., McCoy, 1974). This Holocene sapropel has been the object of most sapropel studies, owing to the fact that this layer can be easily recovered by conventional box, gravity and piston coring. Its occurrence over the eastern Mediterranean extends from the Cilicia basin (Shaw and Evans, 1984) and the Nile Cone (Stanley and Maldonado, 1977) via the Ionian Sea (Stanley, 1978) up into the Adriatic (Van Straaten, 1972). This layer has also been recorded in the Aegean Sea (Perissoratis, 1982; Cramp et al., 1984). In a detailed investigation of the youngest sapropel, Anastasakis and Stanley (1984) clearly showed that a large variety of organic-rich layers may be encountered, indicating that the environment of deposition was not uniform over the entire eastern Mediterranean. Recently Stanley (1986) has shown that turbidity currents can considerably modify the development of sapropels.

Controversial ideas exist about the origin of the organic matter in the Mediterranean sapropels (see Ten Haven et al., 1987) and little is known of the palynology of Late Quaternary Mediterranean sapropels. Calvert (1983) concluded that:

“a detailed examination of the composition of the most recent sapropel is required. It is necessary to identify organic marker compounds that can be used to characterise unequivocally terrestrial and marine organic matter sources...”

The aim of the present study was: (1) to study the lateral organic geochemical variation within the S_1 sapropel; (2) to identify the differential palynofacial units and palynomorph groups; and (3) to look for a correlation between the palynological and the organic geochemical data.

Six S_1 sapropel samples were analyzed (Fig. 1) and also some sediment samples from below and overlying the sapropel. The sapropel samples were chosen in such a way that they form

a transect across the eastern Mediterranean. The samples appear to be ideally suited to test the hypothesis of Rossignol-Strick et al. (1982), who suggested that an excess nutrient-rich freshwater overflow from the river Nile triggered the sapropel formation. The results will be discussed in conjunction with the results of Smith (1984) and compared with those obtained from a S_7 sapropel (Ten Haven et al., 1987). The S_1 sapropel studied by Smith and coworkers (Smith et al., 1983, 1986; Smith, 1984; Sutherland et al., 1984; Poutanen and Morris, 1985) was collected from core 10103, located on the Hellenic Outer Ridge, southwest of the Peloponnesos (Fig. 1).

Within the palynological investigation, the encountered dinoflagellate cysts have been identified on a generic level, other palynomorphs are categorized in large groups, e.g., spores, pollen grains, fungal spores, scytinascas (acid-resistant remains of calcareous planktonic foraminifera).

2. Sampling and analytical methods

Box cores were collected during a cruise of the R.V. “Tyro” to the eastern Mediterranean in 1983. The locations of the box cores from which samples are taken, are presented in Fig. 1, together with a schematic lithological column. Bulk samples for organic geochemical research were taken with a bone spatula and stored at -20°C . Subsamples were taken for organic carbon, $\delta^{13}\text{C}$ and ^{14}C dating analyses. Aliquots of these same samples (~ 3 g) were investigated palynologically using standard techniques (sample 25 was not investigated). Briefly, the mineral matrix was removed by destruction in HCl and HF and the remaining material subsequently separated into a light and a heavy fraction, applying a ZnCl_2 solution with a specific gravity of 2.0 (Funkhauser and Evitt, 1959). The light fraction was then sieved through a $10\text{-}\mu\text{m}$ sieve, homogenized by stirring and subsequently two slides of each sample were prepared using a glycerol–jelly medium for light-

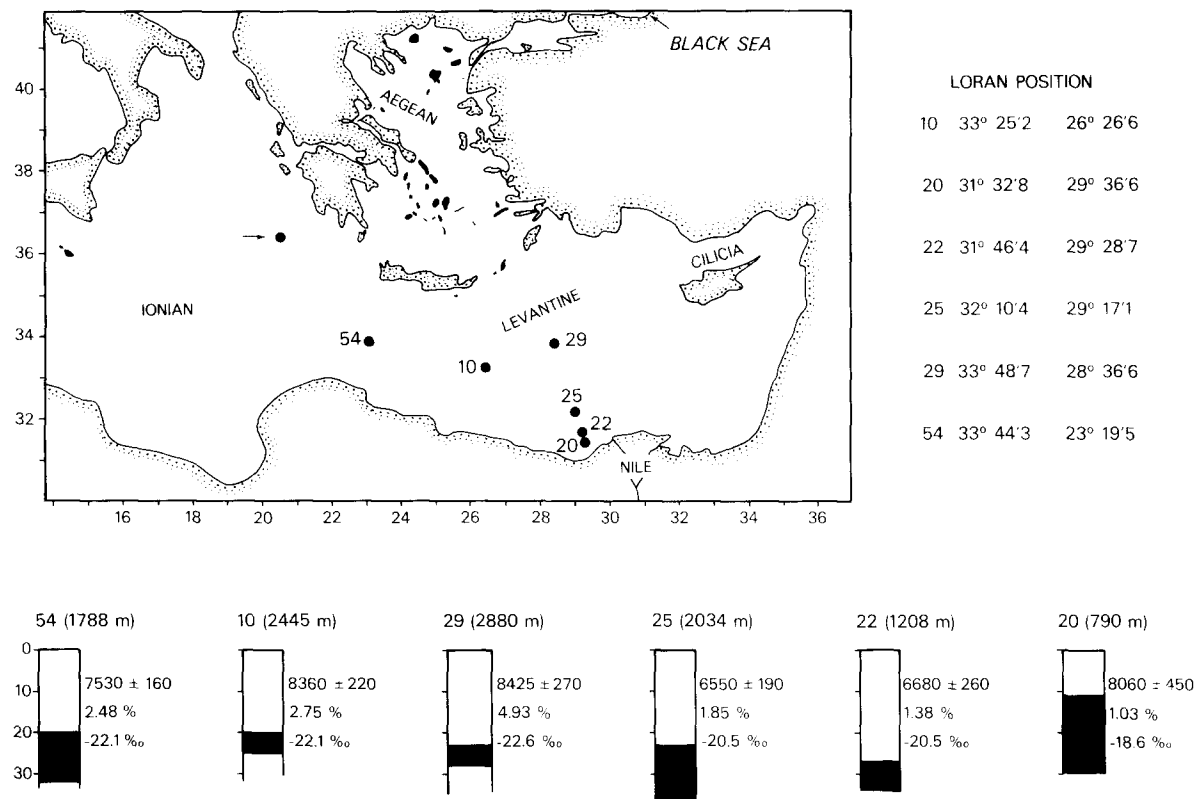


Fig. 1. Location sites of the box cores investigated and their position based on Loran C navigation. Water depth is given between brackets. The gravity core (core 10103) investigated by Smith (1984) is indicated with an arrow. A schematic lithological column indicating the sapropel interval in black is presented. Next to these columns the results of the sapropel subsamples are listed. These are from top to bottom: radio carbon age of the organic matter in years B.P., organic carbon content in %, and $\delta^{13}C$ of the organic matter in ‰.

microscopic investigation. No bleaching techniques were used.

