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Geochemistry of eastern Mediterranean sedimentary cycles

**On the origin of Miocene to Pleistocene sapropels,
laminites and diatomites**

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**On the origin of Miocene to Pleistocene sapropels,
laminites and diatomites**

Geochemie van sedimentaire cycli in de oostelijke Middellandse Zee

**Over het ontstaan van Miocene tot Pleistocene sapropelen,
laminieten en diatomieten**

(met een samenvatting in het Nederlands)

Proefschrift

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ὥς εἰπὼν σύναγεν νεφέλας, ἐτάραξε δὲ πόντον
χερσὶ τρίαιναν ἐλών· πάσας δ' ὀρόθυνεν ἀέλλας
παντοίων ἀνέμων, σὺν δὲ νεφέεσσι, κάλυψεν
γαῖαν ὁμοῦ καὶ πόντον· ὀρώρει δ' οὐρανόθεν νύξ.
σὺν δ' Ἑὐρός τε Νότος τ' ἔπεσον Ζέφυρός τε δυσαῆς
καὶ Βορέης αἰθρηγενέτης μέγα κύμα κυλίνδων.
καὶ τότε Ὀδυσσεύς λύτο γούνατα καὶ φίλον ἦτορ,
ὀχθήσας δ' ἄρα εἶπε πρὸς ὃν μεγαλήτορα θυμόν·
„ὦ μοι ἐγὼ δειλός, τί νύ μοι μήκιστα γένηται;”

Ὅμηρος, Ὀδυσσεύς

*"The limit of man's knowledge in any subject
possesses a high interest, which is perhaps increased
by its close neighbourhood to the realms of imagination."*

Charles Darwin, *The voyage of the Beagle*

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Chapter 1

Introduction and summary

A brief history of sapropels

The word "sapropel" first appears in the literature in 1904, when Potonié mentions that Prof. Dr. Schulze suggested that this word should be used as the international scientific term for *Faulschlamm* [Potonié, 1904]. Sapropel is a contraction of the literal translation of the German words *Fäulniss* and *Schlamm* into ancient Greek (σαπρός and πηλός, meaning putrefaction and mud). Potonié uses the term to describe a dark-coloured sediment, containing decomposing organisms, deposited under stagnant water. Fossil sapropel deposits are subsequently named sapropelites [Twenhofel, 1926]. These terms are commonly used for organic-rich lake sediments or certain oil source rocks, but were introduced to marine geosciences by Olausson who uses the description "sapropelitic mud" for marine sediments containing more than 2% organic carbon [Olausson, 1954].

Without calling them sapropels, Bradley [1938] predicts the occurrence of laminated, organic-rich layers in the Mediterranean, especially in the eastern basin. Kullenberg [1952] first discovered such layers in cores recovered from the Mediterranean seafloor during the 1947-1948 Swedish deep-sea expedition. These layers might have simply been called black shales, if it were not for Olausson [1961] describing them as "sapropelic layers". Many more organic-rich layers were recovered during Deep Sea Drilling Program (DSDP) Legs 13A (1970) and 42A (1975). Examination of these sediments resulted in an official sapropel definition: "a discrete layer, greater than 1 cm in thickness, set in open marine pelagic conditions, and containing greater than 2.0% organic carbon by weight" [Kidd et al., 1978]. The term sapropelic layer was downgraded and since then designates a layer containing between 0.5% and 2.0% organic carbon.

On the origin of sapropels

Especially in the decennia since 1970, numerous researchers have studied the sedimentology, palynology, micropalaeontology and geochemistry of Mediterranean sapropels. The aim of these studies: to reconstruct the climatic conditions and hydrographic regime that resulted in sapropel formation. Currently, the Mediterranean (Fig. 1.1) is a land-locked basin separated from the Atlantic Ocean by the shallow Strait of Gibraltar (284 m deep). Ocean surface water flows eastwards into the Mediterranean, becoming denser as a result of evaporation. Between Sicily and Tunisia, water flows through the shallow Strait of Sicily (330 m deep), which

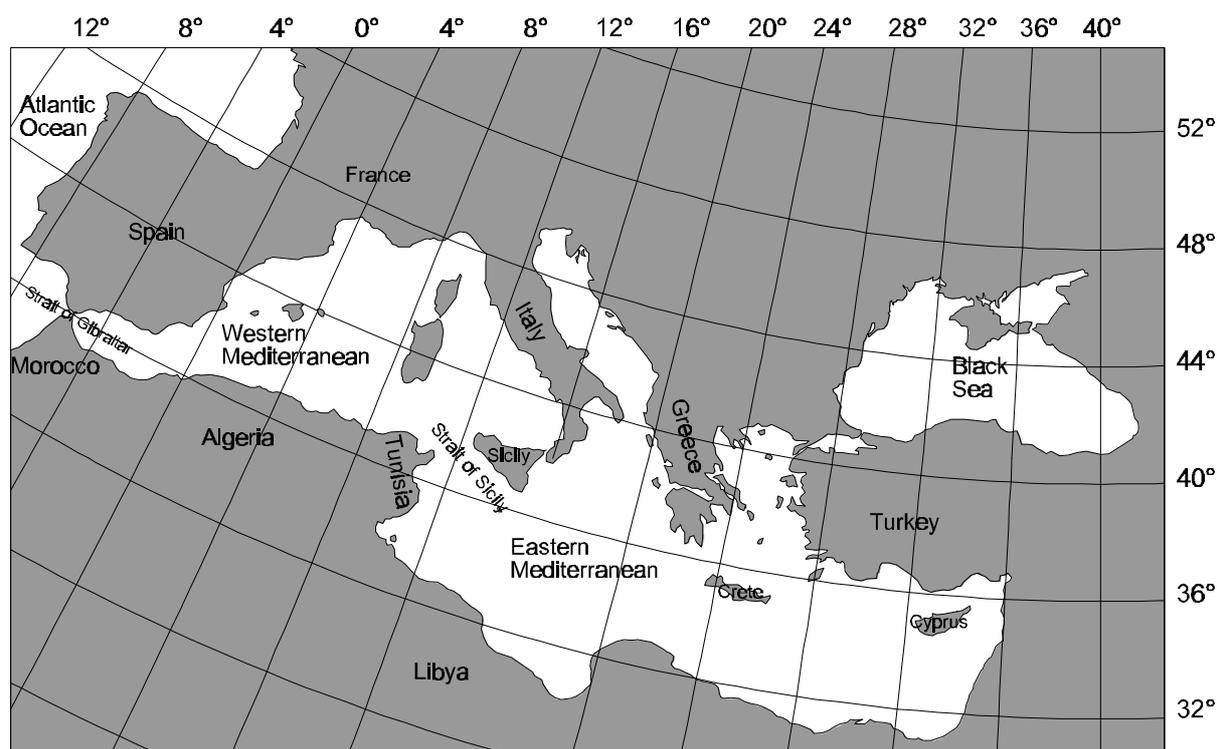


Figure 1.1 Map of the Mediterranean area.

separates the western from the eastern Mediterranean. Continuing evaporation finally makes the surface water so saline and dense that it sinks near Cyprus, where it starts its way back to the Atlantic Ocean as Mediterranean Intermediate Water. This anti-estuarine circulation pattern makes the Mediterranean a nutrient desert: it receives nutrient-depleted surface waters and exports its nutrients received by rivers to the Atlantic with its deep water. The same is true for the eastern basin with respect to the western basin, making the eastern Mediterranean a "nutrient desert within a nutrient desert". Present-day low surface water nutrient levels and oxic bottom waters result in deposition of organic-poor sediments (<0.5% organic carbon). For the deposition of organic-rich sapropels, major changes in this system are clearly necessary.

At first, the occurrence of organic-rich layers in Mediterranean sediments was reported to be linked to improved preservation of organic matter under anoxic bottom water conditions. Anoxia would result from density stratification of the water column, limiting circulation and supply of oxygen to deep water [Bradley, 1938; Olausson, 1961]. In a key paper, Rossignol-Strick *et al.* [1982] correlate the most recent sapropel to a period of heavy precipitation in Africa (late Glacial - early Holocene). They concluded that increased Nile outflow produced a low-salinity layer in the eastern Mediterranean, which stratified the water column, culminating in stagnant (anoxic) bottom waters and sapropel formation. A more extreme theory is that increased Nile outflow did not lead to stagnation, but to a reversal of circulation in the eastern Mediterranean from anti-estuarine to estuarine [Calvert, 1983; Sarmiento *et al.*, 1988]. The simple link between sapropel formation and anoxia was challenged by Calvert, who suggested increased surface

water productivity as an alternative mechanism for sapropel formation [Calvert, 1983; Calvert et al., 1992]. In his view, organic carbon contents of some Mediterranean sapropels were too high to be achieved with present-day productivity even under anoxic bottom water conditions. On the other hand, high productivity in the Mediterranean cannot be achieved with the present-day hydrography. Calvert [1983] invoked the circulation reversal scenario to solve this problem, since with an estuarine circulation the eastern Mediterranean would be a nutrient trap. Alternatively, Rohling and Gieskes [1989] suggested that increased river water input might lead to a shoaling of the density gradient (pycnocline) into the photic zone. This would result in nutrients of intermediate waters becoming available for primary productivity in a so-called "Deep Chlorophyll Maximum". The "productivity versus preservation" debate is still continuing.

De revolutionibus orbium coelestium

Due to the collision of Africa with Europe, some sediments deposited on the Mediterranean seafloor have been uplifted above sea level. In these land sections, mainly in Greece and Italy, layers enriched in organic carbon are also found. "Real" sapropels are uncommon in those sections, because organic carbon levels of more than 2% are rarely attained. Corresponding horizons in carbonate cycles in the Sicilian Trubi, Narbone and Agrigento formations are simply called "grey layers", after their colour. Organic-rich layers in the famous Vrica section are called laminites. All these dark-coloured layers are repeated monotonously and regularly in the sedimentary record. This suggests that they are part of "Milankovitch cycles", linked to the Earth's orbital cycles of eccentricity, obliquity and precession. Eccentricity is a measure of the ellipticity of the shape of the Earth's orbit around the sun, and varies in main periods of 100,000 and 400,000 years. Obliquity is the variation in the angle of the Earth's axis, which has a main period of 41,000 years. Precession describes the movement of this axis around the surface of a cone, completing a full circle every 26,000 years. These variations affect the global, seasonal and latitudinal distribution of solar insolation on Earth and, therefore, result in climatic fluctuations. The correlation of the cyclic occurrence of sapropels in the Mediterranean to these orbital variations is mainly the result of the efforts of Hilgen and coworkers [Hilgen, 1991a, b; Hilgen et al., 1995]. They developed a continuous record of sapropel occurrences down into the Miocene, and correlated each sapropel to a precession cycle. Sapropel deposition occurs during precession minima, when the Northern Hemisphere receives maximum summer insolation, and climate in the Mediterranean region is relatively wet. The correlation of sapropels to the insolation record is of great significance, because it allows accurate age determination, estimation of sedimentation rates, and comparison of individual sapropels in different settings.

Geochemistry of eastern Mediterranean sedimentary cycles

The majority of geochemical studies on sapropels focus on Recent sediments recovered from

Chapter 1

the Mediterranean seafloor by traditional coring techniques. Sediments up to 1 million years old can be obtained in this way. For the study of older sapropels, samples have to be obtained either from land sections, or by seafloor drilling techniques. In the first part of this thesis ("The Miocene"), the geochemistry, micropalaeontology and sedimentology of 7 to 10 million-year-old sapropels from Crete and Gavdos (Greece) are discussed. It has been suggested that formation of such old sapropels did not result from climatic changes caused by the precession, but rather from an overall warm climate [Cita and Grignani, 1982; Thunell et al., 1984]. However, the characteristics of these Miocene sapropels are very comparable to those of Pliocene and Pleistocene sapropels. Therefore, sapropel formation during the last 10 million years must have resulted from one basic mechanism: precession-induced dry-wet oscillations in Mediterranean climate.

Pliocene land sections on Sicily are characterized by a striking alternation of grey-white-beige-white coloured sediments. The grey layers are equivalent to sapropels, but contain much less organic carbon. The formation of these carbonate cycles is still not fully understood, but must result from an intricate interplay of the processes of carbonate productivity, dissolution, and dilution by clays. At the Lido Rossello section on Sicily, six laminated intervals, some of which contain diatoms, are intercalated in the normal grey-white-beige-white sediments. In coeval sediments of the nearby Punta di Maiata section, these laminites are absent. In Chapter 4 it is discussed how these laminites may have formed, and how they are related to the carbonate cycles. It was found that they are productivity events, but there are also indications for the presence of a local anoxic basin during their deposition.

A unique opportunity to study sapropels older than 1 million years in marine cores instead of in land sections was offered by ODP (Ocean Drilling Program) Legs 160 and 161 in 1995. During these campaigns, hydraulic coring techniques were used to obtain excellent sedimentary records extending down into the Pliocene. Some of the Pliocene sapropels recovered were extremely well developed, having a very dark colour, distinct lamination, and sharp boundaries. In Chapter 5, it is shown that some of these sapropels are extremely rich in organic carbon, trace elements and pyrite, and contain isorenieratene derivatives (biomarkers for photosynthetic green sulphur bacteria). These sapropels must have been formed when the eastern Mediterranean water column was almost completely sulphidic as a result of high productivity.

The same sapropels feature in Chapter 6, where a detailed trace element budget of the eastern Mediterranean during their formation is presented. Calculations show that the trace element enrichment is not (solely) the result of diagenesis, and that next to wind, hydrothermal and river input, western Mediterranean seawater is also needed as a trace element source. This indicates that water circulation was not too much restricted during sapropel formation; in fact, it may have been reversed. A very efficient trace element removal mechanism must have been operative, supposedly scavenging by organic matter and sulphides from an almost completely euxinic water column. This mechanism is also operative in the present-day euxinic Black Sea. As such, these Pliocene Mediterranean sapropels are comparable to several worldwide

occurring black shales, especially those of the Caenomanian-Turonian Boundary Event (CTBE). However, because of the shorter duration of sapropel formation, the ultimate trace element sources are different for the sapropels (seawater) than for those black shales (hydrothermal and fluvial input).

In Chapter 7, the geochemical results of all studied ODP sapropels are presented. These (partly coeval) sapropels stem from four different sites that span most of the eastern Mediterranean, and which represent different water depths. Therefore, these data offer unique opportunities to narrow down the possible scenarios for sapropel formation. It is concluded that Pliocene sapropel formation is not the result of *either* increased productivity *or* improved preservation, but that both factors must have played a significant role. Possibly, anoxic conditions developed because of high oxygen demands set by decomposing organic matter, making productivity the key factor determining Pliocene sapropel formation. Sedimentation rates were between 30% lower and 50% higher during Pliocene sapropel formation, which lasted between 1,900 and 10,000 years. Nile runoff and nutrient supply is an important factor in sapropel formation, which is reflected in longer sapropel duration in the eastern part of the eastern Mediterranean than in the western part.

Because uplifted Mediterranean marine sediments in land sections are older than approximately 1 million years, a direct comparison between sapropels in marine cores with their equivalents in land sections had not been possible before ODP Leg 160. In the third part of this thesis ("The Pleistocene"), a comparison is made between a laminite in the Vrica section (Italy) and the coeval sapropel in ODP Sites 967 and 969. The laminite is quite different from the sapropel: it is much thicker, richer in clays, and poorer in organic carbon. Only a small part of the differences between the land section and the marine cores is the result of uplift, weathering and erosion. Most of these differences are due to the different settings: the Vrica sediments were deposited in shallower water, with a higher sedimentation rate, and closer to land than the ODP sapropel.

Where do we go from here: Chaos or community?

Even after several decades of intense research on Mediterranean sapropels, the precise mechanism behind their formation has not been fully elucidated. Clearly, sapropel formation is the result from an intricate interplay of several processes, each with varying intensity in time and place. To improve our understanding of these processes, we primarily need a more detailed knowledge of how palaeoproxies function, and what they register. The ultimate goal should be a model that can explain how sapropels are formed in the eastern and western Mediterranean, from the Miocene to the Holocene. In my view, the only way in which such a model can be attained, is cooperation between all marine disciplines: stratigraphy, sedimentology, micropalaeontology, inorganic and organic geochemistry, palynology, and oceanography. The year 2004 will mark the centennial of the word "sapropel". It would be appropriate if, by then, we will better understand what this term stands for.

Chapter 1

Acknowledgements - Stephen Hawking, Charles Darwin, Nicolaus Copernicus and Martin Luther King are acknowledged for their contributions to the section titles of this introduction.

				Age Myr B.P.	
Cenozoic	Quaternary	Pleistocene		1.6	
		Pliocene		5.3	
	Tertiary	Neogene	Part I: The Miocene		23.7
			Oligocene		36.6
		Palaeogene	Eocene		57.8
	Palaeocene		66.4		

*"Have you ever reflected on what an important sea the Mediterranean is?"
James Joyce (in a letter to Stanislaus)*

Chapter 2

On the origin of upper Miocene sapropels: A case study from the Faneromeni section, Crete (Greece)

I.A. Nijenhuis, S.J. Schenau, C.H. van der Weijden,

F.J. Hilgen, L.J. Lourens, W.J. Zachariasse

Abstract - For the first time, results of an integrated geochemical and micropalaeontological study of upper Miocene sapropels in a land-based section in the Mediterranean are presented. Three sapropels and adjacent homogeneous intervals in the Cretan Faneromeni section have been investigated in detail. The chemical and foraminiferal characteristics were found to be markedly similar to those of Plio-Pleistocene sapropels. As the physiography and climate of the late Miocene Mediterranean were not fundamentally different from those of today, our preferred model for late Miocene sapropel formation is similar to the one recently developed for Plio-Pleistocene sapropels. Increased seasonality and freshwater input during Northern Hemisphere summer insolation maxima triggered high export production and oxygen consumption rates, which, in combination with a concomitant decrease in deep water formation rate, resulted in the observed high organic matter content of the sapropels.

This chapter has been published in *Paleoceanography* 11 (1996): 633-645.

Introduction

Since Potonié, in the beginning of this century, first proposed the word ‘sapropel’ as international scientific expression for the type of deposit till then described by the German word ‘Faulschlamm’ [Potonié, 1907], much research has been devoted to this class of sediments. Marine sapropels and their fossil counterparts, defined as sapropelites [Twenhofel, 1926], have been subject to an increasing interest during the last decades [e.g. Olausson, 1961; Rossignol-Strick et al., 1982; Calvert, 1983; De Lange and Ten Haven, 1983; Howell et al., 1990; Cita, 1991; Rohling, 1994; Van Os et al. 1994]. These studies focus on late Pleistocene sapropels recovered from the eastern Mediterranean in piston cores, and to a lesser extent on Pliocene to early Pleistocene sapropels exposed in land sections. There is growing evidence that despite apparent variations in sedimentological, geochemical, and microfossil characteristics, the formation of Pliocene and Pleistocene sapropels is ultimately controlled by a single mechanism: dry-wet oscillations caused by precession-induced insolation variations [e.g. Rossignol-Strick et al., 1982; Rohling and Hilgen, 1991]. Sapropels are formed during the wetter conditions at times of precession minima, when perihelion occurs during Northern Hemisphere summer. Under these conditions, continental runoff and nutrient-influx to the basin are higher, resulting in enhanced primary productivity and a reduction of excess evaporation and bottom water formation. The relative importance of bottom water anoxia (preservation) in raising the organic matter content of sapropels still is a matter of debate.

Miocene sapropels have received much less attention, partly because Deep Sea Drilling Project/Ocean Drilling Program (DSDP/ODP) safety regulations do not allow drilling through Messinian evaporites. The present scanty literature suggests that these sapropels had a different origin than their younger counterparts. Cita and Grignani [1982] and Thunell et al.

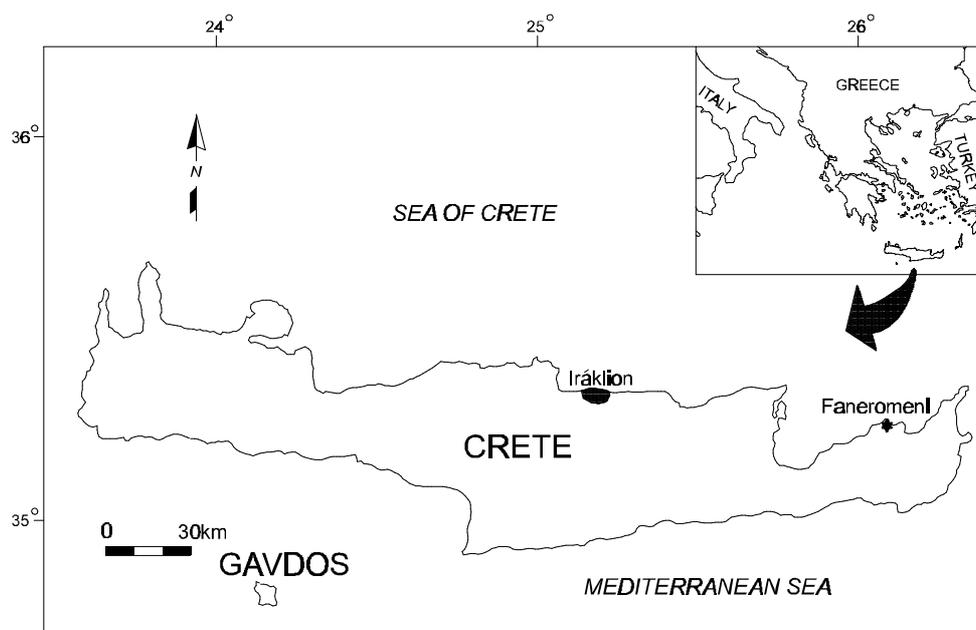


Figure 2.1 Location of the Faneromeni section on the Greek island of Crete.

[1984] have suggested that only the formation of late Pliocene and Pleistocene sapropels was controlled by precession-induced climatic oscillations, whereas the formation of Miocene and early Pliocene sapropels resulted from an overall warm climate and associated sluggish bottom water circulation. *Van der Zwaan and Gudjonsson [1986]* are of the opinion that both Miocene and Pliocene sapropels are formed by climatically induced salinity stratification, albeit caused by other mechanisms in the Miocene (short-term eustatic sea level changes) than in the Pliocene (periodic increase in runoff).

This paper addresses the question of how late Miocene sapropels are formed. For this purpose, three sapropels in the Faneromeni section on Crete were selected for an integrated geochemical and micropalaeontological study.

Lithology and sampling

In the Faneromeni section on the Greek island of Crete (Fig. 2.1), we selected a 4.5 m thick sequence of light-coloured sedimentary rock interbedded by three darker layers (for all of which we will use the name sapropel for reasons of simplicity). The lighter intervals consist of beige marls, which have been homogenized by bioturbation. The lower and upper sapropels are black marls; the middle one, which is thinner, is a grey marl. These darker intervals are faintly laminated, although some bioturbation is discernable. Boundaries between the different lithologies are gradual. The sapropels are coded F18, F19, and F20; astronomical calibration yielded ages of 7.167, 7.146, and 7.123 million years, respectively, for the midpoints of these sapropels [*Hilgen et al., 1995*].

After removal of the weathered surface, core samples (2 cm in diameter, 8 cm long, four at each sampling point) were taken using an electric drill. In the homogeneous layers, samples were collected with larger spacing (15 cm) than in the sapropels (4 cm). Lithologies and sample positions are given in Figure 2.2.

Geochemical analyses

The cores were dried for four days at 40°C and subsequently crushed, powdered, and homogenized. Subsamples were taken for chemical analyses. After removal of inorganic carbon with 1 M HCl, the organic carbon content (C_{org}) was measured by oxidation at 900°C and determination of the resulting CO₂ pressure in a tube of known volume. The stable carbon isotopic composition of organic matter ($\delta^{13}C_{\text{org}}$) was measured in the same tube with a stable isotope ratio analyser (VG SIRA 24). Total nitrogen (N_{tot}) content of the samples was determined with a NA 1500 NCS analyser. The carbonate fraction was determined by Scheibler's method; CO₂ produced was measured gas-volumetrically. For the carbonates and $\delta^{13}C_{\text{org}}$ measurements, all relative errors found in duplicate measurements are better than 0.7%. For C_{org} analyses, relative errors are below 2.6%. The relative standard deviation of a quadruplicate measurement of N is 0.8%.

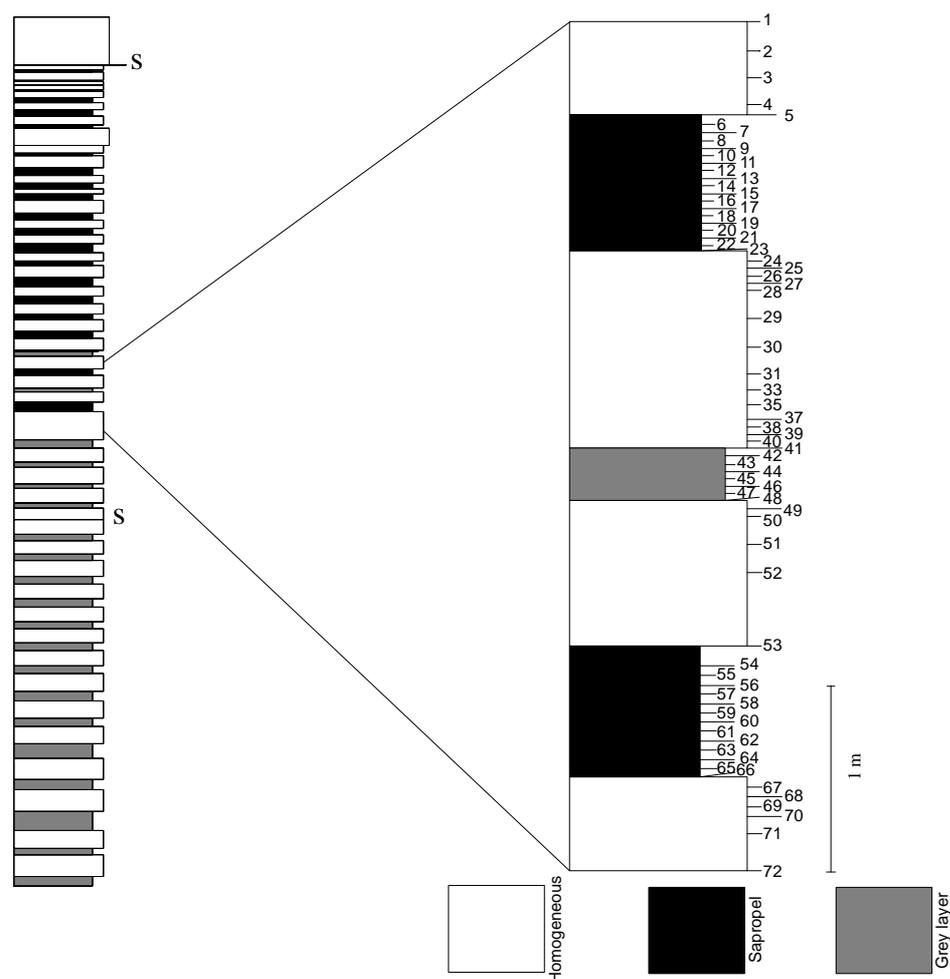


Figure 2.2 Overview of the Faneromeni section (left), sampled interval, and sample locations (right). Total thickness of the section is about 50 m. Bedding parallel shear planes are indicated by the letter S.

For major, minor, and trace element analysis, a 250 mg sample was digested in 10 ml of a 6.5 : 2.5 : 1 mixture of HClO_4 (60%), HNO_3 (65%) and H_2O , and 10 ml HF (40%) at 90°C . After evaporation of the solutions at 190°C on a sand bath, the dry residue was dissolved in 50 ml 1 M HCl. The resulting solutions were analysed by a Perkin Elmer Optima 3000 ICP-AES apparatus for the elements Al, Ba, Ca, Co, Cr, Cu, Fe, K, Li, Mg, Mn, Na, Ni, P, S, Sc, Sr, Ti, V, Y, Zn, and Zr, by a Perkin Elmer 4100 ZL ZGFAAS apparatus for the elements Cd and Mo, and by a Perkin Elmer 5000 G hydride AAS apparatus for the elements As, Sb, and Se. Uranium was measured by X-ray fluorescence analysis on pressed powder tablets (Philips PW 1400 XRF apparatus). Semi-quantitative analysis of Mg-calcite and gypsum was performed by X-ray diffraction (Philips PW 1700 apparatus; CuK_α). Particle sizes were determined on a carbonate and organic matter free basis, using a Malvern Series 2600 laser particle sizer.

The relative error in duplicate measurements for the ICP analyses is better than 3% for all elements except S (5%). The relative errors for Cd, Mo, As, Sb, and Se are, 2%, 5%, 10%, 4%, and 14%, respectively.

Soluble salts were extracted by shaking a 250 mg sample in 50 ml of water at ambient temperature for a week. The resulting solution was analysed by the same ICP as above for Ca, K, Mg, Na, and S. The relative error in duplicate measurements is better than 8% for all elements except K (17%).

All results were checked by using artificial and non-artificial international (e.g. MAG-1, SCo-1, SDC-1 for ICP analyses, SO-1, SO-2, and others for XRF research; data for all standards are given by *Govindaraju [1989]*) and house (MMM 91) standards.

Foraminiferal analyses

Counts on planktonic and benthic foraminifera were made on one and the same split from the 125 to 595 μm fraction using an Otto microsplitter. Specimens were handpicked, mounted on Chapman slides, identified, and counted. Counted numbers of planktonic foraminifera are generally between 100 and 200 and between 50 and 130 for the benthic foraminifera. Preservation is variable, being poor in the carbonate-rich intervals, where many foraminifera are filled and partly covered with sediment, and better in the sapropels.

Oxygen isotopic ratios of carbonates ($\delta^{18}\text{O}_{\text{carb}}$) were measured on the planktonic foraminiferal species *Globigerinoides obliquus* and *Globigerinoides sacculifer*. In order to remove any remaining organic matter, about 100 specimens (10 mg) per sample were roasted for thirty minutes at 470°C under a helium flow. After that, the samples were transferred into glass reaction tubes that were evacuated for fourteen hours. Subsequently, the samples were dissolved in 100% phosphoric acid at 25°C under high vacuum for six hours. The released CO_2 was cryogenically separated from other gases and measured on a VG SIRA 24 mass spectrometer.

Results and interpretation

Geochemistry

Organic matter and related elements - The results of the bulk organic matter analyses are shown in Figure 2.3. In the homogeneous intervals, the C_{org} content is similar to that of oceanic calcareous oozes [*Chester, 1965*]. In the sapropels, however, C_{org} is three to twelve times enriched, reaching top values of more than 3%.

