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THE LIPID GEOCHEMISTRY OF A RECENT SAPROPEL AND ASSOCIATED SEDIMENTS FROM THE HELLENIC OUTER RIDGE, EASTERN MEDITERRANEAN SEA

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Five sections (0–7, 29–36, 53–60, 78–85 and 104–111 cm), of a 0–2 m sediment core from the Hellenic Outer Ridge, in the eastern Mediterranean Sea, have been examined for lipids. Three of these sections were from a 73 cm thick S_1 (*ca.* 6000–9000 years b.p.) sapropel layer, one from an upper ooze layer and one from a lower marl. The lipids were extracted and the major classes analysed in detail by gas chromatography and computerized gas chromatography–mass spectrometry.

In all sections, the *n*-alkanes were dominated by C_{25}–C_{31} components, showing a high odd-over-even predominance, with smaller amounts of lower chain-length components. The acyclic ketone fraction consisted mainly of C_{37}–C_{39} di- and tri-unsaturated alken-2-ones and alken-3-ones. Alkanols, ranging from C_{12}–C_{32} with a high even–odd preponderance, were present in all sections, maximizing at *n*-C_{22} or *n*-C_{26}. The sapropel contained abundant phytol (up to 7000 ng g^{-1} dry sediment), and considerable amounts of 22 : 1, 24 : 1 and 26 : 1 *n*-alkenols; in the non-sapropelic sediment, phytol was only a minor component , and no *n*-alkenols were detected. In addition to these alcohols, the sapropel also contained C_{28}–C_{32} 1,13-, 1,14- and 1,15-diols and 15-keto-alkan-1-ols, the 30 : 0 compound predominating in both series.

In all sections, fatty acids were the most abundant lipid class. These were mainly C_{12}–C_{30} straight-chain compounds, maximizing at 16 : 0 with a high even–odd predominance; most were saturated, but C_{16}, C_{18}, C_{20}, C_{22} and C_{24} monoenoic acids and small amounts of C_{16}, C_{18}, C_{20} and C_{22} polyenoic acids were present. A range of branched and cyclic acids were also identified. The non-sapropelic upper and lower sediments differed from the sapropel in containing higher levels of branched acids (especially C_{15} and C_{17} iso- and anteiso-compounds) and C_{18} monoenoic acids: these differences could be related to differing inputs, especially in terms of microbial communities.

The sterol distributions of the sapropel displayed a wide range of structures (C_{26}–C_{31}), totalling over sixty different components. These included both 4-methyl- and 4-desmethylnuclei, a variety of C_8–C_{11} side-chains, and encompassed Δ^5, $\Delta^{5,22}$, $\Delta^{5,24}$, $\Delta^{5,24\,(28)}$, Δ^{22}, $\Delta^{24,(28)}$, Δ^7 and $\Delta^{8\,(14)}$ unsaturation plus a range of fully saturated stanols. Major components were 4α, 23, 24-trimethyl-5α-cholest-22-en-3β-ol (dinosterol), cholest-5-en-3β-ol (cholesterol), 24-methylcholesta-5,22-dien-3β-ol and 24-ethylcholest-5-en-3β-ol. In contrast, the non-sapropelic sediments contained very low levels of only a few sterols, chiefly cholesterol and dinosterol, probably due to input differences. In addition to sterols, the sapropel also contained small amounts of stanones and sterenes.

A significant terrigenous input of lipids is evident throughout the core (especially from the *n*-alkane data), but the sapropel lipid composition appears to be predominantly of marine origin. Individual 'biological marker' lipids suggest inputs from Dinophycean and Haptophycean algae to the sapropel. Potential contributions of lipids from organisms such as foraminifera and pteropods, remains of which were observed in the sediment, are difficult to assess due to a paucity of data on the lipid compositions of such organisms.

The lipids of the non-sapropelic sediments showed a much less prominent marine signal, especially in terms of the lower levels of phytol and sterols and the higher relative abundance of terrestrial *n*-alkanes.

Two main models have been proposed to explain the formation of organic-rich sapropel facies; (i) stagnation of the water column and the establishment of anoxic conditions in bottom water and sediments, resulting in enhanced preservation of sedimentary organic matter, and (ii) increased biological production providing an increased input of organic matter to the sediments. The lipid composition strongly suggests that this sapropel received a large marine-derived input of organic matter. Since this was less evident in the overlying and underlying sediments, sapropel deposition appears to have been associated with an increased autochthonous input. The anoxic nature of the sapropel, by restricting degradation to anaerobic processes, will also have contributed to the differences in lipid composition between the sediment types.

Little diagenesis of lipids in the sapropel was evident. Small amounts of sterenes and 5β(H)-stanols were present, probably formed by dehydration and reduction, respectively, of precursor sterols. Diagenetic dehydration of phytol may have contributed to the presence of minor amounts of certain other isoprenoid lipids.

1. Introduction

(*a*) *Occurrence of sapropels in the east Mediterranean*

The dark grey or black layers found in the sediments of the east Mediterranean have attracted a great deal of scientific interest since their discovery during the Swedish Deep Sea Expedition (Kullenberg 1952). The realization that the explanation of their formation may also add to knowledge of the relatively recent history of the Mediterranean Basin, the 'cradle of our European civilization' has been a particular incentive. Indeed, it is intriguing to consider that the most recent dark layer, the S_1 sapropel (Cita *et al.* 1977), was laid down during the pre-dynastic Egyptian period and the events involved in its formation may have been seen by this civilization.

One of the most interesting features of these dark layers is that they contain significantly higher levels of organic carbon relative to normal deep-water marine sediments. The terms 'sapropel' and 'sapropelic layer' have been applied to sediments which are generally dark grey or black in colour, with a relatively high organic content (0.5–20% total organic carbon), and the definitions provided by Kidd *et al.* (1978), based on the organic carbon concentration, will be employed here. These define a *sapropel* as: 'a discrete layer, greater than 1 cm in thickness, set in open marine pelagic sediments and containing greater than 2.0% organic carbon by weight'. The definition of a *sapropelic layer* is similar, but specifies an organic carbon content of 0.5–2.0% by mass.

Many sediment cores recovered from the east Mediterranean Basin have contained sapropels (see, for example, Calvert 1983; Cita *et al.* 1977; Kidd *et al*; 1978; Olausson 1960, 1961; Rossignol-Strick *et al.* 1982; Stanley 1978; Thunell *et al.* 1977; Williams & Thunell 1979; Williams *et al.* 1978; Shaw & Evans 1984), which are generally recognizable as distinct bands of dark (i.e. olive grey, dark grey or black) sediment within an otherwise lighter-coloured sediment column (brown or light grey marl or ooze). Only one example of a sapropel has been recorded from the west Mediterranean Basin (Kidd *et al.* 1978).

Sapropels generally differ from the surrounding sediments in that they contain pyrite and iron monosulphides (which cause their dark coloration), and in that benthic faunal remains

and evidence of bioturbation (e.g. burrows) are absent, or occur to a limited extent (Cita *et al.* 1977; Deroo *et al.* 1978; Sigl *et al.* 1978; Shaw & Evans 1984; Sutherland *et al.* 1984).

Several distinct sapropel layers are recognized; three occur in the Recent epoch of the Quaternary, named S_1 (*ca.* 7000–9000 years b.p.), S_2 (*ca.* 23000–25000 years b.p.) and S_3 (*ca.* 38000– over 40000 years b.p.) (Dominik & Mangini 1979; Stanley 1978). Other, older, sapropel layers are known, but have been much less studied; indeed, their ages and areal distributions have not been established (Dominik & Mangini 1979; Thunell 1979*b*).

Correlations of the three Recent sapropels, in cores covering a wide area of the eastern Mediterranean have been made (Stanley 1978), suggesting that formation of these deposits was a basin-wide phenomenon. Stratigraphic correlation of sapropels between different cores, however, is difficult (Dominik & Mangini 1979; Stanley 1978; Stanley *et al.* 1978), owing to:

(i) variable sedimentation rates across the eastern Mediterranean, leading to different sapropel thicknesses and depths of burial; and

(ii) disturbances of the sedimentary sequence. Tectonic activity has been extensive in the eastern Mediterranean. Such activity could have affected the sedimentary record both directly, by inducing slumps, and indirectly, by creating a complex topography (consisting of numerous, often deep, basins and trenches divided by steep ridges), where unconsolidated sediments are prone to slumping. Thus, in some regions, a sapropel layer may have been lost through slumping, or interrupted by the sudden influx of a non-sapropelic turbidite.

Correlation of sapropels across the eastern Mediterranean therefore depends mainly on age determination. ^{14}C dating, the most important technique, is not reliable for ages greater than 40000 years b.p. and so only the most recent sapropels (S_1, S_2 and S_3: see above), have been dated and mapped (Dominik & Mangini 1979; Stanley 1978). Even the use of ^{14}C dating to correlate sapropels presents problems (Jongsma *et al.* 1983; Stanley 1978):

(i) the onset and cessation of sapropel deposition may not have been isochronous across the whole basin, because of local variations in topography and oceanographic conditions;

(ii) sapropel deposition may have been temporarily interrupted, in some areas, owing partly to variations in productivity or water circulation;

(iii) there may have been 'locally produced' sapropels in some areas owing partly to conditions prevailing in an isolated basin, which were not associated with more general sapropel formation (e.g. the sapropel recently reported by de Lange & ten Haven (1983), and Jongsma *et al.* (1983));

(iv) mixing of sediments of different ages (through slumps or turbidites), may affect the apparent age of a sample as determined by ^{14}C dating (which only provides an average age).

The occurrence of sapropel layers in the eastern Mediterranean is thus not well understood, as a result of the difficulties in correlating recovered sapropels over a wide area and the uncertainties regarding the mechanisms of their formation. Nevertheless, it is generally considered that sapropel layers, or at least the three Recent examples, represent periods when the paleoceanographic and environmental conditions over large areas of the eastern Mediterranean were profoundly different from those found today.

(*b*) *Theories of sapropel formation in the east Mediterranean*

(i) *Stagnation scenario*

Bradley (1938) first suggested that climatic and sea-level changes, associated with glacial events, may have led to flooding of the Mediterranean by freshwater and caused profound

changes in its hydrography. He visualized large volumes of freshwater entering the Mediterranean, reversing the normal surface flow pattern (by which Atlantic surface water enters through the Straits of Gibraltar to replace evaporative losses) and forming a surface layer of low-salinity water overlying denser, more saline water. This density gradient, together with the confining effects of the high sills at the Sicily and Gibraltar Straits, would have produced a stable stratification of the water column and inhibited vertical circulation. In the present-day Mediterranean, aeration of deep water is maintained by oxygenated surface water becoming denser (i.e. more saline), through evaporation and sinking, Atlantic surface water being drawn in to replace it (Bradley 1938; Demaison & Moore 1980). A large influx of low-salinity surface water, in excess of that lost by evaporation, would effectively stop this circulation. In a deep, enclosed basin, such as the east Mediterranean, inhibition of vertical mixing, in the absence of other sources of aeration, would lead to the deeper water rapidly becoming depleted in oxygen due to its consumption by decomposing organic matter. Bradley (1938) further suggested that such stagnation of the water column would have resulted in organic-rich sediments being formed and advocated a coring programme to investigate the sedimentary record.

Subsequently, cores containing organic-rich sapropel layers were recovered from the east Mediterranean and were taken to be evidence of past stagnation events (see, for example, Kullenberg 1952; Olausson 1960, 1961). It has generally been accepted that the decomposition of organic matter is less in anoxic than oxic sediments. This is attributed to the lower efficiency of anaerobic, compared with aerobic, respiration, and the fact that anoxic sediments will not contain a permanent population of metazoan benthos, organisms which can considerably increase the rate of reworking of surface sediments (Berner 1980). The first model of sapropel formation (Kullenberg 1952; Olausson 1960, 1961) can be summarized thus: while the water column remained fully oxygenated, the sediments deposited had a low organic content (less than 0.5% organic carbon), caused by extensive remineralization of the organic input. When large influxes of freshwater induced stagnation of the water column and anoxia in the deeper water, as described above, remineralization of organic matter was reduced. This allowed a higher proportion of the organic input to be preserved in the sediments, so giving rise to deposits that were relatively rich in organic content: sapropels (more than 2% organic carbon) and sapropelic layers (0.5–2% organic carbon). When the freshwater input returned to normal, vertical circulation and aeration of the water column was restored, and sapropel deposition ceased.

A number of subsequent studies of sapropel sequences have been made, and these have largely concurred with this model (see, for example, Nesteroff 1973; Cita *et al.* 1977; Thunell *et al.* 1977; Vergnaud-Grazzini *et al.* 1977; Deroo *et al.* 1978; Kidd *et al.* 1978; Sigl *et al.* 1978; Stanley 1978; Williams *et al.* 1978; Luz 1979; Mangini & Dominik 1979; Thunell & Lohman 1979; Williams & Thunell 1979; Rossignol-Strick *et al.* 1982; Thunell & Williams 1982; de Lange & ten Haven 1983; Shaw & Evans 1984). Much of this work has concentrated on the foraminiferal nannofossil assemblages of cores, the species distributions and isotopic compositions of which have been used to reconstruct palaeoclimatic and palaeoceanographic conditions. The ratio of $^{18}O:^{16}O$ ($\delta^{18}O$) in the $CaCO_3$ skeletons of foraminifera in sediment cores has been extensively studied; core profiles of this ratio have consistently shown sapropel layers to correspond to ^{18}O minima (Williams *et al.* 1978; Luz 1979; Williams & Thunell 1979; Rossignol-Strick *et al.* 1982; Thunell & Williams 1982; Shaw & Evans 1984). Furthermore,

within sapropels, the skeletons of planktonic species tend to show greater ^{18}O depletion than those of pelagic and benthic (where present) species. The $^{18}O:^{16}O$ ratio can be affected by several factors, such as temperature and biosynthetic fractionation (Luz 1979), but the consensus of opinion is that the primary cause of the enhanced ^{18}O depletions in the sapropels was a large influx of freshwater (which is depleted in ^{18}O relative to seawater) to the Mediterranean during sapropel formation. The greater ^{18}O depletion of planktonic, compared with deeper-living foraminifera, further suggests that the inflowing water did not mix evenly through the water column but tended to form a low-salinity surface layer. The evidence from $^{18}O:^{16}O$ ratios is supported by studies of microfossil species distributions; remains of planktonic species known to prefer relatively low salinities are often characteristic of late Quaternary sapropels (Thunell *et al.* 1977; Vergnaud-Grazzini *et al.* 1977; Kidd *et al.* 1978; Thunell & Lohman 1979).

Several palaeoclimatic studies have related sapropel deposition to termination of ice ages, when glacial meltwater would have drained into the Mediterranean (Vergnaud-Grazzini *et al.* 1977; Stanley 1978; Williams *et al.* 1978; Luz 1979; Thunell 1979*a*,*b*; Stanley & Blanpied 1980; Thunell & Williams 1982). Specifically, Williams *et al.* (1978) note that 9000 years b.p. (about the time of the onset of deposition of the most recent sapropel) corresponds to the establishment of contact between the Black Sea and the Aegean, due to meltwater from the Fescundinian ice sheet draining into the Black Sea and raising the water level above the sill at the Bosporus. Meltwater would presumably also have entered the Mediterranean via the major European river systems such as the Rhône and the Po.