Circa 300 discrete units ($>10 \mu m$) were counted of each sample and categorized in a palynofacial classification scheme, developed at the Laboratory of Palaeobotany and Palynology (University of Utrecht), comparable with e.g. Staplin (1969), Habib (1979a, b) and Batten (1981). This classification scheme comprises five groups: (1) amorphous organic matter (AOM; dispersed and/or discrete units); (2) opaque non-structured elements; (3) plant tissue remains; (4) palynomorphs (all classes); and (5) animal remains (vertebrate and invertebrate). A full report of the palynofacies clas-

sification is beyond the scope of the present paper.

Prior to organic geochemical analyses the samples were lyophilized, homogenized and divided into two portions. One portion was analyzed according to the "total lipid" method (Klok et al., 1987), which results in one extract containing both free and alkaline-labile compounds. The other sediment portion was analyzed following a method described by Ten Haven et al. (1987). This method results in three extracts, the first one containing free organic compounds, the second one alkaline-labile compounds and the third one acid-labile compounds. This approach offers an insight into

PLATE I



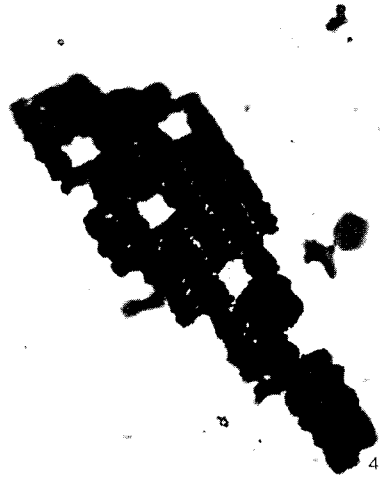
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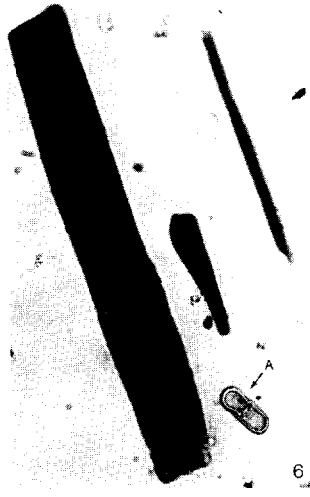
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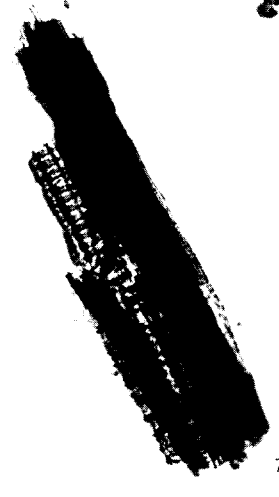
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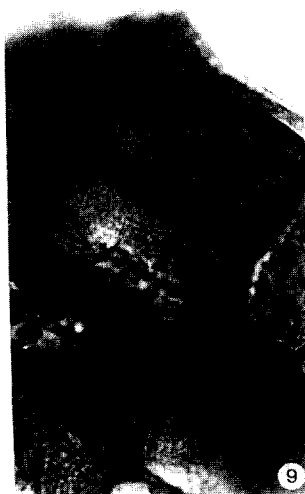
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8



9



10

TABLE I

Palynofacies

	54	10	29	22	20
Amorphous organic matter	+++	++++	++++	++++	++++
Opaque non-structured elements	+++	+	+	+	+
Plant tissue remains general	++++	+++	+++	++	++
Palynomorphs	-	-	-	-	-
Animal remains	-	-	-	-	-

- = rare; + = present; ++ = abundant, +++ = highly abundant; ++++ = dominant. Sample 25 was not investigated.

the mode of occurrence of lipids. Some sapropel samples were subjected to this latter method.

Prior to gas chromatographic (GC) analysis, all extracts were derivatized. The GC and gas chromatographic-mass spectrometric (GC-MS) conditions are described by Ten Haven et al. (1987). In this study however, the gas chromatograph was equipped with a capillary column coated with SE 52[®], instead of CP Sil 5[®].

Quantification of individual compounds was achieved by peak-height and peak-area measurements, processed by computer, in comparison with standard solutions of palmitic acid methylester and *n*-hexacosane. Repetitive analyses of these two standards revealed a quantification error for these two standards of <10%. However, quantification of individual components in the actual extract mixtures is hampered by errors in the work-up procedure, different flame ionization detector (FID) response for different classes of compounds, and coelution and peak broadening at elevated temperatures, resulting in a greater error.

3. Results and discussion

3.1. Palynological investigation

The results are presented in a semi-quantitative manner (Table I). All samples show large quantities of plant tissue remains, including cuticle (Plate I, 2, 5 and 8), wood remains (Plate I, 3), tracheid (Plate I, 1 and 4), and opaque branch-like fragments. The opaque non-structured elements are classified as "abundant" to "present". The AOM (Plate I, 10), in most cases "dominant", possesses a yellowish-brownish colouration. An increase of plant tissue remains, and opaque elements towards the deeper realms can be observed. The palynomorphs form only a minor group within the total organic matter encountered (Table I). Therefore this group will be discussed separately (Table II). In samples 10, 29 and 54, fragments tentatively assigned to arthropoda remains (Plate II, 7 and 10) have been observed.

Important within the fluctuating assemblages of palynomorphs are land-derived ele-

PLATE I

1. Tracheial tissue. $\times 730$, sample 10.
2. Fragment of leaf cuticle with stomata. $\times 300$, sample 54.
3. Wood remains. $\times 300$, sample 10
4. Tracheial tissue. $\times 300$, sample 10.
5. Leaf cuticle. $\times 300$, sample 10.
6. Plant fragment. $\times 300$, sample 54 (A = angiosperm pollen grain).
7. Spiral tracheids. $\times 300$, sample 54.
8. Cuticle fragment. $\times 300$, sample 54.
9. Cuticle fragment, $\times 730$, sample 54.
10. AOM. $\times 300$, sample 54.

