GEOLOGICA ULTRAIECTINA

Mededelingen van het
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No. 46

ORGANIC AND INORGANIC GEOCHEMICAL ASPECTS OF MEDITERRANEAN LATE QUATERNARY SAPROPELS AND MESSINIAN EVAPORITIC DEPOSITS

HANS LODEWIJK TEN HAVEN

STELLINGEN

1

Vaak wordt ten onrechte in de definitie van een sapropeel, zoals geformuleerd door Kidd et al. (1978), de term "organic carbon" vervangen door "organic matter".

R.B. Kidd, M.B. Cita and W.B.F. Ryan, 1978.
In. Rep. Deep Sea Drilling Project 42, 421-443.

2

Bij het gebruik van de "brown-green color transition" als aanwijzing voor de Fe^{3+} - Fe^{2+} redox grens in mariene sedimenten wordt voorbijgegaan aan het verschijnsel kleurenblindheid.

M. Lyle, 1983. Limnol. Oceanogr. 28, 1026-1033.

3

Vergelijking 2, die door Emerson et al. (1980) is gegeven om de "potential alkalinity increase" te beschrijven, is fout.

S. Emerson, R. Jahnke, M. Bender, P. Froelich,
G. Klinkhammer, C. Bowser and G. Setlock, 1980.
Earth Planet. Sci. Lett. 49, 57-80.

4

De door Didyk et al. (1978) gegeven interpretatie van de pristaan/phytaan verhouding als maat voor anoxiciteit van het milieu van afzetting is op onvoldoende grond gebaseerd.

B.M. Didyk, B.R.T. Simoneit, S.C. Brassell and
G. Eglinton, 1978.
Nature 272, 216-222.

5

De verbindingen, die door Palmer en Zumberge (1981) in een Siciliaanse olie geidentificeerd zijn als cycloalkanen, zijn isoprenoide alkylthiophenen.

S.E. Palmer and J.E. Zumberge, 1981.
In: Organic Maturation Studies and Fossil Fuel
Exploration (Ed. J. Brooks), pp. 393-426.
J.S. Sinninghe Damsté, H.L. ten Haven, J.W. de
Leeuw and P.A. Schenck, 1986.
Org. Geochem. 10 (in press).

6

Het manipuleren vam experimentele of literatuur gegevens om de strekking van het eigen betoog niet te ondermijnen, zou aan de kaak gesteld moeten worden (Brassell et al., 1986, vergelijk met Comet, 1982).

S.C. Brassell, G. Eglinton, I.T. Marlowe,
U. Pflaumann and M. Sarnthein, 1986.
Nature 320, 129-133.
P.A. Comet, 1982.
Ph.D. thesis, University of Bristol.

7

Gezien het aanvangssalaris van de promovendus "nieuwe stijl" kan gesteld worden dat de afkorting A.I.O. staat voor Armoedzaaier In Opleiding.

8

Gezien de mate waarin olie, gas en steenkool in Nederland voorkomen lijkt het gerechtvaardigd een organisch geochemische afdeling binnen de Rijks Geologische Dienst op te richten.

Utrecht, 15 december 1986 H.L. ten Haven

Stellingen behorende bij het proefschrift *Organic and inorganic geochemical aspects of Mediterranean Late Quaternary sapropels and Messinian evaporitic deposits.*

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ORGANISCH EN ANORGANISCH GEOCHEMISCHE ASPECTEN VAN MEDITERRANE LAAT KWARTAIRE SAPROPELEN EN EVAPORITISCHE AFZETTINGEN UIT HET MESSINIEN

(MET EEN SAMENVATTING IN HET NEDERLANDS)

PROEFSCHRIFT

TER VERKRIJGING VAN DE GRAAD VAN DOCTOR IN
DE WISKUNDE EN NATUURWETENSCHAPPEN AAN
DE RIJKSUNIVERSITEIT TE UTRECHT, OP GEZAG VAN
DE RECTOR MAGNIFICUS PROF. DR. J.A. VAN GINKEL,
VOLGENS BESLUIT VAN HET COLLEGE VAN DEKANEN
IN HET OPENBAAR TE VERDEDIGEN OP MAANDAG
15 DECEMBER 1986 DES NAMIDDAGS TE 4.15 UUR

DOOR

HANS LODEWIJK TEN HAVEN

GEBOREN OP 13 NOVEMBER 1957 TE 'S GRAVENHAGE

1986
OFFSETDRUKKERIJ KANTERS B.V., ALBLASSERDAM

PROMOTORES: PROF. DRS. P.A. SCHENCK
PROF. DR. C.H. VAN DER WEIJDEN
CO-PROMOTOR: DR. J.W. DE LEEUW

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aan Phia
aan mijn Oma

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CONTENTS

Chapters 2, 6, 7, 8, 9 and 10 have already been published or are accepted for publication and are included in this thesis by permission of the publishers. Chapters 2, 6 and 7 are reproduced by permission of Elsevier Science Publishers, chapters 8 and 10 by permission of Pergamon Press Ltd. and chapter 9 by permission of the Geological Society from "Lacustrine Petroleum Source Rocks".

Chapter 2: H.L. ten Haven, M. Baas, J.W. de Leeuw & P.A. Schenck.
Late Quaternary Mediterranean sapropels I: On the origin of organic matter in sapropel S_7.
Marine Geology 75 (in press).

Chapter 3: H.L. ten Haven, M. Baas, J.W. de Leeuw, P.A. Schenck & H. Brinkhuis.
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Chapter 4: H.L. ten Haven, M. Baas, M. Kroot, J.W. de Leeuw, P.A. Schenck & J. Ebbing.
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Chapter 5: H.L. ten Haven, M. Baas, J.W. de Leeuw J.M. Maassen & P.A. Schenck.
Organic geochemical characteristics of sediments from the anoxic brine-filled Tyro basin (eastern Mediterranean).
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Chapter 6: H.L. ten Haven, G.J. de Lange & G.Th. Klaver.
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eastern Mediterranean. A tentative model.
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The application of biological markers in the recognition of palaeo hypersaline environments.
In : K. Kelts, A. Fleet & M. Talbot (Editors), Lacustrine Petroleum Source Rocks. (in press).

Chapter 10: H.L. ten Haven, J.W. de Leeuw, T.M. Peakman & J.R. Maxwell.
Anomalies in steroid and hopanoid maturity indices.
Geochimica et Cosmochimica Acta 50, 853-855.

SUMMARY

This thesis describes the results of organic and inorganic geochemical investigations obtained for samples collected from the eastern Mediterranean sea floor and from Italy. The samples vary in age from the Late Miocene up to the Holocene. The environmental conditions prevailing during deposition of the samples differ greatly. Sediment samples deposited under both marine anoxic and oxic conditions were studied as well as samples from hypersaline depositional environments.

Late Quaternary eastern Mediterranean sediments are characterized by the occurrence of organic rich layers, so-called sapropels. Detailed investigations of the soluble organic matter of these sapropels indicate that the organic matter is of a mixed marine, terrigenous and bacterial origin (Chapters 2 and 3). A study of the lateral variation in concentration of organic compounds in the youngest sapropel (S_1) revealed a trend of relatively increasing amounts of continentally derived organic matter going from coastal towards more seaward and deeper realms (Chapter 3). Variations in the sea-surface water temperatures during deposition of the sapropels could be inferred from the relative abundance of di- and triunsaturated C_{37} ketones and from the relative abundance of 27-nor-24-methylcholesta-5,22E-dien-3β-ol and cholesta-5,22E-dien-3β-ol (Chapter 4).

Three samples of Holocene age from the anoxic brine-filled Tyro basin were investigated (Chapter 5). Most compounds identified in these samples were also present in the sapropels, but some compounds, such as trisnorhopan-21-one and bishomohopanoic acid, are ascribed to an input from microbiota living at the brine-seawater interface. The brine is thought to be formed by leaching of tectonically exposed Messinian evaporitic deposits, consisting of gypsum, halite and some soluble salts (Chapter 6). The interstitial water chemistry of sedi-

ments from the Tyro basin suggests that selective leaching has taken place, namely halite dissolution followed later by gypsum dissolution (Chapter 7). The interstitial water chemistry of a core collected in the adjacent Kretheus basin, where at present the bottom salinity and oxygen content is at a normal level, is characterized by a strong downward increase of Na and Cl, indicating that conditions similar to the Tyro basin must once have prevailed in the Kretheus basin. The interstitial water chemistry of "normal" Mediterranean sediments is also discussed in chapter 7.

Chapter 8 describes the occurrence and significance of hydrocarbons present in three samples from a Messinian evaporitic basin (northern Apennines). Several new compounds were detected and are discussed. A series of extended hop-17(21)-enes maximizing at the C_{35} members, a very low pristane/phytane ratio, and an even over odd predominance of long chain alkanes seem characteristic for hypersaline conditions prevailing in the past. Using the biological markers described in chapter 8 it is suggested that the source rock of the Rozel Point Oil was deposited under hypersaline conditions (Chapter 9). The investigations of the samples from ancient hypersaline environments also revealed some anomalies in hopanoid and steroid maturity indices (Chapters 8 and 9). Extended 17α(H),21β(H)-hopanes and extended hop-17(21)-enes occur fully isomerized at C-22; 20R- and 20S-5α(H),14β(H),17β(H) steranes are relatively abundant whereas 20S-5α(H),14α(H),17α(H) steranes are virtually absent. Possible diagenetic pathways explaining these phenomena are proposed in chapter 10.

SAMENVATTING

Dit proefschrift beschrijft de resultaten van organisch en anorganisch geochemisch onderzoek van monsters, afkomstig van de bodem van de Middellandse Zee en uit Italie. De monsters variëren in ouderdom van Laat Mioceen tot Holoceen. Hun milieu van afzetting verschilt in hoge mate. Naast sedimenten afgezet onder zowel marien anoxische als oxische omstandigheden zijn ook monsters afkomstig van hypersaline afzettingsmilieus onderzocht.

Karakteristiek voor Laat Kwartaire sedimenten uit de oostelijke Middellandse Zee is, dat in deze sedimenten organisch rijke lagen, z.g. sapropelen, voorkomen. Gedetailleerde analyse van de oplosbare fractie van het organisch materiaal van deze sapropelen heeft aangetoond dat het organisch materiaal van zowel mariene, terrigene als bacteriële oorsprong is (Hoofdstukken 2 en 3). De uitkomsten van een onderzoek naar de laterale variatie in concentratie van organische componenten in de jongste sapropeel (S_1) wijzen op een trend van relatief toenemende hoeveelheden terrigeen materiaal van dichtbij de kust naar meer zeewaarts en dieper gelegen gebieden (Hoofdstuk 3). Verschillen in de temperatuur van het oppervlaktewater van de zee ten tijde van afzetting van de sapropelen konden worden afgeleid uit de relatieve hoeveelheden van twee- en driemaal onverzadigde C_{37}-ketonen en uit de relatieve hoeveelheden van 27-nor-24-methylcholesta-5,22E-dieen-3β-ol en cholesta-5,22E-dieen-3β-ol (Hoofdstuk 4).

Drie monsters van holocene ouderdom, afkomstig uit het anoxische en met pekel gevulde Tyro bekken, zijn onderzocht (Hoofdstuk 5). De meeste componenten die in deze monsters geidentificeerd werden, waren ook al aangetroffen in de sapropelen; enkele componenten echter, zoals trisnorhopan-21-on en bishomohopaanzuur, worden toegeschreven aan microorganismen die op de spronglaag van de pekel met het zeewater leven. In hoofdstuk 6 wordt aannemelijk gemaakt, dat deze pekel is ontstaan door uitloging van een door tektoniek ontsloten evaporitische afzetting van Messinien ouderdom, bestaande uit gips, steenzout en enkele oplosbare zouten. De samenstelling van het poriënwater in sedimenten uit het Tyro bekken doet vermoeden dat er een opeenvolgende uitloging plaatsvond, eerst van steenzout, pas later van gips (Hoofdstuk 7). De samenstelling van het poriënwater uit een kern, genomen in het aangrenzende Kretheus bekken, waar momenteel de saliniteit en het zuurstof gehalte van het bodemwater de normale waarden hebben, wordt gekenmerkt door een sterke toename van Na en Cl met de diepte. Dit wijst er op dat condities gelijk aan die in het Tyro bekken vroeger ook voorkwamen in het Kretheus bekken. Tevens wordt in hoofdstuk 7 de chemie van het poriënwater uit "normale" Middellandse Zee sedimenten besproken.

In hoofdstuk 8 wordt het voorkomen beschreven van koolwaterstoffen geëxtraheerd uit drie monsters, afkomstig uit een Messinien evaporitisch bekken (Noord Apennijnen). Op de betekenis daarvan wordt ook dieper ingegaan. Verscheidene nieuwe componenten werden ontdekt. Een reeks van hop-17(21)-enen met zijketens van meer dan drie C-atomen en een overwegend voorkomen van de C_{35}-R- en S-componenten, een zeer lage pristaan/phytaan verhouding, en een overwegend voorkomen van even lange rechte alkanen ten opzichte van de oneven lijkt karakteristiek te zijn voor hypersaliene afzettingsmilieus. Op grond van de gegevens over de biologische "markers" beschreven in hoofdstuk 8, wordt geconcludeerd dat het olie moeder gesteente van de Rozel Point olie is afgezet onder hypersaliene condities (Hoofdstuk 9). Onderzoek van monsters afkomstig van oude hypersaliene afzettingsmilieus bracht enkele anomalieën aan het licht in de hopanoide en steroide rijpheidsparameters (Hoofdstukken 8 en 9). 17α(H),21 (H)-Hopanen en hop-17(21)-enen met zijketens van meer dan drie C-atomen vertonen volledige isomerisatie aan C-22; 20R- en 20S-5α(H),14β(H),17β(H) steranen zijn relatief sterk aanwezig, terwijl 20S-5α(H),14α(H),17α(H) steranen bijna niet voorkomen. In hoofdstuk 10 wordt een mechanisme voor de diagenese voorgesteld om deze verschijnselen te verklaren.

Chapter 1

INTRODUCTION

The boundary between Eurasia and the African plates, formerly the suture between Eurasia and Gondwana, has been the locality of active tectonism and rapidly changing geography since the Triassic. The Mesozoic seas of this zone are known as the Tethys, while Tertiary seas are usually called Mediterranean. A schematic outline of the tectonic evolution of this zone is given in Figure 1.1. (after Hsü, 1977). This figure is not intended to be complete, but is presented to show the dramatic changes which have taken place. The present-day eastern Mediterranean is thought to be a relic of the Tethys, while other basins of the Mediterranean are of a much younger age (Hsü, 1977). Unconsolidated sediments of Pliocene and Quaternary age, blanketing Late Miocene (Messinian) evaporites, consist largely of terrigenous clays, silt, and sand, and to a lesser extent of organic-rich ooze and volcanic ash (Stanley, 1977).

As early as 1938 Bradley predicted that episodes of stagnation, expressed by organic-rich layers, had occurred during the Quaternary. His hypothesis was later confirmed by the study of cores collected during the Swedish Deep Sea Expedition in 1947-1948 (Kullenberg, 1952), marking the start of numerous investigations of the Mediterranean sea-floor (see e.g. Stanley, 1972; Ryan et al., 1973; Hsü et al., 1978). Many of the above mentioned studies discuss the occurrence of these organic rich layers, so-called sapropels, and speculations are

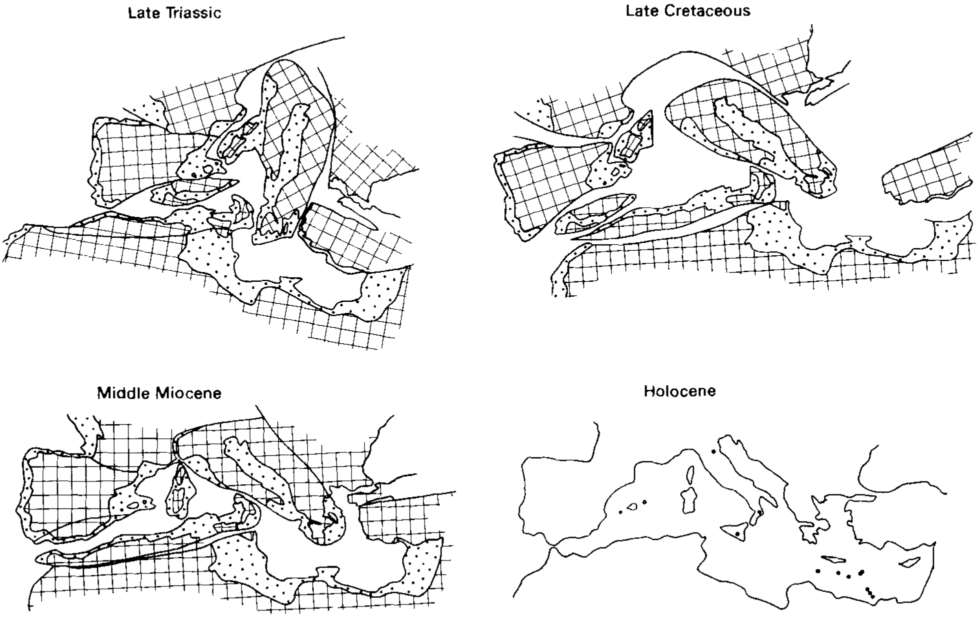

Figure 1.1. Schematic outline of the tectonic evolution of the Mediterranean zone, starting in the Late Triassic (after Hsü, 1977). The location sites of the samples investigated in this thesis are indicated by dots in the Holocene evolutionary stage.

made about the origin of the organic matter. However, no systematic study, using an organic geochemical approach, has been undertaken to support or reject these speculations. The definition of a sapropel, valid for Mediterranean sediments, is given by Kidd et al. (1978): a discrete layer greater than 1 cm in thickness, set in open marine pelagic sediments and containing more than 2% organic carbon by weight. A sapropelic layer is considered to be a similar layer as described above, but having an organic carbon content between 0.5 and 2% by weight (Kidd et al., 1978).

Sapropels occur over wide areas in eastern Mediterranean sediments of Late Quaternary age and are, therefore, commonly used for lithologic correlation studies. Two nomenclature systems were proposed in the literature, symbolizing sapropels either by S_1, S_2, S_3 .... (McCoy, 1974) or by A, B, C .... (Hieke et al., 1973). However, not all sapropels labeled with the S-nomenclature have counterparts in the A, B, C-nomenclature (A = S_1, B = S_3, C = S_5). This is because the cores studied by Hieke et al. (1973) did not contain the fully developed sequence of twelve sapropels as observed in core RC 9-191 (Ryan, 1972; Vergnaud-Grazzini et al., 1977), the most complete core taken sofar. The S-nomenclature is adopted in this thesis.

In 1983 a scientific expedition to the eastern Mediterranean was undertaken with the R.V. Tyro as part of a joint program of the Marine Geology group of the Free University and the University of Amsterdam, and the Marine Geochemistry group of Utrecht University. The scientific program was focussed on the occurrence and origin of Late Quaternary sapropels. During the expedition a brine-filled depression, named Tyro basin, was discovered, where anoxic sedimentation (sapropel formation) takes place at present (Jongsma et al., 1983; de Lange and ten Haven, 1983).

This thesis deals with organic and inorganic geochemical aspects of Late Quaternary eastern Mediterranean sediments, including sediments from the hypersaline Tyro basin. For comparative purposes some samples from ancient (Messinian) hypersaline depositional environments, collected in Sicily and the northern Apennines, were also analyzed (see Fig. 1.1. for location of the sampling sites). Special attention was paid to the interstitial water chemistry and to the study of "biological markers". A biological marker is any organic compound detected in the geosphere whose basic carbon skeleton suggests an unambiguous link to a known contemporary biosynthesized compound. This choice was made for two reasons. Firstly, pore waters are known to be sensitive indicators of diagenetic changes in the solids. An example for this is given by Berner (1980): "a readibly measured 20% increase of dissolved Ca in a marine sediment pore water resulting from the dissolution of calcium carbonate is approximately equivalent, at depth in the sediment, to a decrease in the total solids of only 0.02% $CaCO_3$ by weight (in a sediment containing 50% $CaCO_3$)". Secondly, a study of biological marker compounds can provide insight into the composition of the organic matter with respect to the different kinds of input.

Organic geochemical studies were carried out on several samples in order to decipher the sources of input contributing to the organic matter of the sapropels. The organic geochemistry of sapropel S_7 has been investigated in detail and is discussed in chapter 2. In this chapter also a review is given of the models proposed for the formation of Mediterranean sapropels and of the investigations carried out to elucidate the origin of the organic matter.

The lateral organic geochemical variation of the Holocene sapropel (S_1) over a part of the eastern Mediterranean is discussed in chapter 3, and an attempt is made in this chapter to correlate organic geochemical results with palynological results of this sapropel.

The variation in input of organic matter (allochthonous versus autochthonous) in sapropels S_1, S_5, S_6, S_7 and in a sapropelic layer from southern Italy of Pliocene/Pleistocene age is discussed in chapter 4. Special attention is given to the influences of sea surface temperature variations in the past on the organic geochemical characteristics of the sapropels.

In chapter 5 some organic geochemical characteristics of sediments from the brine-filled, anoxic Tyro basin are discussed, and compared with the results for the other sapropels. The chemical composition of the Tyro brine is discussed in chapter 6, and an origin from dissolution of Messinian evaporitic salt deposits is inferred.

The interstitial water chemistry of Quaternary eastern Mediterranean sediments is highly complicated and generalized models are not applicable (chapter 7). The dissolution of evaporitic salt deposits does not only influence the chemistry of sediments in the Tyro basin, but is also evident at some other sites from which piston cores were recovered.

A detailed investigation of sediments from an ancient (Messinian) hypersaline basin from the northern Apennines revealed the presence of several hitherto unknown biological markers (chapter 8). Moreover some characteristic distribution patterns of biological markers were observed, which could be related to hypersaline conditions, prevailing during time of deposition. The application of these biological markers in the recognition of palaeo hypersaline conditions is discussed in chapter 9. The investigation of the samples from ancient hypersaline environments (chapter 8 and 9) also revealed some anomalies in hopanoid and steroid maturity indices. In chapter 10 possible diagenetic pathways explaining these phenomena are given.

Chapter 2

LATE QUATERNARY MEDITERRANEAN SAPROPELS I: ON THE ORIGIN OF ORGANIC MATTER IN SAPROPEL S_7

Abstract

At least twelve organic rich layers, so-called sapropels (S_1-S_{12}), occur in Late Quaternary sediments from the eastern Mediterranean. Organic matter in sapropel S_7 (organic carbon up to 11 %) is characterized in detail by gas chromatography (GC) and gas chromatography-mass spectrometry (GCMS). Lipids were thus separated to obtain information about their mode of occurrence. This procedure separates the lipids into three classes: (1) free lipids extracted by Soxhlet extraction, (2) residual bound lipids extracted after saponification of the Soxhlet extracted residue and (3) residual bound lipids extracted after acid treatment of the saponified residue. In addition, an extract was obtained after saponification of the free lipids.

The organic matter investigated is of a mixed marine (e.g. dinoflagellates, coccolithophorids), terrigenous (e.g. cuticles) and bacterial origin with the former predominating. The formation of sapropel S_7 is probably caused by a combination of stagnation and high productivity, both induced by a large input of fresh riverine water, carrying nutrients and terrigenous organic material.

2.1. Introduction

The widespread occurrence of "black shales" in Cretaceous and Cenozoic sequences has been well documented at deep sea drilling sites. Organic geochemical research has been focussed on Cretaceous black shales and their possible modern analogues. Several models have been proposed to explain the deposition of these black shales (e.g. Schlanger and Jenkyns, 1976; Arthur et al., 1984) and a general classification for modern aquatic anoxic settings has been proposed by Demaison and Moore (1980). According to these authors the following types of anoxic environments should be considered: (1) large anoxic lakes, (2) anoxic silled basins, (3) anoxic layers caused by upwelling and (4) open ocean anoxic layers. One of the conclusions of Arthur et al. (1984) is: "each region and even each bed within a black shale is likely to have its own particular combination of factors that led to organic matter preservation, so that generalized models may not always be applicable".

The Mediterranean is a landlocked, silled basin with at present a negative water balance and well aerated bottom waters except in some isolated anoxic depressions, recently discovered in the eastern Mediterranean (Jongsma et al., 1983; Scientific staff of Cruise Bannock 1984-12, 1985). At least twelve organic rich layers (referred to as S_1-S_{12} by McCoy, 1974 and Cita et al., 1977) are reported in the Late Quaternary record of the eastern Mediterranean (Cita and Grignani, 1982). Only the youngest (S_1) has been studied in detail for its organic geochemical characteristics (Smith et al., 1983; Smith, 1984; Poutanen and Morris, 1985; Smith et al., 1986).

This paper presents the results of an organic geochemical study of sapropel S_7 from piston core T83-7 (33°39.65′N, 25°59.00′E; water depth 2480 m).

2.2. Models of Mediterranean sapropel formation

Since the discovery of these black organic rich layers (Kullenberg, 1952), numerous studies have been undertaken to understand the occurrence and origin of these so-called sapropels. The principal aim of all these studies was to elucidate the environmental conditions leading to the formation of the sapropels. To this end different approaches were used, such as isotopic studies (e.g. Cita et al., 1977; Thunell et al., 1977; Vergnaud-Grazzini et al., 1977; Williams et al., 1978), faunal studies (e.g. Herman, 1972; Cita et al., 1977; Thunell, 1979a; Mullineaux and Lohmann, 1981; Schrader and Matherne, 1981; Muerdter, 1984), clay mineral distribution studies (e.g. Chamley, 1971; Dominik and Stoffers, 1978) and mineralogical studies (Nesteroff, 1973; Milliman and Müller, 1973; Sigl et al., 1978; Calvert, 1983; Sutherland et al., 1984). As a result of these studies a variety of mechanisms have been proposed to account for the deposition and preservation of these sapropels. Basically two models are invoked to explain the accumulation of the organic rich sediments, "a stagnation model" and "a high productivity model".

The stagnation model, as suggested by Olausson (1961), explains the origin of sapropels by a density stratification induced by a large input of low salinity surface water, which inhibits vertical mixing and aeration of the deeper water, creating anoxic conditions, resulting in the deposition of organic rich sediments. The presence of a low salinity surface water layer during sapropel formation has been confirmed by finding a depletion of ^{18}O in planktonic foraminiferal tests (e.g. Williams et al., 1978). The two major potential sources of fresh water for the invoked low salinity surface water are the Black Sea (e.g. Thunell and Lohmann, 1979; Stanley and Blanpied, 1980) and the river Nile (e.g. Adamson et al., 1980; Rossignol-Strick et al., 1982; Rossignol-Strick, 1985). This has been disputed by Jenkins and Williams (1984), who calculated that neither the river Nile discharge nor the input from the Black Sea (nor both together) can have been sufficient to account for the oxygen isotope depletion associated with the youngest sapropel (S_1).

The high productivity model (e.g. Calvert, 1983) also takes as starting point a large influx of fresh water. This would have induced an outward flow of low salinity surface water from the Mediterranean and a subsurface flow of Atlantic water into the Mediterranean (current reversal). This deep water, rich in nutrients, caused an upwelling effect in the eastern Mediterranean resulting in high primary productivity and an increased amount of organic matter settling through the water column. The high abundance of diatoms and silicoflagellates found in sapropel S_5 south of Crete up to the southern Turkish coastline (Schrader and Matherne, 1981) is in favour of this model. However, in other areas of the eastern Mediterranean, no abundance of diatoms was observed in the S_5 sapropel (Schrader and Matherne, 1981). A large scale upwelling of fertile water rich in silica is therefore not very likely the principal trigger for the regional accumulation of organic matter at those sites (Thunell and Williams, 1982). An alternative high productivity model has been proposed by Rossignol-Strick et al. (1982), who suggested that the enhanced primary productivity is the result of the input of nutrients by an increased fresh water discharge. This hypothesis has also been put forward by Thunell and Williams (1982) and supported by $\delta^{13}C$ values of planktonic foraminifera. Absence of diatoms and silicoflagellates suggests that this low salinity surface layer was not rich in dissolved silica. Calvert (1983) argued that the high organic carbon content of sapropels, up to 20%, cannot be explained merely by a stagnation model without an increase of primary production. Also, the enrichment of Ba in sapropels has been put forward as a support for the high productivity model (Sutherland et al., 1984).

Physiographic parameters, such as water depth and bottom topography, will probably influence the sapropel formation too. The shallowest present-day water depth below which cores have been found to contain sapropels varies between 660 m (McCoy, 1974) and 880 m (Stanley, 1978), although recently so-called sapropelic layers (0.5 - 2.0% Org.C; Kidd et al., 1978) are found at a minimum water depth of 400 m (Shaw and Evans, 1984). The influence of local bottom topography becomes clear from the recent discovery of extant anoxic basins in the eastern Mediterranean. However, these near bottom anoxia are caused by the dissolution of tectonically exposed Messinian evaporitic salt deposits, resulting in a density stratification (Jongsma et al., 1983; de Lange and ten Haven, 1983; Scientific Staff of Cruise Bannock 1984-12, 1985; ten Haven et al., 1985a, see Chapter 6).

Sapropels are considered to be a peculiar feature for the eastern and not for the western Mediterranean, although some organic rich layers have been found in the Tyrrhenian basin (Cita et al., 1973; Kidd et al., 1978). The organic carbon content of these layers is less than 2% and therefore they are not considered to be true sapropels; sapropels by definition have an organic carbon content over 2% (Kidd et al., 1978). Muerdter (1984) has given compelling evidence for westbound low salinity surface water incursions across the Strait of Sicily during times of sapropel formation in the eastern Mediterranean. These incursions did not lead to the deposition of organic rich layers in the western Mediterranean.

2.3. Characterization of the organic matter

The organic material of marine sediments consists of autochthonous marine organic material with superimposed a varying amount of allochthonous terrigenous organic material supplied by rivers and aeolian fall out. Both inputs are controlled by the sinking rate and predation; moreover the input of allochthonous organic matter is also controlled by transport parameters (Didyk et al., 1978). There is disagreement about the nature of the organic material in Mediterranean sapropels. Deroo et al. (1978) and Sigl et al. (1978) concluded that the organic material studied in Mediterranean DSDP cores (Neogene, Pleistocene) is mainly composed of terrigenous material. This is consistent with carbon isotope studies of the organic matter (Hahn-Weinheimer et al., 1978). In contrast, Cita and Grignani (1982) stated on the basis of a dominance of amorphous organic matter that the organic material of Late Pliocene sapropels has a marine origin and that the Late Pleistocene sapropels are mainly composed of marine organic material. Nesteroff (1973) also concluded a marine origin for the organic material based on "a domain between C_1 and C_{12}". C/N ratios of Late Pleistocene sapropels indicate a marine origin (Calvert, 1979, cited in Thunell et al., 1984), while C/N ratios of Early Pleistocene sapropels point to a significant contribution of terrigenous material (Sigl et al., 1978). C/N ratios and $\delta^{13}C$ values of organic matter in the youngest sapropel (S_1) are again in favour of a marine origin (Sutherland et al., 1984).

Only few comprehensive organic geochemical studies have been carried out to elucidate some of these conclusions and statements and their apparent contradictions. One has been carried out on the Late Pliocene and Early Pleistocene sapropels of DSDP drill sites by Comet (1982), whose overall conclusion was that the sapropel lipids were predominantly of marine origin. The only other detailed research has been done on the youngest sapropel S_1 (9000-7000 years BP) (Smith et al., 1983; Smith, 1984; Poutanen and Morris, 1985; Smith et al., 1986). Smith (1984) concluded that lipids of this sapropel indicate a mixed marine and terrigenous origin with the former predominating.

2.4. Objective of this work

Our current research is focussed on organic geochemical characteristics of Late Quaternary Mediterranean sapropels (S_1, S_5, S_6, S_7). This paper reports the results obtained for sapropel S_7. Our ultimate goal is to apply these characteristics to reconstruct the palaeo depositional environment. Sapropel S_7 has been deposited between 180,000 (Thunell et al., 1984) and 200,000 years BP (Cita and Grignani, 1982). Absolute ages have been determined by ^{14}C dating for the S_1 and S_2 sapropels only and there is agreement on an interpolated age of sapropel S_5 (ca. 125,000 years BP). No evidence was found that the sapropel investigated was redeposited, a phenomenon frequently observed (Stanley, 1986). Sapropels usually are correlated with climatic cold-warm stages and sapropel S_7 can be ascribed as an intermediate sapropel if compared with "the warm sapropel S_5" and "the cold sapropel S_6" (Cita and Grignani, 1982; Thunell et al., 1984). A new procedure was developed to decipher the mode of occurrence of lipids in the sapropel. To this end the samples were subjected to a sequential extraction (Soxhlet extraction, saponification and acid treatment). Separated fractions so obtained were derivatized and analyzed by GC and GC-MS. The gas chromatograms were used for a quantitative comparison of compounds belonging to different compound classes, but having the same mode of occurrence. Subsequent separation with thick layer chromatography was minimized to reduce the number of fractions to be analyzed.

In this study only lipids are investigated. Lipids are useful as biogenic indicators, for they show a degree a specifity relating to their biological source. However, because they form a small part of the total organic matter, only semi-quantitative conclusions can be made about the relative contribution of different inputs.

2.5. Experimental

2.5.1. Sampling

Several box cores and piston cores were collected during a 1983 expedition of the R.V. Tyro to the eastern Mediterranean. Piston cores were cut immediately in 1 m sections and horizontally stored at 4 °C. Within 24 hours a core was split lengthwise with a hydraulic cutting device. One half was immediately transferred to a walk-in refrigerator, where interstitial water was recovered, the other half was used for paleontological and sedimentological investigation. Inside the walk-in refrigerator sediment samples were taken with a bone spatula and squeezed in a glove box flushed with high purity nitrogen (see ten Haven et al., 1986c; Chapter 7). After interstitial water recovery the squeezed sediment samples together with the remaining core half were stored at - 20 °C for organic geochemical analysis. To prevent any contamination the equipment, which came in contact with the sediment, was acid cleaned and washed with demineralized water and methanol.

This paper presents data on the organic geochemistry of sapropel layer S_7 of core T83-7. The sapropel layer (37 cm) was divided into two samples on the basis of pollen zones (Ganssen and Troelstra, 1986). These two samples both consisted of a squeezed portion (see above) and an unsqueezed portion.

2.5.2. Organic carbon and $\delta^{13}C$ determination

Prior to analysis, subsamples intended for organic carbon determination and stable isotope measurements were desalted and decalcified (ten Haven et al., 1986c). The organic carbon content was determined with a Perkin Elmer CHN analyzer. $\delta^{13}C$ of the organic matter was measured after combustion at 900 °C. The isotopic difference between the sample CO_2 and an internal standard was determined with a VG Micromass 602C isotopic ratio mass spectrometer. The values are expressed per mil relative to the PDB standard.

2.5.3. Extraction and isolation procedures

The analytical scheme is outlined in Fig. 2.1. The sediment was lyophilized before extraction. The dried sediment samples (27 g and 20 g) were Soxhlet extracted with methanol/toluene (3:1 v/v) for 24 hours. The solvent was removed by means of rotary evaporation and the extract was taken up in CH_2Cl_2 and H_2O in order to desalt the extract. The CH_2Cl_2 layer was removed, using a separatory funnel and the aqueous layer was reextracted with CH_2Cl_2 three times. The combined CH_2Cl_2 extracts were dried with anhydrous Na_2SO_4. A first aliquot of this extract (Extract 1) was methylated with diazomethane, chromatographed over silica with hexane/ethylacetate (3:1 v/v) to remove very polar compounds, and silylated with BSTFA at 40 °C for 1 hour. A second aliquot of extract E1 was methylated also and subsequently subjected to thick layer chromatography according to Skipski et al. (1965). The thick layer plate (Merck, kieselgel 60; 1 mm) was pre-eluted with CH_2Cl_2/CH_3OH (1:1 v/v) and activated at 80 °C. The appro-

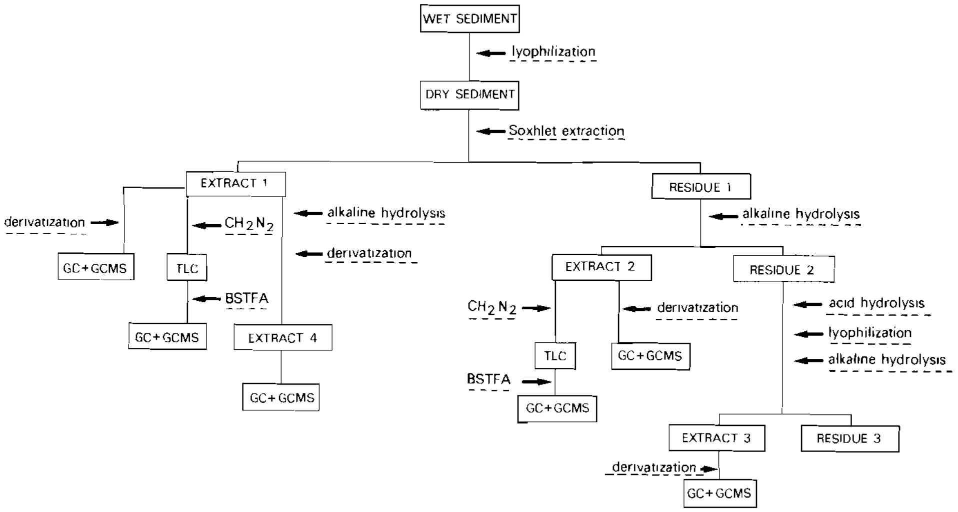

Figure 2.1. Schematic flow chart of the analytical procedures.

priate TLC fractions were silylated.

The residues after Soxhlet extraction (ca. 20 g) were dried under nitrogen and saponified with 1N KOH in 96% methanol under reflux for 1 hour (modified after Klok et al., 1986). After centrifugation the supernatant was transferred to a separatory funnel. The residue was ultrasonically washed with 2 N HCl in water/methanol (1:1 v/v), water/methanol (1:1 v/v), methanol and dichloromethane. The CH_2Cl_2 layer was separated in a separatory funnel by addition of a saturated NaCl solution. The methanol/water layer was washed with CH_2Cl_2 twice. This resulted in Extract 2, which was derivatized, and a residue. An aliquot of Extract 2 was subjected to preparative thick layer chromatography to isolate the sterols (see above).

The residue obtained after saponification was then subjected to acid treatment with 4 N HCl at 100 °C for 6 hours. Afterwards the pH was adjusted to 5 with KOH. The wet residue was lyophilized and subsequently saponified and extracted as described above. This Extract 3 was then derivatized.

A third aliquot of Extract 1 was saponified as described above and derivatized. This resulted in Extract 4.

2.5.4. Gas chromatography and gas chromatography - mass spectrometry

Gas chromatography (GC) was carried out on a Carlo Erba 4160 gas chromatograph equipped with a flame ionization detector, an on-column injector and a capillary column coated with CPSil 5 (25 m, i.d. 0.32 mm). Helium was used as carrier gas. Samples in hexane or ethyl acetate were injected at 80 °C or 100 ° C respectively and the temperature was programmed at 4 °C per minute from 130 °C to 340 °C.

Gas chromatography - mass spectrometry (GC-MS) was carried out using a Varian 3700 gas chromatograph, equipped with a capillary column coated with CPSil 5 (25 m, i.d. 0.32 mm), connected to a Varian Mat 44 quadrupole mass spectrometer, operated at 80 eV with a cycle time of 1.5 sec and a mass range of 50-550 daltons.

2.5.5. Quantitation

Total extract yields were weighed and aliquots of the extracts taken for derivatization as well. After derivatization the extracts were taken up in a known volume of solvent. The injected volume of sample was also determined. No attempts have been made to determine the absolute concentration of compounds in the sediment. The concentration of a compound in different extracts can be made comparable by multiplying the intensity of peaks with a multiplication factor. This factor compensates for dilutions made during the work-up procedure. The multiplication factor for Extracts 1, 2 and 3 is 9x, 3x and 1x respectively.

2.6. Results and discussion

Organic carbon and $\delta^{13}C$ values, as well as extract yields are presented in Fig. 2.2. The organic carbon content is high (up to 11 %)

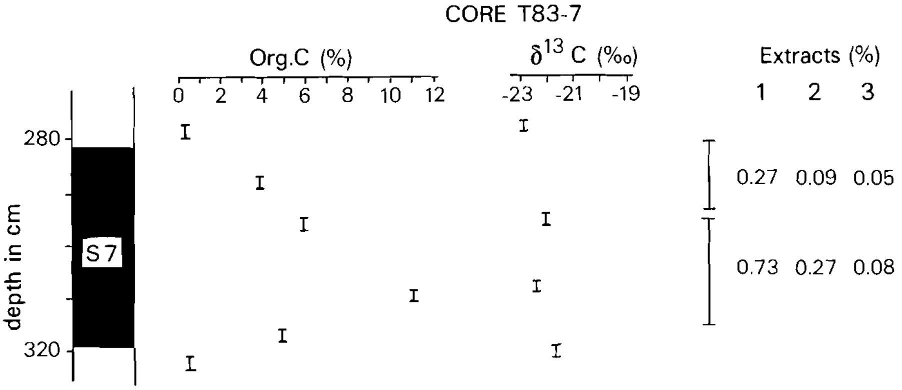

Figure 2.2. Organic carbon content, $\delta^{13}C$ of the organic matter and extract yields (expressed as % of dry sediment) shown against depth.

and varies within the sapropel. Such high values have not yet been reported for Late Quaternary sapropels (S_1-S_{12}), with one exception for sapropel S_5 (ten Haven et al., 1986c). Lunkad (1981) reported a general decrease of organic carbon in sapropels from bottom to top, which contrasts with the results obtained in this study.

Marine organic carbon is isotopically heavier (-18.6 °/oo to -23 °/oo; e.g. Gaskell et al., 1975) than most terrigenous organic carbon (-23 to -27 °/oo, Degens, 1969). Hence $\delta^{13}C$ values of organic carbon in marine sediments are interpreted in terms of relative proportions of marine and terrigenous sources. The $\delta^{13}C$ values of the sapropel organic material do not vary significantly and have values which fall in the upper range of marine organic material. It is striking that the $\delta^{13}C$ values do not vary in view of the organic carbon variations. Therefore it may be tentatively postulated that the ratio between marine organic matter and terrigenous organic matter remains constant during sapropel formation. The characterization of organic matter by means of $\delta^{13}C$ values is not always unambiguous since variable isotope fractionation during marine photosynthesis can occur (Arthur et al., 1985).

The gas chromatograms of extracts E1-E4 and E2-E3 of the lower part of the sapropel are shown in Figs. 2.3. and 2.4., respectively. The peak numbers in these figures correspond with those listed in Tables 2.1. (E1-E4) and 2.2. (E2-E3), respectively. Compound identifications are based on comparison of relative GC retention times and mass spectra with those described in the literature and with coinjection of available standards. The structures of some compounds are given in the Appendix of this chapter, and reference to these structures is made in the text with Roman numbers. We will only discuss the results obtained from the lower part of the sapropel, since the GC and GC-MS data obtained for the upper part of the sapropel were virtually identical.

2.6.1. Extract 1

The major compounds among the free lipids in Extract 1 obtained after Soxhlet extraction are the C_{30} alkan-1,15-diol (46) and a series of long chain unsaturated methyl and ethyl ketones (48-55) (Fig.2.3., upper part).