Other work, however, has suggested that increased fluvial inflow, rather than glacial meltwater, caused a reduction in surface water salinities during deposition of the S_1 sapropel (Rossignol-Strick *et al.* 1982; Shaw & Evans 1984). This increase in river input, especially from the Nile, is believed to have been induced by periods of high precipitation over parts of Africa (Rossignol-Strick *et al.* 1982).

The foraminiferal species distribution and ^{18}O data have provided good evidence in support of the early propositions that climatically induced flooding of the Mediterranean, by freshwater, led to formation of a low-salinity surface water layer, coincident with the deposition of sediments rich in organic material (Bradley 1938). In addition, the absence (or very limited occurrence) of remains of benthic organisms and evidence of bioturbation from sapropels indicates that they were deposited under anoxic conditions (Cita *et al.* 1977; Thunell *et al.* 1977; Vergnaud-Grazzini *et al.* 1977; Kidd *et al.* 1978; Shaw & Evans 1984). It has generally been assumed that reduced degradation of organic matter, resulting from a lack of oxygen, is sufficient to explain the enhanced organic content of sapropels compared to oxic over- and underlying sediments. Arguments regarding sapropel formation have tended to concentrate on the likely events which could have created stagnant, anoxic conditions, rather than whether such conditions really were the primary factor responsible. Thus, alternative sources of freshwater (glacial, fluvial or rainfall), various flow patterns and different river systems for discharging the major input of water have been proposed and discussed, together with features such as topography and water salinity, temperature and depth, to explain the formation and known distribution of sapropels in the east Mediterranean (Thunell *et al.* 1977; Stanley 1978; Williams *et al.* 1978; Lūz 1979; Williams & Thunell 1979; Rossignol-Strick *et al.* 1982; Thunell & Williams 1982; Jongsma *et al.* 1983; de Lange & ten Haven 1983; Shaw & Evans 1984). Recently a small basin has been discovered, south of Crete, where the water column appears

to be density stratified due to the presence of hypersaline bottom water, formed by dissolution of an exposed Messinian evaporite (Jongsma *et al.* 1983; de Lange & ten Haven 1983). The bottom water is anoxic, and preliminary data suggest that sapropelic sediments are currently accumulating there (L. ten Haven, personal communication).

What has not generally been considered to be of specific importance, in producing the characteristic organic-rich nature of sapropels, is an increase in the supply of organic matter to the sediments. Several workers have, however, identified evidence of increased primary productivity or land-derived organic input in sapropels and suggested this to be a contributing factor (Rossignol-Strick *et al.* 1982; Thunell & Williams 1982; de Lange & ten Haven 1983; Shaw & Evans 1984). Recently, a new model of sapropel formation has been proposed which concentrates on high biological productivity as the key factor in sapropel formation. This is discussed below.

(ii) *High productivity scenario*

It is, perhaps, surprising that a mechanism which is known to produce deposits rich in organic content in some present day shallow water marine environments, i.e. the sedimentation of large amounts of detritus from phytoplankton blooms (see, for example, Calvert & Morris 1977; Cronin & Morris 1982; Poutanen & Morris 1983; Gagosian *et al.* 1983; Smith *et al.* 1982, 1983*b*, *c*), has not been specifically considered in relation to the formation of sapropels in the east Mediterranean. Doubt has recently been cast on the feasibility of forming sapropel facies without an increase in the normal supply of organic material to the sediments. In a review of several anoxic water columns, Richards (1970) proposed that the relatively high organic content of sediments in some anoxic basins (e.g. the Black Sea and Cariaco Trench) may represent high sedimentation rates rather than slow decomposition. This led Calvert (1983) to suggest that a similar consideration might apply to Mediterranean sapropels; by using relations published by Muller & Suess (1979) and Suess (1980) applied to average values for sedimentation rates, sediment density and porosity and primary production, he concluded that 'it is not possible to produce a sapropel containing substantially more than a few percent carbon at the present production rate in the Mediterranean'. Since some sapropels have been found to contain up to 20% organic carbon by mass, he further concluded that it is doubtful if anoxic conditions alone could have been responsible for the formation of such organic-rich deposits, but that an increase in biological production, with a concurrent rise in the flux of organic matter to the sediments, must have been involved.

In the present-day Mediterranean, Atlantic surface water enters through the Straits of Gibraltar, drawn by evaporative losses. Circulation is maintained by an outflow of deeper Mediterranean water. Bradley (1938) proposed that large influxes of low-salinity surface water would have reversed the normal circulation pattern, causing an outflow of surface water and an inflow of deeper Atlantic water. He further speculated that this hydrographical change might be recorded in the sediments as varves rich in organic material, formed from seasonal phytoplankton blooms and preserved by water column stagnation in the eastern basin. Calvert (1983), in his study of Pleistocene sapropels, suggested that their formation was related to high productivity induced by such a circulation reversal, in an analagous fashion to the organic-rich phytoplankton oozes found in the Namibian and Peruvian upwelling régimes (Morris & Calvert 1977; Demaison & Moore 1980; Calvert & Price 1983). He envisaged that the subsurface inflow of Atlantic water would have created an upwelling effect in the eastern basin,

carrying nutrients into the euphotic zone, and supporting an increase in primary production. This productivity may have been further enhanced by the flux of nutrients likely to have been carried directly into the surface waters by the increased run-off, and the climatic warming which often parallels sapropel formation (Olausson 1960, 1961; Ryan 1972). The higher biological productivity would have provided an increased flux of organic matter to the sediments, producing a raised sedimentary organic content and so forming a sapropel or sapropelic layer. Decomposition of the high organic input would have maintained oxygen depletion in the lower water column and sediments.

(*c*) *Evidence for increased productivity during sapropel deposition*

The two major types of model for sapropel formation ('stagnation' and 'high productivity', outlined above) both take as a starting point large influxes of water to the Mediterranean at the beginning of an interglacial period, but diverge when explaining how this could have led to deposition of anoxic, organic-rich sediments. If increased biological production was a major factor, then evidence of an enhanced marine input should be detectable in the sapropel. In a sapropel-containing core from east of Crete, studied by Thunell & Williams (1982), there was a sharp increase in the abundance of diatom frustules in the sapropel layer, compared with the underlying and overlying sediments, which the authors attributed to localized high productivity. De Lange & ten Haven (1983) suggested that periods of increased production in the surface water contributed to the variable organic carbon content which they found in a sapropel from south of Crete.

This paper reports the organic geochemical data for a core, containing an S_1 sapropel, from the Hellenic Outer Ridge; the lithology, inorganic geochemistry, ^{13}C data and C:N ratios for this core have been published by Sutherland *et al.* (1984). These authors found an enrichment of several trace metals (Ba, Cr, Cu, Mo, Ni, Zn), which together with a distinctly marine carbon isotopic signature, $\delta^{13}C = -18.5$ to $-21.6‰$ (see figure 2*a*, *b*), and C:N ratios of *ca.* 10, were taken as evidence of an increased carbon flux from marine sources to the sea floor during the formation of the sapropel, probably as a result of an increase in marine primary production. Other work on this same S_1 sapropel found that the distribution patterns of the various molecular weight fractions of humic and fulvic acids resembled those previously found in young marine sediments rich in organic material underlying areas of high productivity, rather than those found in sediments where the overwhelming input of organic matter was from terrigenous sources (Poutanen & Morris 1985).

On the other hand, some workers have considered the majority of the organic matter in some sapropels to be of terrestrial origin (Deroo *et al.* 1978; Sigl *et al.* 1978), including some who proposed that an increase in terrestrial input was a factor in sapropel formation (Rossignol-Strick *et al.* 1982; Shaw & Evans 1984). Evidence for terrestrial inputs has been based mainly on the presence of higher plant fragments (especially pollen), high C:N values, *n*-alkane distributions, the composition of humic fractions and particular pyrolysis products (Deroo *et al.* 1978; Sigl *et al.* 1978; Shaw & Evans 1984). Clearly, the precise nature of the immediate source of the organic matter, terrestrial vegetation or marine planktonic, is of primary importance in studies of Mediterranean sapropels. Yet little detailed work on this specific aspect has been published; particularly lacking are detailed data on the lipids of sapropels, compounds which are known to have good potential as source indicators (Simoneit 1978).

(*d*) *Objectives of this study*

Two main types of sapropel are recognized (Nesteroff 1973); pelagic sapropels found on topographic highs and present in sequences of pelagic nannofossil oozes, and turbidite sapropels found in trenches and depressions which usually show evidence of reworking by currents, or slumping. Few of the studies on the Mediterranean sapropels have concentrated on the most recent, S_1, deposit (Cita *et al.* 1977) yet, in the older deposits, clues as to the origins of the organic matter tend to become less clear and may be lost. It was therefore decided to investigate in detail the composition of a recent S_1 sapropel taken from a topographic high.

A sapropel from the Hellenic Outer Ridge, shown by ^{14}C dating to be an S_1 layer, was chosen for study; the mineralogy, major and minor element geochemistry and the radiocarbon and stable carbon isotope data have been reported by Sutherland *et al.* (1984). The work described herein presents detailed analyses of the extractable lipids. These data are used particularly to evaluate the sources of organic matter (marine versus terrestrial) in the sapropel, the likely major contributing organisms and possible input differences between sapropel and non-sapropelic sediments. The implications in relation to the theories of sapropel formation (outlined above) are then considered.

2. Experimental methodology

(*a*) *Coring and sampling*

Full details of core collection and sampling have been given previously (Sutherland *et al.* 1984) but it is appropriate to give certain additional details here.

We wished to collect samples of the Recent S_1 sapropel from an area which had suffered little postdepositional disturbance and hence had received little lateral input from bottom currents, (i.e. a site which would mainly record the sedimentary input from the overlying water column). To this end, a site (figure 1) was chosen on the northern arm of the Hellenic Outer Ridge (see Sutherland *et al.* 1984 for details of topography). It was protected from lateral influences to the north, east and west by deep water basins and to the south by the east-west ridge system. Narrow and wide beam echo sounders revealed the site to have a fairly complex local topography. After a detailed echo sounder search within a 2 mile square, using satellite fixes and a live track plot, a local high spot (under 2900 m depth of water) was chosen which, it was hoped, had received minimal additional input from slumping and ponding (site 10103, 36° 9.4′ N, 20° 28.6′ E). While the loss of part of the sediment to deeper-lying areas by the winnowing action of deep currents and slumping had to be expected, it was considered that at least the remainder should be in the original time sequence of deposition.

Over a period of 2 days (1st–2nd August 1979) four cores were collected from as close to the top of the chosen topographic high as possible. Cores were opened, their stratigraphy described and samples taken for smear slide analysis. Sections of 7 cm length were taken for lipid analysis from core 10103 # 8K (core A; figure 2*a*) and immediately frozen at −20 °C under N_2, in specially cleaned containers until analysis at the laboratory. Nine sections were taken in all (table 1).

FIGURE 1. Location of core site 10103 on the Hellenic Outer Ridge, eastern Mediterranean Sea. A full description of the site is given in the text and in Sutherland *et al.* (1984).

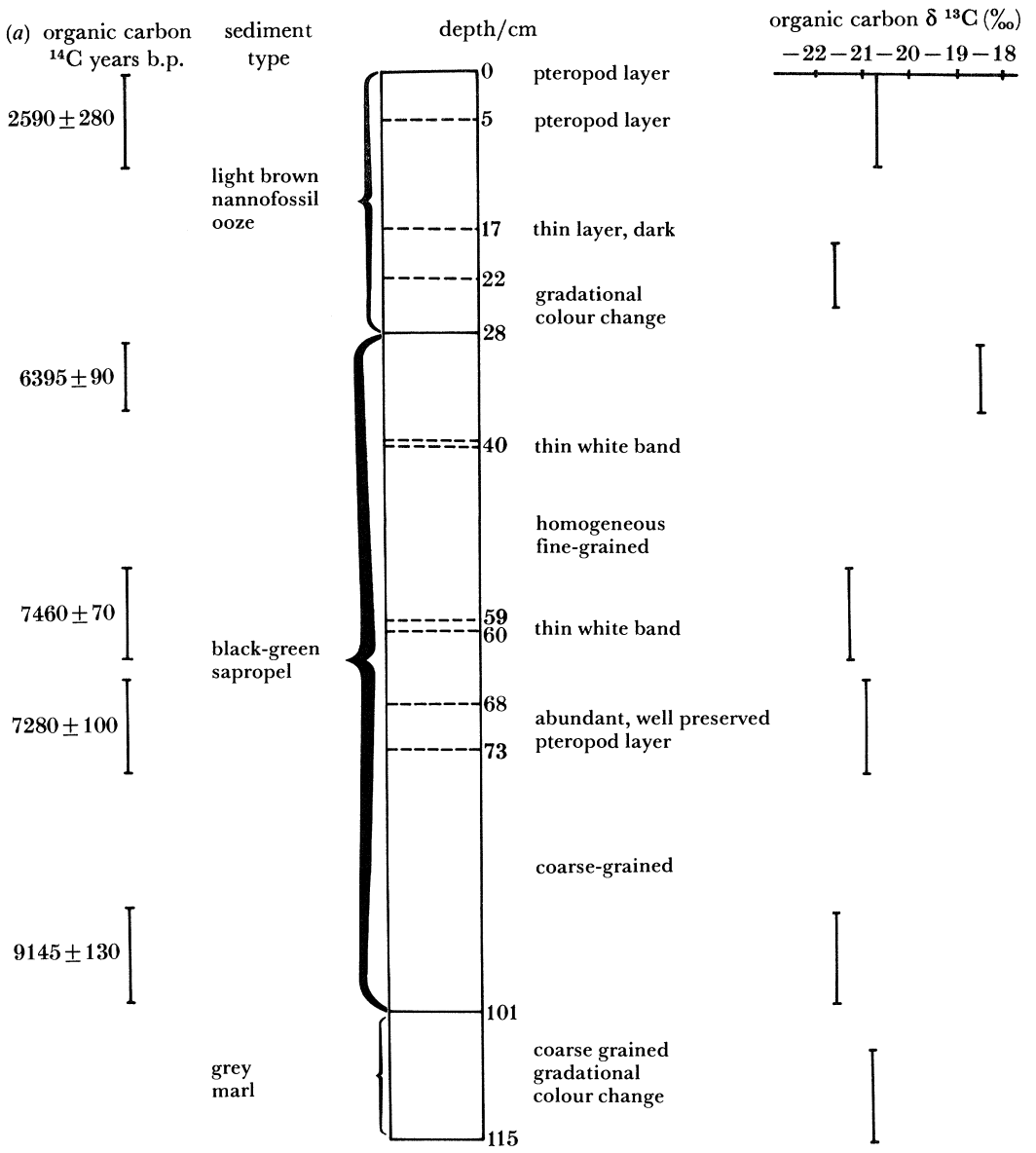
TABLE 1. WATER CONTENT OF CORE 10103A (AS PERCENTAGE OF WET SEDIMENT MESS)

section no.	depth in core/cm	water (%)	sediment type
1	0–7	48	brown ooze
2	17–24	45	
3	29–36	59	sapropel
4	41–48	58	
5	53–60	61	
6	65–72	65	
7	78–85	60	
8	91–98	62	
9	104–111	29	grey marl

(*b*) *Lipid analysis*

(i) *Extraction of lipids*

Lengthwise subsections of core sections 1, 3, 5, 7 and 9 (table 1 and figure 2*a*) were thawed and extracted with chloroform/methanol in the laboratory. Each section, wet weight 117–243 g, was suspended in 500 ml of $CHCl_3/CH_3OH$ (2 : 1 by volume) in a glass vessel which was then flushed with pure N_2, stoppered and placed in a Mettler ultrasonic tank for 1 h. The resulting suspension was allowed to stand overnight, then centrifuged (3000 r.p.m., 10 min)



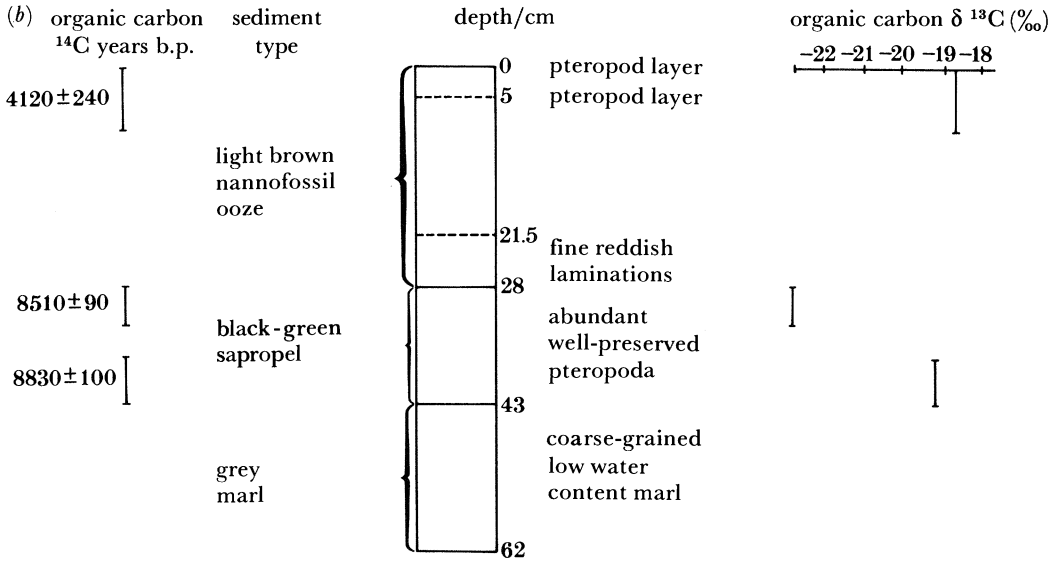


FIGURE 2 (*a*, *b*). For legend see page 386.