PLATE II

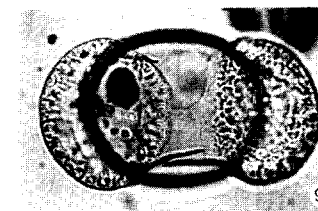
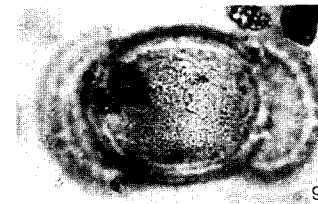
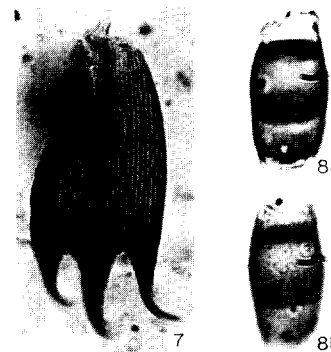
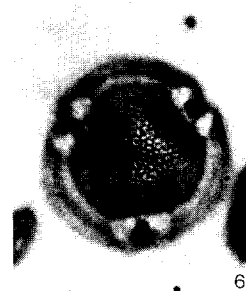
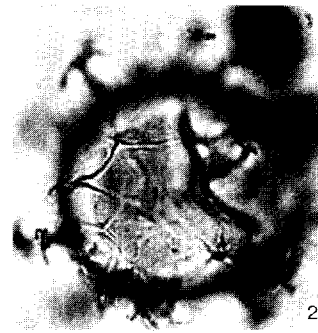
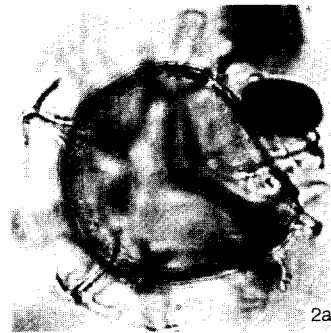
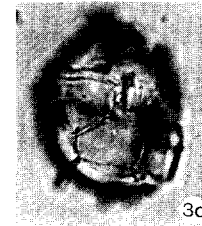
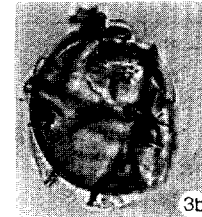
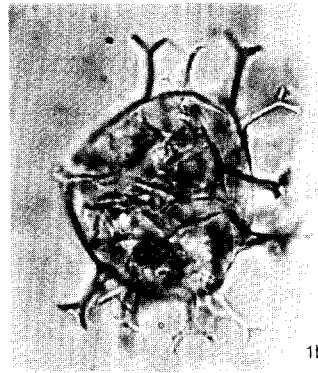
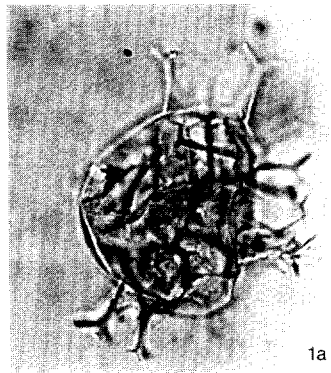


TABLE II

Palynomorphs

	54	10	29	22	20
Palynomorphs general	++	++	-	-	+
<i>Land:</i>					
Spores	+	++	+	-	+
Pollen	++	+	+	-	++
Fungal spores	-	+	-	-	+
<i>Aquatic:</i>					
Dinoflagellate cysts	+	++	+	-	+
Acritarchs	+	+	-	-	+
Scytinasc	+	+	+	+	-
<i>Pediastrum</i>	-	-	+	+	+
Other algal remains	+	+	++	+	+

- = rare; + = present; ++ = abundant.

ments (spores, pollen and fungal spores) (Table II; Plates I and II). In addition to these categories of palynomorph scytinasc, dinoflagellate cysts, acritarchs and representatives of the multicellular alga *Pediastrum* Meyen, 1829 are observed. Other algal remains (Table II) are those unassignable to the above-mentioned groups.

A relative abundance of these "aquatic" palynomorphs has been observed in sample 10. Within the group of dinoflagellate cysts, species assignable to the genera *Spiniferites* Mantell, 1850, emend. Sarjeant, 1970 (Plate II, 1 and 2) and *Impagidinium* Stover and Evitt, 1978 (Plate II, 3) are dominant (see Lentini and Williams, 1985, and references cited therein).

Similar observations were made by Wall et al. (1977) and Harland (1983). Many of the observed aquatic palynomorphs may have a fresh- or brackish-water origin, especially the encountered forms assignable to *Pediastrum* (Plate II, 4), a genus known to occur exclusively in these kind of environments (Evitt, 1963). Only the encountered species of dinoflagellate cysts and acritarchs are certainly of marine origin, in addition to most forms assignable to the scytinasc group (e.g., Plate II, 5).

3.2. Geochemical investigation

Data of the sapropel subsamples are given next to the schematic lithological column (Fig. 1). Ordered are from top to bottom ^{14}C dating of the organic matter, organic carbon content and $\delta^{13}\text{C}$ -values of the organic matter, respectively.

The radio carbon data point to a range in age from 6600 to 8500 yr. B.P., corresponding with data reported before for the S₁ sapropel (e.g., McCoy, 1974; Stanley and Maldonado, 1977). The three cores collected on the Nile Cone (samples 20, 22 and 25) contain sapropelic sequences instead of true sapropels. In these cores the bottom of the sapropelic layer was not penetrated. These cores are collected in a zone where the highest sedimentation rates in the Nile Cone area are measured; up to 88 cm/1000 yr. (Stanley and Maldonado, 1977). Therefore, it is not surprising that these cores bear sapropelic intervals with expanded thicknesses and a "diluted" organic carbon content in compar-

PLATE II

1. *Spiniferites* sp.: (a) high focus; and (b) low focus. $\times 730$, sample 10.
2. *Spiniferites* sp.: (a) mid-focus; and (b) low focus. $\times 730$, sample 29.
3. *Impagidinium* sp.: (a) high focus, showing precingular archeopyle; (b) mid-focus; and (c) low focus. $\times 300$, sample 22.
4. *Pediastrum simplex* (Meyen) Lemmermann 1897. $\times 300$, sample 20.
5. Scytinasc (planktonic foraminiferal remain). $\times 300$, sample 10.
6. Angiosperm pollen grain, high focus. $\times 730$, sample 29.
7. Arthropodal remains (?). $\times 300$, sample 10.
8. Multicellular fungal spore: (a) low focus; and (b) high focus. $\times 300$, sample 29.
9. Bisaccate pollen grain: (a) high focus; and (b) low focus. $\times 300$, sample 29.
10. Arthropodal remains (?). $\times 300$, sample 54.

ison with the other cores. However, it is equally possible that the expanded thickness and relatively low organic carbon content is the result of redepositional events (Stanley, 1986). The sapropels in cores 10 and 54 have a similar organic carbon content to the sapropel in the core studied by Smith and coworkers (Sutherland et al., 1984). The sapropel in core 29 is characterized by a higher organic carbon content. The $\delta^{13}\text{C}$ -values show a remarkable trend. Near the mouth of the Nile the $\delta^{13}\text{C}$ -value resembles marine organic matter, while in the middle of the Mediterranean (core 29) a certain amount of the organic matter seems to be of a terrigenous origin. The mean $\delta^{13}\text{C}$ -value of core 10103 (-20.6‰ ; Sutherland et al., 1984) corresponds with the values measured in cores 22 and 25, suggesting that the (relative) input of terrigenous organic matter is highest in the middle of the Mediterranean. A somewhat analogous situation was observed in plankton tows in the Black Sea (Deuser, 1970), where the site nearest the Danube Delta had plankton with heavier $\delta^{13}\text{C}$, possibly caused by high productivity. Another explanation for the ^{13}C -enriched values near the mouth of the Nile is a relative large contribution of so-called "C₄ plants" from the hinterland of the Nile which are isotopically heavier, displaying average $\delta^{13}\text{C}$ -values between -12 and -14‰ (Schidlowski, 1986).