The $\delta^{13}\text{C}_{\text{org}}$ profile is complex and therefore difficult to interpret. The lower and upper sapropels, however, show a pattern of heavier values at their boundaries and lighter values in the middle. $\delta^{13}\text{C}_{\text{org}}$ is often used as an indicator for the source (marine versus terrestrial) of organic matter, because carbon isotopic values of marine organic matter are normally less negative ($\sim -20.6\text{‰}$) than those of terrestrial organic matter ($\sim -26.6\text{‰}$; e.g. *Jasper and Gagosian [1990]*). If the profile is interpreted in this way, the sapropels show an enrichment of marine

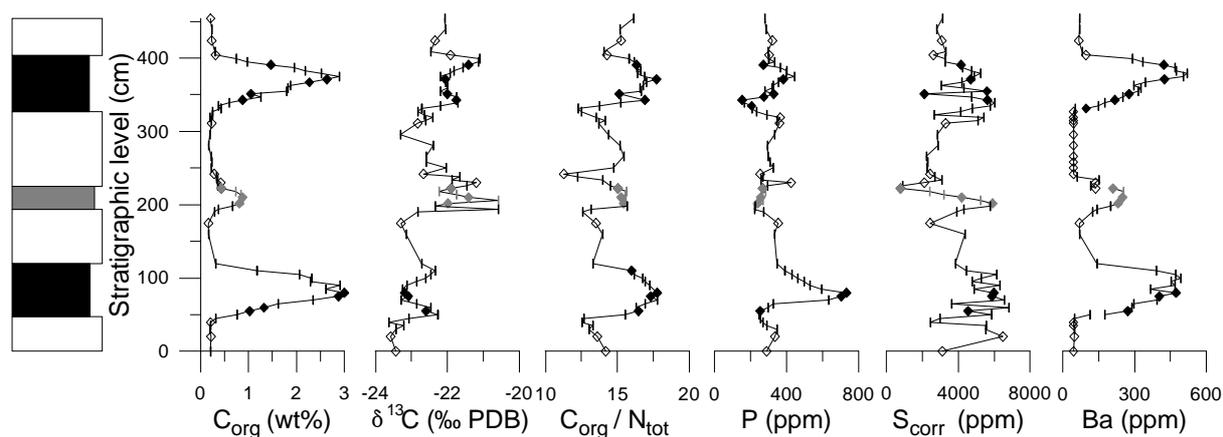


Figure 2.3 Profiles of C_{org} , $\delta^{13}C_{org}$, C/N ratio, P , S (corr) and Ba .

organic matter at their borders, which is partly compensated by an increase in production or preservation of terrestrial organic matter in the middle. Other factors, like variation in primary productivity, temperature, and diagenesis, however, may also have contributed to the observed variations.

The correlation between C_{org} and N_{tot} is almost perfect ($r^2=0.99$). Yet, a plot of the C_{org}/N_{tot} ratio (Fig. 2.3) does show a correlation with lithology. This is the result of varying contents of clay with associated inorganic nitrogen. Therefore, in this case, the C_{org}/N_{tot} ratio cannot be used as an indicator of the source of organic matter.

Total phosphorus shows an increase in the middle of the sapropels and a decrease at the bottom. The enrichment is probably due to the higher organic matter content of the sediments. Early diagenesis may result in release or immobilization of P, depending on the phase to which it is bound and on the environmental conditions in the sediment [De Lange, 1992a]. Both factors may contribute to the observed complex phosphorus profile.

Sulphur shows a profile that we cannot fully explain (Fig. 2.3). S is mainly present in sulphates (gypsum, pore water sulphate) and sulphides. Proof for the presence of gypsum was found neither macroscopically nor by XRD (X-ray diffraction) analysis. Therefore $S(corr)$ (elements designated with (corr) are corrected for the amount of that element present in extractable salts by subtracting this from the total content) represents organic sulphur and the sulphide content (mainly pyrite) of the sediments. XRD analysis did not confirm the presence of pyrite, indicating that the amount of this mineral present (a few percent at most) is lower than the detection limit. Pyrite contains reduced iron, which, together with manganese and C_{org} , gives sediments a dark colour [Olausson, 1961]. Some of the lighter spots in the sapropels correlate with dips in the sulphur profile. As neither C_{org} nor manganese show depletions at these locations, oxidation of pyritic iron must be the cause of the colour change. So these sulphur depletions are due to local weathering and subsequent removal of pyrite-derived sulphate.

In marine sediments, the Ba content often correlates well with C_{org} , but the exact mechanism that causes this relationship is still a matter of debate. Microenvironments containing decaying organic matter and the remains of siliceous plankton that become enriched in sulphate may provide the intermediary for barite precipitation [e.g. Bishop, 1988]. This knowledge, combined with the fact that Ba is enriched in sediments underlying highly productive surface waters [Dehairs et al., 1980], have led to a wide acceptance of sedimentary Ba content as a proxy for surface water palaeoproductivity. Although there are some caveats, which have been listed by De Lange et al. [1994], we believe that the Ba content in our samples (Fig. 2.3) indicates a higher palaeoproductivity during sapropel formation.

Carbonates - The carbonate profile (Fig. 2.4) shows values up to ~70% in the homogeneous intervals with depletions of about 20% in the sapropels. The carbonate content measured by Scheibler's method exceeds the $CaCO_3$ content obtained when converting all Ca determined by ICP-AES to calcite. This implies the presence of Mg calcites, which are also important in modern eastern Mediterranean sediments [Milliman and Müller, 1973]. The presence of a few percent Mg calcite was confirmed by XRD.

Strontium (Fig. 2.4) is slightly enriched in the sapropels, but the main feature of the Sr profile is the presence of sharp peaks at the boundaries of the sapropels. A possible explanation

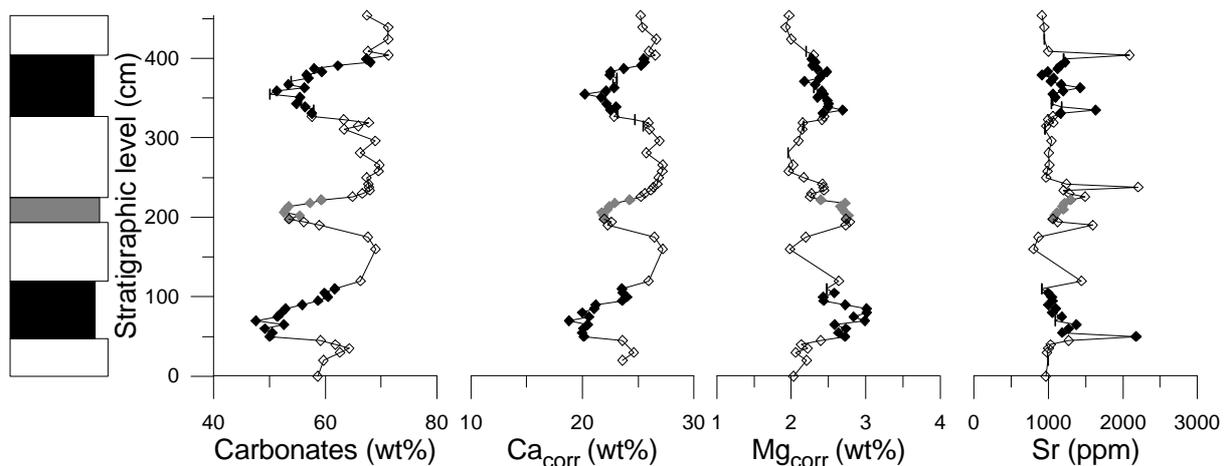


Figure 2.4 Profiles of total carbonate content, Ca, Mg and Sr.

for the increase in Sr content in the sapropels is a higher input of organisms with aragonitic tests, like pteropods, because aragonite is relatively rich in Sr [Sutherland et al., 1984]. During and after sapropel formation, acids may be released as a result of organic matter oxidation. As aragonite is more soluble than calcite, aragonite will be dissolved first, giving rise to Sr fluxes which may precipitate as celestite ($SrSO_4$) under or above the sapropel where sulphate concentrations are higher [Baker and Bloomer, 1988].

Terrestrial elements - Elements that are mainly associated with terrestrial matter are Al, Fe, K, Na, Li, Ti, Co, Cr, Sc, Y, and Zr. All these elements are enriched in the sapropels. Aluminium mainly resides in clays and is, therefore, used as an indicator of the terrestrial fraction: the

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contents of the other terrestrial elements are divided by the Al content for each sample (denoted with an asterisk) in order to reveal subtle differences in the chemical characteristics of terrestrial matter. Although the Al content in clays may vary, this method is frequently used [e.g. Calvert and Pedersen, 1993]. Fe^* and Li^* (Fig. 2.5) show no systematic elevation or depletion in sapropels. Cr^* , Sc^* , and $Na^*(corr)$ (Fig. 2.5) are enriched in sapropels. The enrichment of Cr^* can be due to the redox-sensitive character of this element (qv. next section). The $Na^*(corr)$ and

S c * p r o f i l e m a y

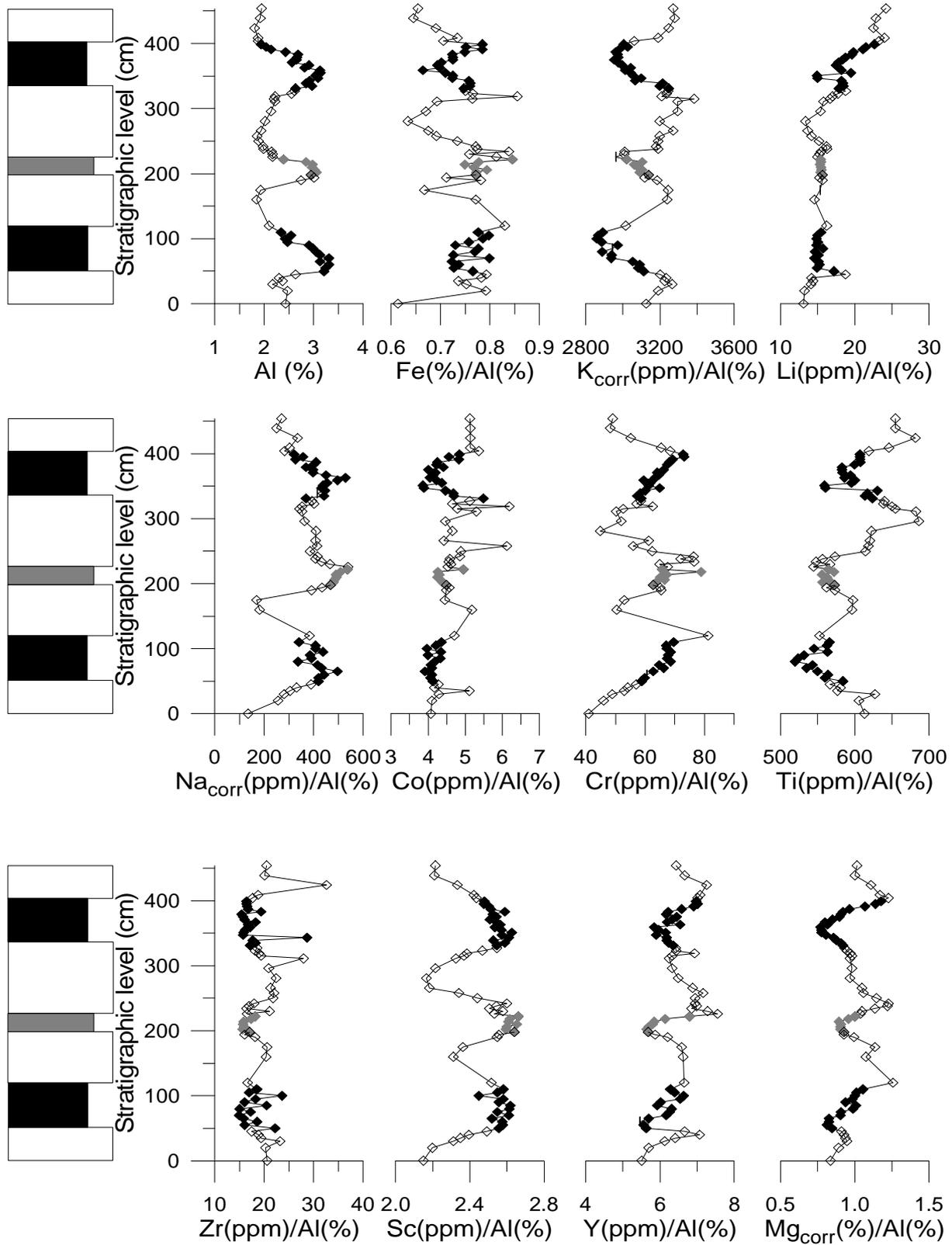


Figure 2.5 *Terrestrial elements and Mg. The graphs shown are the contents of the elements divided by the Al content; uncorrected profiles of these elements are all similar to that of Al. All percentages are weight percentages.*

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indicate a different source region during sapropel formation. K^+ , Co^+ , Ti^+ , Y^+ , and Zr^+ (Fig. 2.5) are slightly depleted in sapropels, which may again indicate a different source region. Zr^+ and Ti^+ are considered indicators of the aeolian terrestrial fraction [e.g. Shimmiel, 1992]. The slightly lower values of these elements in the sapropels seem to suggest a relative decrease of wind-borne terrestrial input during sapropel formation. This can be the result of the wetter conditions prevailing at those times, resulting in a relatively higher fluvial and lower aeolian input.

Chalcophilic and redox-sensitive elements - As, Se, Sb, Cr, Cu, V, Mo, and U (Fig. 2.6) are redox-sensitive elements. Owing to transition in oxidation states, they are immobilized under reducing (anoxic) conditions, whereas they are more mobile under oxidizing conditions. Chalcophilic elements are, a.o. Ni, Zn, Cu, As, Se, Mo, and Cd (Fig. 2.6). These elements can coprecipitate with sulphides, which are formed under anoxic conditions. The observed strong enrichment of both groups of elements in the sapropels can be caused by their precipitation out of an anoxic water column or by diffusion from the (oxic) water into the sediment (which may be completely anoxic or which may still have a thin oxic top layer) due to an Eh gradient [Arthur et al., 1990; Calvert and Pedersen, 1993; Van der Weijden, 1993].

Manganese (Fig. 2.6) shows a different kind of redox-sensitive behaviour: it is mobile under anoxic conditions and precipitates as (hydr)oxy particles and carbonate coatings in an oxic environment. This element shows peaks near the edges of the upper and lower sapropels and is depleted within them, which is in accordance with intensified oxygen depletion during sapropel formation.

Extractable salts - The results of the extraction with water were used for correcting the concentrations of the elements Ca, K, Mg, Na, and S for the presence of soluble salts. Profiles of these extracted elements do not show a correlation with lithology.

Grain size analysis - Changes in fluvial and aeolian terrestrial input would be expected to be reflected in grain size distribution. However, grain size analysis on selected samples indicated no significant difference between sapropels and homogeneous intervals.

Foraminifera

Planktonic foraminifera - The planktonic foraminiferal fauna consists of thirteen species, with *Globigerina bulloides* and *Globigerina falconensis* lumped together into one category, because the distinction between both species becomes faint in cases of poor preservation and small-sized specimens. The varying state of preservation also obliged us to identify *Globigerinoides obliquus* by the flattened final chamber(s), since supplementary openings are generally concealed in the poorly preserved specimens. Figure 2.7 gives the percentage distribution of eleven species plus the combination of *G. falconensis* and *G. bulloides* and shows that the overall planktonic foraminiferal fauna is dominated by the species *Globoturbotalita apertura*. Species showing systematic changes with lithology are *Globigerinoides sacculifer* and *Neogloboquadrina acostaensis* (left-coiled). Modern neogloboquadrinids flourish under eutrophic conditions such as associated with (seasonal) upwelling [e.g. Thunell and Reynolds, 1984; Ravelo et al., 1990; Reynolds

On the origin of upper Miocene sapropels

Sautter and Thunell, 1991; Pujol and Vergnaud-Grazzini, 1995] or spring/fall blooms [e.g.

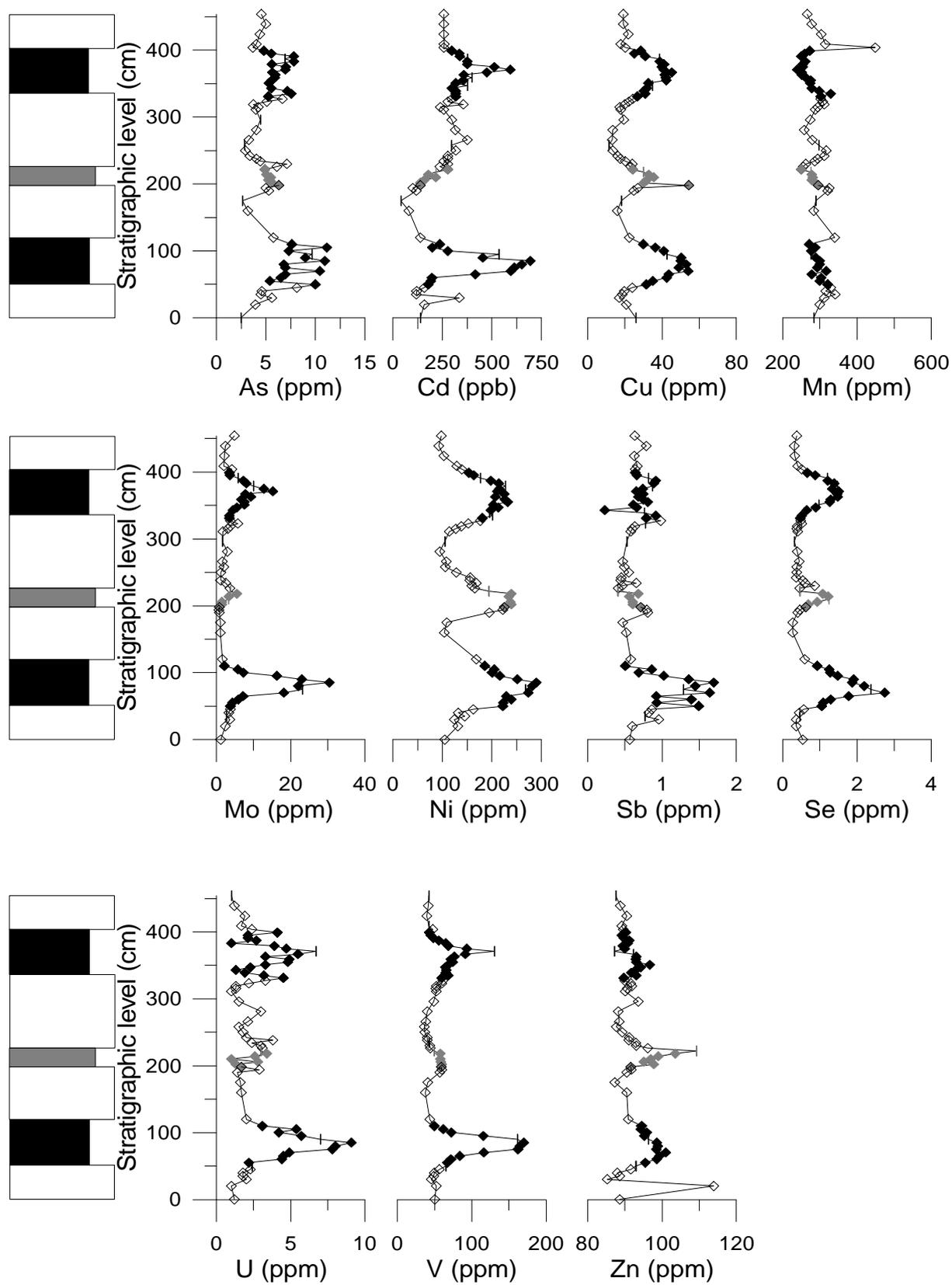


Figure 2.6 Profiles of redox-sensitive and chalcophilic trace elements.

Tolderlund and Bé, 1971; Reynolds and Thunell, 1986]. There is some evidence in the literature that extinct neogloboquadrinids preferred eutrophic conditions as well [Lourens et al., 1992]. Living *G. sacculifer* inhabits warm and oligotrophic surface waters [e.g. Hemleben et al., 1989].

The contrasting habitat characteristics of *N. acostaensis* and *G. sacculifer* suggest that the flourishing of both species in the Faneromeni sapropels occurred in different seasons. The eutrophicated surface water conditions preferred by *N. acostaensis* probably occurred in spring at the onset of thermal stratification after deep winter mixing. Warm and oligotrophic conditions preferred by *G. sacculifer* on the other hand represent summer conditions. The flourishing of both species in the Faneromeni sapropels and their (near) absence in the homogeneous intervals suggest that the seasonal cycle of eutrophication and surface water warming was more pronounced during sapropel formation than during intervening periods. *Benthic foraminifera* - The benthic foraminiferal fauna is characterized by a large number of species that generally occur in low abundances. We simplified the set of census data by combining the percentages of individual species into four major groups. Group 1 (see caption Fig. 2.8) includes species considered tolerant to low-oxygen conditions [Van der Zwaan, 1982; Jonkers, 1984; Katz and Thunell, 1984].

Group 2 (Fig. 2.8) contains species that are indicative of normal marine (well-oxygenated) conditions [Van der Zwaan, 1982; Jonkers, 1984; Verhallen, 1991].

Group 3 (Fig. 2.8) consists of *Bolivina pseudoplicata*. This species is treated separately because opinions about its habitat requirements vary from mud-dwelling and low-oxygen tolerant [Van der Zwaan, 1982] to epiphytic in well-oxygenated environments [Jonkers, 1984]. According to Verhallen [1991] this is a mud-dwelling species indicative of normal marine

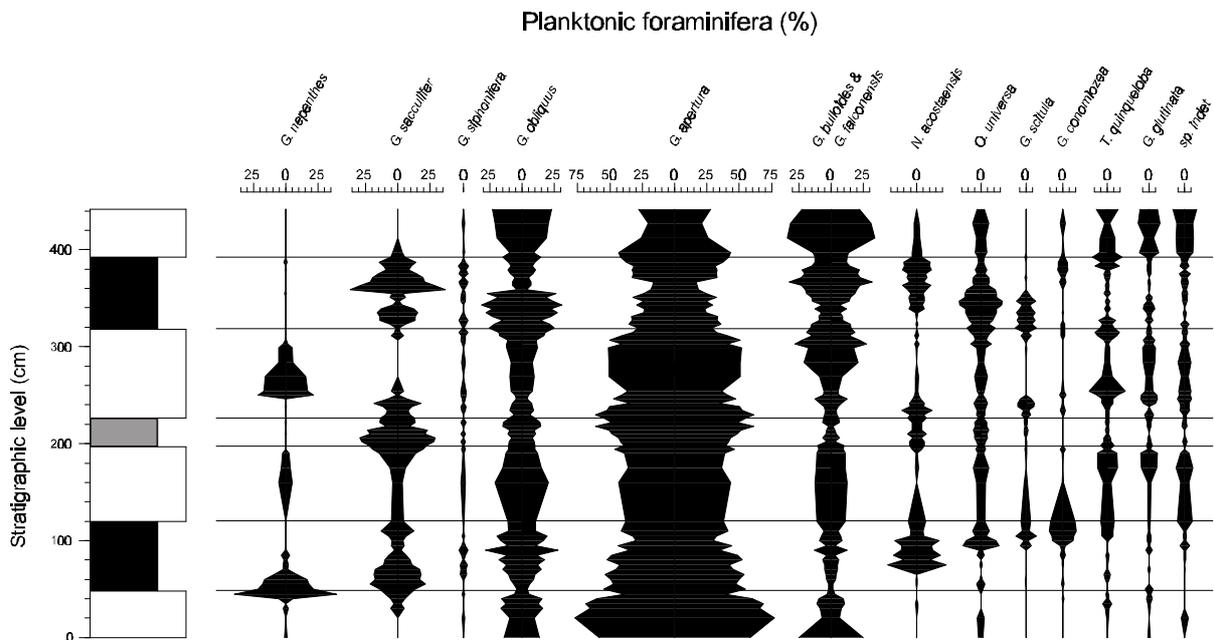


Figure 2.7 Planktonic foraminiferal species abundance in the Faneromeni section.

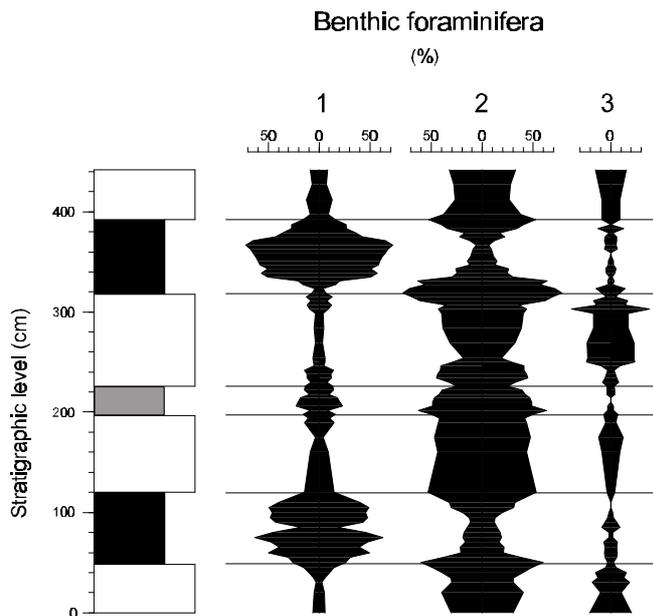


Figure 2.8 Percentages of three major groups of benthic foraminifera. Group 1 represents a low-oxygen tolerant association and consists of the species *Cancris auricula*, *Bulimina costata*, *Bulimina elongata*, *Bolivina spathulata*, *Bolivina dilatata*, *Uvigerina cylindrica cylindrica*, *Uvigerina cylindrica gaudryinoides*, *Uvigerina pygmaea*, and *Globobulimina pyrula*. Group 2 includes species indicative of oxic environments such as: *Planulina ariminensis*, *Lenticulina spp.*, *Reusella spinulosa*, *Cibicides pseudoungerianus*, *Siphonina planoconvexa*, *Gyroidina soldanii*, *Oridorsalis stellatus*, *Cassidulina subglobosa*, *Cassidulina leavigata*, *Anomalinoidea helicinus*, *Karreriella bradyi*, *Spiroplectammina carinata*, and several unilocular and uniserial species. Group 3 consists of *Bolivina pseudoplicata*.

Rohling et al., 1993], however, did not occur during the deposition of the late Miocene sapropels of Faneromeni.

The average P/B ratio for non-sapropel samples is 64. Using the palaeodepth equation of Van der Zwaan et al. [1990], a water depth of 350 m can be calculated.

Oxygen isotope ratios - The planktonic foraminiferal $\delta^{18}\text{O}$ record shows systematic changes with lithology (Fig. 2.9). Lowest $\delta^{18}\text{O}$ values ($\sim -1.4\text{‰}$) are reached in the lower and upper sapropels, whereas the middle one shows less depleted values. In the homogeneous layers, $\delta^{18}\text{O}$ values are significantly higher, up to $\sim 0.7\text{‰}$. These $\delta^{18}\text{O}$ shifts of about 2‰ resemble the ^{18}O depletions often observed in Plio-Pleistocene sapropels from the eastern Mediterranean [e.g. Vergnaud-Grazzini et al., 1977; Williams et al., 1978; Gudjonsson and Van der Zwaan, 1985; Lourens

conditions. Group 4 represents the rest and includes a mixture of notorious epiphytes (probably allochthonous), undeterminable species, and rare elements.

Figure 2.8 shows that group 3 (*B. pseudoplicata*) has a strong affinity with group 2. The species of group 2 and 3, therefore, seem to be indicative of oxic environments, in contrast with those of group 1, which are characteristic of dysoxic environments. The lower and upper sapropels are characterized by peak abundances of group 1 and minimum values of group 2 and 3, whereas the reverse is shown above and below these sapropels (Fig. 2.8). The dominance of group 1 during sapropel formation suggests (seasonal) near-bottom oxygen depletion. The much less pronounced increase of group 1 in the middle sapropel indicates that near-bottom oxygen conditions were less depleted than during the deposition of the lower and upper sapropels. Truly anoxic bottom water conditions, such as inferred from the lack of autochthonous benthic foraminifera in some Pliocene and Pleistocene sapropels [Nolet and Corliss, 1990; Verhallen, 1991;

et al., 1992]. Usually, light $\delta^{18}\text{O}$ values in sapropels are attributed to reduced surface water salinity due to increased freshwater input.

Discussion

The sedimentary cycles in the Faneromeni section show marked variations in the organic, carbonate, and terrestrial fractions. The carbonate fraction is depleted and the organic carbon and terrestrial fractions are enriched in the sapropels. Similar variations in Plio-Pleistocene Mediterranean sapropels, laminites, and carbonate cycles have been attributed to changes in productivity, preservation, terrestrial dilution, and/or diagenesis [Howell et al., 1990; Thunell et al., 1991; Van der Weijden, 1993; Van Os et al., 1994]. In the next section, after considering the effects of diagenesis on the characteristics of the sapropels, we will discuss these hypotheses in order to constrain the underlying mechanism(s) which led to the formation of these sapropels.

Early diagenesis

Two geochemical aspects may play an important role in early diagenesis: mobilization of some elements (e.g. Mn, Fe) and the occurrence of a burn-down front. Manganese and iron oxides within sapropels dissolve under reducing conditions. When oxic conditions have been reestablished on top of the sapropel, upward moving Mn^{2+} and Fe^{2+} will be oxidized and precipitated there [De Lange et al., 1989]. Manganese peaks have indeed been observed at the top of the sapropels (Fig. 2.6), but iron peaks are vaguer, probably because they are obscured by other iron species (only a small fraction of total iron present can be mobilized; Wallace et al. [1988]). The iron and manganese peaks of the middle sapropel are situated well above its top. This can be the result of a burn-down front: after reventilation of the dysoxic bottom water, a downward moving oxidation front may remove organic matter from the sapropel, making it thinner [Higgs et al., 1994]. Other chemical and micropalaeontological indicators confirm the fact that a burn-down front modified this sapropel. Barium shows high

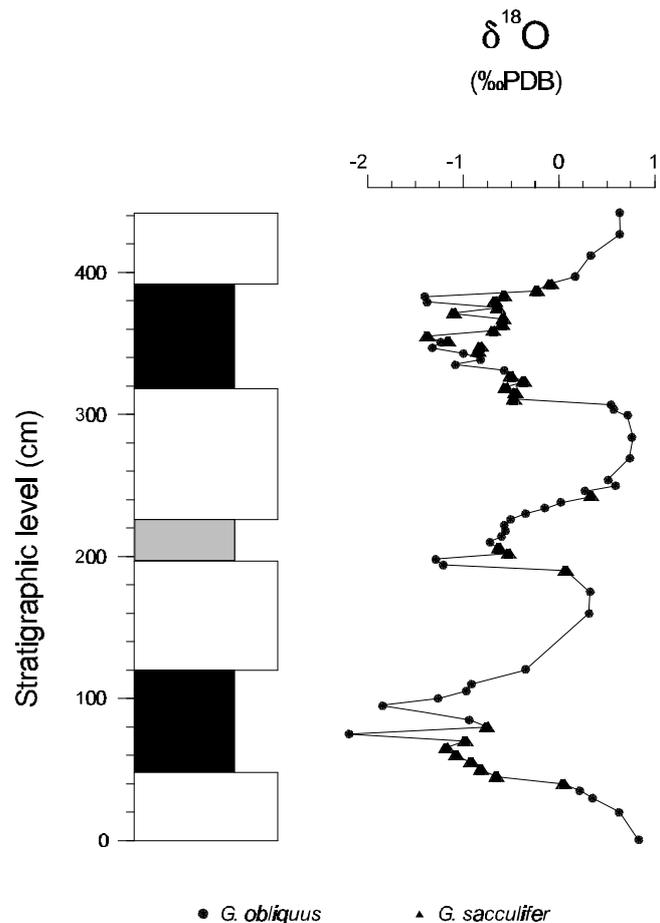


Figure 2.9

● *G. obliquus* ▲ *G. sacculifer*
 Compilation of planktonic foraminiferal $\delta^{18}\text{O}$ values derived from two foraminiferal species, *Globigerinoides obliquus* (circles) and *Globigerinoides sacculifer* (triangles). Note that an adjustment for the interspecific isotopic difference between both species was not used.