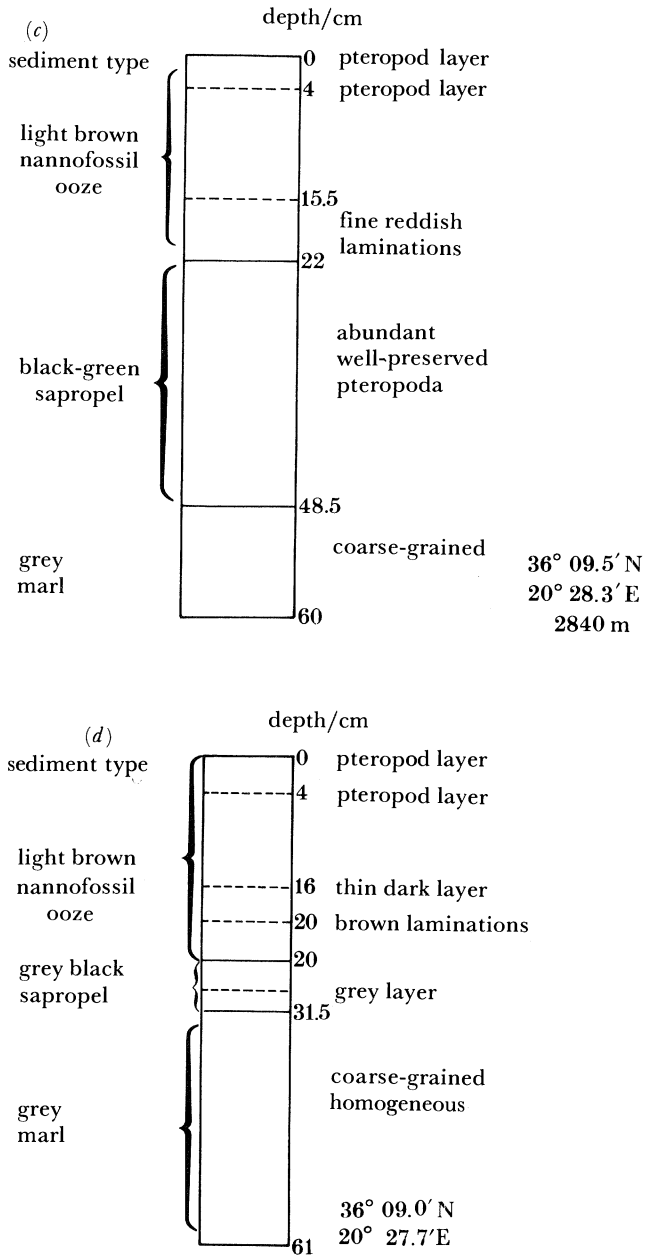


FIGURE 2. Stratigraphy of the four cores recovered from site 10103: (*a*) core A (10103 # 8K); (*b*) core B (10103 # 1BX); (*c*) core C (10103 # 6K); (*d*) core D (10103 # 3K).

and the supernatant extract decanted. The sediment residue was resuspended in a further 500 ml of $CHCl_3/CH_3OH$, sonicated for 1 h, centrifuged and the supernatant decanted. The two solvent extracts were combined and washed with 0.05 M KCl to produce a two-phase system. The organic phase was separated, evaporated to dryness using a rotary evaporator at 30 °C, and the total extracted lipids weighed. They were then dissolved in 2 ml CH_2Cl_2 and stored under N_2 at −20 °C. All operations were carried out at ambient temperature and the lipid extract maintained under an atmosphere of N_2 as far as possible.

(ii) *Separation of lipid classes and derivatization*

Saponification: an aliquot of the total lipid extract was saponified; 200 µl of lipid extract, in CH_2Cl_2, were added to 4 ml of 10% KOH in CH_3OH and the mixture left to stand, under N_2, overnight. Then a further 4 ml of CH_3OH and 2 ml of H_2O were added, the pH checked (pH > 10), and the mixture refluxed for 1 h. After cooling, the neutral fraction was extracted by liquid–liquid partitioning with *n*-C_6H_{14}/Et_2O (4:1 by volume, 3 × 10 ml). The acid fraction was obtained from the residual CH_3OH/H_2O solution by acidifying to pH 2 with aqueous HCl and then extracting with *n*-C_6H_{14}/Et_2O (4:1 by volume, 3 × 10 ml). The neutral and acid fractions were evaporated by using a rotary evaporator and stored, under N_2, in CH_2Cl_2 at −20 °C.

Neutral fraction: an aliquot of the neutral fraction was derivatized with bis(trimethylsiloxy)-trifluoroacetamide (BSTFA) for 1 h at 40 °C, and analysed by gas chromatography and gas chromatography–mass spectrometry (see below).

The remainder of the neutral fraction was separated by preparative thin layer chromatography using 0.4 mm thick silica gel G on 20 × 20 cm glass plates. The plates were developed in *n*-C_6H_{14}/EtOAc (85:15 by volume) for 45 min. Standard lipids (cholesterol, *n*-octadecan-1-ol, cholest-4-en-3-one, 5α(H)-cholestan-3-one, 5β(H)-cholestan-3-one and tetracosane) were applied as discrete spots beside the neutral fraction and, after development, the standards were visualised by spraying with rhodamine 6G (in CH_3OH) and irradiation with a UV lamp. Bands corresponding to these standards were marked on the sample area of the plate, and then the standards were completely removed to avoid possible contamination of the sample. The marked sample bands were then scraped off and the adsorbed compounds eluted with 3 × 10 ml CH_2Cl_2 (hydrocarbons and ketones) or 1 × 10 ml CH_2Cl_2 and 2 × 10 ml EtOAc (other lipid classes). Each TLC fraction was evaporated and stored as above. Alcohols were derivatized to their trimethylsilyl ethers (TMS ethers), by using BSTFA as described above, before analysis by gas chromatography and gas chromatography–mass spectrometry (see below).

Acid fraction: the acid fraction from the saponified lipid extract was methylated by addition of 2 ml BF_3–CH_3OH reagent (14% BF_3 in CH_3OH) and warming to 40 °C for 30 min. After cooling, 2 ml of CH_3OH and 1 ml H_2O were added and the fatty acid methyl esters (FAME) extracted by partitioning with 3 × 10 ml *n*-C_6H_{14}/Et_2O (4:1 by volume). The recovered FAME were stored as above.

(iii) *Gas chromatography* (GC)

All samples were analysed on a 25 m × 0.25 mm (i.d.) OV-1 coated fused silica capillary column in a Carlo Erba 2150 gas chromatograph fitted with a flame ionization detector (FID). The column was temperature programmed from 80 to 280 °C at 4 K min^{-1}, with He carrier gas at 1.2 kg cm^{-2}, and with the injector and detector held at 300 °C. Quantitative analyses were performed on a Carlo Erba 4160 gas chromatograph by using cold, 'on-column' injection, which eliminated the discrimination against the less volatile components in a sample associated with hot, vaporizing injectors. The GC column and conditions used were similar to above and the data were acquired onto a VG 'Multichrom' data system for quantitation (see below). In addition, the FAME samples were analysed on a 75 m × 0.3 mm (i.d.) glass capillary column coated with a 3:2 mixture of DEGS/PEGS, in a Carlo Erba 2150 instrument. The column was temperature programmed from 80 to 180 °C at 4 K min^{-1} with

H_2 carrier gas at 2.0 kg cm^{-2}. This relatively polar phase gave better separation of unsaturated FAME than OV-1 and was used to assist identification by retention time.

(iv) *Gas chromatography–mass spectrometry* (GC–MS)

All samples were analysed using a Finnigan 4000 quadrupole GC–MS linked to an on-line INCOS 2300 computer data system. A 25 m × 0.3 mm (i.d.) OV-1 coated fused silica capillary column was used in the GC, passing, via an interface box maintained at 280 °C, directly into the ion source of the MS. The column was temperature programmed from 50 to 280 °C at 4 K min^{-1}, with He carrier gas at 0.8 kg cm^{-2}. The MS ion source was maintained at 250 °C, with a filament current of 35 μA, an electron energy of 35 eV and an accelerating voltage of 1750 V. Mass spectra were repetitively scanned from 50 to 550 or 50 to 600 u with a total scan time of 1 s. Mass spectra were acquired onto magnetic discs and processed using the INCOS data system.

(v) *identification of lipids*

The individual components of lipid fractions were identified by a combination of GC relative retention times (RRT) and co-injection with standards, and by mass spectral data (as discussed in Smith *et al.* 1982, 1983*a*, *b*). The mass spectra were examined for the presence of molecular ions and characteristic fragment ions and, where possible, were compared with authentic reference spectra published in the literature or held in the INCOS data system library of mass spectra.

(vi) *Quantitation of lipids*

Wherever possible, individual components of lipid fractions were quantitated from the on-column GC–FID response, by comparison of peak areas with those of known quantities of standards added to samples before GC analysis. The standards used were: *n*-C_{24} alkane (for alkanes and acyclic ketones), iso-16:0 alcohol–TMS ether (for fatty alcohols, diols and keto-ols), iso-16:0 FAME (for FAME) and 5α(H)-cholestane (for steroids). An equal FID response to both sample and standard compounds was asssumed in quantitation. Peak areas were measured using a VG 'Multichrom' GC data system.

Where two or more compounds co-eluted, mass chromatography of characteristic MS ions was used to estimate the relative contribution made to the peak by each component.

(*c*) *Radiocarbon and* $\delta^{13}C$ *measurements*

Radiocarbon and stable carbon isotope measurements, on the organic carbon fraction of several sections of core 10103A, were made at the Scottish Universities Research Reactor Centre, East Kilbride, Scotland. $\delta^{13}C$ values are expressed per mille relative to the PDB standard (figure 2*a*).

3. Results and discussion

(*a*) *Sedimentological data*

(i) *Core lithologies*

The lithologies of the four cores are shown in figure 2*a–d*. The sequences are identical. In each case the sapropel was overlaid by the laminated light brown marl ooze of relatively constant thickness (22–28 cm). This would indicate that sedimentary conditions during the

post sapropel period have been similar at the four sites. Certainly, approximately the same sediment accumulation rates have occurred at two of the four sites for which ^{14}C data are available (see below). The sapropel layer, however, varies markedly in thickness (6.5–73 cm), some cores containing laminae of well preserved pteropod tests which might indicate reworking (figure 2). The water content data for core A (10103 # 8K) (table 1) show the sapropel to contain a considerably higher water content than do the enclosing sediments, although their mineralogical compositions were similar (Sutherland *et al.* 1984). The variation in sapropel thickness and the high water content are consistent with the sapropel being relatively unconsolidated during deposition. This may be the result of a relatively rapid accumulation rate compared with the overlying sediment.

(ii) *Radiocarbon dating*

The radiocarbon data for cores A and B clearly suggest an enhanced sedimentation rate during sapropel formation (figure 2*a*, *b*).

Core A appears to record a relatively continuous period of sapropel formation (*ca.* 9000–6500 years b.p.), the ^{14}C data giving a sedimentation rate of around 23 cm ka^{-1}, compared with 4.6 cm ka^{-1} for the upper marl ooze and 7.2 cm ka^{-1} for the lower calcareous clay (see discussion in Sutherland *et al.* 1984). Core B appears to have lost the upper part of the sapropel and only the 8000–9000 year sequence remains, corresponding to a sedimentation rate of approximately 20 cm ka^{-1}.

Thus, ^{14}C dating of two cores from this study area indicates that the sapropel accumulated at a faster rate than did the surrounding sediments. As discussed by Sutherland *et al.* (1984), these ^{14}C data are at variance with the ^{230}Th results of Thompson (1982), who concluded that the sapropel in the local area as a whole probably accumulated at a rate similar to, or slightly higher than, the carbonate ooze subsequently deposited. The ^{230}Th inventory of the core may have been affected by inputs of material from sources other than the overlying water column (Thompson 1982), and therefore the high sedimentation rates, given by ^{14}C data, for the sapropel may partly reflect lateral transport as well as simple vertical settling (Sutherland *et al.* 1984). In view of the topography of the coring site (described earlier), it would seem that any lateral transport of sediment must have been very local.

Calculations for different sapropels have derived a wide range of sedimentation rates: from less than 1 to over 25 cm ka^{-1} (Dominik & Mangini 1979; Mangini & Dominik 1979; Stanley *et al.* 1978; Sutherland *et al.* 1984). This reflects the great variety of depositional environments in the east Mediterranean Basin, in terms of topography, circulation and sediment dispersal patterns (Dominik & Mangini 1979; Stanley 1978; Stanley *et al.* 1978; Sutherland *et al.* 1984). Current data do not provide a generalized relation between sapropels and sedimentation rates, and each core must be considered separately with regard to its particular depositional situation.

(iii) *Smear slide analysis*

Smear slide analysis of samples taken at intervals down the sapropel in cores A and D showed the presence of pteropods, planktonic foraminifera, coccoliths, plant debris, silicious spines and shell fragments (Sutherland *et al.* 1984; S. Crease, personal communication). Pteropod tests were particularly abundant both in the sapropel and the overlying ooze. No diatom, silicoflagellate or dinoflagellate remains were found. Some evidence of a terrigenous higher plant input was present in the form of wood fragments and pollen grains, plus some fragments which appeared to be carbonized wood, possibly derived from forest fires.