The C_{30}-alkan-1,15-diol (46, II) is the most abundant diol of a series of C_{28}-C_{32} diols. The corresponding 15-keto compound (46), coeluting on this capillary column, is the most abundant keto-ol. Gas chromatography, applying a column coated with SE 52, separated these two compounds, and it became thus clear that the C_{30}-diol is the most abundant compound. Both compounds were found in Black Sea sediments for the first time (de Leeuw et al., 1981) and were also abundantly present in sapropel S_1 (Smith et al., 1983; ten Haven et al., 1986b; see Chapter 3) and Early Pleistocene sapropels (Comet, 1982). Since these compounds have not (yet) been reported in lacustrine environments, it may be assumed that these compounds are indicators of marine

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Figure 2.3. Gas chromatograms of Extract 1 and Extract 4 of the lower part of sapropel S_7. Numbers refer to identifications listed in Table 2.1.

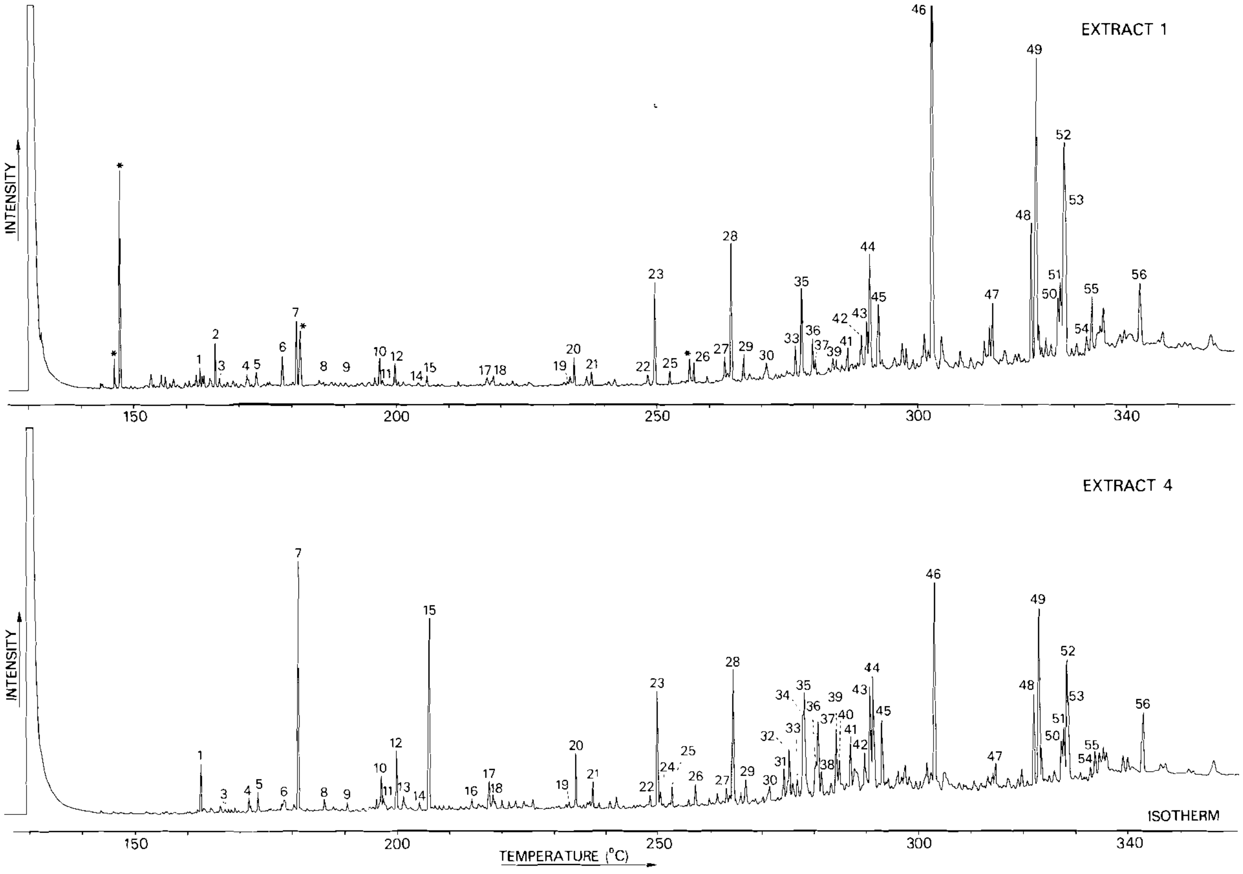
EXTRACT 1
INTENSITY
* 1 2 3 4 5 6 7 * 8 9 10 11 12 14 15 17 18 19 20 21 22 23 25 * 26 27 28 29 30 33 35 36 37 39 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56
150
200
250
300
340
EXTRACT 4
INTENSITY
1 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31 32 33 34 35 36 37 38 39 40 41 42 43 44 45 46 47 48 49 50 51 52 53 54 55 56
ISOTHERM
150
200
250
300
340
TEMPERATURE (°C)

Table 2.1. Major compounds identified by GC-MS in E1 and E4 of sapropel S_7 (Figure 2.3)

1.	n-$C_{14:0}$-FA	
2.	loliolide	
3.	i-$C_{15:0}$-FA + ai-$C_{15:0}$-FA	
4.	n-$C_{15:0}$-FA	
5.	6,10,14-trimethylpentadecan-2-one	
6.	n-$C_{16:1}$-FA	
7.	n-$C_{16:0}$-FA	
8.	n-$C_{16:0}$-OH	
9.	n-$C_{17:0}$-FA	
10.	n-$C_{18:1}$-FA	
11.	phytanic acid	
12.	n-$C_{18:0}$-FA	
13.	n-$C_{16:0}$-βOH-FA	
14.	n-$C_{18:0}$-OH	
15.	phytol	
16.	n-$C_{16:0}$-ωOH-FA	
17.	n-$C_{20:0}$-FA	
18.	n-$C_{18:0}$-βOH-FA + n-$C_{18:0}$-αOH-FA + n-$C_{18:0}$-12-OH-FA	
19.	n-C_{25}-HC	
20.	n-$C_{22:0}$-FA	
21.	n-$C_{22:0}$-OH	
22.	n-C_{27}-HC	
23.	n-$C_{24:0}$-FA	
24.	n-$C_{24:1}$-OH	
25.	n-$C_{24:0}$-OH	
26.	n-$C_{25:0}$-FA	
27.	n-C_{29}-HC	
28.	n-$C_{26:0}$-FA contaminant	
29.	n-$C_{26:0}$-OH	
30.	n-$C_{27:0}$-FA	
31.	27-nor-24-methylcholesta-5,22E-dien-3β-ol	
32.	cholesta-5,22E-dien-3β-ol	
33.	n-C_{31}-HC	
34.	cholest-5-en-3β-ol	
35.	n-$C_{28:0}$-FA	
36.	n-$C_{28:0}$-OH	
37.	24-methylcholesta-5,22-dien-3β-ol	
38.	24-methyl-5α(H)-cholest-22-en-3β-ol	
39.	24-methylcholesta-5,24(28)-dien-3β-ol	
40.	n-$C_{29:0}$-FA + 24-methylcholest-5-en-3β-ol	
41.	24-ethylcholesta-5,22-dien-3β-ol	
42.	n-C_{33}-HC + Δ^5-C_{29}-sterol ?	
43.	1,13-$C_{28:0}$-diol + 1,14-$C_{28:0}$-diol + 24-ethylcholesta-5-en-3β-ol	
44.	n-$C_{30:0}$-FA + 24-ethyl-5α(H)-cholestan-3β-ol	
45.	4α,23,24-trimethyl-5α(H)-cholest-22-en-3β-ol + n-$C_{30:0}$-OH	
46.	1,15-$C_{30:0}$-diol + C_{30}-15-keto-1-ol	
47.	1,15-$C_{32:0}$-diol ?	
48.	heptatriacontatrien-2-one	($C_{37:3}$-methylketone)
49.	heptatriacontadien-2-one	($C_{37:2}$-methylketone)
50.	octatriacontatrien-3-one	($C_{38:3}$-ethylketone)
51.	octatriacontatrien-2-one	($C_{38:3}$-methylketone)
52.	octatriacontadien-3-one	($C_{38:2}$-ethylketone)
53.	octatriacontadien-2-one	($C_{38:2}$-methylketone)
54.	nonatriacontatrien-3-one	($C_{39:3}$-ethylketone)
55.	nonatriacontadien-3-one	($C_{39:2}$-ethylketone)
56.	unknown	

derived organic matter. They might be derived from planktonic cyanobacteria (Brassell, pers. comm., 1986).

The long chain poly unsaturated methyl and ethyl ketones (48-55; e.g. I), are important compounds also. These compounds were first identified in Black Sea sediments (de Leeuw et al., 1980) and in the coccolithophore Emiliania huxleyi (Volkman et al., 1980). Recently Marlowe et al. (1984) have shown that these ketones occur also in species of Isochrysidales (prymnesiophyte algae), which are not known to bear coccoliths, thus expanding their occurrence in living algae. Coccolithophorid algae are abundant in sapropels, hence they are a likely source for the long chain ketones. These ketones are relatively more abundant in the S_7 sapropel than in the S_1 sapropel (Smith, 1984; ten Haven et al., 1986b). Sapropel S_7 is the oldest sapropel in which the presently widespread occurring coccolithophore Emiliania huxleyi appears (Cita and Grignani, 1982). As the Emiliania huxleyi acme zone begins at ca. 70,000 years BP (Gartner, 1977), the high abundance of these ketones cannot be explained merely by a contribution from Emiliania huxleyi. Moreover, Marlowe et al. (1984) have shown that these ketones occur in sediments of Eocene age and this far extends beyond the fossil record of Emiliania huxleyi, its first occurrence being dated at ca. 268,000 years BP (Thierstein et al., 1977). These ketones very likely are of marine origin and as coccolithophorid algae are abundant in sapropels they are a likely source for these compounds, but not necessary exclusively from Emiliania huxleyi.

Other relatively important classes of compounds encountered in Extract 1 are fatty acids and sterols. Recently, it has been shown that the typical distribution patterns of long chain alkanes (C_{23}-C_{33}) with a strong odd over even predominance, and their coocurrence with fatty acids (C_{20}-C_{30}) and alcohols (C_{20}-C_{30}) both with a strong even over odd predominance are not only markers for a terrigenous input, but - in more detail - for plant cuticles (de Leeuw, 1986). This points to a contribution of terrigenous organic matter, probably fluvially transported from the continent (de Leeuw, 1986). Marine fatty acids have predominantly a chain length of C_{14}-C_{22}; however the distribution pattern of fatty acids (both short and long chain) of cuticles reflects almost completely the fatty acid distribution observed in this sapropel. Hence, at least a partial terrigenous origin for the short-chain fatty acids is likely.

The major free sterol is dinosterol (45, IXi). This compound is not so abundant as in the S1 sapropel, where it is the major compound (Smith, 1984; ten Haven et al., 1986b). The biological source of this compound is believed to be dinoflagellates (Boon et al., 1979). Dinoflagellate cysts, although not abundant, were observed in this sapropel (Brinkhuis, pers. comm., 1985). The 4-desmethyl sterols are relatively minor compounds in this extract.

Loliolide (2, VI) and dihydroactinidiolide were also observed among the free lipids and the former is relatively abundant. These compounds are thought to be oxidation products of carotenoids with an origin from diatoms and/or dinoflagellates (Klok et al., 1984). As no diatoms were encountered in this sapropel (Troelstra, pers. comm., 1985) an origin from dinoflagellates seems more likely.

2.6.2. Extract 4

This extract was obtained after saponification of Extract 1. Hence, it should contain essentially the same compounds as encountered in Extract 1, plus those compounds that were originally linked by an ester bond. The saponified free extract yielded a chromatogram shown in the lower part of Fig. 2.3. The long chain ketones (48-55) are known to occur only as free compounds. Therefore differences between Extract 1 and Extract 4 are easily observed using these compounds as internal standards. The major differences of E4 with E1 are the increase of the amounts of C_{16} fatty acid (7) and phytol (15). The latter is believed to be derived from phytoplankton chlorophylls (Johns et al., 1980) and it is clear that most of the phytol, encountered at this stage, is still in its esterified form, because free phytol is only a minor compound in E1. Also, relatively important increases in concentration are observed in the steroid region, e.g $\Delta^{5,22}$ C_{27} (32; VIIa), Δ^{5} C_{27} (34; VIId), $\Delta^{5,22}$ C_{28} (37; VIIe), $\Delta^{5,24(28)}$ C_{28} (39; VIIg) and Δ^{5} C_{29} (43, VIIl) sterols are quantitatively important compounds in E4, while they were minor in E1. Fatty acids with the exception of the C_{16} component and fatty alcohols show minor increases in comparison with the long chain ketones. These phenomena can be ascribed to the presence of unhydrolyzed wax- and sterylesters and triglycerides in E1. It may be concluded that the triglycerides and sterylesters are the major contributors for the observed differences between E1 and E4, as the saponification of waxesters would produce equal amounts of fatty acids and fatty alcohols (e.g. Boon and de Leeuw, 1979). This tentative conclusion could not be verified since triglycerides and sterylesters are not amenable by the GC-MS system available.

2.6.3. Extract 2

The gas chromatogram of the extract obtained after alkaline hydrolysis of the Soxhlet extracted sediment residue (Extract 2) is shown in the upper part of Fig. 2.4. The C_{30}-alkan-1,15-diol, long chain ketones and alkanes are virtually absent in this fraction, indicating that the Soxhlet extraction has been effective. The major compounds are fatty acids (3,12,22,31,34,41,44), phytol (25) and other mono unsaturated fatty alcohols (e.g. 42), 6,10,14-trimethyl-pentadecan-2-one (7; IV), 11,18-diOH-C_{18}-fatty acid (39; III), 1,12-, 1,13- and 1,14-C_{24}-diols (45) and sterols. Minor compounds are iso- and anteiso-fatty acids (e.g. 15), mono unsaturated fatty acids, mainly $C_{16:1}$ (10) and hydroxy-acids (α-OH,β-OH,ω-OH) (e.g. 13, 17, 29).

The presence of short and long chain fatty acids in this extract indicates that these fatty acids were not only present as such (see Extract 1), but also as esterified moieties in polar and/or macromolecular structures.

The isoprenoid ketone (7) is believed to be an oxidation product of phytol originally derived from chlorophyll and it was suggested therefore that this ketone might be a marker for oxic conditions during sedimentation (Ikan et al., 1973). However, its low presence in Extract 1 and its relatively high presence in Extracts 2 and 3 seems to contradict this suggestion, since in such cases the isoprenoid ketone should be in its free form and thus present in Extract 1 only.

An alternative suggestion that this ketone is formed by microbial degradation of phytol (Brooks and Maxwell, 1974) cannot explain its occurrence in Extracts 2 and 3 either. It is hard to imagine that this compound is the result of cleavage of an ester linkage and we therefore tend to believe that it is artificially formed during both base and acid treatment.

The origin of the mono unsaturated straight chain fatty alcohols (22:1, 24:1, 26:1) is still unclear. They have been ascribed to a terrigenous origin (Gaskell et al., 1975) and to a bacterial reduction of unsaturated fatty acids (Comet, 1982). Evidence for either one of these suggestions is lacking. Their exclusive presence in Extract 2 indicates that these compounds occur as esterified moieties in polar and/or macromolecular compounds.

The 11,18-diOH fatty acid (39), with diagnostic fragment ions of 287 and 289 daltons and a rearrangement ion 258 daltons, is relatively important. This compound is reported to occur in Black Sea sediments, where it is tentatively ascribed to a cutin/suberin source (Cardoso and Eglinton, 1983). However the 11,18-diOH-C_{18} fatty acid occurs as a minor constituent in plant cuticles and when it is present other dihydroxyacids are much more abundant, such as 10,18-diOH-C_{18} acid (Holloway, 1972). Since no other cutin and suberin markers, such as 10,16-diOH-C_{16} and 9,18-diOH-C_{18} fatty acids and 9,10,18-triOH-C_{18} fatty acids (see e.g. Cardoso and Eglinton, 1983) were found, one is tempted to believe that 11,18-diOH-C_{18} fatty acid is derived from sources other than higher plants.

The odd numbered iso- and anteiso-fatty acids point to a bacterial origin (e.g. Boon et al., 1975). The even numbered fatty acids ($C_{16:0}$ (12), $C_{16:1}$ (10), $C_{18:0}$ (22)) do not preclude such a bacterial origin.

The sterol composition in this fraction is very complex and there-

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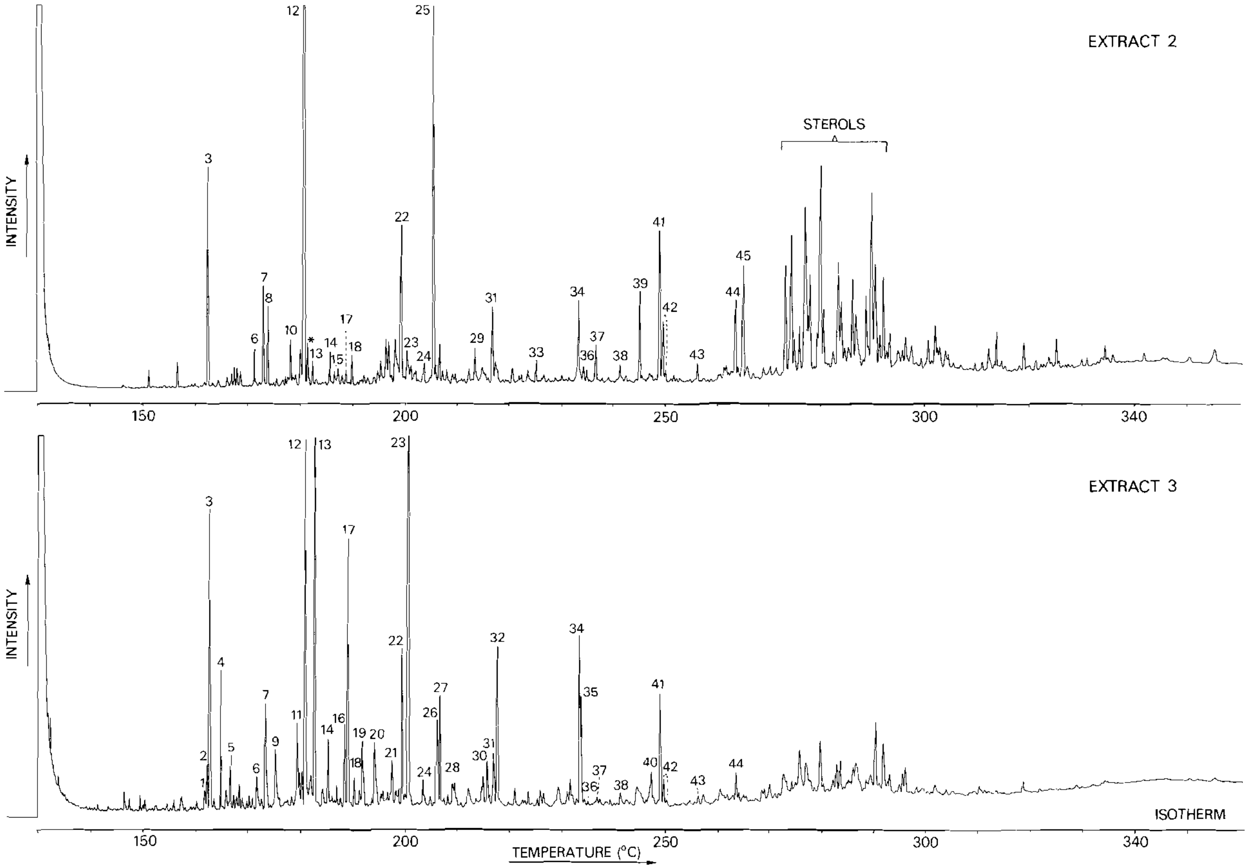
Figure 2.4. Gas chromatograms of Extract 2 and Extract 3 of the lower part of sapropel S_7. Numbers refer to identifications listed in Table 2.2.


EXTRACT 2
INTENSITY
STEROLS
3
7
8
6
10
12
*
13
14
15
17
18
22
23
24
25
29
31
33
34
36
37
38
39
41
42
43
44
45
150
200
250
300
340
EXTRACT 3
INTENSITY
1
2
3
4
5
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9
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28
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32
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35
36
37
38
40
41
42
43
44
ISOTHERM
150
200
TEMPERATURE (°C)
250
300
340

Table 2.2. Major compounds identified by GC-MS in E2 and E3 of sapropel S_7 (Figure 2.4)

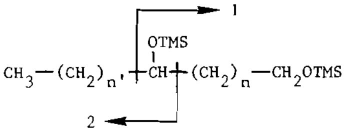
1. i-$C_{12:0}$-βOH-FA
2. n-$C_{14:1}$-FA
3. n-$C_{14:0}$-FA
4. n-$C_{12:0}$-βOH-FA
5. unknown
6. n-$C_{15:0}$-FA
7. 6,10,14-trimethylpentadecan-2-one + n-$C_{13:0}$-βOH-FA (E3) + n-$C_{13:0}$-αOH-FA (E3)
8. unknown, most prabably contaminant
9. n-$C_{15:0}$-OH
10. n-$C_{16:1}$-FA
11. i-$C_{14:0}$-βOH-FA + i-$C_{14:0}$-αOH-FA
12. n-$C_{16:0}$-FA
13. n-$C_{14:0}$-βOH-FA
14. n-$C_{16:0}$-OH
15. i-$C_{17:0}$-FA + ai-$C_{17:0}$-FA
16. i-$C_{15:0}$-βOH-FA + i-$C_{15:0}$-αOH-FA
17. ai-$C_{15:0}$- OH-FA
18. n-$C_{17:0}$-FA
19. n-$C_{15:0}$-βOH-FA + n-$C_{15:0}$-αOH- FA
20. n-$C_{16:0}$-FA (as TMS-ester)
21. i-$C_{16:0}$-βOH-FA
22. n-$C_{18:0}$-FA
23. n-$C_{16:0}$-βOH-FA
23. right shoulder n-C_{16}-9-OH-FA + n-C_{16}-10-OH-FA
24. n-$C_{18:0}$-OH
25. phytol
26. i-$C_{17:0}$-βOH-FA
27. ai-$C_{17:0}$-βOH-FA
28. n-$C_{17:0}$-βOH-FA
29. n-$C_{16:0}$-ωOH-FA
30. n-$C_{18:1}$-βOH-FA
31. n-$C_{20:0}$-FA
32. n-$C_{18:0}$-βOH-FA
33. n-$C_{21:0}$-FA
34. n-$C_{22:0}$-FA
35. n-$C_{20:0}$-βOH-FA
36. n-$C_{22:1}$-OH (2 x)
37. n-$C_{22:0}$-OH
38. n-$C_{23:0}$-FA + n-$C_{21:0}$-βOH-FA
39. 11,18-diOH-$C_{18:0}$-FA
40. n-$C_{22:0}$-βOH-FA + unknown
41. n-$C_{24:0}$-FA
42. n-$C_{24:1}$-OH (2 x)
43. n-$C_{25:0}$-FA
44. n-$C_{26:0}$-FA
45. 1,12- + 1,13- + 1,14-$C_{24:0}$-diol

fore it was decided to isolate the sterols by thick layer chromatography. The gas chromatogram of the appropriate fraction containing the residual bound sterols, fatty alcohols and several diols is partly shown in Fig. 2.5. The corresponding identifications are listed in Table 2.3.

In this TLC fraction a suite of C_{24}-C_{26} diols, not yet reported in the literature, was encountered. Four residual bound alkanediols were identified (a, c, g and a´). The chain length and the position of the midchain hydroxyl group, as a trimethylsilylether, could be determined from typical fragment ions (Table 2.4). Peak a represents three isomers, a 1,12-, a 1,13- and a 1,14-diol and peak g represents two isomers, a 1,13- and a 1,14-diol. This suite of new diols was only encountered in this extract, in contrast with the C_{28}-C_{32} diols, occurring as free compounds in Extract 1. This indicates that the short chain diols exclusively occur as esterified compounds. Although these compounds are probably potential biological markers no biological source can be suggested presently.

Table 2.4. Major fragment ions observed in mass spectra of alkandiols (a, c, g, a' in Fig. 2.5)

Compound	1	2	Identification
a	345	271	1,12-C_{24}-diol
	359	257	1,13-C_{24}-diol
	373	243	1,14-C_{24}-diol
c	359	271	1,13-C_{25}-diol
g	359	285	1,13-C_{26}-diol
	373	271	1,14-C_{26}-diol
a'	387	313	1,15-C_{30}-diol



Fragment ions are given as their di(trimethylsilyl)ethers.

As was already mentioned before, Extract 2 is ca. 3 x less concentrated than Extract 1. Still it is clear from Figs. 2.3. and 2.4. that most sterols are residual bound; the major exception being dinosterol. To eliminate the possibility that the sterols are entrapped in the calcareous mineral matrix and are released upon acidification with 2N HCl/MeOH (see experimental section), the saponification of residue R1 was also carried out omitting the neutralization step. The gas chromatogram thus obtained was similar to the gas chromatogram of Extract 2. Since the sterol composition with and without neutralization is identical, it is concluded that the sterols are bound by ester linkages to substrates, other than sterol esters. A potential source for these

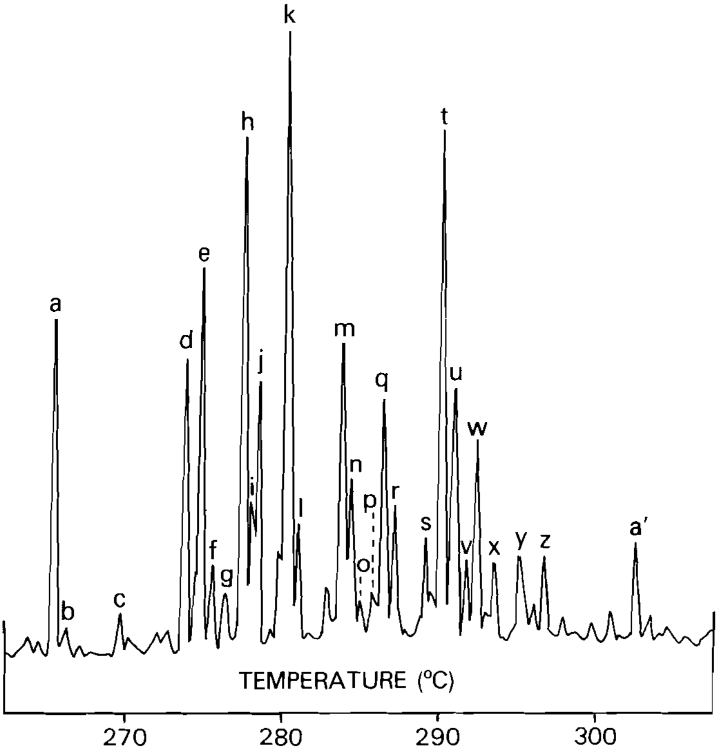


Figure 2.5. Part of the gas chromatogram of a TLC fraction of Extract 2. Letters correspond to identifications listed in Table 2.3. Compound 'a' corresponds with compound 45 in Fig. 2.4.

sterols might be polar sulphate sterols, which have been encountered in some organisms (Kates et al., 1978)

In this fraction the 4-desmethyl sterols are more abundant than the 4-methyl sterols (Fig. 2.5.), in contrast with Extract 1 where dinosterol is the most abundant sterol. This contrasts also with the results obtained from Black Sea sediments, where the 4-methyl sterols are prominent and most sterols are present as free sterols (de Leeuw

Table 2.3. Compounds identified in the sterol fraction of E2 (Figure 2.5)

Comp.	Struct.	Identification
a		1,12-dihydroxytetracosane + 1,13-dihydroxytetracosane + 1,14-dihydroxytetracosane
b	VII a	24-norcholesta-5,22-dien-3β-ol
c		1,13-dihydroxypentacosane
d	VII b	27-nor-24-methylcholesta-5,22-dien-3β-ol
e	VII c	cholesta-5,22E-dien-3β-ol
f	VIII c	5α(H)-cholest-22E-en-3β-ol
g		1,13-dihydroxyhexacosane + 1,14-dihydroxyhexacosane
h	VII d	cholest-5-en-3β-ol
i	VIII d	5α(H)-cholestan-3β-ol
j	VIII e	27-nor-24-methyl-5α(H)-cholestan-3β-ol
k	VII f	24-methylcholest-5,22-dien-3β-ol
l	VIII f	24-methyl-5α(H)-cholest-22-en-3β-ol
m	VII g	24-methylcholesta-5,24(28)-en-3β-ol
n	VII h	24-methylcholest-5-en-3β-ol +
	VIII g	24-methyl-5α(H)-cholest-24(28)-en-3β-ol ? +
	IX d	4α-methyl-5α(H)-cholestan-3β-ol
o	VIII h	24-methyl-5α(H)-cholestan-3β-ol
p	VII i	23,24-dimethylcholesta-5,22-dien-3β-ol
q	VII k	24-ethylcholesta-5,22-dien-3β-ol +
	V	12-hydroxyoctacosanoic acid
r	IX f	4α,24-dimethyl-5α(H)-cholest-22-en-3β-ol
s	?	Δ^5-C_{29}-sterol ?
t	VII l	24-ethylcholest-5-en-3β-ol +
	VIII j	23,24-dimethyl-5α(H)-cholestan-3β-ol ?
u	VIII l	24-ethyl-5α(H)-cholestan-3β-ol
v	IX h	4α,24-dimethyl-5α(H)-cholestan-3β-ol
w	IX i	4α,23,24-trimethyl-5α(H)-cholest-22-en-3β-ol
x	VII m	24-ethylcholesta-5,24(28)E-dien-3β-ol ?
y	VII n	24-ethylcholesta-5,24(28)Z-dien-3β-ol ?
z	IX j	4α,23,24-trimethyl-5α(H)-cholestan-3β-ol (two isomers)
a'	II	1,15-dihydroxytriacontane

See appendix for structural formulae.

et al., 1983). The 4-methyl sterols (r, v, w) are major compounds in Black Sea sediments and ascribed to a dinoflagellate input (de Leeuw et al., 1983). The 5α(H) stanols (i, j, o, u) might be derived from dinoflagellates (Robinson et al., 1984) also, although a microbial conversion from Δ^5-sterols cannot be ruled out (de Leeuw et al., 1983). The most abundant sterol is 24-methylcholesta-5,22-dien-3β-ol (k), which is biosynthesized by many diatoms (e.g. Lee et al., 1980), but also by Haptophycae algae such as Emiliania huxleyi (Volkman et al., 1981). Most Haptophycae also contain cholest-5-en-3β-ol (h), 24-ethyl-cholesta-5,22-dien-3β-ol (q) and 24-ethylcholest-5-en-3β-ol (t), all of them relatively significant components in this sapropel. The latter might also be derived from terrigenous detritus. An intriguing observation is the high abundance of 27-nor-24-methylcholesta-5,22-dien-3β-ol (d), which was also present as a relatively major compound in sapropel S1 and in Black Sea sediments. It is still unclear which organism or group of organisms biosynthesize this sterol. The distribution pattern of the 4-desmethyl sterols is similar to that found in the S1 sapropel (Smith, 1984). This similarity suggests a similar input, which might be mainly phytoplankton.

Coeluting with compound q is a compound with mass spectral fragmentation ions of 197, 301, 327 daltons and a rearrangement ion of 272 daltons. This compound was tentatively identified as a 12-hydroxy octacosanoic acid (V). The origin of this compound is unknown.

6.4. Extract 3

The gas chromatogram of the lipids released after subsequent acid hydrolysis of the second residue (Extract 3) is shown in the lower part of Fig. 2.4. This fraction consists almost totally of hydroxy fatty acids and fatty acids. The most important compounds in this mixture are the n-C_{14} and n-C_{16} β-hydroxy fatty acids (peaks 13 and 23). Fig. 2.6. shows part of the mass chromatogram of m/z 175, indicative of β-hydroxy fatty acids (Eglinton et al., 1968). The branched chain β-hydroxy fatty acids were not positively identified but the presence of iso-C_{12}, C_{14}, C_{16}, C_{18} and C_{20} and both iso- and anteiso-C_{13}, C_{15}, C_{17} and C_{19} acids is based on their elution behaviour and mass spectra (Boon et al., 1977). A few other compounds with characteristic ions at m/z 133 and 175 are present in minor amounts (unlabeled peaks in Fig. 2.6.). They were not further identified. One relatively important compound is tentatively identified as a $C_{18:1}$ β-hydroxy fatty acid (30 in Fig. 2.4.) based on an important fragment ion at m/z 369 (M-15). The β-hydroxy fatty acids are thought to reflect a microbial contribution (e.g. Cranwell, 1981a; Cardoso and Eglinton, 1983). Goossens et al. (1986) have shown, applying the same isolation procedure, that amide bound β-hydroxy fatty acids from lipopolysaccharides (LPS) of gram negative bacteria exclusively occur in the acid hydrolysable fraction. Although present in small quantities the presence of α-hydroxy fatty acids, almost coeluting on this capillary column with the β-hydroxy fatty acids, could be inferred with diagnostic ions M-59 and m/z 129 and by scanning the front- and rearside of a GC peak. α-Hydroxy fatty acids were observed also in the acid labile fraction of some bacteria (Goossens et al., 1986).

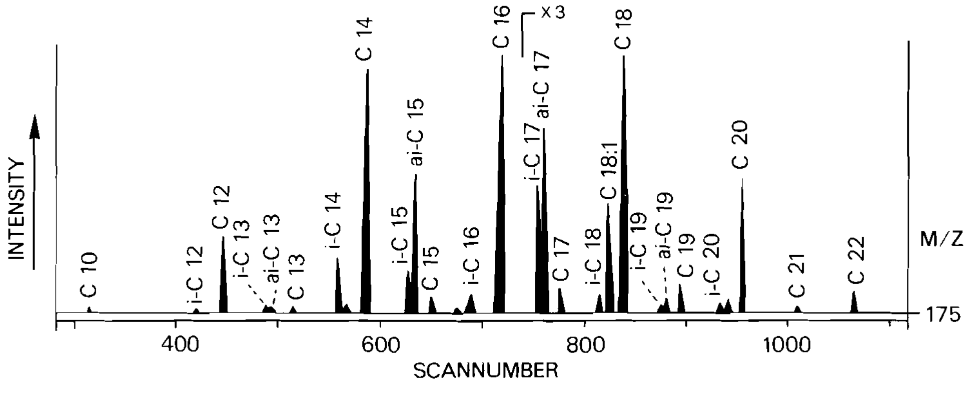


Figure 2.6. Mass chromatogram of m/z 175 in Extract 3, indicative of β-hydroxy fatty acids.

The question remains whether these bacteria are actually living in the sapropel or whether remnants of bacteria living at the time of deposition are left behind. The lower pH measured in interstitial waters recovered from this sapropel sequence (ten Haven et al., 1986c) might be ascribed to ongoing bacterial activity.

2.7. Conclusions

The lipids investigated make up only a small part of the total organic matter present. Nevertheless they carry valuable information with respect to their original biological source. Assuming that the lipids can be used as a representative reflection of the total organic matter, it can be concluded that the organic matter of sapropel S_7 is of mixed marine, terrigenous and bacterial origin with the former probably predominating. This conclusion is to some extent supported by the $\delta^{13}C$ values of the organic matter. The long chain unsaturated ketones, the alkandiols, phytol, loliolide and most sterols reflect a marine input. The long chain alkanes, fatty acids and alkanols, occurring as free extractable compounds, are ascribed to a terrigenous input. A bacterial contribution to the organic matter is exemplified by the presence of iso and anteiso fatty acids and β-hydroxy fatty acids, the latter compounds almost exclusively occurring in the acid labile fraction. It is clear that the analysis of only free extractable organic compounds would lead to an overestimation of the terrigenous input and an underestimation of the bacterial contribution. The sequential analyses provide more detailed information, whereby a better estimate of different sources of input can be made.

Compelling evidence exists for a low salinity surface layer (e.g. Cita et al., 1977; Vergnaud-Grazzini et al., 1977; Thunell et al., 1977; Williams et al., 1978), which could be nutrient rich (cf. Rossignol-Strick et al., 1982) and inducing a concomitant high primary productivity. This low salinity surface layer could also have prevented thermohaline convection, resulting in a density stratification (Olausson, 1961), although a completely stratified water column is no prerequisite for sapropel formation (de Lange and ten Haven, 1983; see also Morris et al., 1984). A model for the formation of sapropel S_7 is depicted in Fig. 2.7. This model combines stagnation and high productivity. The high organic carbon content and its variation within the samples of sapropel S_7 supports a high varying productivity (see also Calvert, 1983). High productivity can either be induced by nutrient rich upwelling waters containing silica or by nutrient rich, low silica river discharge. As no diatoms were found at

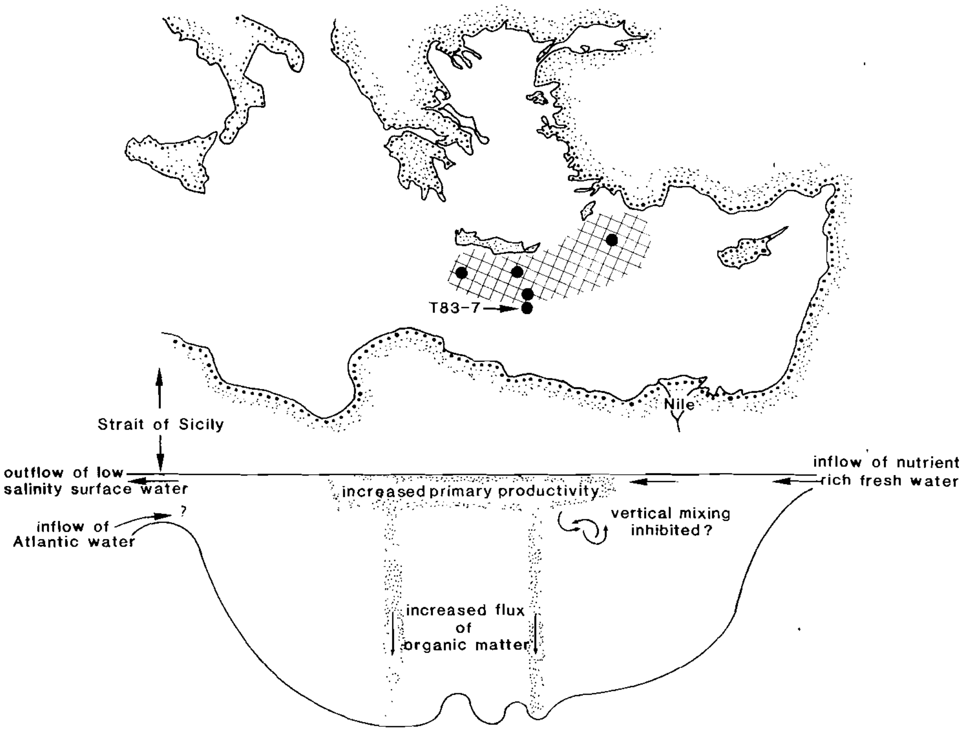
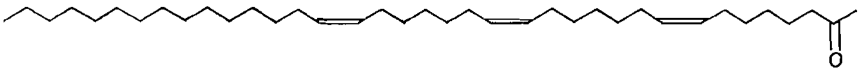


Figure 2.7. Map and schematic profile of the eastern Mediterranean. The map shows the location of core T83-7 and the locations of the four cores, where diatoms were encountered in the S_5 sapropel. The inferred areal distribution of diatom occurrence in sapropel S_5 is hatched (after Schrader and Matherne, 1981). The profile illustrates the proposed model for formation of sapropel S_7.

site T83-7 and because of the relatively high amounts of fluvial terrigenous material, it is thought that the high productivity is induced by increased river discharge (Rossignol-Strick et al., 1982) and not by upwelling. However, this particular model cannot be generalized, because diatoms were found in other sapropels at other sites (Schrader and Matherne, 1981). Judging from the distribution pattern of diatoms in sapropel S_5 over the eastern Mediterranean (Fig. 2.7., Schrader and Matherne, 1981), it is clear that upwelling, as a cause of sapropel formation, is restricted to a small area.

APPENDIX

I



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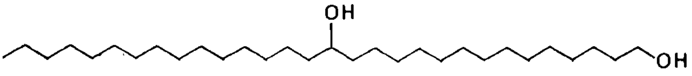

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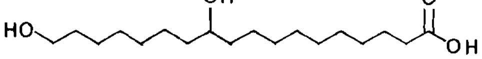

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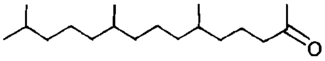

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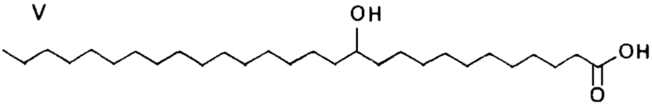

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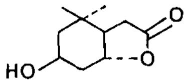

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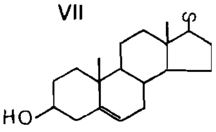

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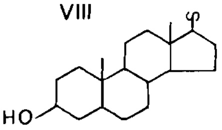

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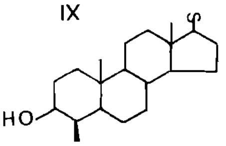

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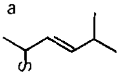

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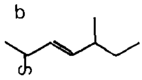

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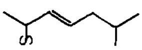

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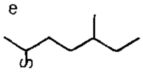

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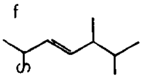

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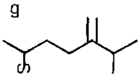

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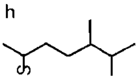

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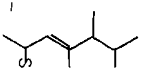

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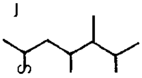

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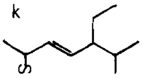

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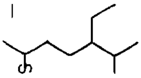

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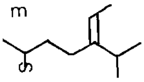

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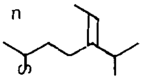


Chapter 3

LATE QUATERNARY MEDITERRANEAN SAPROPELS II: ORGANIC GEOCHEMISTRY AND PALYNOLOGY OF S_1 SAPROPELS AND ASSOCIATED SEDIMENTS

Abstract

Six S_1 sapropel samples from the eastern Mediterranean were investigated organic geochemically to study the lateral variation within this organic rich layer. Five of these samples were also analyzed palynologically. In addition, some sediment samples from below and overlying the sapropel intervals were investigated for their organic geochemical characteristics.

Organic matter of S_1 sapropels is of a mixed marine, terrigenous and bacterial origin. A trend of relatively increasing amounts of continentally derived organic matter towards more seaward and deeper realms can be observed from both palynological and organic geochemical data. This trend is supported to some extent by $\delta^{13}C$ values of the organic matter.

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

caused by better preservation conditions.

An increasing discharge from the Nile seems to be the driving force for formation of the S_1 sapropels. Based on this assumption a model for sapropel formation is proposed. Although not all the data could be explained properly by this model, most phenomena are explained.