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values up to 15 cm above the top, indicating that C_{org} values were originally higher here. The Ba spike is probably caused by an increase in sulphate concentration accompanying a burn-down front, resulting in supersaturation and precipitation of barite near the upper boundary of the sapropel [Van Os et al., 1991]. The upper Sr spike of the middle sapropel is also situated above the top, and the redox-sensitive elements Se, Cr, As, and U remain enriched above this sapropel. These elements may have remained immobilized during the burn-down period due to adsorption. There is also micropalaeontological evidence: the planktonic foraminiferal species *G. sacculifer* and *N. acostaensis* and the benthic foraminiferal group 1 show elevated percentages up to 25 cm above the middle sapropel. From all this evidence it can be concluded that the middle sapropel was originally thicker. However, even if we take the position of the Ba and Sr peaks as its original top, this sapropel remains thinner than the other two. The upper and lower sapropels show no signs of a burn-down front. Because their organic matter content is higher, the oxidation front may have been unable to seriously modify the characteristics of these sapropels [De Lange et al., 1989].

Changes in the carbonate and terrestrial fractions

The carbonate and terrestrial fractions show a cyclicity that is slightly out of phase with the organic carbon cyclicity: the carbonate fraction is depleted (and the terrestrial fraction enriched) within sapropels, but this depletion starts earlier than the C_{org} enrichment. Three explanations exist for carbonate diminution: (1) dilution by terrestrial material, (2) lower carbonate production, and (3) post-depositional dissolution, caused by oxidation of organic material. The percent changes in terrestrial input, carbonate production, and C_{org} (due to oxidation) needed to explain the observed carbonate depletion, have been calculated with equations of Van der Weijden [1993]:

$$\Delta_{terr} = \left[\frac{x(100-y)}{y(100-x)} - 1 \right] \times 100\% \quad (1)$$

$$\Delta_{carb} = \left[1 - \frac{y(100-x)}{x(100-y)} \right] \times 100\% \quad (2)$$

$$\Delta C_{org} = \left[x - \frac{y(100-x)}{100-y} \right] \times 0.103\% \quad (3)$$

in which x is the mean carbonate percentage of all homogeneous intervals, y is the mean carbonate percentage of all sapropels, Δ_{terr} is the increase of the terrestrial fraction in the sapropels with respect to the homogeneous intervals (in percent), Δ_{carb} is the decrease of the

carbonate fraction in the sapropels with respect to the homogeneous intervals (in percent); and ΔC_{org} is the amount of organic carbon that has to be oxidized to cause the observed decrease in carbonates (in percent). The results are presented in Table 2.1. This table shows that if the decrease of the carbonate fraction is due to dilution only, the terrestrial input would have to increase by some 60%. Geochemical indicators of terrestrial input ($\delta^{13}\text{C}$, C/N ratio, mean grain size) do not support such a strong increase. Oxidation of 3-4% C_{org} may have occurred, and some carbonate has been dissolved, as can be inferred from the Sr peaks at the boundaries of the sapropels. However, if this had resulted in dissolution of as much as 20% carbonate, this would have been manifest in etching and fragmentation of foraminifera in the sapropels, which is not the case. Therefore a decrease of biogenic carbonate production is needed as well, to explain the observed profile.

If the terrestrial input remains constant and the carbonate production decreases during sapropel formation, the sedimentation rate also decreases. The average sedimentation rate of the interval in this study is 6.5 cm/1,000 yr. To form 65 cm thick sapropels at this or a lower sedimentation rate would imply sapropel formation periods of 10,000 years or more, which is considerably longer than estimated for modern sapropels (e.g. 3,000 years for the S1 sapropel [Hilgen et al., 1993]). To shorten the duration of sapropel formation, an increase in the terrestrial input is needed after all.

Table 2.1 *Changes in the terrestrial, carbonate, and organic fractions for all sapropels needed to explain the observed carbonate decrease in the sapropels.*

	Δ_{terr} (%)	Δ_{carb} (%)	ΔC_{org} (%)
upper sapropel	65.9	39.7	3.43
middle sapropel	60.9	37.7	3.13
lower sapropel	49.3	33.0	3.96

Cycles in the organic carbon fraction

There are three main factors (which are partly interrelated) that can explain the enrichment of marine organic matter in Plio-Pleistocene sapropels.

1. The theory that used to be most widely accepted is that organic matter preservation is enhanced by anoxic bottom water, which may be caused by stratification [Rossignol-Strick et al., 1982; Mangini and Schlosser, 1986]. Degradation in anoxic environments is lower because of the absence of benthos and consequent lack of bioturbation [Demaison and Moore, 1980; Bralower and Thierstein, 1987].

2. The main control on sedimentary organic matter content is not preservation but surface water productivity if anoxic degradation is as rapid as oxic decomposition [Calvert, 1983; Pedersen and Calvert, 1990].

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3. An additional important factor is the sedimentation rate. If the sedimentation rate is high, organic matter is buried quickly, inhibiting its decomposition by benthos [Hartman et al., 1976; Müller and Suess, 1979; Howell et al., 1988].

We concluded from the Ba profile that palaeoproductivity was higher during the formation of the Faneromeni sapropels. This is substantiated by the high abundances of *N. acostaensis* in the sapropels. Modern representatives of this planktonic foraminiferal species flourish in eutrophic regions. Suppression of calcareous species by organic-walled (dinoflagellates) and/or siliceous organisms may explain the decrease of carbonate productivity that coincides with this increase in total palaeoproductivity.

Müller and Suess [1979] concluded that very high variations in sedimentation rate are needed for relatively small fluctuations in sedimentary organic matter content. In the part on carbonate cycles we calculated that a 60% increase of terrestrial input is needed to explain all of the decrease of the carbonate fraction in the sapropels. However, oxidation of organic matter and a decrease in carbonate production also contribute to the low carbonate values. Therefore, we conclude that very high variations in sedimentation rate are unlikely.

As we have seen in the section on redox-sensitive and chalcophilic elements and in the section on benthic foraminifera, oxygen depletion was more intense during sapropel formation, but the Faneromeni sapropels were not deposited under completely anoxic conditions. From all of this we conclude that the main reason for the C_{org} enrichment is higher palaeoproductivity and that increased preservation may have played a role as well.

On the origin of the Faneromeni sapropels

The geochemical and micropalaeontological characteristics of the Faneromeni sapropels are markedly similar to those observed in their Pliocene and Pleistocene equivalents. Thus, it can be assumed that all late Neogene sapropels were deposited at times of precession minima when perihelion occurred during Northern Hemisphere summer [Rossignol-Strick, 1983; Hilgen, 1991a]. It has been argued that this orbital configuration led to an intensification of the summer monsoon [e.g. Prell and Kutzbach, 1992] and possibly also to a greater influence in the Mediterranean of Atlantic-born depressions [Rohling and Hilgen, 1991], resulting in increased river discharge of the Nile [Rossignol-Strick, 1983] and rivers draining the northern sector of the Mediterranean [Rossignol-Strick, 1987; Rohling and Hilgen, 1991; Aksu et al., 1995]. Increased river discharge is commonly believed to have elevated the nutrient level and decreased the rate of deep water formation due to a steepening of the density gradient [Rossignol-Strick et al., 1982; Mangini and Schlosser, 1986]. Rohling [1994], however, argued that Mediterranean intermediate water (MIW) was less dense during periods of late Quaternary sapropel formation and that the mixing between this less dense MIW and Adriatic Sea winter water caused reduced rates of deep water formation. The elevated percentages of neogloboquadrinids and *Florisphaera profunda* furthermore suggest that the density loss of MIW resulted in a shoaling of the pycnocline and the development of a deep chlorophyll maximum (DCM) layer [Rohling, 1994; Castradori, 1993]. Reduced buoyancy loss of MIW therefore could explain the inferred increase

in primary production, decrease in surface water salinity and the decrease in bottom water oxygen during the deposition of the Faneromeni sapropels. Prerequisite for this is the presence of an anti-estuarine circulation during the late Miocene, which requires that the physiography (in the sense of being an elongated marginal basin of the Atlantic) and climate (with evaporation dominating precipitation and runoff) of the Mediterranean were not so much different from those of today.

Geological evidence suggests that the Mediterranean has been an elongated satellite basin of the Atlantic at least since the late Miocene [Rögl and Steininger, 1983; Orszag-Sperber *et al.*, 1993]. Also, late Miocene climatic conditions were not fundamentally different from those prevailing today [Suc and Bessais, 1990; Quade *et al.*, 1994], although floral remains in marine sediments of late Miocene age on Crete [Sachse and Mohr, 1996] and the widespread occurrence of late Miocene coral reefs in the Mediterranean [Esteban, 1979] suggest that mean annual precipitation values and annual sea surface water temperatures were slightly higher. Even the Nile River reached present-day (pre-Aswan) dimensions during the late Miocene [Ross and Uchupi, 1977; Barber, 1981], providing a pathway for transmitting signals of increased rainfall via increased Nile outflow into the Mediterranean.

Increased seasonality and freshwater input during the formation of the Faneromeni sapropels (leading to increased winter mixing, shoaling, and nutrient-enrichment of MIW) could have increased spring bloom conditions resulting in higher export production and oxygen consumption rates. Near-bottom oxygen depletion may have been strengthened by reduced deep water formation rates. Maximum surface water warming in summer on the other hand might have caused conditions preferred by *G. sacculifer*. The less well-developed middle sapropel reflects the less pronounced insolation maximum at that time, which resulted from the interference between precession and obliquity [Hilgen *et al.*, 1995]. The processes at work were therefore less intense, resulting in a lower C_{org} content, whereas this sapropel was more prone to diagenetic alteration.

Conclusion

Geochemical and micropalaeontological characteristics of the Faneromeni sapropels are markedly similar to those of Plio-Pleistocene counterparts. This similarity implies that a single mechanism is responsible for Mediterranean sapropel formation throughout the late Neogene. This conclusion is consistent with the fact that Mediterranean late Miocene physiography and climate were not so much different from today.

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Chapter 3

Organic-rich layers in the Metochia section (Gavdos, Greece): Evidence for a single mechanism of sapropel formation during the past 10 Myr

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I.A. Nijenhuis, C.H. van der Weijden, W.J. Zachariasse*

Abstract - Three well-developed 10 Ma old sapropels from the island of Gavdos (Greece) were selected for a detailed geochemical, micropalaeontological and sedimentological study. The sapropels are characterized by a high organic carbon and a low carbonate content. Productivity was higher during sapropel formation, as indicated by increased Ba contents and higher percentages of the planktonic foraminiferal species *Neogloboquadrina acostaensis*. Enrichment of Mo and V in the sapropels indicates less oxygenated bottom water conditions, which is supported by the flourishing of low oxygen tolerant benthic foraminifera. Variation in grain size and the Ti/Al ratio point to an alternating dominance of fluvial (sapropels) and aeolian (homogeneous intervals) terrestrial clastics. Evidence for a local origin of the enhanced fluvial input comes from the gradual replacement of the sapropels by cyclic turbidite sequences which were fed by bed-load type rivers. The increased fluvial input during sapropel formation increased the sedimentation rate and caused the observed carbonate depletion. Results obtained for the Gavdos sapropels are consistent with those of previous studies of younger sapropels and related CaCO₃ cycles in the Mediterranean. This consistency in most of the geochemical and micropalaeontological characteristics indicates that all sapropels and related layers are the result of a single mechanism for at least the past 10 Myr, namely precession-induced dry-wet oscillations in the Mediterranean climate. Still, the effect of this mechanism on the intensity of surface water productivity, dilution and diagenetic signals may differ from

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site to site, depending on location, depositional environment and intensity of the astronomical forcing.

Introduction

Organic-rich layers known as sapropels occur widespread in marine sequences throughout the Mediterranean Neogene. Their occurrence is cyclic and can unambiguously be correlated to variations in the eccentricity of the Earth's orbit and in the tilt (obliquity) and precession of the Earth's axis [Rossignol-Strick, 1983; Hilgen, 1991a, b; Hilgen et al., 1995; Lourens et al., 1996a]. Most studies concerning sapropel formation focus on upper Pleistocene sapropels [e.g. Rossignol-Strick et al., 1982; Calvert, 1983; De Lange and Ten Haven, 1983; Howell et al., 1990; Rohling, 1994] which are recovered from the seafloor by gravity coring techniques. Recently, excellent continuous Plio-Pleistocene sequences with numerous sapropels from the eastern and western Mediterranean were drilled during ODP Legs 160 and 161 [Emeis et al., 1996; Comas et al., 1996]. Similar sequences have been studied in land sections that experienced rapid uplift [e.g. Sprovieri et al., 1986; De Visser et al., 1989; Lourens et al., 1992; Rio et al., 1991; Thunell et al., 1991; Rohling et al., 1993; Van der Weijden, 1993; Van Os et al., 1994]. Miocene sapropels, however, have not been recovered by deep-sea drilling because safety regulations do not allow drilling through Messinian evaporites. Therefore, older sapropels can only be studied in land sections. Results of a previous study on three late Miocene sapropels in the Faneromeni section on Crete [Nijenhuis et al., 1996 (Chapter 2)] suggested, in contrast to previous reports [Cita and Grignani, 1982; Thunell et al., 1984], that they had the same origin as their Plio-Pleistocene counterparts.

Two important mechanisms have been proposed to explain the formation of eastern Mediterranean sapropels. One implies that an increase in freshwater input resulted in the development of a low salinity layer which in turn reduced deep water circulation. The reduction of deep water formation may have led to anoxic bottom water conditions and a better preservation of organic matter [Olausson, 1961; Cita et al., 1977; Nolet and Corliss, 1990]. The alternative mechanism invokes an increase in marine productivity rather than enhanced preservation of organic matter as the driving mechanism behind sapropel formation [Calvert, 1983; Calvert et al., 1992]. Rohling and Gieskes [1989] combined both scenarios and argued that a distinct Deep Chlorophyll Maximum (DCM) may have developed within the euphotic zone, thereby enhancing primary productivity. Studies of Plio-Pleistocene carbonate cycles and sapropels have further shown that dilution with terrestrial material [De Visser et al., 1989; Howell et al., 1990; Thunell et al., 1990; Van der Weijden, 1993; Foucault and Mélières, 1995] and diagenetic (dissolution) processes [Sprovieri et al., 1986] may have played an important role during their formation. The relative importance of these two processes is still a matter of debate [Van Os et al., 1994; Nijenhuis et al., 1996 (Chapter 2); Chapter 4]. Although the mechanisms differ, it is generally accepted that sapropel formation is initiated by more humid conditions in circum-Mediterranean climate at times of precession minima when perihelion occurred in Northern Hemisphere summer [Rossignol-Strick, 1983; Prell and Kutzbach, 1987; Hilgen 1991a; Rohling and Hilgen, 1991].

In this study we present the geochemical, micropalaeontological, and sedimentological results of a study of three well-developed sapropels from the Metochia section on Gavdos,

Greece. There are two reasons for selecting these sapropels. First, we wanted to investigate whether early Tortonian sapropels are formed by the same mechanism as Messinian and younger sapropels. If so, this would imply that the climatic oscillations responsible for sapropel formation can be traced back to 10 Ma, thus predating the intensification of the Asian monsoon at 8 Ma [Prell and Kutzbach, 1992]. Secondly, because these sapropels are replaced upwards in the section by turbidites. This link between runoff-related turbidites and sapropels [Postma *et al.*, 1993] permits a closer study of the significance of increased terrestrial supply in sapropel formation.

Material and methods

Lithology and sampling

The Metochia B section is located on the small island of Gavdos south of Crete (Greece; Fig. 2.1). The sedimentary sequence is shown in Figure 3.1. The basal part of the sequence consists of a palaeosol, overlain by estuarine sediments with oyster banks and strongly bioturbated shallow marine sandstones. On top of these sandstones, light-coloured marls alternate with dark-coloured sapropels (L1-L7). These sapropels are gradually replaced by turbidites (L8-L11), which in turn are succeeded by another series of sapropels (L12-L20) and marls. The transition from the shallow marine sandstones to the sapropels/marls reflects a rapid deepening of the basin to approximately 850 m as calculated by the ratio of planktonic to benthic foraminifera [Postma *et al.*, 1993].

For this study we sampled sapropels L5-L7 with the adjacent marls and turbidites L8-L9 (Fig. 3.1). The sapropels are finely laminated with no macroscopic traces of bioturbation. The light-coloured marls are homogeneous and contain locally red-coloured burrows. Some silty turbidites occur in sapropel L7, ranging in thickness from 0.5 to 3 cm. The true turbidite sequences (L8-L11) are thinly-bedded and covered by a hemipelagic marl layer. Turbidites L8 and L9 show a coarsening and thickening upward trend. After removal of the weathered surface rock, core samples (2 cm in diameter, 8 cm long) were taken using an electric drill.

Geochemical and micropalaeontological analyses

Samples were dried for four days at 40°C and subsequently crushed and powdered. After homogenization, subsamples were taken for geochemical analyses. After removal of inorganic carbon with 1 M HCl the organic carbon (C_{org}) content was measured by oxidation at 900°C and determination of the resulting CO_2 -pressure in a tube of known volume. The isotopic composition of organic matter ($\delta^{13}C_{org}$) was measured in the same tube, using a Stable Isotope Ratio Analyser (VG SIRA 24). $\delta^{13}C_{org}$ values are reported relative to the PDB standard. The carbonate fraction of the samples was determined by subtracting the amount of C_{org} from the total carbon content measured on a NA 1500 NCS analyser. The carbonate content was checked with Scheibler's method (gas-volumetrically). For the carbonate and $\delta^{13}C_{org}$ measurements, all relative errors found in duplicate measurements are better than 0.6%. For C_{org} analyses, relative errors are below 0.5%.

Evidence for a single mechanism of sapropel formation during the past 10 Myr

For major, minor and trace element analysis, a 250 mg sample was digested in 10 ml of a 6.5 : 2.5 : 1 mixture of HClO₄ (60%), HNO₃ (65%) and H₂O, and 10 ml HF (40%) at 90°C. After evaporation of the solutions at 190°C on a sand bath, the dry residue was dissolved in 50 ml 1 M HCl. The resulting solutions were analysed for the elements Al, Ba, Ca, Cu, Fe, K, Mn, Ni, P, S, Sc, Sr, Ti, V, Y, and Zr, by a Perkin Elmer Optima 3000 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES), for the elements Cd and Mo by a Perkin Elmer 4100 ZL ZGFAAS, and by a Perkin Elmer 5000 G hydride AAS for the elements As, Sb and Se. Particle sizes were determined on a carbonate and organic matter free basis, using a Malvern Series 2600 Laser Particle Sizer. The relative error in duplicate measurements for the ICP analyses is better than 3% for all elements. The relative errors for Cd, Mo, Sb and Se are better than 2%, for As better than 6%.

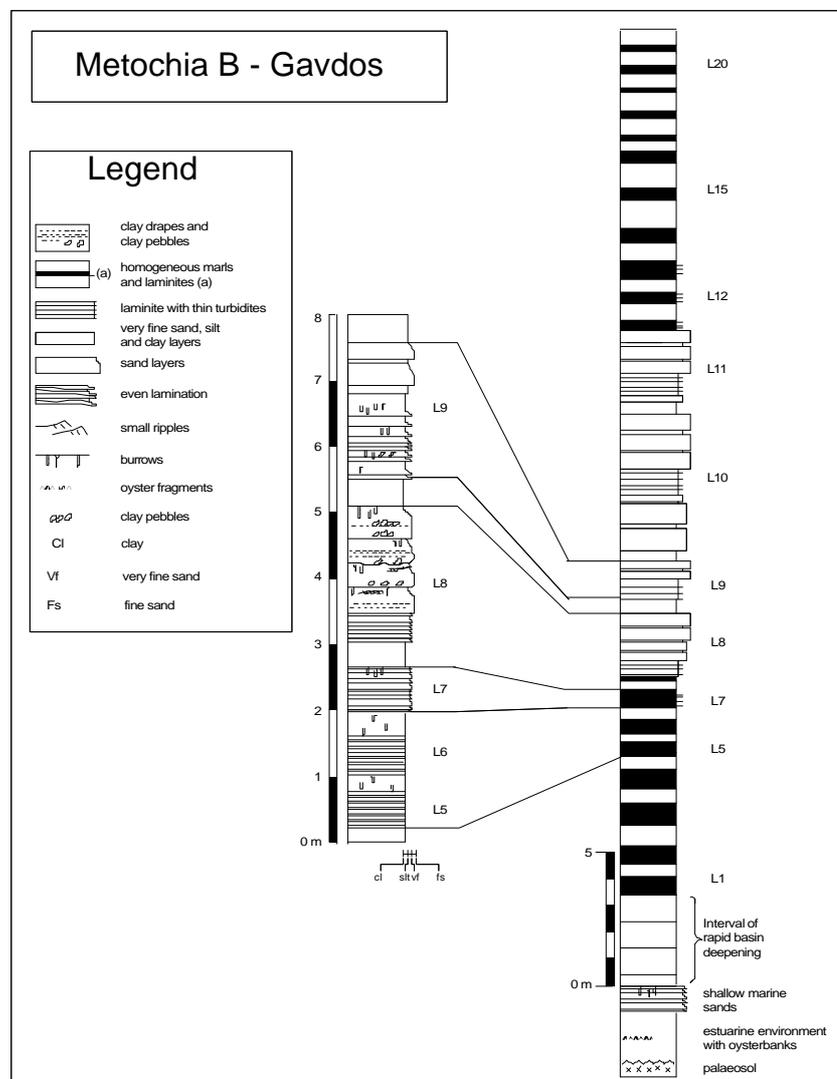


Figure 3.1 *The sedimentary sequence of the Metochia B section (right) and the enlarged section of the sampled interval (L5-L9, left).*

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Soluble salts were extracted by shaking a 250 mg sample in 50 ml water at ambient temperature for a week. The resulting solutions were analysed by ICP for the element S. All results were checked using international (a.o. SO₃, SO₄ and PACS-1 for ICP analyses, see *Govindaraju [1989]*) and house (MMM 91) standards.

Counts on planktonic (100-200 specimens) and benthic foraminifera (10-100) were made on the same split in the size range between 125 and 595 µm. Specimens were hand-picked, mounted on Chapman slides, identified and counted. Preservation is moderate in the lower (L5) and slightly better in the middle and upper sapropel (L6, L7).

Oxygen and carbon isotopic ratios of carbonates ($\delta^{18}\text{O}_{\text{carb}}$, $\delta^{13}\text{C}_{\text{carb}}$) were measured on the planktonic foraminiferal species *Globigerinoides obliquus*, *Globigerinoides apertura* and *Globigerinoides sacculifer*. To remove any remaining organic matter, about 100 specimens (10 mg) per sample were roasted for thirty minutes at 470 °C under a helium flow. After that, the samples were transferred into glass reaction tubes that were evacuated for fourteen hours. Subsequently, the samples were dissolved in 100% phosphoric acid at 25 °C under high vacuum for six hours. The released CO₂ was cryogenically separated from other gases and measured on a VG SIRA 24 mass spectrometer. The results are reported relative to the PDB standard.

Results

Geochemical analyses

The four layers enriched in C_{org} correspond to sapropels L5, L6, L7 and the basal part of L8 (Fig. 3.2). The maximum C_{org} content of the sapropels increases upwards from approximately 1.5% to 3.0%. The homogeneous marls and turbidites are low in C_{org} (0.25%). L6, L7 and L8 have C_{org} contents higher than 2% and, therefore, classify as sapropels [*Kidd et al., 1978*]. For reasons of simplicity, the term sapropel will be used for all organic-rich laminated layers in this study.

The barium content (divided by aluminium to correct for the contribution of Ba from a terrestrial source) is much higher within the sapropels and correlates well with the C_{org} pattern (Fig. 3.2), except for the lower part of L8. In the turbiditic layers Ba is high and C_{org} low. The sulphur profile (Fig. 3.2) is the total amount of sulphur (S) minus the water soluble sulphate content (S*) obtained by water extraction (S_{corr}). This gives an indication of the amount of sulphides (mainly pyrite), which is high in the sapropels. Sulphur and Fe/Al peaks in the homogeneous marls are associated with red-coloured burrows. These burrows were probably filled with organic-rich material and pyritized after burial. The sulphur concentration in the turbiditic layers is low. The S* concentration correlates well ($r^2=0.98$) with Ca* (the amount of Ca released during water extraction), indicating the presence of gypsum. Total phosphorus (Fig. 3.2) is enriched in the homogeneous marls. Ca (Fig. 3.2) is lower in the sapropels and higher in the homogeneous marls; it correlates inversely with C_{org}. Sr/Ca is lower in the homogeneous marls.

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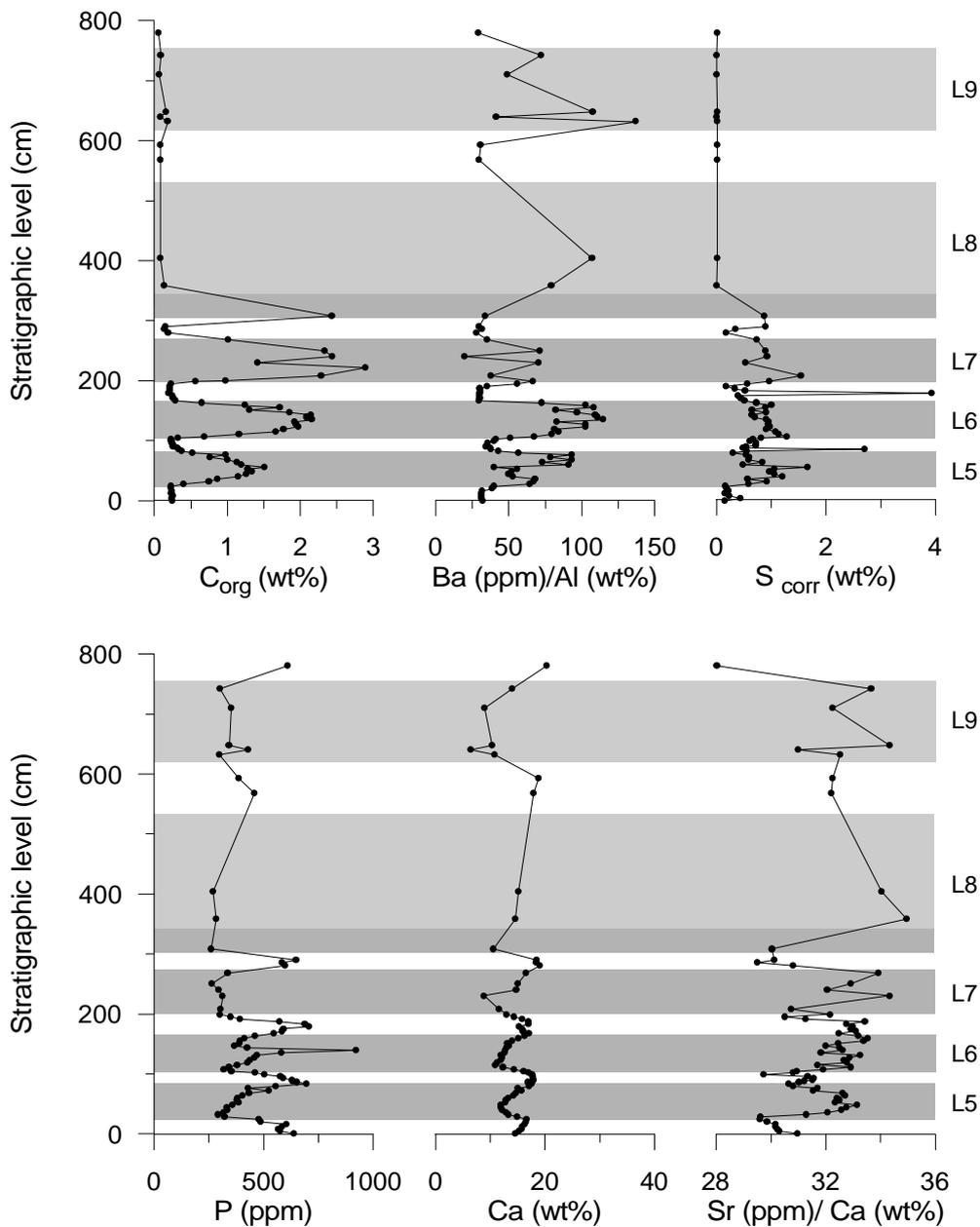


Figure 3.2 C_{org} , Ba/Al , S_{corr} , P , Ca and Sr/Ca profiles in the Metochia section. Dark shaded intervals correspond to the sapropels; light shaded intervals to turbidites.

Elements that are mainly associated with the terrestrial fraction are Al, Fe, Sc, Y, Ti, and Zr. All these elements are enriched in the sapropels and turbiditic layers (Fig. 3.3). Aluminium resides mainly in clay minerals and is, therefore, used as a proxy for the terrestrial fraction. The

terrestrial elements have been divided by the Al content to reveal differences that are not related to variations in clay content (Fig. 3.3). Changes in the Fe/Al ratio can be explained by the varying pyrite content. Values for Sc/Al are higher in sapropel L7 and in the turbidites.