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(*b*) *Lipid composition and inputs*

(i) *General survey*

The concentrations of total carbon, organic carbon, extractable lipid and the major lipid classes in the five sections from core A are shown in figure 3. These profiles illustrate the similarities within the sapropel (sections 3, 5 and 7) on the one hand and the non-sapropelic sediment (sections 1 and 9) on the other. The total organic carbon content (TOC) of the sapropel was much higher than that of the sediments above and below it, and this is reflected in the yields of extractable lipid. Relative to the dry mass of the sediment, all lipid classes follow a similar pattern, being much more abundant in the sapropel than in the non-sapropelic sediment (figure 3). However, if the abundance is expressed relative to the TOC of the core, it can be seen that some lipid classes form a relatively higher proportion of the TOC in the non-sapropelic sediment (sections 1 and 9) than they do in the sapropel (sections 3, 5 and 7) (figure 3). This is especially true of the alkanes and, to a lesser extent, applies to the *n*-alcohols and fatty acids. The fact that these classes of lipid are enhanced relative to the other classes in the non-sapropelic sediments, compared to the sapropel, could be due to two factors; either (i) the non-sapropelic sediments received relatively larger initial inputs of alkanes, *n*-alcohols and fatty acids than did the sapropel, or, (ii) greater degradation of alkenones, phytol, sterols, diols and keto-ols, has occurred in the oxic non-sapropelic sediments compared to the anoxic sapropel.

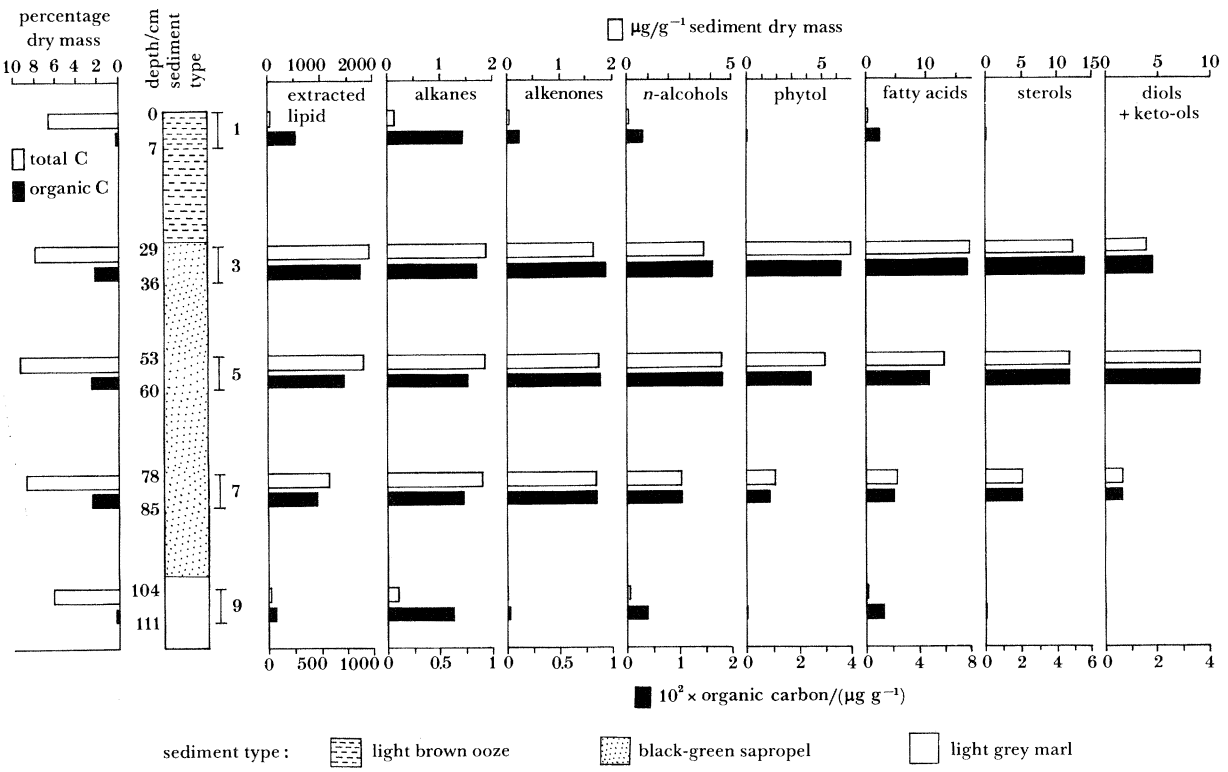

FIGURE 3. Profile of core A (10103 # 8K) showing the abundances of total carbon, organic carbon, extractable lipid and the major lipid classes in the five sections (1, 3, 5, 7, 9) analysed. Abundances are expressed relative to both the sediment dry mass and the organic carbon content.

It is most likely that a combination of these factors was involved. As discussed below, the alkanes and *n*-alcohols are believed to be predominantly of terrestrial, higher plant origin. These compounds are generally considered to be relatively refractory and to be degraded at a slower rate than other, more labile, lipids (Simoneit 1978; Cranwell 1981). If degradation is generally faster in oxic, compared with anoxic sediments, a greater differentiation between the more resistant and the more labile components might be expected in the oxic overlying and underlying sediments compared to the anoxic sapropel. The much higher abundances of phytol, sterols and possibly diols and keto-ols in the sapropel, however, may also implicate an increased contribution from marine primary production, as discussed below.

It would be interesting to see if other sapropels could be differentiated from their non-sapropelic overlying and underlying sediments on the basis of the relative abundances of different lipid classes.

(ii) *Acyclic hydrocarbons*

The sedimentary *n*-alkanes were the lipid class showing the greatest terrigenous component. Their distributions were dominated by longer chain alkanes (C_{25}–C_{35}, with an odd–even chain-length predominance of 5.1–7.4 (figure 4), which provide good indicators of higher plant material (Brassell *et al.* 1978; Simoneit 1978; Tissot & Welte 1978; Tulloch 1984). These long-chain alkanes are not easily decomposed (Cranwell 1981; Simoneit 1978), and hence survive transport from the land and post depositional degradation more readily than labile lipids; this may account for their relatively high abundance in the oxic sediments of core sections 1 and 9 (as discussed above).

The hydrocarbons of marine organisms have not been well characterized, and most reported analyses are not recent (pre-1972). These data indicate that hydrocarbons from marine sources tend to be of relatively short chain length (less than C_{20}), notably C_{15} and C_{17} alkanes and alkenes in algae (Han & Calvin 1969; Gelpi *et al.* 1970; Blumer *et al.* 1971; Lee & Loeblich 1971). All core sections show secondary maxima in their alkane distributions in this carbon range, but neither *n*-C_{15} nor *n*-C_{17} are particularly prominent (figure 4). Furthermore, no short chain alkenes were identified. The secondary mode at *n*-C_{22} in section 7 is not readily explicable; a similar distribution, with a mode at *n*-C_{20}, was found in an older (Pleistocene) east Mediterranean sapropel analysed by Comet (1982), who suggested it was most likely of 'marine origin'.

A possible source of these shorter-chain *n*-alkanes is bacteria although, again, interpretation is hampered by a lack of data, especially from recent analyses. Several species of bacteria have been reported to contain a range of *n*-alkanes (Albro & Dittmer 1970; Davis 1968; Han & Calvin 1969), while the results of Johnson & Calder (1973) suggest that sedimentary bacteria may be able to break down the original input of alkanes and then resynthesize a new suite of these compounds. Similarly, experiments by Cranwell (1976) showed that bacterial decomposition of an alga changed the *n*-alkane distribution originally present in the alga, producing an increased proportion of shorter-chain compounds and a lowered CPI. Many of the shorter-chain *n*-alkanes in core 10103 may well be the result of bacterial activity, although the amount of information currently available is too limited for definite conclusions to be drawn.

The isoprenoid alkanes pristane and phytane, (2,6,10,14-tetramethylpentadecane and 2,6,19,14-tetramethylhexadecane, respectively) were present, in similar concentrations, as minor components of the alkane fraction of all core sections. These components could have

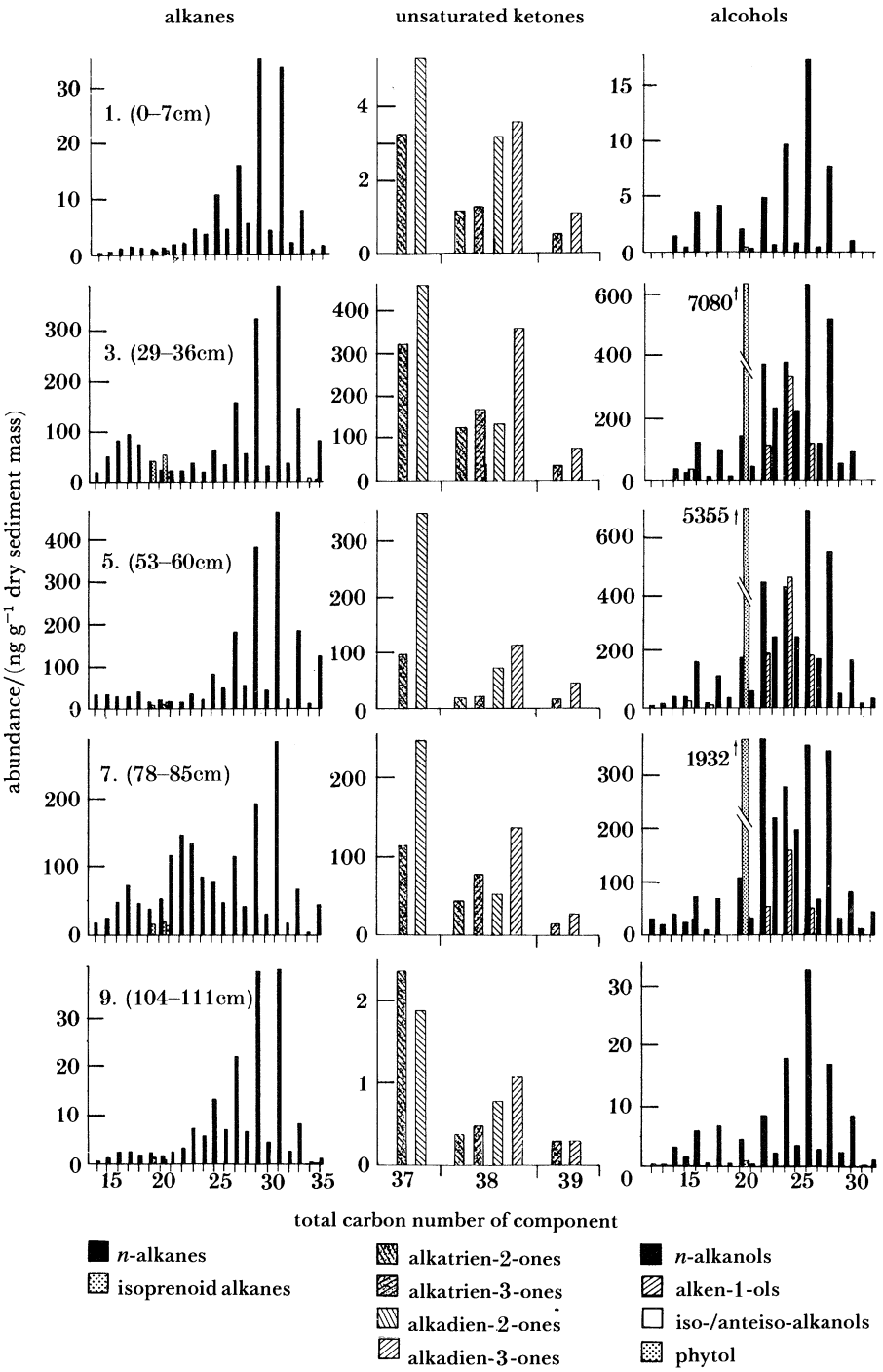

FIGURE 4. Distributions of (*a*) alkanes, (*b*) long-chain unsaturated ketones and (*c*) fatty alcohols in sections 1 (0–7 cm), 3 (29–36 cm), 5 (53–60 cm), 7 (78–85 cm) and 9 (104–111 cm) of core A.

originated from several sources. Direct inputs from organisms are possible; zooplankton are believed to contribute pristane (but not phytane) to some sediments (Blumer & Snyder 1965), and certain archaebacteria contain various isoprenoids, including phytane (Tornabene *et al.* 1979). Alternatively, early diagenetic reactions of phytol are reported to give rise to both phytane and pristane: the former via dehydration (to phytenes) and subsequent hydrogenation, the latter via oxidation to phytanic acid followed by decarboxylation, reviewed in Rowland

(1982) and Tissot & Welte (1978). Phytol was abundant in the sapropel, (although not in the over- and underlying sediments: figures 3 and 5), and may have given rise to at least a part of the pristane and phytane, along with other acyclic isoprenoids (Rowland 1982; Tissot & Welte 1978).

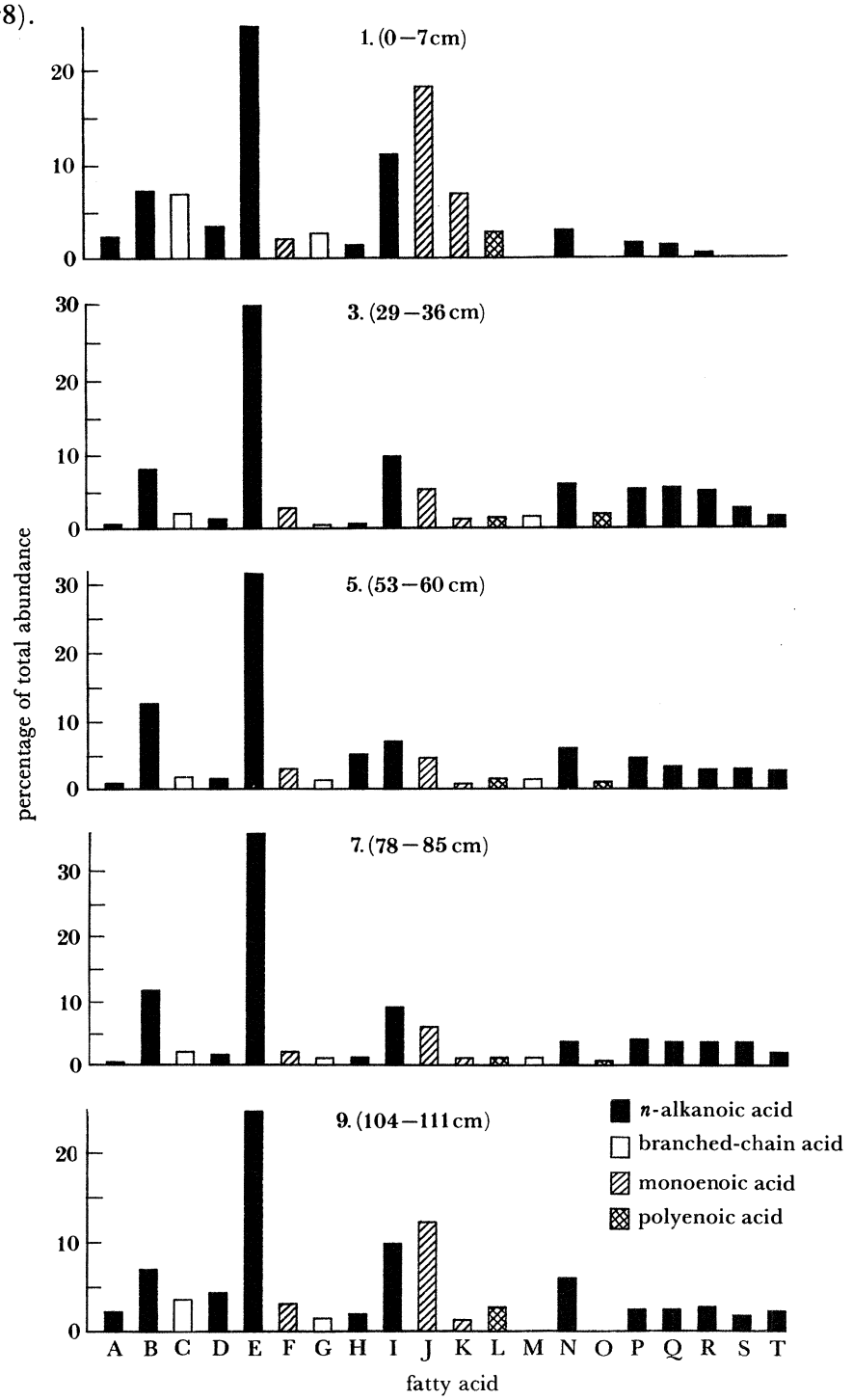

FIGURE 5. The major fatty acids of core A; distributions in sections 1 (0–7 cm), 3 (29–36 cm), 5 (53–60 cm), 7 (78–85 cm) and 9 (104–111 cm). The figure is intended to provide only a general comparison of the acid distributions down the core and the minor components (less than *ca.* 1% of total) have been omitted in the interests of clarity. Full data, including the identities of the acids represented by the letters A–T, are presented in table 3.