3.1. Introduction

Black organic rich layers, so-called sapropels, are widely distributed over the eastern Mediterranean. Sapropel layers in the Mediterranean are defined as those containing more than 2% organic carbon and having a thickness greater than 1 cm (Kidd et al., 1978). Therefore, not all reported organic rich layers are true sapropels, as sometimes the organic carbon content is below 2%. Layers, containing 0.5 - 2% organic carbon are defined as sapropelic layers (Kidd et al., 1978). In the Late Quaternary the occurrence of at least twelve sapropels has been recorded (Cita and Grignani, 1982). The youngest one (S_1) has been dated by the ^{14}C method at 7000-9000 yr BP (e.g. McCoy, 1974). This Holocene sapropel has been the object of most sapropel studies, owing to the fact that this layer can be easily recovered by conventional box, gravity and piston coring. Its occurrence over the eastern Mediterranean extends from the Cilicia basin (Shaw and Evans, 1984) and the Nile Cone (Stanley and Maldonado, 1977) via the Ionian Sea (Stanley, 1978) up into the Adriatic (Van Straaten, 1972). This layer has also been recorded in the Aegean sea (Perissoratis, 1982; Cramp et al., 1984). In a detailed investigation of the youngest sapropel Anastasakis and Stanley (1984) clearly showed that a large variety of organic rich layers may be encountered, indicating that the environment of deposition was not uniform over the entire eastern Mediterranean. Recently Stanley (1986) has shown that turbidity currents can considerably modify the development of sapropels.

Controversial ideas exist about the origin of the organic matter in the Mediterranean sapropels (see ten Haven et al., 1986a; Chapter 2) and little is known of the palynology of Late Quaternary Mediterranean sapropels. Calvert (1983) concluded that "a detailed examination of the composition of the most recent sapropel is required. It is necessary to identify organic marker compounds that can be used to characterise unequivocally terrestrial and marine organic matter sources ...".

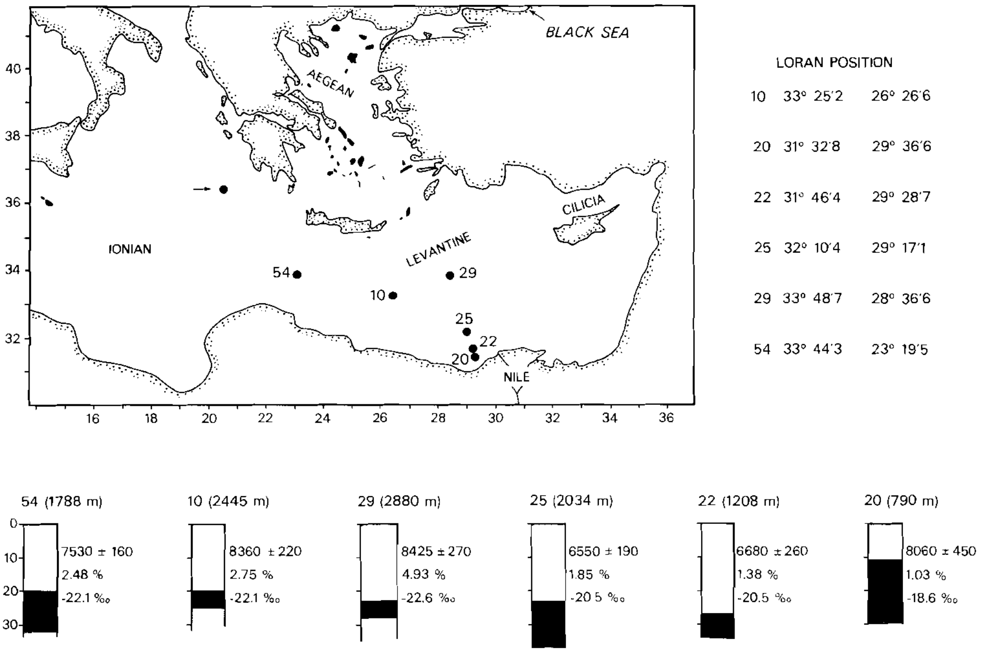
The aim of present study was (1) to study the lateral organic geochemical variation within the S_1 sapropel, (2) to identify the differential palynofacial units and palynomorphs groups and (3) to look for a correlation between the palynological and the organic geochemical data.

Six S_1 sapropel samples were analyzed (Fig. 3.1.) and also some sediment samples from below and overlying the sapropel. The sapropel samples were chosen in such a way that they form a transect across the eastern Mediterranean. The samples appear to be ideally suited to test the hypothesis of Rossignol-Strick et al. (1982), who suggested that an excess nutrient rich fresh-water overflow from river Nile triggered the sapropel formation. The results will be discussed in conjunction with the results of Smith (1984) and compared with those obtained from a S_7 sapropel (ten Haven et al., 1986a). The S_1 sapropel studied by Smith and co-workers (Smith, 1984; Smith et al., 1983; 1986; Poutanen and Morris, 1985) was collected from core 10103, located on the Hellenic Outer Ridge, south west of the Peloponnesos (Fig. 3.1.).

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

3.2. Sampling and analytical methods

Box cores were collected during a cruise of the R.V. Tyro to the eastern Mediterranean in 1983. The locations of the box cores from which samples are taken, are presented in Figure 3.1., together with a schematic lithological column. Bulk samples for organic geochemical



LORAN POSITION

10	33° 25'2	26° 26'6
20	31° 32'8	29° 36'6
22	31° 46'4	29° 28'7
25	32° 10'4	29° 17'1
29	33° 48'7	28° 36'6
54	33° 44'3	23° 19'5

Figure 3.1. Location sites of the box cores investigated and their position based on Loran C navigation. Water depth is given between brackets. The gravity core (core 10103) investigated by Smith (1984) is indicated with an arrow. A schematic lithological column indicating the sapropel interval in black is presented. Next to these columns the results of the sapropel subsamples are listed. These are from top to bottom: radio carbon age of the organic matter in years BP, organic carbon content in %, and $\delta^{13}C$ of the organic matter in $^{o}/oo$.

research were taken with a bone spatula and stored at -20°C. Subsamples were taken for organic carbon, $\delta^{13}C$ and ^{14}C dating analyses. Aliquots of these same samples (ca. 3 g) were investigated palynologically using standard techniques (sample 25 was not investigated). Briefly, the mineral matrix was removed by destruction in HCl and HF and the remaining material subsequently separated in a light and a heavy fraction, applying a $ZnCl_2$ solution with a specific gravity of

2.0 (Funkhauser and Evitt, 1959). The light fraction was then sieved through a 10 µm sieve, homogenized by stirring and subsequently two slides of each sample were prepared using a glycerol-jelly medium for light-microscopic investigation. No bleaching techniques were used.

Circa 300 discrete units (> 10 µm) were counted of each sample and categorized in a palynofacial classification scheme, developed at the Laboratory of Palaeobotany and Palynology (State University of Utrecht) comparable with a.o. Staplin (1969), Habib (1979a, b) and Batten (1981). This classification scheme comprises five groups: 1. Amorphous Organic Matter (AOM) (dispersed and/or discrete units), 2. Opaque non-structured elements, 3. Plant tissue remains, 4. Palynomorphs (all classes) and 5. Animal remains (vertebrate and invertebrate). A full report of the palynofacies classification is beyond the scope of the present paper.

Prior to organic geochemical analyses the samples were lyophilized, homogenized and divided into two portions. One portion was analyzed according to the "total lipid" method (Klok et al., 1986), which results in one extract containing both free and alkaline labile compounds. The other sediment portion was analyzed following a method described by ten Haven et al. (1986a). This method results in three extracts, the first one containing free organic compounds, the second one alkaline labile compounds and the third one acid labile compounds. This approach offers an insight into the mode of occurrence of lipids. Some sapropel samples were subjected to this latter method.

Prior to gas chromatographic analyses all extracts were derivatized. The gas chromatographic and gas chromatographic - mass spectrometric conditions are described by ten Haven et al. (1986a). In this study, however, the gas chromatograph was equipped with a capillary column coated with SE 52, instead of CP Sil 5.

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

3.3. Results and Discussion

3.3.1. Palynological investigation

The results are presented in a semi quantitative manner (Table 3.1.). All samples show large quantities of plant tissue remains, including cuticle (Plates I.2., I.5., I.8.), wood remains (Plate I.3.), thracheid (Plates I.1., I.4.), and opaque branch like fragments. The opaque non-structured elements are classified as "abundant" to "present". The AOM (Plate I.10.), in most cases "dominant", possesses a yellowish-brownish colouration. An increase of plant tissue remains, as well as opaque elements towards the deeper realms can be observed. The palynomorphs form only a minor group within the total organic matter encountered (Table 3.1.). Therefore this group will be

Table 3.1. Palynofacies

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

- = rare; + = present; ++ = abundant; +++ = highly abundant

++++ = dominant Sample 25 was not investigated.

discussed separately (Table 3.2.). In samples 10, 29, and 54 fragments tentatively assigned to arthopoda remains (Plates II.7., II.10.) have been observed.

Important within the fluctuating assemblages of palynomorphs, are land derived elements (spores, pollen, and fungal spores) (Table 3.2.; Plates I. and II.). In addition to these categories of palynomorphs scytinascs, dinoflagellate cysts, acritarchs and representatives of the multicellular alga Pediastrum Meyen, 1829 are observed. Other algal remains (Table 3.2.) are those unassignable to the above mentioned groups.

Table 3.2. Palynomorphs

		54	10	29	22	20
Palynomorphs general		++	++	-	-	+
LAND	Spores	+	++	+	-	+
	Pollen	++	+	+	-	++
	Fungal spores	-	+	-	-	+
AQUATIC	Dinoflagellate cysts	+	++	+	-	+
	Acritarchs	+	+	-	-	+
	Scytinascs	+	+	+	+	-
	Pediastrum	-	-	+	+	+
	Other algal remains	+	+	++	+	+

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

A relative abundance of these "aquatic" palynomorphs has been observed in sample 10. Within the group of dinoflagellate cysts, species assignable to the genera Spiniferites Mantell, 1850, emend.

Sarjeant, 1970 (Plates II.1., II.2.) and Impagidinium Stover and Evitt, 1978 (Plate II.3.) are dominant (see Lentin and Williams, 1985 and references cited therein). Similar observations were made by Wall et al. (1977) and Harland (1983). Many of the observed aquatic palynomorphs may have a fresh or brackish water origin, especially the encountered forms assignable to Pediastrum (Plate II.4.), a genus known to occur exclusively in these kinds of environments (Evitt, 1963). Only the encountered species of dinoflagellate cysts and acritarchs are certainly of marine origin, in addition to most forms assignable to the scytinasc group (e.g. Plate II.5.).

3.3.2. Geochemical investigation

Data of the sapropel subsamples are given next to the schematic lithological column (Fig. 3.1.). Ordered are from top to the bottom ^{14}C dating of the organic matter, organic carbon content and $\delta^{13}C$ values of the organic matter respectively.

The radio carbon data point to a range in age from ca. 6,600 to 8,500 years B.P., corresponding with data reported before for the S_1 sapropel (e.g. McCoy, 1974; Stanley and Maldonado, 1977). The three cores collected on the Nile Cone (samples 20, 22 and 25) contain sapropelic sequences instead of true sapropels. In these cores the bottom of the sapropelic layer was not penetrated. These cores are collected in a zone, where the highest sedimentation rates in the Nile Cone area are measured, up to 88 cm per 1,000 yr (Stanley and Maldo-

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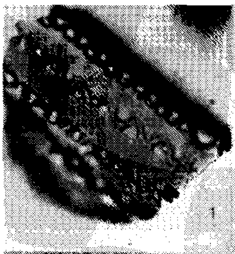
Plate I.1. Tracheial tissue, x 1000 (sample 10); 2. Fragment of leaf cuticle with stomata, x 400 (sample 54); 3. Wood remains, x 400 (sample 10); 4. Tracheial tissue, x 400 (sample 10); 5. Leaf cuticle, x 400 (sample 10); 6. Plant fragment, x 400 (sample 54) A = angiosperm pollen grain; 7. Spiral tracheids, x 400 (sample 54); 8. Cuticle fragment, x 400 (sample 54); 9. Cuticle fragment, x 1000 (sample 54); 10. AOM, x 400 (sample 54).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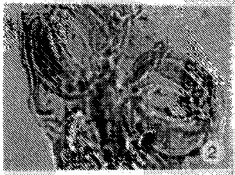
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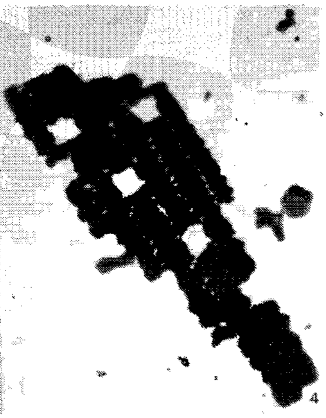
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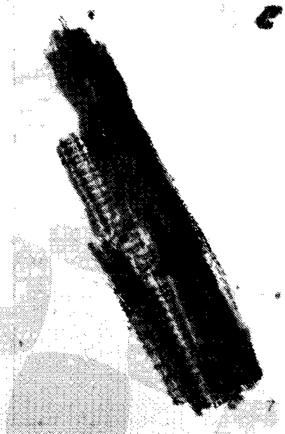
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8

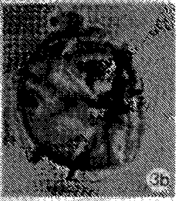

9


10


1a


1b


3a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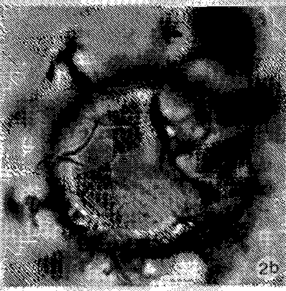
2a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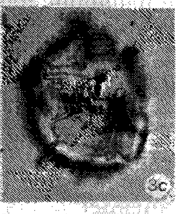
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9a


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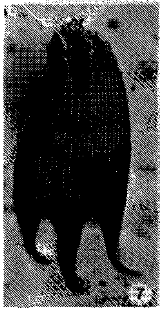
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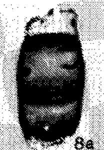
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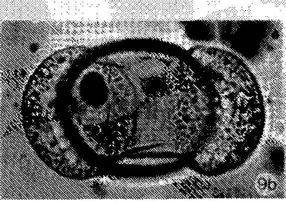
8b


9b

nado, 1977). Therefore, it is not surprising that these cores bear sapropelic intervals with expanded thicknesses and a "diluted" organic carbon content in comparison with the other cores. However, it is equally possible that the expanded thickness and relatively low organic carbon content is the result of redepositional events (Stanley, 1986). The sapropels in cores 10 and 54 have a similar organic carbon content to the sapropel in the core studied by Smith and co-workers (Sutherland et al., 1984). The sapropel in core 29 is characterized by a higher organic carbon content. The $\delta^{13}C$ values show a remarkable trend. Near the mouth of the Nile the $\delta^{13}C$ values resemble marine organic matter, while in the middle of the Mediterranean (core 29) a certain amount of the organic matter seems to be of terrigenous origin. The mean $\delta^{13}C$ value of core 10103 (-20.6 $^{o}/oo$; Sutherland et al., 1984) corresponds with the values measured in cores 22 and 25, suggesting that the input of terrigenous organic matter is highest in the middle of the Mediterranean.

Plate II.1. Spiniferitis sp., a: high focus, b: low focus, x 1000 (sample 10); 2. Spiniferitis sp., a: mid focus, b: low focus, x 1000 (sample 29); 3. Impagidinium sp., a: high focus showing precingular archeopyle, b: mid focus, c: low focus, x 400 (sample 22); 4. Pediastrum simplex (Meyen) Lemmermann 1897, x 400 (sample 20); 5. Scytiniasc (planktonic foraminiferal remain), x 400 (sample 10); 6. Angiosperm pollen grain, high focus, x 1000 (sample 29); 7. Arthopodal remains (?), x 400 (sample 10); 8. Multicellular fungal spore, a: low focus, b: high focus, x 400 (sample 29); 9. Bisaccate pollen grain, a: high focus, b: low focus, x 400 (sample 29); 10. Arthopodal remains (?), x 400 (sample 54).

3.3.3. Vertical organic geochemical variation

Samples from below and overlying the sapropel interval were investigated in order to obtain information about the vertical organic geochemical variation within a box core. The "total lipid" gas chromatograms of extracts from three sections in box core 29 including a S_1 sapropel are presented in Figure 3.2. Identifications of labeled compounds is given in Table 3.3. Quantitative results of selected compounds are presented in Table 3.4.

The major differences beween sapropel and non-sapropel sediments are, of course, the high organic carbon content of the sapropel layer and the concomitant high concentration of extractable organic compounds. Other characteristic differences are the low concentration of sterols (e.g. 52, 53, 60), phytol (16) and long chain diols (49, 62, 65), and the relative high concentration of $C_{18:1}$ fatty acids in non-sapropel samples. Further, differences in the ratios between n-alkanes, n-fatty acids and n-alkanols are noticed (Fig. 3.2. and Table 3.4.). Typical compounds, such as 9,16-C_{16}- (25) and 11,18-C_{18}- (31) dihydroxy fatty acids were only observed in the sapropel samples. Most of these differences were also observed by Smith (1984). In all sapropel samples the following intensity distribution is observed in the C_{20}-C_{30} fatty acid range (peaks 20-58): n-C_x-FA > n-C_x-ROH > n-C_{x+3}-HC whereas in the non-sapropel samples the sequence n-C_{x+3}-HC > n-C_x-FA > n-C_x-ROH is mostly observed ($x = 20,21,..,30$). These compounds are considered to be of a terrestrial origin. The distribution pattern of these compounds in the sapropels mimics the distribution pattern observed in cuticles (de Leeuw, 1986; Nip et al., 1986). Cuticles, which are indeed observed in the sapropels (Plate I.), are likely to be fluvially transported during periods of excessive fresh water inflow (e.g. Rossignol-Strick et al., 1982; Pratt, 1984). The dihydroxy fatty acids also point to a terrigenous input during sapropel formation. The explanation of Smith (1984) that this alternating distribution pattern is the result of a relative enrichment of n-alkanes, due to a faster degradation of more labile compounds (fatty

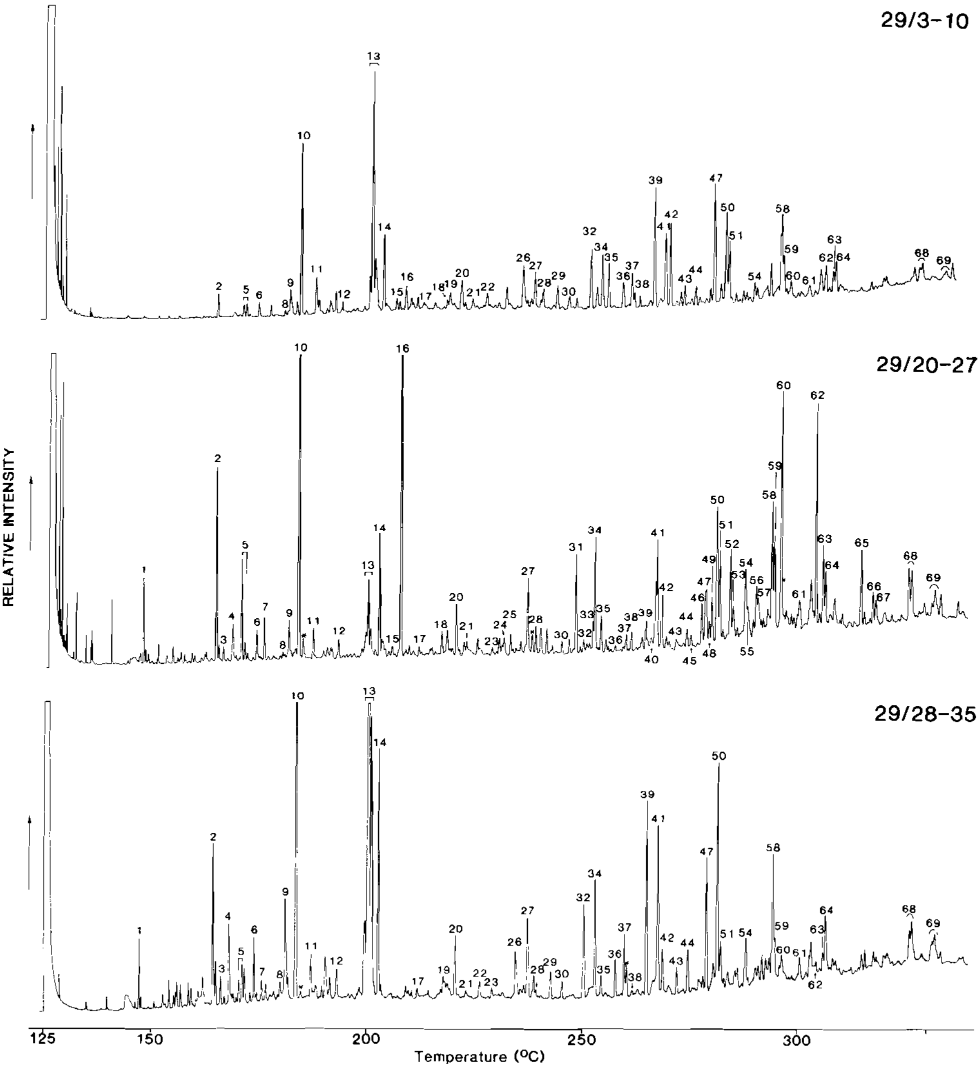


Figure 3.2. Gas chromatograms of the "total lipid" extracts from three samples of box core 29. Section 20-27 (depth in cm from sediment-water interface) represents the S_1 sapropel. Peak numbers correspond to the numbers mentioned in Table 3.3. Contaminants are labeled with an asterisk.

Table 3.3. Compounds identified by GC-MS, indicated in Figure 3.2.

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

* tentative assignment

acids, alcohols) under oxic conditions prevailing during time of deposition might be too limited. This distribution pattern can also be explained by two different mechanisms of input, viz. an eolian transport and a fluvial transport. The distribution pattern in the non-sapropel samples is dominated by n-alkanes, and shows similarities with distribution patterns observed in eolian dusts (Simoneit, 1977).

It might equally be possible that the characteristics of the non-sapropel sediments are mainly the result of an eolian input. As long-chain alkanes are very refractory compounds (Cranwell, 1981b), it can be concluded from the quantitative results (Table 3.4.), that the input of continentally derived organic matter is higher during sapropel formation. As it is unlikely that anoxic conditions are solely responsible for the enhanced concentration of these compounds in sapropels, an increase of fluvially transported terrigenous material can be inferred.

Table 3.4. Quantitative results of selected compound in box core 29.

Compound		3-10 cm	13-19 cm	20-27 cm	28-35 cm
n-C_{16}-FA	(10)	340	800	18650	440
n-C_{27}-HC	(32)	115	100	550	80
n-C_{24}-FA	(34)	100	80	3580	100
n-C_{24}-OH	(35)	90	50	1120	20
dinosterol	(60)	40	<10	7770	25
C_{30}-diol	(62)	60	<10	7300	15
C_{37}-ketones	(68)	65	<10	3360	70

Values are expressed in ng/g dry sediment. Numbers between brackets correspond with those listed in Table 3.3.

The position of the double bond in the monounsaturated fatty acids was not determined. However, with a view on the results of Smith (1984), it is assumed that Δ^9- and Δ^{11}-C_{18} fatty acids are the most abundant monounsaturated fatty acids. These compounds and the iso and anteiso C_{15} and C_{17} fatty acids most probably reflect a contribution from bacterial lipids (e.g. Boon et al., 1975; 1978). β-Hydroxy fatty acids (C_{12}-C_{20}) are important compounds in the acid labile fraction of sapropels (not shown here, see ten Haven et al., 1986a), supporting a bacterial contribution to the organic matter (Goossens et al., 1986).

Sterols are relatively important compounds in the sapropel, 4α,23,24-trimethyl-cholest-22-en-3β-ol (dinosterol) being dominant. This compound and other observed 4-methyl sterols can be attributed to a dinoflaggelate input (Boon et al., 1979; de Leeuw et al., 1983; Robinson et al., 1984). Dinosterol is also the most important sterol in the S_1 sapropel investigated by Smith (1984). Smith attributed the predominance of sterols in sapropel samples to a higher degree of preservation (i.e. anoxic environment of deposition) and to a higher productivity during sapropel formation. The latter was deduced from the observation that fatty acids are more abundant than sterols in the non-sapropel samples, whereas these compounds probably degrade faster than sterols (Cranwell, 1981b).

The isoprenoid alcohol, phytol, is the second most abundant compound in the sapropel sample, and is for the larger part present in the sediment in an esterified form. This compound is present in the non-sapropel samples in very low concentrations. These low concentrations are probably due to an enhanced degradation of chlorophyll under oxic conditions. Also, an additional input of chlorophyll during sapropel formation as a result of an increased primary productivity increases the phytol concentration, but a quantitative estimate of this additional input cannot be made. Phytol reflects an autochthonous rather than an allochthonous input, because it is not expected to survive intact during transportation from the continent to the deep sea (Brassell et al., 1980).

Othercharacteristic compounds occurring in varying amounts in all samples, are the C_{30}-alkan-1,15-diol and a series of long chain unsaturated ketones. The former compound might reflect an input of planktonic cyanobacteria (Morris and Brassell, 1986), the latter compounds can be ascribed to an input of the coccolithophorid algae _Emiliania huxleyi_ (de Leeuw et al., 1980; Volkman et al., 1980). An origin for the long chain ketones from _Emiliania huxleyi_ is inferred from the fact that the samples investigated are deposited well within the _Emiliania huxleyi_ acme zone (Gartner, 1977), although the long chain ketones are also found in other algae (Marlowe et al., 1984).

In section 29/3-10 some compounds, all with a C_{29} skeleton, were observed, which were virtually absent in the sapropel. These compounds (not indicated in Fig. 3.2. and Table 3.3.) are tentatively identified as 24-ethyl-cholest-2-ene, 24-ethyl-cholest-4-en-3-one and 4-methyl-24-ethyl-19-nor-cholesta-1,3,5(10)-trien. Δ^2 sterenes occur ubiquitously in recent sediments and are believed to be intermediates in the diagenetic degradation of sterols (Dastillung and Albrecht, 1977). The occurrence of the A-ring monoaromatic steroid is, to our knowledge, the first report of this compound in such recent sediments. Although it has been suggested that the aromatization of ring A of the precursor sterols begins at a very early stage of diagenesis (Hussler et al., 1981), we tend to believe, based on its limited occurrence in our samples, that this compound reflects an input of reworked organic matter.

3.3.4. Lateral organic geochemical variation

The GC and GC-MS data of all other S_1 sapropel samples are virtually identical to the results described above. Overall the organic geochemical characteristics of the S_1 sapropels are similar to the characteristics of the older sapropel S_7 (ten Haven et al., 1986a). Differences, however, are observed in the relative abundancies of the compounds encountered. The discussion of the lateral variation is focussed on differences in concentration of some selected compounds (Table 3.5.). An assessment of the data in terms of lateral input variation is difficult, since the absolute concentrations of compounds is influenced by variations in sedimentation rates, in primary productivity and in preservation conditions. Throughout the following discussion two assumptions have been made:

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

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

A terrestrial input to the organic matter is not only evident from the palynological investigation, but also from "terrestrial" biological markers, such as long straight chain alkanes, alkanols and fatty acids. Figure 3.3. shows a typical distribution pattern of alkanes of sample 54 with a strong odd over even predominance of long chain alkanes (CPI_{24-34}). This kind of distribution pattern is indicative for an origin from higher plant material and also confirms the low maturity of the sediment. Other compounds which might be attributed to a terrigenous origin are the dihydroxy fatty acids, such as 9,16-diOH-

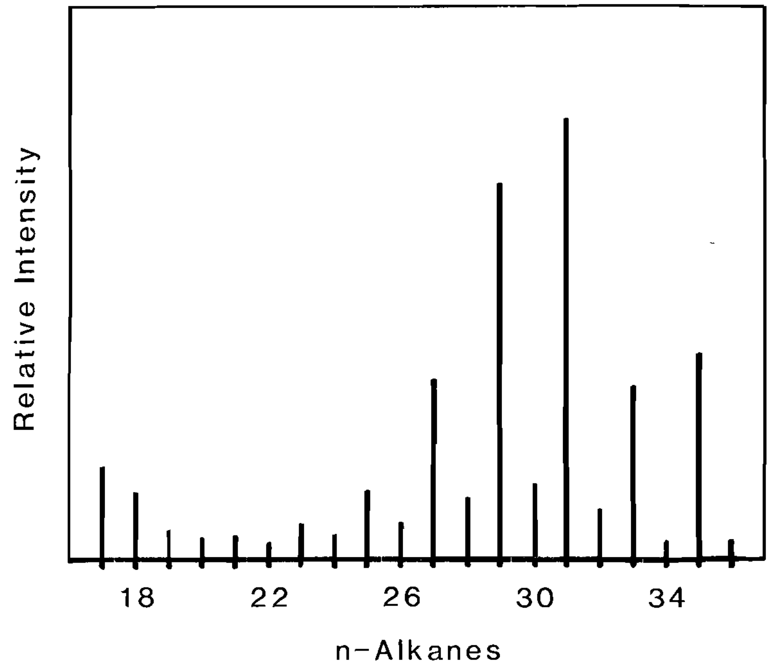


Figure 3.3. Relative distribution of n-alkanes in the S_1 sapropel of box core 54.

$C_{16:0}$ fatty acid and 11,18-diOH-$C_{18:0}$ fatty acid. A contribution from another source (especially for the 11,18 dihydroxy fatty acid) can at present not be precluded (Cardoso and Eglinton, 1983; ten Haven et al., 1986a). The relative high abundance of 24-ethylcholest-5-en-3β-ol (Fig. 3.2., peak 58) might also be attributed to a terrigenous input, although Volkman (1986) pointed out that the application of this compound as a biological marker for terrigenous organic matter can lead to erroneous conclusions.

The variation in concentration of the n-C_{27} alkane (as ng/g dry sediment, Table 3.5.A.) is visualized in Figure 3.4. The distribution pattern of this alkane provides an insight in the input variation of continentally derived organic matter. This input seems to most pronounced at site 29, a conclusion supported by the $\delta^{13}C$ values of the organic matter (Fig. 3.1., correlation coefficient r between $\delta^{13}C$ and n-C_{27} is 0.75) and to some extent by the palynological investigation. This phenomenon can not be observed when the data are normalized for differences in the organic carbon content (Fig. 3.4. and Table 3.5.B.). The objective of this normalization is to correct for organic carbon dilution, caused by different sedimentation rates at different sampling sites and for redepositional events. Based on these normalized data the input of terrestrial organic matter, as exemplified by n-C_{27}, is relatively low at site 29, contradicting the $\delta^{13}C$ results. This discrepancy might be caused by differences in primary productivity and preservation conditions. It is postulated that at site 29 the environment of deposition was more favourable for preservation of organic matter than at the other sites. A comparison can be made with the sapropel of box core 10, which has a comparable thickness as the sapropel of box core 29 and an equal sedimentation rate might be suspected. The sapropel at site 29 is, however, marked by a higher organic carbon content (4.93 %) and a concomitant higher concentration of extractable organic compounds (Table 3.5.). The preservation conditions might be indirectly linked with the water depth, as box core 29 was collected from deeper realms. It is generally assumed that sapropels are deposited under anoxic conditions and it can be imagined that

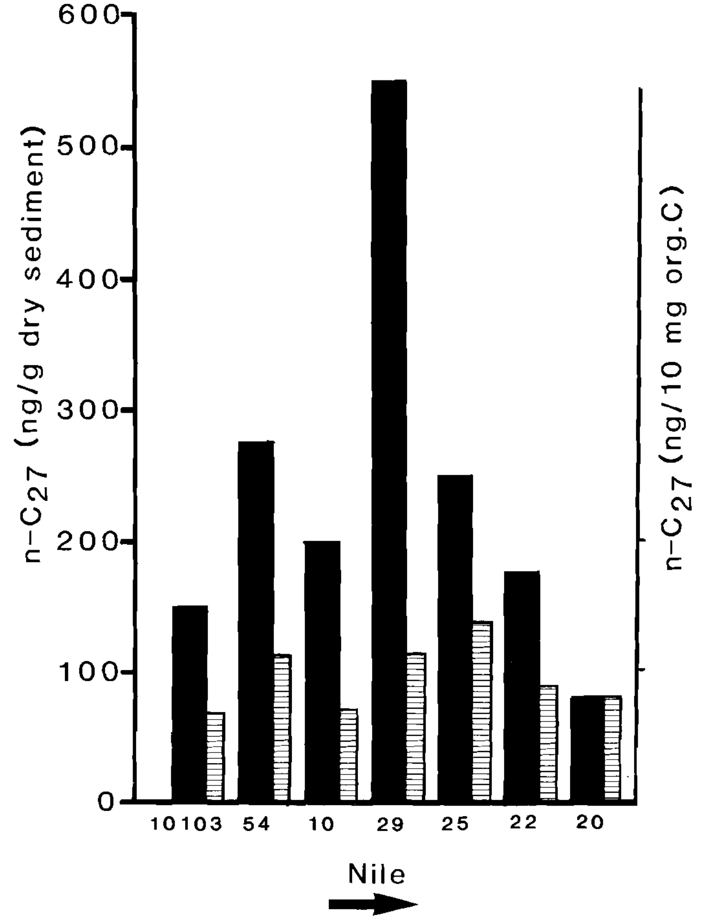


Figure 3.4. Distribution of n-C_{27} alkane (in ng/g dry sediment, black bars; in ng/10 mg org. C., hatched bars) in the sapropel samples ordered towards the mouth of the river Nile. The concentration of core 10103 represents an average value of three S_1 samples from this core, taken from Smith (1984).

oxygen is more exhausted in the deeper parts of the basin and in isolated depressions. This is supported by the observation that the shallowest present-day water depth below which cores containing sapropelic intervals are found is 400 m (Shaw and Evans, 1984), whereas cores containing sapropels are found at a minimum water depth of 660 m (McCoy, 1974). Benthic activity will be minimal at depths where oxygen is exhausted, and consequently the preservation will be better. The interpretation of the n-C_{27} data is thus not straightforward, but based on the palynological data, the $\delta^{13}C$ values and the correlation between the absolute concentrations of n-C_{27} and the $\delta^{13}C$ values a relative increase of terrigenous organic input towards more seaward and deeper deposited sapropels might be inferred.

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

The variations of the normalized data of phytol, dinosterol and the C_{30}-diol are shown in Figure 3.5. A high correlation between these compounds is evident. The correlation between the C_{30}-diol and dinosterol ($r = 0.90$) is surprising, as these two compounds reflect two different marine inputs (dinoflagellates and planktonic cyanobacteria respectively). Also the correlation of these two compounds with phytol can not be explained properly, because it is unlikely that phytol is solely derived from dinoflagellates and planktonic cyanobacteria. Even more surprising is the fairly good correlation ($r = 0.80$) between the continentally derived n-C_{27} and the marine derived C_{37} ketones (not shown in Fig. 3.5.). These correlations might indicate that the communities of photosynthetic organisms in the surface water have been rather uniform over the eastern Mediterranean during formation of sapropel S_1 and that the influx of continentally derived matter caused parallel variations in the primary productivity.

The distribution of dinosterol (Table 3.5.) does not mimic the distribution of dinoflagellate cysts (Table 3.2.). However, all reports on the lipid composition of dinoflagellates deal with investi-

Table 3.5.A. Quantitative results of selected compound in S_1 sapropels

	10103	54	10	29	25	22	20
n-C_{16}-FA	3325	6100	4950	18650	3750	5050	5050
i-$C_{20:1}$-OH	4790	2050	1950	16150	1450	1500	550
n-C_{27}-HC	150	275	190	550	250	180	80
n-C_{24}-FA	470	1150	950	3580	450	1150	250
n-C_{24}-OH	360	250	350	1120	600	300	130
dinosterol	2550	1150	1250	7770	1100	450	150
C_{30}-diol	3980	850	1350	7300	1700	450	150
C_{37}-ketones	540	950	750	3360	1500	900	450

Values are expressed in ng/g dry sediment. Values of core 10103 are an average of three S_1 sapropel samples, taken from Smith (1984).

Table 3.5.B. Quantitative results calculated on 1% organic carbon.

	10103	54	10	29	25	22	20
n-C_{16}-FA	1500	2460	1800	3800	2030	3660	4900
i-$C_{20:1}$-OH	2160	830	710	3280	780	1090	530
n-C_{27}-HC	70	110	70	110	135	90	80
n-C_{24}-FA	210	460	350	730	240	830	240
n-C_{24}-OH	160	100	130	230	320	220	125
dinosterol	1150	460	450	1590	600	330	145
C_{30}-diol	1790	340	490	1490	920	330	145
C_{37}-ketones	240	380	270	690	810	650	440

Values are expressed in ng/10 mg organic carbon. Average organic carbon values of sections analyzed by Smith (1984) is 2.22% (Sutherland et al., 1984).

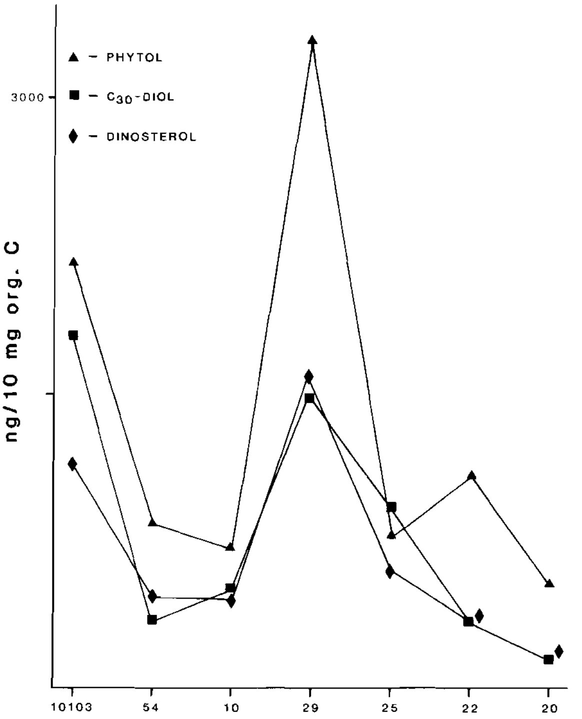


Figure 3.5. Distribution of phytol, dinosterol and C_{30}-diol in the sapropel samples, calculated on the organic carbon content (Table 3.5.B.) ordered towards the mouth of the river Nile.

gations of total dinoflagellate populations. Dale (1976) showed that only 5-10% of a given dinoflagellate population forms acid-resistant cysts with a high fossilization potential. Hence, a discrepancy between the palynology, which only studies acid-resistant remains, and the organic geochemistry is not surprising in this respect. Smith et al. (1982) attributed dinosterol and several other 4-methylsterols to an unknown uncharacterised phytoplankton source, based on the absence of dinoflagellate cysts in their samples from the Namibian shelf. However, only relatively few living species produce fossilizable remains. Moreover, dinocysts are probably not the only fossil remains of dinoflagellates. It is equilly possible that a considerable amount of the acid-resistant AOM is of a dinoflagellate origin (Dale, pers. comm., 1986). The suggestion of Smith et al. (1982) seems therefore equivocal.

Figure 3.6. shows some of the basic parameters thought to be responsible for the sapropel formation, assuming that an increase of Nile water discharge is the driving force for sapropel formation (cf. Rossignol-Strick et al., 1982). This assumption is supported by the distribution pattern of the representatives of the fresh to brackish water genus Pediastrum encountered in samples 20, 22 and 29 (Table 3.2.). Evitt (1963) suggested that the resistant cells of this genus may have been transported into the marine environment by streams rather than living in the area in which they were fossilized.

The input of nutrient-rich riverine water will induce a higher autochthonous production of marine organisms in the water column, an effect which diminishes with increasing distance from the source of mixing (Fig. 3.6.). Also the input of continentally derived organic matter will be enhanced. Assuming that the organic detritus passing from the sea surface through the water column to the sea floor is a reflection of the sea surface organic matter, it can be suggested that organic matter reaching the sea floor near the distributary mouth is predominantly of marine origin, whilst towards a more seaward direction the relative concentration of terrigenous organic material is increasing (Fig. 3.6.). In a situation with uniform sedimentation rates and "good" preservation conditions, it is thus expected that layers with the highest organic carbon values are found near the distributary mouth. A similar observation can be suspected when there are "poor" preservation conditions, only the contribution of labile marine organic matter will decrease relatively to the contribution of refractory terrigenous organic matter. The sapropels collected from

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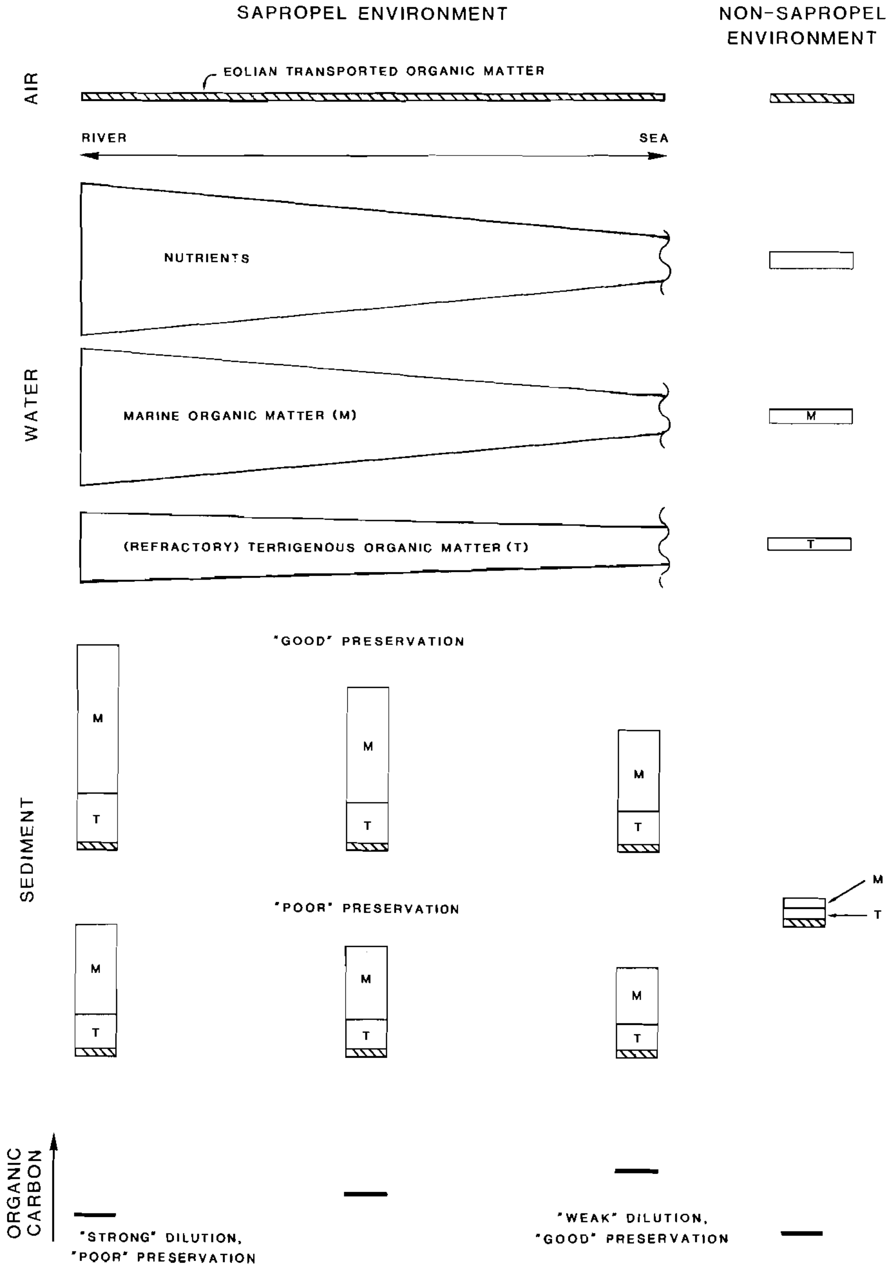
Figure 3.6. Schematic model for the formation of sapropel S_1.