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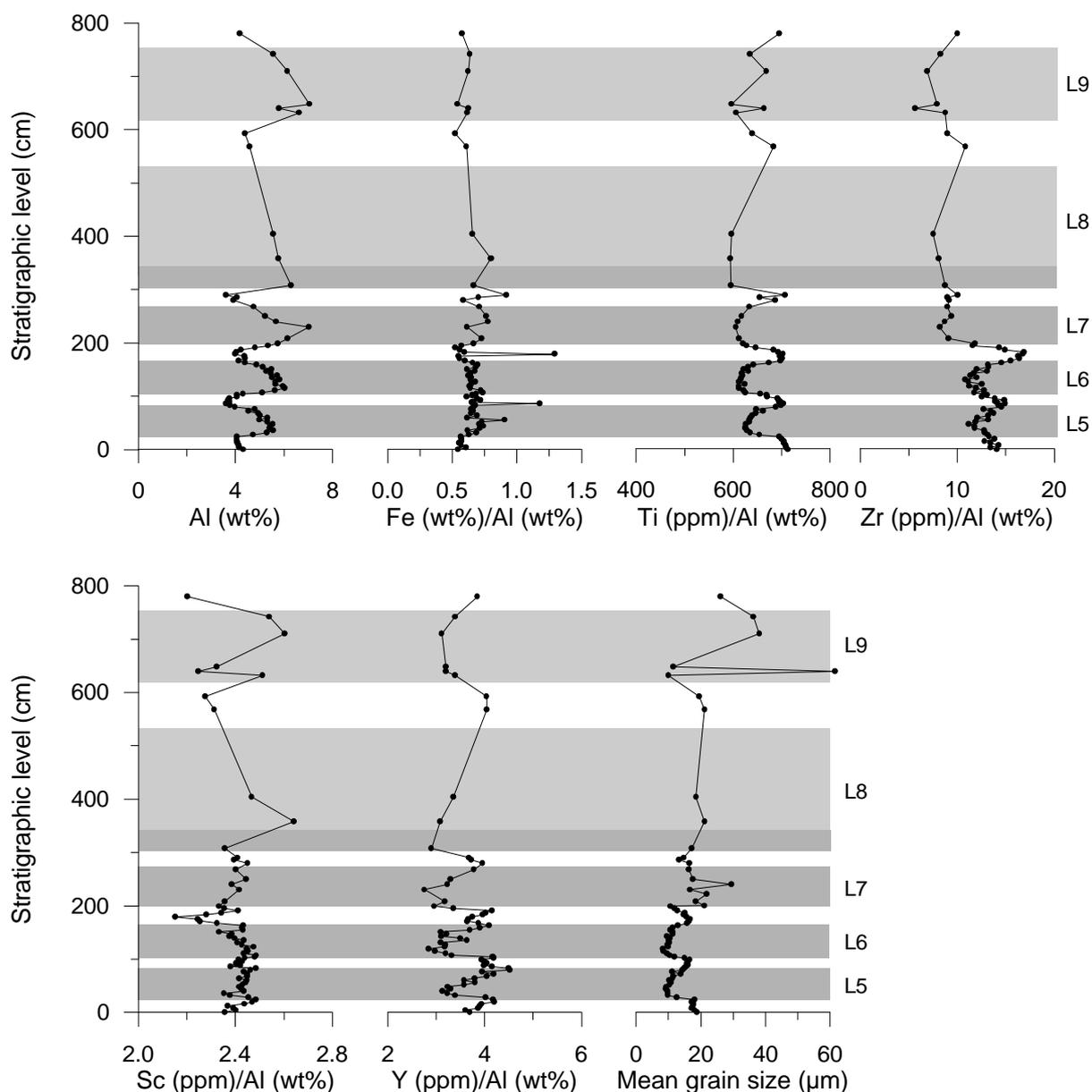


Figure 3.3 *Terrestrial elements and mean grain size profiles.*

Ti/Al, Y/Al and Zr/Al ratios are higher in the homogeneous marls and lower in the sapropels and turbiditic layers.

The redox-sensitive and chalcophilic elements Cu, Ni, V, Cd and Mo were measured in all samples; Cd, Se, As and Sb were only measured in sapropels L5 and L6 (Fig. 3.4). The contents of these elements have also been divided by the Al content to correct for the contribution of the

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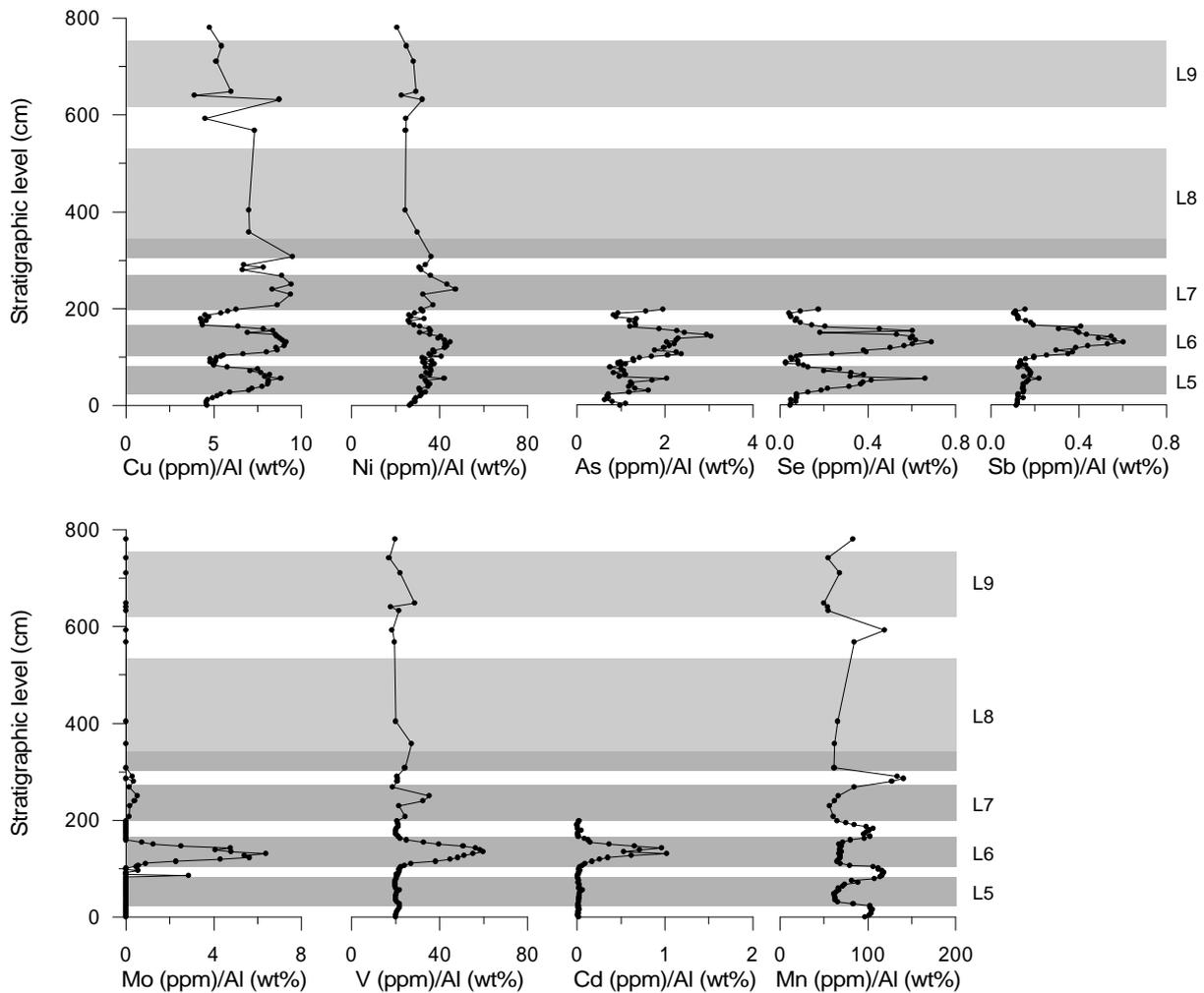


Figure 3.4 *Redox-sensitive and chalcophilic trace elements.*

detrital fraction. All redox-sensitive and chalcophilic elements analysed are enriched in L6, whereas sapropel L5 has only increased Cu, As and Se contents. Sapropel L7 is slightly enriched in V and Mo.

Grain size

Sapropels L5 and L6 contain more fine-grained material than the homogeneous marls (Fig. 3.3). Sapropel L7 is coarser than L5 and L6 and the turbiditic layers consist of fine- as well as coarse-grained material. A closer inspection of the grain size distributions reveals a dominance of the 4 μm grain size in the sapropels, versus a more even distribution of 6 to 20 μm in the homogeneous marls. In the turbidites a 6 to 80 μm distribution prevails. The fine-grained material in the sapropels is best sorted.

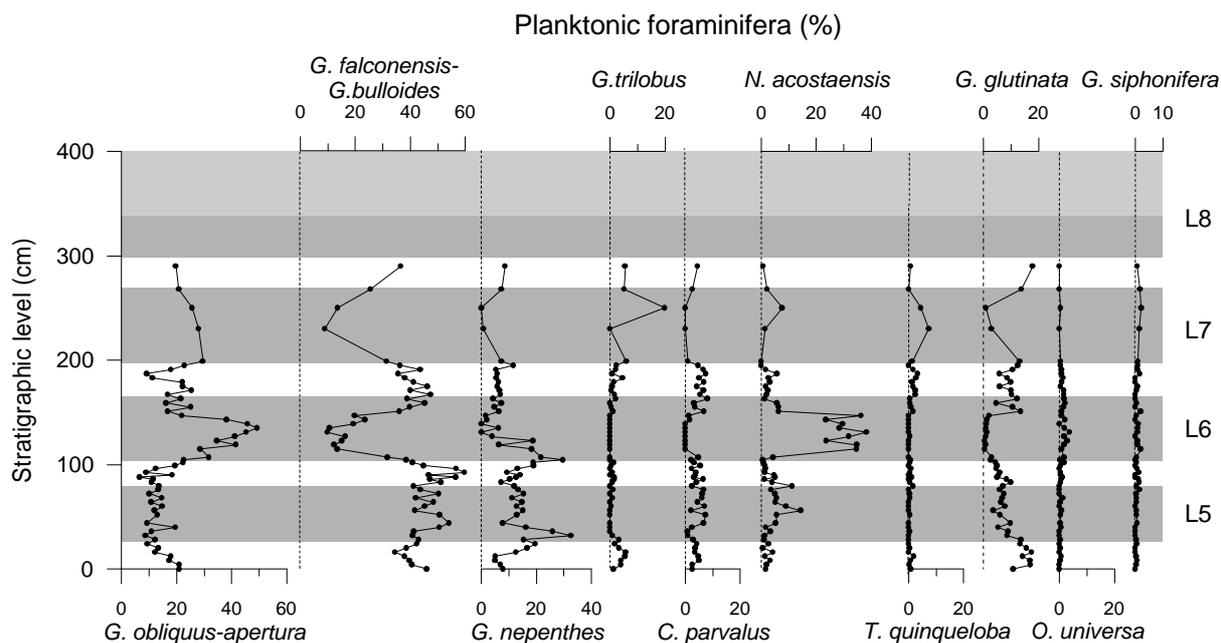


Figure 3.5 Distribution of planktonic foraminiferal taxa.

Foraminifera

The planktonic foraminiferal fauna consists of twelve species. Moderate preservation obliged us to lump the species *Globigerinoides obliquus* and *Globoturborotalita apertura* into one category. This also applies to the species *Globigerina falconensis* and *Globigerina bulloides*. The planktonic foraminiferal fauna is generally dominated by the group of *Globigerina falconensis-bulloides* (Fig. 3.5).

Benthic foraminiferal species have been combined into three major groups. Group 1 includes *Uvigerina semiornata*, *Uvigerina cylindrica gaudryinoides*, *Cancris auricula*, *Bulimina costata*, *Bulimina elongata*, *Bolivina spathulata*, *Bolivina dilatata*, and *Globobulimina pyrula*. All these species are tolerant to low-oxygen conditions [Van der Zwaan, 1982; Jonkers, 1984; Katz and Thunell, 1984; Van der Zwaan and Gudjonsson, 1986]. Group 2 includes species that are indicative of normal marine conditions [Van der Zwaan, 1982; Jonkers, 1984; Verhallen, 1991]. The most abundant species in this group are *Reussella spinulosa*, *Cibicides pseudoungerianus*, *Siphonina* spp., *Uvigerina proboscidea*, *Gyroidina soldanii*, *Pullenia* spp., *Bolivina antiqua*, *Bolivina scalprata miocenica*, and *Anomalinoidea* spp. Group 3 represents a mixture of notorious epiphytes (probably allochthonous) and undeterminable elements. Group 1 proliferates in the sapropels, whereas group 2 dominates the homogeneous intervals (Fig. 3.6).

Stable isotopes

The oxygen isotopic composition of planktonic foraminiferal carbonate ($\delta^{18}\text{O}_{\text{carb}}$) shows variations which are correlated to changes in lithology (Fig. 3.7). Lowest $\delta^{18}\text{O}_{\text{carb}}$ values are observed in sapropel L6 (-2.0‰), whereas less negative values are found in L5. The $\delta^{13}\text{C}_{\text{carb}}$ record is more complex, but some relation with lithology can be observed (Fig. 3.7). Lowest $\delta^{13}\text{C}_{\text{carb}}$ values (-0.5‰) are found in the sapropels. $\delta^{13}\text{C}_{\text{org}}$ varies around -22‰. L5 has less

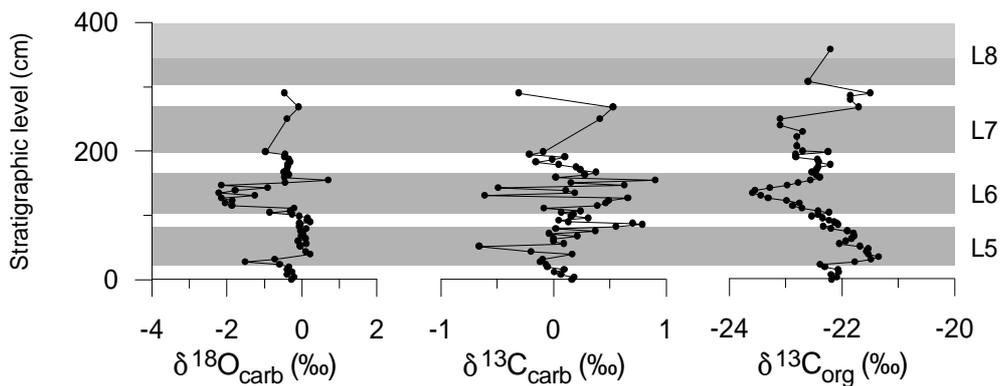


Figure 3.7 Oxygen and carbon isotopic ratios of planktonic foraminiferal carbonate, and carbon isotopic ratio of organic matter.

negative values; L6 and L7 more negative $\delta^{13}\text{C}_{\text{org}}$ values.

Discussion

The main characteristics of the Gavdos sapropels are the higher C_{org} content and the lower carbonate content. Organic matter enrichment in sapropels can be attributed to different processes: diagenesis (preservation), primary productivity and dilution. The oxygen content of the bottom water is often believed to be the determining factor for organic matter

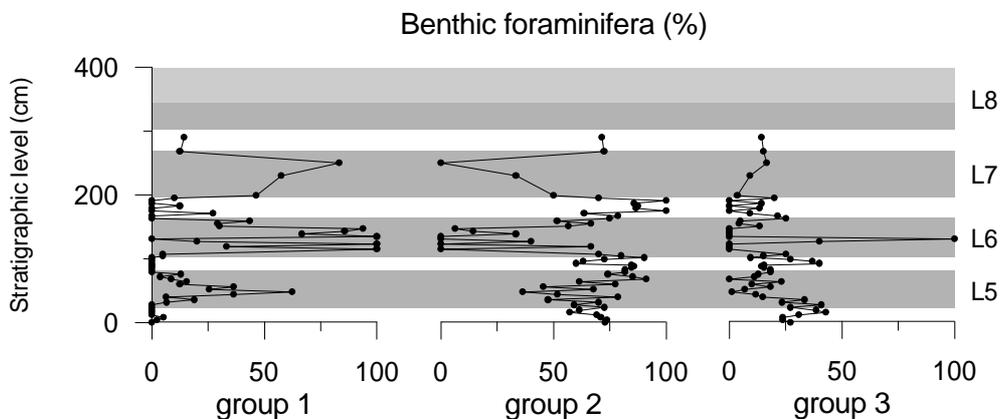


Figure 3.6 Distribution of benthic foraminifera (see text for the composition of the groups).

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preservation [Demaison and Moore, 1980; Pratt, 1984; Canfield, 1993]: oxic degradation is energetically more favourable than anoxic degradation, and bioturbation, which is more intense during oxic conditions, may enhance the decomposition of organic matter. However, it has also been argued [Henrichs and Reeburgh, 1987; Pedersen and Calvert, 1990; Calvert and Pedersen, 1993] that the flux of organic matter to the sediment controls the organic matter distribution since experiments have shown that rates of oxic organic matter degradation are approximately the same as anoxic degradation. The main problem in assessing the role of oxygen on C_{org} preservation is that there is often a relation between oxygen depletion and productivity: in areas of high productivity a high organic matter flux to the bottom waters will consume the oxygen in the water column causing oxygen depletion. Canfield [1994] states that the sedimentation rate is the determining factor controlling the degradation of organic matter: at a sedimentation rate > 30 cm/kyr the rate of anoxic degradation equals that of oxic degradation because rapid burial causes most organic material to be degraded via anoxic pathways, regardless of the bottom water conditions. At lower sedimentation rates, as in the Gavdos sapropels (4 cm/kyr), sediments deposited under aerobic conditions will remain much longer in an oxygenated environment than their anoxic counterparts. Therefore, differences in the aerobic/anaerobic pathways may be manifested more clearly at low sedimentation rates.

In the following sections we will discuss the geochemical and micropalaeontological evidence for each of these processes in order to unravel the most important factor that controlled the organic matter enrichment and the carbonate depletion in the Gavdos sapropels.

Diagenesis

Evidence for variations in oxygen deficiency in the sediment or bottom water is provided by redox-sensitive elements, the laminated character of the sapropels and the composition of the benthic fauna. Fluctuations in the benthic foraminiferal associations indicate that the oxic-anoxic interface was (seasonally) shallower, possibly even in the water column, during the deposition of the Gavdos sapropels. The low-oxygen tolerant association in the L5 sapropel is dominated by *Uvigerina semiornata* and in the L6 and L7 sapropels by *Uvigerina cylindrica gaudryinoides* (except near the top of the upper sapropel where *Cancris auricula* dominates). *Uvigerina cylindrica gaudryinoides* and *Cancris auricula* can tolerate severe oxygen deficiency [Jonkers, 1984] and their abundance in sapropels L6 and L7 suggests that oxygen deficiency was most intense in these periods. The very fine laminations observed in the sapropels could indicate that bioturbation by benthic organisms was limited due to oxygen depletion in the bottom water. Oxygen conditions during turbidite deposition cannot be determined adequately, even though the occurrences of small *chondrites* in the top of the turbidites as observed by Postma *et al.* [1993] indicate reduced oxygen levels [Wetzel, 1991].

The sharp contrast between sapropels L5 and L6 is also indicated by the redox-sensitive elements Cd, V, Mo, Sb and As. These elements can be immobilized under reducing (anoxic) conditions by precipitation, coprecipitation with iron sulphides or scavenging by organic matter [Piper and Isaacs, 1995b]. The extent and degree of bottom water anoxia, therefore,

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influence their content in the sediment. Elevated concentrations may indicate a shallower position of the oxic-anoxic boundary (as a result of a high input of reactive organic material). The enrichment, however, could also be due to increased scavenging by organic matter. Mo, V, Cd and Sb contents are higher in the L6 sapropel, but not in the other C_{org} -rich intervals. The Mo and V profiles are remarkable. Mo has a relatively high concentration in seawater (10 ppb) compared with other trace elements and is only moderately enriched in organic matter. Peak abundances of Mo are, therefore, expected if seawater is the source for the enrichment. This obviously is the case for L6, but the absence of Mo peaks in L5 and L7 indicates that redox conditions of the bottom water were different, unless later diagenesis removed Mo from these sapropels. Dissolved vanadate (V^V) predominates in oxic seawater and is, under more anoxic conditions, reduced to the vanadyl ion (V^{IV}) which readily adsorbs to particle surfaces [Breit and Wanty, 1991]. This redox transition occurs at the $\text{NO}_3^-/\text{SO}_4^{2-}$ redox boundary. Therefore, denitrifying conditions in the water column in combination with a large flux of organic matter will promote high sedimentary V contents. The profiles of Mo and V indicate that not all enrichments of organic matter cooccur with more reducing conditions in the water column. Less oxygenated conditions during sapropel formation can explain the lower Mn/Al and P concentrations. Under reducing conditions in the sediment Mn is mobilized and escapes to the water column. If bottom waters are well oxygenated, the Mn pore water concentration can build up leading to Mn carbonate precipitation [Calvert and Pedersen, 1993]. The benthic regeneration of phosphorus is higher under reducing conditions [Ingall and Jahnke, 1994].

The palaeoredox indicators all reveal less oxygenated conditions during sapropel formation which could have increased the preservation of organic matter. Periods of bottom water anoxia, as suggested by the profiles of Mo and V during formation of sapropel L6, must have been short because the occurrence of (autochthonous) benthic foraminifera indicates that the bottom water could not have been anoxic for long periods.

Because bottom waters have not been continuously anoxic during sapropel formation, it is possible that oxic decomposition of organic matter and subsequent dissolution of CaCO_3 occurred during sapropel deposition. It has been calculated that 2 to 3% organic matter must have been decomposed to cause a 20% reduction of the carbonates content at times of sapropel formation (Table 3.1). During the very early stages of sulphate reduction some carbonate may have been dissolved due to a decrease in pH [Canfield and Raiswell, 1991]. Pervasive sulphate reducing conditions, however, will produce HCO_3^- that will prevent CaCO_3 dissolution. We, therefore, assume that carbonate dissolution due to sulphate reduction in the sediment was of minor importance at times of sapropel formation.

The presence of gypsum probably indicates that some carbonate was dissolved during acid production upon oxidation of pyrite. This gypsum could have precipitated soon after formation of the sapropels, but oxidation of sulphides during weathering of the section seems more likely. Still, we consider dissolution of carbonates to be of minor importance, because this would have been manifest in etching and fragmentation of foraminifera, which were not

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observed. In addition, Sr peaks, which may indicate the dissolution of aragonite and precipitation of celestite [Nijenhuis *et al.*, 1996 (Chapter 2)], were not found.

Primary productivity

Barium is often used to estimate variations in primary productivity [Goldberg and Arrhenius, 1958; Calvert, 1983; Dymond *et al.*, 1992]. The enhanced Ba contents of the sapropels could, therefore, indicate higher primary productivity. This must be considered with caution, however, because dissolution and reprecipitation of barite may occur during sulphate reduction [De Lange *et al.*, 1994]. Sulphate reduction occurred, as is indicated by the presence of a few percent of sulphides. The overall effect, however, is probably insignificant, since no Ba mobilization peaks have been observed outside the sapropels. The turbiditic layers are also rich in Ba but very low in organic matter, which may indicate that the organic matter has been oxidized.

Another indication of increased surface water productivity at times of sapropel formation is suggested by peak abundances of the planktonic foraminiferal species *Neogloboquadrina acostaensis*. Modern representatives of neogloboquadrinids proliferate under **Table 3.1** Changes in (1) terrestrial input, (2) carbonate production and (3) oxidation of organic matter needed to explain the decrease in carbonate content in the sapropels, calculated using the equations [Van der Weijden, 1993]:

$$\Delta_{terr} = \left[\frac{x(100-y)}{y(100-x)} - 1 \right] \times 100\% \quad (1)$$

$$\Delta_{carb} = \left[1 - \frac{y(100-x)}{x(100-y)} \right] \times 100\% \quad (2)$$

$$\Delta C_{org} = \left[x - \frac{y(100-x)}{100-y} \right] \times 0.103\% \quad (3)$$

in which *x* represents the mean carbonate percentage in all homogeneous intervals and *y* the mean carbonate percentage in all sapropels.

	Δ_{terr}	Δ_{carb}	ΔC_{org}
sapropels L5, L6	62%	38%	2.1%
sapropel L7	91%	48%	2.7%

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	Δ_{terr}	Δ_{carb}	ΔC_{org}
upper turbidite L9	130%	56%	3.0%

eutrophic conditions, such as those associated with upwelling [Ravelo *et al.*, 1990; Reynolds Sautter and Thunell, 1991; Pujol and Vergnaud-Grazzini, 1995], spring blooms [e.g. Tolderlund and Bé, 1971; Reynolds and Thunell, 1986] or DCM [Fairbanks *et al.*, 1982; Ravelo *et al.*, 1990], and there is some evidence in the literature that this is also true for their fossil equivalents [Van der Zwaan, 1982; Rohling and Gieskes, 1989; Lourens *et al.*, 1992]. Modern representatives of *Globigerinoides obliquus* and *Globoturborotalita apertura* (*Globigerinoides ruber* and *Globoturborotalita rubescens*) inhabit warm and oligotrophic surface waters [e.g. Bé and Hutson, 1977]. The concomitant increase in abundance of neogloboquadrinids and the *Globigerinoides obliquus*-*Globoturborotalita apertura* group in sapropel L6 and L7, thus seem to indicate increased seasonal contrasts in surface water productivity.

Changes in surface water productivity may also have contributed significantly to the distribution of the redox-sensitive elements in the sediment. In shelf-slope environments, where rates of organic matter accumulation are high, the biogenic source is the most important factor in the trace element budget [Piper and Isaacs, 1995b]. The enrichments of the trace elements Ni and Cu in the sapropels correlate well with the organic matter content and may, therefore, be explained by increased surface water productivity. However, quantifying the contribution of the biogenic source remains difficult, because an increase in surface water productivity may also lead to more reducing conditions in the sediment and bottom water.

Van Os *et al.* [1994] proposed that the carbonate depletion in Pliocene sapropels was caused by lower carbonate production due to partial replacement of non-opportunistic calcareous plankton taxa by siliceous plankton. The decrease in carbonate production, needed to explain the observed carbonate pattern, is in the order of 40 to 60% (Table 3.1). This hypothesis is, however, difficult to prove since siliceous plankton, which is easily dissolved, was not found in the sediment.

Dilution

The greater thickness of the sapropels relative to the homogeneous intervals in combination with estimates of 4-6 kyr for the duration of Plio-Pleistocene sapropel formation [Lourens *et al.*, 1996a] suggest an increase in sedimentation rate during sapropel formation. Even if sapropel formation lasted as long as 10-12 kyr (i.e. half a precession cycle) the sedimentation rate must have been higher. The sapropels gradually pass upwards into river-flood generated turbidite layers [Postma *et al.*, 1993]. Thin turbidites occur within the sapropels (L7) and eventually substitute them (L8). The sapropels also increase in thickness from 46 cm (L5) to 68 cm (L7), suggesting a gradual increase in sedimentation rate.

The influence of terrestrial dilution is clearly reflected in the geochemical data and the mean grain size variation. In general, a higher fluvial discharge leads to a relative increase of

fine-grained particles. In contrast, the wind-borne fraction consists of both fine (< 6 μm) and coarser material, and its importance depends on prevailing winds and distance to the source [e.g. Koopmann, 1981; Sarnthein et al., 1981]. The decrease in grain size during sapropel formation can, therefore, best be explained by a higher input of river-derived material which dilutes the coarser wind-borne fraction. In the homogeneous marls the wind-borne fraction predominates. Sapropel L7 forms the transition to the cyclic turbidite sequences: the grain size increases in this sapropel, therefore, seem to be associated with the growth of a river-fed subfan-lobe, bringing coarser material to the site. The turbidites are mixtures of coarse and fine fluvial material.

Other evidence for the variability in the wind-borne versus fluvial input comes from the Ti/Al and Zr/Al ratios. High Ti/Al and Zr/Al values generally indicate that the input of wind-borne material has increased with respect to that of fluvial origin [Shimmield, 1992]. The patterns of Ti/Al and Zr/Al correlate well with the mean grain size of sapropels L5-L7 and the homogeneous marls. The increase in grain size in L7 and the turbidites, however, is not associated with higher values of Ti/Al and Zr/Al. Variations in Sc/Al and Y/Al also indicate changes in the source of the terrestrial material.

To explain the reduction in CaCO_3 by dilution, the increase in the terrestrial clastic component must have been in the order of 60 to 130% (Table 3.1). The estimated increase in terrestrial clastics from L5/L6 to L9 parallels the gradual increase in sedimentation rate, indicating that an increase in fluvial-terrestrial clastics may be the most important factor in controlling the reduction in CaCO_3 in the Gavdos sapropels. This could also imply that the increase in organic matter was mainly caused by enhanced supply of land-derived organic matter. In that case, one may expect lighter $\delta^{13}\text{C}_{\text{org}}$ values in the sapropels, because the $\delta^{13}\text{C}_{\text{org}}$ signal of marine organic matter is normally less negative ($\sim -20.6\text{‰}$) than that of terrestrial origin ($\sim -26.6\text{‰}$) [Jasper and Gagosian, 1990]. The $\delta^{13}\text{C}_{\text{org}}$ values in the entire section vary around -22‰ , which indicates a predominantly marine origin. The $\delta^{13}\text{C}_{\text{org}}$ values, however, are significantly lower in sapropels L6 and L7, suggesting an increase in the relative contribution of land-derived organic matter.

On the origin of the Gavdos sapropels

All Neogene sapropels and related beds are associated with precession minima during which perihelion occurred in the Northern Hemisphere summer [Rossignol-Strick, 1983; Prell and Kutzbach, 1987; Hilgen 1991a, b; Rohling and Hilgen, 1991; Hilgen et al., 1995; Lourens et al. 1996a]. It has been argued that this orbital configuration resulted in an intensification of the summer monsoon [e.g. Prell and Kutzbach, 1987], thereby enhancing fluvial discharge from the river Nile [Rossignol-Strick, 1983]. In addition, a greater influence of Atlantic-born depressions in the Mediterranean could have increased the river discharge from the northern borderlands of the Mediterranean [Rohling and Hilgen, 1991]. Evidence for increased river discharge at times of sapropel formation has been obtained from significant shifts in the $\delta^{18}\text{O}_{\text{carb}}$ record to lighter values [e.g. Vergnaud-Grazzini et al., 1977; Williams et al., 1978; Thunell and Williams, 1989;

Evidence for a single mechanism of sapropel formation during the past 10 Myr

Gudjonsson and Van der Zwaan, 1985; Tang and Stott, 1993; Aksu et al., 1995]. Similar shifts are found in the Gavdos sapropels (Fig. 3.7). The most depleted $\delta^{18}\text{O}_{\text{carb}}$ values are observed in sapropel L6, suggesting that river input was highest during deposition of this layer. Alternatively, it has been argued that the oxygen isotope depletions have been caused by a reduction in excess evaporation and variations in water exchange with the western Mediterranean Sea and the Atlantic Ocean [e.g. *Van Os and Rohling, 1993; Bigg, 1995*].