In addition, the hydrocarbon fractions did contain a small component comprising a complex mixture of unresolved branched and cyclic alkanes (estimated to account for *ca.* 10% of the total hydrocarbons) which may be indicative of minor contamination by some type of mineral oil (Farrington 1980). If so, part of the pristane and phytane could be associated with this; without more definitive evidence, however, for example from stereochemical determination of pristane configuration (Patience *et al.* 1978; Smith *et al.* 1983*c*), this remains an unknown quantity. No definite conclusions can therefore be drawn from the presence of pristane and phytane in this core.

As well as the alkanes shown in figure 5, the unusual, branched C_{20} alkane, 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane was identified in small amounts (15–20 ng g^{-1} dry sediment) in core sections 3, 5 and 7. This compound has been identified in a number of marine and freshwater sediments (Comet 1982; Rowland 1982; Yon 1981; Yon *et al.* 1982). Additionally, a series of C_{20} and C_{25} alkenes, believed to be pseudohomologues, have been found in lake, estuarine and marine sediments (Barrick *et al.* 1980; Yon 1981; Rowland 1982; Smith *et al.* 1983; Volkman *et al.* 1983). These hydrocarbons probably have a common biological source, which may be a direct input from some type of green alga; 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane, the corresponding monoene and a C_{25} diene (probably pseudohomologous) have recently been identified in the lipids of several species of *Enteromorpha*, a filamentous green macroalga (Rowland 1982). In view of the limited data currently available, there is no reason to suppose that these compounds are unique to this one genus. Their subsequent discovery in a planktonic genus, for example, might explain their occurrence in a variety of different sediments.

(iii) *Acyclic ketones*

Three types of acyclic ketone were identified in core A; a C_{18} isoprenoid alkan-2-one, a series of C_{21}–C_{33} alkan-2-ones, and several C_{37}–C_{39} alken-2-ones and alken-3-ones (figure 4).

The C_{18} isoprenoid ketone 6,10,14-trimethyl-pentadecan-2-one, was present in relatively low concentrations in all the sapropel sediment sections (25–30 ng g^{-1} dry sediment), but was not detected in the under- and overlying sediments. This compound is believed to derive from the phytyl side chain of chlorophyll (Ikan *et al.* 1973); phytol, its precursor, was an abundant component of the sapropel total alcohols (figure 4). Experiments have demonstrated the formation of this ketone, by bacterial action, from phytol and from decaying algae (reviewed in Rowland 1982). Its occurrence in sediments and water column particulates has generally been ascribed to phytol diagenesis (Ikan *et al.* 1973; Brassell *et al.* 1980; Comet 1982; Smith *et al.* 1983*c*; Volkman *et al.* 1983).

Section 3 of the core, alone, contained low concentrations of *n*-alkan-2-ones. These ranged from C_{21}–C_{33}, maximizing at *n*-C_{25} (17 ng g^{-1} dry sediment), with an overall odd–even chain length preference of 12.2. Such compounds have been found in a variety of different sediments (see, for example, Cranwell 1977; Simoneit *et al.* 1979; Brassell *et al.* 1980; Volkman *et al.* 1981*b*, 1983), including Pleistocene east Mediterranean sapropels (Comet 1982). The chain length distribution has generally been similar in these reports, as has the high odd–even predominance. Two diagenetic routes for their formation from higher plant lipids have been suggested; (i) oxidation of long-chain alkanes (Brassell *et al.* 1980), (ii) β-oxidation, followed by decarboxylation, of long-chain fatty acids (Arpino *et al.* 1970). However, consideration of the alkane (figure 4) and fatty acid (figure 5) distributions for this sapropel indicates that

neither route would produce the observed pattern of alkan-2-ones, unless the reactions were highly specific to particular chain lengths. A similar conclusion was reached by Volkman *et al.* (1981*b*, 1983) for sediments from an Australian intertidal zone and the Peru Continental Shelf. A direct input for these compounds should therefore be considered. Since alkan-2-ones have been identified in soil (Morrison & Bick 1966), in a higher plant (*Brassica napus*; Richter & Krain 1981) and in sediment from a lake which receives a large terrigenous input (Cranwell 1977), it is thought most likely that they are associated with the terrigenous sedimentary contribution.

In contrast, the C_{37}–C_{39} alken-2-ones and alken-3-ones are present in all sediment sections (figure 4), and are undoubtedly of marine origin. These unusual, long-chain lipids are biosynthesized by a few species of planktonic Haptophycean algae (Marlowe *et al.* 1983, 1984), which represent their only known biological sources. The most likely known source of these is a coccolithophorid alga, *Emiliania huxleyi* (Volkman *et al.* 1980*b*, 1980*c*), which is widely distributed in the World's oceans (Okada & McIntyre 1977); the ketones have accordingly been found in marine sediments throughout the world (see, for example, Brassell *et al.* 1980; Comet 1982; De Leeuw *et al.* 1980; Marlowe *et al.* 1983; Smith *et al.* 1983*c*). Coccoliths, from coccolithophorid algae such as *E. huxleyi*, were common in the sapropel, which implies that these algae did form a significant input, and most likely they contributed the long-chain ketones. Information on the known occurrences of ketone-containing Haptophyceae suggests that *E. huxleyi* is probably the major source of these compounds in recent marine sediments (Marlowe *et al.* 1983), although many other such algae remain to be studied.

(iv) *Alcohols*

All core sections contained a distribution of *n*-alkan-1-ols, ranging from C_{12}–C_{32}, dominated by components greater than C_{20} with a high even–odd predominance (figure 4).

Some higher plants produce wax esters, and these typically contain mostly longer chain (over C_{20} alkanols (Cranwell & Volkman 1981; Eglinton 1967; Tulloch & Hoffman 1979; Tulloch 1984), with a distribution similar to those in this core. There is thus little doubt that the alkanols in core A derive mainly from terrigenous higher plant debris (Simoneit 1978). Originally, they were probably mostly associated with fatty acids as wax esters; indeed, small amounts of wax esters were identified in the unsaponified lipids of section 5. These ranged from C_{30}–C_{48}, maximizing at 38:0 (34 ng g^{-1} dry sediment) and 44:0 (33 ng g^{-1} dry sediment), and were exclusively straight-chain, saturated esters. The mass spectral data for the wax esters indicated their component acids to be predominantly C_{16}–C_{20} and their component alcohols to be predominantly C_{20}–C_{28}. Such esters are common constituents of the leaf waxes of higher plants (Cranwell & Volkman 1981; Eglinton & Hamilton 1967; Tulloch 1984; Tulloch & Hoffman 1979), and inputs of higher plant debris would very likely contribute both wax esters and their component long-chain acids and alcohols to sediments.

The sapropel (but not the non-sapropelic sediment) also contained substantial quantities of monounsaturated *n*-alcohols (22:1, 24:1 and 26:1) (figure 4). The origin of these is not clear. Alkenols have not, so far, been reported as significant components of plant waxes. Some marine zooplankton contain abundant wax esters, most analyses of which have identified 20:1 and 22:1 as the major alcohol moiety (Morris & Culkin 1976; Sargent 1976, 1981). However, 24:1 and 26:1 occur only as trace components in zooplankton (Sargent 1976, 1981), while they are the major unsaturated *n*-alcohols in the sapropel. Various other marine organisms, such

as fish and some bacteria, also contain alcohols (mainly in the form of wax esters), but not, apparently, significant amounts of any with chain length greater than C_{20} (Sargent 1976, 1981; Bryn *et al.* 1977). Thus, current data do not suggest a likely source of the *n*-alkenols.

The alcohol distributions of the non-sapropelic sediments differed from those of the sapropel in several ways; (i) a lower proportion of 22:0 alcohol, (ii) a lower proportion of C_{21}–C_{29} odd-chain alkanols, and (iii) a much lower proportion of phytol. It is difficult to attribute these differences purely to increased degradation in the oxic over- and underlying sediments. Known degradation products of phytol (e.g. phytanic acid, 6,10,14-trimethylpentadecan-2-one) (Ikan *et al.* 1973; Tissot & Welte 1978) were not detected in the non-sapropelic sediments (but were present, in small quantities, in the sapropel), while the degradation of *n*-alcohols would have needed to be quite specific, with regard to chain length, to produce the differences in distribution. It is therefore proposed that the differences in alcohol distributions are mainly due to an input difference; possibly the non-sapropelic sediment alcohols represent a predominantly higher plant wax input (since they resemble quite closely reported compositions for several plant waxes: Eglinton & Hamilton 1967), while the sapropel alcohols, especially the alkenols, include additional contributions from other sources. The abundance of phytol in the sapropel suggests that this additional input was rich in chlorophyll (probably the major source of sedimentary phytol) and hence may have derived from marine productivity.

Two other types of alcohol were present in the sediment: a series of C_{28}–C_{32} 1,13-,1,14- and 1,15-diols, and a similar series of 15-keto-l-ols (table 2). These data, and a detailed discussion of them, have been presented previously (Smith *et al.* 1983*d*) and so will not be considered in detail here. No source organisms for either the diols or the keto-ols are yet known. When this information is available, it may provide useful indications of the type of water column which existed during sapropel formation.

TABLE 2. ALKA-DIOLS AND KETO-OLS IDENTIFIED IN CORE 10103A

(Previously published in Smith *et al.* (1983*d*).)

	component/(ng g^{-1} sediment (dry mass))				
	section	section	section	section	section
Alka-diol/keto-ol†	1	3	5	7	9
		(*a*) *Alka-diols*			
28:0 1,13-diol	—	43	160	35	—
28:0 1,14-diol	—	15	57	12	—
28:0 1,15-diol	—	7	35	8	—
29:0 1,13-diol	—	3	16	tr	—
29:0 1,14-diol	—	2	7	tr	—
29:0 1,15-diol	—	6	50	5	—
30:0 1,15-diol	1	2142	5756	1050	3
30:1 1,14-diol	—	21	118	—	—
31:0 1,15-diol	—	84	184	32	—
32:0 1,15-diol	—	80	166	28	—
		(*b*) *Keto-ols*			
28:0 keto-ol	—	tr	tr	tr	—
29:0 15-keto-1-ol	—	27	69	14	—
30:0 15-keto-1-ol	tr‡	1162	2135	399	1
31:0 15-keto-1-ol	—	35	74	10	—
32:0 15-keto-1-ol	—	230	285	40	—
32:1 15-keto-1-ol	—	99	103	15	—

† Structures are designated as $x:y$, where x = carbon number and y = number of double bonds.
‡ tr; Trace component (less than 1 ng g^{-1}); —, not detected (less than *ca.* 0.5 ng g^{-1}).

(v) *Fatty acids*

These constituted the most abundant class of lipid in all samples (table 3, figure 5). Carbon number ranged from C_{12} to C_{30}, with hexadecanoic acid (16:0) as the major acid in all core sections.

The fatty acid distribution was very similar throughout the sapropel (core sections 3, 5 and 7), being dominated by saturated, straight-chain components of even carbon number (table 3, figure 5). Branched-chain acids, (mainly iso- and anteiso-15:0, -17:0 and phytanic acid), constituted only *ca.* 5% of the total fatty acids. Significant quantities of monounsaturated acids (principally 16:1 and 18:1) were present, with lower levels of polyunsaturated acids. Among the latter, 16:2, 18:2 and 18:3 were readily identified from the mass spectra of their methyl esters, but the other polyunsaturated acids did not give unambiguous spectra and their assignments remain tentative, being based on GC retention times.

On the basis of chain-length distribution, the sedimentary fatty acids, being predominantly C_{14}–C_{18} compounds, appear to be dominated by marine inputs. The acids of chain length greater than C_{24} probably represent a mainly terrigenous contribution (Simoneit 1978; Simoneit *et al.* 1979; Brassell *et al.* 1980), since such compounds are components of many higher plant leaf waxes (Eglinton & Hamilton 1967; Tulloch & Hoffman 1979; Tulloch 1984), and marine organisms generally contain only trace amounts of fatty acids longer than C_{22} (Ackman *et al.* 1968; Morris & Culkin 1976). In contrast, whereas higher plants usually possess little C_{14} or unsaturated fatty acid, many marine organisms contain abundant C_{14}–C_{22} acids with a large unsaturated component. In particular, a considerable number of phytoplankton species have been analysed (see, for example, Ackman *et al.* 1968; Chuecas & Reily 1968; De Mort *et al.* 1972; Kates & Volcani 1966; Moreno *et al.* 1979*a*; Morris & Culkin 1976; Orcutt & Patterson 1975; Pugh 1971; Volkman *et al.* 1980*a*, 1981*a*). Such analyses have been used to help assess inputs of fatty acids to a number of sediments (Boon *et al.* 1975; Volkman & Johns 1977; Volkman *et al.* 1980*e*; Smith *et al.* 1983*b*, *c*). A notable difference between the sedimentary fatty acids and those reported for phytoplankton is the relative lack of polyunsaturated components in the sediment, compounds which are often abundant in phytoplankton. Indeed, polyunsaturated acids have rarely been reported in sediments, a fact which has been attributed to their lability, and hence rapid degradation, relative to monounsaturates and saturates (Farrington & Quinn 1971; Boon *et al.* 1975; Smith *et al.* 1983*b*, *c*). It has been demonstrated that faecal pellets released by zooplankton, after feeding on phytoplanktonic algae, show a selective depletion of polyunsaturated fatty acids compared to the algae (Volkman *et al.* 1980*d*; Prahl *et al.* 1984); this indicates that reworking of primary production by pelagic animals may significantly influence the fatty acid composition of underlying sediments and could, at least in part, account for the relatively low levels of polyunsaturated acids.