SAPROPEL ENVIRONMENT
NON-SAPROPEL ENVIRONMENT
AIR
EOLIAN TRANSPORTED ORGANIC MATTER
RIVER
SEA
WATER
NUTRIENTS
MARINE ORGANIC MATTER (M)
M
(REFRACTORY) TERRIGENOUS ORGANIC MATTER (T)
T
SEDIMENT
'GOOD' PRESERVATION
M
T
'POOR' PRESERVATION
M
T
ORGANIC CARBON
'STRONG' DILUTION, 'POOR' PRESERVATION
'WEAK' DILUTION, 'GOOD' PRESERVATION

the Nile Cone are, however, strongly influenced by a high sedimentation rate, resulting in expanded thicknesses and low organic carbon contents (Fig. 3.6.), but still characterised by the initial $\delta^{13}C$ values. The relation between marine organic matter and terrigenous organic matter as proposed in this model also explains the observed correlation between n-C_{27} and the long chain ketones. This model explains most of the phenomena observed, although some questions remain to be answered.

On the right side in Figure 3.6. the present-day situation is shown, indicating the relative importance of eolian transported organic material (see section 3.3.3.). A non-sapropel environment is characterized by both low productivity as well as poor preservation.

3.4. Conclusions

Organic matter of S_1 sapropels is of a mixed marine, terrigenous and bacterial origin. A trend of relatively increasing amounts of continentally derived organic matter towards more seaward and deeper deposited sapropels can be observed. The planktonic communities present during formation of the S_1 sapropel in the eastern Mediterranean were probably uniform. It is further postulated that in deeper realms conditions were more favourable for preservation of organic matter than in shallower areas. However, varying sedimentation rates hamper a straightforward interpretation.

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

Chapter 4

LATE QUATERNARY MEDITERRANEAN SAPROPELS III: ASSESSMENT OF SOURCE OF INPUT AND PALAEOTEMPERATURE AS DERIVED FROM BIOLOGICAL MARKERS

Abstract

Sources of input contributing to the organic matter of Mediterranean sapropels (S_1, S_5, S_6, S_7) are inferred from the relative distributions of terrigenous and marine biological markers. The relative terrigenous contribution does not vary significantly. Within the marine contribution there is a significant compositional variation. A contribution from dinoflagellates is relatively important in the S_1 sapropel, whereas sapropels S_6 and S_7 are characterized by a relatively large contribution from prymnesiophyte algae and planktonic cyanobacteria. The abundance of diatoms in sapropel S_5, as deduced from microscopic observations, is probably reflected by a high concentration of loliolide.

Variations in sea-surface water temperatures can be deduced from the relative abundance of di- and triunsaturated C_{37} ketones (U^k_{37} index) and from the relative abundance of esterified 27-nor-24-methylcholesta-5,22E-dien-3β-ol and cholesta-5,22E-dien-3β-ol (S_{TI} index). These two molecular geothermometers are consistent with the $\delta^{18}O$ record and with the pollen record of the sapropels investigated.

4.1. Introduction

A major key to understanding the origin and occurrence of Cretaceous black shales lies in the understanding of their modern day analogues. The Quaternary sedimentary record of the eastern Mediterranean offers an excellent opportunity to study such modern day analogues. The Mediterranean is a landlocked isolated basin. Hence, any significant global or regional environmental change usually has a pronounced effect in the sedimentary record. As a result of such environmental changes a number of organic rich layers, so-called sapropels, have been deposited in a relatively short time span (Cita and Grignani, 1982). These sapropels can be easily recovered by conventional piston coring and have been the subject of numerous investigations (ten Haven et al., 1986a and references cited therein; see chapter 2). Although much geological information is available there is still disagreement about the mechanism leading to their formation, and about the origin of the organic matter (ten Haven et al., 1986a). A study of lipid distributions in sapropels can help to identify the different sources of input contributing to the organic matter, which in its turn can provide insight into the environment of deposition. As lipids form a small part of the total organic matter in sediments, no absolute quantifications can be made of the different biogenic contributors. Estimations of the different sources of input (e.g. marine versus terrigenous) can only be made on a semiquantitative level. Due to the isolated character of the Mediterranean, it can be expected that at least part of the organic matter in the sapropel stems from the continent either via run-off and/or eolian transport. Moreover, the Mediterranean sapropels offer a good possibility to study the usefulness of distribution patterns of specific lipids as indicators for variations in seawater temperatures, because the sapropels have been deposited under both warm and cold climatic conditions (Cita and Grignani, 1982). Recently, the distribution pattern of long chain unsaturated methyl ketones, originating from prymnesiophyte algae, has been shown a powerful tool for the elucidation of palaeotemperature variations (Brassell et al., 1986a).

4.2. Experimental

Four sapropels (S_1, S_5, S_6, S_7) from two piston cores were analyzed in this study. The cores, T83-7 (33°39.65'N, 25°59.00'E, 2480 m water depth) and T83-30 (33°48.20'N, 28°36.60'E, 2810 m water depth) were collected during an expedition of the R.V. Tyro in 1983. Sapropels S_1 and S_5 were obtained from core T83-30; sapropels S_6 and S_7 from core T83-7. The samples from sapropels S_6 and S_7 were divided into three and two subsamples respectively on the basis of pollen analyses (Ganssen and Troelstra, 1986), in order to assess variations in seawater temperatures prevailing during deposition of these sapropels. No pollen data were available for the two other sapropel samples. For comparative purposes, an organic rich interval (Late Pliocene) from the Vrica section (Calabria, Italy), comparable to sapropel layer c of Selli et al. (1977), was also analyzed.

The shipboard handling and the laboratory work-up procedure, as well as the GC and the GC-MS conditions are described by ten Haven et al. (1986a). Briefly, four extracts were obtained from each sample, Extract 1 by Soxhlet extraction with methanol/toluene (3:1), Extract 2 after saponification of the Soxhlet extracted residue, Extract 3 after acid-hydrolysis of the saponified residue, and Extract 4 after saponification of an aliquot of Extract 1.

4.3. Results and discussion

The most complete record of Late Quaternary sapropel sequences is found in core RC 9-181 recovered from the Mediterranean Ridge south of Crete (Vergnaud-Grazzini et al., 1977), encompassing twelve sapropels (S_1-S_{12}). Most cores do not contain such a complete record, and the cores collected during the Tyro expedition only contained sapropels S_1, S_5, S_6 and S_7. Some geological information and bulk parameters of the sapropels investigated, as well as data for the same sapropels at

Table 4.1. Background information of the samples investigated.

	S_1	S_5	S_6	S_7	Vrica
isotope stage chronology	1	5e	6	7a	
thickness (cm)	7	18	56	37	≈ 550
climate	temp./warm	warm	cold	temp.	temp.
$\delta^{13}C$ (org. C)	-22.6	-22.2/-22.1	-22.7/-24.0	-22.0/-22.0	-25.2
$CaCO_3$ (%)	34	28-33[a]	48-57[a]	44-51[a]	n.d.
org. C (%)	4.8	8.5-18.9[a]	2.4-6.0[a]	3.9-11.0[a]	0.8
org. C (%) from literature	1.03-4.93[b]				
	1.15-2.95[c]	6.33[c]	3.21-4.43[c]		
	1.71-3.34[d]				
		4.66-6.63[e]	2.12-4.42[e]	4.76-5.34[e]	

a. from ten Haven et al. (1986c)
b. from ten Haven et al. (1986b)
c. from Cita and Grignani (1982)
d. from Sutherland et al. (1984)
e. from Cita et al. (1982)
n.d. = not determined

other sites, are summarized in Table 4.1. The percentages of organic carbon vary widely, even within one sapropel layer, and are generally higher than those reported in the literature. The carbonate content seems to be related to the location of the core site, i.e. the sapropels from core T83-30 are characterized by lower carbonate contents than those from core T83-7. This could be the result of dilution by current-transported aluminosilicate detritus at site T83-30, absent at site T83-7 (Venkatarathnam et al., 1972). The $\delta^{13}C$ values of the organic matter point to enhanced contribution of terrigenous organic matter during deposition of sapropel S_6 and the sapropelic layer of the Vrica section.

Analyses of the planktonic foraminiferal fauna of several cores point to warm water conditions for all sapropels with the exception of sapropels S_6 and S_8 (e.g. Cita et al., 1977, 1982; Thunell and Williams, 1983; Thunell et al., 1983). Sapropel S_5 is especially characterized by a warm faunal assemblage (e.g. Globigerinoides ruber and Globigerinoides sacculifer), whilst sapropel S_6 is characterized by a cold assemblage (e.g. Globigerina bulloides and Globigerina quinqueloba). Another characteristic feature of the sapropel S_5 sample investigated is the high abundance of diatoms (Troelstra, pers. comm., 1986). This phenomenon is restricted to the S_5 sapropel in a relatively small area south of Crete up to the southern Turkish coastline (Schrader and Matherne, 1981; Thunell and Williams, 1982).

The climatic conditions prevailing during deposition of the layer from the Vrica section are not known exactly. According to Selli et al. (1977) the Late Pliocene of the Vrica section is marked by a moderately cool climate, but Thunell (1979b) stated that warm conditions returned in the latest Pliocene.

4.3.1. Sources of input

Detailed descriptions of the organic geochemical characteristics of sapropel S_7 and the lateral variation in the concentrations of organic compounds in the S_1 sapropel over the eastern Mediterranean are given by ten Haven et al. (1986a, b; see chapters 2 and 3). Both studies showed that the organic matter of the sapropels is of mixed marine, terrigenous and bacterial origin (see also Smith, 1984). It was also shown that the concentration of organic compounds is strongly dependent on sedimentation rate, preservation conditions prevailing during deposition and primary productivity (ten Haven et al., 1986b). These parameters are not uniform over the eastern Mediterranean. For instance, sedimentation rates and primary productivity are much higher near the mouth of the river Nile than in the middle of the Mediterranean due to an increased supply of inorganics and nutrients via the Nile.

In order to obtain a semiquantitative estimate of different sources of input contributing to the sapropel organic matter, a number of organic compounds were selected, whose origin can be linked to specific biological sources from analyses of contemporary organisms. The saponified free extract (Extract 4) was chosen for the selection of the compounds. An example of a gas chromatogram of Extract 4 indicating the selected compounds is given in Fig. 4.1. It should be noted

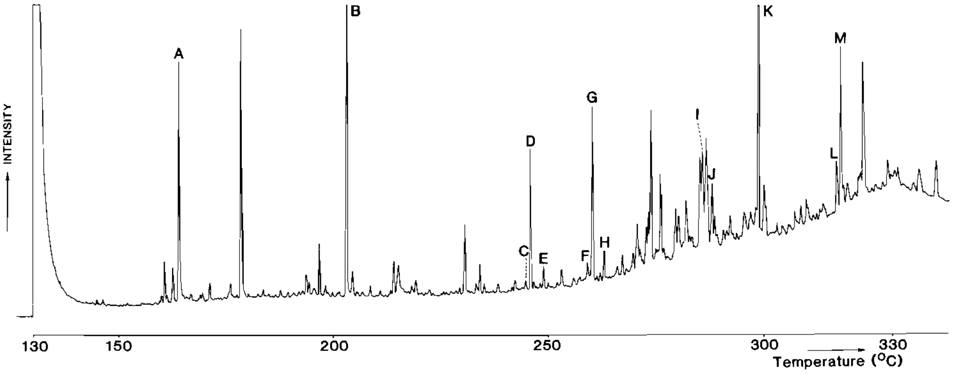


Figure 4.1. Gas chromatogram of Extract 4 of sapropel S_5, indicating the selected compounds. A = loliolide, B = Phytol, C = n-C_{27}-HC, D = n-C_{24}-FA, E = n-C_{24}-OH, F = n-C_{29}-HC, G = n-C_{26}-FA, H = n-C_{26}-OH, I = 24-ethylcholest-5-en-3β-ol, J = 4α,23,24-trimethyl-5α(H)-cholest-22-en-3β-ol, K = n-C_{30}-1,15-diol + n-C_{30}-15-one-1-ol, L = $C_{37:3}$-methylketone and M = $C_{37:2}$-methylketone. Conditions: Carlo Erba 4160 gas chromatograph equipped with on column injection and SE 52 capillary column, programmed from 130°C to 330° at a rate of 4°C/min.

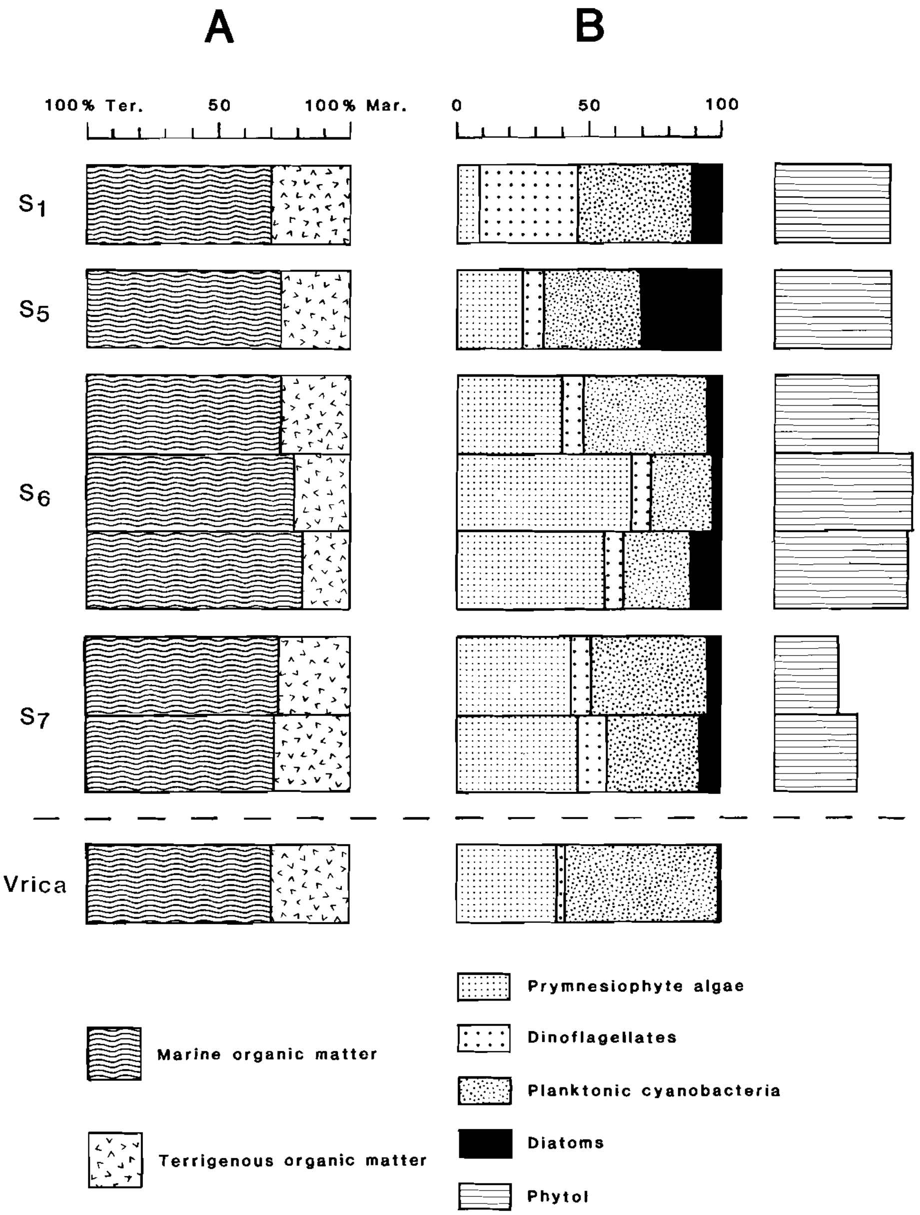
that no semiquantitative estimate of the bacterial contribution can be made as specific bacterial biological markers, such as iso and anteiso fatty acids and β-hydroxy fatty acids occur predominantly in Extracts 2 and 3 (ten Haven et al., 1986a). Two important premises of this approach are that the diagenetic influence is the same for all samples investigated and that these lipids can be considered to be representative for the original input.

The following compounds were selected: n-C_{27} + n-C_{29} alkanes (C and F), n-C_{24} + n-C_{26} fatty acids (D and G) and n-C_{24} + n-C_{26} alkanols (E and H), all of them attributed to a terrigenous origin (e.g. Simoneit, 1978). 24-Ethylcholest-5-en-3β-ol (I) was also selected although its value as a terrigenous input marker (e.g. Huang and Meinschein, 1976) has been questioned by other investigators (e.g. Mackenzie et al., 1982; Volkman, 1986). $C_{37:2}$ + $C_{37:3}$ ketones (L and M) are thought to be characteristic for prymnesiophyte algae (e.g. Volkman et al., 1980; Marlowe et al., 1984; Brassell et al., 1986a), dinosterol (J) for dinoflagellates (e.g. Boon et al., 1979; Robinson et al., 1984), C_{30}-diol + C_{30}-keto-ol (K) for planktonic cyanobacteria (Morris and Brassell, 1986), loliolide (A) for diatoms and/or dinoflagellates (Klok et al., 1984), and phytol (B) was selected for a non-specific marine input.

The compounds selected comprise the most abundant and/or characteristic compounds present in the extracts studied and are virtually always well separated in the gas chromatograms of Extract 4 (see Fig. 4.1.). Figure 4.2.A. shows the normalized distribution of the terrigenous (except 24-ethylcholest-5-en-3β-ol) and marine compounds. Based on this selected set of biological markers one might conclude that the relative terrigenous input is similar in all samples investigated. There seems to be a small relative increase of terrigenous organic matter in sapropel S_6 towards its top. This increase can also be inferred from the $\delta^{13}C$ values of organic matter of the sapropels, since a value of -22.7 $^{o}/oo$ was measured at the base, -23.6 $^{o}/oo$ in the middle and -24.0 $^{o}/oo$ at the top. However, the $\delta^{13}C$ values of sapropel S_6 are significantly more negative than those of the other sapropels (Table 4.1.), whilst the relative terrigenous input, as calculated from the biological markers mentioned, seems to be similar. Moreover, in a previous study of S_1 sapropels the opposite observation was made: a relative increase of marine marker compounds co-occurred with more negative values for the $\delta^{13}C$ (ten Haven et al., 1986b). Hence, at this stage interpretation of the above results is not straightforward either because of the simplicity of our assumptions or because of the fact that for instance the $\delta^{13}C$ variations between the sapropels are the result of variations in the sea-surface temperatures (Sackett, 1986). A normalization including 24-ethylcholest-5-en-3β-ol does not change the pattern described above. Hence, it can not be established from our data whether this compound stems from a terrigenous or a marine source in this instance. Figure 4.2.B. shows the normalized distribution of the marine biological markers. Phytol has not been included in this figure since it is of non-specific marine origin, but its percentile contribution is shown. The contribution from dinoflagellates is most pronounced in sapropel S_1. The relatively high abundance of loliolide in sapropel S_5 suggests a high input of diatoms (Klok et al., 1984), a suggestion supported by microscopic observations. It thus appears that loliolide is a useful biological marker for diatoms indeed. The older sapropels (S_6 and S_7) are characterized by a high input of prymnesiophyte algae, and the sample from the Vrica section by a high input of planktonic cyanobacteria.

Diagenetic alterations will influence the concentration of certain biological markers. The extent of these diagenetic changes is hard to predict, but as the relative phytol concentration does not decrease dramatically in the older sapropels diagenetic effects are thought to be minimal. However, in the Vrica sample phytol is virtually absent and the interpretation of the organic geochemical characteristics of this sample is thus hampered by a diagenetic overprint.

Figure 4.2.A Normalized distribution of total terrigenous and marine biological markers. The scale is relative and does not imply exact percentages. B: Normalized distribution of marine biological markers ($C_{37:3}$ + $C_{37:2}$ ketones, dinosterol, C_{30}-alkan-1,15-diol + C_{30}-15-keto-1-ol, and loliolide). The percentile contribution of phytol is also presented.


A
B
100% Ter.
50
100% Mar.
0
50
100
S1
S5
S6
S7
Vrica
Marine organic matter
Terrigenous organic matter
Prymnesiophyte algae
Dinoflagellates
Planktonic cyanobacteria
Diatoms
Phytol

4.3.2. Palaeotemperature assessment

Recently Brassell et al. (1986a) have shown that variations in sea-surface temperatures can be inferred from the relative abundances of the long chain $C_{37:2}$ and $C_{37:3}$ methyl ketones. The changes in the alkenone unsaturation with increasing or decreasing temperatures are a consequence of the ability of aquatic organisms to match to some extent changes in the environmental conditions. Brassell et al. (1986a) defined an alkenone unsaturation index as: $U^k_{37} = [C_{37:2}] - [C_{37:4}]/[C_{37:2} + C_{37:3} + C_{37:4}]$, which can be simplified to $U^k_{37} = [C_{37:2}]/[C_{37:2} + C_{37:3}]$ where $C_{37:4}$ ketones are absent, as in the sediments discussed herein. The authors found a good correlation between the U^k_{37} and the oxygen isotope signal of surface dwelling foraminifera, a correlation which deteriorates in older sediments (> 550 ky).

Variations in the palaeotemperature and palaeosalinities of the (sub)surface water prevailing during deposition of Late Quaternary sapropels are well documented by oxygen isotopes ($\delta^{18}O$) of foraminiferal tests (e.g. Cita et al., 1977; Thunell, 1979b; Thunell and Williams, 1982, 1983; Thunell et al., 1984; Vergnaud-Grazzini et al., 1977; 1986). Contrary to the open Atlantic Ocean, the general isotope record of the semi-isolated Mediterranean possesses strong overprints of local origin, due to increased continental run-off as a result of periodical deglaciation. Fluctuations in the $\delta^{18}O$ composition of planktonic foraminifera therefore indicate cycles with amplitudes greater than those which can be attributed to global ice volume changes only.

The general isotope record for open Atlantic Ocean sediments is shown in Fig. 4.3.A., in which the coeval deposition of the Mediterranean sapropels is indicated (after Thunell et al., 1984). This figure shows that sapropel S_5 was deposited during warm climatic conditions, and sapropel S_6 during a glacial maximum. In most isotopic studies the $\delta^{18}O$ record is determined for the planktonic foraminifer Globigerinoides ruber. Since this species is absent in the S_6 samples investi-

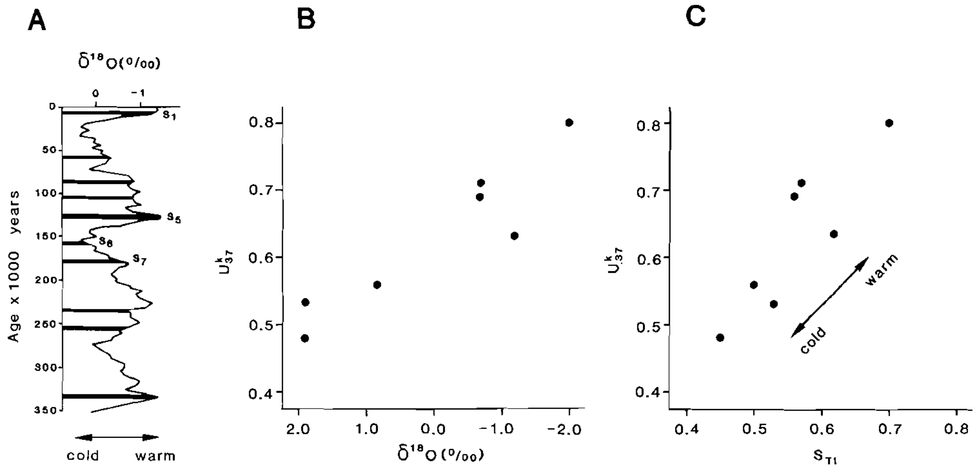


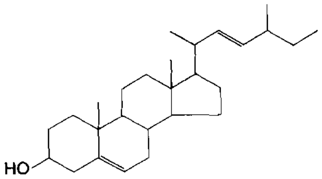
Figure 4.3.A Generalized open-ocean oxygen isotopic record with superimposed the coeval deposition of Mediterranean sapropels (after Thunell et al., 1984). B: Plot of U^k_{37} index against $\delta^{18}O$ for G. ruber (from Vergnaud-Grazzini et al., 1977). C: Plot of the U^k_{37} index against the Sterol Temperature Index (S_{TI}).

gated (Ganssen and Troelstra, 1986) the U^k_{37} index for the sapropels is here compared with $\delta^{18}O$ data published for the same sapropels at other sites.

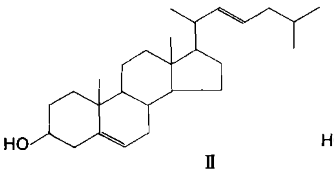
A plot of the U^k_{37} index against the $\delta^{18}O$ of Mediterranean sapropels (data from core RC 9-181, Vergnaud-Grazzini et al., 1977) is shown in Fig. 4.3.B. The $\delta^{18}O$ curve of core RC 9-181 is most similar to the $\delta^{18}O$ record of the open ocean, and therefore isotope data of this core are selected. The correlation between these two climatic indices is evident, although there is some scatter. This scatter is probably the result of the selection of the isotopic data since even within one sapropel layer different isotopic signals are measured over the eastern Mediterranean (e.g. Vergnaud-Grazzini et al., 1977). The maximum glacial/interglacial temperature difference in the Mediterranean has been estimated to be not greater than 8°C (Cita et al., 1977). If the relatively negative $\delta^{18}O$ values associated with sapropels are solely due to temperature changes, one has to invoke unrealistic large temperature differences (e.g. Thunell et al., 1983). The maximum U^k_{37} difference between the warm sapropel S_5 and the cold sapropel S_6 is 0.32, corresponding with a temperature difference of 5-10°C (estimated from Fig. 1.B of Brassell et al., 1986a). This value is comparable with the 8° estimate of Cita et al. (1977) and suggests that a low salinity surface water layer does not significantly influence the U^k_{37} index.

The U^k_{37} ratio of the Vrica sample (0.87), indicating a very warm climate, is much higher than that of sapropel S_5 (0.80). This climatic interpretation seems unreliable in the light of the statement by Cita and Grignani (1982) that sapropel S_5 records the warmest conditions ever experienced by the eastern Mediterranean and by the pollen data of the Vrica section, pointing to a moderately cool climate (Selli et al., 1977). Comet (1982) reported also a U^k_{37} ratio of 0.87 for an organic-rich sample of Late Pliocene age from DSDP site 376 (eastern Mediterranean). This discrepancy might result from inputs of different species of prymnesiophyte algae with a different U^k_{37} temperature dependence. The age of the sample from the Vrica section as well as the sample investigated by Comet (1982) (> 10^6 years) predates the first appearance of Emiliania huxleyi. This latter species is thought to be the main contributor of the long chain unsaturated alkenones in Late Quaternary sediments (Brassell et al., 1986a). Another, more speculative, explanation is that the triunsaturated alkenone has a better chance to be oxidized than the diunsaturated alkenone. The Vrica sample is from a land outcrop well exposed to oxidation in contrast to the sapropel samples, presently buried at depths where dissolved oxygen is already exhausted (ten Haven et al., 1986c). However, this suggestion cannot explain the results of Comet (1982).

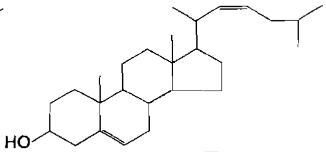
In addition to the long chain alkenones, another pair of organic compounds shows an internal ratio which seems to be temperature dependent. These two compounds are: 27-nor-24-methylcholesta-5,22E-dien-3β-ol (occelasterol, I) and cholesta-5,22E-dien-3β-ol (II). The identification of occelasterol is based on its mass spectrum and relative retention time. Occelasterol coelutes with cholesta-5,22Z-dien-3β-ol (III), but Kobayashi and Mitsuhashi (1974) point out that reports of the latter compound are questionable. They suggest that GC peaks assigned to III are largely, if not entirely, due to occelasterol. Moreover, the mass spectrum of occelasterol is characterized by m/z 111 > m/z 129, whereas cholesta-5,22Z-dien-3β-ol exhibits a fragmentation pattern of m/z 129 > m/z 111 (Wardroper, 1979). However, the presence of an unknown sterol also with a $\Delta^{5,22}$ unsaturation but a slightly different retention time (Wardroper et al., 1979) can not be precluded, as no occelasterol standard was available for coinjection. It should be emphasized that these two sterols occur as non-extractable esterified moieties in the sediment (see also ten Haven et al., 1986a). They occur in Extract 2, obtained after saponification of the Soxhlet extracted residue. This implies that these sterols are probably protected against biotransformation processes such as bacterial hydrogenation (cf. Eyssen et al., 1973) and can therefore survive the early stages of diagenesis.



I



II



III

Analogous to the U^k_{37} index, the variations of these two sterols can be expressed as a Sterol Temperature Index defined as $S_{TI} = [\Delta^{5,22}] / [\Delta^{5,22} + 27\text{-nor-}24\text{-Me-}\Delta^{5,22})$. Figure 4.3.C. shows that there is a good correlation (r = 0.9) between the U^k_{37} and the S_{TI} index of Late Quaternary sapropels. The free extractable analogs of these steroid compounds do not show this correlation. The virtual absence of these sterols in the Vrica sample together with the possibility that the alkenones are oxidized in this sample, makes it impossible to check this relation in a more ancient sediment.

The biological origin of these two sterols is at present unknown, but based on their esterified mode of occurrence and their temperature dependent behaviour, a direct biological input can be postulated. Whether these sterols originate from different organisms, their growth conditions being temperature dependent (i.e. one is dominant at elevated temperatures, the other at lower temperatures), or that the S_{TI} index reflects changes in sterol moieties of the membrane of one organism or one group of organisms remains to be seen. It is noteworthy to mention that Betouhim-el et al. (1977) have shown that the phytoflagellate _Ochromonas danica_ has a higher sterol content when cultured at low temperatures than when cultured at higher temperatures. The suggestion that occelasterol might be formed by demethylation of 24-methylcholesta-5,22E-dien-3β-ol (Minale and Sodano, 1977; Schmitz, 1978) cannot explain its behaviour in the Mediterranean sapropels.

As was already explained before, the isotopic record of Late Quaternary Mediterranean sediments is strongly influenced by continental run-off. Another possibility to check the climatic assessment by the U^{k}_{37} and S_{TI} indices is a comparison of these two indices with the pollen record of sapropels. The relative concentrations of the long chain ketones and of the two sterols (drawn as bars) as well as the pollen record of the S_6 and S_7 sapropel (from Ganssen and Troelstra, 1986) are presented in Fig. 4.4. It is clear from this figure that the U^{k}_{37} and the S_{TI} indices are consistent with the pollen record. The replacement of "cold" steppe elements (_Artemisia_ and Chenopodiaceae) by temperate deciduous trees is closely followed by an increase of the organic geochemical temperature indices. Figure 4.5. shows plots of a pollen index P_I (defined as P_I = [Trees]/[Steppe + Trees]) against the

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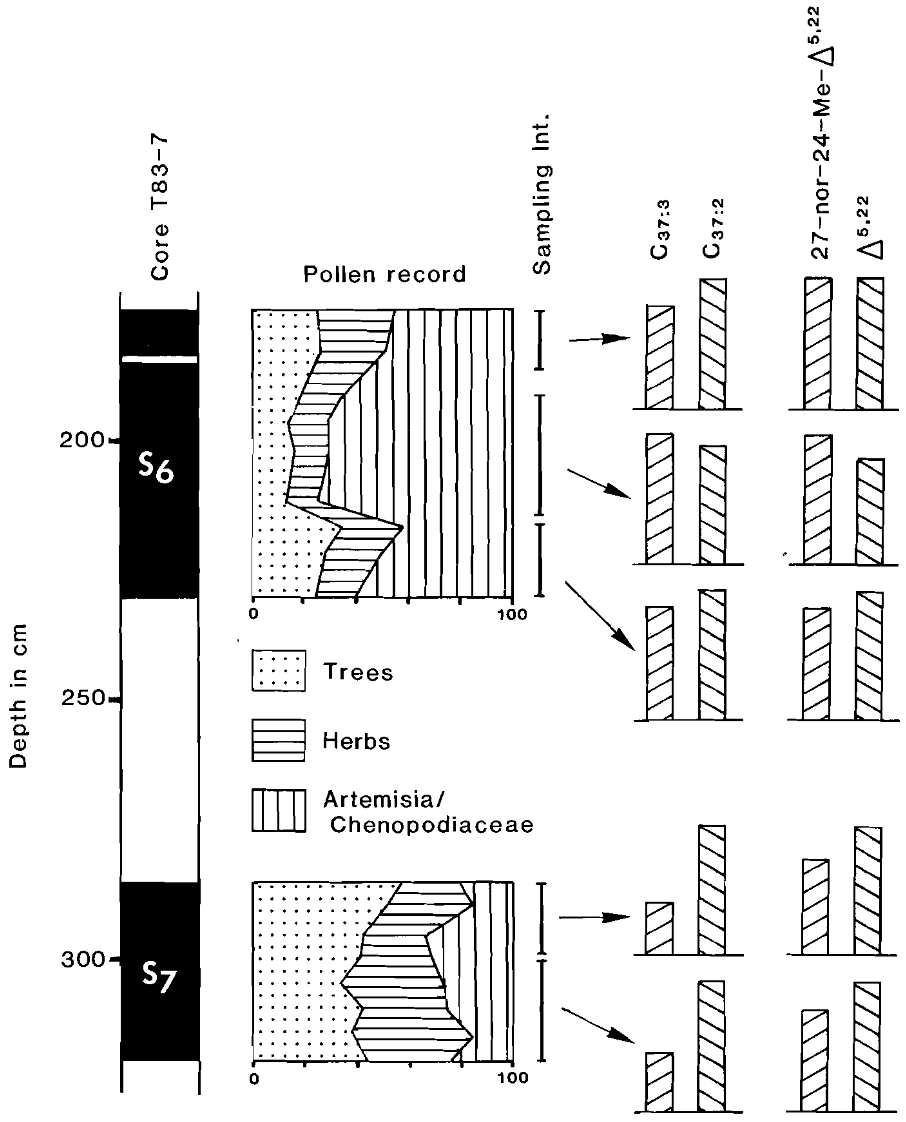
Figure 4.4. Pollen record of the S_6 and S_7 sapropel (data from Ganssen and Troelstra, 1986), and a graphical expression of the two molecular temperature indices (U^{k}_{37} and S_{TI}) both normalized to the highest component.


Core T83-7
Depth in cm
200
250
300
S6
S7
Pollen record
0
100
0
100
Trees
Herbs
Artemisia/ Chenopodiaceae
Sampling Int.
C37:3
C37:2
27-nor-24-Me-Δ5,22
Δ5,22

U^k_{37} and the S_{TI} index respectively. Although these plots are only based on five samples significant correlations of 0.98 and 0.96, respectively, are observed.

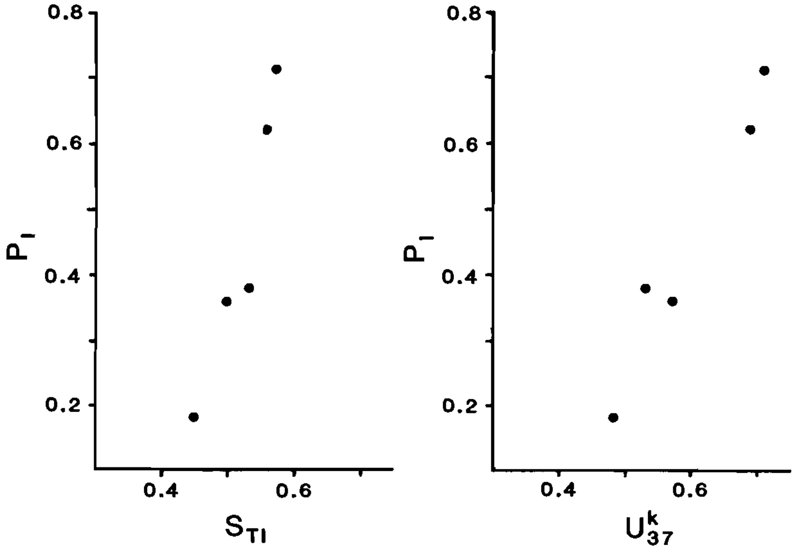


Figure 4.5. Plots of P_I index against U^k_{37} index and against S_{TI} index for samples from sapropel S_6 and S_7.

4.4. Conclusions

The relative terrigenous contribution to organic matter in Mediterranean sapropels in comparison with the marine input is generally the same in all samples investigated. Varieties within the marine input can be recognized by diagnostic organic compounds.

Variations in the sea-surface water temperatures are reflected by variations in the abundances of tri- and diunsaturated methyl ketones and in the relative abundances of esterified 27-nor-24-methylcholesta-5,22E-dien-3β-ol (occelasterol) and cholesta-5,22E-dien-3β-ol. Both temperature indices show a strong correlation with the pollen record (in terms of temperature dependence) of sapropel S_6 and S_7.

The virtual absence of the two temperature dependent sterols in the oldest sample investigated makes it impossible to check the S_{TI} index in older sediments. When the calibration of these two geothermometers is firmly established, it should be possible to correct the $\delta^{18}O$ isotopic data of the Mediterranean sapropels for temperature variations and hence make better estimates of the salinity decrease, always invoked to explain the large oxygen isotopic depletion associated with sapropels. The remarkably good correlation of the pollen record with the temperature dependent sterol and ketone ratios indicates that this approach might have future applications in micropalaeontological investigations.

Chapter 5

ORGANIC GEOCHEMICAL CHARACTERISTICS OF SEDIMENTS FROM THE ANOXIC BRINE-FILLED TYRO BASIN (EASTERN MEDITERRANEAN)

Abstract

Soxhlet extractable organic compounds of sediments from the anoxic brine-filled Tyro basin (eastern Mediterranean) were analyzed by gas chromatography and gas chromatography - mass spectrometry. Cholesterol and 22,29,30-trisnorhopan-21-one are the major compounds identified. The occurrence of this triterpenoid ketone, as well as bishomohopanoic acid and diplopterol (tentatively identified) is ascribed to an input of microbiota living at the brine-seawater interface. Sterols occur for the greater part as free moieties, in contrast with the esterified mode of occurrence of sterols in eastern Mediterranean sapropels. This may be attributed to reworking at the brine-seawater interface.

5.1. Introduction

The Tyro basin is a depression located in the Strabo Trench (eastern Mediterranean) at a depth of 3450 m, containing anoxic hypersaline water in the bottom 100 m (Jongsma et al., 1983; de Lange and ten Haven, 1983). The brine has a density of 1.199 mg/ml and a chloride concentration of 5.7 mol/l, as a result of leaching of tectonically exposed Messinian evaporitic salt deposits (ten Haven et al., 1985a; see chapter 6). Only few of such depositional environments are known in the modern Ocean. Orca basin (Gulf of Mexico) and Atlantis II Deep and Discovery Deep (Red Sea), are other examples. In contrast with the Tyro and Orca brines, the Red Sea brines are thought to be formed from recharge by seawater which leaches evaporitic deposits at depth, and which subsequently rises and discharges through vents (Craig, 1969). Requejo et al. (1986) reported on the hydrocarbon geochemistry of sediments from the Orca basin (Gulf of Mexico), a basin comparable with the Tyro basin. However, it is uncertain whether the DSDP sediments investigated by Requejo et al. (1986) were deposited under hypersaline conditions, since Addy and Behrens (1980) estimated that the brine began flowing into the Orca basin ca. 8.000 years ago.

The environmental conditions, prevailing in the Tyro basin, offer the unique possibility for studying the influences of such a brine on organic compounds biosynthesized in the photosynthetic zone and for studying the organic input of microbiota living at the brine-seawater interface. The large density gradient across this interface functions as a barrier for organic matter settling from the sea surface through the water column. As a consequence, large amounts of organic matter (Ryan et al., 1969) and high microbial activity (Wiesenburg et al., 1985) are observed at such haloclines.

One of the remarkable phenomena of Tyro basin sediments is the occurrence of so-called gelatinous pellicles, which are thought to be formed at the interface (Erba et al., 1986).

5.2. Experimental

During an expedition of the R.V. Tyro in 1983 one piston core (T83-46; 33°52.02'N, 26°02.30'E) was collected from the basin floor of the Tyro basin. The core was split lengthwise and one half was deepfrozen until sampling. The stratigraphy of core T83-46 is described in detail by Troelstra (1986). Three intervals with a vertical thickness of 5 cm each were sampled, corresponding with a ^{14}C age of 1100, 3300 and 6200 years BP respectively (see Troelstra, 1986). These samples all have an organic carbon content of 1.7 % (ten Haven et al., 1986c, see chapter 7).

Sediment samples were Soxhlet extracted with methanol/toluene (3:1) for 24 hours. Following the extraction, the solvent was removed by means of rotary evaporation and the extract was taken up in CH_2Cl_2 and H_2O. The CH_2Cl_2 was separated in a separatory funnel and the aqueous layer was reextracted with CH_2Cl_2 three times. The combined CH_2Cl_2 extracts were dried on anhydrous Na_2SO_4. Extracts, thus obtained, were methylated with diazomethane, evaporated to dryness, chromatographed over a column filled with silica 60 (Merck 70-230 mesh) using hexane/ethylacetate (3:1) as eluent (four column volumes), again evaporated to dryness and silylated in pyridine with BSTFA plus 1% TMCS at 60°C for one hour.

An aliquot of the Soxhlet extract (not derivatized) was subjected to thin layer chromatography and separated into hydrocarbon, several ketone, fatty acid, alcohol and sterol fractions by elution according to the method of Skipski et al. (1965). The fatty acid, alcohol and sterol fraction were derivatized as described above.

Gas chromatography (GC) was carried out on a Carlo Erba 4160 gas chromatograph equipped with a flame ionization detector, an on-column injector and a capillary column coated with CPSil 5 (25 m, i.d. 0.32 mm). Hydrogen was used as carrier gas. Samples in ethyl acetate were injected at 100°C and the temperature was programmed at 4°C per minute from 130°C to 325°C. Gas chromatography - mass spectrometry (GC-MS) was carried out using a Varian 3700 gas chromatograph, equipped with a similar column as described above, connected to a Varian Mat 44 quadrupole mass spectrometer, operated at 80 eV with a cycle time of 1.5 sec and a mass range of 50-550 daltons. The TLC fraction, containing the fatty acids was reanalyzed after the Varian 3700 gas chromatograph was equipped with an on-column injector.

5.3. Results

The organic carbon content of sediments from the Tyro basin varies between 0.75 and 2.63% (ten Haven et al., 1986c). Low values reflect probably a dilution effect caused by redepositional events (Troelstra, 1986). The highest values are comparable to the values measured in sediments from the Orca basin (Northam et al., 1981). The three samples selected for this study were sampled at those intervals of core T83-46, which are thought to be no result of redeposition.