3.3. Vertical organic geochemical variation

Samples from below and overlying the sapropel interval were investigated in order to obtain information about the vertical variation of organic compounds within a box core. The "total lipid" gas chromatograms of extracts from three sections in box core 29 including a S₁ sapropel are presented in Fig. 2. Identifications of labelled compounds are given in Table III. Quantitative results of selected compounds are given in Table IV.

The major differences between sapropel and non-sapropel sediments are, of course, the rel-

atively high organic carbon content of the sapropel layer and the concomitant high amount of extractable organic compounds. Other characteristic differences are the low concentration of sterols (e.g., 52, 53, 60), phytol (16) and long-chain diols (49, 62, 65), and the relatively high concentration of C_{18:1} fatty acids (13) in non-sapropel samples. Further, differences in the ratios between *n*-alkanes, *n*-fatty acids and *n*-alkanols are noticed (Fig. 2; Table IV). Typical compounds, such as 9,16-C₁₆- (25) and 11,18-C₁₈- (31) dihydroxy fatty acids were only observed in the sapropel samples. Most of these differences were also observed by Smith (1984). In all sapropel samples the following intensity distribution is observed in the C₂₀-C₃₀ fatty acid range (peaks 20-58): *n*-C_{*x*}-FA > *n*-C_{*x*}-ROH > *n*-C_{*x*+3}-HC, whereas in the non-sapropel samples the sequence *n*-C_{*x*+3}-HC > *n*-C_{*x*}-FA > *n*-C_{*x*}-ROH is mostly observed (*x* = 20, 21, ..., 30). These compounds are considered to be mainly of a terrestrial origin. The distribution pattern of these compounds in the sapropels mimics the distribution pattern observed in cuticles (De Leeuw, 1986; Nip et al., 1986). Cuticles, which are indeed observed in the sapropels (Plate I), are likely to be fluvially transported during periods of excessive freshwater inflow (e.g., Rossignol-Strick et al., 1982; Pratt, 1984). The dihydroxy fatty acids also point to a terrigenous input during sapropel formation. The explanation of Smith (1984), that this alternating distribution pattern is the result of a relative enrichment of *n*-alkanes, due to a faster degradation of more labile compounds (fatty acids, alkanols) under oxic conditions prevailing during time of deposition, might be too limited. This distribution pattern can also be explained by two different mechanisms of input, viz. an eolian transport and a fluvial transport. The distribution pattern in the non-sapropel sample is dominated by *n*-alkanes, and shows similarities with distribution patterns observed in eolian dusts (Simoneit, 1977). It might equally be possible that the characteristics of the non-sapropel sediments are mainly the result of an

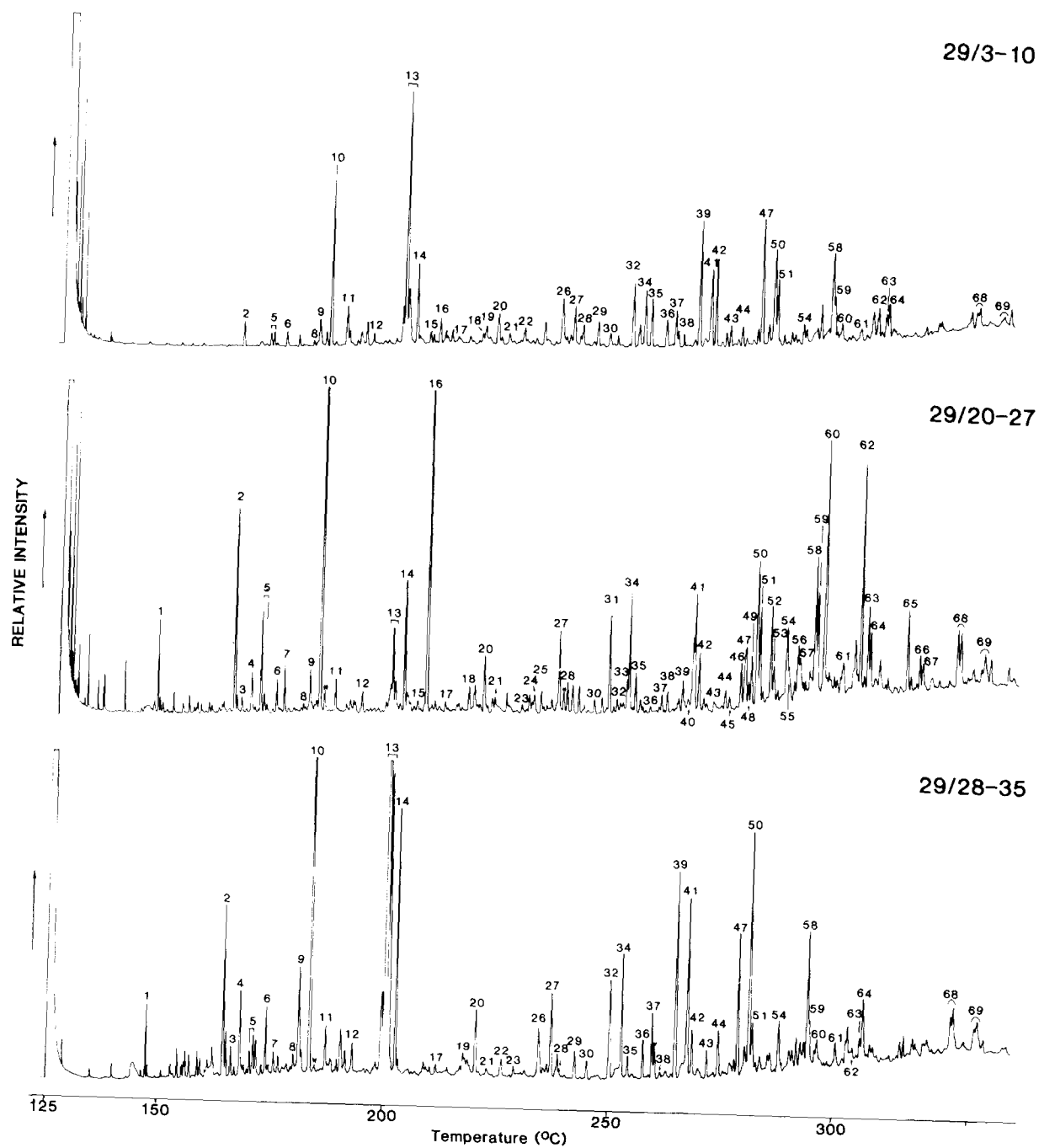


Fig. 2. Gas chromatograms of "total lipid" extracts from three samples of box core 29. Section 20-27 (depth in cm from sediment-water interface) represents the S_1 sapropel. Peak numbers correspond to the numbers mentioned in Table III. Contaminants are labelled with an *asterisk*.