Allowing for the likely loss of polyunsaturated components, some useful comparisons may still be drawn between the fatty acids of a sediment and those reported for the main classes phytoplankton (discussed in Smith *et al.* 1983*b*). For the sapropel, the following points emerge: (i) diatoms (Bacillariophyceae) are characteristically rich in 16:1 but contain only low levels of C_{18} acids; in the sapropel 16:1 is a relatively minor component while C_{18} acids are quite abundant; (ii) in the Haptophyceae (which includes the coccolithophorids), as well as in the sapropel, 18:1 is generally more abundant than 16:1; (iii) in 'green algae' (Chlorophyceae),

Table 3. Fatty acids identified in core 10103A

figure 5†	fatty acid	component/(ng g^{-1} sediment (dry mass)) section 1	section 3	section 5	section 7	section 9
	(a) acyclic acids					
—	i-12 : 0	tr	38.1	tr	—	tr
A	12 : 0	5.4	100.1	76.7	22.6	8.7
—	i-13 : 0	tr	42.6	tr	tr	tr
—	a-13 : 0	tr	24.0	tr	tr	tr
—	13 : 0	tr	24.0	15.3	8.1	tr
—	i-14 : 0	tr	30.0	25.6	12.9	—
B	14 : 0	17.0	1360.3	1227.7	588.5	29.1
—	14 : 1	—	24.0	23.0	15.8	—
C	i-15 : 0	7.5	147.3	80.5	38.5	4.9
	a-15 : 0	8.6	187.0	90.8	61.1	10.2
D	15 : 0	7.9	219.1	140.6	81.5	17.9
—	isop-16 : 0	3.6	43.2	44.7	20.4	1.5
—	i-16 : 0	tr	46.9	27.8	17.2	tr
E	16 : 0	58.3	5116.2	3027.0	1832.9	102.9
F	16 : 1 Δ^{9}	4.6	446.4	281.3	102.6	13.1
—	16 : 1 Δ^{11}?	tr	39.4	24.5	9.5	tr
—	16 : 1 Δ^{13}?	tr	70.4	67.2	16.3	tr
—	16 : 2	—	11.5	6.8	tr	—
—	16 : 3?	—	tr	tr	—	—
—	16 : 4?	—	19.2	30.5	—	—
—	br-17 : 0	—	14.8	—	—	—
G	i-17 : 0	2.2	27.7	95.9	13.6	1.9
	a-17 : 0	4.0	38.8	24.3	36.2	4.5
H	17 : 0	3.1	95.4	48.6	54.3	7.5
—	17 : 1	—	tr	—	—	—
—	i-18 : 0	—	77.9	31.8	21.4	—
I	18 : 0	26.1	1631.1	682.6	457.2	41.4
J	18 : 1 Δ^{9}	43.0	879.8	448.9	303.3	51.2
K	18 : 1 Δ^{11}	16.1	197.6	73.9	45.3	5.0
—	18 : 1 Δ^{13}	1.5	37.2	14.1	10.1	2.0
L	18 : 2	6.5	141.4	92.7	46.2	11.3
—	18 : 3	—	11.0	28.8	4.1	—
—	18 : 4?	—	71.1	16.6	4.5	—
—	i-19 : 0	tr	tr	tr	tr	tr
—	a-19 : 0	tr	tr	tr	tr	tr
—	19 : 0	tr	130.7	74.2	18.6	4.8
M	isop-20 : 0	—	251.4	130.6	61.4	—
N	20 : 0	6.8	991.9	575.3	181.1	25.1
—	20 : 1	—	20.7	14.7	5.9	—
—	20 : 2	—	20.7	12.7	—	—
—	20 : 2	—	75.8	10.7	—	—
O	20 : 5?	—	227.9	89.9	27.2	—
—	21 : 0	tr	210.6	97.1	21.7	5.7
P	22 : 0	3.6	866.5	434.7	196.9	9.6
—	22 : 1	—	60.2	52.1	10.0	—
—	22 : 6?	—	45.6	81.9	22.6	—
—	23 : 0	tr	117.2	44.7	24.9	2.2
Q	24 : 0	3.2	903.7	319.6	176.5	9.7
—	24 : 1	—	tr	tr	—	—
—	25 : 0	tr	101.9	46.0	25.8	2.7
R	26 : 0	1.1	838.0	268.5	178.8	10.9
—	27 : 0	tr	88.3	15.3	27.2	1.9
S	28 : 0	tr	440.0	281.3	176.5	6.7
—	29 : 0	tr	38.1	51.1	25.3	1.4
T	30 : 0	tr	251.4	260.5	99.6	8.6

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TABLE 3 (*cont.*)

figure 5†	fatty acid	component/(ng g^{-1} sediment (dry mass)) section 1	section 3	section 5	section 7	section 9
	(*b*) *cyclic acids*					
—	cholan-24-oic acid	—	49.3	—	—	—
—	C_{25} steroidal acid	—	15.4	—	—	—
—	C_{31} ββ-homo-hopanoic acid	tr	96.9	25.0	37.6	tr
—	C_{32} ββ-bis-homo-hopanoic acid	1.7	692.2	175.6	162.9	3.4
	(*c*) *others*					
—	36 : 2 methyl ester	—	11.4	9.2	7.3	—
—	36 : 2 ethyl ester	—	24.8	19.0	13.9	—

Symbols: i, iso-; a, anteiso-; isop, isoprenoid; br, branched acid of unknown structure; tr, trace component (less than 1 ng g^{-1}); —, not detected (less than *ca.* 0.5 ng g^{-1}) .

† The letters (A–T) indicate those fatty acids whose relative abundance is illustrated in figure 5.

16 : 1 and 18 : 1 are of variable abundance, but the ratio of 14 : 0/16 : 0 is generally considerably smaller than in the sapropel; (iv) the fatty acids of dinoflagellates (Dinophyceae) contain variable amounts of C_{18} acids but, like those of the sapropel, are relatively low in 16 : 1; and (v) all the above classes of algae tend to contain 16 : 0 as a major acid, which was the predominant sedimentary acid.

Thus, from considering the fatty acid compositions reported for the four major classes of marine phytoplankton, it appears that members of the Dinophyceae and Haptophyceae were more important as constituents of the phytoplankton, during sapropel formation, than were Bacillariophyceae or Chlorophyceae. This conclusion is supported by other lipid data (discussed elsewhere), while the relative unimportance of diatoms is also suggested by smear slide studies (discussed above) and mineralogical analysis (Sutherland *et al.* 1984).

Such conclusions represent an oversimplification of the situation. The usefulness of comparisons between the sediment data and data from phytoplankton analyses is restricted by the limited number of phytoplankton species which have been examined using modern analytical techniques, and the fact that nearly all analyses have used single, cultured species rather than natural populations from the field (see discussions in Ballantine *et al.* 1979; Smith *et al.* 1983*b*; Morris 1984). There is evidence that both the growth stage of the organism and the conditions under which it was cultured may influence its fatty acid composition (Pugh 1971; Wright *et al.* 1980), which suggests that cultured algae may not necessarily be good models for natural populations in terms of assessing their lipid contributions to sediments. In addition, contributions from pelagic organisms, either directly, or indirectly via faecal pellets, and microbial reworking will undoubtedly have influenced the sedimentary lipid compositions. Limitations of present data make it impossible to assess such factors quantitatively; for example, mineralogical and microscopic analyses of the sediments studied here indicated inputs of foraminifera and pteropods, but an appreciation of the significance of these organisms as contributors of lipids to sediments must wait until detailed data on their lipid composition are available. Similarly, more information is needed on the changes in lipid composition effected, during assimilation and excretion of primary production, by higher tropic levels in the water column.

The non-sapropelic sediments (core sections 1 and 9) contained lower levels of extractable fatty acids than the sapropel; there were also qualitative differences between the compound

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distributions (table 3, figure 5). Compared to the sapropel, the under- and overlying sediments contained higher proportions of unsaturated C_{18} acids and branched acids (especially iso- and anteiso-15:0) but, apart from the 18:2, no polyunsaturated acids were detected. No definite explanation for these differences can be given, but it is proposed that they are due to a combination of factors: differences in input, possibly associated with a higher input from marine sources to the sapropel (as discussed elsewhere), and the effects of an oxic, as opposed to anoxic, sedimentary environment. Unlike the anoxic sapropel, the under- and overlying sediments would have supported metazoan benthos which affect the lipid composition by scavenging organic detritus and producing their own lipids. Furthermore, the bacterial communities of the oxic and anoxic sediments would certainly have differed substantially. Sulphate-reducing bacterial activity is indicated by the presence of pyrite in the sapropel (Sutherland *et al.* 1984), while the iso- and anteiso-, odd-chain-length acids, and possibly the vaccenic acid (18:1 Δ^{11}, probably reflect a contribution from bacterial lipids (Boon *et al.* 1975; Gillan *et al.* 1983; Leo & Parker 1965; Parkes & Taylor 1983; Perry *et al.* 1979; Volkman & Johns 1977; Volkman *et al.* 1980*e*). Bacterial communities may be characterized by different fatty acid compositions (Parkes & Taylor 1983; Gillan *et al.* 1983), but data are insufficient to suggest how this might be reflected in this core.

Small quantities of cyclic acids were identified in core A (table 3). The origin of the steroidal acids in section 3 is not clear; such compounds have been found in other marine sediments and may be formed by microbial degradation of sterols (Mackenzie *et al.* 1982), but their source here is uncertain.

The hopanoid acids, present in all core sections are, like various other sedimentary hopanoids (Van Dorsselaer *et al.* 1974), generally believed to derive from the polyhydroxylated hopanes found in a wide variety of bacteria (Rohmer & Ourisson 1976; Ourisson *et al.* 1979). Oxidative cleavage of the tetrahydroxylated side-chain of bacteriohopanetetrol, (a widespread bacterial hopanoid: Ourisson *et al.* 1979), could generate 17β(H), 21β(H)-bishomohopanoic acid; (Ourisson *et al.* 1979; Rohmer & Ourisson 1976). This compound was the major cyclic acid in core A (table 3) and has been reported as the dominant hopanoid acid of several other sediments (see, for example, Brassell 1980; Rohmer & Ourisson 1976; Van Dorsselaer *et al.* 1974). The minor, C_{31}, hopanoid acid in core A, 17β(H), 21β(H)-homohopanoic acid, has an analogous structure to the C_{32} compound discussed above, with a C_4 side chain. It could arise by oxidative decarboxylation of the C_{32} acid, or by oxidative cleavage of a different polyhydroxyhopane precursor (Brassell 1980; Rohmer & Ourisson 1976), possibly a C_{35} pentahydroxyhopane.

The 36:2 fatty acid methyl and ethyl esters present in the sapropel (table 3) provide further evidence of an input from Haptophycean algae. Such compounds were first identified in *Emiliania huxleyi* (Volkman *et al.* 1981*a*) and have subsequently been found in several other species of Haptophyceae (Marlowe *et al.* 1983, 1984). The positions of the double bonds have not been elucidated, but it seems probable that they correspond to those of the diunsaturated long-chain ketones, also present in the algae (de Leeuw *et al.* 1980), which would make them $\Delta^{14,21}$ fatty acid esters; the ketones and esters may well be biosynthetically related (Marlowe *et al.* 1984; Volkman *et al.* 1981*a*).

(vi) *Sterols*

Sterols were abundant in the sapropel; their structures ranged from C_{26} to C_{31}, encompassing Δ^5,Δ^7,$\Delta^{8(14)}$-stenols and nuclear-saturated stanols, various side-chains with Δ^{22}, Δ^{24}, $\Delta^{24(28)}$

and fully saturated structures, and included both 4-methyl and 4-desmethyl nuclei (table 4, figure 6).

The wide range of sterols is typical of a marine system (Boutry *et al.* 1979; Djerassi 1981; Morris & Culkin 1977) and most of the major sterols in the sapropel, especially cholesta-5,22-dien-3β-ol, cholest-5-en-3β-ol, 24-methylcholesta-5,22-dien-3β-ol, 24-methylcholesta-5,24(28)-dien-3β-ol and 24-ethylcholesta-5,22-dien-3β-ol are common constituents of marine phytoplankton (see, for example, Alam *et al.* 1978, 1979*a*, *b*, 1981; Ballantine *et al.* 1979*a*; Kates *et al.* 1978; Kokke *et al.* 1981*a*, *b*, 1982; Lin *et al.* 1982; Marlowe *et al.* 1984; Orcutt & Patterson 1975; Paoletti *et al.* 1976; Rubinstein & Goad 1974; Volkman *et al.* 1980*a*, 1981*a*; Withers *et al.* 1978, 1979*a*, *b*). Several discussions relating sedimentary sterol composition to biological input have appeared in the literature (De Leeuw *et al.* 1983; Lee *et al.* 1980; Robinson *et al.* 1984; Smith *et al.* 1982, 1983*a*; Wardroper *et al.* 1978). Similar considerations here suggest that Haptophycean algae (e.g. coccolithophorids) and dinoflagellates contributed major inputs of sterols to the sapropel, as discussed below.

The major sterol of the sapropel was 4α,23,24-trimethyl-5α-cholest-22-en-3β-ol (dinosterol; table 4 and figure 6). This was accompanied by a range of other, C_{28}–C_{30}, 4-methyl-sterols. The most important biological sources of these compounds are generally believed to be dinoflagellates (Mackenzie *et al.* 1982; Brassell & Eglinton 1983); many of these 4-methyl-sterols have been identified in various dinoflagellate species (Alam *et al.* 1978, 1979*a*, *b*, 1981; Kokke *et al.* 1981*a*, *b*, 1982; Robinson *et al.* 1984; Steudler *et al.* 1977; Shimizu *et al.* 1976; Withers *et al.* 1978, 1979*a*, *b*; Zielinski *et al.* 1983). Other organisms which have been reported to contain 4-methyl-sterols, such as bacteria (Bird *et al.* 1971; Bouvier *et al.* 1976) and yeasts (Barton *et al.* 1970), are not regarded as important sources; the range of these sterols reported in such organisms is much more limited than that in the sapropel, and does not include the major sedimentary sterols (e.g. dinosterol). Currently, dinoflagellates appear to be the only group of organisms which could have contributed the bulk of the sedimentary 4-methyl-sterols (Brassell & Eglinton 1983). Although no remains of dinoflagellates (e.g. cysts) were observed in the sediment, it appears that many dinoflagellate species do not necessarily leave visible remains in sediments (Dale 1976).

Dinoflagellates could also have contributed some of the sedimentary 4-desmethyl-sterols, including some which are not recognized as being widespread in organisms. These include sterols with a 23,24-dimethyl side chain (Kokke *et al.* 1982). Dinoflagellates may also contribute significant amounts of 5α(H)-stanols to sediments (Kokke *et al.* 1982; Robinson *et al.* 1984) and could have been the major source of these compounds in core A.