All three samples investigated gave similar gas chromatograms and the same compounds were identified by GC-MS. A representative gas chromatogram is shown in Figure 5.1. The numbers in this figure correspond with those listed in Table 5.1. Identifications are based on comparison of mass spectra with those described in the literature and by coinjection of available standards.

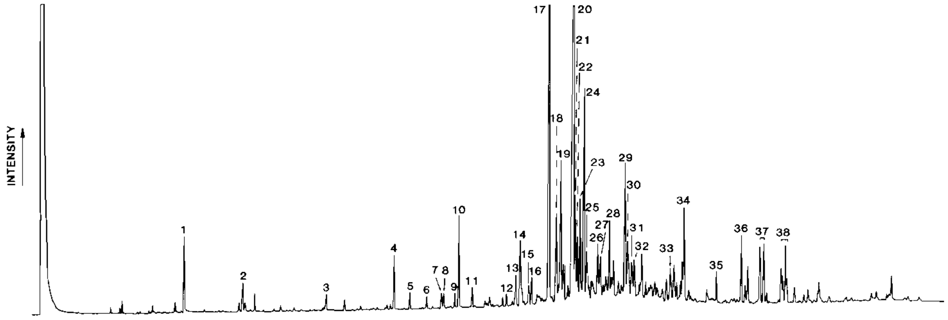


Figure 5.1. Representative gas chromotogram of the free extractable compounds of sediments from the Tyro basin. Identifications of numbered compounds are given in Table 5.1.

Table 5.1. Compounds identified by GC-MS, indicated in Figure 5.1.

1. n-$C_{16:0}$-FA
2. n-$C_{18:1}$-FA + phytanic acid
3. n-$C_{20:0}$-FA
4. n-$C_{22:0}$-FA
5. n-$C_{22:0}$-OH
6. n-$C_{23:0}$-FA
7. n-$C_{23:0}$-OH
8. unknown
9. n-C_{27}-HC
10. n-$C_{24:0}$-FA
11. n-$C_{24:0}$-OH
12. cholestadien
13. n-C_{29}-HC
14. n-$C_{26:0}$-FA
15. 22,29,30-trisnorhopen-21-one*
16. n-$C_{26:0}$-OH
17. 22,29,30-trisnorhopan-21-one
18. 27-nor-24-methylcholesta-5,22-dien-3β-ol
19. cholesta-5,22E-dien-3β-ol
20. cholest-5-en-3β-ol
21. 5α(H)-cholestan-3β-ol
22. n-$C_{28:0}$-FA
23. cholestenone*
24. 24-methylcholesta-5,22-dien-3β-ol
25. 24-methyl-5α(H)-cholest-22-en-3β-ol
26. 24-methylcholesta-5,24(28)-dien-3β-ol
27. 24-methylcholest-5-en-3β-ol
28. 24-ethylcholesta-5,22-dien-3β-ol
29. 24-ethylcholest-5-en-3β-ol
30. 24-ethyl-5α(H)-cholestan-3β-ol
31. n-$C_{30:0}$-FA
32. 4α,23,24-trimethyl-5α(H)-cholest-22-en-3β-ol
33. hopan-22-ol*
34. 1,15-C_{30}-diol + C_{30}-15-keto-1-ol
35. unknown (m/z 191,203)
36. 17β(H),21β(H)-bishomohopanoic acid
37. $C_{37:3}$-methylketone +
    $C_{37:2}$-methylketone
38. $C_{38:3}$-ethylketone +
    $C_{38:3}$-methylketone +
    $C_{38:2}$-ethylketone +
    $C_{38:2}$-methylketone

* tentative assignment

The major compounds are identified as cholest-5-en-3β-ol (20) and 22,29,30-trisnorhopan-21-one (17). The mass spectrum of the latter compound, almost purely isolated by TLC, is presented in Figure 5.2.A. In the same TLC fraction another compound occurred (15), the mass spectrum of which is presented in Figure 5.2.B. Its occurrence in the same TLC fraction suggests that we are dealing with a similar kind of compound. The molecular ion m/z 382 suggests one unsaturation and the fragment ion m/z 189 points to the presence of unsaturation in ring A or B. Fragment ion m/z 119 may be formed by loss of 70 a.m.u. from m/z 189 (Boon et al., 1978).

Apart from cholesterol, several other sterols are identified as well as their 5α(H) counterparts (Fig. 5.1. and Table 5.1.). Other

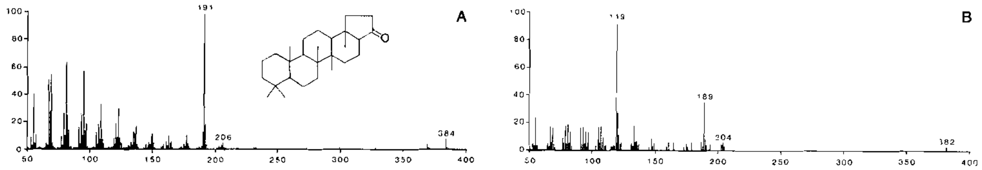


Figure 5.2. (A) Mass spectrum of a compound identified as 22,29,30-trisnorhopan-21-one (17) and (B) mass spectrum of a compound tentatively identified as a 22,29,30-trisnorhopen-21-one (15). Numbers between brackets refer to Figure 5.1. and Table 5.1.

relatively important compounds identified are fatty acids (e.g. 1, 10, 14, 36), long chain polyunsaturated methyl- and ethylketones (37, 38) and a C_{30}-diol coeluting with a C_{30}-keto-ol (34). Compound 23, having a base peak m/z 124 and other characteristic fragment ions m/z 229 and 261 is tentatively identified as a cholestenone. Long straight chain alkanes (9, 13) and alkanols (11, 16) are present in low concentrations.

A gas chromatogram of a TLC fraction, showing the fatty acid distribution, is presented in Figure 5.3. Unsaturated fatty acids are present in minor amounts. Branched fatty acids (iso and anteiso C_{15} and C_{17}) were also identified but are not indicated. The two peaks, labeled with bold numbers 33 and 36, are identified as hopan-22-ol (diplopterol) and 17β(H),21β(H)-bishomohopanoic acid respectively. The tentative identification of the former compound as diplopterol needs some clarification. At first, the fatty acid TLC fraction was not silylated and in the total ion current several compounds showed up which had no counterparts in the gas chromatogram, viz. two hop-17(21)-enes, hop-21(22)-ene and hop-22(29)-ene. These compounds were probably formed in the injector of the GC-MS system due to a cleavage of H_2O from the original compound. Therefore it was decided to silylate and reanalyze this fraction. This analysis was performed with the same GC-MS apparatus as descibed above, but the GC was equipped with an on-column injector. The mass spectrum of compound 33 is characterized by a base peak m/z 131 and fragment ions at m/z 73 (TMS), 189 and 191. This fragmentation is interpreted as side-chain cleavage of the C-21/C-22 bond to give m/z 131 (C_3H_6OTMS), and skeleton cleavage of C-8/C-14 and C-9/C-11 to give m/z 191 on the one hand and on the other hand cleavage through C-8/C-14 and C-12/C-13 to give m/z 279 which after additional loss of TMSO (+2H) gives m/z 189. To our knowledge, no mass spectrum of silylated diplopterol is described in the literature.

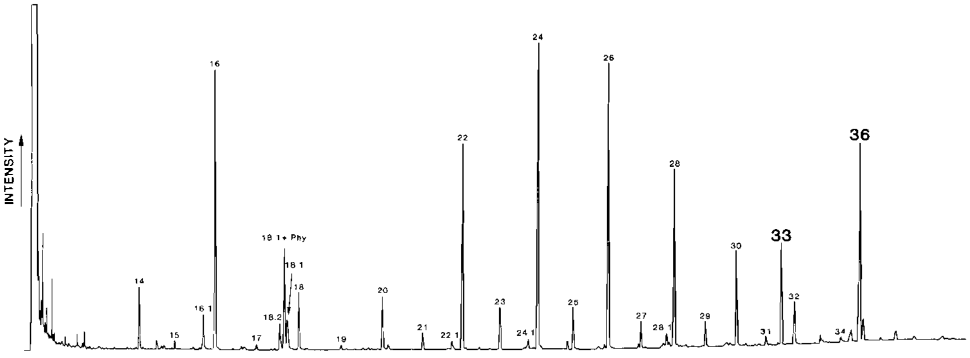


Figure 5.3. Gas chromatogram of a TLC fraction, containing fatty acids. Straight chain fatty acids are indicated by numbers, corresponding with the number of carbon atoms. Unsaturated fatty acids are indicated in a similar way, but the label is followed by the number of unsaturations. Phy is phytanic acid. Bold numbering 33 and 36 corresponds with the numbering of Figure 5.1. and Table 5.1.

5.4. Discussion

It is suspected that sediments from the Tyro basin are characterized by organic matter produced in the photosynthetic zone, by organic matter from microbiota living at the brine-seawater interface, and by continentally derived organic matter. The microbiota living at the interface will probably considerably modify the organic matter produced in the photosynthethic zone, although the extent of this reworking cannot be estimated. A microbial input might be inferred from the presence of compounds, which were not observed in the Mediterranean sapropels (ten Haven et al., 1986a, b; see chapters 2 and 3). Sapropels, referred to as S_1, S_2, etc., are a common feature of Late Quaternary eastern Mediterranaen sediments, and are thought to be the sedimentary expression of anoxic conditions prevailing in the past. A microbial assignment of certain compounds can only be made under the assumption that the overall composition of the primary producers has not changed between the time of deposition of the sapropels and the time of deposition of the sediments investigated in this study. This seems a reasonable approach, since the ^{14}C age of the oldest sample investigated (6200 years BP) is only slightly younger than the age of the most recent sapropel (S_1, 9000-7000 years BP).

Terrestrial compounds in sediments from the Tyro basin, as reflected by n-C_{27} and n-C_{29} alkanes and long chain fatty acids and alkanols, are present in minor amounts only, in contrast with the results obtained for the S_1 sapropel (ten Haven et al., 1986b). This contrast is not surprising, since an increasing discharge from the river Nile has been invoked for the formation of the S_1 sapropel (Rossignol-Strick et al., 1982). This mechanism for sapropel formation is likely to supply relatively large amounts of continentally derived organic matter, a situation which ended approximately 7000 years ago. The samples investigated in this study are of a younger age. The compositional characteristics of these samples are therefore thought to indicate that the organic matter present in the Tyro basin is mainly of an autochthonous origin.

Most compounds identified were also observed in sapropel S_1 and older sapropels investigated; however, their mode of occurrence differs strongly. While sterols occur for the greater part as esterified moieties in the sapropels (ten Haven et al., 1986a), they occur as free compounds in the Tyro basin. Also the relative concentration of the sterols is different: cholesterol being dominant in the Tyro basin, dinosterol in the S_1 sapropel (Smith, 1984; ten Haven et al., 1986b). It is difficult to trace the origin of cholesterol, since it is a ubiquitously occurring compound, but its preponderance in the Tyro basin is remarkable.

Some compounds are observed, which were absent or present in very low concentrations in the sapropels. These compounds are: trisnorhopan-21-one, bishomohopanoic acid, trisnorhopen-21-one and diplopterol (the identification of the latter two compounds is tentative). The occurrence of the 3-desoxy hopanoids in the Tyro basin sediments is therefore ascribed to an input from and/or caused by the microbiota living at the interface.

Smith (1984) reported the occurrence of bishomohopanoic acid in sapropel S_1, although present in relatively low concentrations. Bishomohopanoic acid is thought to be derived from bacteriohopanetetrol (Ourisson et al., 1979), a compound occurring in aerobic and/or photosynthetic prokaryots. The relatively high abundance of bishomohopanoic acid in Tyro basin sediments may point to an origin from non-photosynthetic prokaryots. Trisnorhopan-21-one is probably a diagenetic product of diplopterol (Albaiges and Albrecht, 1979), which in its turn is derived from the microbiota living at the interface.

Chapter 6

THE CHEMICAL COMPOSITION AND ORIGIN OF THE TYRO BRINE, EASTERN MEDITERRANEAN. A TENTATIVE MODEL

Abstract

Tyro basin, located within the Strabo Trench (eastern Mediterranean) is an anoxic, brine-filled depression at a depth of 3300 m. The chemical composition of the brine is similar to that of the Orca basin, although it is somewhat more concentrated. Its composition is most likely determined by an outcropping Messinian evaporitic sequence from gypsum up to soluble salts. The Br content of the halite is estimated from the brine composition and the result (200 ppm) is in fair agreement with the data from DSDP site 374 from the Ionian basin (118-218 ppm).

6.1. Introduction

After the discovery of the brine-filled, anoxic Orca basin (Gulf of Mexico) it was speculated that similar conditions could exist in other areas of the world oceans (Shokes et al., 1977). Indeed a similar brine-filled basin was discovered during a cruise with the Dutch R.V. Tyro in the eastern Mediterranean (Jongsma et al., 1983) (Fig. 6.1.). The brine has a Cl content of 5.7 mol/l, while dissolved O_2 is below the detection limit of the analytical method (de Lange and ten Haven, 1983). The Cl concentration in the interstitial water of sediments from the Tyro basin remains constant in contrast to the Orca basin where it decreases with depth. The source of this brine has been attributed to Messinian salt (Jongsma et al., 1983; de Lange and ten Haven, 1983). This salt was frequently encountered in cores collected during DSDP leg 13 (Ryan et al., 1973) and DSDP leg 42A (Hsü et al., 1978) in the Mediterranean. The presence of salt diapirs in the vicinity of the Tyro basin has been described by Peters and Huson (1985). The ´M´ reflector, associated with Messinian evaporites, is exposed in the side wall of the basin (Jongsma et al., 1983) (Fig 6.1.). Very recently another anoxic brine-filled basin, "Bacino Bannock", was discovered on the southwestern margin of the Mediterranean ridge, probably also originating from dissolution of Messinian evaporites (Scientific Staff of Cruise Bannock 1984-12., 1985).

6.2. Experimental and Results

Bottom water samples were taken with Nansen bottles at 0.5 and 1.5 m above the sediment-water interface. Pore waters were extracted following the shipboard working procedure described by de Lange (1983). On board NH_4, PO_4, NO_3 and NO_2 were analyzed spectrophotometrically using a Skalar 400 autoanalyzer. Dissolved O_2 was determined according to the Winkler method. Na, K, Ca, Mg and Sr were determined by AAS, Cl by the Mohr-titration and SO_4 by conductivity after separation with an Amolex ion-chromatograph. Br was determined according to

Kuehn and Hsü (1975). The chemical composition of the Tyro brine is given in Table 6.1. and compared with the Orca brine and average seawater. The charge balance was checked and the result found to be within the combined analytical errors.

Table 6.1. The chemical composition of the Tyro brine compared to the Orca brine (from Shokes et al., 1977) and average seawater.

	Tyro brine	Orca brine	Average seawater
$d_{22.5}$	1.199 (20°C)	1.185	1.025
Cl (mmol/l)	5700	5000	560
Na (mmol/l)	5300	4720	480
K (mmol/l)	17	19	10
Mg (mmol/l)	76	51	54
Ca (mmol/l)	25	32	10
Sr (mmol/l)	0.29	--	0.10
SO_4 (mmol/l)	43*	45	29
Br (mmol/l)	1.6	1.2[a]	0.8
NH_4 (µmol/l)	750	--	4[b]
PO_4 (µmol/l)	40	81.5	<0.1[b]
NO_3 (µmol/l)	0	0	1.8[b]
NO2 (µmol/l)	16	--	0.5[b]
O_2 (ml/l)	0	0	4-5

a) from Trabant and Presley (1978).

b) an average of 40 eastern Mediterranean surface water samples, analyzed within 24 hours after collection.

* the sulphate concentration of the bottom water (36.8 mmol/l; indicated with an asterisk in Fig. 6.2) is thought to be inaccurate (see Chapter 7) and therefore the value of the uppermost interstitial water sample from the piston core is given.

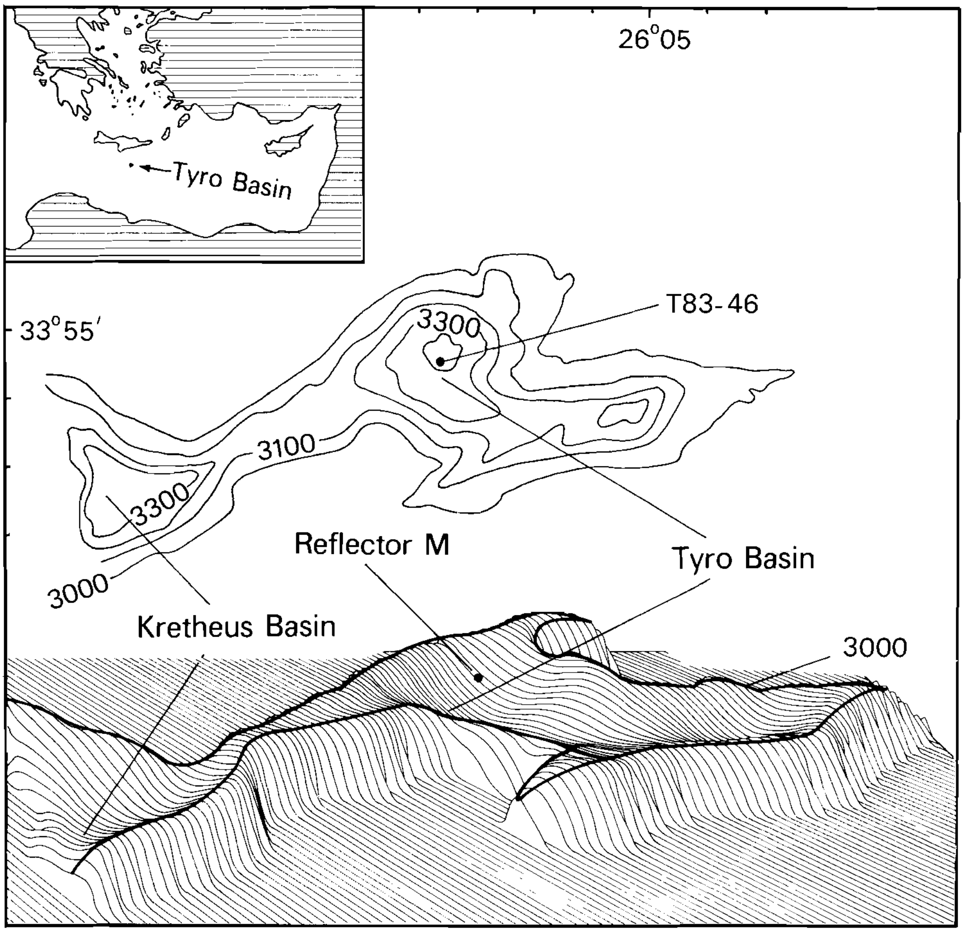


Figure 6.1. Location map of the Tyro basin indicating core T83-46, together with a three dimensional view of the Tyro basin. The position of the 'M' reflector associated with Messinian evaporites is also indicated.

6.3. Discussion

The geomorphology of the Tyro basin is visualized in a three dimensional view (Fig. 6.1.), constructed with the Symap/Symvu plot program of Dougenik and Sheehan (1976) . The resemblance to the three dimensional picture of the Orca basin presented by Trabant and Presley (1978) is striking. These authors suggest that the observed hummocky trend may be indicative of an underlying salt mass or a former salt ridge.

The Tyro brine is more concentrated than the Orca brine (Table 6.1.). The density of the brine (1.199 g/ml at 20°C) is also shown by a midwater sound reflector about 70 m above the basin floor (Jongsma et al., 1983). The stratification of the water column limits vertical exchange resulting in a depletion of O_2 and NO_3 by organic degradation, and a corresponding increase of NH_4, PO_4 and NO_2 (Table 6.1.).

In a gross approximation, the volume of the brine is 3×10^8 l water. This value is calculated from seafloor topography based on Sea Beam surveying (Huchon et al., 1982). Assuming that the brine was formed through dissolution of Messinian evaporitic sequence by seawater (containing 0.5 mol Na/l), that the surplus of Na is all from halite, and that no exchange of brine water with seawater above the depression occurred, it can be calculated that 8.5×10^7 Kg halite is dissolved. The SO_4 profile versus depth of interstitial water from piston core T83-46 (Fig. 6.2.) shows a strong decrease downwards indicating sulphate reduction. In the Orca basin no evidence for sulphate reduction was found (Addy and Behrens, 1980). Considering the quantities of salt dissolved and the observed SO_4 gradient, it seems impossible to attribute the origin of the brine solely to diffusion from sediments underneath.

Solubility calculations of the chemical composition using the computer program of Shapley and Cutler (1970, modified by A. van Genderen) revealed that the brine is still undersatured with respect to halite and that dissolution of salt still takes place. The brine is supersaturated with respect to dolomite. The high SO_4 content can be attributed to the dissolution of gypsum. It can be calculated, with the same assumptions as above for Na, that 7.7×10^5 Kg gypsum is dissolved. Since diagenesis consumes SO_4 (Fig. 6.2.) then the estimate

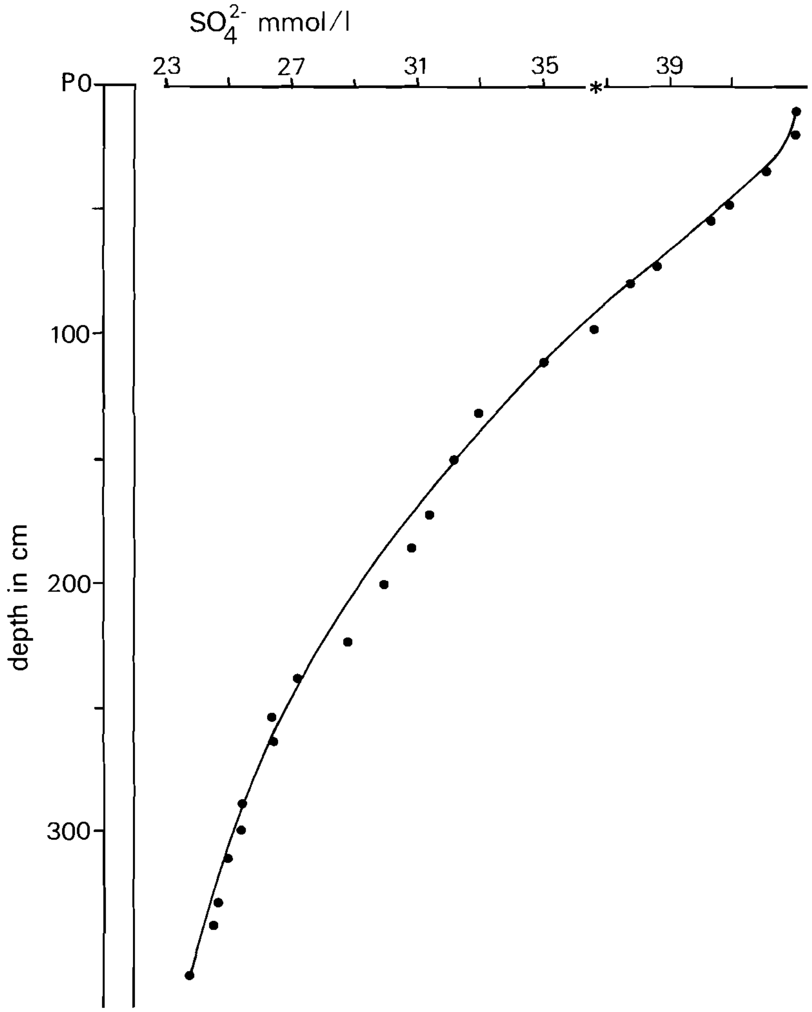


Figure 6.2. Sulphate profile versus depth in interstitial water of sediments from core T83-46. P0 stands for the top level of the piston core.

of dissolved gypsum is too low. The high Mg content can be attributed to soluble salts. Such salts were recovered in the centre of the eastern Mediterranean during DSDP leg 42A (Kuehn and Hsü, 1978). Also the K enrichment can be ascribed to soluble salts.

Calculations were also made to estimate the Br and Sr content of the original salt deposits, in both cases assuming that all the surplus Br and Sr originates from halite and gypsum respectively. The partitioning of Br between brine and precipitating minerals at various stages of seawater evaporation is well known (e.g. Decima, 1976). The Br content may therefore be indicative of the paragenesis of its source rock. These estimations gave a 200 ppm Br content for the halite and 5800 ppm Sr for the gypsum, the latter being extremely high. The Br value corresponds to a marine halite precipitated with polyhalite; similar values were also found at DSDP site 374 in the Ionian basin (Kuehn and Hsü, 1978). These authors report a Br content of halite ranging from 114 to 218 ppm. Normal gypsum precipitating with halite from seawater contains 2100-2300 ppm Sr (Usdowski, 1973). This suggests that there is also another source for Sr, or that our estimate of dissolved gypsum is indeed too low.

Another source for Sr could be celestite. This mineral has not been reported from DSDP drill sites, but has been found in Messinian land sections in the northern Apenninnes (ten Haven, unpublished results). Recycled evaporitic deposits are marked by low Br and Sr contents and can therefore be rejected as the source rock. Most likely the evaporitic sequence consists of normal precipitated gypsum, halite and some soluble salts. The recent discoveries of anoxic basins indicate that the presence of similar basins associated with outcropping Messinian evaporites is likely to cause stagnant conditions and shows that sapropelic sediments do not necessarely have to be formed over the entire eastern Mediterranean.

Chapter 7

INTERSTITIAL WATER STUDIES OF LATE QUATERNARY EASTERN MEDITERRANEAN SEDIMENTS WITH EMPHASIS ON EARLY DIAGENETIC REACTIONS AND EVAPORITIC SALT INFLUENCES

Abstract

Interstitial waters of five piston cores from the eastern Mediterranean were recovered by shipboard squeezing and analyzed for their major elements. Additionally organic carbon, $CaCO_3$ and HCl extractable Mg were determined in the sediments from these cores. Three cores contain sapropels, which are considered to be the sedimentary expression of anoxic periods during the Quaternary. The pH in the interstitial waters extracted from the sapropels is significantly lower than the pH of the interstitial waters from the surrounding sediment. It is suggested that the low pH in sapropel interstitial waters is induced by bacterial activity. Other dissolved elements are not influenced by these sapropel layers.

Core T83-46, taken in the hypersaline anoxic Tyro basin, shows a strong downward SO_4 decrease, accompanied by a strong NH_4 increase. The interstitial water chemistry of the Tyro basin sediment is attributed to selective leaching of evaporitic salt, first halite dissolution later followed by gypsum dissolution. The interstitial water

chemistry of core T83-45, taken in the adjacent Kretheus basin, is dominated by diffusive processes, which became important ever since oxic conditions returned in this formerly anoxic hypersaline basin

7.1. Introduction

The Quaternary stratigraphy of eastern Mediterranean sediments is characterized by sapropels that are considered to be the sedimentary expressions of stagnation and development of anoxic conditions. These sediments are therefore interesting objects for interstitial water studies. Apart from the results of the DSDP program, Leg 13 (Sayles et al., 1972; Presley et al., 1972) and Leg 42 A (McDuff et al., 1978; Bode and Sotelo, 1978), to our knowledge only one deep sea piston core from the western Mediterranean has been studied in detail for its interstitial water chemistry (Church et al., 1971; Michard et al., 1974). Milliman and Müller (1973) reported some preliminary interstitial water results from piston and gravity cores from the eastern Mediterranean. Most of the interstitial water data obtained from DSDP drill sites in the Mediterranean show a significant increase in Cl with depth. The same feature is also found at many other locations overlying salt deposits (Gieskes, 1983 and references therein). In the Mediterranean this Cl increase is caused by underlying Messinian salt deposits.

Small anoxic basins are found in the eastern Mediterranean, which find their origin in the dissolution of outcropping Messinian salt deposits (ten Haven et al., 1985a). Two similar anoxic hypersaline basins are known; viz. Tyro basin (Jongsma et al., 1983) and Bacino Bannock (Scientific Staff of cruise Bannock 1984-12., 1985). Preliminary interstitial water analyses of sediments from the Kretheus basin, adjacent to the Tyro basin, suggested that hypersaline and anoxic conditions existed in this basin up to very recently (de Lange and ten Haven, 1983). Anoxic conditions, that also lasted until a few thousand years ago in basins of the Katia area, are reported by the Scientific staff of cruise Bannock 1984-12 (1985).

The present paper describes the interstitial water results obtained from five piston cores, including a core from the Tyro basin and a core from the Kretheus basin.

7.2. Sampling procedures

The cores were collected during a 1983 cruise with the R.V. Tyro to the eastern Mediterranean. The cores were recovered with a piston corer and a gravity trip corer, serving as trigger weight, with attached Nansen bottles at 0.5 and 1.5 m above the sediment-water interface. The location of the cores is shown in Fig. 7.1.

The shipboard working procedure is described in detail by de Lange (1984). Briefly the PVC lined core is cut into 1 m sections , sealed and stored horizontally at 3-4 °C. Interstitial water extraction is started within 24 hours. The core is split lengthwise with a hydraulic cutting device and one half is immediately transferred to a nitrogen filled glove bag in a walk-in refrigerator, which is kept at in situ temperature (ca. 13 °C). After a subsample is taken for porosity determination, an interval of 5 to 15 cm of sediment is sampled for interstitial water extraction. The samples are then transferred via a sluice to a glove box flushed with high purity nitrogen and squeezed with modified Reeburgh-type squeezers (Reeburgh, 1967), using pressures up to 15 bar. The oxygen concentration and temperature inside the glove box are monitored continuously. Oxygen was generally below 0.005 %. The interstitial water is collected in polyethylene bottles, which were acid cleaned, thoroughly rinsed with demineralized water and dried prior to their use. Subsequently the interstitial water is separated into four portions; one for shipboard analyses, one of 4 ml for alkalinity determination, one of 8 ml, which is immediately acidified with 200 µl of 4N HCl for on shore analyses, and the remainder, which is deep frozen. The bottom water samples are divided into two portions; one in a polyethylene bottle, which is deep frozen after on board analyses, the other for oxygen analysis. The squeezed sediment is divided into two portions, one stored under nitrogen at 4 °C, the

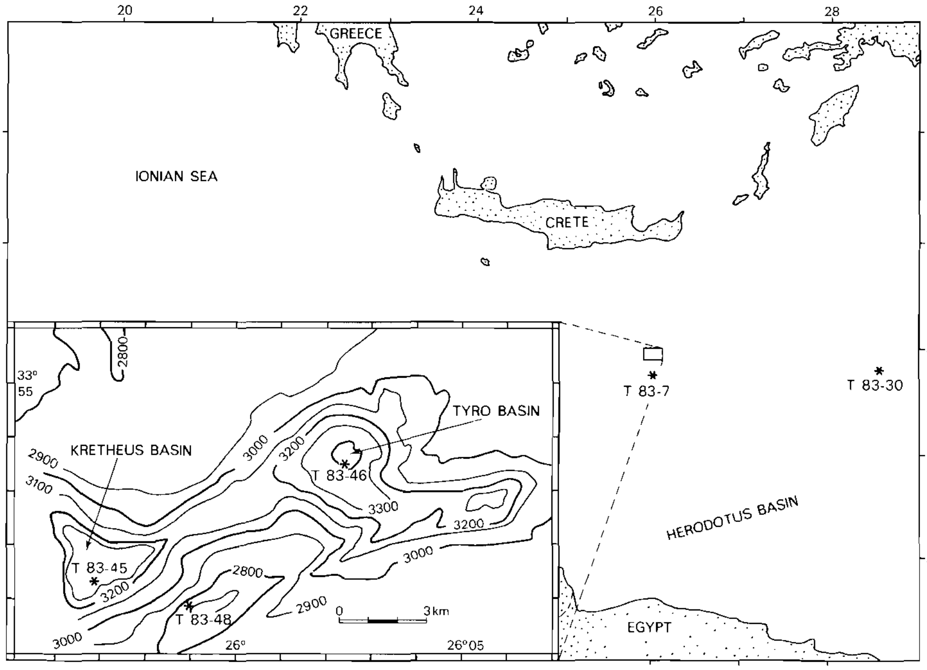


Figure 7.1. Location of the five piston cores. Core T83-7: 33°39.65´N, 25°59.00´E, water depth 2479 m; Core T83-30: 33°48.20´N, 28°36.60´E, water depth 2812 m; Core T83-45: 33°50.54´N, 25°56.73´E, water depth 3316 m; Core T83-46: 33°52.02´N, 26°02.30´E, water depth 3473 m; Core T83-48: 33°50.10´N, 25°59.05´E, water depth 2724 m. The positions are based on Loran C navigation.

other stored at - 20 °C for organic geochemical studies (cf ten Haven et al., 1986a, b; see e.g. chapters 2 and 3).

7.3. Experimental

A total of 10 to 80 ml of interstitial water was obtained per sample. On board NH_4, NO_3 and NO_2 were analyzed with a Skalar SA-400 autoanalyzer. Standards and blanks were prepared in a stock of nutrient depleted Atlantic surface water. The pH of the interstitial water was measured with a pH/Eh meter, Radiometer model 471. Alkalinity was determined titrimetrically according to a method adapted from Strickland and Parsons (1968). Dissolved oxygen was determined by the Winkler method (Grasshoff et al., 1983) .

The following constituents were analyzed within eight months after collection. If the amount of the retrieved water was too small for the subdivision mentioned above, the analyses were carried out on the portions previously used for alkalinity determination, correcting for the extra dilution. Results obtained during the last few years in our laboratory have shown that these data are less accurate than those obtained by direct determination in the interstitial waters. Na, Mg, K and Ca were analyzed by routine flame Atomic Absorption Spectrometry with a Perkin Elmer 2380 model, using Cs and La as spectroscopic buffers. Sr was determined by electrothermal atomization AAS, using a Perkin Elmer 5000 atomic absorption spectrometer equipped with a HGA 400 graphite furnace model and Zeeman background correction. Standards were prepared in artificial seawater in order to minimize matrix effects. Cl was determined by Mohr titration with silver nitrate (Vogel, 1961). SO_4 was determined by ion chromatography with conductivity detection using an Amolex 81 Ion-Chromatograph. The SO_4 standards were made from Atlantic surface water.

Porosity of the sediment was calculated after wet and dry weighing of an aliquot of sediment, using the expression by Berner (1971).

$$\text{Porosity} = \frac{W\ p_s}{W\ p_s + (1-W)\ p_w}$$

where W = % H_2O obtained by difference (wet wt/100), p_s = dry density of solid sediment material, assumed to be constant (2.65 g/cm^3) and p_w = density of interstitial water (1.03 g/cm^3). No corrections were made for layers with an extremely high organic carbon content, which have usually a lower density (Müller and Suess, 1979) resulting in a lower porosity. To make the proper corrections for samples taken in core T83-46, the density of the interstitial water is assumed to be the same as the density of the brine (1.199 g/cm^3) (ten Haven et al., 1985a; see chapter 6).

Detailed subsamples of the sediment cores were taken at irregular intervals, taking into account the visible changes in the sediment stratigraphy. In order to compare the "normal" Mediterranean sediment samples with sediment samples from the hypersaline Tyro basin, all samples were desalted by dialysis against a continuous flow of demineralized water until the electroconductivity was below 100 µS. The desalted sediment suspension was then freeze dried and homogenized. A weighed amount of dry sediment (ca. 0.5 g) was reacted with 1 M HCl until the effervescence ceased. The HCl solution was decanted after centrifugation and the residue washed three times with distilled water. The combined supernatants (HCl plus distilled water portions) were collected. Ca, Mg and Sr were determined in this HCl/water fraction with Inductively Coupled Plasma Emission Spectrometry (ARL type 34000). The sediment was oven dried (40 °C) and organic carbon and nitrogen were determined by combustion with a Perkin Elmer 240 Elemental Analyzer. From the ICPES analyses the percentage $CaCO_3$ was calculated and the organic carbon values were corrected for the $CaCO_3$ content. The organic nitrogen was only accurate in samples with a high organic carbon content.

7.4. Results

The interstitial water data are shown in Figs. 7.2.A, 7.3.A, 7.4.A, 7.6.A and 7.8.A. The results obtained from the sediment analyses are shown in Figs. 7.2.B, 7.3.B, 7.4.B, 7.6.B and 7.8.B. A simplified lithological column, indicating the sapropels, is also presented in these figures. Detailed descriptions of the cores can be found in Ganssen and Troelstra (1986) and Troelstra (1986).

The loss of sediment during coring with a piston corer is often difficult to estimate (e.g. McCoy, 1980), especially in an area such as the Mediterranean with highly varying sedimention rates. Sometimes a gap even exists between the bottom of the trip core and the top of the piston core. In two cases, cores T83-7 and T83-45, a rough estimate of the sediment loss with the piston corer could be made from some of the observed interstitial water gradients (NH_4 profile for core T83-7; the Na and Cl profile for core T83-45). This approach could not be used for the other three cores, but a top layer of at least 40 cm can reasonably be assumed to be missing. The lines in the interstitial water figures were drawn after first, second or third order polynomial fitting calculations. Bottom water samples, indicated with an asterisk, generally show deviations for Ca, Sr and SO_4 probably caused by the storage procedure of these samples (deepfrozen). A likely explanation is that $CaSO_4$ incorporating Sr precipitated during freezing and that this preciptate was not completely dissolved at the time of subsampling for the analyses. These data together with the data between brackets were excluded from the polynomial fitting calculations.

The gap in the profile of Mg, Ca and Sr between the piston core and trip core of core T83-7 can best be explained by an underestimate of the sediment loss during coring, although an artifact induced by a difference in compression during coring between the trip core and piston core cannot be excluded. The gap is most pronounced in the Mg profile. Perhaps exchange processes occur between interstitial water and the tephra layer at the top of the piston core, providing a sink for magnesium (Gieskes, 1983), but additional information on the isotopic composition of dissolved strontium ($^{87}Sr/^{86}Sr$) and the oxygen isotopic composition of the interstitial water ($^{18}O/^{16}O$) is needed to verify this (e.g. Hawkesforth and Elderfield, 1978).

7.5. Discussion

The interstitial water data are divided into three groups for the purposes of discussion: cores with a normal Mediterranean stratigraphy (T83-7, T83-30, T83-48), the core from the anoxic brine filled Tyro basin (T83-46), and the core from the Kretheus basin (T83-45).

7.5.1. Cores T83-7, T83-30, T83-48

Oxidation/reduction reactions, involving the oxidation of organic matter, dominate the diagenetic processes near the sediment-water interface. These chemical reactions are presented in Table 7.1., but instead of applying the Redfield gross molecule $C_{106}H_{263}O_{110}N_{16}P$ (Redfield, 1958; Froelich et al., 1979; Emerson et al., 1980) the reac-

Table 7.1. Oxidation of Mediterranean sedimentary organic matter.

Oxidation reactions of organic matter

(a) Oxygen reduction:

$$126\ O_2 + C_{106}H_{245}O_{110}N_{10}P + 12\ HCO_3^- \rightarrow 118\ CO_2 + 10\ NO_3^- + HPO_4^{2-} + 128\ H_2O$$

(b) Nitrate reduction:

$$90.8\ NO_3^- + C_{106}H_{245}O_{110}N_{10}P \rightarrow 17.2\ CO_2 + 88.8\ HCO_3^- + 50.4\ N_2 + 77.6\ H_2O + HPO_4^{2-}$$

(c) Mn^{4+} reduction:

$$227\ MnO_2 + C_{106}H_{245}O_{110}N_{10}P + 346\ CO_2 + 104\ H_2O \rightarrow 452\ HCO_3^- + 5\ N_2 + 227\ Mn^{2+} + HPO_4^{2-}$$

(d) Fe^{3+} reduction:

$$212\ Fe_2O_3 + C_{106}H_{245}O_{110}N_{10}P + 740\ CO_2 + 313\ H_2O \rightarrow 846\ HCO_3^- + 424\ Fe^{2+} + 10\ NH_3 + HPO_4^{2-}$$

(e) Sulphate reduction:

$$53\ SO_4^{2-} + C_{106}H_{245}O_{110}N_{10}P \rightarrow 45\ CO_2 + 61\ HCO_3^- + 10\ NH_4^+ + 53\ HS^- + 45\ H_2O + HPO_4^{2-}$$

$CaCO_3$ dissolution/precipitation

(f) $CO_2 + H_2O + CaCO_3 \leftrightarrow 2\ HCO_3^- + Ca^{2+}$

The stoichiometric reactions are listed in order of their occurrence, based on thermodynamical grounds (modified from Emerson et al., 1980). The C:N ratio (106:10) is chosen according to the results of the C:N ratio of Mediterranean sapropels of this study and the C:N results of Sutherland et al. (1984)

tions are given according to the C:N ratio for organic matter as found in Mediterranean sapropels (the N analyses of non-sapropel samples were inaccurate, and therefore the C/N ratios of the sapropels were arbitrary considered to be characteristic). The C:N ratio of the sapropels encountered varies between 9 and 9.6, which is in fair agreement with the results of Sutherland et al. (1984). They reported a C:N ratio equal to about 10 for the organic matter in the S_1 sapropel. A similar approach was also proposed by Hartmann et al. (1973) (applying $C_{106}H_{239}O_{110}N_8P_{(.2-.7)}$ as the organic reactant in the oxidation reactions).