The substitution of the Gavdos sapropels by turbidites points to a local origin of the fluvial runoff [*Postma et al., 1993; this study*]. The delta plain and front were most likely located in the southern parts of central and west Crete, and fed by bed-load type rivers draining the uplifted Hellenic Arc [*Postma et al., 1993*]. Evidence of a local origin of enhanced fluvial runoff in the eastern Mediterranean at times of precession minima further comes from early Pliocene turbidite sequences of Corfu (Greece) [*Weltje and de Boer, 1993*] and from oxygen isotope profiles from the youngest Holocene sapropel in the Aegean Sea [*Perissoratis and Piper, 1992; Aksu et al., 1995; Zachariasse et al., 1997*].

Increased runoff supplied additional nutrients to the eastern Mediterranean, resulting in maximum primary productivity during deposition of sapropels L6 and L7 as indicated by neogloboquadrinid peak abundances and higher Ba concentrations. A concomitant reduction in excess evaporation may have resulted in pycnocline shoaling into the euphotic zone, thereby promoting DCM formation [*Rohling and Gieskes, 1989; Rohling, 1994*]. Erosion of the pycnocline during winter by deep mixing (resulting from minimum boreal winter insolation), may have favoured spring bloom conditions and, hence, higher export productivity and oxygen

	Productivity indicators					Continental indicators						Redox indicators						
	CaCO ₃	C _{org}	Ba	neogl.	infl.	bull.	clay	Ti/Al	Zr/Al	grain size	S/D	δ ¹³ C	δ ¹⁸ O	δ ¹³ C _{org}	redox	benthos	G.noides	
Late Pleistocene sapropels																		
<i>Aksu et al. [1995]</i>	--	++	++			++	+	+				--	--		++	++		
<i>Calvert [1983]</i>	±	++	++					-	-						++			
<i>Fontugne and Calvert [1992]</i>												--	--	--				
<i>Rohling and Gieskes [1989]</i>				++														
<i>Pruysers et al. [1991]</i>	±	++	++												++			
summary	±	++	++	++		++	+	±	-			--	--	--	++	++		
Late Pliocene-Early Pleistocene sapropels																		
<i>Gudjonsson and Van der Zwaan [1985]</i>												--	--					
<i>Howell et al. [1988]</i>	--	+											--					
<i>Howell et al. [1990]</i>	--	+		++	++								--					
<i>Wehausen and Brumsack [1998]</i>	--	++	++					--	--									
<i>Nijenhuis et al. [1998]</i>	--	++	++											-	++			
<i>Van der Weijden [1993]</i>	--	+						-	--				--		++			
<i>Spaak [1983]; Verhallen [1991]</i>				++	++	++										++		
<i>Lourens et al. [1992]; Versteegh [1994]</i>				++	++	++					++		--					
<i>Van Os et al. [1994]</i>	--	++	++	--	++			--	--			-	--	±				
<i>Foucault and Mélières [1995]</i>							++											
summary	--	++	++	++	++	++	++	--	--		++	-	--	±	++	++		
Early Pliocene CaCO₃ cycles and sapropels																		
<i>Sprovieri [1993]</i>																		++
<i>Spaak [1983]; Jonkers [1984]</i>				++		++										++		±
<i>Gudjonsson [1987]</i>												-	--					
<i>De Visser [1991]; De Visser et al. [1989]</i>	--	++	++	++	++		++	--		--	++	±	--	±				
summary	--	++	++	++	++	++	++	--		--	++	-	--	±		++		+
Miocene sapropels																		
<i>Sprovieri et al. [1996]</i>																		++
<i>De Visser [1991]</i>							±											
<i>Nijenhuis et al. [1996] (Chapter 2)</i>	--	++	++	++				--	--	±	++	±	--	±	++	++		++
<i>this paper</i>	--	++	++	++				--	--	--		±	--	±	++	++		++
summary	--	++	++	++			±	--	--	-	++	±	--	±	++	++		++

Table 3.2 Published characteristics of Mediterranean Miocene to Late Pleistocene sapropels. + higher in sapropel; - lower in sapropel; ± no systematic change with respect to adjacent sediments; + for clay minerals indicates smectite maxima and kaolinite and palygorskite minima in the sapropels. neogl. = neogloboquadrinids; infl. = *Globorotalia inflata* group; bull. = *Globigerina bulloides*; clay = clay minerals; S/D = sporomorphs/dinophlagellate cysts ratio; redox = redox-sensitive elements; benthos = low-oxygen-tolerant benthic foraminifera; *G.noides* = *Globigerinoides* spp.

consumption rates. On the other hand, increased thermal stratification and decreased nutrient replenishment during summer (resulting from maximum boreal summer insolation) resulted in maximum surface water temperatures and oligotrophy at times of sapropel formation as indicated by peak abundances of the *Globigerinoides obliquus*-*Globoturborotalita apertura* group. The combination of abundant *Globigerinoides sacculifer* (having a higher optimum temperature than the modern representatives of the *Globigerinoides obliquus*-*Globoturborotalita apertura* group [Bé and Hutson, 1977]) and neogloboquadrinids suggests that seasonal contrast reached a maximum during L7. Seasonal contrasts were weaker during the formation of L5, because neogloboquadrinids and the *Globigerinoides obliquus*-*Globoturborotalita apertura* group hardly rise above background level. The low oxygen bottom water concentrations, possibly strengthened by reduced deep water formation rates [Rohling, 1994], in combination with the large downward organic matter flux caused the high C_{org} contents of the sapropels.

Comparison with younger sapropels

In Table 3.2 we compare our results with those of previous studies on younger sapropels and related $CaCO_3$ cycles in the Mediterranean. A complete comparison is not possible because the same spectrum of proxies is not always available for all time intervals. For instance, there is an obvious lack of granulometric data for the late Pleistocene. Another problem is that some of the research focussed almost entirely on the sapropels, thereby neglecting the adjacent homogeneous marls which are equally important from a palaeoclimatic point of view.

The most obvious geochemical characteristics of sapropels are the high C_{org} and Ba contents, elevated contents of redox-sensitive and chalcophilic elements, and low $CaCO_3$ content. Irrespective of their age, these characteristics are shared by all sapropels and related grey coloured layers of the $CaCO_3$ cycles, although the latter are less enriched in C_{org} . The planktonic and benthic foraminiferal signal is also remarkably constant through time, with peak occurrences of neogloboquadrinids (with the exception of the Holocene sapropel S1; Rohling and Gieskes, [1989]) and high abundance of low-oxygen tolerant benthic foraminifera in sapropels. This is also the case for some of the continental indicators with maxima in the ratio of continental versus marine palynomorphs (S/D), and minima in Ti/Al, Zr/Al, grain size and $\delta^{18}O_{carb}$ values in sapropels. The consistency in most of the diagnostic geochemical and micropalaeontological characteristics between the Gavdos sapropels and their younger counterparts (Table 3.2) indicates that all sapropels and related layers are driven by one single

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mechanism for at least the last 10 Myr, although diagenesis, primary productivity and dilution may differ from site to site, depending on location, proximity to land, depositional environment, and intensity of the astronomical forcing.

The importance of terrestrial input during sapropel formation has been the subject of much debate [e.g. *De Visser et al., 1989; Howell et al., 1990; Thunell et al., 1990; Van der Weijden et al., 1993; Van Os et al., 1993; Nijenhuis et al. 1996 (Chapter 2)*]. Continental indicators (Table 3.2: grain size, S/D, Ti/Al, Zr/Al, and $\delta^{18}\text{O}_{\text{carb}}$), however, point in the same direction with river dominated input during periods of sapropel deposition and increased aeolian input during the intervening periods. The alternating dominance of fluvial and aeolian-derived terrestrial clastics is also evidenced by changes in the clay mineral composition in the grey layers of Pliocene CaCO_3 cycles [*De Visser et al., 1989; Foucault and Mélières, 1995; Chapter 4*], although clay mineral patterns in the Mediterranean are complex and difficult to interpret because enrichment depends on factors as source rocks, local climate and relief. Results obtained from grain size analyses are not always consistent (Table 3.2), but usually point to enhanced fluvial input in sapropels as well [*De Visser et al., 1989; this study*]. The inconsistency in the $\delta^{13}\text{C}_{\text{org}}$ signal can be explained by a varying degree of post-burial diagenesis or by uncertainties in the interpretation of bulk organic matter $\delta^{13}\text{C}$ values [*Hayes, 1993*].

Conclusions

Consistency in most of the diagnostic geochemical and micropalaeontological characteristics between the Gavdos sapropels and their younger equivalents indicates that all sapropels and related layers are driven by a single mechanism during the last 10 Myr. On Gavdos, these characteristics clearly point to an alternating dominance of fluvial- (sapropels) and aeolian-derived (homogeneous marls) terrestrial clastics causing the carbonate cyclicity. Evidence for a local origin of enhanced fluvial input comes from the gradual replacement of the sapropels by cyclic turbiditic layers which were fed by bed-load type rivers. The sapropels of Gavdos were deposited during periods of increased productivity and less oxygenated bottom water conditions resulting in the high organic matter content.

Acknowledgements - We thank M. van Alphen for performing the geochemical analyses. The help of G.J. van der Zwaan and T. Kouwenhoven in the determination of the benthic foraminifera is appreciated. For technical assistance we are grateful to G. Ittman, A van Dijk, H. de Waard, G.J. van 't Veld and G. Nobbe. Two anonymous reviewers are thanked for their constructive remarks.

		Age Myr B.P.			
Caenozoic	Quaternary	Pleistocene		1.6	
		Part II: The Pliocene		5.3	
	Tertiary	Neogene	Miocene		23.7
			Oligocene		36.6
		Palaeogene	Eocene		57.8
			Palaeocene		66.4

*"The Mediterranean is beautiful
in a different way from the ocean,
but it is as beautiful."*

Chapter 4

Diatomites at Lido Rossello: Geochemistry and implications for formation models of the "Trubi" marls

I.A. Nijenhuis, L.J. Lourens, G.J. de Lange

Abstract - The geochemistry and micropalaeontology of three coeval marine sedimentary cycles of the Pliocene "Trubi" formation have been investigated in two land sections. The Punta di Maiata and the nearby Lido Rossello sections at Sicily show the same grey-white-beige-white coloured quadripartite carbonate cycles. At Lido Rossello, however, a laminite and a diatomite are intercalated in this pattern.

Palaeoproductivity, as inferred from barium contents, was high during deposition of the grey layers, the diatomite and the laminite. In contrast, the planktonic foraminiferal shell flux is low in the grey layers. Dilution by clays, which has occurred by aeolian input in the beige layers, and by fluvial input in the grey layers, is insufficient to explain the low shell flux in the grey layers, but may account for the decrease in total carbonate content in the beige layers. Carbonate dissolution has taken place in the grey layers and the laminites, as evidenced by strontium mobilization peaks around these layers.

Apart from increased productivity, the presence of a local depression at Lido Rossello may have contributed to the formation of the laminite and the diatomite.

This chapter will be submitted together with *Lourens et al. [in prep.] to Paleoceanography.*

Introduction

Rhythmic limestone-marl cycles are common in the geological record [e.g. Einsele and Seilacher, 1982, and references therein], and are often driven by variations in the Earth's orbit [e.g. Fischer, 1980; De Boer, 1991]. These so-called periodites may develop when sediments are deposited under oxic conditions with a carbonate/clay ratio in the order of four, and when the alternating beds are too thick to become obliterated by bioturbation [Einsele, 1982]. The origin of periodites is discussed in terms of carbonate productivity and dissolution, terrestrial dilution, and diagenetic processes such as pressure solution [e.g. Einsele, 1982].

The marls of the "Trubi" formation of the Sicilian and Calabrian Pliocene are a special example of such periodites. These sedimentary rocks vary not only in carbonate, but also in organic carbon (C_{org}) content. As a result, quadripartite cycles occur, consecutively consisting of a grey marl, slightly enriched in C_{org} , a white limestone, a beige marl (poor in C_{org}), and another white limestone. More commonly, Mediterranean Neogene and Quaternary sediments are characterized by bipartite cycles consisting of limestones or marls alternating with sapropels, sedimentary layers containing more than 2% C_{org} . Both quadripartite and bipartite cycles have been linked to the precession of the Earth's equinoxes, the grey layers and sapropels representing humid periods at times of precession minima (Northern Hemisphere insolation maxima) [Hilgen, 1991a, b; Lourens et al., 1996a]. Mediterranean sapropels have been studied intensively in the last few decades [e.g. Kidd et al., 1978; Cita and Grignani, 1982; Rossignol-Strick et al., 1982; Calvert, 1983; De Lange and Ten Haven, 1983; Mangini and Schlosser, 1986; Rohling and Hilgen, 1991; Nijenhuis et al., 1996 (Chapter 2)]. Their origin is thought to be the result of increased continental runoff, which on the one hand supplies nutrients, raising productivity, and on the other hand stabilizes the water column, possibly resulting in anoxic bottom waters and improved organic matter preservation. Quadripartite cycles have received much less attention. De Visser et al. [1989] conducted an integrated low-resolution micropalaeontological, palynological, geochemical and clay mineralogical research on four cycles of the Punta di Maiata section. They concluded that an alternation of increased terrestrial input (grey layers) and decreased carbonate production (beige layers) caused the carbonate cycles. Based on a combined geochemical and micropalaeontological survey of the first sapropel-containing carbonate cycle of the Narbone formation which directly overlies the "Trubi" marls, Van Os et al. [1994] concluded that productivity changes were the main cause of the cyclicity: low productivity in the beige layers, intermediate (mainly carbonate) productivity in the white layers and very high (mainly organic/opal) productivity in the grey layers. Thunell et al. [1991], on the other hand, concluded on the basis of mainly foraminiferal data that marl-limestone duplets in the Calabrian "Trubi" formation were caused by low productivity in the marls (equivalent to the grey layers) and upwelling-type conditions in the limestones (equivalent to the beige and white layers).

Whatever the best model may be, it seems that the origin of the "Trubi" quadripartite cycles lies in an intricate interplay of the processes of marine productivity, terrestrial dilution,

and carbonate dissolution. Further constraining these processes is essential to our understanding of the formation of these sediments and their link to climatic variations. An excellent opportunity for achieving this may lie in the occurrence of local deviations in the monotonous grey-white-beige-white successions. The irregular occurrence of six laminated intervals (some containing diatoms) in cycles 26-31 of the Lido Rossello section [Brolsma, 1978] is such a local deviation. These laminites are absent in coeval sediments of the nearby Punta di Maiata section. We conducted an integrated high-resolution geochemical and micropalaeontological survey of three sedimentary cycles at Lido Rossello (containing the top two laminites) and their lateral equivalents at Punta di Maiata (where these laminites are absent). It was found that the laminites are productivity events unrelated to precessional forcing [Lourens *et al.*, *in prep.*]. In this paper, we will further constrain the processes involved in the formation of the laminites, and discuss the implications of their occurrence for existing formation models of the "Trubi" marls.

Material and methods

Geological setting

The Lido Rossello and Punta di Maiata sections are exposed along the beach at the south coast of Sicily in some four kilometres of continuous cliff outcrops (Fig. 4.1A). These outcrops cover the lower part of the Pliocene "Trubi" formation, and the contact with the underlying upper Miocene "Arenazzolo" formation is locally visible. The cliff-face is dissected by numerous NW-SE trending faults (every fifty metres), which show displacements of up to fifteen metres [Brolsma, 1978].

The marine sediments of the "Trubi" formation have been deposited at a water depth between 500 and 800 metres [Brolsma, 1978]. Weathered sediments are characterized by a distinct grey-white-beige-white colour alternation, with the grey and beige layers being less indurated. The fresh sediments show a markedly different colour alternation of dark blue - light blue (or white) - light blue with dark blue bands - light blue.

At Lido Rossello, approximately twenty-nine metres above the local base of the "Trubi" formation, six brownish-rose, finely bedded limestone marls are intercalated [Brolsma, 1978]. These laminated beds vary in thickness from 10 to 145 cm and contain, with the exception of the uppermost bed, siliceous organisms (radiolaria and diatoms) [Zachariasse *et al.*, 1978].

Sampling

Samples were taken during three campaigns. In October 1994, we sampled an interval at Lido Rossello which contains carbonate cycles 29 and 30 (cycle coding after Langereis and Hilgen, [1989]) and the uppermost laminated bed (no. 6 of Brolsma [1978]), which has a distinct brown colour. In June 1995 we sampled the time-equivalent cycles at Punta di Maiata (about one kilometre to the southeast) and extended our 1994 sampling trajectory at Lido Rossello downwards. This latter interval was sampled in another gully approximately ten metres to the

east with respect to the 1994 trajectory, and contains carbonate cycle 29, part of cycle 28, and a second laminated interval (no. 4 of Brolsma [1978]). In August 1996, we sampled the time-

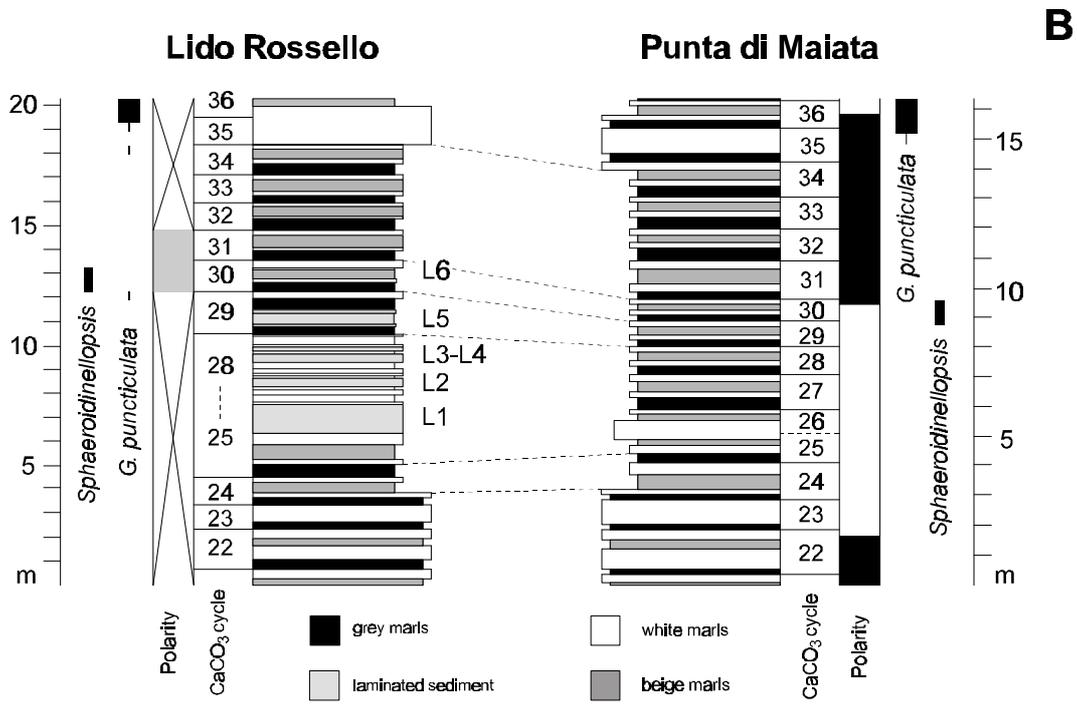
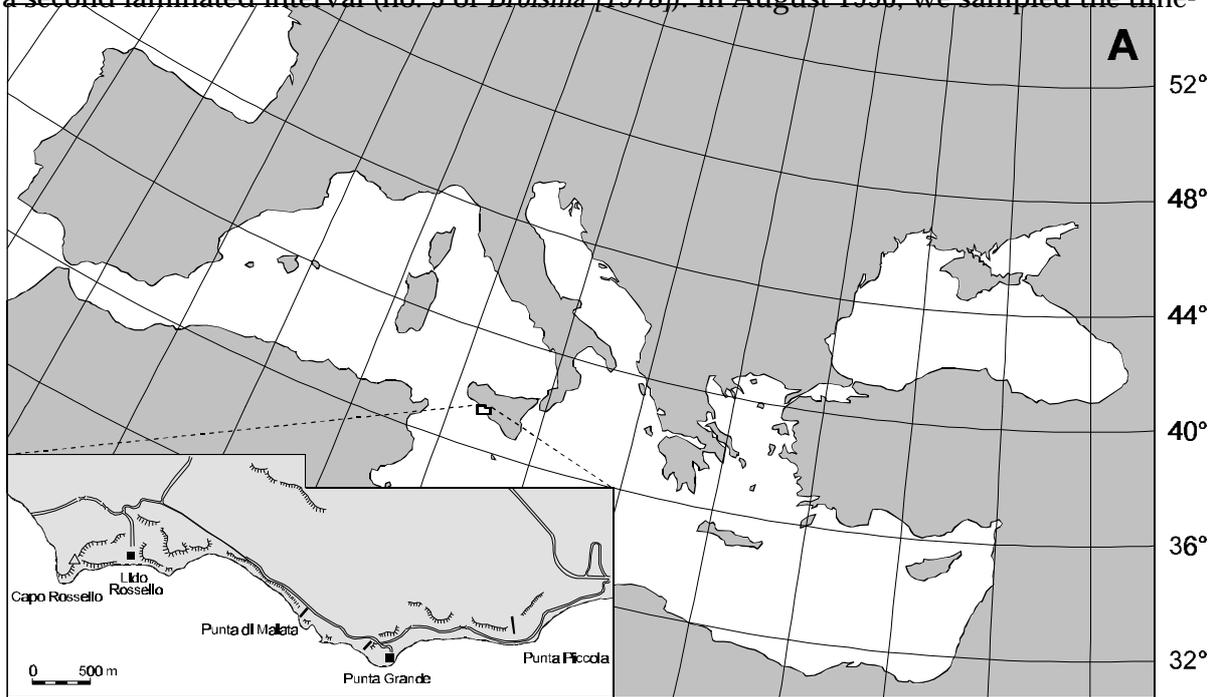


Figure 4.1 Location of the sections (A) and composite stratigraphic columns of carbonate cycles 22-36 at Lido Rossello and Punta di Maiata (B). The laminated intervals at Lido Rossello as described by Brolsma [1978] are indicated by L1-L6.

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equivalent interval at Punta di Maiata in an outcrop approximately fifteen metres to the east of the 1995 sampling trajectory. A composite stratigraphic column of cycles 22-36 in both sections is shown in Fig. 4.1B.

Considerable effort was taken to remove the weathered surface to expose the fresh sediment. After that, small cores with a diameter of 2.5 cm were drilled and packed in aluminium foil. During the 1994 campaign, separate samples for geochemical purposes were taken by scraping off sediments parallel to the bedding plane using a stainless steel spatula. These samples were transported in glass jars. All other geochemical analyses were performed on the drilled cores after cleaning their surface by scraping with a stainless steel knife.

Micropalaeontology

Counts of planktonic foraminiferal species, siliceous organisms and palynomorfs were made on splits from the 125 to 595 μm fraction. Between 200 and 400 specimens of planktonic foraminifera were picked per sample, mounted on Chapman slides, identified and counted. For each slide, we also counted the amount of siliceous organisms, benthic foraminiferal specimens and palynomorfs. Counted species/groups are: *Globigerinoides obliquus*, *Globigerinoides trilobus*, *Globoturborotalita apertura* + *Globoturborotalita nepenthes*, sinistral- and dextral-coiled *Neogloboquadrina acostaensis*, *Sphaerodinellopsis seminulina* + *Sphaerodinellopsis subdehiscens*, *Globigerina falconensis*, *Globigerina quinqueloba*, *Globigerinata glutinata*, *Orbulina universa*, *Globigerinella siphonifera* and *Globorotalia margaritae*.

In the laminated intervals, organic compounds of small spherical objects were observed, and larger ones which were always wrinkled. *Brolsma [1978]* had these forms tentatively identified by G.T. Boalch as possible representatives of the genus *Pachysphaera* (division Chlorophyta (green algae), class Prasinophyceae).

Geochemistry

The samples were freeze-dried and powdered in an agate mortar. After removing inorganic carbon with 1 M HCl, C_{org} was measured with a Fisons NA 1500 NCS analyser. Stable organic carbon isotopes ($\delta^{13}C_{\text{org}}$) were determined with a Stable Isotope Ratio Analyser (VG SIRA 24), and are reported relative to the PeeDee Belemnite (PDB) standard. The carbonate content was determined gas-volumetrically. Opal analyses were performed on selected samples, following the method of *Müller and Schneider [1993]*, using a Technicon TRAACS 800 auto-analyser. For major, minor and trace element analyses, a 250 mg sample was digested in 10 ml of a 6.5 : 2.5 : 1 (v/v) mixture of HClO_4 (60%), HNO_3 (65%) and H_2O , and 10 ml HF (40%) at 90°C. After evaporation to dryness on a sand bath at 190°C, the residue was dissolved in 50 ml 1 M HCl. The resulting solutions were analysed with a Perkin Elmer Optima 3000 Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES) for Al, Ca, Fe, S, Ti, Ba, Sr, Ni, and V. For selected samples from Lido Rossello, these solutions were also analysed for As and Se with a Perkin Elmer 3100 hydride-Atomic Absorption Spectrometer (AAS).

All results were checked with international and house standards. Absolute standard deviations in $\delta^{13}\text{C}_{\text{org}}$ analyses are below 0.2‰. Relative standard deviations in duplicate measurements are lower than 1% for carbonate analyses, and lower than 5% for C_{org} and ICP duplicate measurements. As and Se were measured in triplicate with a standard deviation below 10%.

Age model

We assigned astronomical ages to the midpoints of the grey layers of Punta di Maiata as given by Lourens *et al.* [1996a]. Hereafter, we tuned the Lido Rossello succession to Punta di Maiata by using the characteristic faunal patterns of three planktonic foraminiferal species/groups: *Sphaeroidinellopsis seminulina* + *Sphaeroidinellopsis subdehiscens*, *Globigerinoides trilobus* and *Globorotalia margaritae*. A comparison between the sedimentation rates of the two localities is shown by their ratios (Fig. 4.2). This ratio indicates that the sedimentation rates of both sections are almost similar during deposition of cycles 30, 31 and the top of cycle 28, whereas they are significantly higher at Lido Rossello during deposition of cycle 29.

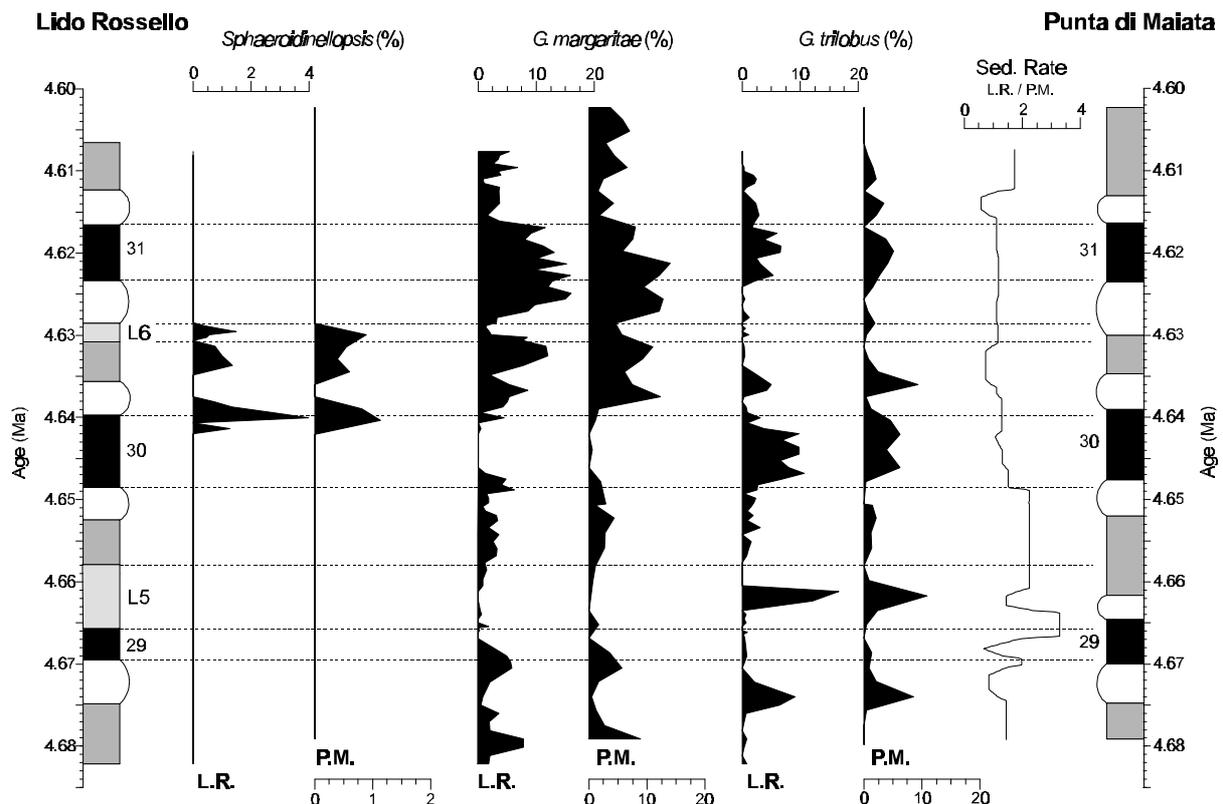


Figure 4.2 Abundance of the planktonic foraminifera species used for constructing the age model, and the ratio of the inferred sedimentation rates at Lido Rossello and Punta di Maiata.

Results

Micropalaeontology

Distribution of the planktonic foraminiferal species used in constructing the age model are shown in Fig. 4.2; the total foraminiferal shell flux per cubic centimetre is shown in Fig. 4.3. Distribution patterns of other individual planktonic foraminiferal species are reported elsewhere [Lourens *et al.*, *in prep.*]. The ratio of benthic to total foraminifera is highest in the grey layers and low in the laminites. Diatoms and radiolaria have only been found in the lower part of the diatomite in cycle 29 at Lido Rossello.

Geochemistry

First, the geochemistry of the “normal” grey-white-beige-white sediments at Punta di Maiata will be reported. Subsequently, we will show in how far this pattern is different at Lido Rossello, due to the occurrence of the diatomaceous laminite in the white intervals of cycle 29 (“the diatomite”) and the brown laminite in the beige interval of cycle 30 (“the laminite”).