Stanols can be formed by bacterial reduction of sterols, which is probably an important process in some sediments (Gagosian *et al.* 1980; Smith *et al.* 1982) but, in the present case, the evidence suggests that such production has only been minor. There is no tendency for the proportion of stanols to increase with depth in the core, as might be expected if progressive conversion of Δ^5-sterols to stanols was occurring, and which has been observed in some cores (Gaskell & Eglinton 1976; Nishimura & Koyama 1977; Smith *et al.* 1982). The compounds (stenones and stanones) believed to be intermediate in the microbiological stenol–stanol conversion (Gagosian *et al.* 1980), were present in only very low abundance (table 5, and discussed below) and their distributions did not correspond well with the sterols. The small quantities of C_{27}, C_{28} and C_{29} 5β(H)-stanols (table 4) probably are the result of microbial transformation of Δ^5-stenols. Eukaryotic sterol biosynthetic pathways produce exclusively the 5α(H)-epimer (Goad 1978; Morris & Culkin 1977), but both 5α(H)- and 5β(H)-stanols have

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Table 4. Sterols identified in core 10103A

figure 6†	sterol‡	structure§	component/(ng g^{-1} sediment (dry mass)) section 1	section 3	section 5	section 7	section 9
	(a) 4-desmethyl-sterols						
A	24-nor-cholesta-5,22*E*-dien-3β-ol	1a	—	131	131	60	—
B	24-nor-5α-cholest-22*E*-en-3β-ol	2a	—	92	100	35	—
—	24-nor-cholest-5-en-3β-ol?	1b	—	6	6	—	—
—	24-nor-5α-cholestan-3β-ol	2b	—	20	19	tr	—
C	27-nor-24-methylcholesta-5,22*E*-dien-3β-ol	1c	—	300	311	125	—
D	27-nor-24-methyl-5α-cholest-22*E*-en-3β-ol	2c	—	122	114	44	—
E	cholesta-5,22*E*-dien-3β-ol	1e	0.2	582	609	273	tr
F	5α-cholest-22*E*-en-3β-ol	2e	tr	202	172	65	0.3
G	cholest-5-en-3β-ol	1f	2.4	811	876	441	4.0
H	5α-cholestan-3β-ol	2f	0.2	270	292	116	0.3
—	27-nor-24-methyl-5α-cholestan-3β-ol	2d	—	10	12	14	—
—	cholesta-5,24-dien-3β-ol	1g	—	52	62	26	—
—	cholest-7-en-3β-ol	5f	—	12	—	32	—
—	5β-cholestan-3β-ol	3f	—	10	20	27	—
—	5β-cholestan-3α-ol	4f	—	15	30	37	—
I	24-methylcholesta-5,22-dien-3β-ol	1h	0.1	895	908	390	—
J	24-methyl-5α-cholest-22-en-3β-ol	2h	tr	233	238	95	—
—	C_{28} steradienol	?	—	30	—	—	—
—	C_{28} Δ^5-stenol	?	—	9	tr	tr	—
K	24-methylcholesta-5,24(28)-dien-3β-ol	1i	—	566	616	265	—
L	24-methyl-5α-cholest-24(28)-en-3β-ol	2i	—	79	113	19	—
M	24-methylcholest-5-en-3β-ol	1j	0.2	214	210	122	—
N	24-methyl-5α-cholestan-3β-ol	2j	—	92	96	37	—
—	24-methylcholest-7-en-3β-ol	5j	—	9	tr	tr	—
—	24-methyl-5β-cholestan-3β-ol	3j	—	10	10	tr	—
—	24-methyl-5β-cholestan-3α-ol	4j	—	10	10	tr	—
O	23,24-dimethylcholesta-5,22-dien-3β-ol	1k	—	140	139	44	—
P	23,24-dimethyl-5α-cholest-22-en-3β-ol	2k	—	201	145	23	—
Q	24-ethylcholesta-5,22-dien-3β-ol	1m	—	340	437	182	—
R	24-ethyl-5α-cholest-22-en-3β-ol	2m	—	119	122	37	—
—	23,24-dimethylcholest-5-en-3β-ol	1l	–	32	41	19	—
—	23,24-dimethyl-5α-cholestan-3β-ol	2l	—	14	14	32	—
S	24-ethylcholest-5-en-3β-ol	1p	1.3	915	1127	404	1.9
T	24-ethyl-5α-cholestan-3β-ol	2p	0.6	369	388	107	0.5
—	24-ethycholesta-5,24(28)*E*-dien-3β-ol	1n	—	19	19	12	—
—	24-ethyl-5α-cholest-24(28)*E*-dien-3β-ol	2n	—	17	21	9	—
—	24-ethylcholesta-5,24(28)*Z*-dien-3β-ol	1o	tr	76	96	65	—
—	24-ethyl-5α-cholest-24(28)*Z*-dien-3β-ol	2o	—	36	55	25	—
—	C_{29} Δ^7-stenol	51/p	—	46	61	tr	—
—	C_{29} 5β(H),3β(OH)-stanol	31/p	—	20	30	17	—
—	C_{29} 5β(H),3α(OH)-stanol	41/p	—	25	40	17	—
—	C_{30} Δ^{22}-stanol	?	—	45	47	28	—
—	24-propylcholesta-5,24(28)*E*-dien-3β-ol	1q	—	71	62	25	—
—	24-propyl-5α-cholest-24(28)*E*-en-3β-ol	2q	—	43	59	17	—
—	24-propylcholesta-5,24(28)*Z*-dien-3β-ol	1r	—	92	107	11	—
—	24-propyl-5α-cholest-24(28)*Z*-en-3β-ol	2r	—	26	31	tr	—
—	22(23)-methylene-23,24-dimethyl-cholest-5-en-3β-ol	1u	—	14	tr	tr	—
—	22(23)-methylene-23,24-dimethyl-5α-cholestan-3β-2ol	2u	—	12	tr	tr	—
	(b) 4-methyl-sterols						
—	C_{28} Δ^{22}-4-methyl-stanol?	?	—	12	11	10	—
—	C_{28} Δ^{22}-4-methyl-stanol?	?	—	10	9	10	—
—	4α-methyl-5α-cholestan-3β-ol	7f	—	—	—	47	—
—	C_{29} Δ^{22}-4-methyl-stanol?	?	—	69	59	20	—
—	C_{29} Δ^{22}-4-methyl-stanol?	?	—	133	115	51	—
—	4α,24-dimethylcholest-24(28)-en-3β-ol?	4i	—	—	—	41	—
U	4α,24-dimethyl-5α-cholestan-3β-ol	4j	0.1	655	587	380	—
—	4α,23,24-trimethylcholesta-5,22-dien-3β-ol	6k	—	—	—	54	—

TABLE 4 (*cont.*)

figure 6†	sterol‡	structure§	component/(ng g^{-1} sediment (dry mass)) section 1	section 3	section 5	section 7	section 9
V	4α,23,24-trimethyl-5α-cholest-22-en-3β-ol	7k	4.2	3567	3034	1094	1.8
—	4α-methyl-24-ethyl-5α-cholest-22-en-3β-01	7m	—	39	44	20	—
—	4α,23,24-trimethyl-5α-cholest-8(14)-en-3β-ol?	81?	—	49	15	—	—
—	4α-methyl-24-ethyl-5α-cholest-8(14)-en-3β-ol?	8p?	—	65	20	—	—
W	4α,23(*S*),24(*R*)-trimethyl-5α-cholestan-3β-ol	71	—	140	100	68	—
X	4α,23(*R*),24(*R*)-trimethyl-5α-cholestan-3β-ol	71	—	501	187	122	0.6
—	22(23)-methylene-4α,24-dimethyl-5α-cholestan-3β-ol	7t	—	—	—	13	—
—	22(23)-methylene-4α,23,24-trimethyl-5α-cholestan-3β-ol	7u	—	tr	98	71	—

Symbols: tr, Trace component (less than 0.1 ng g^{-1} for sections 1 and 9, less than 1.0 ng g^{-1} for sections 3, 5 and 7); —, Not detected (less than *ca.* 0.1 ng g^{-1}).

† The letters (A–X) indicate those sterols whose relative abundance is illustrated in figure 6.

‡ Identifications based on GC retention times and mass spectra of the trimethylsilyl ethers, as discussed previously (Smith *et al.* 1982, 1983*a*).

§ The structures of the sterols are illustrated in figure 7; numbers refer to nuclei and letters to side-chains.

been formed in experiments in which bacteria have metabolized radiolabelled Δ^5-sterol substrates (Bjorkhem & Gustaffson 1971; Eyssen *et al.* 1973; Gaskell & Eglinton 1975; Parmentier & Eyssen 1974; Taylor *et al.* 1981). However, the sedimentary 5β(H)-stanols may have been formed in the guts of pelagic zooplankton and transported to the sediments in faecal material, or been formed by bacterial activity on sinking particles, rather than be the result of postdepositional diagenesis. Overall, the evidence suggests that diagenetic transformation of sterols has only been a minor process, and the majority of the 5α(H)-stanols have probably resulted from direct input, most likely from dinoflagellates.

Diatoms have been the most thoroughly investigated group of phytoplankton as regards lipid composition; some species have 24-methylcholesta-5,22-dien-3βol (quite abundant in the sapropel) as their major sterol, which has thus been regarded as a 'diatom marker' (see, for example, Lee *et al.* 1980). Diatoms however, do not appear to have formed a major sedimentary input to core A (see earlier discussion), unlike some other sapropel-containing cores (Thunell & Williams 1982). A number of species of Haptophycean algae have also been found to produce 24-methylcholesta-5,22-dien-3β-ol as their principal sterol (Volkman *et al.* 1981*a*; Lin *et al.* 1982; Marlowe *et al.* 1984). Since the presence of coccoliths and long-chain ketones in the sediment indicates that such algae have formed a significant input, then they are a more likely source of this sterol here. The Haptophyceae so far examined also contained, between them, cholest-5-en-3β-ol, 23,24-dimethylcholesta-5,22-dien-3β-ol, 24-ethylcholesta-5,22-dien-3β-ol and 24-ethylcholest-5-en-3β-ol, all of which were significant components of the sapropel sterols, plus small amounts of several of the minor sedimentary sterols. Few species of this class have yet been analysed, and most of these have contained very simple sterol distributions, with two or three components usually accounting for over 90% of the total sterols (reviewed in Marlowe *et al.* 1984), which is unlike the complex sedimentary distribution. This complexity no doubt

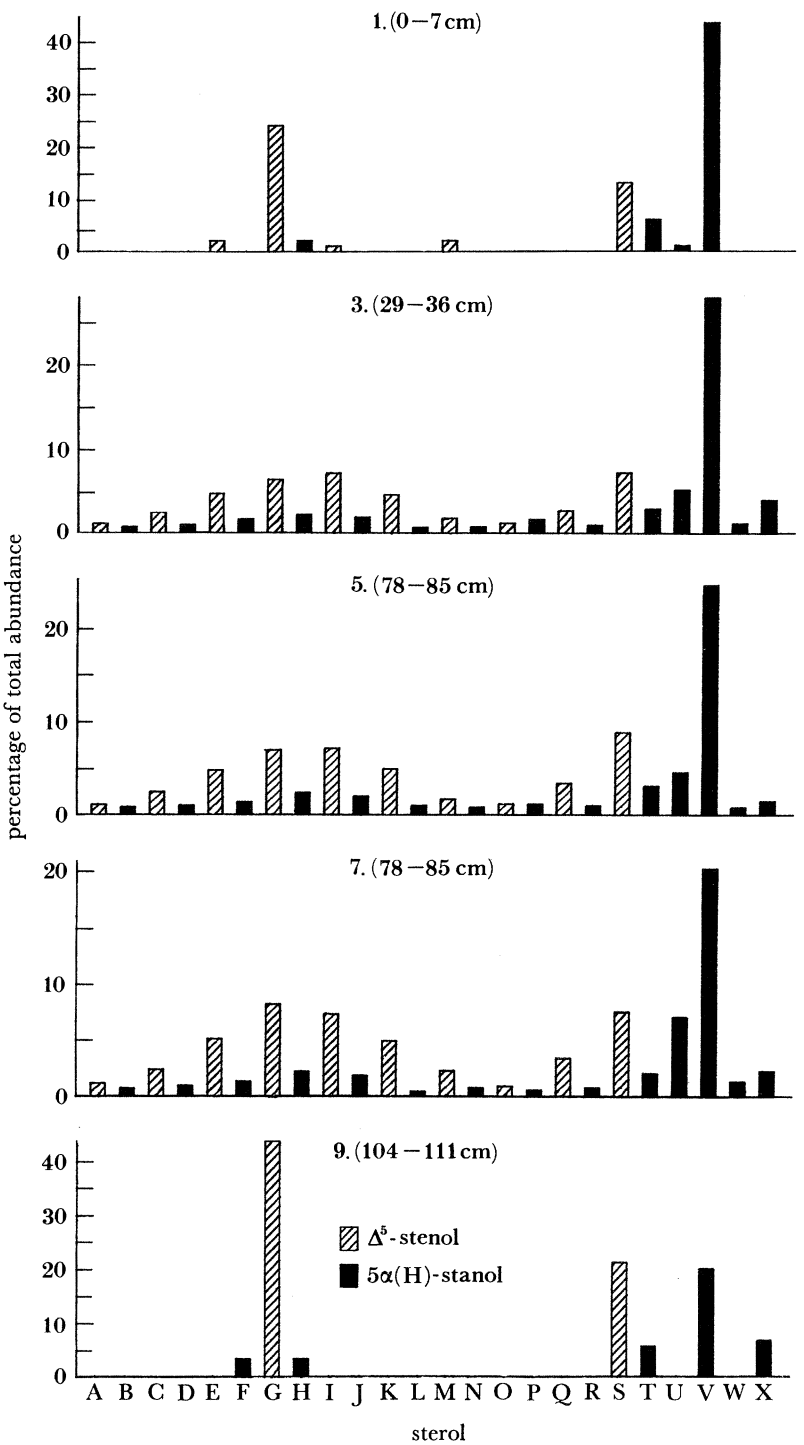

FIGURE 6. The major sterols of core A; distributions in sections 1 (0–7 cm), 3 (29–36 cm), 5 (53–60 cm), 7 (78–85 cm) and 9 (104–111 cm). The figure is intended to provide only a general comparison of the sterol distribution down the core and the minor sterols (less than *ca.* 1 % of total) have been omitted in the interests of clarity. Full data, including the identities of the sterols represented by the letters A–X, are given in table 4.

reflects contributions from many sources, including changes in the lipid composition brought about by passage through the food web before final deposition in the sediments.

Another group of phytoplankton whose sterol composition has not been thoroughly investigated is the Chlorophyceae (green algae). These organisms are ubiquitous in the oceans, though rarely as a major component of the phytoplankton. Most analyses of Chlorophyceae have shown them to contain mainly cholesterol, C_{28} and C_{29} Δ^7, $\Delta^{5,7}$ and $\Delta^{5,7,22}$-sterols (Orcutt & Richardson 1970; Patterson 1971; Bard *et al.* 1978; Wright 1979; Zielinski *et al.* 1982). Recent work has revealed a diverse range of other, additional, sterols in several species of *Dunaliella* (Prahl *et al.* 1984). The small quantities of Δ^7-sterols, and possibly some of the other minor sterols, in this sediment could well derive from planktonic green algae.

Some of the minor sterols, such as the C_{26} sterols and the 24-propyl-$\Delta^{24(28)}$-compounds, have been identified in filter-feeding invertebrates; sponges and bivalve molluscs (Idler *et al.* 1976; Ballantine *et al.* 1979*b*). Such organisms have been proposed as possible souces of these sterols in some sediments (Brassell 1980), but in the case of this sapropel the absence of remains from such benthic fauna (e.g. sponge spicules) argues against this. Some marine algae also contain these minor sterols (Boutry *et al.* 1979; Rohmer *et al.* 1980), while their occurrence in certain larger invertebrates may be related to the presence of symbiotic zooxanthellae in the animals (Goad 1978; Kokke *et al.* 1981*b*; Steudler *et al.* 1977). Hence, algae are the most likely source of these minor sterols in the sapropel.

Numerous foraminifera tests were present throughout core A, suggesting that foraminifera were probably a significant source of sedimentary lipids. As with fatty acids, however, there have been no detailed analyses of the sterols of these organisms with which to compare the sedimentary sterol distributions.