In sediments with high sedimentation rates redox processes, involving reactions a-d of Table 7.1., generally occur at very shallow burial depths (Froelich et al., 1979; Emerson et al., 1980). In order to monitor the subtle changes in NO_3 and NO_2 it is necessary to sample at very close intervals, starting from the sediment-water interface. Due to the large sampling intervals and the loss of the top of the sediment in the piston cores, we have clearly missed the zone of nitrification (reaction a) and of denitrification (reaction b). Therefore NO_3 (all samples < 10 µmol/l) and NO_2 (all samples < 1 µmol/l) results are omitted. The results of the Fe and Mn analyses will be discussed elsewhere. The oxidation of organic matter in these cores is marked by an increase in NH_4 with depth. The decrease in SO_4 with depth in core T83-30 and T83-48 gives evidence for sulphate reduction (Figs. 7.3.A and 7.4.A). Considering that this decrease in SO_4 is not observed in core T83-7 (Fig. 7.2.A), and that the stratigraphy and the environmental conditions of the cores (e.g. water depth and oxygen content of the bottom water) are quite similar, either a difference in redox conditions exists or the decrease in SO_4 is obfuscated by upward diffusion of SO_4 (possibly due to the dissolution of underlying evaporitic deposits). The sulphate reduction and the concomitant oxidation of organic matter takes place under anaerobic conditions and is represented by reaction e of Table 7.1. The increase in NH_4 in core T83-7 (ca. 70 µmol) should theoretically correspond with a decrease of about 0.4 mmol SO_4, which is however within the analytical error of the SO_4 determination. The reduction of 5 mmol SO_4 in core T83-30 and 3 mmol SO_4 in core T83-48 should generate ca. 950 µmol NH_4 and ca. 550 µmol NH_4 respectively. However the increase in NH_4 in core T83-30 amounts only to ca. 160 µmol and is negligible in core T83-48. The deficit of NH_4 could be partly explained by exchange reactions with clay minerals, whereby up to half of the ammonium produced in diagenetic reactions can be fixed onto the ion-exchange sites (Rosenfeld, 1981), however we do not consider this to be a completely satisfactory explanation for the deficit of ammonium. A slight decrease in alkalinity is observed in core T83-7 (Fig. 7.2.A) which is difficult to explain. Both SO_4 reduction and other oxidation reactions are accompanied by an increase in alkalinity. However, in a system open to molecular diffusion and assuming a constant calcite saturation, reactions c and d coupled with reaction f can cause a decrease in alkalinity, accompanied with a decrease in Ca (Emerson et al., 1980; 1982). The alkalinity in cores T83-30 and T83-48 remains nearly constant with depth. It is frequently difficult to rationalize alkalinity profiles in carbonate-bearing sediments (e.g. Emerson et al., 1980). A decrease in alkalinity may result from the reduction in pressure caused by bringing the sediment to sea-level pressure (Murray et al., 1980), but quantitative prediction of this pressure effect is difficult to establish (Emerson et al., 1982). Loss of alkalinity and Ca due to $CaCO_3$ precipitation after squeezing is reported by Gieskes (1973). This

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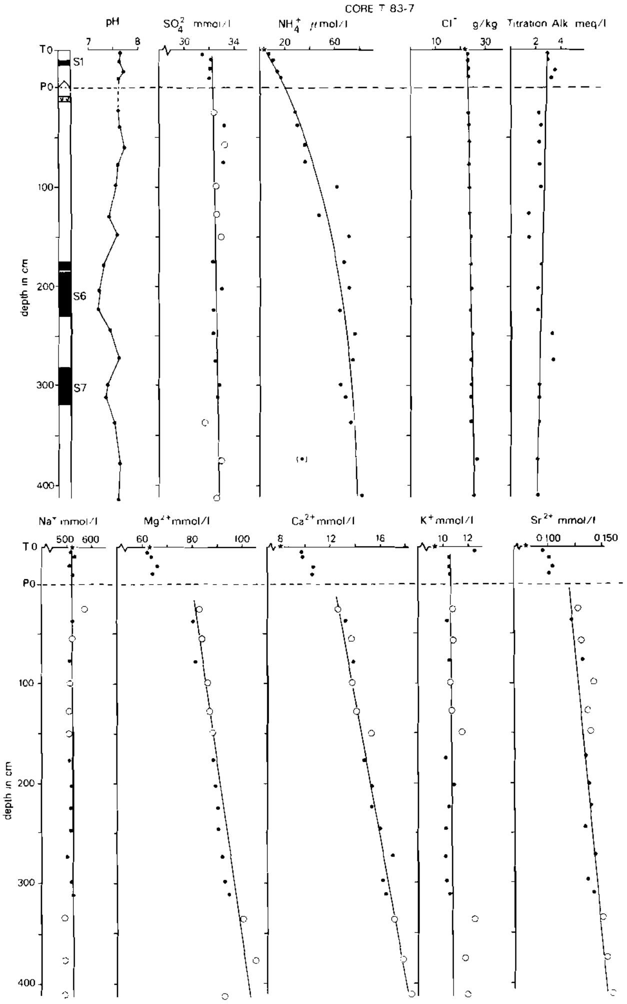
Figure 7.2.A Plot of interstitial water data versus depth in piston- and trip core T83-7. Data represented by open symbols are determined in portions used for determination of alkalinity, because small amounts of interstitial water were recovered at these sample points. Oxygen concentration of the bottom water is 6.11 mg/l. The measured sulphate concentration of the bottom water is 24 mmol/l. Note that the Cl values are reported in g/Kg. The values are, as a consequence of the applied analyses, dependent on the density, which increases with depth in core T83-45 (Fig. 7.8.).

phenomenon is observed in sediments in which SO_4 is strongly reduced and alkalinity exceeds over 20 meq/kg. This is not the case in these cores, however. The percentage of calcium carbonate in the sediment (Figs. 7.2.B, 7.3.B and 7.4.B) varies between 16 and 59%, indicating that the interstitial water is saturated with respect to calcium carbonate. Precipitation of calcium carbonate would lower the alkali-



nity and the concentration of Ca. This could partly be the controlling mechanism in core T83-30 where Ca decreases with depth. Other precipitation reactions, such as the formation of siderite and rhodochrosite, can also control the carbonate system (Gieskes, 1983).

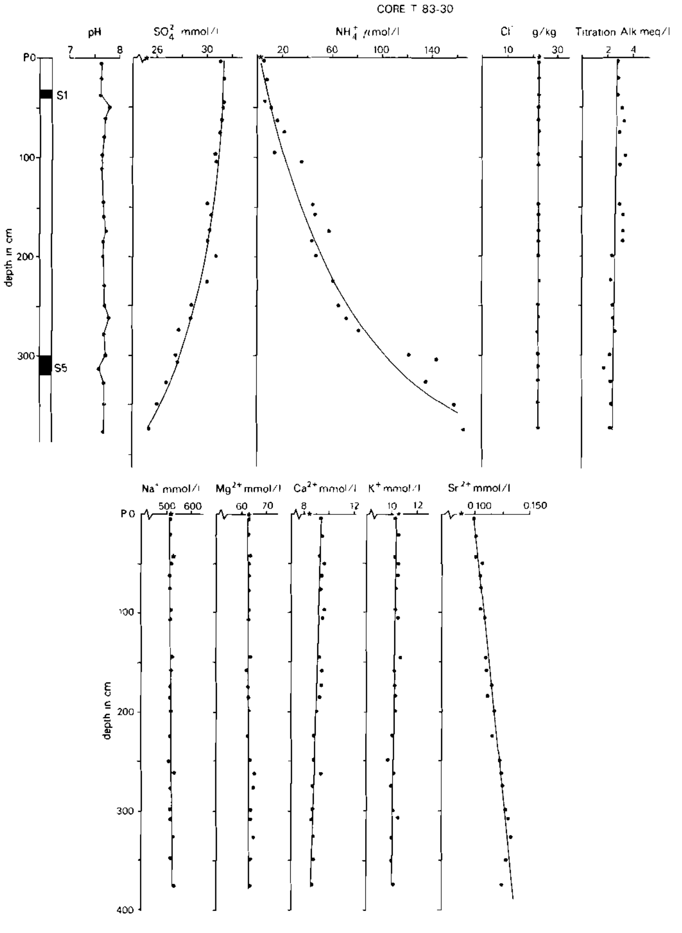


Figure 7.3.A Plot of interstitial water data versus depth in piston core T83-30. Oxygen concentration of the bottom-water is 5.89 mg/l. Ammonium in the deepest five samples was determined after 4 days and these values are therefore not reliable.

The discrepancies in the predictions of the increase of alkalinity with depth might be traced back to the stoichiometric reactions of Table 7.1., where it is assumed that the organic matter is completely mineralized. In fine grained sediment under deep oceanic conditions organic matter is only partly and selectively decomposed. However the reduction of SO_4 will produce some anion (e.g. weak organic acids), which will certainly add alkalinity.

The increase in concentration of Mg, Ca, Sr and Cl as well as the constant concentrations of K and Na in core T83-7 correspond precisely with interstitial water data from the western Mediterranean, that were published by Michard et al. (1974). Two mechanisms have been suggested to explain these features. Michard et al. (1974) proposed that underlying salt deposits are responsible for these profiles and suggested that either halite was missing or the mechanism is selective for alkaline earths. Milliman and Müller (1973) proposed that the breakdown of magnesian calcite, defined as calcite containing more than 4

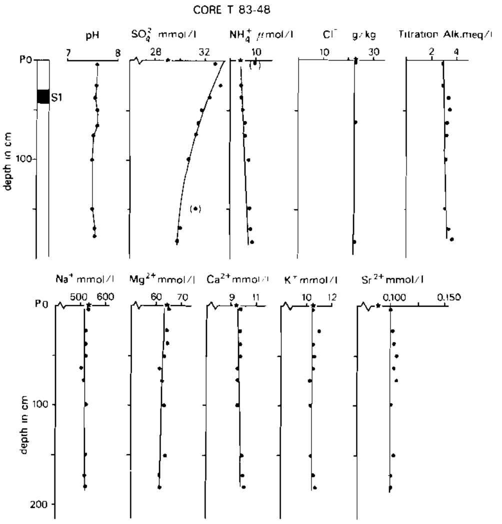


Figure 7.4.A Plot of interstitial water data versus depth in piston core T83-48. Oxygen concentration of the bottom water is 6.14 mg/l.

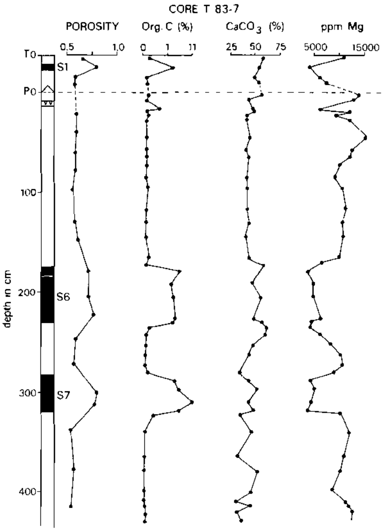


Figure 7.2.B Porosity, Organic Carbon, $CaCO_3$ and HCl extractable Mg in piston and trip core T83-7. To save space the organic carbon scale has been reduced. Maximum Org. C. value is 11.0 %. The T 0 and P 0 mark indicate the top level of the trip core and of the piston core respectively.

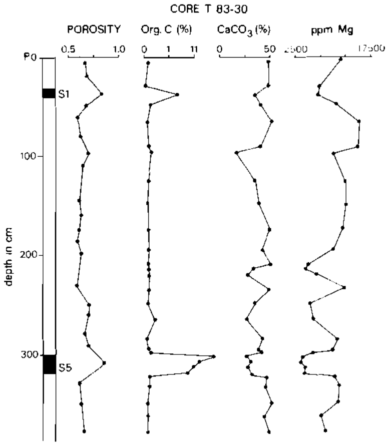


Figure 7.3.B Porosity, Organic Carbon, $CaCO_3$ and HCl extractable Mg in piston core T83-30. Note the scale of the organic carbon. Maximum Org. C. value is 18.9 %.

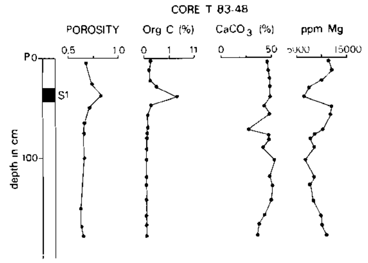


Figure 7.4.B Porosity, Organic Carbon, $CaCO_3$ and HCl extractable Mg in piston core T83-48. Note the scale of the organic carbon. Maximum Org. C. value is 4.3 %.

mol % $MgCO_3$ in solid solution (Chave, 1952), is the principal source of the increase of the concentrations of Mg and Ca in interstitial waters of the eastern Mediterranean. Magnesian calcite comprises 20-50% of the carbonate fraction in the deep sea sediments of the eastern Mediterranean (Milliman and Müller, 1973). Unfortunately no alkalinity data were reported by Milliman and Müller (1973) nor by Michard et al. (1974), which could support the suggestion of magnesian calcite dissolution.

Messinian diapirs in the vicinity of coring site T83-7 are reported by several workers (Leite and Mascle, 1982; le Pichon et al., 1979; Jongsma et al., 1983; Peters and Huson, 1985) and it seems reasonable to attribute the features in core T83-7 to salt influences. How then can the lack of Na enrichment with depth be explained?

One possibility is that a completely developed evaporitic sequence lies underneath, whereby the most soluble salts, the K and Mg salts, are present at the top. Development of such a sequence with a "bull's eye" zonation of saline minerals, according to the desiccated deep basin model of Hsü (1972), was found during leg 42A of DSDP. The dissolution of the most soluble salts will cause a concentration increase of K, Mg and Cl and this functions as a barrier for the dissolution of underlying halite. Such a model of selective dissolution of salt minerals can explain the profiles found in DSDP site 374, where a lack of Na enrichment with depth was also observed (McDuff et al., 1978). Soluble salts were encountered at this DSDP site (Kuehn and Hsü, 1978). The Mg/Cl, Ca/Cl and Sr/Cl ratios of core T83-7 and T83-30 and the top sample of DSDP site 374 (McDuff et al., 1978) are depicted in Figs. 7.5.B, C and D. Bearing in mind that in core T83-7 no increase in K is observed and that this core differs on that basis already from site 374, these figures show that, compared with DSDP site 374, Mg and Ca are relatively more enriched than is Cl. The increase in Cl with depth (ΔCl^- = 100 mmol/l) is counterbalanced by an increase in Ca, Mg and Sr ($\Delta Ca^{2+} + \Delta Mg^{2+} + \Delta Sr^{2+}$ = 50 mmol/l). Although differences in interstitial water chemistry exist between core T83-7 and DSDP site 374, we believe that the observed profiles in

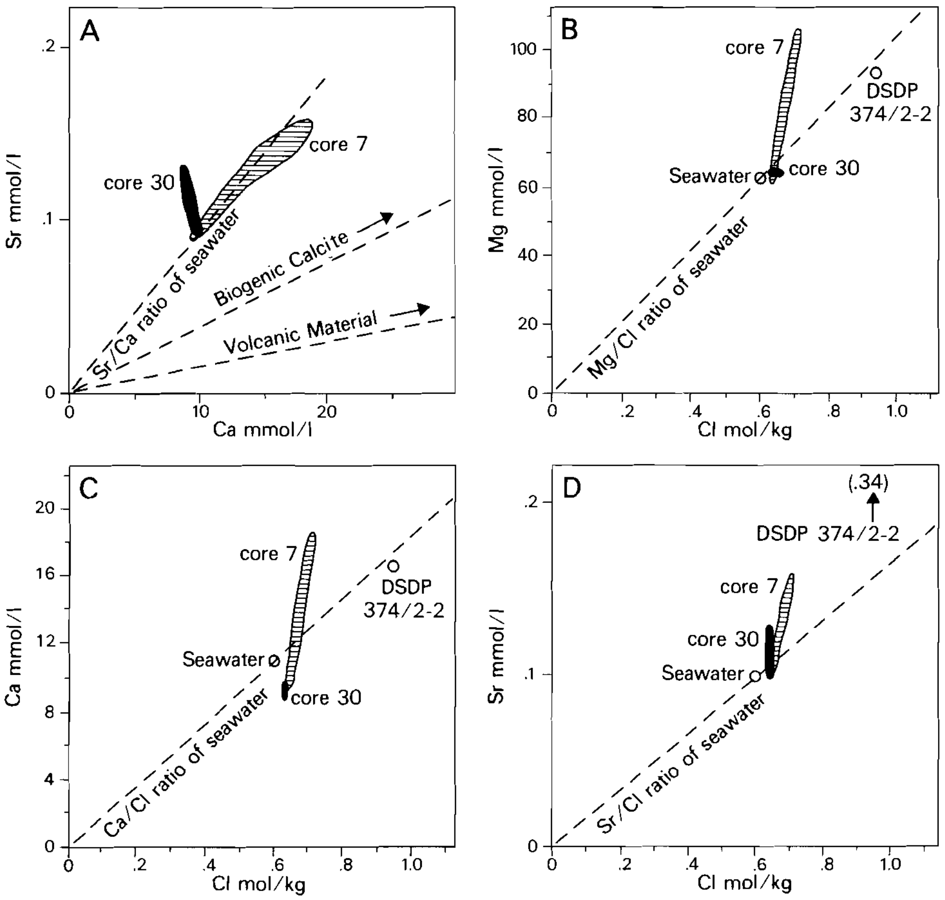


Figure 7.5. Cross plots of Sr versus Ca, Mg versus Cl, Ca versus Cl and Sr versus Cl for interstitial waters in piston core T83-7 and T83-30. DSDP 374/2-2 data after McDuff et al. (1978). Fig. A is drawn according to Hawkesforth and Elderfield (1978). Mediterranean seawater data are from Michard et al. (1974).

core T83-7 can best be explained by selective dissolution of Messinian salt deposits at depth and subsequent upward diffusion with additional exchange of alkaline earth ions (Mg, Ca) for alkaline ions (K, Na) similar to that observed at DSDP site 374. Note that the constancy of

K and Na does not reflect quantitative exchange rather is simply the upper few meters of a diffusion dominated profile extending over several hundred meters.

The suggestion of Milliman and Müller (1973) that magnesian calcite is the principal source for Mg and Ca increase (possibly Sr) is uncertain because of the following observations:

- In cores T83-30 and T83-48 the HCl extractable Mg of the sediment varies in the same range between 4000 and 15000 ppm as in core T83-7 (Figs. 7.2.B, 7.3.B and 7.4.B), but no increase in Mg with depth is observed in interstitial waters of core T83-30 and T83-48. In this approach we assume that the trends in concentrations of acid-extractable Mg as observed in Figs. 7.2.B, 7.3.B and 7.4.B are due to differences in the magnesian calcite content. This is supported by the fact that the sapropel sequences are marked by a low content of magnesian calcite, which was reported by Milliman and Müller (1973). The results are presented in the figures as total acid-extractable Mg concentrations, but approximately the same trends are observed when the concentrations are normalized to total $CaCO_3$ content.
- The alkalinity profile of core T83-7 gives no evidence for dissolution of magnesian calcite and there seems to be no decrease of magnesian calcite with depth as was observed in the cores investigated by Milliman and Müller (1973).

The increase in Sr concentration with depth in core T83-30 (Fig. 7.3.A) can be attributed to a preferential release during recrystallization of Sr-rich biogenic carbonate to form Sr-poor carbonate (Gieskes et al., 1975; Hawkesforth and Elderfield, 1978). The Sr/Ca ratio of interstitial waters from core T83-7 falls on the seawater ratio line (Fig. 7.5.A), but carbonate recrystallization, which causes a deviating Sr/Ca ratio (see core T83-30 in Fig. 7.5.A) can here be obscured by upward diffusion of Ca.

All three cores contain sapropel sequences, which are defined as "a discrete layer greater than 1 cm in thickness, set in open marine pelagic sediments and containing more than 2% organic carbon by weight" (Kidd et al., 1978). Although several hypotheses have been proposed to explain the occurrence and formation of these sapropels, it is generally accepted that they are formed in anoxic environments (see ten Haven et al., 1986a for a review). Recently such conditions were discovered in the Tyro Basin (Jongsma et al., 1983) and in Bacino Bannock (Scientific staff of cruise Bannock 1984-12, 1985) in the eastern Mediterranean . The NH_4 concentration in interstitial waters from the Tyro Basin increases from 1000 µmol/l up to 3000 µmol/l at 4 m. depth (de Lange and ten Haven, 1983; see also Fig. 7.6.A) and the pH of the interstitial waters is ca. 7 (Fig. 7.6.A). Assuming that these concentrations are characteristic and thus representative for the anoxic periods, which led to sapropel formation during the Quaternary, it is interesting to observe that they are completely obliterated in the sapropel sequences of cores T83-7, T83-30 and T83-48. Approximately 7000 - 9000 years ago the last basin-wide anoxic event took place in the eastern Mediterranean, leading to the formation of sapropel S_1. This period of time is sufficiently long to remove all NH_4 by diffusion into the bottom water. Post-depositional oxidation of ammonium via nitrite to nitrate and subsequent diffusion of the latter species into the bottom water can also play an important role. The low pH of interstitial waters extracted from sapropels S_5, S_6 and S_7 (Figs. 7.2.A and 7.3.A) cannot be a remnant of anoxic periods, because the diffusion coefficient of H is much higher than the diffusion coefficient of NH_4 (Li and Gregory, 1974). The vertical extent of the sapropels in conjunction with their organic carbon content seems to control the pH. The most prominent sapropel, S_6 in core T83-7, shows the largest decrease in pH. Oxidation of pyrite ($FeS_2 + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4{}^{2-} + 2\ H^+$) produces low pH conditions. The occurrence of gypsum in sapropels has been explained by precipitation of Ca released from dissolving biogenous carbonate, and SO_4 released from pyrite oxidation (Calvert, 1983). The oxidation of pyrite can be caused by post-depositional diffusion of oxygen into the sediment, when aerobic conditions returned after the period of sapropel formation. This mechanism is consistent with the absence of gypsum below sapropels, becoming rare at their base and increasing towards their top (Cita et al., 1977). Such a sequence can be expected when oxygen diffuses downwards and starts to oxidize pyrite at the top of the sapropel. Because the older sapropels are presently buried at a depth where oxygen is already exhausted (a conclusion based on the SO_4 profile in core T83-30), we suggest that the decrease in pH, observed in interstitial water recovered from the sapropels, results from bacterial activity producing organic acids under anaerobic conditions. Bacterial organic geochemical marker molecules were indeed found in sapropel sequences (ten Haven et al., 1986a, b). The sediments of lower porosity bounding the sapropels (Figs. 7.2.B, 7.3.B, 7.4.B) will limit the dispersal of H by diffusive processes. To test this hypothesis it is necessary to analyze the interstitial water for volatile fatty acids.

7.5.2. Core T83-46

This core, collected in the anoxic hypersaline Tyro basin, is unique for the Mediterranean (Jongsma et al., 1983). The brine is thought to be derived from dissolution of outcropping Messinian salt (ten Haven et al., 1985a). The Cl and Na concentrations are extremely high and show no variation with depth (Fig. 7.6.A). No estimate can be made of the time of accumulation of the brine, as was successfully carried out by Addy and Behrens (1980) for the Orca brine on basis of a Cl profile. The SO_4 decrease of 19 mmol/l is again not accompanied by an NH_4 increase of 3.7 mmol/l as would be expected from the stoichiometry of reaction 5 of Table 7.1. Small authigenic gypsum crystals were found in a box core from the Tyro basin, but not in the piston core (Troelstra, 1986). The brine is presently undersaturated with respect to gypsum (ten Haven et al., 1985a) and a SO_4 decrease due to gypsum precipitation is therefore excluded. The alkalinity seems to be controlled by precipitation of calcite and degradation of organic matter. In the upper 100 cm the calcite precipitation causes a decrease in the alkalinity, whereas in the lower part degradation of organic matter predominates causing an increase in alkalinity. There

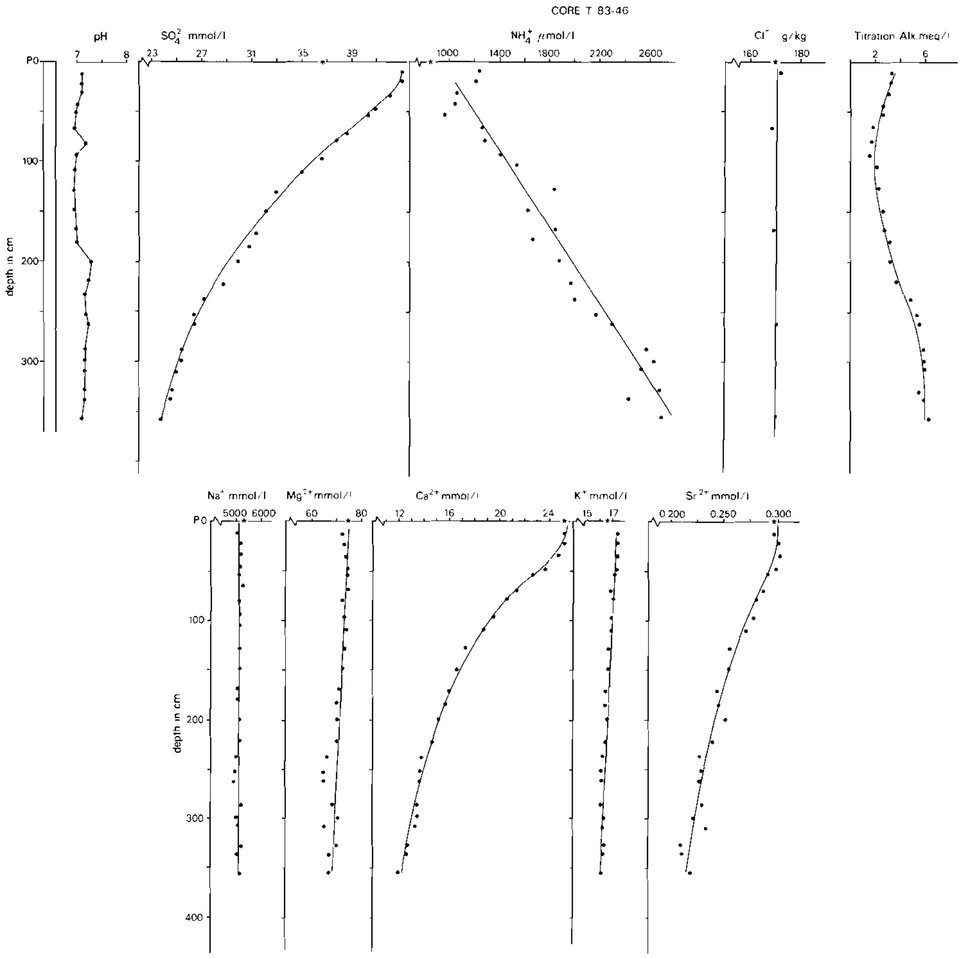


Figure 7.6.A Plot of interstitial water data versus depth in piston core T83-46. Oxygen concentration of the bottom water is 0 mg/l (de Lange and ten Haven, 1983).

seems to be a relationship between Ca and Sr suggesting that calcite may also remove Sr. However incorporation of Sr in calcite is unlikely to be sufficient, as the Sr content of calcite is low. An alternative explanation is that the Tyro brine is selectively formed, first by halite dissolution, later followed by gypsum dissolution (perhaps induced by continued tectonic activity), releasing Ca and SO_4 as well as Sr. The Sr profile is then only controlled by diffusion into sediment, whereas the SO_4 and Ca profiles are also influenced by sulphate reduction and calcite precipitation respectively. A plot of Ca versus Sr (Fig. 7.7.) shows indeed a depletion of Ca when compared with the seawater ratio line.

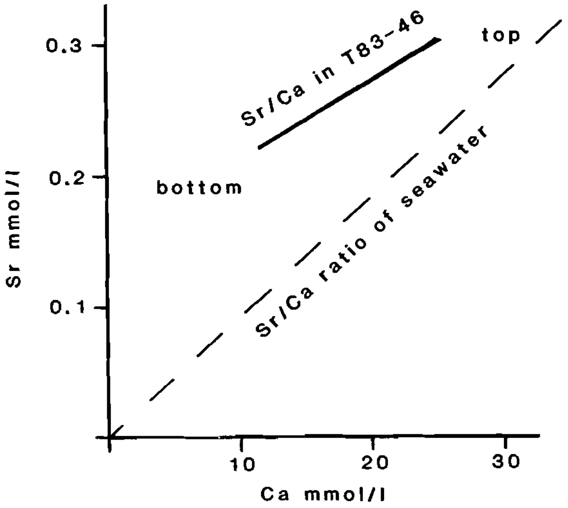
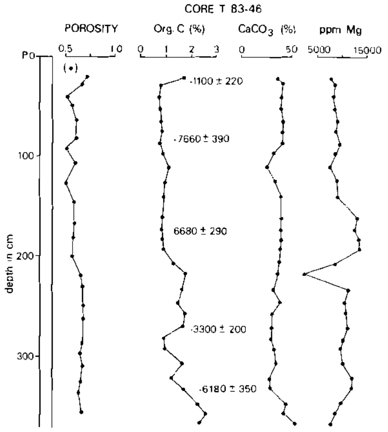


Figure 7.7. Ca versus Sr for interstitial waters in core T83-46.

Two mechanisms have been proposed to explain a decrease of Mg with depth in a reducing environment. Sholkovitz (1973) proposed that the cation exchange capacity of clay minerals is increased with depth, because of removal of iron coatings, thereby making blocked sites available for Mg uptake. Drever (1971) suggested that Mg is removed by replacement of iron in a silicate phase. In trying to elucidate which of the two mechanisms prevail, Bischoff et al. (1975) showed on basis of laboratory experiments that both mechanisms could account for a decrease of Mg. A decrease of K with depth is also attributed to either

Figure 7.6.B Porosity, Organic Carbon, $CaCO_3$ and HCl extractable Mg in piston core T83-46. The results of the ^{14}C dating of organic carbon are taken from Troelstra (1986).



cation exchange processes (Russell, 1970) or to replacement in an insoluble, probably silicate phase (Zaitseva, 1962, in Mannheim, 1976). Sayles (1979) observed a relationship between the K depletion in interstitial water and the amount of continentally derived kaolinite in sediments from the Brasil basin.

McCoy and Stanley (1984) suggested that the sedimentation rate is probably extremely high in the Tyro basin due to resedimentation processes triggered by active tectonism. These resedimentation processes became evident from the carbon dating analyses of organic carbon (Fig. 7.6.B, see also Troelstra, 1986). The porosity and organic carbon profiles are both influenced by these resedimentation processes (Troelstra, 1986). The carbonate content varies little with depth in contrast with HCl extractable Mg which shows a sharp negative peak at the "turnover" point from the partly pelagic to the totally resedimented sediment (Fig. 7.6.B). We have no explanation for this phenomenon, but it is remarkable that above this point Mg is slightly enriched.

7.5.3. Core T83-45

This core was collected in the presently oxic Kretheus basin, separated by a sill at a depth of 3100 m from the anoxic, brine-filled

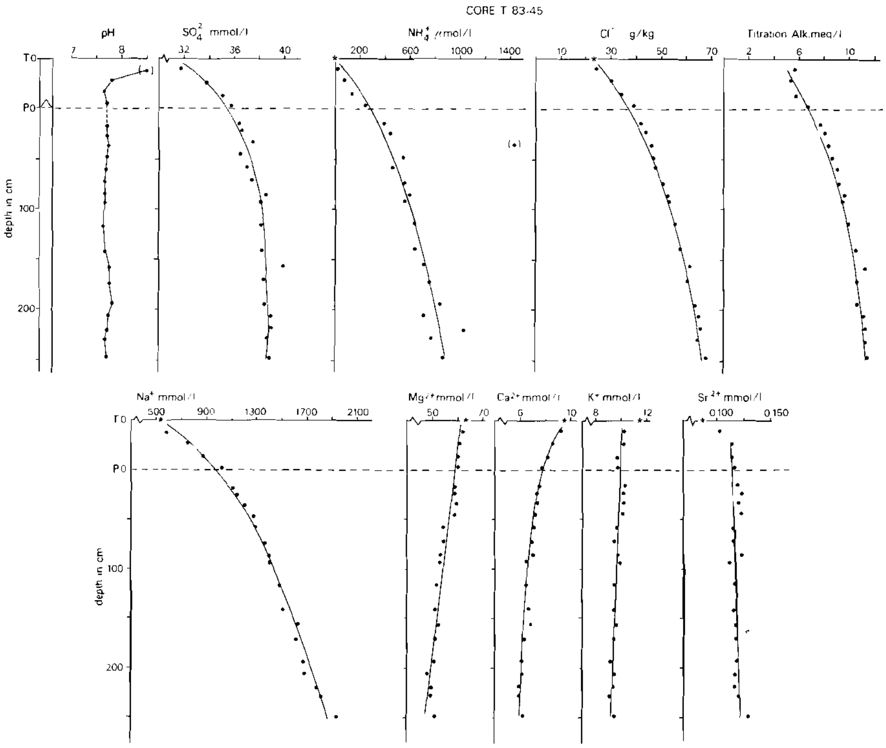
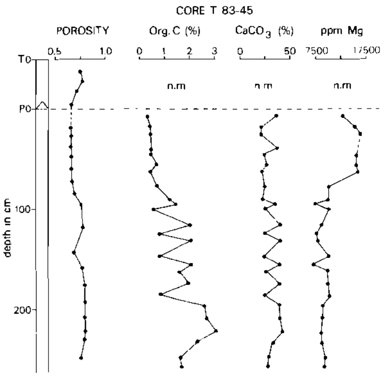


Figure 7.8.A Plot of interstitial water data versus depth in piston- and trip core T83-45. Oxygen concentration of the bottom water is 6.03 mg/l. The measured sulphate concentration of the bottom water is 24 mmol/l. The T 0 and P 0 mark indicate the top level of the trip core and of the piston core respectively.

Tyro basin (Fig. 7.1.). The uppermost 3 cm of the piston core sediment is brown coloured, whereas the rest of the sediment has a greyish green colour similar to the sediment colour of core T83-46. This observation in combination with the Cl profile (Fig. 7.8.A) was interpreted as evidence for the presence of anoxic hypersaline conditions in the Kretheus basin up untill very recently (Jongsma et al., 1983; de Lange and ten Haven, 1983). Preliminary diffusion calculations

Figure 7.8.B Porosity, Organic Carbon, $CaCO_3$ and HCl extractable Mg in piston and trip core T83-45. N.M. = not measured.



showed the turnover time to be ca. 3000 years ago (de Lange and ten Haven, 1983), suggesting a link with the Minoan eruption (see Troelstra, 1986)

As starting point for modelling and interpreting the observed profiles of core T83-45 (Fig. 7.8.A), we assume that the brine formerly present in the Kretheus basin was essentially the same as the Tyro brine (Jongsma, 1986). At the time that normal Mediterranean seawater conditions returned diffusive processes became important. The Cl and Na profiles are excellent examples for diffusive controlled processes. Sjöberg et al. (1984) found similar profiles of Cl and Na in interstitial waters from postglacial black clays, but the chlorinity range (0-7 °/oo) in their study is different. The increase in Cl (1372 mmol/l) is almost exactly counterbalanced by the increase of Na (1365 mmol/l), which is a logical consequence of the restriction of electro neutrality. (The Cl values in g/kg were transformed to values in mmol/l assuming a linear relationship between density and chlorinity of Mediterranean seawater, with Cl = 22 °/oo, p_w = 1.03 g/cm^3, and density and chlorinity of the Tyro brine, with Cl = 170 °/oo, p_w = 1.19 g/cm^3). It is noteworthy that the Cl content of the bottom water in the Kretheus basin (23 °/oo) is slightly higher than that of the bottom waters collected at other sites (22 °/oo). A number of possible diffusion scenarios were constructed (see for theoretical background

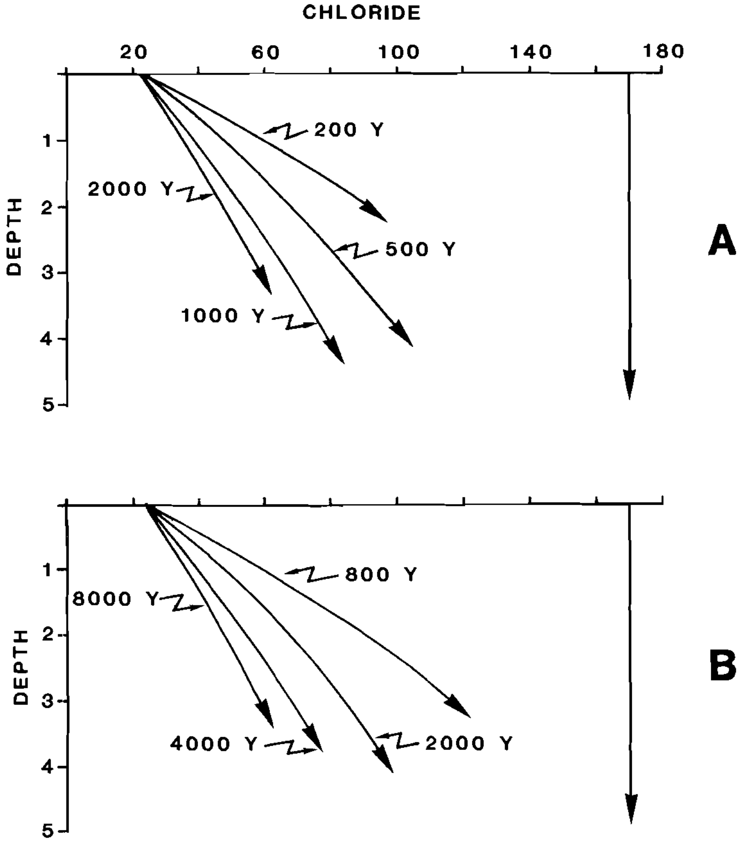


Figure 7.9. Model plots of chloride diffusion calculations. Boundary conditions: initial concentration 170 ^{o}/oo shifted to 21 ^{0}/00 at T = 0. Calculated for diffusion coefficient D = 1.34×10^{-5} cm^{2}/sec and cross-coupling term 0.78. Fixed depth at 50 m (A) and 25 m (B).

McDuff and Gieskes, 1976) and compared to the concentration gradient observed in the sediment. Cross-coupling terms, resulting from the electroneutrality requirement, were taken into account in the diffusion calculations (calculated according McDuff and Ellis, 1979). It is noteworthy to mention that there is especially an acceleration of Sr and SO$_4$ compared to Ca, due to their cross-coupling terms. Using the models which gave the best fit (e.g. Fig. 7.9.), the calculated range for the turnover time is estimated to be 250-4000 years, depending on the boundary conditions (i.e the depth at which the Kretheus chlorinity is equal to the chlorinity of the Tyro basin, see Figs. 7.9.A and B). The NH_4 profile also reflects a diffusion controlled intermediate between values found in the normal Mediterranean cores and the Tyro core. The contribution of NH_4 due to oxidation of organic matter since the cessation of anoxic bottom water conditions, cannot be estimated. Like Cl and Na the SO_4 profile can be explained by diffusion of sulphate in to the bottom water, taking as starting point, a profile found in the Tyro basin (the only requirement was to have the proto-

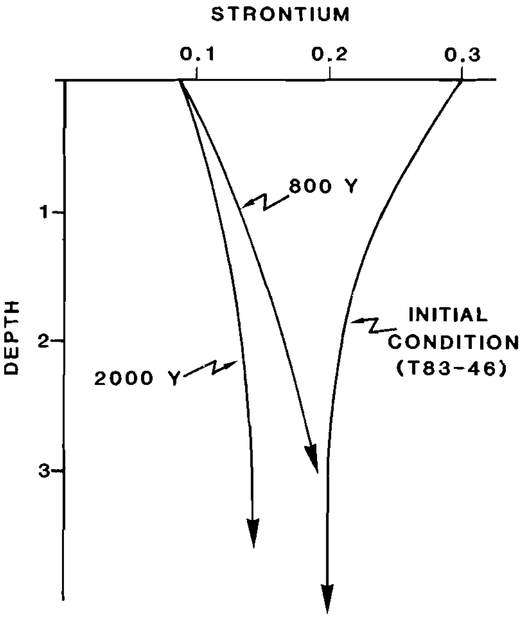


Figure 7.10. Model plot of strontium diffusion calculation. Boundary conditions: initial concentration 0.3 mmol/l shifted to 0.09 mmol/l at T = 0. Calculated for diffusion coefficient D = 4.90×10^{-6} cm^2/sec and cross coupling term 3.55. Fixed depth at 25 m.

Kretheus not quite as sulphate reducing as the present Tyro). A test would be provided by a longer core, in order to show the relic effects of sulphate reduction at deeper levels in the Kretheus basin. The origin of Ca, Sr and SO_4 enrichment is most likely from the dissolution of calcium sulphate phases. However, the high alkalinity values makes it difficult to interpret the Ca profile as calcite precipitation will dominate the transport terms. The Sr data follow the diffusion relaxation seen in other anions and cations. This is illustrated in Figure 7.10.

Chapter 8

ORGANIC GEOCHEMICAL STUDIES OF A MESSINIAN EVAPORITIC BASIN, NORTHERN APENNINES (ITALY) I: HYDROCARBON BIOLOGICAL MARKERS FOR A HYPERSALINE ENVIRONMENT

Abstract

This paper describes the occurrence and significance of hydrocarbons present in two bituminous marl layers and one distinct gypsum layer from a Messinian sedimentary basin, where hypersaline conditions prevailed. Several new compounds were detected and tentatively identified: of these 20R- and 20S-4α,24-dimethyl-5α(H),14β(H),17β(H) and 20R- and 20S-4β,24-dimethyl-5α(H),14β(H),17β(H) cholestanes; 4-methylspirosterenes; 4,4-dimethyl-5α(H),14β(H),17β(H) pregnanes and homopregnanes are discussed in this paper. Several of these compounds might be considered as biological markers for a (hyper) saline environment. The short side chain 4-desmethylsteranes, 5α(H),14β(H),17β(H)-, 5α(H),14β(H),17α(H)- and 5α(H),14α(H),17α(H) pregnanes and homopregnanes, are the most abundant compounds in the extract from the gypsum sample. It is suggested that in this case these compounds do not reflect the stage of diagenesis but are related to certain organisms exclusively occurring in hypersaline environments. In addition the very low pristane/phytane ratio, often considered as an indicator for anoxicity, could also be interpreted as a useful indicator for hypersalinity.

8.1. Introduction

The Messinian formations (Late Miocene, 6.5 to 5.0 My. Bp) characterise the salinity crisis throughout the Mediterranean area. These formations consist essentially of evaporitic sediments e.g. limestones, gypsum, anhydrite, halite and K-Mg salts and are studied extensively (e.g. Drooger, 1973; Cita, 1982 and references therein).

In Italy part of the Messinian is described as "formazione gessososolfifera" (gypsum and sulphur bearing formation). From this formation sulphur, halite, potash salts and gypsum are mined; also "bitumina" occur, which are usually very rich in sulphur (up to 11.4%; Colombo and Sironi, 1961). These bitumina occur in the basal bituminous marls, in diatomaceous shales, evaporitic limestones and almost always in marly intercalations within the evaporitic strata. According to Selli (1973) the hydrocarbon content is sometimes so high that the Messinian is assumed to be the source rock for most of the Italian gas in the Po plain. However gas producing reservoirs of Trias age are also known (Mattavelli et al., 1983). The fine-grained hemipelagic sediments of the early Pliocene function as the caprock (Cita, 1982). Apart from a preliminary study on Miocene evaporitic deposits in Sicily by Palmer and Zumberge (1981), to our knowledge no organic geochemical studies of Messinian samples are reported in the literature.

This paper describes the hydrocarbon geochemistry of three samples from a small evaporitic Messinian basin in the northern Apennines (Fig. 8.1.). The purpose of this study was to search for biological markers for a hypersaline environment and to compare the data obtained in this study with those obtained from contemporary depositional environments such as Solar Lake (Boon et al., 1983) and Gavish Sabkha (de Leeuw et al., 1985).

8.2. Geological setting and organic geochemistry

The samples were collected in the Perticara basin (Fig. 8.1.a).

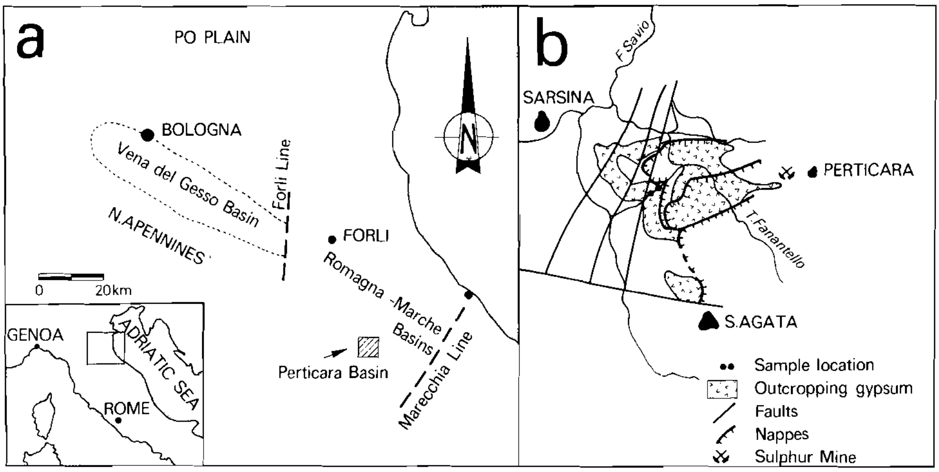


Figure 8.1. Location map of the Vena del Gesso and Romagna Marche evaporitic basins. The Messinian gypsum formation in the Perticara basin, together with the sample location is shown in Figure b.