Punta di Maiata - Contents of C_{org} (Fig. 4.4) are low in the white and beige layers (~0.08%) and high in the grey layers (up to 0.30%). Barium (shown as $Ba^* = (Ba_{sample}/Al_{sample}) \times Al_{average}$ (Fig. 4.4) in order to correct for carbonate dilution effects) covaries with C_{org} , but the transitions to high values are more abrupt. The carbonate content of the sediments is high, on average 77% (representative for the grey layers), varying between ~83% in white and ~70% in the beige layers (Fig. 4.3). Note that the shell flux and the carbonate content do not show the same pattern. The Sr/ $CaCO_3$ ratio (Fig. 4.3) is constant, but slightly higher in the top and bottom of the grey layers than in the middle of these layers. Aluminium (Fig. 4.5) correlates inversely with $CaCO_3$. The Ti/Al curve is of a duplet type, with low values in grey and high values in beige layers, the inverse of the 65°N summer insolation pattern (Fig. 4.5). Sedimentary Fe^* and S contents are nearly constant (Fig. 4.6). There is considerable scatter in the trace element data, but the contents of Ni and V (shown as ratios to Al; Fig. 4.7A) are higher in the grey layers than in the white and beige sediments.

Lido Rossello - The grey-white-beige-white cyclicity patterns at Lido Rossello are almost identical to those observed at Punta di Maiata, but the carbonate contents are slightly lower (Fig. 4.3). At Lido Rossello, Sr/ $CaCO_3$ ratios are higher, and peaks around the grey interval of cycle 30 are much more pronounced than they are at Punta di Maiata (Fig. 4.3). Except for the part above the brown layer, Fe^* and especially S are higher at Lido Rossello (Fig. 4.6). In this section $\delta^{13}C_{org}$ and opal have been analysed as well. These parameters do not show a correlation with the grey-white-beige-white lithologies (Fig. 4.4). The samples at 4.634 and 4.678 Ma show particularly negative $\delta^{13}C_{org}$ values. The presence of a constant amount of 1 wt% opal in these sediments is not accompanied by the presence of siliceous organisms, and may, therefore, be an artefact of the indirect method used for its analysis [Müller and Schneider, 1993].

The diatomite in cycle 29 stands out in the Lido Rossello profiles because it is characterized by the highest contents of C_{org} (up to 0.8%), opal (4%), Ba (900 ppm), Fe, S, V, As and Se (Figs. 4.4, 6 and 7). The lower, well-laminated part of the diatomite is clearly enriched

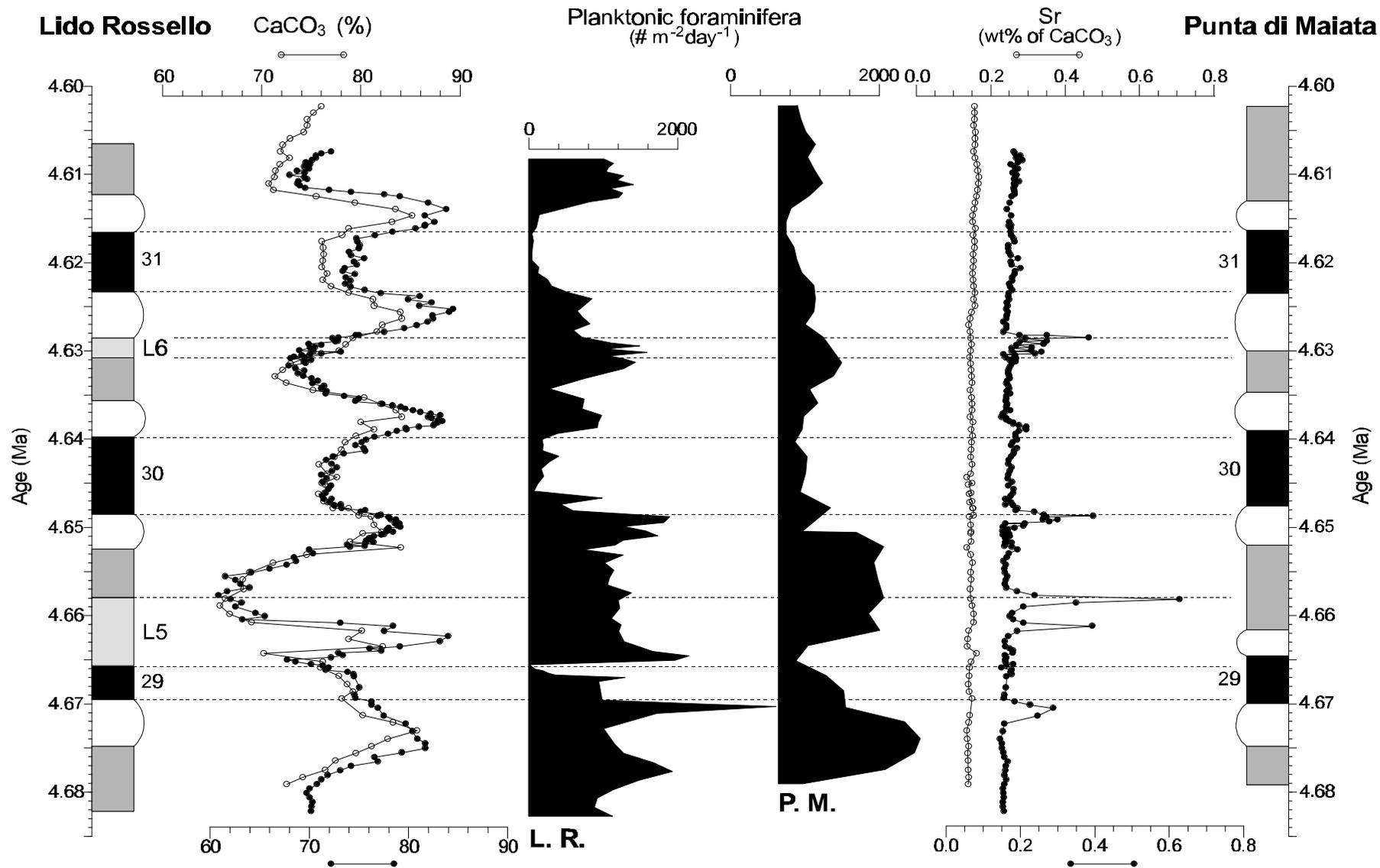


Figure 4.3 Profiles of CaCO_3 , flux of planktonic foraminifera, and Sr/CaCO_3 at Lido Rossello (closed symbols/L.R.) and Punta di Maiata (open symbols/P.M.). Note that there is a small offset in the horizontal axes of the CaCO_3 and Sr/CaCO_3 profiles.

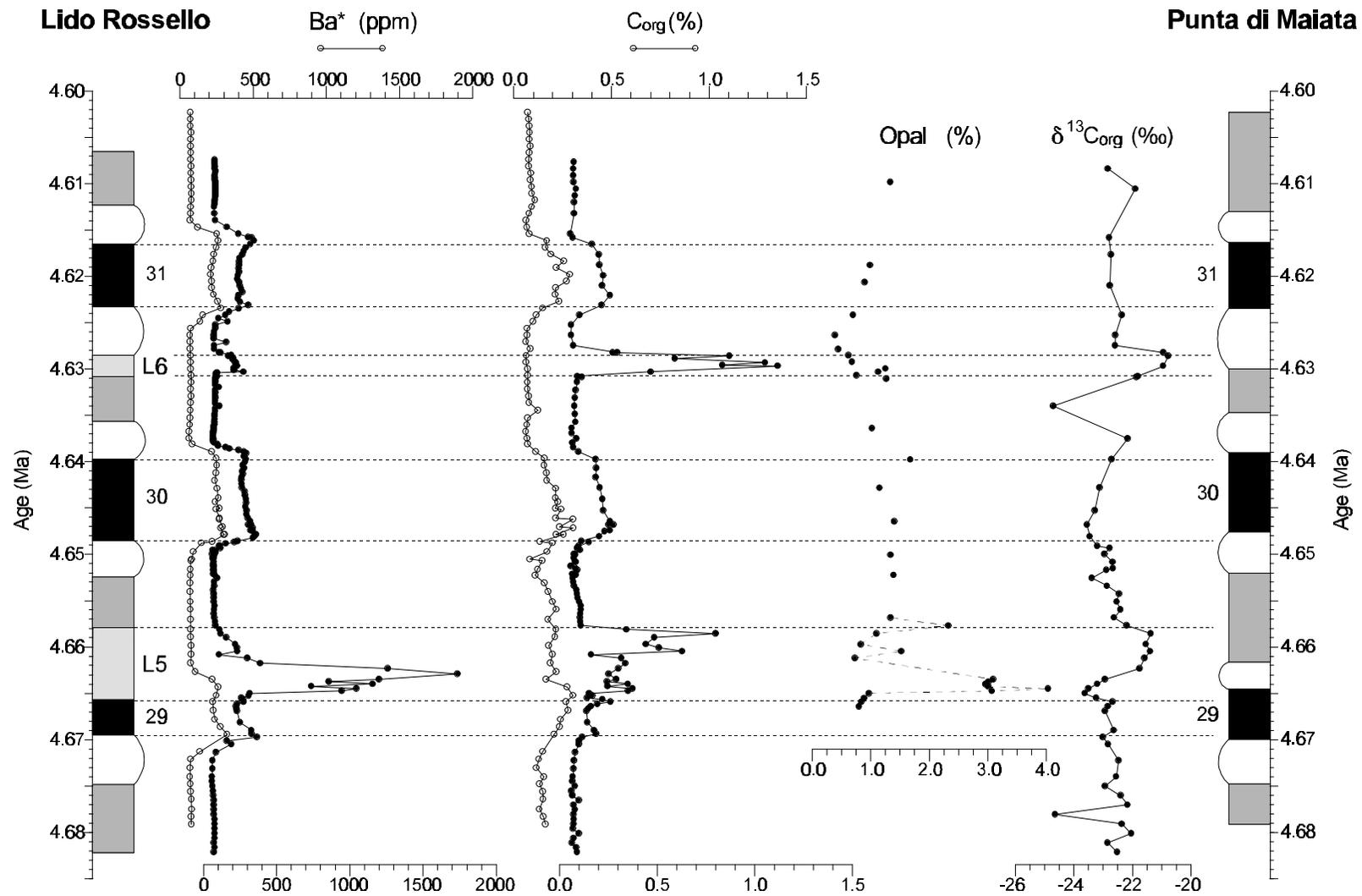


Figure 4.4 Profiles of Ba^* and C_{org} at Lido Rossello (closed symbols) and Punta di Maiata (open symbols), and opal and $\delta^{13}C_{org}$ at Lido Rossello only. Note the small offset in the horizontal axes of the Ba and C_{org} profiles.

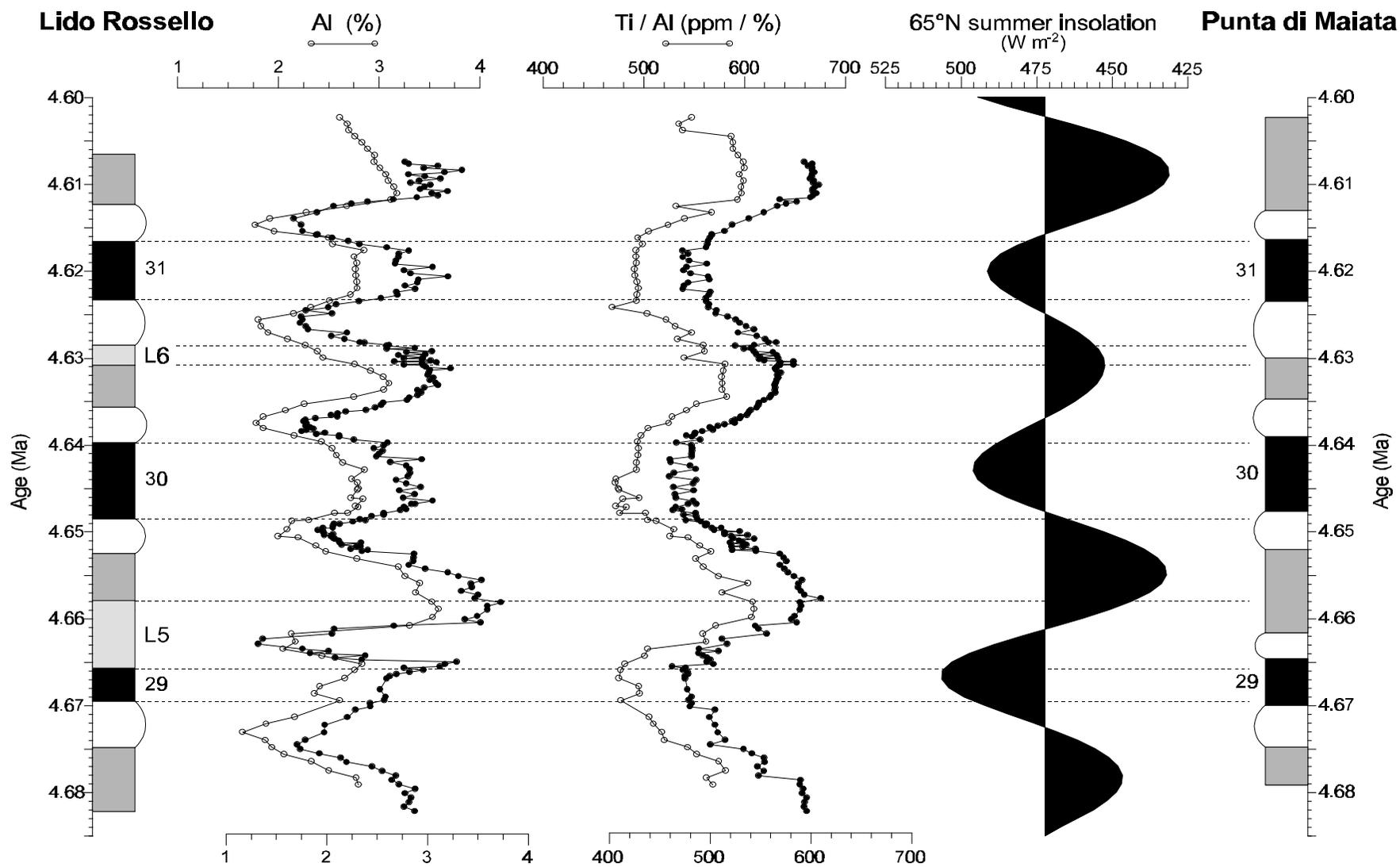


Figure 4.5 Profiles of Al and Ti/Al at Lido Rossello (closed symbols) and Punta di Maiata (open symbols) and 65°N summer insolation. Note that there is a small offset in the horizontal axes of the Al and Ti/Al profiles, and that the horizontal axis of the insolation curve is reversed.

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in opal, and is further characterized by highest Ba, trace element, Fe and S contents, but by intermediate C_{org} contents. In the upper part of the diatomite, lamination is less well developed, and highest C_{org} contents are reached. Additionally, the transition from the lower to the upper part is characterized by a shift from more to less negative $\delta^{13}C_{org}$ values (Fig. 4.4). The highest Sr/ $CaCO_3$ peaks are observed around the upper part of the diatomite. The brown laminite has C_{org} contents comparable to the diatomite, and Ba enrichments comparable to those in the grey layers. Opal and trace elements are not enriched in this layer.

Discussion

The observed differences in geochemical parameters in cycles 28-31 between Lido Rossello and Punta di Maiata appear to be related to the occurrence of the laminite and the diatomite in between the typical "Trubi" grey-white-beige-white sediment alternations. Here, the occurrence of the laminated intervals will be discussed in terms of the different models invoked to explain the carbonate cyclicity. In particular, we will focus on the relative importance of productivity, dilution, and carbonate dissolution processes.

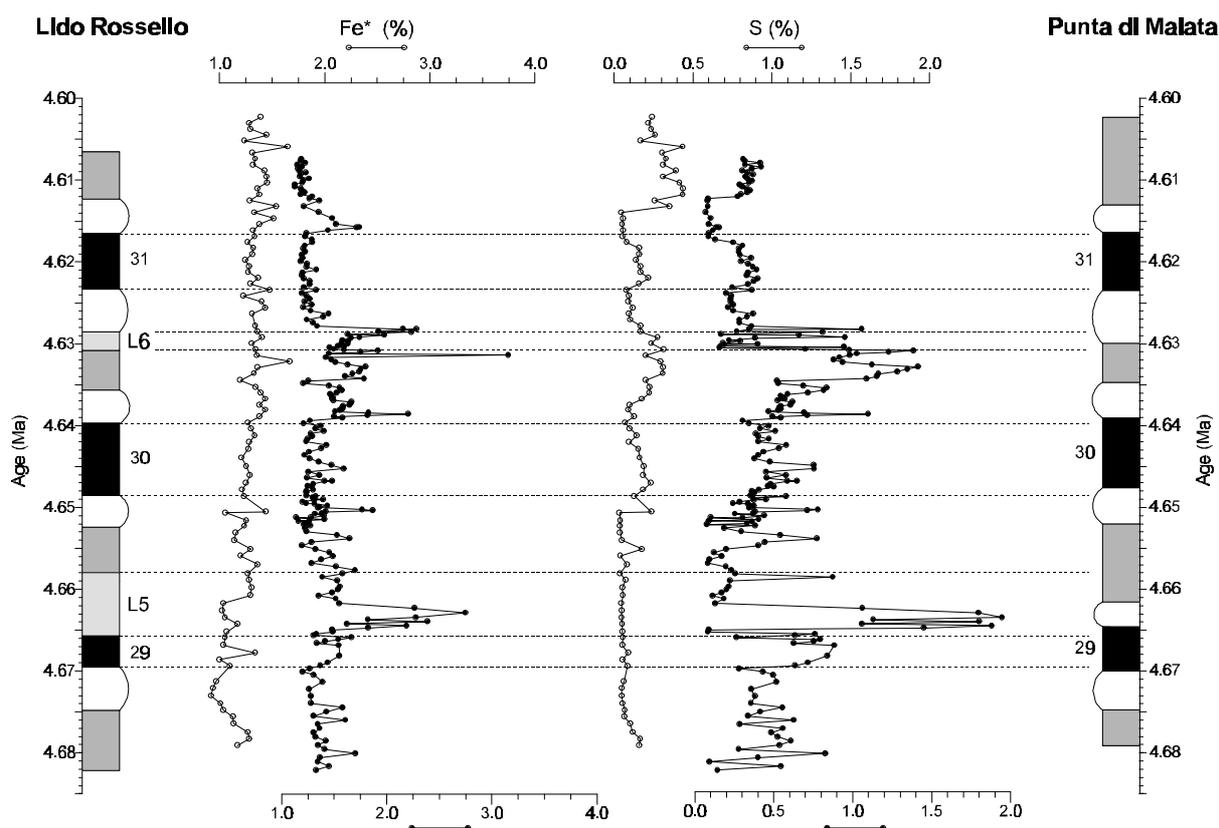


Figure 4.6 Profiles of Fe^* and S at Lido Rossello (closed symbols) and Punta di Maiata (open symbols). Note the small offset in the horizontal axes.

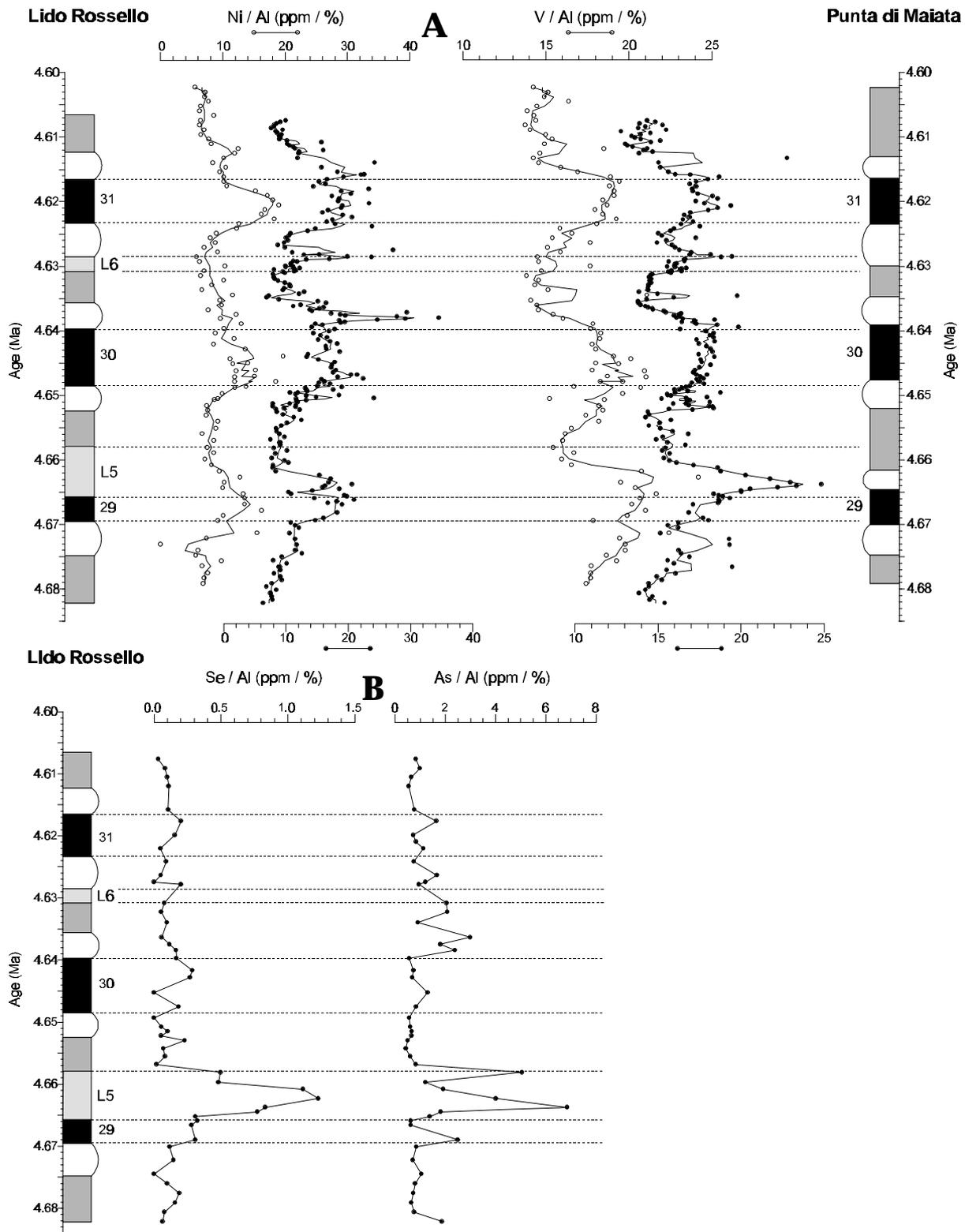


Figure 4.7 A: Profiles of Ni/Al and V/Al at Lido Rossello (closed symbols) and Punta di Maiata (open symbols). Solid lines are 3-point moving average curves. Note the offset in the horizontal axes. B: Profiles of Se/Al and As/Al at Lido Rossello.

Productivity

Sedimentary barium is considered a reliable palaeoproductivity indicator. It originates from barite formed in settling particles with microenvironments containing decaying organic matter [Dehairs *et al.*, 1980; Dymond *et al.*, 1992]. In the "Trubi" marls, Ba^* covaries well with C_{org} , both being higher in the grey layers, and low and constant in the beige and white layers. The existence of a constant relation between Ba^* and C_{org} is indicated by almost identical levels of these parameters in Lido Rossello and Punta di Maiata. The elevated Ba^* values in the grey layers and the laminated intervals at Lido Rossello, therefore, indicate that these layers were formed under conditions of increased productivity. This is confirmed by the oxygen and carbon stable isotope composition of different planktonic foraminiferal species, which indicate higher nutrient levels during deposition of these layers [Lourens *et al.*, *in prep.*]. Moreover, the high Ba contents within the diatomite at Lido Rossello are accompanied by enhanced opal contents and the occurrence of diatoms and radiolarians. These siliceous organisms are abundant in highly productive surface waters associated with, e.g., upwelling [Takahashi, 1986].

High Ba contents are accompanied by high planktonic foraminiferal shell fluxes in the laminated intervals at Lido Rossello, but by low shell fluxes in the grey layers (Fig. 4.3). Moreover, the shell flux is higher at Lido Rossello than at Punta di Maiata, whereas the Ba contents are almost identical. In other words, high surface water palaeoproductivity inferred from Ba contents and from planktonic shell fluxes are not always related. Similar low carbonate shell fluxes associated with high Ba contents in a grey layer of a younger carbonate cycle in the nearby Punta Piccola section (Fig. 4.1A) have been attributed to outcompetition of calcareous organisms by siliceous plankton and opportunistic foraminifera under high productivity conditions [Van Os *et al.*, 1994]. The absence of the expected diatoms and radiolarians in those grey layers has been explained by dissolution of opal [Van Os *et al.*, 1994]. The presence of a diatomite at Lido Rossello shows that siliceous organisms can be preserved in this setting. The absence of diatoms and radiolarians in the grey layers of Lido Rossello, therefore, suggests that they were never abundantly present in these layers. Furthermore, the presence of siliceous organisms apparently does not necessarily result in low carbonate shell fluxes. Therefore, the low shell flux in the grey layers is more likely to be explained by dilution with clays or dissolution of carbonates. We will now discuss these processes.

Dilution

Total sedimentation rate probably did not fluctuate much in the Lido Rossello and Punta di Maiata sections (Fig. 4.2). Nevertheless, variations in the relative contributions of the marine (carbonate) and terrestrial (clay) fractions may have occurred, leading to dilution effects.

A striking observation is the sinusoidal bipartite cyclicity of the Ti/Al curve (Fig. 4.5) in these quadripartite sedimentary cycles. This ratio is highest in the beige layers, and lowest in the grey intervals, and is, therefore, the opposite of the insolation curve (Fig. 4.5). Titanium is representative of heavy minerals, which are thought to be mainly transported to deep marine sediments by wind [*e.g.* Boyle, 1983; Shimmield, 1992]. Therefore, lower Ti/Al values indicate

a relatively higher contribution of river with respect to wind input. This explains the inverse correlation between the Ti/Al profile and the insolation curve: at precession minima (insolation maxima, grey layers) climate around the Mediterranean is relatively wet, resulting in high river and low wind input, whereas the reverse situation occurs at precession maxima (insolation minima, beige layers).

The relative changes in aeolian and fluvial input can be quantified using the Ti/Al curve once the Ti/Al value of wind-blown dust and of river particles is known. The Ti/Al value of recent dust storms in the Mediterranean area is 623 ± 75 (ppm/%; *Bonelli et al. [1996]; Güllü et al. [1996]*). The Ti/Al value of suspended matter in world rivers varies between 485 and 667 [*Gordeyev and Lisitsyn, 1978; Martin and Meybeck, 1979*]. However, this value will surely decrease with increasing distance from the river mouth because of preferential settling of heavy particles; indeed the lowest Ti/Al value in our samples (459) is below this river value. Assuming a Ti/Al ratio of 459 for the river end-member and 623 for the aeolian end-member in the Lido Rossello area, we can calculate the percentage aeolian input in the beige (86%), white (37%) and grey layers (13%). This implies that, compared with the white intervals, aeolian input is a factor 2.3 higher in the dryer beige interval, and fluvial input is a factor 1.4 higher in the wetter grey intervals. These values strongly depend on the assumed Ti/Al ratios of the end-members. Applying our selected values for river and aeolian input to top sediment (Ti/Al = 530) in box core UM 42 located in the Ionian Sea yields a present-day wind input of 80%, which is consistent with sediment trap data for this area [*Rutten et al., submitted*]. Still, the actual Pliocene Ti/Al aeolian dust and river Ti/Al values may have been considerably different from the applied values. Therefore, these numbers only give an idea of the relative changes in fluvial and aeolian input that may occur. The large differences between the grey, white and beige layers, however, suggest that the absolute amount of detrital input may have varied as well. Thus, dilution of carbonates by detrital material may have occurred, by aeolian input in beige, and by river input in grey layers. Evidence for such changes has also been inferred from palynological and grain size data [*De Visser et al., 1989*], from clay mineral data [*Foucault and Mélières, 1995*], and from strontium isotope data [*Blenkinsop et al., 1994*]. $\delta^{13}\text{C}_{\text{org}}$ values have also been used to determine the relative contributions of terrestrial and marine input [*Van Os et al., 1994*], but this parameter cannot be used for these purposes in a simple and straightforward manner in eastern Mediterranean sediments [*Chapter 7*].

The variations in total carbonate content observed in the sediments can be achieved by a 75% higher detrital flux in grey and beige compared with white intervals. Therefore, our estimated variations in detrital input may account for the lower total carbonate content in the beige layers, but not for the carbonate decrease in the grey intervals. Also, the variations in planktonic foraminiferal shell flux of more than $1,600 \text{ shells m}^{-2} \text{ day}^{-1}$ in beige and white layers to $200 \text{ shells m}^{-2} \text{ day}^{-1}$ in grey layers cannot be explained by dilution alone. As we already excluded productivity as the main cause for these variations, carbonate dissolution probably played a significant role as well.

Early diagenesis, redox levels and carbonate dissolution

Carbonate dissolution may be a factor contributing to the low carbonate contents and foraminiferal shell fluxes in the grey layers. The fact that foraminifera shells in these layers appear well preserved does not prove that dissolution did not occur: selective dissolution of microfossils is possible [Einsele, 1982; De Lange et al., 1994]. Also, the "clean" appearance of foraminifera in the grey layers compared with those in the beige and white layers which often have carbonate overgrowths, may indicate that shells were "etched" by acids in the organic-enriched layers, and that carbonate precipitated on shells in the organic-poor layers. Such processes may enhance the original differences in sedimentary carbonate content [Einsele, 1982] and contribute to the decoupling of foraminiferal shell flux and total carbonate content.