TABLE III

Compounds identified by GC-MS, indicated in Fig. 2

(1) Dihydroactinidiolide	(36) <i>n</i> -C _{28:0} -HC
(2) <i>n</i> -C _{14:0} -FA	(37) <i>n</i> -C _{25:0} -FA
(3) Isololiolide	(38) <i>n</i> -C _{25:0} -OH
(4) Loliolide	(39) <i>n</i> -C _{29:0} -HC
(5) <i>i</i> -C _{15:0} -FA + <i>ai</i> -C _{15:0} -FA	(40) <i>n</i> -C _{27:0} -ketone
(6) <i>n</i> -C _{15:0} -FA	(41) <i>n</i> -C _{26:0} -FA
(7) 6,10,14-trimethylpentadecan-2-one	(42) <i>n</i> -C _{26:0} -OH
(8) <i>i</i> -C _{16:0} -FA	(43) <i>n</i> -C _{30:0} -HC
(9) <i>n</i> -C _{16:1} -FA	(44) <i>n</i> -C _{27:0} -FA
(10) <i>n</i> -C _{16:0} -FA	(45) <i>n</i> -C _{27:0} -OH
(11) <i>n</i> -C _{16:0} -OH	(46) 27-nor-24-methylcholesta-5,22-dien-3 β -ol
(12) <i>n</i> -C _{17:0} -FA	(47) <i>n</i> -C _{31:0} -HC + cholesta-5,22-dien-3 β -ol (esp. 29/20-27)
(13) C _{18:1} -FA + phytanic acid (29/20-27)	(48) 5 α (H)-cholest-22-en-3 β -ol
(14) <i>n</i> -C _{18:0} -FA	(49) 1,13-C ₂₆ -diol* + 1,14-C ₂₆ -diol*
(15) <i>n</i> -C _{18:0} -OH	(50) <i>n</i> -C _{28:0} -FA + cholest-5-en-3 β -ol (esp. 29/20-27)
(16) Phytol	(51) <i>n</i> -C _{28:0} -OH + 5 α (H)-cholestan-3 β -ol (esp. 29/20-27)
(17) <i>n</i> -C _{19:0} -FA	(52) 24-methylcholesta-5,22-dien-3 β -ol
(18) <i>n</i> -C _{16:0} - ω OH-FA	(53) 24-methyl-5 α (H)-cholest-22-en-3 β -ol
(19) <i>n</i> -C _{23:0} -HC	(54) <i>n</i> -C _{29:0} -FA + 24-methylcholesta-5,24(28)-dien-3 β -ol
(20) <i>n</i> -C _{20:0} -FA	(55) <i>n</i> -C _{29:0} -OH + 24-methylcholest-5-en-3 β -ol
(21) <i>n</i> -C _{20:0} -OH	(56) 24-ethylcholesta-5,22-dien-3 β -ol
(22) <i>n</i> -C _{24:0} -HC	(57) 4 α ,24-dimethyl-5 α (H)-cholest-22-en-3 β -ol
(23) <i>n</i> -C _{21:0} -FA	(58) <i>n</i> -C _{30:0} -FA + 24-ethylcholest-5-en-3 β -ol (esp. 29/20-27)
(24) 8,16-diOH-C _{15:1} -FA	(59) 24-ethyl-5 α (H)-cholestan-3 β -ol + <i>n</i> -C _{30:0} -OH
(25) 9,15-diOH-C _{16:0} -FA	(60) 4 α ,23,24-trimethyl-5 α (H)-cholest-22-en-3 β -ol
(26) <i>n</i> -C _{25:0} -HC	(61) <i>n</i> -C _{31:0} -FA + <i>n</i> -C _{31:0} -OH
(27) <i>n</i> -C _{22:0} -FA	(62) 1,15-C ₃₀ -diol
(28) <i>n</i> -C _{22:0} -OH	(63) C ₃₀ -15-keto-1-ol
(29) <i>n</i> -C _{26:0} -HC	(64) <i>n</i> -C _{32:0} -FA + <i>n</i> -C _{32:0} -OH
(30) <i>n</i> -C _{23:0} -FA	(65) 1,15-C ₃₂ -diol*
(31) 11,18-diOH-C _{18:0} -FA	(66) Unknown
(32) <i>n</i> -C _{27:0} -HC	(67) <i>n</i> -C _{34:0} -FA* + <i>n</i> -C _{34:0} -OH*
(33) <i>n</i> -C _{24:1} -OH	(68) C _{37:3} + C _{37:2} -methylketones
(34) <i>n</i> -C _{24:0} -FA	(69) C _{38:3} + C _{38:2} -methyl and -ethylketones
(35) <i>n</i> -C _{24:0} -OH	

*Tentative assignment.

olian input. As long-chain alkanes are very refractory compounds (Cranwell, 1981), it can be concluded from the quantitative results (Table IV), that the absolute input of continentally derived organic matter is higher during sapropel formation. As it is unlikely that anoxic conditions are solely responsible for the enhanced concentration of these compounds in sapropels, an increase of fluviially transported terrigenous material can be inferred.

The position of the double bond in the mono-unsaturated fatty acids was not determined.

However, with a view on the results of Smith (1984), it is assumed that Δ^9 - and Δ^{11} -C₁₈-fatty acids are the most abundant mono-unsaturated fatty acids. These compounds and the *iso*- and *anteiso*-C₁₅- and C₁₇-fatty acids most probably reflect a contribution from bacterial lipids (e.g., Boon et al., 1975, 1978). β -Hydroxy fatty acids (C₁₂-C₂₀) are important compounds in the acid-labile fraction of sapropels (not shown here, see Ten Haven et al., 1987), supporting a bacterial contribution to the organic matter (Goossens et al., 1986).

TABLE IV

Quantitative results of selected compounds in core 29

Compound		3-10 cm	13-19 cm	20-27 cm	28-35 cm
<i>n</i> -C ₁₆ -FA	(10)	340	800	18,650	440
<i>n</i> -C ₂₇ -HC	(32)	115	100	550	80
<i>n</i> -C ₂₄ -FA	(34)	100	80	3,580	100
<i>n</i> -C ₂₄ -OH	(35)	90	50	1,120	20
Dinosterol	(60)	40	< 10	7,770	25
C ₃₀ -diol	(62)	60	< 10	7,300	15
C ₁₇ -ketones	(68)	65	< 10	3,360	70

Values are expressed in ng/g dry sediment. Numbers between brackets correspond with those listed in Table III.

Sterols are relatively important compounds in the sapropel, 4 α ,23,24-trimethyl-cholest-22-en-3 β -ol (dinosterol) being dominant. This compound and other 4-methyl sterols observed can be attributed to a dinoflagellate input (Boon et al., 1979; De Leeuw et al., 1983; Robinson et al., 1984). Dinosterol is also the most important sterol in the S₁ sapropel investigated by Smith (1984). Smith attributed the predominance of sterols in sapropel samples to a higher degree of preservation (i.e. anoxic environment of deposition) and to a higher productivity during sapropel formation. The latter was deduced from the observation that fatty acids are more abundant than sterols in the non-sapropel samples, whereas these compounds probably degrade faster than sterols (Cranwell, 1981).