This basin is one of the Romagna Marche evaporitic basins, which are separated by structural highs (the Forli Line and the Marecchia Line) from adjacent basins. All these evaporitic sediments were deposited in the Periadriatic trough where no halite and potash salts precipitated. The description of the setting as given here is based on a compilation of papers by several Italian geologists e.g. Parea and Ricci Lucchi (1972), Ricci Lucchi (1973), Selli (1973), Carloni et al. (1974), Borsetti et al. (1975), Vai and Ricci Lucchi (1977) and on our own field observations. Although most of the information available from the literature refers to the adjacent Vena del Gesso Basin (Fig. 8.1.a), it may be also valid for the Perticara basin.

Vai and Ricci Lucchi (1977) found a six facies sequence in the Vena del Gesso basin which is repeated several times. The idealised depositional cycle, starting from the bottom, is as follows:

- a bituminous marl/shale, deposited in a lagoonal environment with euxinic conditions near the bottom due to halocline stratification.

These layers contain a high plant debris, bituminous matter, authigenic pyrite, calcite and gypsum. Fossilized fishes, insects and leaves can be detected.

- a calc-gypsum algal stromatolite. Algal mats cemented by carbonate and/or gypsum.
- a massive gypsum (selenite) due to extensive autochthonous precipitation of gypsum. Algae cover the selenite crystals during minor interruptions of the gypsum growth.
- a banded gypsum (selenite) due to evaporitic precipitation within algal mats.
- a nodular and lenticular gypsum (selenite). The growth of the selenite and algal mats was increasingly interrupted by sheet floods carrying terrigenous material.
- a chaotic gypsum due to debris flow deposits (subaerial).

In the Perticara basin (Fig. 8.1.b) from which the samples are taken, this idealised six facies sequence is only partly encountered. Many varieties of gypsum can be distinguished. The evaporitic sequence starts with a laminated gypsum (Fig. 8.2.), which is the most common variety of primary gypsum in this basin. These layers are deposited autochthonously and characterize the central part of the basin (Parea and Ricci Lucchi, 1972). The gypsum here most likely is a hydrated anhydrite and thus a secondary mineral (Dronkert, 1985). Another occurring variety is bituminous gypsum, in which tiny gypsum crystals are enveloped in a dark pelitic bituminous matrix.

The most common and impressive variety of gypsum encountered is the so-called chaotic gypsum, reaching a thickness of 40 m. This facies was explained by Ricci Lucchi (1973) in the following way; gypsum was deposited in a Sabkha environment on narrow tops of structural highs. During periods of tectonic activity these gypsum deposits subsequently slided into the basin. Later the name of a "cannibalistic evaporitic basin" is proposed by Vai and Ricci Lucchi (1977) to explain the character and volumetric importance of such resedimented evaporites.

Interbedded with all these varieties of gypsum deposits, bituminous marls smelling strongly with H_2S occur, with thicknesses varying from

1 to 500 mm. At the contact between the bituminous marl and the gypsum native sulphur can often be found. A detailed stratigraphic description cannot be given due to post depositional tectonic activity, as indicated by the faults in Fig. 8.1.b.

Figure 8.2. A well developed lamination of primary gypsum and bituminous marls, showing the location site of the gypsum sample.

Organic geochemical studies of hypersaline environments have been focussed mainly on recent sediments (e.g. Nissenbaum et al., 1972; Cardoso et al., 1978; Philp et al., 1978; Boon et al., 1983; de Leeuw et al., 1985) and on the lipid composition of halotolerant and halophilic bacteria (e.g. Kates et al., 1982). Studies on ancient sediments have only been carried out on a limited scale. Green River shale is an ancient sediment, which was deposited sometimes under hypersaline conditions (Hall and Douglas, 1983). However, the results of organic geochemical studies of this shale have not been related to hypersalinity. Several investigations report the occurrence of compounds probably related to an evaporitic environment of deposition. An even over odd predominance of the n-alkanes in the C_{20} - C_{34} range is thought to reflect evaporitic facies (Welte and Waples, 1973; Dembicki et al., 1976; Spiro and Aizenshtat, 1977; Tissot et al., 1977; Guoying et al., 1980). Since most of the recent hypersaline environments are marked by reducing conditions at the bottom due to halocline stratification of the water column, it is sometimes suggested that the mechanism to produce an even over odd n-alkane predominance is a reduction of alcohols, carboxylic acids and esters in a reducing environment, instead of a decarboxylation of these compounds, which yields an odd over even predominance (Guoying et al., 1980). However many reducing environments are known, which do not show hydrocarbon patterns with an even over odd predominance. In samples with an even over odd predominance of n-alkanes the pristane/ phytane ratio - when reported - is below 1.0 (Schenck, 1969; Welte and Waples, 1973; Albaiges and Torradas, 1974; Hall and Douglas, 1983). The even over odd predominance is also attributed to a maturation effect instead of an environmental effect (Leythaeuser et al., 1980; Shi Ji-Yang et al., 1982), but in these studies no positive correlation is observed between a low pristane/phytane and a low carbon preference index. Waples et al. (1974) suggested that the regular C_{25} isoprenoid hydrocarbon (2,6,10,14,18-pentamethyleicosane) is a biological marker for saline environments. These authors also found an abundance of phytane over pristane. The irregular C_{25} isoprenoid hydrocarbon (2,6,10,15,19-

pentamethyleicosane) is thought to be a biological marker for methanogenic bacteria (Holzer et al., 1979; Brassell et al., 1981; Rowland et al., 1982), although both regular and irregular C_{25} isoprenoid have been found in neutral lipids of Archaebacteria (Langworthy et al., 1982). The pristane/ phytane ratio has been suggested as an indicator for the degree of anoxicity in the environment of deposition (Didyk et al., 1978). Recent results have shown that this ratio should be used with caution as an indicator of depositional environment (Mackenzie et al., 1981; Goossens et al., 1984).

8.3. Experimental

The samples were collected from a location along the river Torrente Fanantello (point 2 from Borsetti et al., 1975). A 40 cm and a 10 cm thick bituminous marl layer, interbedded between two hugh chaotic gypsum layers, and a 10 cm thick gypsum layer (Fig. 8.2.) were sampled after removing the outer weathered rock material.

After grinding in a rotary disc mill the powdered samples (2 x 150 g marl and 300 g gypsum) were Soxhlet extracted with toluene/methanol (1/3 v/v) for eight hours. The solvent was removed and the extracts were taken up in pentane. This pentane soluble part of the extract was fractionated by column chromatography on activated silica/alumina using pentane, toluene and toluene/ethanol (1/1 v/v) as eluents. Elution of the pentane fraction over a column filled with activated copper removed the sulphur. The saturated straight chain and branched/ cyclic hydrocarbons were separated by urea adduction. Gas chromatography was performed using a Carlo Erba 4160 instrument equipped with a 21 m glass WCOT column (0.32 mm) coated with SE 52, programmed from 150-330^{o}C at 4^{o}/min with He as carrier gas. Gas chromatography-mass spectrometry was carried out on a Varian 3700 gas chromatograph equipped with a 25 m glass WCOT column (0.25 mm) coated with CP-Sil 5, coupled to a MAT 44 quadrupole mass spectrometer operating at 70 eV with mass range m/z 50-500 and a cycle time of 2 s. Helium was used as carrier gas. The results described here were obtained on the desulphurized pentane eluates of the three samples and their urea adduct and non adduct fractions.

The amounts of the extractable material obtained were 1.156 g (0.75%) and 6.730 g (4.83%) for the two marl samples and 0.013 g (0.004%) for the gypsum sample respectively. The small amount of extract obtained from the gypsum sample meant that only the major hydrocarbons present in the total saturated hydrocarbon fraction could be identified by GC-MS.

The clay fraction (< 2 µm) of one marl sample was separated by sedimentation and its percentage calculated (22.5 %). The major clay minerals were determined after K and Mg saturation by sedimentation on porous ceramic slides, atmospheric drying (K + Mg), glycolation (Mg) and heating (K) at 550 °C. X-ray diffraction analyses were carried out with a Philips diffractometer model PK 1050. Montmorillonite is the most abundant clay mineral; illite, kaolinite and chlorite are present in minor amounts.

8.4. Results

The gas chromatograms of the pentane eluates of one marl and the gypsum sample are shown in Figures 8.3. and 8.4. The peak numbers in these figures correspond with those listed in Tables 8.1. and 8.2. Identifications are based on comparision of relative GC retention times and mass spectra with those described in the literature. When no literature data are available, tentative assignments are made. The hydrocarbon fractions from the two marl layers gave similar gas chromatograms and the same compounds were identified.

Figure 8.4. Gas chromatogram of the saturated hydrocarbon fraction of the gypsum sample. Identification of numbered compounds is given in Table 8.2. n-Alkanes are indicated with an asterisk.

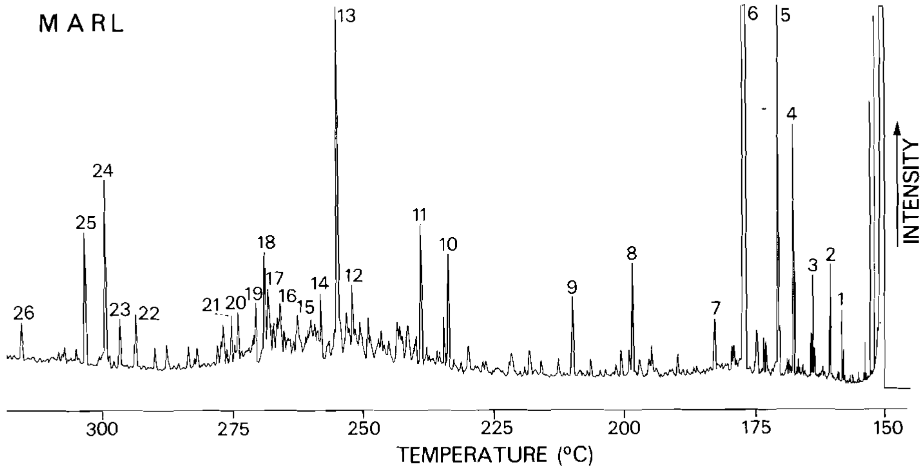


Figure 8.3. Gas chromatogram of the urea non-adduct saturated hydrocarbon fraction of the marl sample. Identification of numbered compounds is given in Table 8.1. For clarity only the major peaks are numbered.

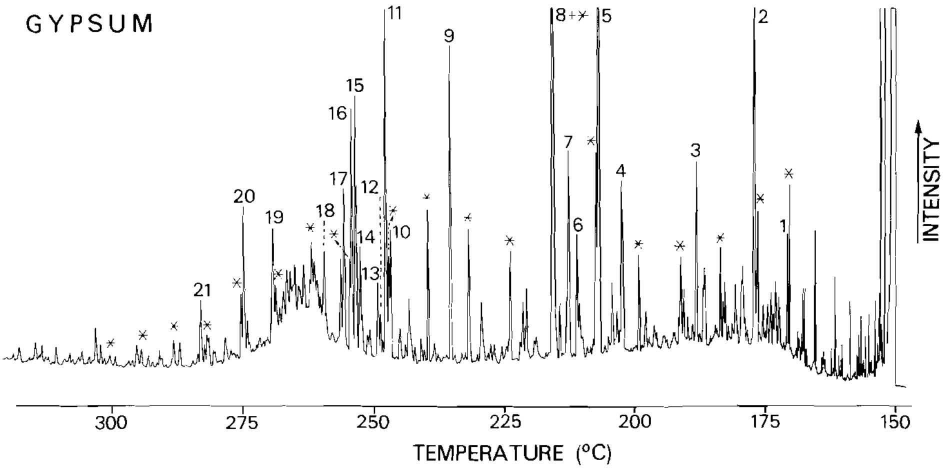


Table 8.1. Compounds identified by GC-MS in the hydrocarbon fraction of the marl sample

1. 2,6,10-trimethyldodecane
2. 2,6,10-trimethyltridecane
3. 2-methylpentadecane
4. 2,6,10-trimethylpentadecane
5. 2,6,10,14-tetramethylpentadecane (pristane)
6. 2,6,10,14-tetramethylhexadecane (phytane)
7. 2,6,10,14-tetramethylheptadecane
8. 2,3-dimethyl-5-(2,6,10-trimethylundecyl)-thiophene* +
   2,6,10,14-tetramethylnonadecane
9. 2,6,10,14,18-pentamethyleicosane
10. 20S-diacholestene
11. 20R-diacholestene
12. 5β(H),14α(H),17α(H)-20R-cholestane
13. 5α(H),14α(H),17α(H)-20R-cholestane
14. unknown 4-methylsteroid
15. 5α(H),14α(H),17α(H)-20R-24-methylcholestane
16. 5α(H),14β(H),17β(H)-20R-24-ethylcholestane +
    5α(H),14β(H),17β(H)-20S-24-ethylcholestane
17. 4β,24-dimethyl-5α(H),14β(H),17β(H)-20R-cholestane* +
    4α,14-dimethyl-5α(H),14α(H),17α(H)-20R-cholestane*
18. 5α(H),14α(H),17α(H)-20R-24-ethylcholestane +
    4β,24-dimethyl-5α(H),14β(H),17β(H)-20S-cholestane*
19. 4β,24-dimethyl-5α(H),14α(H),17α(H)-20R-cholestane
20. 4α-methyl,24-ethyl-5α(H),14α(H),17α(H)-20R-cholestane*
21. neohop-13(18)-ene
22. 22S-tetrakishomohop-17(21)-ene
23. 22R-tetrakishomohop-17(21)-ene
24. 22S-pentakishomohop-17(21)-ene
25. 22R-pentakishomohop-17(21)-ene
26. unknown.

* Tentative assignments. The 24-ethyl assignment could not be distinguished from the 23,24-dimethyl. The n-alkanes were clathrated with urea.

8.4.1. n-Alkanes and branched alkanes

The distributions of the n-alkanes are given in Figure 8.5. The marl sample contains n-alkanes with a moderate odd over even predomi-

Table 8.2. Compounds identified by GC-MS in the hydrocarbon fraction of the gypsum sample

1. 2,6,10,14-tetramethylpentadecane (pristane)
2. 2,6,10,14-tetramethylhexadecane (phytane)
3. unknown
4. 5α(H),14β(H),17α(H)-pregnane
5. 5α(H),14β(H),17β(H)-pregnane + 5α(H),14α(H),17α(H)-pregnane
6. 5α(H),14 (H),17α(H)-homopregnane
7. 4-methyl-5α(H),14β(H),17β(H)-pregnane* + 4-methyl-5α(H),14α(H),17α(H)-pregnane*
8. 5α(H),14β(H),17β(H)-homopregnane + 5α(H),14α(H),17α(H)-homopregnane + n-tricosane
9. phtalate ester (contaminant)
10. 5α(H),14β(H),17β(H)-norcholestane
11. 5α(H),14α(H),17α(H)-norcholestane
12. 5α(H),14β(H),17β(H)-norcholestane
13. 5α(H),14α(H),17α(H)-norcholestane
14. 5α(H),14α(H),17α(H)-20S-cholestane
15. 5α(H),14β(H),17β(H)-20R-cholestane
16. 5α(H),14β(H),17β(H)-20S-cholestane
17. 5α(H),14α(H),17α(H)-20R-cholestane
18. 17α(H)-22,29,30-trisnorhopane
19. 17α(H),21β(H)-norhopane
20. 17α(H),21β(H)-hopane
21. gammacerane

* Tentative assignments. The n-alkanes are indicated with an asterisk in Figure 8.4.

nance (CPI_{24-34} = 2.20), whereas the gypsum shows an even over odd predominance (CPI_{24-34} = 0.95). In the gypsum sample the relative n-C_{23} concentration is too high due to coelution of homopregnane, the most abundant component from Figure 8.4. in the pentane eluate, which was not fully removed after urea adduction. Taking this into account the n-C_{22} is in both samples the most important n-alkane. Isoprenoid alkanes range from 2,6,10-trimethyldodecane to 2,6,10,14,18-pentamethyleicosane, the latter one being relatively important (nr. 9 in Fig. 8.3). In the gypsum only pristane and phytane could be definitely identified. In both samples the pristane/phytane ratio is extremely low (0.1) and in the marl phytane is the most abundant component.

Branched alkanes are abundant in the marl. The most important single branched alkane is 2-methylpentadecane (nr. 3 in Fig. 8.3.).

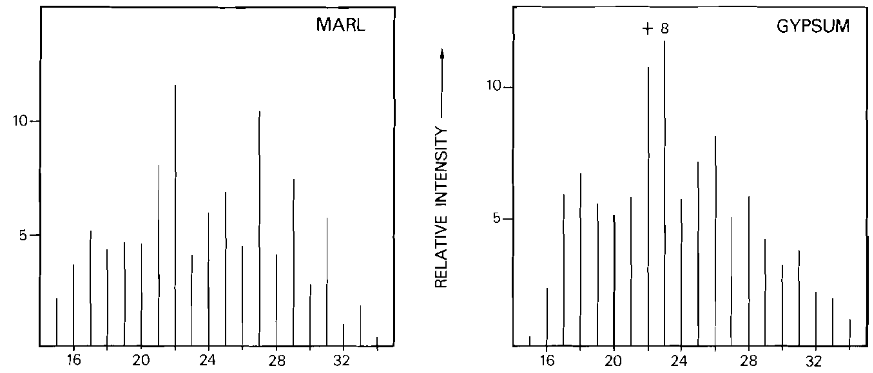


Figure 8.5. Distributions of n-alkanes in the marl and gypsum sample.

8.4.2. Steranes

Marl Sample

Figure 8.6. shows a series of mass chromatograms from scan 1000 to 1250. The m/z 217 and 218 traces reveal the presence of 4-desmethyl steranes. The steranes with the biological configuration 5α(H), 14α(H),17α(H)-20R C_{27}, C_{28} and C_{29} are clearly present (the A series; peaks 13, 15, 18 in Fig. 8.3.). The 5β(H),14α(H),17α(H)-20R C_{27} component is also observed (B 27; peak 12 in Fig. 8.3.). The presence of

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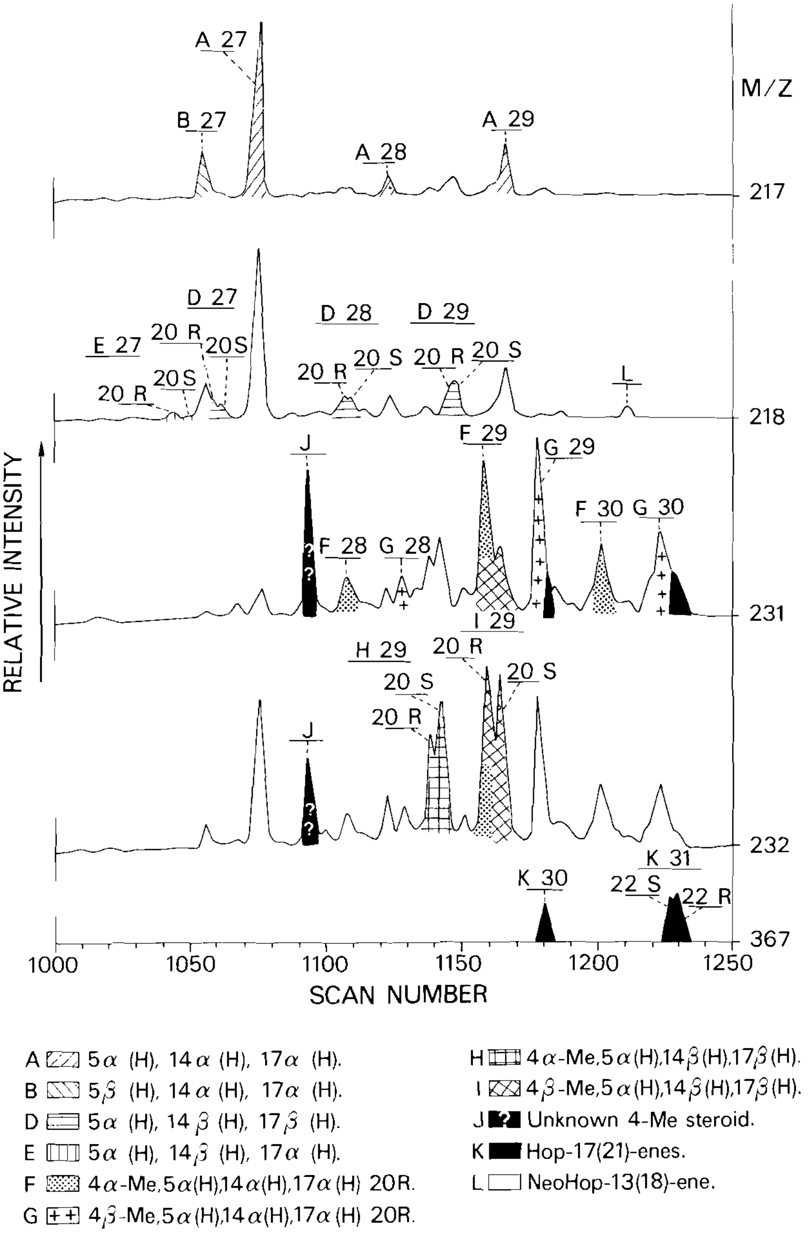
Figure 8.6. Mass chromatograms of m/z 217, 218, 231, 232 and 367 in the steroid region of the TIC-trace of the marl sample. The 4α-methyl-5α(H),14α(H),17α(H)-20R C_{28} coelutes with the 4β-methyl-5α(H),14β(H),17β(H)-20R C_{28}. This coelution influence is symbolically indicated.


M/Z
217
218
231
232
367
A 27
B 27
A 28
A 29
D 27
E 27
20 R
20 S
20 R
20S
D 28
D 29
20 R
20 S
20 R
20 S
L
J
F 29
G 29
F 28
G 28
F 30
G 30
I 29
H 29
20 R
20 S
20 S
20 R
J
K 30
K 31
22 S
22 R
RELATIVE INTENSITY
1000
1050
1100
1150
1200
1250
SCAN NUMBER
A ▨ 5α (H), 14α (H), 17α (H).
B ▨ 5β (H), 14α (H), 17α (H).
D ▤ 5α (H), 14β (H), 17β (H).
E ▥ 5α (H), 14β (H), 17α (H).
F ▩ 4α-Me,5α(H),14α(H),17α(H) 20R.
G ⊞ 4β-Me,5α(H),14α(H),17α(H) 20R.
H ▦ 4α-Me,5α(H),14β(H),17β(H).
I ▧ 4β-Me,5α(H),14β(H),17β(H).
J ? Unknown 4-Me steroid.
K ■ Hop-17(21)-enes.
L ☐ NeoHop-13(18)-ene.

the 5α(H),14β(H),17β(H)-20R and -20S steranes, characterized by the m/z 217, 218, 219 pattern in the mass spectra (Wardroper, 1979) is indicated in the m/z 218 trace (the D series). The stereochemical assignment at C-20 is based on GC retention data reported by Mackenzie et al. (1980) and Moldowan et al. (1980). The C_{29} components (D 29) are the most abundant within this series (peak 16 in Fig. 8.3.). Minor amounts of 5α(H),14β(H),17α(H)-20R and -20S cholestanes (E 27) and possibly C_{28} and C_{29} homologues (not shown) are present. Their identification is based on the GC retention times reported by Mackenzie (1980) and the m/z 217, 218, 219 pattern in their mass spectra (Wardroper, 1979).

The mass chromatograms of m/z 231 and 232 reveal the 4-methyl steranes (F and G series in Fig. 8.6.). The identification of the 4α- and 4β-methyl-5α(H),14α(H),17α(H)-20R steranes is based on data reported by Rubinstein and Albrecht (1975) and by McEvoy (1983). Several new 4-methyl steranes were detected, which were tentatively identified as 20R- and 20S-4α,24-dimethyl-5α(H),14β(H),17β(H) cholestanes and 20R- and 20S-4β,24-dimethyl-5α(H),14β(H),17β(H) cholestanes (H 29 and I 29 respectively). The stereochemical assignments at positions 5, 14, 17 and 20 are based on the criteria applied for the 4-desmethyl assignments (Wardroper, 1979).

Compound J is an unknown 4-methyl steroid. Its mass spectrum is characterized by m/z 231, 232 and 398. The m/z 367 trace, characteristic for extended hop-17(21)-enes, is included since these hopenes also give a fragment ion at m/z 231 and therefore influence the 231 trace. In the m/z 218 trace peak L corresponds to neohop-13(18)-ene (see below).

Gypsum Sample

The most abundant steranes, in fact the most abundant compounds present in the hydrocarbon fraction, are identified as 5α(H),14β(H),17β(H) and 5α(H),14α(H),17α(H) pregnanes and homopregnanes (peaks 5 and 8 in Fig. 8.4.) (Restle, 1983). The 14β(H),17β(H) and 14α(H),

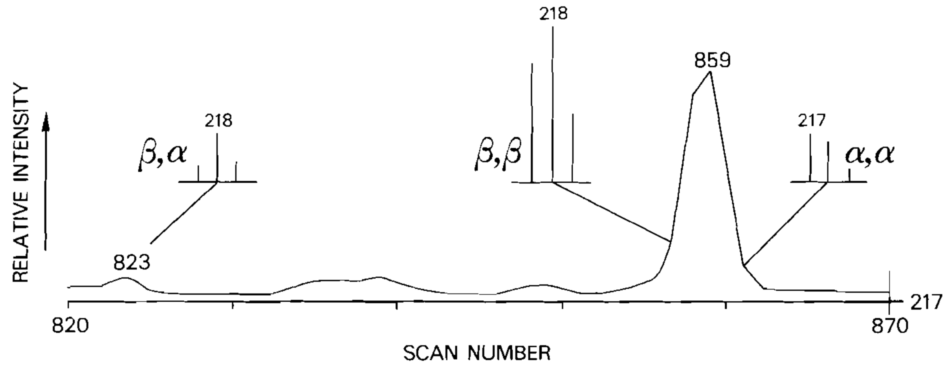


Figure 8.7. Mass chromatogram of m/z 217 in the gypsum sample. The m/z 217, 218, 219 pattern of three scans is included. Scan 823 corresponds with peak 6 and scan 859 with peak 8 in Fig. 8.4.

17α(H) isomers of these C_{21} and C_{22} steranes almost coelute. Careful inspection of the mass spectral data, giving attention to the m/z 217, 218, 219 patterns, reveals that the 14β(H),17β(H) component elutes just before the 14α(H),17α(H) component (Fig. 8.7., scans 859 and 861). Other relatively abundant C_{21} and C_{22} steranes are identified as 5α(H),14β(H),17β(H) pregnane and homopregnane (peaks 4 and 6 in Fig. 8.4.; scan 823 in Fig. 8.7.) (Restle, 1983).

4-Methyl and 4,4-dimethyl pregnanes and homopregnanes are also encountered. Both the 5α(H),14β(H),17β(H) and 5α(H),14α(H),17α(H) configurations are thought to be present, based on the m/z 231, 232, 233 (Restle, 1983) and 245, 246, 247 patterns in the mass spectra. Figure 8.8. shows a mass spectrum, which is ascribed to 4,4-dimethyl-5α(H),14β(H),17β(H)-homopregnane. The enhanced intensity of m/z 177 indicates a 4,4- dimethyl moiety, and not a 4,14-dimethyl moiety (Kimble, 1972). The 14β(H),17β(H) configuration is concluded from the 245, 246, 247 pattern. The stereochemistry at C-4 in the 4-methyl pregnanes and homopregnanes cannot be established from our data.

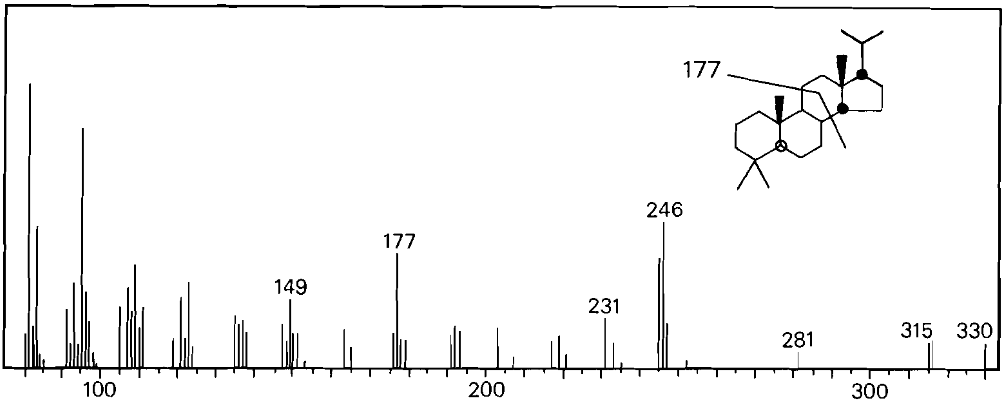


Figure 8.8. Mass spectrum of a compound, tentatively identified as 4,4-dimethyl-5α(H),14β(H),17β(H)-homopregnane.

The steranes with the longer side chains are dominated by C_{26} and C_{27} compounds. The cholestanes encountered are, in order of elution: 20S-5α(H),14α(H),17α(H); 20R-5α(H),14β(H),17β(H); 20S-5α(H),14β(H),17β(H) and 20R-5α(H),14α(H),17α(H) (peaks 14, 15, 16 and 17 in Fig. 8.4.). This elution sequence and the mass spectral data are in full agreement with data reported by Seifert and Moldowan (1979), Mackenzie et al. (1980) and Moldowan et al. (1980). By analogy with the C_{27} steranes the same pattern might be expected for the C_{26} compounds. However the mass spectral data indicate a different elution sequence: 5α(H),14β(H),17β(H); 5α(H),14α(H),17α(H); 5α(H), 14β(H),17β(H) and 5α(H),14α(H),17α(H) (peaks 10, 11, 12, 13 in Fig. 8.4.). This unexpected behaviour might be attributed to two types of C_{26} steranes viz. 24-nor and 27-nor cholestanes. Some C_{28} and C_{29} steranes are encountered in minor amounts and could therefore not be further identified.

8.4.3. Sterenes

Two series of sterenes are identified in the marl sample: rearranged sterenes and spirosterenes. In the gypsum sample no sterenes could be detected.

20R- and 20S-C_{27} diasterenes (peaks 10 and 11 in Fig. 8.3.) are abundant. Traces of 20R- and 20S-C_{28} and C_{29} diasterenes are also observed but not further indicated. The identification of the diasterenes is based on GC retention time and mass spectral data reported by Rubinstein et al. (1975).

The mass spectra of spirosterenes are characterized by a base peak m/z 206 + 14n (n=0-2) and an abundant ion at m/z 121 due to subsequent cleavage through the C-20/C-22 bond (Fig. 8.9.) (Anastasia et al., 1978b; Peakman et al., 1984). Mass chromatograms of m/z 206, 220 and 234 are presented in Fig. 8.9. The 20R- and 20S- isomers of 12,14-cyclo-12,13-seco-5α(H)-cholest-13(17)-ene and their pseudohomologues, the 24-methyl and the 24-ethyl and/or 23,24-dimethyl all occur. Assignments are based on mass spectral data and GC retention times reported earlier (Peakman et al., 1984).

Four other compounds with a base peak at m/z 220 are also encountered (Fig. 8.9.). Two of these spirosterenes show a molecular ion at m/z 398, indicating a C_{29} carbon skeleton. Since these compounds obviously possess a 24-methyl substituted side chain we speculate that these compounds are 4-methylspirosterenes. This tentative identification is supported by the fact that the 4-methyl steranes encountered in this sample (see above) are almost exclusively composed of the 4,24-dimethyl cholestanes.

Before each doublet of 4-desmethyl spirosterenes another doublet of spirosterenes with low intensity elute. These compounds might represent the 5β(H) counterparts, because of their relative retention times. No specific features were observed in their mass spectra.

8.4.4. Triterpanes and triterpenes

Figure 8.10. shows mass chromatograms of m/z 191 for both samples and m/z 367 for the marl sample. In the marl sample a series of 17α(H),21β(H) hopanes could be detected based on relative retention times and mass spectral data. 17α(H),21β(H) hopane is the most abun-

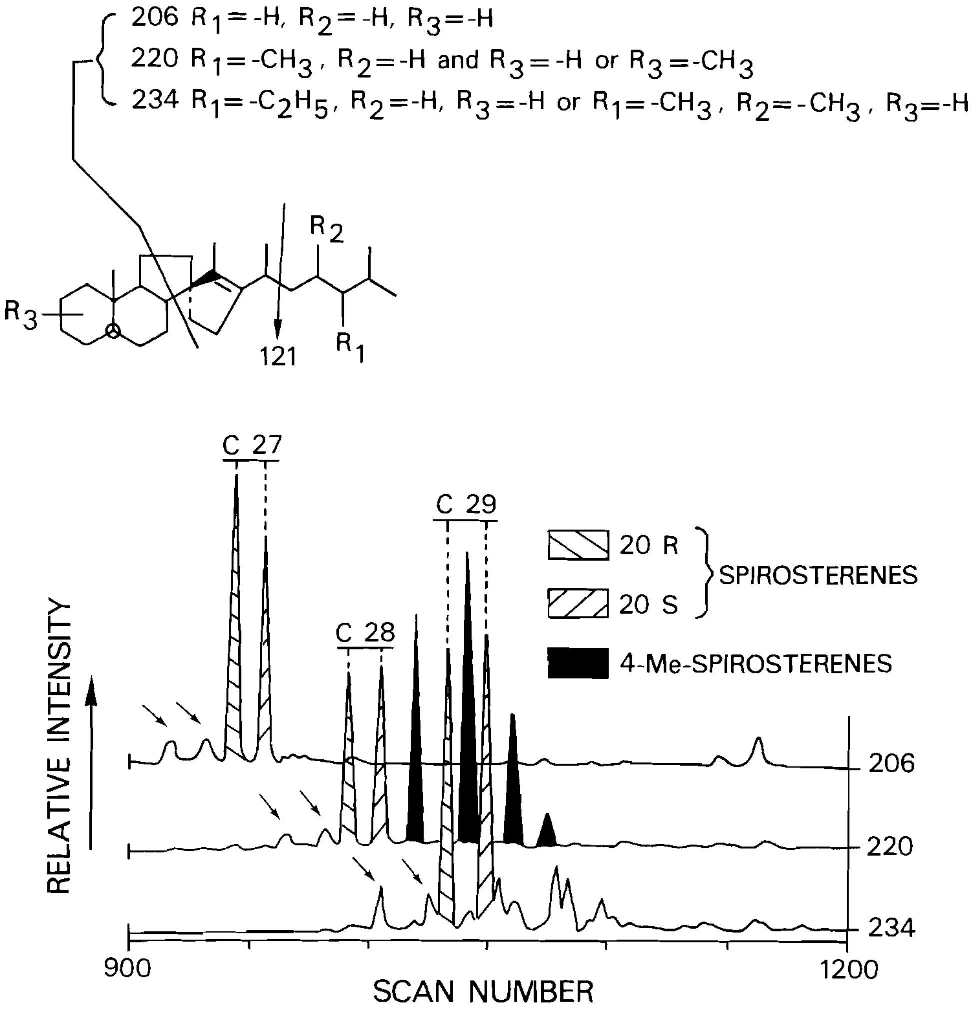


Figure 8.9. Mass chromatograms of m/z 206, 220, 234 (indicative of spirosterenes) in the marl sample. A spirosterene skeleton indicating the major cleavages is presented. Arrows indicate the tentative assigned 5β(H) counterparts.

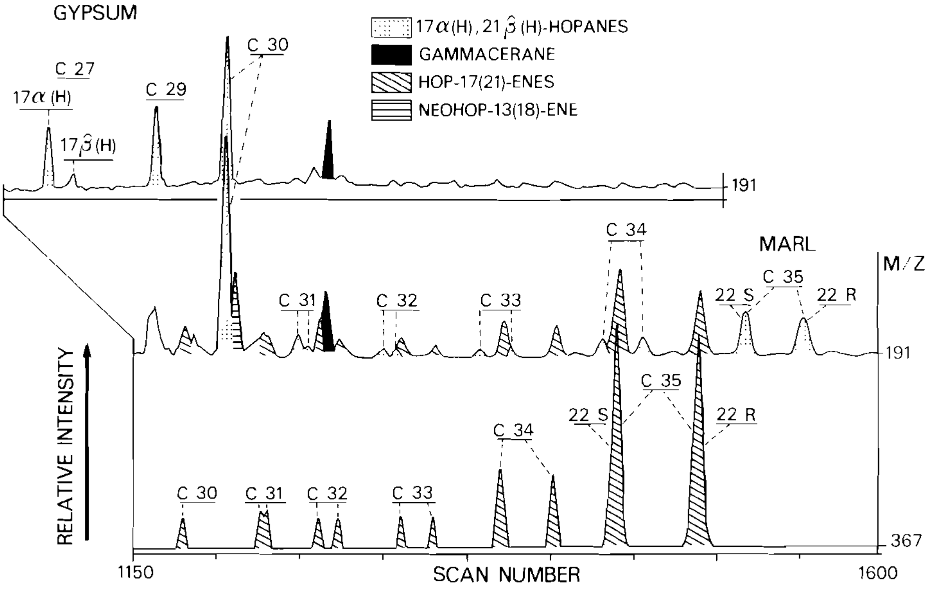


Figure 8.10. Mass chromatograms of m/z 191 (both samples) and m/z 367 (marl sample) in the hopanoid region of the TIC-trace. The mass chromatogram m/z 367 is also partly presented in Fig. 8.6. The identification of 17β(H)-trisnorhopane in the gypsum sample is tentative.

dant component. 22R- and 22S-17α(H),21β(H) pentakishomohopanes are present in high amounts, when compared with the other extended hopanes. Gammacerane is tentatively identified on basis of retention time (Shi Ji-Yang et al., 1982) and mass spectral data. Minor amounts of 17β(H),21α(H) 20R and 20S hopanes are also encountered but not indicated in Fig. 8.10.

In the gypsum sample the hopanes are relatively more abundant. The following compounds are identified: 17α(H)-22,29,30-trisnorhopane, 17α(H),21β(H)-norhopane, 17α(H),21β(H)-hopane and gammacerane (peaks 18, 19, 20, 21 in Fig. 8.4.). 17β(H)-22,29,30-trisnorhopane is tentatively identified.

The mass chromatogram of m/z 367 reveals the presence of series of hop-17(21)-enes (see also Fig. 8.6.). Both 22S and 22R isomers are present in almost equal amounts. The 22S- and 22R-pentakishomohop-17(21)-enes are the most abundant hopenes (peaks 24 and 25 in Fig. 8.3). The identification is based on mass spectral data and retention times reported by McEvoy (1983). Another triterpene present in the marl sample is neohop-13(18)-ene (peak 21 in Fig. 8.3.; compound L in Fig. 8.6.).

8.4.5. Thiophenes

Recently the 3-methyl-2-(2,6,10-trimethyldodecyl)-thiophene has been synthesized (Brassell et al., 1986b), the mass spectrum of which shows a base peak at m/z 111 and a molecular ion peak at m/z 308. This compound was observed in the marl sample. The most abundant thiophene encountered is tentatively identified as 4,5-dimethyl-2-(2,6,10-trimethylundecyl)-thiophene (peak 8 in Fig. 8.3.) on the basis of similarities and differences of the mass spectrum compared with those of the synthesized compound (Brassell et al., 1986b). This thiophene has a base peak at m/z 125 and also a molecular ion peak at m/z 308. Similar spectra with base peaks at m/z 111 + 14n (n=0-5) and molecular ion peaks at 294 + 14n (n=0-5) are observed in the total ion current trace. We believe that these compounds are all thiophenes. These compounds are only detected in the marl sample and are the subject of current detailed investigation in our laboratory.

8.5. Discussion

Although post-depositional tectonic movements make it impossible to correlate the marl samples and the gypsum sample stratigraphically the three samples are definitely from the same epoch (Messinian) (Carloni et al., 1974; Borsetti et al., 1975). The Messinian formation is about 200 m. thick in the Perticara basin and the maximum difference in the depth of burial between the marl and the gypsum is 75 m. at the most.

The maximum depth of burial of the Messinian gypsum formation in the Perticara basin is about 600 m (van Wamel, pers. comm., 1984). As the gypsum layer investigated is collected from the bottom of the evaporitic sequence, the maximum depth of burial of the gypsum sample is estimated at 800 m. The diagenetic history is therefore expected to be almost the same for both samples, and the differences in the hydrocarbon fractions are therefore probably caused by different environments of deposition, by different autochthonous inputs and/or by transformations catalyzed by superacid sites of clay minerals in the marl samples.

8.5.1 n-Alkanes and branched alkanes

A predominance of the C_{22} n-alkane occurs in both samples (Fig. 8.5.). This phenomenon has been reported by Schenck (1969) and by Powell and McKirdy (1973) in extracts from samples of sediments ranging in age from Pliocene to Permian. Also in the recently deposited Gavish Sabkha sediments the C_{22} n-alkane is predominant (de Leeuw et al., 1985). The origin of this straight chain alkane is not known, but it could well be a biological marker for saline environments. The distribution patterns of the long straight chain alkanes (C_{24}-C_{34}) for the marl and the gypsum sample are quite different. The latter possesses a slight even over odd predominance, whereas the former has a pronounced odd over even predominance. The longer chain n-alkanes point to a contribution of terrigenous material (Eglinton and Hamilton, 1963). The CPI value of the marl is representative of an immature sediment. The observed differences between the samples cannot be explained straightforwardly by a maturation effect as suggested by Leythaeuser et al. (1980), because both samples have had more or less the same diagenetic history. The mechanism of dehydration under reducing conditions instead of decarboxylation (Guoying et al., 1980) is a possibility, but it is unlikely that reducing conditions stopped abruptly when salinity decreases to a point where gypsum no longer precipitated. The even over odd predominance probably reflects the presence of precursors typical for evaporitic environments. An input of reworked organic matter, which obscures the even predominance in the marl cannot be precluded. The regular C_{25} isoprenoid hydrocarbon, described as a biological marker for saline environments (Waples et al., 1974), only occurs in the marl sample. This may imply that this molecule is a marker for certain organisms which only live in a restricted salinity range. The occurrences of monomethyl branched alkanes can be ascribed to origins from cyanobacteria (Cardoso et al., 1978; Philp et al., 1978) or purple sulphur bacteria (de Leeuw et al., 1985).

The pristane/phytane ratio in both samples is extremely low. Chlorophyll has been assumed to be the precursor of these isoprenoids, but recent results have shown that other possibilities cannot be precluded, such as tocopherol as a precursor of pristane (Goossens et al., 1984). Kaplan and Baedecker (1970) and Nissenbaum et al. (1972) suggested in their studies of the Dead Sea that phytane might be derived from phosphatidyl glycerophosphate. This phospholipid with ether linked alkyl chains is found in halophilic bacteria. The natural breakdown of the isoprenoid glycerol ether lipid will increase the phytane concentration during diagenesis and this explains the low pristane/phytane ratio in ancient sediments from saline environments (Welte and Waples, 1973; Waples et al., 1974; Albaiges and Torradas, 1974; Hall and Douglas, 1983). We therefore suggest that the pristane/phytane ratio not only can be used as an indicator for the degree of anoxicity (Didyk et al., 1978), but also as an indicator for salinity. Different precursors for the C_{19} and C_{20} isoprenoids in combination with different ratios of these precursors will of course give different pristane/phytane ratios, which should therefore be used with caution.