Pteropod tests were also abundant throughout the core, representing another possible source of sterols. A north Atlantic species, *Spiratella helicina*, analysed by Idler & Wiseman (1971), contained cholesterol as its major sterol, with smaller amounts of other C_{26}, C_{27}, C_{28} and C_{29} compounds. These included 24-nor-cholesta-5,22-dien-3β-ol, cholesta-5,22-dien-3β-ol, cholesta-5,24-dien-3β-ol, 24-ethylcholest-5-en-3β-ol and both the 24(28)*E* and 24(28)*Z* isomers of 24-ethylcholesta-5,24(28)-dien-3β-ol, all of which were present in the sapropel and may thus partly have derived from the pteropods. This would represent a reworking of the primary production by zooplankton, but the extent of such reworking and its influence on the sedimentary lipids is unknown.

Some authors (e.g. Huang & Meinschein 1976) have considered the presence of 24-ethylcholest-5-en-3β-ol in a sediment as evidence of terrigenous input, since the 24(*R*)-isomer of this compound is common among higher plants (Patterson 1971). This is not necessarily true, since a number of marine algae also contain this sterol (Ballantine *et al.* 1979*a*; Lin *et al.* 1982; Marlowe *et al.* 1984; Paoletti *et al.* 1976; Rohmer *et al.* 1980; Volkman *et al.* 1981*b*; Morris 1984). The 24-ethylcholest-5-en-3β-ol in core A may well represent a mixture of marine and terrigenous inputs.

The non-sapropel core sections contained detectable amounts of only a few sterols (table 4, figure 6). These correspond to the major sterols in the sapropel, but the great diversity of structural types which appears to characterize a rich marine input was lacking. The presence of dinosterol is probably indicative of some phytoplankton (dinoflagellate) input, but the other sterols present cannot be attributed to any particular sources. The very low levels of sterols in core sections 1 and 9, compared with sections 3, 5 and 7, are probably due to a combination

of lower initial input and greater degradation. Sterols were much less abundant than fatty acids in the non-sapropelic sediment, while in the sapropel sterols and fatty acids were of similar abundance. This is difficult to explain on the basis of greater general degradation of lipids in the non-sapropelic sediment, since sterols appear to be *less* susceptible than fatty acids to degradation in sediments (Cranwell 1981). The more important factor may well have been an increased input from relatively sterol-rich organisms to the sediments during sapropel formation. The sapropel sterol distributions show many similarities to those of sediments from the Namibian and Peruvian upwellings, which receive inputs predominantly from phytoplankton blooms (Smith *et al.* 1982, 1983*a*; Wardroper *et al.* 1978); this suggests that the sapropel did indeed receive a major phytoplankton input.

(vii) *Steroidal ketones*

The major sedimentary steroidal ketone present in core A, 4,23,24-trimethylcholest-22-en-3-one, or 'dinosterone' (table 5), has been identified in a marine dinoflagellate (Withers *et al.* 1978) and is probably mainly associated with inputs from dinoflagellates (discussed above). The other stanones have not been recognised as significant components of the lipids of marine organisms and, at present, cannot be ascribed to a direct biological input. The corresponding Δ^4-unsaturated analogues of several of the ketones in table 5 have been identified in a few marine organisms, including a dinoflagellate (Ha *et al.* 1982; Kokke *et al.* 1982; Sheikh & Djerassi 1974); Δ^4-stenones, however, were not detected.

Table 5. Steroidal ketones identified in core 10103A†

	component		
	ng g^{-1} sediment (dry mass)		
steroidal ketone	section 3	section 5	section 7
5α(H)-cholestan-3-one	—	—	26.0
5β(H)-cholestan-3-one	—	8.1	3.0
cholesta-3,5-dien-7-one	1.1	—	—
24-methyl-5α(H)-cholestan-3-one	—	3.1	—
C_{29} 5α(H)-stanone	—	7.0	—
C_{29} 4-methyl-5α(H)-stanone	2.8	—	—
C_{29} 4-methyl-5α(H)-stanone	2.8	—	—
4,23,24-trimethyl-5α(H)-cholest-22-en-3-one	75.5	15.9	13.2
4,23(*S*),24(*R*)-trimethyl-5α(H)-cholestan-3-one?‡	6.9	—	2.5
4,23(*R*),24(*R*)-trimethyl-5α(H)-cholestan-3-one?‡	20.7	—	—

—, not detected (less than *ca.* 0.5 ng g^{-1}).

† No steroidal ketones were detected in core sections 1 and 9.

‡ Tentative identifications based on analogy with the sterols and comparison of GC data with that presented in Zielinski *et al.* (1983).

In some sediments, a source of stanones appears to be as diagenetic transformation products (Gagosian *et al.* 1980; Smith *et al.* 1982); some bacteria can reduce Δ^5-sterols to stanols via Δ^4-sten-3-one and stan-3-one intermediates (Bjorkhem & Gustaffson 1971; Eyssen *et al.* 1973; Parmentier & Eyssen 1974; Taylor *et al.* 1981). In the sapropel analysed here, however, the low levels of stanones, the very limited range of structures compared with the sterols and the

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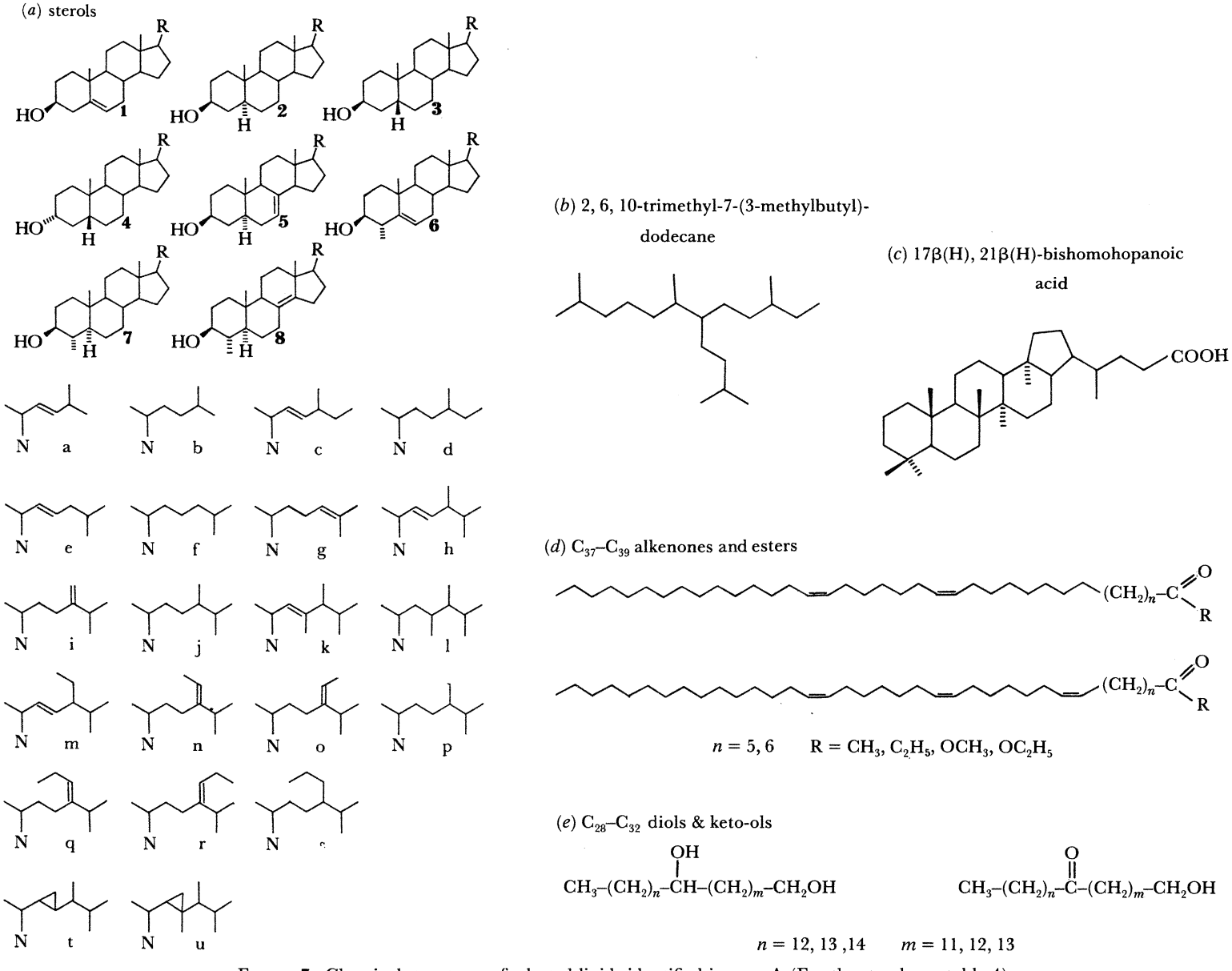

FIGURE 7. Chemical structures of selected lipids identified in core A (For the sterols see table 4).

absence of detectable amounts of Δ^4-stenones provide no compelling evidence that such transformations have been of importance. At least some of the sedimentary steroidal ketones (e.g. dinosterone), therefore, probably represent inputs from dinoflagellates.

(viii) *Steroidal hydrocarbons*

An early stage in sterol diagenesis is dehydration to produce sterenes (initially mainly the Δ^2-sterenes and $\Delta^{3,5}$-steradienes) (Dastillung & Albrecht 1977; Mackenzie *et al.* 1982). No significant biological sources of these compounds are known (Mackenzie *et al.* 1982) and the small quantities of sterenes in the sapropel (table 6) are presumed to have formed by diagenetic dehydration of the corresponding sterols. The amounts involved are very small relative to the total sterols, and further reduction to steranes (Mackenzie *et al.* 1982) was not evident.

TABLE 6. STEROIDAL HYDROCARBONS (STERENES) IDENTIFIED IN CORE 10103A†

		component		
		ng g^{-1} sediment (dry mass)		
sterene‡	double bond positions§	section 3	section 5	section 7
C_{27} sterene	Δ^2	12.6	22.4	11.0
C_{27} steratriene	?	tr	—	—
C_{28} sterene	Δ^2	2.4	2.5	6.0
C_{27} steradiene	$\Delta^{3,5}$	6.0	16.3	12.1
C_{28} sterene	Δ^2	2.2	5.0	—
C_{28} sterene	Δ^2	—	12.6	—
C_{28} steradiene	$\Delta^{N,24}$	5.4	—	—
C_{28} steradiene	$\Delta^{N,24}$	11.4	—	—
C_{28} steratriene	$\Delta^{X,X,24}$	5.4	9.9	—
C_{28} steratriene	$\Delta^{N,N,24}$	13.2	14.9	—
C_{29} sterene	Δ^2	6.6	10.8	—
C_{29} sterene	Δ^2	15.0	24.9	9.7
C_{29} sterene	Δ^{24}	tr	17.9	—
C_{29} steradiene	?	4.2	18.1	tr
C_{30} steratriene	?	tr	5.1	—
C_{30} steratriene	?	tr	1.7	—

Symbols: tr, trace component (less than 1 ng g^{-1}); —, not detected (less than *ca.* 0.5 ng g^{-1}).

† No sterenes were detected in core sections 1 and 9. No steranes were detected in any core section.

‡ Sterenes are listed in order of GC retention time (on OV-1, conditions as given in text).

§ Sterene double bond positions are generally not well characterized. N indicates a double bond somewhere in the sterene nucleus; X indicates a double bond in an unknown position. The low levels of sterenes present precluded more detailed interpretation.

4. GENERAL DISCUSSION

The distributions of the major lipid classes in the sapropel facies from core A (10103 # 8K) clearly suggest that marine sources dominated the input of lipids. More specifically, it appears from the sterols that dinoflagellates were important source organisms, while the presence of coccoliths and C_{37}–C_{39} unsaturated ketones points to certain Haptophycean algae as having also been important contributors.

The lipids of the sapropel show many similarities to those of certain marine sediments, formed under upwelling areas, which are known to receive a very large phytoplankton input, for example on the Namibian and Peruvian continental shelves (Boon *et al.* 1975; Gagosian *et al.* 1983*a*; Lee *et al.* 1980; Smith *et al.* 1982, 1983*a*,*b*,*c*; Wardroper *et al.* 1978). Particular similarities are evident among the fatty acids and sterols; the fatty acids of all these sediments show a preponderance of C_{14}–C_{22} acids, dominated by 16:0, with 14:0 and 18:0 as other

major components. In each case, the sterols display a similar, diverse range of structures, with cholest-5-en-3β-01, 24-methylcholesta-5, 22-dien-3β-ol and 24-ethylcholest-5-en-3β-ol as major components, while the Namibian shelf sterols, like those of the sapropel, were found to be dominated by 4-methyl-sterols, especially dinosterol (Smith *et al.* 1982). These similarities are observed despite major differences in the sediment types: a silicious ooze in the case of Namibia and Peru, compared with a calcareous mud in the case of the sapropel. The lipid distributions may thus indicate that the sapropel, like the Namibian and Peruvian shelf sediments, received a major input derived from marine productivity. Such an input was less evident in the lipids of the non-sapropelic, overlying and underlying sediments, suggesting that an increase in biological production in the water column was associated with sapropel formation.

The most likely cause of an increase in production would have been an increase in nutrient supply to the euphotic zone. Extra nutrients could have been carried in by the meltwater–fluvial influx (Rossignol-Strick *et al.* 1982; Thunell & Williams 1982) and/or by an inflow of Atlantic deep water induced by circulation reversal in the Mediterranean (Bradley 1938; Calvert 1983). In the latter situation, a subsurface inflow of denser, nutrient-bearing Atlantic water would have been forced to rise over the sill at the Straits of Sicily into the euphotic zone of the Eastern Basin, providing a source of nutrients for phytoplankton growth. These nutrients, perhaps supplemented by an increased supply in run-off, could have triggered and sustained a higher than usual level of biological production, until the freshwater input and the circulation returned to normal.

An examination of both the inorganic geochemistry (Sutherland *et al.* 1984) and organic geochemistry (this study) of an S_1 sapropel from the Ionian Sea has thus demonstrated the need to include increased biological productivity, contributing an increased organic input to the sediments, as a factor in theories of sapropel formation. Further work is needed to address matters such as (i) the extent and intensity of this productivity, (ii) the precise nature and sources of nutrient inputs, (iii) the involvement of high productivity in forming other, older sapropel facies and (iv) the possible use of organic geochemistry to help correlate sapropel facies across the Mediterranean.

5. Summary and conclusions

Samples of an S_1 sapropel and the underlying and overlying sediments, in a core from the Hellenic Outer Ridge, east Mediterranean Sea, have been analysed for lipids. The sapropel contained an abundant and diverse range of hydrocarbons, ketones, fatty alcohols, fatty acids and steroids; the non-sapropelic sediment contained generally lower levels, and a more limited range, of these compounds.

Comparisons of the sapropel lipid distributions with those reported for various organisms suggest the following:

(i) the sapropel lipids were derived predominantly from marine planktonic organisms, with a smaller terrestrial (higher plant) contribution;

(ii) the major recognizable inputs of lipids probably derived from Dinophycean and Haptophycean algae. A minor bacterial influence was evident, but contributions from potential sources such as foraminifera and pteropods are difficult to assess due to inadequate data on these organisms;

(iii) the lipids were well preserved, in the sense that little diagenetic alteration was recognizable.

The differences between the lipid distributions of the sapropel and of the enclosing sediments are probably the result of both the prevailing anoxic conditions in the former (compared with oxic conditions in the latter) and an increased supply of planktonic material to the sediments during sapropel formation. This is consistent with the concept that sapropel deposition was associated with periods of increased biological production in the water column.

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