The isoprenoid alcohol, phytol, is the second most abundant compound in the sapropel sample, and is for the larger part present in the sediment in an esterified form. This compound is present in the non-sapropel samples in very low concentrations. These low concentrations are probably due to an enhanced degradation of chlorophyll under oxic conditions. Also, an additional input of chlorophyll during sapropel formation as a result of an increased primary productivity increases the phytol concentration in the sapropels, but a quantitative estimate of this additional input cannot be made. Phytol reflects an autochthonous rather than an allochthonous input, because it is not expected to survive intact during transporta-

tion from the continent to the deep sea (Brassell et al., 1980).

Other characteristic compounds occurring in varying amounts in all samples are the C₃₀-alkan-1,15-diol and a series of long-chain unsaturated ketones. The former compound might reflect an input of planktonic cyanobacteria (Morris and Brassell, 1987), the latter compounds can be ascribed to an input of the coccolithophorid algae *Emiliania huxleyi* (De Leeuw et al., 1980; Volkman et al., 1980). An origin for the long-chain ketones from *E. huxleyi* is inferred from the fact that the samples investigated are deposited well within the *E. huxleyi* acme zone (Gartner, 1977), although these long-chain ketones are also found in other algae (Marlowe et al., 1984).

In section 29/3-10 some steroids, all with a C₂₉ skeleton, were observed, which were virtually absent in the sapropel. These compounds (not indicated in Fig. 2 and Table III) are tentatively identified as 24-ethyl-cholest-2-ene, 24-ethyl-cholest-4-en-3-one and 4-methyl-24-ethyl-19-nor-cholesta-1,3,5(10)-trien. A²-sterenes occur ubiquitously in Recent sediments and are believed to be intermediates in the diagenetic degradation of sterols (Dastillung and Albrecht, 1977). The occurrence of the A-ring monoaromatic steroid is, to our knowledge, the first report of this compound in such Recent sediments. Although it has been suggested that the aromatization of the A ring of the precursor sterols starts at a very early stage of diagenesis (Hussler et al., 1981), we tend to believe, based on its limited occurrence in our samples, that this compound reflects an input of reworked organic matter.

3.4. Lateral organic geochemical variation

The GC and GC-MS data of all other S₁ sapropel samples are qualitatively similar to the results described above. Overall the organic geochemical characteristics of the S₁ sapropels

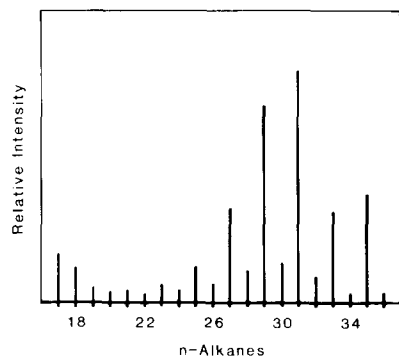


Fig. 3. Relative distribution of *n*-alkanes in the S₁ sapropel of box core 54.

are similar to the characteristics of the older sapropel S₇ (see Ten Haven et al., 1987). Differences, however, are observed in the relative abundances of the compounds encountered. The discussion of the lateral variation is focussed on differences in concentration of some selected compounds (Table V). An assessment of the data in terms of lateral input variation is difficult, since the absolute concentrations of compounds is influenced by variations in sedimentation rates, in primary productivity and in preservation conditions. Throughout the following discussion two assumptions have been made:

(1) The $\delta^{13}\text{C}$ bulk parameter does indeed reflect a ratio between marine and terrigenous organic matter (it should be emphasized that the organic geochemical results are obtained from total sapropel sequences as recovered in the box core, whereas the bulk parameters were determined on a pin-pointed subsample).

(2) The lipids are representative for the total organic matter, although they make up only a small part of the total organic matter (extract yields per gram organic carbon varied between 1% and 4%).

A terrestrial contribution to the organic matter is not only evident from the palynological investigation, but also from "terrestrial" biological markers, such as long straight-chain alkanes, alkanols and fatty acids. Fig. 3 shows a typical distribution pattern of alkanes of sapropel sample 54 with a strong odd-over-even

predominance of long-chain alkanes ($\text{CPI}_{24-34} = 5.4$). This kind of distribution pattern is indicative for an origin from higher-plant material and also confirms the low maturity of the sediment. Other compounds which might be attributed to a terrigenous origin are the dihydroxy fatty acids, such as 9,16-diOH-C_{16:0} fatty acid, and 11,18-diOH-C_{18:0} fatty acid. A contribution from another source (especially for the 11,18-dihydroxy fatty acid) can at present not be precluded (Cardoso and Eglinton, 1983; Ten Haven et al., 1987). The relatively high abundance of 24-ethyl-cholest-5-en- β -ol (Fig. 2, peak 58) might also be attributed to a terrigenous input, although Volkman (1986) pointed out that the application of this compound as a biological marker for terrigenous organic matter can lead to erroneous conclusions.

The variation in concentration of the *n*-C₂₇ alkane [as ng/g dry sediment, Table V, (A)] is visualized in Fig. 4. The distribution pattern of this alkane may provide an insight into the input variation of continentally derived organic matter. This input seems to be most pronounced at site 29, a conclusion supported by the $\delta^{13}\text{C}$ -values of the organic matter (Fig. 1; correlation coefficient *r* between $\delta^{13}\text{C}$ and *n*-C₂₇ is 0.75) and to some extent by the palynological investigation. This phenomenon cannot be observed when the data of Table V, (A) are normalized for differences in the organic carbon content [Fig. 4; Table V, (B)]. The objective of this normalization is to correct for organic carbon dilution, caused by different sedimentation rates at different sampling sites, and for redepositional events. Based on these normalized data the input of terrestrial organic matter, as exemplified by *n*-C₂₇, is relatively low at site 29, contradicting the $\delta^{13}\text{C}$ results. This discrepancy might be caused by differences in primary productivity and preservation conditions. It is postulated that at site 29 the environment of deposition was more favourable for preservation of organic matter than at other sites. A comparison can be made with the sap-

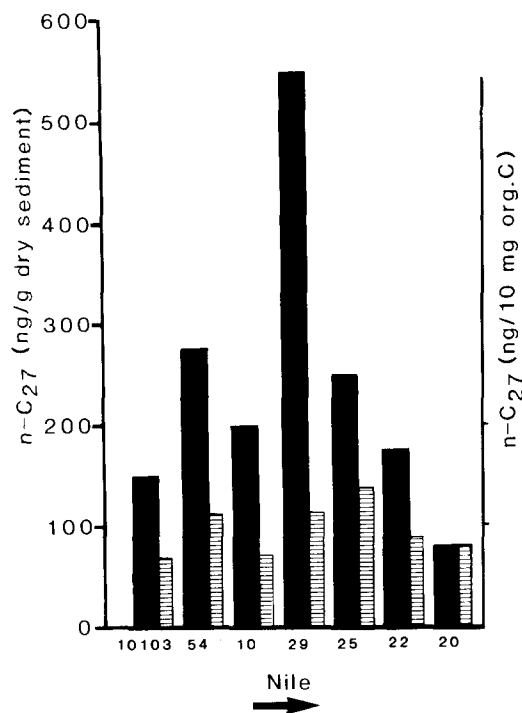


Fig. 4. Distribution of $n\text{-C}_{27}$ alkane (in ng/g dry sediment, black bars; in ng/10 mg org. C, hatched bars) in the sapropel samples ordered towards the mouth of the river Nile. The concentration of core 10103 represents an average value of three S_1 samples from this core, taken from Smith (1984).