8.5.2. Steranes and sterenes

According to the relation between maturity parameters proposed by Mackenzie et al. (1982) for the Paris basin, the gypsum and marl samples correspond to vitrinite reflectances of about 1.0 % and 0.4 - 0.9 % respectively. There is thus not only a discrepancy between the marl and the gypsum, but also a large variability in the marl itself. The extract of the gypsum sample is "more mature" than the extract of the marl, as it contains higher proportions of the products of diagenetic isomerization (20R- and 20S-5α(H),14β(H),17β(H) C_{27} steranes and 20S-5α(H),14α(H),17α(H) C_{27} sterane). The 20S- and 20R-5α(H),14β(H), 17β(H) C_{27}, C_{28} and C_{29} steranes, with the latter relatively important, are present in the marl, but the 20S-5α(H),14α(H),17α(H) configuration is virtually absent. Rearranged sterenes are present in relatively large quantities in the marl, whereas rearranged steranes were not observed. To explain the apparent differences in maturity we speculate that either both samples contain reworked mature material from different sources or that the observed discrepancies are induced by the specific kind of environment. Hollerbach (1980) suggested that the diagenesis of organic matter in evaporites progresses differently from that in clastic sediments, resulting in a different interpretation of the vitrinite reflectance values in both cases.

The presence of rearranged sterenes and spirosterenes in the marl and the absence of these compounds in the gypsum can be attributed to differences in the lithology. Both types of rearranged compounds are only found in the marl, where the transformation is probably catalyzed by superacid sites in clay minerals (Sieskind et al., 1979). In view of this it is noteworthy that the transformation experiments of sterols by Sieskind et al. (1979) were successful with kaolinite and montmorillonite, the latter being the most abundant clay mineral in one marl sample. Spirosterenes have been observed in Cretaceous black shales from the Deep Sea Drilling Project (Brassell et al., 1984), from the northern Apennines (van Graas, 1982) and in Miocene sediments (McEvoy, 1983), but up till now no 4-methyl spirosterenes have been reported. The cooccurrence of these spirosterenes with the tentatively identified 4α-methyl- and 4β-methyl-5α(H),14β(H),17β(H) 20R and 20S steranes both with a C_{29} skeleton, are probably all products originating from the same precursor. It might be speculated that such precursor steroids contain a double bond at the 7, 8 or 8(14) position, since Anastasia et al. (1978a) have demonstrated that such steroidal compounds are easily converted to Δ^{14}-sterenes with an inversed side chain via the intermediate spirosterenes. Subsequent hydrogenation of the Δ^{14} double bond will yield 14α(H),17β(H)- and 14β(H),17β(H)-steranes with the latter being dominant (van Graas et al., 1982). Steroids with a Δ^{7}, Δ^{8} or $\Delta^{8(14)}$ double bond occur in cyanobacteria, fungi, sponges, starfishes and some green algae (Nes and McKean, 1977). The 4-methyl-5α(H),14α(H),17α(H)- steranes point to a dinoflagellate origin (Boon et al., 1979; de Leeuw et al., 1983; Robinson et al., 1984), but a bacterial origin cannot be totally precluded (Bird et al., 1971), although the distribution given by these authors is very different.

The 14β(H),17β(H) and 14α(H),17α(H) pregnanes and homopregnanes are the most abundant compounds in the gypsum. The 4-methyl and 4,4-dimethyl short side chain steranes are present in smaller amounts. Little is known about the precursors of these pregnanes and homopregnanes. Some sterols with a short side chain were isolated from marine organisms, such as gorgonians and sponges, but a relation with pregnanes and homopregnanes could not be established up till now (Restle, 1983). Because of their dominant presence we suggest that these compounds are related to unknown precursors present in certain organisms, which exclusively occur in a hypersaline environment. In view of this suggestion it is noteworthy that traces of 5α(H) pregnane were observed by Gallegos (1971) in the Green River shale. The pristane/phytane ratio in some Green River shale extracts is 0.3 (Gallegos, 1971) and it is known that there were periods during the time of deposition of this shale, in which hypersaline conditions developed (Hall and Douglas, 1983 and references therein).

8.5.3. Triterpanes and triterpenes

The series of extended C_{31}-C_{35} 22S- and 22R hop-17(21)-enes and 22S- and 22R-17α(H),21β(H) hopanes maximize at the C_{35} components in the marl sample. Despite the low thermal maturity of the sediment, concluded from the CPI value, both series are fully isomerized at C-22 to the isomerization endpoint of 50-60% 22S isomer (Seifert and Moldowan, 1980). The obvious correlation between the distribution of the hopenes on the one hand and the distribution of the hopanes on the other hand, in combination with the same degree of isomerization at C-22 suggests that the 17α(H),21β(H) hopanes are formed via a reduction of the hop-17(21)-enes in this sample and not via an isomerization of the unstable 17β(H),21β(H) hopanes. The origin of the series of extended hopenes is unclear. McEvoy (1983) suggested that the precursors are attached to the kerogen via an ether linkage side chain and that the hopenes are released during the onset of the catagenesis. This contradicts with the low thermal maturity of the sediment and again an interpretation of these compounds as biological markers for hypersaline environments might be suggested. This similar distribution pattern of hopenes and hopanes is encountered in other studies of saline environments (Barwise, pers. comm., 1984). Boon et al. (1983) detected in Solar Lake sediments large quantities of triterpenoids which may be the precursors of the hopenes (e.g. a bishomohopenoic acid). The abundance of hop-17(21)-ene and neohop-13(18)-ene can be ascribed to a bacterial input (De Rosa et al., 1971; Howard, 1980). Gammacerane, which is only tentatively identified in both samples, is also found in Green River shale (Hills et al., 1966). The precursor of gammacerane is still unknown but it has been suggested that it is derived from tetrahymanol (Henderson et al., 1969). The typical distribution pattern of norhopane, hopane and gammacerane, observed in the gypsum sample, is also found in other hypersaline environments (Barwise, pers. comm., 1984) and may therefore be also indicative for hypersaline environments.

8.6. Palaeoreconstruction of the Perticara basin

Conflicting ideas exist concerning the origin of the Messinian evaporite deposits in the Periadriatic trough. Parea and Ricci Lucchi

(1972) and Ricci Lucchi (1973) stated that the thick chaotic gypsum layers are the result of large scale resedimentation processes due to slope instability and indicative for deep water conditions in the Periadriatic trough. In 1977 Vai and Ricci Lucchi also propose a shallow water environmental setting (lagoon) with varying water depths for the Vena del Gesso basin. The maximum water depth in this lagoonal environment is estimated to have been in the orders of some tens of meters, with a shallowing during or after deposition of the bituminous marls. In other words the maximum water depth in the lagoon is reached during the deposition of the bituminous marls. The organic geochemical results point to shallow water conditions or even a Sabkha environment for the Perticara basin. The results obtained in this study show resemblance with the results from Solar Lake (Boon et al., 1983) and Gavish Sabkha (de Leeuw et al., 1985). All these studies show a large input from photosynthetic bacteria such as cyanobacteria. Vai and Ricci Lucchi (1977) described algal crusts in the Vena del Gesso basin, which could be remnants of cyanobacterial mats. Of particular interest is the suggestion by Ricci Lucchi (1973) that Sabkha conditions existed on structural highs in the Perticara basin. The gypsum layer, investigated in this study, is thought to be an autochthonous gypsum, deposited in the central part of the Perticara basin at the beginning of the evaporitic facies. From the organic geochemical data we deduce that during the time of deposition of this gypsum shallow water conditions existed. The marl samples investigated are both interbedded between hugh chaotic resedimented gypsum layers, which suggests that the basin was deeper than during the time of deposition of the gypsum sample. However the organic geochemistry still points to shallow water conditions. During times of tectonic activity autochthonous gypsum was removed and slided into the relatively deeper parts of the basin, resulting in the chaotic gypsum layers. The palaeoreconstruction described here is summarized in Fig. 8.11., where the major stages of deposition and their interrelationships are visualized. This figure also shows a hypothetical lithological column.

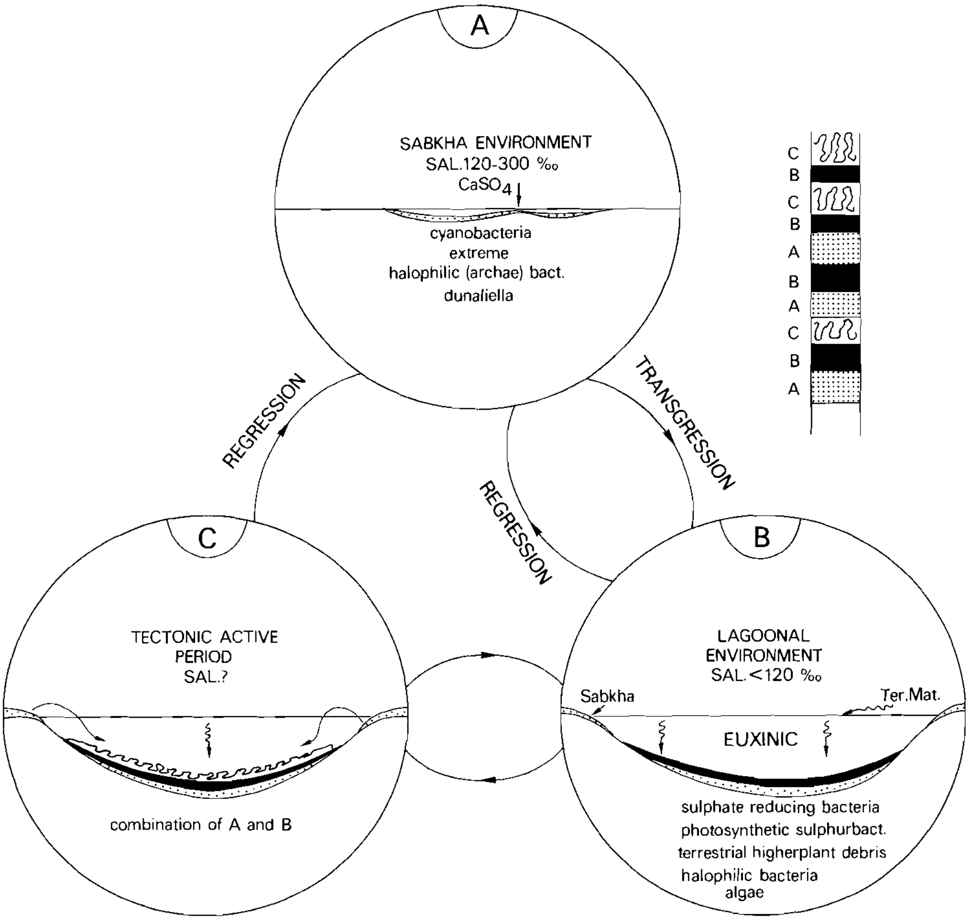


Figure 8.11. Schematic palaeoreconstruction of the Perticara basin, representing three different stages of deposition. A: deposition of authochthonous gypsum. B: deposition of bituminous marls. C: deposition of chaotic gypsum. A hypothetical stratigraphic column is also presented.

Chapter 9

APPLICATION OF BIOLOGICAL MARKERS IN THE RECOGNITION OF PALAEO HYPERSALINE ENVIRONMENTS

Abstract

In this study the saturated and aromatic hydrocarbon fractions of a marl sample from a Messinian (Late Miocene) evaporitic basin located in the northern Apennines, and four oils, Rozel Point oil (Utah, USA; Miocene) and three seep oils from Sicily (Messinian), have been studied by GC with simultaneous FID and FPD detection and by GC-MS.

All samples show characteristics which might be linked to hypersaline conditions prevailing during the time of deposition. Some of these characteristics are: a very low pristane/phytane ratio (< 0.1), a relatively high abundance of docosane (C_{22}) and gammacerane and a series of extended hopanes and/or hop-17(21)-enes maximizing at C_{35}. The aromatic hydrocarbon fraction of all samples is dominated by organic sulphur compounds of which 2,3-dimethyl-5-(2,6,10-trimethylundecyl)-thiophene is the most abundant compound.

The suggestion of Meissner et al. (1984), that the source rock of Rozel Point oil was deposited under hypersaline conditions, is supported by the organic geochemical characteristics of this oil.

9.1. Introduction

Biological markers, compounds which originate from specific structures occurring in living organisms, are widely used in petroleum exploration. Mostly, they are applied to discriminate between a continental versus a marine origin, for oil/source rock correlations and for thermal maturity estimates of source rocks (e.g. Tissot and Welte, 1984). The different sources of marine input can, at present, be specified more exactly by biological markers. For example, it is believed that 4-methylsteranes are the diagenetically altered imprints of dinoflagellates (Boon et al., 1979; Robinson et al., 1984; de Leeuw, 1986).

Recently several characteristic biological markers and their specific distribution patterns have been correlated with hypersaline conditions prevailing during time of deposition (ten Haven et al., 1985b, see Chapter 8; Sinninghe Damsté et al., 1986).

It is the intention of this paper to present similar characteristics observed in a marl layer from the northern Apennines and seep oils from Sicily, of which the palaeoenvironmental conditions during deposition are known, and to apply the information obtained to reconstruct the palaeoenvironmental facies of the source rock of the Rozel Point oil. We will, therefore, discuss only those compounds which are relevant to this subject.

Detailed descriptions of the geological setting of the northern Apennines marl layer (NAM) and of the saturated hydrocarbon fraction extracted from this sample are given by ten Haven et al. (1985b). The aromatic hydrocarbon fraction is described by Sinninghe Damsté et al. (1986). Some preliminary geochemical results of the Sicily seep oils (SSO) and their geological setting were published by Palmer and Zumberge (1981). The Italian samples are all Messinian (Late Miocene) in age. It is thought that during the Late Miocene the geographically most widespread anoxic event since the Cretaceous took place (Thunell et al., 1984), resulting in the deposition of organic-rich sediments, such as the Monterey shale and its contemporary deposits from the circum Pacific. In and around the Mediterranean area the Late Miocene is characterized by thick evaporitic deposits, interbedded with organic-rich layers (Cita, 1982). The origin and age of the Rozel Point oil is not exactly known. Meissner et al. (1984) suggested that this oil is sourced by playa-lake deposits of the Miocene Salt Lake group.

9.2. Experimental

The extraction procedure and the separation of the extracts and oils into saturated hydrocarbon, aromatic hydrocarbon and polar fractions are described by Sinninghe Damsté et al. (1986). Prior to gas chromatography the elemental sulphur was removed with activated copper. Gas chromatography of the saturated hydrocarbon fractions was performed using a Carlo Erba 4160 instrument with on-column injection, equipped with a 25 m fused silica column (0.32 mm) coated with CP-sil 5, programmed from 125 - 330 °C at 4°/min with H_2 as carrier gas. Gas chromatography of the aromatic hydrocarbon fraction was performed using a Varian 3700 instrument with simultaneous flame ionization detection (FID) and flame photometric detection (FPD), equipped with a 50 m fused silica column (0.22 mm) coated with CP-sil 5. The conditions of the gas chromatography - mass spectrometry analyses are described by Sinninghe Damsté et al. (1986). Identifications of compounds are based on comparison of relative retention times and mass spectra with those of standards and data reported in the literature (e.g. Sinninghe Damsté et al., 1986; Philp, 1985 and references cited therein).

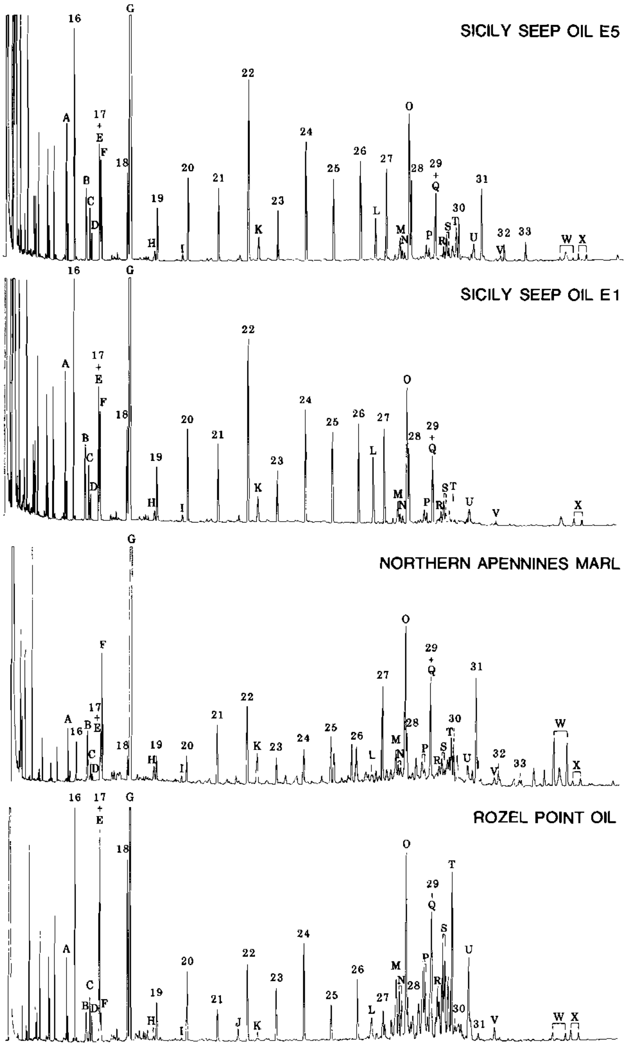
9.3. Results and Discussion

9.3.1. Saturated Hydrocarbon Fraction

The gas chromatograms of the saturate fraction of four samples are shown in Figure 9.1. The numbers in this figure indicate n-alkanes and correspond with their number of carbon atoms. The R_{22} index, defined as 2 x $C_{22}/(C_{21} + C_{23})$, is greater than one for all samples (RPO = 1.7; NAM = 1.9; SSO E1 = 3.0; SSO E5 = 3.1). This predominance of docosane is interpreted as a marker for hypersaline environments (ten Haven et al., 1985b) and is also observed in Chinese oils, the source rock of which was deposited in saline lakes (Wang et al., 1986). Tetracosane is even more abundant than docosane in the RPO sample, a phenomenon sometimes also observed in Chinese oils (Wang et al., 1986). The alkanes of RPO show an even over odd predominance (CPI_{24-34} = 0.82) in contrast with those of the NAM (CPI = 2.20) and SSO E5 (CPI = 1.20). SSO E1 possesses a remarkable n-alkane distribution. It mimics the distribution pattern of SSO E5 up to n-C_{29}, but no longer chain alkanes are observed. It has been postulated several times that an even over odd predominance of n-alkanes characterizes a hypersaline environment (see ten Haven et al., 1985b and references cited therein). Sometimes such an even over odd predominance could be obscured due to an additional input of continentally-derived alkanes. We believe that the R_{22} index is, therefore, a better criterion for hypersaline environments as heneicosane (C_{21}) and tricosane (C_{23}) are relatively low components among continentally-derived hydrocarbons.

Monomethyl branched alkanes, such as 2-methylpentadecane (A in Fig. 9.1) and 2-methylhexadecane (C) are relatively abundant and are thought to reflect the original presence of heterotrophic bacteria. Also in the RPO sample 7-methyl- and 8-methylheptadecane were observed and these compounds are thought to be derived from cyanobacteria (Gelpi et al., 1970).

Isoprenoid alkanes are abundant and phytane (G) is the most abundant compound in the saturate fraction of all samples. The pristane/phytane ratio is very low (<0.1), which is indicative of hypersaline environments (ten Haven et al., 1985b; see also Albaiges and Torradas, 1974; Fu Jiamo et al., 1986; Wang et al., 1986). The C_{25} isoprenoid (K), either 2,6,10,14,18- and/or 2,6,10,14,19-pentamethyleicosane, is also present in all samples and it is noteworthy to mention that the 2,6,10,14,18-C_{25} isoprenoid has been suggested as a biological marker


SICILY SEEP OIL E5

SICILY SEEP OIL E1

NORTHERN APENNINES MARL

ROZEL POINT OIL

Figure 9.1. Gas chromatograms of the saturated hydrocarbon fraction of Sicily seep oil E1 and E5 (two SSO's, E1 and E5, gave identical gas chromatograms), northern Apennines marl sample and Rozel Point oil. Identifications of letter-labeled compounds are given in Table 9.1.

Table 9.1. Selected compounds identified in the saturated hydrocarbon fraction

A	2-methylpentadecane
B	2,6,10-trimethylpentadecane
C	2-methylhexadecane
D	3-methylhexadecane
E	2,6,10-trimethyl-7-(3-methylbutyl)-dodecane
F	2,6,10,14-tetramethylpentadecane (pristane)
G	2,6,10,14-tetramethylhexadecane (phytane)
H	2,6,10,14-tetramethylheptadecane
I	2,6,10,14-tetramethyloctadecane
J	5α(H),14α(H),17α(H)-pregnane + 5α(H),14β(H),17β(H)-pregnane
K	2,6,10,14,18-pentamethyleicosane and/or 2,6,10,14,19-pentamethyleicosane
L	2,6,10,15,19,23-hexamethyltetracosane (squalane)
M	5β(H),14α(H),17α(H)-20R-cholestane + 5α(H),14α(H),17α(H)-20S-cholestane (especially Rozel Point Oil)
N	5α(H),14β(H),17β(H)-20R-cholestane + 5α(H),14β(H),17β(H)-20S-cholestane
O	5α(H),14α(H),17α(H)-20R-cholestane
P	5α(H),14β(H),17β(H)-20R-24-methylcholestane + 5α(H),14β(H),17β(H)-20S-24-methylcholestane
Q	5α(H),14α(H),17α(H)-20R-24-methylcholestane
R	4α,24-dimethyl-5α(H),14β(H),17β(H)-20R-cholestane + 5α(H),14α(H),17α(H)-20S-24-ethylcholestane (especially Rozel Point Oil)
S	4α,24-dimethyl-5α(H),14β(H),17β(H)-20S-cholestane + 5α(H),14β(H),17β(H)-20R-24-ethylcholestane + 5α(H),14β(H),17β(H)-20S-24-ethylcholestane
T	5α(H),14α(H),17α(H)-20R-24-ethylcholestane
U	4α-methyl,24-ethyl-5α(H),14α(H),17α(H)-20R-cholestane + 17α(H),21β(H)-hopane
V	gammacerane
W	22R-pentakishomohop-17(21)-ene + 22S-pentakishomohop-17(21)-ene
X	17α(H),21β(H)-22R-pentakishomohopane 17α(H),21β(H)-22S-pentakishomohopane

for hypersaline environments (Waples et al., 1974). The 2,6,10,15,19-C_{25} isoprenoid is virtually absent. The presence of squalane (L) suggests that halophilic bacteria were present in the original depositional environment, although a contribution from other bacteria such as methanogenic bacteria cannot be precluded. Recently large quantities of highly branched alkanes and alkenes were found in sediments from some hypersaline basins of Western Australia (Dunlop and Jefferies, 1985). The isoprenoid alkane 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane (E) is an important compound occurring in the RPO (Yon et al., 1982) and is also present in small quantities in the other samples. This compound might be a biological marker for Enteromorpha prolifera (Rowland et al., 1985), a species which is known to have a salinity tolerance up to 65 °/oo (Ehrlich and Dor, 1985).

Figure 9.2 shows mass chromatograms of m/z 191 and 367 of the RPO. The distribution patterns of the extended hop-17(21)-ene series, exemplified by the m/z 367 trace, and the extended 17α(H),21β(H)-hopane series are very similar if not identical and maximize at C_{35}. This

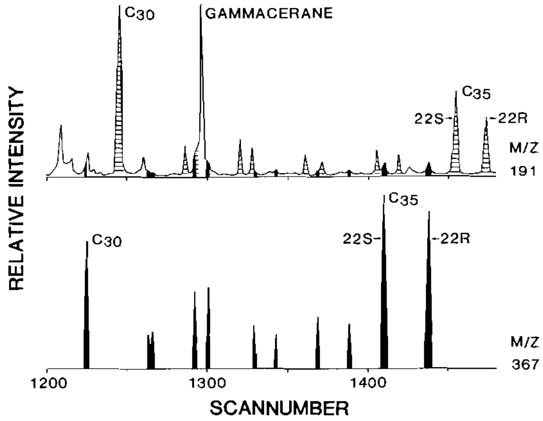


Figure 9.2. Mass chromatograms of m/z 191 and 367 in the hopanoid region of the RPO. Hop-17(21)-enes are indicated black and 17α(H), 21β(H) hopanes are shaded.

phenomenon is thought to be very typical for hypersaline environments (ten Haven et al., 1985b) . Similar distribution patterns of the hopanoids are observed in the other samples (Fig. 9.1) and also in marl extracts from Sicily evaporitic deposits (Palmer and Zumberge, 1981) and in some Chinese oils derived from salt lake evaporitic formations (Fu Jiamo et al., 1986). There are, however, some similar distribution patterns reported from non hypersaline environments (e.g. McEvoy, 1983). A reduction of hopenes to the corresponding hopanes was suggested to explain the similar distribution patterns of these compounds (ten Haven et al., 1985b; 1986d, see Chapter 10) Another feature which all samples have in common, is the presence of gammacerane (V in Fig. 9.1; see also Fig. 9.2). Gammacerane is also ubiquitous in Chinese oils derived from saline environments (Fu Jiamo et al., 1986; Xie Taijun et al., 1986). In the RPO 5α(H),14α(H),17α(H)- and 5α(H),14β(H),17β(H) pregnane (J), homopregnane and 4-methylpregnane were encountered, but only in small amounts. Sometimes pregnanes and homopregnanes are present as the major steranes in samples from hypersaline environments (ten Haven et al., 1985b; see also Fu Jiamo et al., 1986).

The sterane composition and distribution of the Italian samples (NAM, SSO's) are almost identical (Fig. 9.1), supporting the presumed origin of the seep oils from Messinian formations in Sicily (Palmer and Zumberge, 1981). One of the remarkable phenomena is the almost complete absence of 20S 5α(H),14α(H),17α(H) sterane isomers, whereas the 20S and 20R 5α(H),14α(H),17α(H) steranes (N, P, S) are present in relatively high amounts. This "maturity" discrepancy can be explained by an alternative diagenetic pathway of steroids, assuming precursor steroids with an Δ^{7}, Δ^{8} and/or $\Delta^{8(14)}$ double bond (ten Haven et al., 1986d). Other relatively important steranes are 4-methylsteranes (R, S, U). These compounds may point to an input of dinoflagellates (Boon et al., 1979; Robinson et al., 1984; de Leeuw, 1986), which is not surprising considering the wide salinity tolerance of dinoflagellates (Wall and Dale, 1974). However, a bacterial origin for the 4-methyl steranes can at present not totally be precluded, since Bouvier et al.

(1976) reported the occurrence of a 4-methyl-$\Delta^{8(14)}$-sterol and a 4-methyl-$\Delta^{8(14),24}$-sterol in the bacterium Methylococcus capsulatus.

9.3.2. Aromatic Hydrocarbon Fraction

The majority of compounds present in the so-called aromatic hydrocarbon fraction consists of organic sulphur compounds (OSC). In view of this it is noteworthy that Thompson (1981) reported a sulphur content of 13.95 % for the RPO and Colombo and Sironi (1961) measured up to 10.10 % sulphur in Messinian seep oils. Figure 9.3 shows the gas chromatograms as recorded with an FPD giving a selective response for OSC. A detailed description of the OSC of the NAM sample is reported by Sinninghe Damsté et al. (1986) and OSC of the RPO are reported by de Leeuw (1986) and by Sinninghe Damsté and de Leeuw (1986). The most abundant compound in all samples is identified as 2,3-dimethyl-5-(2,6,10-trimethylundecyl)-thiophene (c in Fig. 9.3). The co-occurrence of this C_{20} isoprenoid thiophene and phytane as the most important compounds in the respective component classes, seems to favour the hypothesis that this isoprenoid thiophene results from an early diagenetic incorporation of sulphur in, e.g., archaebacterial phytenes (Brassell et al., 1986b). In all samples a mixture of uncommon isoprenoid thiophenes (b) is observed. Although the exact structures of these compounds are not yet elucidated, it is speculated that they result from sulphur incorporation into 2,6,10-trimethyl-7-(3-methylbutyl)-dodecene (Sinninghe Damsté et al., 1986). These types of sulphur compounds are relatively abundant in RPO and in the saturated fraction the corresponding alkane, 2,6,10-trimethyl-7-(3-methylbutyl)-dodecane, is an important compound, which supports the incorporation theory. More information concerning the OSC of the seep oils investigated here will be published elsewhere (Sinninghe Damsté et al., in prep; Schmid and Albrecht, in prep.).

As the precise nature of the OSC is still poorly understood, a direct link with the depositional environment seems rather speculative. However, in view of their dominant presence in all samples, the

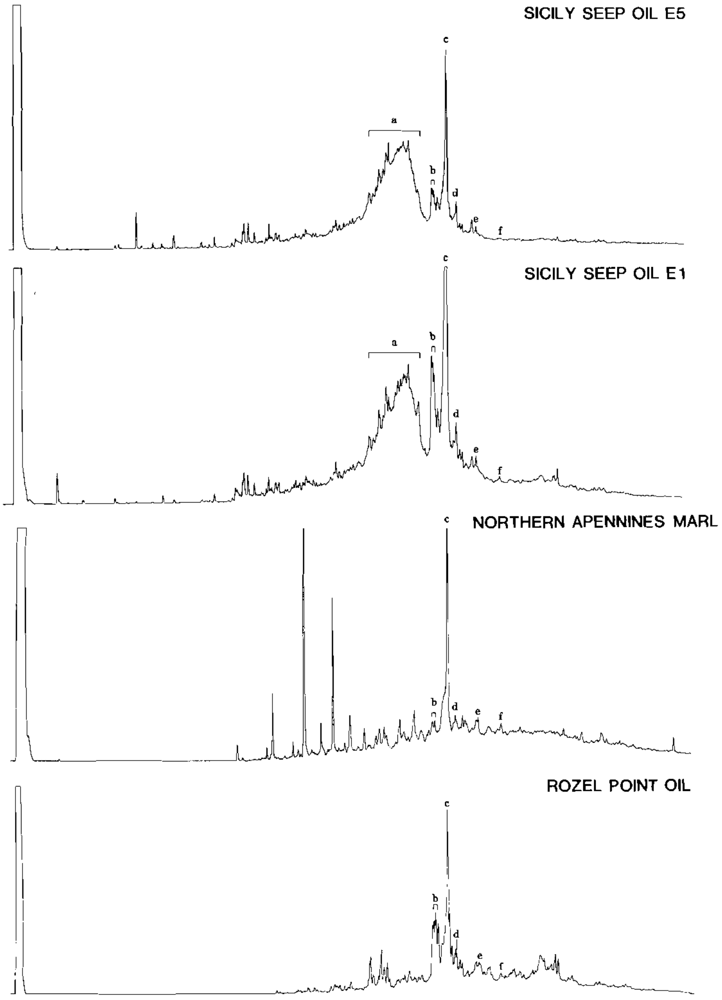


Figure 9.3. FPD-gas chromatograms of the aromatic hydrocarbon fraction of Sicily seep oils E1, E5, northern Apennines marl and Rozel Point oil. Identifications of selected compounds are given in Table 9.2.

Table 9.2. Selected compounds identified in the aromatic hydrocarbon fraction

a	unresolved hump of amongst others thiolanes
b	mixture of uncommon C_{20} isoprenoid thiophenes
c	2,3-dimethyl-5-(2,6,10-trimethyl)-thiophene
d	3-methyl-2-(3,7,11-trimethyldodecyl-thiophene
e	3,5-dimethyl-2-(3,7,11-trimethyldodecyl)-thiophene
f	5-ethyl-3-methyl-2-(3,7,11-trimethyldodecyl)-thiophene

suggestion of Sinninghe Damsté et al. (1986) that these OSC characterize hypersaline depositional environments, seems to be justified. Moreover the existence of high-sulphur petroleums has been ascribed to sulphur incorporation into organic matter in carbonate-evaporate environments (Tissot and Welte, 1984).

9.4. Conclusions

All samples show similar biological marker characteristics, which can be attributed to the environment of deposition. Table 9.3 summarizes these biological markers and their typical distribution patterns.

The Rozel Point oil has been suggested to be sourced by playa-lake deposists of the Miocene Salt Lake group (Meissner et al., 1984), and based on the distribution of biological markers and their relative quantities observed in the saturated and aromatic hydrocarbon fractions, we support this suggestion.

It seems that the phenomena as described in Table 9.3, can be used as a key to the past to recognize palaeo hypersaline environments.

Table 9.3. Organic geochemical phenomena related to hypersaline depositional environments

- phytane $\gg$ pristane
- $R_{22} = \frac{2 \times n\text{-}C_{22}}{n\text{-}C_{21} + n\text{-}C_{23}} > 1.5$
- high abundance of regular C_{25} isoprenoid
- high abundance of squalane
- high abundance of organic sulphur compounds, especially 2,3-dimethyl-5-(2,6,10-trimethylundecyl)-thiophene
- 14β(H),17β(H)-sterane concentration relative high in comparison with the 14α(H),17α(H)-20S-steranes
- relative high abundance of gammacerane
- typical distribution pattern of C_{31}-C_{35} hop-17(21)-enes and 17α(H),21β(H)-hopanes, both maximizing at C_{35}

Chapter 10

ANOMALIES IN STEROID AND HOPANOID MATURITY INDICES

Abstract

The purpose of this letter is to put forward new interpretations of previously-published data relating to ancient hypersaline environments.

Recent hypersaline environments are often characterized by high amounts of relatively uncommon sterols, such as Δ^7 sterols. The diagenetic pathway of such sterols, tentatively proposed here, might "rapidly" lead to formation of 20R- and 20S-5α(H),14β(H),17β(H)-steranes, providing such immature samples with a mature appearance. Extended 17α(H),21β(H)-hopanes and extended hop-17(21)-enes, present in ancient hypersaline environments, occur fully isomerized at C-22 and a diagenetic pathway explaining this phenomenon is proposed. The use of these specific stereoisomers as maturity parameters in the reconstruction of the thermal and burial history of sediments, could therefore lead to erroneous conclusions.

10.1. Introduction

The degree of isomerisation in biological markers, such as steranes and triterpanes, is now widely applied to indicate maturity of source rocks and petroleums (e.g. Mackenzie and McKenzie, 1983). Isomerisation parameters can be used to understand and reconstruct the thermal and burial history of sediments since their deposition (e.g. Beaumont et al., 1985). These studies clearly show that the isomerisation of steranes at C-14, C-17 and C-20 and of hopanes at C-17, C-21 and C-22 are all related to increasing maturity and can also be correlated with each other and with other maturity parameters such as vitrinite reflectance. However, in recent organic geochemical studies of ancient hypersaline environments of deposition (ten Haven et al., 1985b, see chapter 8; 1986e, see chapter 9), "anomalies" were observed in maturation indices of steranes and triterpanes in comparison with the other maturity parameters proposed by Mackenzie and Maxwell (1981).

The purpose of this letter is to put forward new interpretations of previously-published data from ancient hypersaline environments, rather than provide experimental solutions. Alternative diagenetic pathways of hopanoids and steroids are proposed here, which may explain the observed maturity discrepancies.

10.2. Discussion

In samples from ancient hypersaline environments series of extended 17α(H),21β(H)-hopanes and/or extended hop-17(21)-enes, both maximizing at the C_{34} or C_{35} members, are observed (e.g. Palmer and Zumberge, 1981; Palacas et al., 1984; ten Haven et al., 1985b; 1986e; Fu Jiamo et al., 1986). Both series of hopanoids are fully isomerized at C-22 to their isomerisation endpoint of 50-60 % 22S isomer (Seifert and Moldowan, 1980). The hopenes are indicative for a rather immature stage, whereas the fully isomerized 17α(H),21β(H)-hopanes, together with the presence of relatively abundant 14β(H),17β(H)-steranes (see below) are indicative for a mature stage. It was therefore suggested that the extended hopanes were formed via reduction of the extended hopenes and not via isomerisation of the 22R-17β(H),21β(H)-hopanes (ten Haven et al., 1985b). The ratio of extended hopenes/hopanes well above 1 in a sediment sample (ten Haven et al., 1985b) on the one hand, and a value of this ratio well below 1 in more mature oils on the other hand (ten Haven et al., 1986e) might support such a diagenetic process. A reduction of extended hop-17(21)-enes to the corresponding 22R- and 22S-hopanes, based on data from the three most mature samples of DSDP Leg 63 (not hypersaline), was also suggested by McEvoy (1983); an increase in the 22S/22R hopane ratio was explained by a reduction of the corresponding hop-17(21)-enes, which had already a 22S/22R ratio of about unity. The isomerisation at C-22 in these hopanoids can be attributed to either a temporary migration of unsaturation from $\Delta^{17(21)}$ to the Δ^{21} position, followed by a reprotonation at C-22 from either the α- or the β-face, and a return of the unsaturation to its former, probably more stable, location, or to a defunctionalization of the presursor hopanoids followed by a double bond migration from the side chain to the $\Delta^{17(21)}$, "en passant" isomerizing chiral centers in the side chain.

The sterane composition of these hypersaline samples is often markedly different from that of other samples. The 20R- and 20S-5α(H),14β(H),17β(H)- and 20R-5α(H),14α(H),17α(H)-steranes are relatively abundant, whereas the 20S-5α(H),14α(H),17α(H)-steranes are virtually absent. This contradicts the relationship proposed by Mackenzie and Maxwell (1981) (see also Mackenzie et al., 1980). Rullkötter et al. (1984) also observed a similar kind of "maturity" discrepancy and explained this by variations in the composition of the steroid precursors. A careful inspection of the literature reveals that their samples are also from a hypersaline environment. Their most mature sample (BI-9) appeared to contain alkanes with an even over odd predominance (Spiro and Aizenshtat, 1977; Spiro et al., 1983), a low pristane/phytane ratio (Spiro, 1984), and a postulated relatively high abundance of gammacerane (Rullkötter et al., 1984), later confirmed by coinjection (Rullkötter et al., 1985). All these phenomena can be ascribed to a hypersaline depositional environment (ten Haven et al., 1985b; 1986e).

Like Rullkötter et al. (1984) we also suggest that the maturity anomalies must be induced by specific steroid precursors present in the original depositional environment.

Sterols with a double bond at the Δ^7 position are often abundant in hypersaline environments (e.g. Boon et al., 1983; de Leeuw et al., 1985). A possible diagenetic pathway starting from such sterols is visualized in Figure 10.1. It is suggested that the precursor sterols are altered during diagenesis to sterenes with a double bond at positions Δ^7, Δ^8, $\Delta^{9(11)}$, $\Delta^{8(14)}$, Δ^{14}. Based on deuterium incorporation experiments (Akporiaye et al., 1981) and molecular mechanics (van Graas et al., unpublished results) isomerisation to structures with a double bond at positions Δ^6, Δ^{11} and Δ^{15} is unlikely due to their relatively high energy contents. Also it is not expected that the common Δ^4 and Δ^5 sterenes isomerize to Δ^7 sterenes, because of the relatively high energy content of Δ^6 sterenes (van Graas et al., unpublished results). Indeed, Turner et al. (1957) have shown in the laboratory that treatment of cholest-6-ene with Brønsted acids gives the 4-ene and 5-ene and none of the 7-ene. Although Δ^7, $\Delta^{8(14)}$, Δ^{14} sterenes have not yet been detected in sediments, it is known that these sterenes can be easily converted to spirosterenes (Anastasia et al., 1978a), compounds often observed in sediments (e.g. Brassell et al., 1984). Spirosterenes were also observed in sediments deposited under hypersaline conditions (ten Haven et al., 1985b). Hence, via the isomerisation scheme depicted in Figure 10.1 we can ultimately arrive, after hydrogenation of these sterenes, at steranes with various configurations, viz. 14β(H),17β(H); 14α(H),17α(H); 14β(H),17α(H) and 14α(H),17β(H)- steranes (ordered according to decreasing thermodynamic stabilities, after van Graas et al., 1982). It is assumed that the natural configuration is retained at positions 8, 9 and 13. Since it has been demonstrated that the 14β(H),17β(H) configuration is the most stable one, it may be concluded that upon hydrogenation of the appropriate sterenes, i.e. 17β(H)-8(14)-ene or 14-ene, on the least hin-

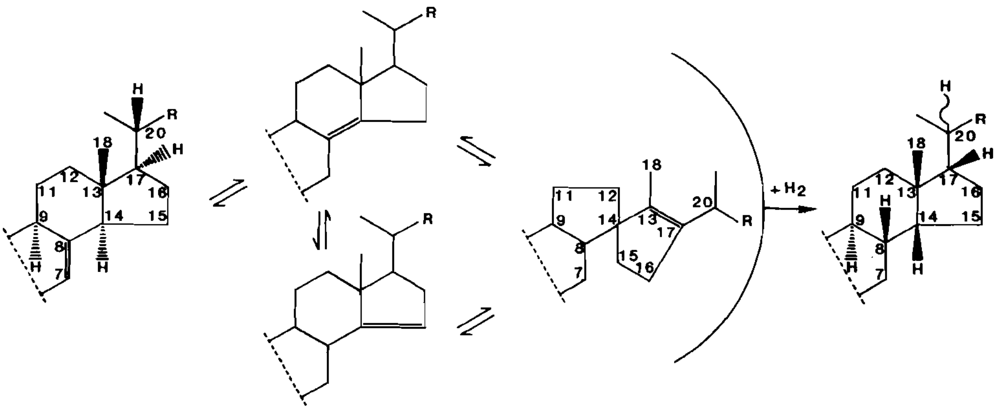


Figure 10.1. Proposed diagenetic pathway of Δ^7 sterols. Only the 14β(H),17β(H)-steranes are shown, as these are the thermodynamically most stable steranes. $R = C_6H_{13}$, C_7H_{15} or C_8H_{17}.

dered face, the thermodynamically most stable steranes are preferentially formed in this particular case. Such a generation of 14β(H),17β(H)-steranes from Δ^7, $\Delta^{8(14)}$, Δ^{14} sterenes has been shown to occur in the laboratory after initial isomerisation at the 17-position (with dry HCl at -78°C), giving the 17β(H)-14-ene after dechlorination, followed by catalytic hydrogenation (Caspi et al., 1975; Anastasia et al., 1978a). The side chain epimerization may involve the intermediate formation of spirosterenes (Anastasia et al., 1978b). It should be noted here that the hydrogenation could also yield spirosteranes, compounds which have not been reported to occur in sediments.

It is generally believed that the superacid sites of clay minerals play an important role in carbonium ion-initiated isomerisations (e.g. Sieskind et al., 1979). The absence or virtual absence of diasteranes noted in carbonate environments (McKirdy et al., 1983; Rullkötter et al., 1985). supports this. To what extent the mineral matrix of a hypersaline environment of deposition (e.g. gypsum) can catalyze carbonium-ion triggered isomerisation is as yet unknown.

10.3. Conclusions

From the above it is clear that it is not always possible to apply the degree of isomerisation of steranes and triterpanes as maturity indices. Care should be taken in the application of these indices, since obviously specific steroidal and extended hopanoidal precursors strongly influence the occurrence of certain stereoisomers at an early stage of diagenesis.

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