An indication that carbonate dissolution did in fact occur in the Lido Rossello and Punta di Maiata sediments comes from Sr/CaCO₃ peaks around some grey layers, the laminite, and the diatomite. Calcite contains about 0.14 wt% Sr, whereas aragonite, which is more soluble than calcite, contains ~ 1 wt% of this element [Milliman, 1974]. Carbonate dissolution, therefore, may result in mobilization of Sr, which can precipitate outside the zone of carbonate dissolution in Sr-rich carbonates, or as celestite (SrSO₄). Carbonates may be dissolved by acids released when organic matter is oxidized during diagenesis or weathering. In the grey layers, the diatomite, and the laminite, contents of redox-sensitive and chalcophilic trace elements as well as pyrite (inferred from Fe⁺ and S levels) are high, indicating that these layers have been formed under more oxygen-depleted conditions than the other sediments, and that sulphate reduction may have occurred during and after their deposition. During organic matter oxidation by sulphate reduction, bicarbonate addition causes supersaturation of calcite and aragonite [Morse and Mackenzie, 1990]. However, carbonate undersaturation occurs in the initial stages of sulphate reduction [Canfield and Raiswell, 1991]. Severe oxygen depletion and high levels of sulphate reduction during formation of the grey layers are unlikely because benthic foraminifera are present. Furthermore, bioturbation may have occasionally led to oxidation of pyrites and organic matter, producing additional acidity that may dissolve carbonates. The laminites, on the other hand, are devoid of benthos. Concluding, some carbonate may have dissolved during early diagenesis at least in the grey layers, but since pervasive sulphate reduction will result in carbonate supersaturation, this cannot have amounted to more than a few percent. Strontium mobilized by this mechanism may move outside the zone of sulphate reduction and precipitate when it encounters SO₄²⁻, giving rise to celestite peaks [Baker and Bloomer, 1988; Nijenhuis et al., 1996 (Chapter 2)]. Alternatively, carbonate dissolution took place during subaerial weathering. In this case, organic matter is not oxidized by sulphate, but by oxygen, and carbonate supersaturation does not occur [Canfield and Raiswell, 1991]. Mobilized Sr may subsequently move outside the zone where carbonate is undersaturated, and precipitate as Sr-rich carbonate, also giving rise to Sr/CaCO₃ peaks.

A remarkable difference between the Lido Rossello and Punta di Maiata sections is the presence of much higher Sr/CaCO₃ peaks in the former (in fact, these peaks are so small in Punta di Maiata that they cannot be discerned in Fig. 4.3). In the Punta di Maiata section, the

(calculated) Sr content of carbonates gradually increases from 0.14 wt% at the bottom to 0.16 wt% at the top, without variation with lithology. This would imply an increase of aragonite in the carbonate-fraction from 0% at the bottom to 2% at the top of the section (assuming 0.14 wt% Sr in calcite; 1 wt% in aragonite). At Lido Rossello, the Sr content of carbonates is slightly higher, 0.17 wt% on average, increasing from 0.16 in the bottom to 0.19 wt% (or 6% aragonite in carbonates) at the top of the section. We can calculate the amount of Sr mobilized, the associated dissolved carbonate, and the original Sr/CaCO₃ value from the Sr peaks around, for example, the grey layer of cycle 30, assuming that the Sr/CaCO₃ peaks only result from carbonate dissolution in that layer. The amount of dissolved carbonate corresponding to the mobilized Sr depends on whether aragonite (containing 1 wt% Sr) or calcite (containing 0.14 wt% Sr) dissolved. If we assume that only aragonite dissolved from the grey layer, then the Sr quantity in the spikes represents 4% of the carbonate originally present in that layer. In this case, 8% aragonite must have been present in the initial grey layer. If we assume that only calcite dissolved, then the Sr quantity in the spikes represents 14% of the carbonate originally present in the grey layer, and 6% aragonite was initially present. Obviously, the real amount of carbonate that dissolved must lie somewhere between these two values. Dissolution of 10-14% of the carbonate initially present in the grey layer can account for the difference in carbonate content between the white and the grey layers; dissolution of 4-10% is insufficient but may have emphasized the differences between the grey and white layers. It may also account for the clean appearance of foraminifera in the grey layers and the overgrowths in the white intervals (precipitation of dissolved carbonate). Concluding, some grey layers were originally richer in aragonite, which subsequently dissolved when organic matter was oxidized by sulphate reduction or during diagenesis.

Sulphate reduction may result in barite dissolution [e.g. De Lange et al., 1994]. The M-shaped Ba* profiles around the grey layers (Fig. 4.4) indicate that some Ba mobilization took place. The diatomite constitutes the only interval in these sediments where the C_{org} and Ba* profiles are decoupled: in the upper part, highest C_{org} contents are reached whereas relatively little Ba is present, and in the lower part maximum Ba contents are accompanied by C_{org} contents only slightly higher than in the grey intervals. Barium may have migrated outside the upper part of the diatomite and precipitated in the lower part, enhancing the Ba productivity signal there. However, if sulphate reduction continued in the organic rich layer after deposition of younger, organic-poor strata, a mobilization peak would also be expected above the diatomite. Such a Ba spike is not found. Thus, the relatively low Ba content in the upper diatomite is probably not the result of barium mobilization. A comparison with the brown layer shows that the Ba and C_{org} of this layer are very similar to those of the upper diatomite. Perhaps then, it is not the Ba content of the upper diatomite that is relatively low, but that of the lower part that is relatively high. The highest opal contents also occur in the lower diatomite, and Ba may particularly be associated with diatoms [Bishop, 1988]. In anoxic hypersaline basins in the Mediterranean, bottom waters contain increased silica contents [De Lange et al., 1990], and well-preserved opaline species are encountered [Erba, 1991]. During deposition of the diatomites,

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the Lido Rossello area may have been similar to such an anoxic basin, where a build-up of silica concentration at times of high productivity resulted in preservation of diatoms and associated barium. Redox-sensitive trace elements are enriched in the lower diatomite, confirming stronger oxygen depletion. In the Lido Rossello section, up until the brown layer, the pyrite content is higher than at Punta di Maiata, indicating that sulphate reduction may have been more persistent in this interval. Additionally, there is a slump level directly below the first of the six diatomites [Brolsma, 1978], possibly indicating the formation of a small basin. The presence of a depression at Lido Rossello may explain some of the features and the local occurrence of the diatomites, but it cannot account for all characteristics. For example, Lourens *et al.* [in prep.] showed that there are distinct changes in the water column characteristics at times of diatomite formation, which do not occur at Punta di Maiata. Also, it cannot be explained why the occurrence of diatomites is not restricted to a specific part of the cycles, e.g. only to the high productivity grey layers.

Weathering

Whereas variations of $\delta^{13}\text{C}_{\text{org}}$ with lithology are lacking in the grey-white-beige-white sequence, there is a distinct shift to lighter values in the lower, opal-rich part of the diatomite, and a shift to heavier values in the upper, C_{org} -rich part. The laminite in cycle 30 also shows heavier $\delta^{13}\text{C}_{\text{org}}$. These heavier values may result from a contribution of organic matter derived from diatoms, which is 3-4‰ heavier in $\delta^{13}\text{C}_{\text{org}}$ than dinoflagellate and coccolithophore organic matter [Tyson, 1994]. Additionally, planktonic archaea found in the laminite also have relatively heavy $\delta^{13}\text{C}_{\text{org}}$ values of around -20‰ [Hoefs *et al.*, 1997]. The highest abundance of diatoms in the lower part of the diatomite is accompanied by lighter instead of heavier $\delta^{13}\text{C}_{\text{org}}$ values. Prasinophyceae are characterized by a particularly light $\delta^{13}\text{C}_{\text{org}}$ of -28.6‰ [Prauss and Riegel, 1989], but these are present in similar quantities in the upper and lower part of the diatomite [Lourens *et al.*, in prep.]. $\delta^{13}\text{C}_{\text{org}}$ is often interpreted in terms of marine/terrestrial input, and this would mean that the diatom-rich interval would be characterized by relatively more terrestrial organic matter. This is highly unlikely and fits in the pattern that this classic interpretation does not hold in the Mediterranean [Chapter 7]. An alternative interpretation is that the light values in the lower diatomite and the lower C_{org} contents are the result of organic matter oxidation during weathering. Oxidation after uplift might be stronger in this part because of better developed lamination, providing a pathway for fluids containing oxidants. A similar effect of weathering on $\delta^{13}\text{C}_{\text{org}}$ has been reported in a laminated part of the nearby Punta Piccola section [Van Os *et al.*, 1996]. The light values at 4.634 and 4.678 Ma (Fig. 4.4) may also result from weathering in less fresh samples. If organic matter oxidation did indeed occur in the lower diatomite, Sr-mobilization peaks resulting from carbonate dissolution would be expected around this layer. A Sr/ CaCO_3 peak is observed above this layer, but not below; since the upper Sr peak only consists of one sample, however, the lower peak may have been missed because of insufficient sample density (3-4 cm).

Conclusions

- Although Ba indicates that palaeoproductivity in the quadripartite cycles was highest in the grey layers, planktonic foraminiferal shell fluxes are higher in the white and beige layers. There is no direct evidence for an increase in diatom/radiolarian productivity in the grey layers.
- Ti/Al profiles indicate that significant changes in the relative contribution of aeolian and fluvial detrital matter occurred. A 75% relative increase in detrital input in the grey and beige layers with respect to the white layers may explain the decrease in total carbonate content, but cannot account for the low shell flux in the grey layers.
- Carbonate dissolution occurred in some of the grey layers (4-14% of the carbonate initially present) and in the laminites, resulting in Sr/CaCO₃ peaks around these layers.
- There may have been a local depression at Lido Rossello during formation of the laminated intervals at Lido Rossello. Stagnant bottom water in such a basin can account for high opal and barium contents in these layers.

Chapter 5

Sulphidic eastern Mediterranean surface waters during Pliocene sapropel formation

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Abstract - Sapropels (organic matter rich layers) are common in the eastern Mediterranean Neogene sedimentary record. Their formation is thought to have been initiated by climate-related enhanced organic matter productivity [Rossignol-Strick *et al.*, 1982; Calvert *et al.*, 1992; Rohling, 1994] and/or by increased organic matter preservation due to oxygen depletion in more stagnant bottom waters [Rossignol-Strick *et al.*, 1982; Rohling, 1994]. Exceptionally organic matter rich Pliocene sapropels were recovered during the recent Leg 160 of the Ocean Drilling Program [Emeis *et al.*, 1996]. Here we report that these sapropels contain molecular fossils derived from photosynthetic green sulphur bacteria, indicating that during Pliocene sapropel formation euxinic (sulphidic) conditions in the water column extended into the photic zone. The sapropels also have a high content of trace metals, likely due to the efficient scavenging of these metals by sulphides in the euxinic water column. In addition, the abundance of pyrite and its isotopic composition are consistent with iron sulphide formation in the water column during sapropel deposition. This study provides the first evidence for basin-wide water column euxinia over substantial periods during Pliocene sapropel formation in the eastern Mediterranean. Palaeoflux calculations indicate that increased organic matter productivity was an important factor in generating and sustaining these euxinic conditions.

This chapter has been accepted for publication in *Nature*.

Material and methods

Geochemical analyses were performed on seven Upper Pliocene sapropels obtained from several eastern Mediterranean ODP Leg 160 sites (Table 5.1; Fig. 5.1). The sediment samples (0.5-1 cm resolution) were freeze-dried and ground. Organic carbon (C_{org}) contents were determined with a CNS analyser after carbonate removal with 1M HCl [Nijenhuis *et al.*, 1998]. Sediments were dissolved in $HClO_4$ - HNO_3 -HF; dried residues were dissolved in 1M HCl for analysis with ICP-AES (Mo, Ni, V, Ba), Zeeman AAS (Cd), and FIAS (Se) [Nijenhuis *et al.*, 1998]. Pyritic sulphur (S_{pyr}) was extracted by Cr(II) reduction [Passier *et al.*, 1996]. Evolved sulphide was trapped in 1M NaOH and measured polarographically, or trapped as Ag_2S and measured for stable sulphur isotope composition ($\delta^{34}S_{pyr}$) by C-irmMS relative to the V-CDT standard [Passier *et al.*, 1998]: $R = {}^{34}S/{}^{32}S$, $\delta^{34}S_{pyr}(\text{‰}) = 1000 \times [(R_{pyr}/R_{V-CDT}) - 1]$. Organic compounds were extracted with methanol/dichloromethane. Elemental sulphur was removed with activated Cu. Apolar fractions were isolated on activated Al_2O_3 , and analysed by GC and GC-MS [Bosch *et al.*, 1998].

Results and discussion

Astronomical tuning of the sapropels revealed that they are time-equivalent to three sapropels in the Punta Piccola section (Sicily, Italy), i-292, i-290, and i-282, and sapropel i-176 of the Vrica and Singa sections (Calabria, Italy), which have ages of 3.058, 3.036, 2.943, and 1.808 Ma, respectively [Lourens *et al.*, 1996a]. The sapropels are distinct, dark grey to black sediment layers

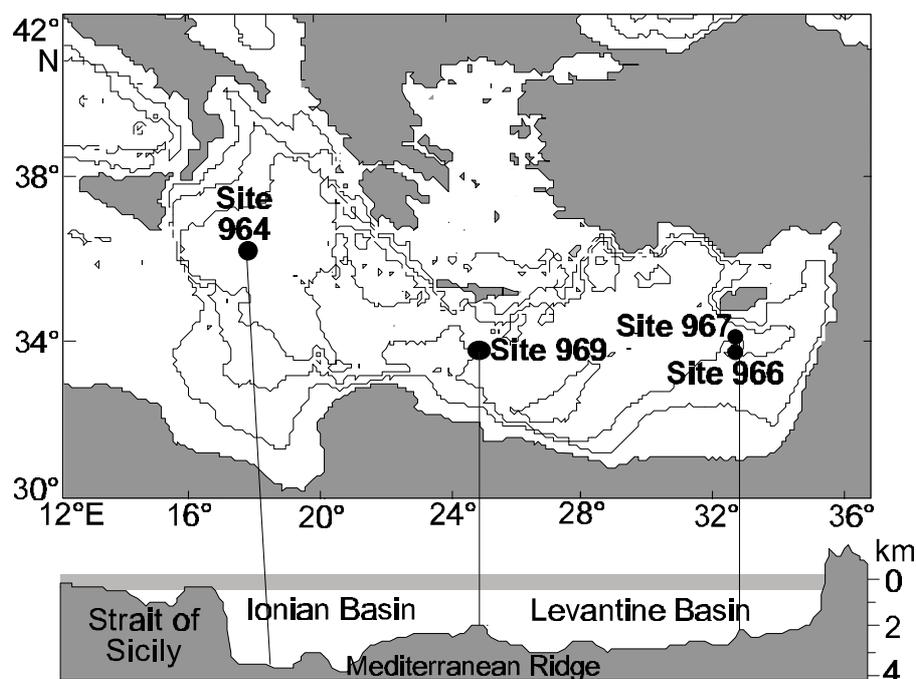


Figure 5.1 Locations of the drilling sites in the eastern Mediterranean.

with a thickness ranging from centimetres to decimetres, embedded in light grey to brown

Table 5.1 The sapropels studied, their age, water depth, depth in sediment, average trace element and C_{org} contents and enrichment factors with respect to average non-sapropel sediments (in brackets). C_{org} and pyritic sulphur contents, stable sulphur isotopic composition of pyrite and abundance of isorenieratene derivatives (ID: ++ abundant; + trace; - not detected) of specific subsamples.

sapropel code	sapropel position (cm) in ODP sample coding Position subsample (cm)	Age (Ma)	Water depth (m)	Depth (mbsf ¹)	Cd (ppm)	Mo (ppm)	Ni (ppm)	Se (ppm)	V (ppm)	C_{org} (wt%)	AR ³ (gCm ⁻² yr ⁻¹)	Ba (ppm)	S_{pyr} (wt%)	$\delta^{34}S_{pyr}$ (‰)	ID
i-176	160-967C-6H-2, 30-44 36-37.7	1.808	2553	48.4	n.d. ²	98 (32)	190 (2)	13 (121)	430 (5)	5.0 (37) 7.4	1.8	n.d. ²	5.8	-41.4	++
i-282A	160-964D-10H-1, 103-110 107.5-108	2.943	3660	80.2	34 (130)	195 (16)	317 (9)	29 (131)	1317 (13)	15.3 (149) 21.1	6.2	1603 (13)	2.4	-36.1	+
i-282B	160-967C-8H-4, 114-130 122.5-123	2.943	2553	72.2	3 (45)	202 (6)	183 (4)	22 (52)	555 (6)	8.4 (63) 14.5	3.4	1029 (8)	2.8	-37.4	+
i-282C	160-969E-6H-6, 27-39 32-33	2.943	2201	50.7	31 (270)	407 (26)	299 (4)	24 (17)	1937 (19)	17.7 (81) 23.5	7.1	1316 (11)	2.1	-42.0	++
i-290	160-964E-6H-5, 77-103 99-100	3.036	3661	82.9	6 (61)	45 (6)	291 (9)	n.d. ²	304 (5)	5.0 (76) 23.6	2.0	n.d. ²	3.6	-39.5	+
i-292A	160-966C-5H-3,4, 148-13 10-11	3.058	926	42.6	1 (9)	133 (21)	101 (3)	n.d. ²	340 (4)	6.0 (24) 11.6	1.2	n.d. ²	1.1	-39.1	-
i-292B	160-967C-8H-6, 40-57 46-47	3.058	2553	74.5	8 (51)	224 (18)	174 (4)	n.d. ²	918 (7)	13.2 (64) 20.3	5.3	n.d. ²	1.9	-37.3	+

¹ mbsf: metres below seafloor

² n.d.: no data

³ AR= accumulation rate of organic carbon = $(C_{org}[\text{wt}\%] \times \text{sediment accumulation rate} [\text{cm kyr}^{-1}] \times \text{dry density} [\text{g cm}^{-3}]/10)/n$, n : number of samples in the sapropel.

hemipelagic carbonate oozes. Fine lamination of the sapropels indicates the absence of bioturbation and, therefore, bottom water oxygen depletion [Emeis *et al.*, 1996]. The sapropels contain considerable amounts of isorenieratene derivatives, trace metals and pyrite (Table 5.1; Fig. 5.2). The occurrence of isorenieratene derivatives in the sapropels analysed indicates a periodic overlap of the photic and euxinic zones during sapropel formation. Isorenieratene is a carotenoid believed to be biosynthesized exclusively by the brown strain of photosynthetic green sulphur bacteria (Chlorobiaceae) [Liaaen-Jensen, 1978]. Since Chlorobiaceae are phototrophic and require free sulphide as an electron donor to fix CO₂, their occurrence is restricted to euxinic waters in the photic zone. These bacteria fix CO₂ in the reverse tricarboxylic acid cycle, resulting in a biomass anomalously enriched in ¹³C [Quandt *et al.*, 1977]. The isorenieratene derivatives are indeed 13-14‰ enriched in ¹³C relative to algae-derived biomarkers, which confirms that they originate from green sulphur bacteria [Summons and Powell, 1986; Kohnen *et al.*, 1992; Sinnighe Damsté *et al.*, 1993; Hartgers *et al.*, 1994]. The presence of ¹³C-enriched isorenieratene-derived compounds in the Pliocene sapropels, therefore, provides strong evidence that the lower photic zone contained sulphide over substantial periods of time during sapropel formation. This situation is comparable to the present-day euxinic Black Sea, where green sulphur bacteria occur at the lower photic zone [Repeta *et al.*, 1989] and isorenieratene derivatives are found in the sediment [Sinninghe Damsté *et al.*, 1993].

Euxinic conditions in the water column during sapropel deposition explain the exceptionally high contents in the sapropels of trace metals (Table 5.1; Fig. 5.2) scavenged by organic matter and by metal sulphide precipitation. These trace metal enrichments strongly exceed the maximum amount that can be supplied to the sapropels by plankton or diagenesis [Nijenhuis *et al.*, 1998]. Therefore, scavenging by metal sulphide precipitation under euxinic conditions, which is also thought to have played an important role in transferring trace metals to similarly enriched Cretaceous black shales [Arthur *et al.*, 1990], must have been operative during formation of the studied sapropels.

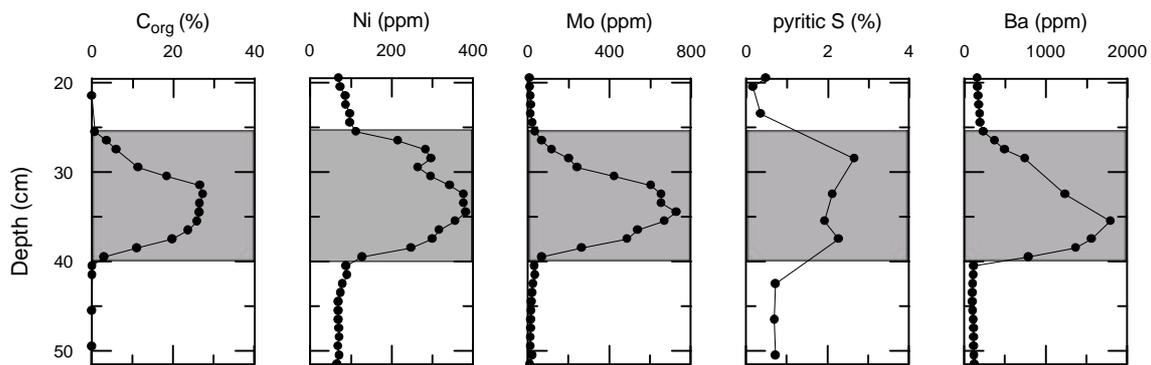


Figure 5.2 Content versus depth profiles of C_{org} , Ni, Mo, pyritic S and Ba in and around the ODP sapropel in core section 160-969E-6H-6; the shaded area indicates the position of the sapropel.

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Pyrite (FeS_2) enrichments in the sapropels (Fig. 5.2; Table 5.1) are attributed to organic matter decomposition via microbial sulphate reduction and subsequent reaction of the reduced sulphur with iron during sapropel formation [Passier *et al.*, 1996; Passier *et al.*, 1998]. Supply of detrital iron and iron diffusion towards the sapropels cannot adequately explain the amount of pyrite found in the sapropels. The integrated pyritic iron content of sapropel i-282C is 6 mmol cm^{-2} , whereas the supply of detrital iron and upward iron diffusion from underlying sediments during sapropel formation is only 2 mmol cm^{-2} (calculated at Site UM26 [Passier *et al.*, 1997] near Site 969). A euxinic water column provides an additional iron source because of iron-sulphide formation in the water column. Additional iron for this iron-sulphide formation can be supplied after its liberation from (hydr)oxides at the margins of a euxinic basin in response to a fluctuating oxycline, as occurs at present in the Black Sea [Kempe *et al.*, 1991; Canfield *et al.*, 1996]. Isotopic compositions of pyritic sulphur ($\delta^{34}\text{S}_{\text{pyr}}$) are consistent with a euxinic water column. Values of $\delta^{34}\text{S}_{\text{pyr}}$ in the sapropels are about -40‰ (Table 5.1), indicating a depletion by 60‰ compared with seawater sulphate (present-day value: $+20.6\text{‰}$ [Passier *et al.*, 1996]). To achieve sulphur isotopic fractionations between sulphate and pyrite of this magnitude, sulphate reduction must proceed under continuous supply of abundant dissolved sulphate (open system) and must be followed by further ^{34}S depletion in the sulphide pool by reoxidation and disproportionation processes in the sulphur cycle [Canfield and Thamdrup, 1994]. In the present-day Black Sea [Fry *et al.*, 1991; Canfield and Thamdrup, 1994], sulphide reoxidation occurs at the chemocline, which results in lighter isotopic compositions of sulphide in the euxinic water column. Directly below sapropels (e.g. Fig. 5.2), pyrite is enriched relative to normal organic matter poor marine sediments. This indicates that sulphide diffused into the organic matter poor sediment below as a result of iron limitation for pyrite formation within the sapropel [Passier *et al.*, 1996; Passier *et al.*, 1998].

The combined observations (presence of ^{13}C -rich isorenieratene, enrichments of trace metals and ^{32}S -rich pyrite, and lamination of the sapropels) indicate that the eastern Mediterranean water column must have been euxinic from the bottom up into the lower photic zone over substantial periods during Pliocene sapropel formation. This is the first evidence for such extreme oxygen depletion during sapropel deposition. Both increased primary productivity (leading to a higher oxygen demand) and the development of more stagnant conditions (resulting in reduced oxygen replenishment of bottom waters) have been proposed to cause sapropel formation [Rossignol-Strick *et al.*, 1982; Calvert *et al.*, 1992; Rohling, 1994] and are probably related to the climate-induced [Rossignol-Strick, 1985; Hilgen, 1991a] increase in freshwater inputs from the African and European continents [Rossignol-Strick *et al.*, 1982; Rossignol-Strick, 1985; Rohling, 1992].

Did primary productivity increase during Pliocene sapropel formation? The euxinic eastern Mediterranean and the present-day euxinic Black Sea have similar depths, and the sapropelic organic matter of both basins is predominantly of marine origin [Emeis *et al.*, 1996; Arthur *et al.*, 1994]. Thus, applying the euxinic preservation efficiency observed in the modern

deep Black Sea (at maximum 5% of the primary produced organic matter [Arthur *et al.*, 1994]) to the present-day average primary productivity in the open eastern Mediterranean ($26 \text{ gC m}^{-2} \text{ yr}^{-1}$ [Béthoux, 1989]) we find a maximum C_{org} accumulation rate of $1 \text{ gC m}^{-2} \text{ yr}^{-1}$. In contrast, the C_{org} accumulation rate in Pliocene sapropels (Table 5.1) calculated from the C_{org} contents and sediment properties [Emeis *et al.*, 1996] is $4 \text{ gC m}^{-2} \text{ yr}^{-1}$ on average, illustrating that primary productivity must have increased significantly during Pliocene sapropel formation.

The enrichment of barium (Table 5.1; Fig. 5.2) in the sapropels also strongly points to a productivity increase. Sedimentary barium may serve as a palaeoproductivity indicator because it originates from barium uptake into barite in decaying organic matter associated with primary productivity in the surface waters [Dymond *et al.*, 1992; Falkner *et al.*, 1993; François *et al.*, 1995]. Sapropel i-282C has an intermediate barium accumulation compared with its lateral equivalents i-282A and i-282B (Table 5.1; Fig. 5.1), thus the barium enrichment is representative for the average deep basin, minimizing possible sediment focussing effects. The barium profile (Fig. 5.2) is smooth, so no dissolution and remobilization of barite took place after burial, indicating that the barium enrichment is original. This is because pore water sulphate was never depleted, which is also indicated by $\delta^{34}\text{S}_{\text{pyr}}$ [Passier *et al.*, 1998]. Because the barium enrichment in i-282C is original and representative, barium contents can be used to calculate export palaeoproductivity (the part of the primary productivity of organic matter exported from the photic zone to deep waters) via an empirical formula [François *et al.*, 1995], yielding an average export productivity of $46 \text{ gC m}^{-2} \text{ yr}^{-1}$ during sapropel deposition. Some limitations are associated with this calculation. The formula was determined for the oxic ocean [François *et al.*, 1995], which may not be comparable to the eastern Mediterranean during sapropel deposition. However, the upper part of the photic zone, where barite predominantly forms [Dymond *et al.*, 1992; Falkner *et al.*, 1993; François *et al.*, 1995], remained oxic. Also, barite accumulation was not limited by sulphate, because the concentration of sulphate in seawater is so high that it was not significantly depleted by sulphate reduction in the water column, which is also indicated by $\delta^{34}\text{S}_{\text{pyr}}$ [Passier *et al.*, 1998]. Barite formation related to productivity has been shown to occur in euxinic basins [Falkner *et al.*, 1993] and in oxygen minimum zones [Dean *et al.*, 1997] as well as in the open ocean [Dymond *et al.*, 1992; François *et al.*, 1995]. Euxinic conditions may, however, lead to reduced formation and poorer preservation of barite [Dymond *et al.*, 1992; Falkner *et al.*, 1993; François *et al.*, 1995], which means that the calculated export productivity is a minimum value.

Could the extreme oxygen depletion in the water column result from the observed productivity increase? This oxygen depletion can be estimated from the average export productivity calculated from sedimentary barium (e.g. $46 \text{ gC m}^{-2} \text{ yr}^{-1}$ for sapropel i-282C) and the amount of organic matter that accumulated in the sediment ($7 \text{ gC m}^{-2} \text{ yr}^{-1}$ for sapropel i-282C), corrected for the part of the organic matter mineralized by microbial sulphate reduction. Sulphate reduction produces 1 mole of sulphide for every 2 moles of organic matter mineralized ($2 \text{ "CH}_2\text{O" + SO}_4^{2-} \rightarrow \text{H}_2\text{S} + 2 \text{ HCO}_3^-$). Any sulphide that escaped from burial was reoxidized at the chemocline, so part of the organic matter was indirectly mineralized by

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oxygen. The sulphide buried represents the part of organic matter truly mineralized by sulphate reduction; in sapropel i-282C this is 20% of the originally accumulated C_{org} . The oxygen demand in the water column during sapropel deposition calculated from carbon fluxes is $1 \cdot 10^{13}$ mole O_2 yr^{-1} , assuming that 138 moles of O_2 are required for 106 moles of “ CH_2O ” [Béthoux, 1989] and that sapropels occur in 80% of the eastern Mediterranean (excluding the area shallower than 200 m). The estimated present-day oxygen supply to the eastern Mediterranean through deep water formation in the Levantine and Adriatic basins is also $1 \cdot 10^{13}$ mole O_2 yr^{-1} [Béthoux, 1989]. In the present-day eastern Mediterranean (export production is 6 to 12 gC m^{-2} yr^{-1} ; [Béthoux, 1989]), the amount of oxygen used for organic matter decomposition is less than the amount supplied, resulting in an oxic water column [Béthoux, 1989]. In contrast, our estimates indicate that the oxygen demand resulting from increased export production of organic matter during Pliocene sapropel formation is of the same order of magnitude as the present-day oxygen supply, meaning that oxygen in the water column may have become depleted so that sulphate reduction led to euxinic conditions. The calculated oxygen demand is a good first order estimate, based on the average deep eastern Mediterranean. Variations in the content, composition and burial efficiency of organic matter, especially across the basin margins, however, may affect the oxygen demand.

These palaeoflux calculations suggest that water column euxinia could have been achieved even when continued circulation supplied oxygen to deep waters. The trace metal budget for the studied Pliocene sapropels strongly favours continued circulation during deposition, since this would have provided an extra input of trace metals, required to account for the observed amounts of trace metals in the sapropels. For example, the total amount of nickel sequestered in sapropel i-282 (average of Sites 964, 967, and 969), assuming 80% coverage, is $8 \cdot 10^{13}$ g. The water column in a fully stagnant eastern Mediterranean, however, contains only $\sim 2 \cdot 10^{12}$ g (ca. 3%) [Nijenhuis et al., 1998] and rivers, assuming global average river composition and a present-day discharge, can supply only $\sim 8 \cdot 10^{12}$ g (i.e. $\sim 10\%$) during sapropel formation. Unfortunately, exact river discharges of trace metals during sapropel formation are unknown. A tenfold increase in river water discharge during sapropel formation, however, is highly unrealistic [Rossignol-Strick, 1989; Rohling, 1994]. Consequently, it is unlikely that Ni discharge increased to such an extent. Budgets for other trace metals in sapropel i-282 and i-292 yield comparable results [Nijenhuis et al., 1998].