ropel of box core 10, which has a comparable thickness as the sapropel of box core 29 and an equal sedimentation rate might be suspected. The sapropel at site 29 is, however, marked by a higher organic carbon content (4.93%) and a concomitant higher concentration of extractable organic compounds (Table V). The preservation conditions might be indirectly linked with the water depth, as box core 29 was collected from deeper realms. It is generally assumed that sapropels are deposited under anoxic conditions and it can be imagined that oxygen is more exhausted in the deeper parts of the basin and in isolated depressions. This is supported by the observation that the shallowest present-day water depth below which cores containing sapropelic intervals (0.5–2.0% org. C) are found is 400 m (Shaw and Evans, 1984), whereas cores containing sapropels (>2.0% org. C) are found at a minimum water depth of

660 m (McCoy, 1974). Benthic activity will be minimal at depths where oxygen is exhausted, and consequently the preservation will be better. The interpretation of the $n\text{-C}_{27}$ data is thus not straightforward, but based on the palynological data, the $\delta^{13}\text{C}$ data and the correlation between the absolute concentrations of $n\text{-C}_{27}$ and the $\delta^{13}\text{C}$ -values a relative increase of terrigenous organic input towards more seaward and deeper deposited sapropels might be inferred.

The sapropel investigated by Smith and coworkers is from a core collected in a water depth of 2895 m (Sutherland et al., 1984). The organic carbon content is not that high (1.71–3.34%; Sutherland et al., 1984), which might be the result of “dilution”. Features, such as expanded thickness, a fining-upward sequence, and a ^{14}C age of 7460 yr. B.P. measured above a ^{14}C age of 7280 yr. B.P. (Sutherland et al., 1984), may point to redepositional events.

The variations of the normalized data of phytol, dinosterol and the C_{30} -diol are shown in Fig. 5. A high correlation between these compounds is evident. The correlation between the C_{30} -diol and dinosterol ($r=0.91$) is surprising, as these two compounds reflect two different marine inputs (dinoflagellates and planktonic cyanobacteria, respectively). Also the correlation of these two compounds with phytol cannot be explained properly, because it is unlikely that phytol is solely derived from dinoflagellates and planktonic cyanobacteria. Even more surprising is the fairly good correlation ($r=0.80$) between the continentally derived $n\text{-C}_{27}$ - and the marine derived C_{37} -ketones. These correlations might indicate that the communities of photosynthetic organisms in the surface water have been rather uniform over the eastern Mediterranean during the formation of sapropel S_1 and that the influx of continentally derived matter cause parallel variations in the primary productivity.

The distribution of dinosterol (Table V) does not mimic the distribution of dinoflagellate

TABLE V

Quantitative results of six S₁ sapropels*¹

(A) Quantitative results of selected compounds

Sample Compound	10103* ²	54	10	29	25	22	20
<i>n</i> -C ₁₆ -FA	3,325	6,100	4,950	18,650	3,750	5,050	5,050
<i>i</i> -C ₂₀₋₁ -OH	4,790	2,050	1,950	16,150	1,450	1,500	550
<i>n</i> -C ₂₇ -HC	150	275	190	550	250	180	80
<i>n</i> -C ₂₄ -FA	470	1,150	950	3,580	450	1,150	250
<i>n</i> -C ₂₄ -OH	360	250	350	1,120	600	300	130
Dinosterol	2,550	1,150	1,250	7,770	1,100	450	150
C ₃₀ -diol	3,980	850	1,350	7,300	1,700	450	150
C ₃₇ -ketones	540	950	750	3,360	1,500	900	450

(B) Quantitative results normalized to 1% organic carbon*³

Sample Compound	10103	54	10	29	25	22	20
<i>n</i> -C ₁₆ -FA	1,500	2,460	1,800	3,800	2,030	3,660	4,900
<i>i</i> -C ₂₀₋₁ -OH	2,160	830	710	3,280	780	1,090	530
<i>n</i> -C ₂₇ -HC	70	110	70	110	135	90	80
<i>n</i> -C ₂₄ -FA	210	460	350	730	240	830	240
<i>n</i> -C ₂₄ -OH	160	100	130	230	320	220	125
Dinosterol	1,150	460	450	1,590	600	330	145
C ₃₀ -diol	1,790	340	490	1,490	920	330	145
C ₃₇ -ketones	240	380	270	690	810	650	440

*¹Values are expressed in ng/g dry sediment.*²Values of core 10103 are an average of three S₁ sapropel samples, taken from Smith (1984).*³Average org. C values of sections analyzed by Smith (1984) is 2.22% (Sutherland et al., 1984).

cysts (Table II). However, all reports on the lipid composition of dinoflagellates deal with investigations of total dinoflagellate populations. Dale (1976) showed that only 5–10% of a given living dinoflagellate population forms acid-resistant cysts with a high fossilization potential. Hence, a discrepancy between the palynology, which only studies acid-resistant remains, and the organic geochemistry is not surprising in this respect. Smith et al. (1982) attributed dinosterol and several other 4-methylsterols to an unknown uncharacterised phytoplankton source, based on the absence of dinoflagellate cysts in their samples from the Namibian Shelf. However, only relatively few living species produce fossilizable remains. Moreover, dinocysts are probably not the only

fossil remains of dinoflagellates. It is equally possible that a considerable amount of the acid-resistant AOM is of a dinoflagellate origin (B. Dale, pers. commun., 1986). The suggestion of Smith et al. (1982) seems therefore equivocal.

Fig. 6 shows some of the basic parameters thought to be responsible for the sapropel formation, assuming that an increase of Nile water discharge is the driving force for the sapropel formation (cf. Rossignol-Strick et al., 1982). This assumption is supported by the distribution pattern of the representatives of the fresh-to brackish-water genus *Pediastrum* encountered in samples 20, 22 and 29 (Table II). Evitt (1963) suggested that the resistant cells of this genus may have been transported into the marine environment by streams rather than

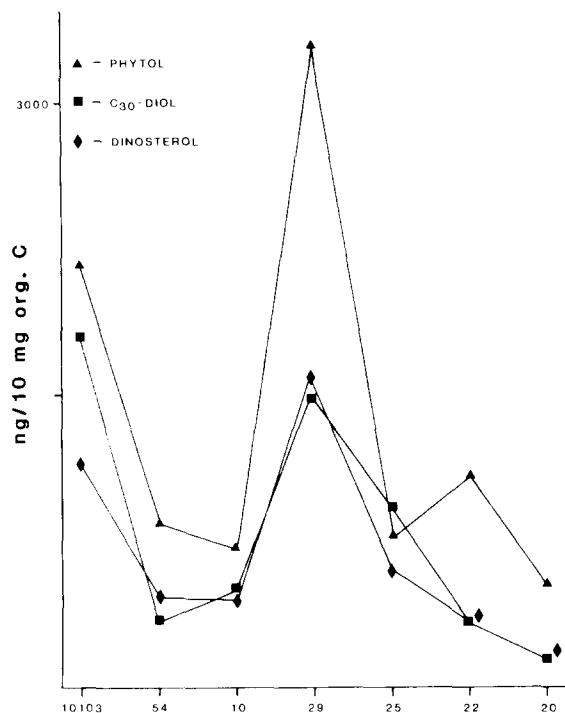


Fig. 5. Distribution of phytol, dinosterol and C₃₀-diol in the sapropel samples, calculated on the organic carbon content [Table V, (B)] ordered towards the mouth of the river Nile.

living in the area in which they were fossilized.

The input of nutrient-rich riverine water will induce a higher autochthonous production of marine organisms in the water column, an effect which diminishes with increasing distance from the source of mixing (Fig. 6). Also the input of continentally derived organic matter will be enhanced. Assuming that the organic detritus passing from the sea surface through the water column to the sea floor is a reflection of the sea-surface organic matter, it can be suggested that organic matter reaching the sea floor near the distributary mouth is predominantly of marine origin, whilst in a more seawards direction the relative concentration of terrigenous organic material increases (Fig. 6). In a situation with uniform sedimentation rate and "good" preservation conditions, it is thus expected that layers with the highest organic carbon values are found near the distributary mouth. A similar observation can be suspected when there are

"poor" preservation conditions, only the contribution of labile marine organic matter will decrease relative to the contribution of refractory terrigenous organic matter. The sapropels collected from the Nile Cone are, however, strongly influenced by a high sedimentation rate, resulting in expanded thicknesses and low organic carbon contents (Fig. 6), but still characterized by the initial $\delta^{13}\text{C}$ -values. The relation between marine organic matter and terrigenous organic matter as proposed in this model also explains the observed correlation between the $n\text{-C}_{27}$ and the long-chain ketones. This model explains most of the phenomena observed, although some questions remain to be answered.

On the right in Fig. 6, the present-day situation is shown, indicating the relative importance of eolian transported organic material (see Section 3.3). A non-sapropel environment is characterized by both low productivity as well as poor preservation.

4. Conclusions

Organic matter of S₁ sapropels is of a mixed marine, terrigenous and bacterial origin. A trend of relatively increasing amounts of continentally derived organic matter towards more seaward and deeper-deposited sapropels can be observed. The planktonic communities present during formation of the S₁ sapropel in the eastern Mediterranean were probably relatively uniform. It is further postulated that in the deeper realms conditions were more favourable for preservation of organic matter than in shallower areas. However, varying sedimentation rates hamper a straightforward interpretation.

The driving force for sapropel formation seems to be an increased run-off from the river Nile, based on the $\delta^{13}\text{C}$ -values, on the distribution of the fresh/brackish water genus *Pediastrum*, and on the concentration and distribution of terrestrial biological markers in sapropel and non-sapropel samples.

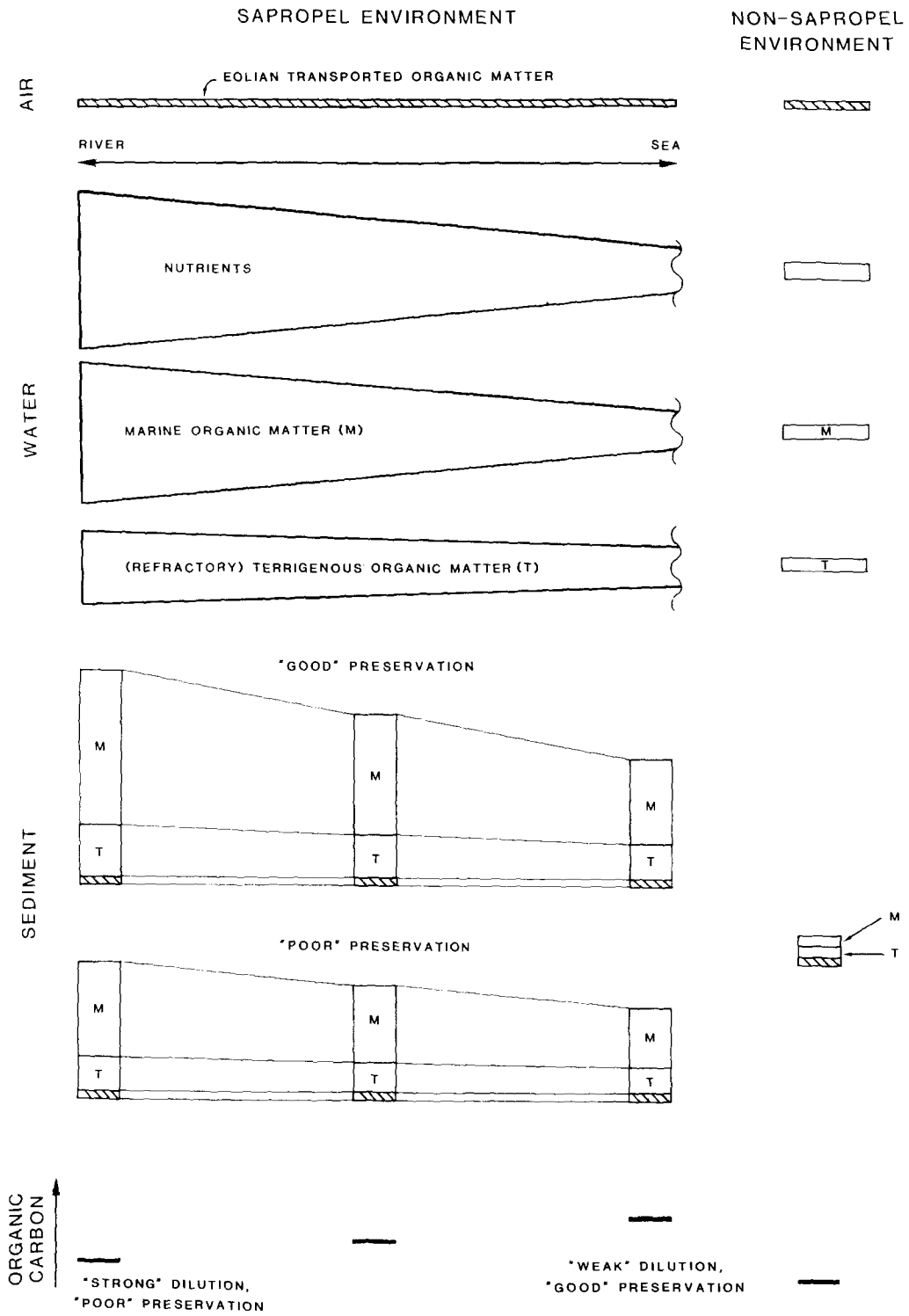


Fig. 6. Schematic model for the formation of sapropel S₁.

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