Conclusions

Our results demonstrate that during Pliocene sapropel formation euxinia reached up into the photic zone. Our calculations indicate that increased productivity was an important factor in establishing this condition, while continued circulation was essential for the delivery of trace metals to the sapropel. Therefore, stagnation of the water column was not as important as generally believed. These findings shed a completely new light on sapropel formation.

Sulphidic eastern Mediterranean surface waters during Pliocene sapropel formation

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Chapter 6

Organic matter and trace element rich sapropels and black shales: A geochemical comparison

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Abstract - A distinct Pliocene eastern Mediterranean sapropel (i-282) recovered from three Ocean Drilling Program (ODP) Leg 160 sites, has been investigated for its organic and inorganic composition. This sapropel is characterized by high organic carbon (C_{org}) and trace element contents, and the presence of isorenieratene derivatives. The latter indicates that the base of the photic zone was sulphidic during formation of the sapropel. Combined with evidence of bottom water anoxia (preservation of laminae, high redox-sensitive trace element contents, and the abundance and isotopic composition of pyrite) this leads to the tentative conclusion that almost the entire water column may have been euxinic. This anoxia resulted from high productivity and not from stagnation, because an approximation of the trace element budget during sapropel formation shows that water exchange with the western Mediterranean is needed. Entire water column euxinia has been suggested earlier for several black shales. With regard to the depositional environment and the C_{org} content, however, only the Caenomanian/Turonian Boundary Event (CTBE) black shales appear to be comparable to this sapropel. The proposed trace element removal mechanism of scavenging and (co)precipitation in an anoxic water column, is thought to be similar for both types of deposits. The ultimate trace element source for the sapropel, however, is seawater, whereas it is hydrothermal and fluvial input for the CTBE black shale (because of the larger temporal and spatial distribution of that event). Nonetheless, the C_{org} -rich eastern Mediterranean Pliocene sapropel discussed here may be considered to be a younger analogue of CTBE black shales. As the type euxinic basin, the Black Sea is a contemporaneous analogue, which has, however, low sedimentary C_{org} and trace element contents because of local conditions.

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Introduction

Organic matter rich marine sediments (sapropels) in the eastern Mediterranean have been reported as possible younger analogues, or precursors, of C_{org}-rich black shales [Calvert, 1983; Thomson *et al.*, 1995]. The commonly used definition of a (marine) sapropel is: 'a discrete layer, greater than 1 cm in thickness, set in open marine pelagic conditions and containing greater than 2% C_{org} by weight' [Kidd *et al.*, 1978]. The term black shale is less precisely defined and is applied to any fine-grained, dark-coloured sediment (usually rich in organic matter). Thus, sapropels can be considered a specific subclass of black shales, although it is as yet unknown in how far these deposits have been formed under comparable conditions.

Two mechanisms have been proposed to explain C_{org} enrichment in both sapropels and black shales: (1) increased production of marine and/or enhanced input of terrestrial organic matter, and (2) improved preservation of organic matter (because of an anoxic water column, expanded oxygen minimum zone, or higher sedimentation rates). However, the proposed formation models for sapropels and black shales differ in time control, basin physiography, and scale of the events. It has been demonstrated that the cyclic occurrence of Mediterranean sapropels between organic matter poor, bioturbated sediments correlates to variations in the eccentricity of the Earth's orbit and the obliquity and precession of the Earth's axis [Rossignol-Strick, 1983; Langereis and Hilgen, 1991; Lourens *et al.*, 1996a]. At Mediterranean latitudes, the precession has the largest effects on climate. Since one precession cycle lasts 21,000 years on average, that is also the presumed duration of one sapropel-homogeneous cycle. Cyclicity in black shales has also been reported [Arthur *et al.*, 1990; De Boer, 1991; Wetzel, 1991; Wignall, 1994], but a precise time control on the formation of those sediments is often lacking [Wignall, 1994]. Black shales have been found in environments ranging from open marine to shallow shelves, whereas Mediterranean sapropels were formed in a satellite basin separated from the open marine environment by a shallow sill (the Strait of Gibraltar). In fact, most sapropels only occur in the eastern Mediterranean, which in its turn is separated by shallow sills from the western Mediterranean (Strait of Sicily) and the Black Sea (Bosporus). Such a setting is more sensitive to inhibition of circulation and water column stratification than an open marine setting. Finally, eastern Mediterranean sapropel formation occurred in a relatively small area, whereas some black shales are thought to have formed in extensive parts of the Atlantic and the equatorial Pacific during so-called oceanic anoxic events (OAEs [Arthur *et al.*, 1990]). Alternative models for black shale formation do not invoke OAEs, but only increased productivity [Pedersen and Calvert, 1990].

Contradictory to the suggestion implied by using the term OAE, it is not generally believed that the whole ocean was anoxic, but rather that an extended oxygen minimum zone caused increased organic matter preservation [Wignall, 1994]. However, recent evidence, based on the presence of molecular fossils derived from isorenieratene, suggests that the southern North Atlantic Ocean was completely anoxic during the formation of the Caenomanian/Turonian Boundary Event (CTBE) black shales [Sinninghe Damsté and Köster, 1998].

Isorenieratene is a pigment exclusively biosynthesized by the brown-coloured strain of photosynthetic green sulphur bacteria (Chlorobiaceae). These bacteria require sunlight and hydrogen sulphide and are, therefore, restricted to a very specific habitat at the chemocline in the photic zone of euxinic basins. Isorenieratene and its dia- and catagenetically formed derivatives have also been encountered in other black shales [Koopmans *et al.*, 1996], and in the water column and Unit I and II sapropels of the Black Sea [Repeta *et al.*, 1989; Repeta, 1993; Sinnighe Damsté *et al.*, 1993]. In this paper, data are presented from eastern Mediterranean sapropels that also contain such molecular fossils.

Black shales are often enriched not only in organic matter but also in trace elements like Co, Cr, Cu, Mo, Ni, V, and Zn [e.g. Vine and Tourtelot, 1970; Brumsack, 1980]. These elements usually show a strong positive correlation with organic matter and/or sulphides. Their enrichment in the sediment is thought to be the result of accumulation in organic tissues, (co)precipitation with sulphides under anoxic conditions, or (post-depositionally) by diagenetic processes. Although sapropels may also be enriched in these elements, their contents reported thus far are generally not as high as those of some black shales [Calvert, 1983; Pruysers *et al.*, 1991; Thomson *et al.*, 1995; Nijenhuis *et al.*, 1996 (Chapter 2)]. In contrast, the Pliocene eastern Mediterranean sapropels of this study do have very high C_{org} and trace element contents.

In this paper the possible sources of trace elements in sapropels and black shales will be discussed in order to compare their respective modes of formation.

Material and methods

The sapropel selected for this study is i-282 in the Mediterranean Precession Related Cycle (MPRC) coding, which is equivalent to cycle 107 of the Rossello Composite section [Langereis and Hilgen, 1995]. It has been dated by astronomical tuning at 2.943 Ma, Upper Pliocene (Piacenzian) [Lourens *et al.*, 1996a]. It is identified unambiguously in Sites 964, 967 and 969 of ODP Leg 160 [pers. comm. L. Lourens, 1997]. This sapropel is compared with i-292 (corresponding to cycle 102 in the Rossello Composite), dated at 3.058 Ma [Lourens *et al.*, 1996a]. The intervals studied are listed in Table 6.1, the site locations are shown in Fig. 5.1.

Table 6.1 Specification of the studied intervals. Cycle coding after Lourens *et al.*, 1996a.

Leg	Hole	Core	Section	Interval studied (cm)	Sapropel interval (cm)	Depth of section top (mbsf)	Abbreviation	Cycle coding
160	964D	10H	1	90-132.5	103-110	80.1	964D10/1	i-282
160	967C	8 H	4	95-151	114-130	66.5	967C8/4	i-282
160	969E	6H	6	19-52	26-40	50.4	969E6/6	i-282
160	964E	6H	5/6	128-045	5-13	82.0	964E6/5	i-292
160	966C	5H	3/4	135-025	147-016	41.0	966C5/3	i-292

Slices with a thickness of 0.5 to 2 cm were cut from the split cores, using Teflon cutters. The slices were freeze-dried, after which subsamples were taken. These samples were crushed and homogenized in an agate mortar, and subsequently used for all geochemical analyses. After removal of inorganic carbon with 1M HCl, C_{org} contents were measured with a Fisons NA 1500 NCS analyser. For trace element analyses, a 250 mg sample was digested in 10 ml of a 6.5 : 2.5 : 1 mixture of $HClO_4$ (60%), HNO_3 (65%) and H_2O , and 10 ml HF (40%) at 90°C. After evaporation to dryness on a sand bath at 190°C, the residue was dissolved in 50 ml 1M HCl. The resulting solutions were analysed with a Perkin Elmer Optima 3000 inductively coupled plasma atomic emission spectrometer (ICP-AES) for Mo, V, Cu, Co, Ni, Zn and Cr. As, Se and Sb were measured in the same solutions with a Perkin Elmer 3100 hydride atomic absorption spectrometer (AAS); Cd with a Perkin Elmer 4100 ZL ZGFAAS (AAS with Zeeman correction).

Precision of the analyses is better than 5%, except for the determination of Se and Sb, for which it is better than 10% for sediments that contain >1 ppm of each element. Accuracy was checked with international (SO1, SO3) and house (MMM91) standards and is also better than 5% for each element except As (+9%), Co (-9%) and Zn (-9%). Detection limits for trace elements are reported in Table 6.2.

Selected subsamples were ultrasonically extracted using 8 ml of methanol (MeOH) (4x), 8 ml of dichloromethane (DCM) (4x) and 8 ml of DCM (4x). Elemental sulphur was removed from the combined extracts by stirring with activated copper (24 hours). The obtained extractable organic matter was separated into an apolar and a polar fraction on an activated Al_2O_3 column. An aliquot of the apolar fraction, obtained by elution with four column-volumes of hexane:DCM (9:1 v/v), was further separated by argentation thin layer chromatography, using hexane as developer [Bosch *et al.*, 1998]. Four fractions were isolated. The polar fractions, obtained by elution of the column with four column-volumes of DCM:MeOH (1:1 v/v), were desulphurized by Raney nickel [Sinnighe Damsté *et al.*, 1988]. Fractions obtained were analysed by gas chromatography (GC), GC/mass spectrometry (GC/MS) and isotope ratio monitoring GC/MS (irm-GC/MS) [Bosch *et al.*, 1998].

Results

C_{org} contents in the sapropels are very high (up to 27%), and trace element contents are up to several orders of magnitude higher than in average shales. The highest concentrations of C_{org} and trace elements are reached within the sapropels, but in several cases elevated trace element contents also occur in adjacent non-sapropel intervals. Numeric data are reported in Table 6.2; results for 969E6/6 are shown graphically (Fig. 6.1) and are representative of the other sites except for Zn, which is not enriched in sapropel 964D10/1 (Table 6.2).

For an extensive report on the organic geochemical results we refer to Bosch *et al.* [1998]. Here we report that the apolar fraction of sample 160-969E-6H-6, 34-35, contains abundant novel aromatic compounds, which were identified as being diagenetically derived from

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isorenieratene [Bosch et al., 1998]. $\delta^{13}\text{C}$ values of these compounds as determined by irm-GC/MS

Table 6.2 *Detection limits of the equipment used for trace element analyses. Average and maximum (in brackets) contents of C_{org} (%) and trace elements (ppm) in the sapropels and homogeneous intervals of this study. ID: presence of isorenieratene derivatives (++ abundant; +trace; - not detected).*

	I.D.	C-org (%)	As (ppm)	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Mo (ppm)	Ni (ppm)	Sb (ppm)	Se (ppm)	V (ppm)	Zn (ppm)
detection limit			0.2	0.03	3.3	3.3	3.3	3.3	3.3	0.4	0.2	3.3	6.7
964D10/1	+												
sapropel		15.3 (25.3)	112 (297)	34 (65)	76 (147)	182 (265)	264 (388)	195 (392)	317 (727)	26 (37)	29 (44)	1317 (2235)	115 (142)
homogeneous		0.1	20	0.3	12	54	47	13	36	3	0.2	99	120
967C8/4	+												
sapropel		8.4 (15.4)	58 (88)	3 (8)	48 (75)	77 (96)	110 (138)	202 (410)	183 (251)	8 (17)	22 (38)	555 (884)	90 (114)
homogeneous		0.1	22	0.1	19	46	48	32	51	2	0.4	99	55
969E6/6	++												
sapropel		17.7 (27.3)	41 (62)	31 (88)	37 (66)	168 (197)	207 (334)	407 (728)	299 (382)	9 (14)	24 (36)	1937 (3575)	163 (181)
homogeneous		0.2	13	0.1	14	96	53	16	80	2	1	99	135
964E6/5	+												
sapropel		12.0 (24.2)	n.d. ¹	22 (55)	112 (206)	245 (414)	265 (378)	151 (363)	280 (379)	n.d. ¹	n.d. ¹	923 (2061)	121 (161)
homogeneous		0.1	n.d. ¹	0.1	19	45	47	6	40	n.d. ¹	n.d. ¹	75	43
966C5/3	-												
sapropel		6.0 (11.6)	n.d. ¹	1 (3)	22 (46)	47 (61)	74 (137)	133 (295)	101 (159)	n.d. ¹	n.d. ¹	340 (797)	57 (86)
homogeneous		0.3	n.d. ¹	0.1	10	38	31	7	37	n.d. ¹	n.d. ¹	84	42
967C8/6	+												
sapropel		13.2 (20.3)	n.d. ¹	8 (18)	35 (59)	76 (90)	135 (177)	224 (515)	174 (327)	n.d. ¹	n.d. ¹	918 (1630)	98 (144)
homogeneous		0.2	n.d. ¹	0.2	17	57	51	13	49	n.d. ¹	n.d. ¹	126	58

¹ n.d.: no data

Table 6.3 Average and maximum (in brackets) contents of C_{org} (%) and trace elements (in ppm) and the presence or absence of isorenieratene derivatives (I.D.) for sapropels i-282 (this study), S1 [Calvert, 1983], S1-S7 [Pruysers et al., 1991], from the Black Sea [Brumsack, 1989] and Faneromeni (Crete; Nijenhuis et al., 1996 (Chapter 2)), and black shales from the CTBE [Arthur et al., 1990; Thurow et al., 1988], the Monterey Formation [Piper and Isaacs, 1995a], the Kimmeridge Clay [Tribovillard et al., 1994] and the Posidonia Shale [Brumsack, 1991].

	sapropel i-282	sapropel S1(DSDP Leg 13)	sapropels S1-S7	Unit I/II Black Sea sapropels	Miocene sapropels Faneromeni	CTBE ODP Leg 103	CTBE ODP Site 641A	Monterey Formation	Kimmeridge Clay	Posidonia Shale
C_{org}	13.1 (27.3)	6.1 (20.2)	2.5 (4.7)	6.4 (14)	1.6 (3)	9.3	8.5 (35.6)	6.2 (17.3)	4.4 (35)	9.2 (18.3)
As	70 (297)	7 (128)	(40)	25 (49)	7 (11)	35	126 (210)	10 (24)	n.d. ¹	28 (57)
Cd	23 (88)	n.d. ¹	n.d. ¹	1 (2)	0.4 (0.7)	14	54 (197)	7 (32)	4 (14)	3 (5)
Co	54 (147)	n.d. ¹	21 (34)	27 (51)	12 (14)	38	468 (600)	8 (15)	21 (26)	22 (64)
Cr	142 (265)	n.d. ¹	117 (158)	70 (105)	182 (225)	122	141 (430)	146 (570)	118 (146)	60 (140)
Cu	194 (388)	129 (404)	58 (122)	87 (175)	38 (55)	190	353 (921)	51 (177)	76 (104)	73 (159)
Mo	268 (728)	73 (228)	(85)	80 (185)	8 (30)	163	1950 (5050)	26 (101)	81 (220)	33 (125)
Ni	266 (727)	130 (261)	139 (195)	96 (150)	219 (289)	145	464 (870)	130 (373)	127 (230)	109 (285)
Sb	14 (37)	n.d. ¹	(5)	n.d. ¹	0.9 (2)	16	35 (118)	4 (12)	n.d. ¹	n.d. ¹
Se	25 (44)	n.d. ¹	n.d. ¹	n.d. ¹	1.2 (3)	n.d. ¹	n.d. ¹	15 (56)	n.d. ¹	n.d. ¹
V	1270 (3575)	n.d. ¹	142 (401)	173 (415)	79 (170)	647	968 (3627)	204 (564)	249 (437)	178 (305)
Zn	123 (181)	117 (274)	70 (107)	83 (108)	80 (93)	1273	6866 (17170)	146 (460)	170 (628)	235 (695)
I.D.	yes	no	no	yes ²	n.d. ¹	yes ³	no ³	no ⁴	yes ⁵	yes ⁶

¹ n.d.: no data

² Repeta, [1993]; Sinnighe Damsté et al. [1993]

³ Sinnighe Damsté and Köster [1998]

⁴ Schouten [1995]

⁵ Van Kaam-Peters et al. [1997]

⁶ Van Kaam-Peters [1997]

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were +8‰ enriched relative to algal derived organic compounds measured in the same sample, confirming their origin from isorenieratene derived from photosynthetic green sulphur bacteria. The presence of isorenieratane among the released hydrocarbons after desulphurization of the polar fraction was confirmed by coelution with an authentic standard. Identical isorenieratene derivatives were also found in individual samples of the other sapropels (Table 6.2). Because of the lower amounts of these compounds, $\delta^{13}\text{C}$ analyses were not performed on those samples, but the very specific biological source of isorenieratene indicates that photosynthetic green sulphur bacteria are in these cases also the most probable

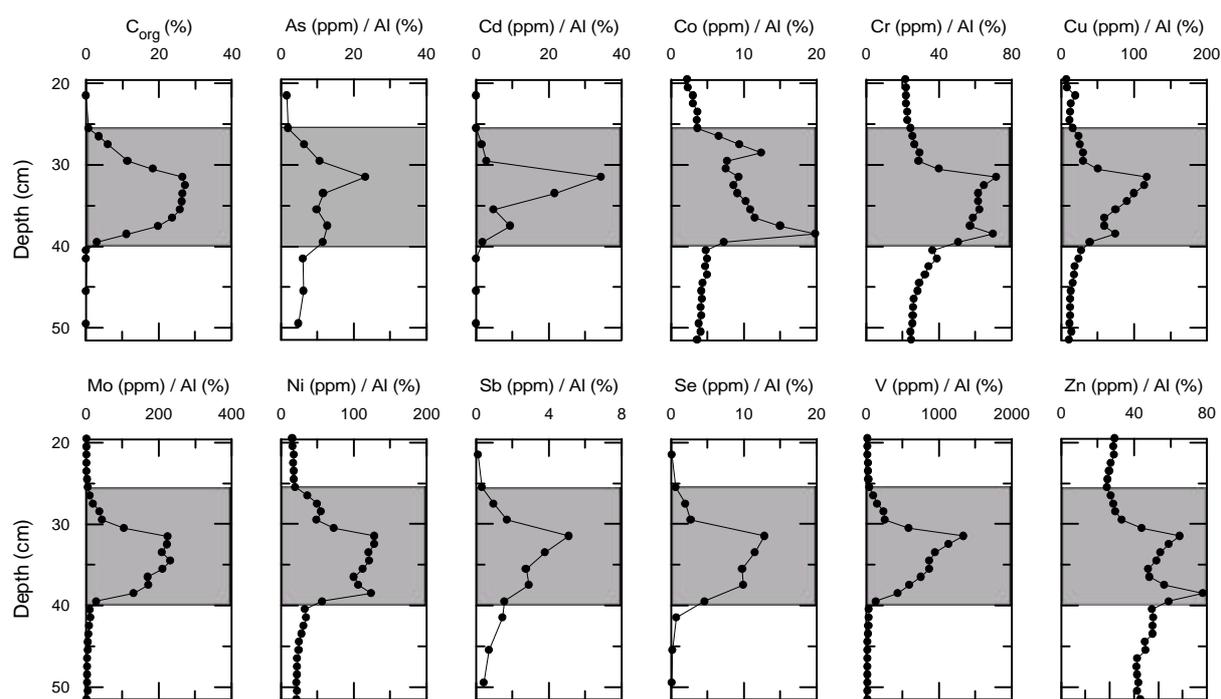


Figure 6.1 C_{org} and trace element contents of interval 969E6/6. Sapropel indicated by shading.

origin.

Discussion

The distribution patterns of trace elements and C_{org} are comparable to those previously reported for Mediterranean sapropels [e.g. Calvert 1983; Pruyers *et al.*, 1991; Nijenhuis *et al.*, 1996 (Chapter 2)]. Average and maximum C_{org} and trace element contents of the sapropels of this study, however, are considerably higher than ever reported before (Table 6.3). Furthermore, the occurrence of intact isorenieratene in sapropels has been reported only once before for a Mediterranean (Pleistocene) sapropel [Tibbets, 1980]. The presence of isorenieratene and its derivatives in the Pliocene eastern Mediterranean sapropels of this study point to sulphidic conditions at the base of the photic zone [Bosch *et al.*, 1998]. Bottom water anoxia is indicated by the presence of laminae in the sapropels (absence of benthic life) and the abundance and

isotopic composition of pyrite [Passier and De Lange, 1998]. Consequently, during the formation of these sapropels, a large part of the water column, or even all of it except the upper part of the photic zone, must have been euxinic. These specific water column conditions may have resulted in more effective scavenging and (co)precipitation of redox-sensitive and chalcophilic trace elements, resulting in the observed high contents in the sapropels. In the following we will approximate the trace element budget of the eastern Mediterranean during the formation of these Pliocene sapropels, in order to derive the ultimate trace element sources.

Possible trace element sources

The enrichment of trace elements in marine sediments may, in general, originate from six sources:

- (1) super- and subjacent sediments, through diagenesis
- (2) suboxic shelf and slope sediments
- (3) hydrothermal input
- (4) aeolian input
- (5) fluvial runoff
- (6) seawater.

The relative importance of these sources may be assessed by evaluating the trace element budget of the eastern Mediterranean during formation of the i-282 sapropel. The accompanying calculations will be simplified by taking the average composition and thickness of the sapropel at the three sites. These sites form a transect and are, therefore, thought to be representative for the whole of the eastern Mediterranean (Fig. 5.1). In our calculations we will assume that **b** of the eastern Mediterranean seafloor has been covered with this sapropel (excluding near-coastal areas), and that there are no significant effects of a 'burn-down front' [Thomson *et al.*, 1995; Van Santvoort *et al.*, 1996]. The formation time of Pliocene sapropels is estimated to be between 3,000 and 6,000 years [Wehausen and Brumsack, 1998].

(1) *Super- and subjacent sediments, through diagenesis* - Sapropels are deposited under anoxic-sulphidic conditions whereas the underlying sediments are suboxic [Passier *et al.*, 1996; Passier and De Lange, 1998]. Sapropels may, therefore, act as sinks for chalcophilic elements (which coprecipitate with sulphides) and certain redox-sensitive elements (which are immobilized under anoxic conditions) that are mobilized in the suboxic parts of the sediment [Thomson *et al.*, 1995].

Assuming that trace element maxima in the sediment are only caused by diagenesis, we can calculate the initial concentration by redistributing the total trace element amount equally over the sapropels and homogeneous intervals. Such calculations for cycle i-282 result in very high hypothetical contents (Table 6.4, in bold) comparable to the average or even maximum contents reported for *sapropels* by previous studies (cf. Table 6.3). If these hypothetical contents of cycle i-282 are compared with values obtained by the same method for other sapropels in the same cores (same site for 964), we find distinct differences for most elements, whereas we would expect similar contents if diagenesis were the only cause of the

enrichment. These comparisons show that diagenesis can be ruled out as the single source of the trace element excess in the sapropel.

Table 6.4 Contents (in ppm) obtained by equally distributing trace element contents over the entire intervals 964D10/1, 964E6/5, 967C8/4, 967C8/6, 969E6/1 (160-969E-6H-1, 110-150 combined with 160-969E-6H-2, 0-20) and 969E6/6. Values for cycle i-282 are in bold. n.d.: no data

Interval	Cd (ppm)	Co (ppm)	Cr (ppm)	Cu (ppm)	Mo (ppm)	Ni (ppm)	V (ppm)	Zn (ppm)
964D10/1	9	23	75	82	41	83	299	119
964E6/5	2	29	68	72	27	68	173	52
967C8/4	1	27	54	64	92	84	213	64
967C8/6	4	26	66	93	116	110	512	77
969E6/1	n.d.	53	72	68	37	126	241	53
969E6/6	n.d.	23	127	119	182	173	879	147

(2) (Sub-)oxic shelf and slope sediments - Trace elements are mobilized in suboxic sediments and may subsequently escape to the water column. In the case of eastern Mediterranean sapropel formation, this may lead to a transfer of trace elements from the (sub-)oxic shelf and slope sediments to the seawater, and subsequently to anoxic sapropel sediments in the deeper parts of the basin. Recycling of trace elements is linked to the iron and manganese cycles, and is commonly thought to be an important mechanism in the Black Sea [Kempe *et al.*, 1991]. However, there are virtually no quantitative data on the amount of trace elements mobilized and the related fluxes out of the sediment. Still, we would like to quantify the potential of this source. We, therefore, have assumed that the maximum trace element quantity that can be mobilized is the amount present in the upper half metre of sediment in 30% of the eastern Mediterranean surface area. The actual maximum quantity is probably lower, since not all of the trace elements present in those sediments will be mobilized, and because 30% of the surface area is most likely an overestimate. Still, for Cd (1%), Mo (9%), Se (3%) and V (16%), only a small fraction of the excess trace element quantity in the sapropel can be supplied under these assumptions. However, for some other trace elements, this maximum amount is a higher fraction of the total sapropel trace element quantity, and, therefore, this mechanism could be important, if the flux out of the (sub-)oxic sediments is high enough. We have used data from Shaw *et al.* [1990] to quantify fluxes out of (sub-)oxic sediments and to calculate the fraction of the trace element amount in the sapropel that can be supplied in this way during the maximum assumed sapropel formation period of 6,000 years (Table 6.5). Although there are considerable uncertainties in the flux estimates, and in their applicability to the Mediterranean region, these data suggest that trace element mobilization from (sub-)oxic shelf and slope sediments could potentially be a significant source for Co, Cr and Zn.

(3) Hydrothermal input - The cyclic occurrence of sapropels in the Mediterranean region is not likely to be caused by hydrothermal venting, but the total amount of trace elements available

Table 6.5 Results of calculations for establishing the possible sources of the trace elements in sapropels i-282 and i-292 with a composition that is the average of the three sites, a thickness of 12 cm (16 cm for i-292), and a dry density of 1.8 gr/cm³, covering **b** of the eastern Mediterranean (total surface area: 1.66 million km²). Values for homogeneous intervals have been calculated in the same way.

Column 1:	Excess trace element content of the sapropel (the average content of the sapropel minus the average content of the homogeneous interval).
Column 2:	The total excess trace element quantity of the sapropel over b of the eastern Mediterranean.
Column 3:	The fraction of the trace element amount that may be supplied by mobilization from (sub-)oxic shelf and slope sediments in 6,000 years. Based on suboxic flux ranges estimated from Shaw et al. [1990]; values in brackets are based on our assumed maximum (see text) because no flux data were available. Lowest values based on 10% (sub-)oxic sediments and lowest flux estimate; highest values based on 30% (sub-)oxic sediment and highest flux estimate. Numbers used (element, flux coefficient (10 ⁻⁶ cm/s), lower flux (nM/cm), higher flux): Co (5, 5,10), Cr (7, 18, 60), Cu (4, 15, 20), Mo (6, 200, 400), Ni (5, 33, 50), V (6, 87, 800).
Column 4:	The trace element content of the C _{org} present in the sapropel assuming that all (excess) trace elements are fixed to organic matter.
Column 5:	The trace element content of marine organic matter (converted to C _{org} by multiplication with 2.5, assuming that the dry matter of marine organisms contains 40% C _{org} [Brumsack, 1980; Arthur et al., 1990]).
Column 6:	Trace element concentration of seawater [Broecker and Peng, 1982; Bruland, 1983].
Column 7:	Trace element concentration of river water [Broecker and Peng, 1982; Martin and Whitfield, 1983; Brumsack, 1989].
Column 8:	The total trace element amount present in the eastern Mediterranean (EM) with a composition of column 6.
Column 9:	The excess trace element quantity present in the sapropel expressed in multiples of the amount present in the eastern Mediterranean (EM).
Column 10:	The period of river water input needed to supply the excess amount of trace elements present in the sapropel to the Mediterranean, based on a river composition as in column 7, and 1.5 times the present-day riverine input of 514 km ³ /yr plus 400 km ³ /yr from the Black Sea [Lacombe and Tchernia, 1972]. The trace elements already present in the eastern Mediterranean have been deducted from the sapropel total; trace element fixation in the western Mediterranean is neglected.
Column 11:	The period of seawater exchange with the western Mediterranean needed to supply the excess trace element content of the sapropel. The trace elements already present in the

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Mediterranean have been deducted from the sapropel total. The water input from the western Mediterranean is 39,800 km³/yr [Béthoux, 1980].

		1	2	3	4	5	6	7	8	9	10	11
		Excess	Total	Shelf /	Content	Content in C_{org}	Seawater	River	Total	Seawater	Period river	Period
		content	excess	slope	in C_{org}	marine organ-	conc.	water	in EM	volume	water input	seawater
		(ppm)	(10¹²g)	fraction	(ppm)	isms (ppm)	(ppb)	conc. (ppb)	(10¹²g)	(#-EM)	(kyr)	input (kyr)
i-282	As	51	12	(77%)	371	12.5	1.7	1.7	4.34	3	3	0.1
	Cd	22	5	(1%)	159	30	0.08	0.02	0.2	26	188	1.7
	Co	39	10	4-28%	286	2.5	0.001	0.2	0.003	3779	35	253
	Cr	88	21	9-91%	638	5	0.21	1	0.543	40	15	2.6
	Cu	150	37	3-12%	1091	27.5	0.25	1.5	0.637	58	18	3.8
	Mo	257	63	<9%	1868	5	10.6	0.5	27.03	2	52	0.089
	Ni	224	55	5-24%	1627	18.75	0.47	0.5	1.19	46	78	3
	Sb	12	3	(44%)	86	1.25	0.15	1	0.38	8	2	0.4
	Se	25	6	(3%)	179	2.5	0.14	0.2	0.35	17	21	1.1
	V	1206	296	<16%	8781	9	1.8	0.77	4.59	64	276	4.3
Zn	21	5	(100%)	151	275	0.39	0.35	0.99	5	9	0.3	
i-292	Cd	8	2	(3%)	74	30	0.08	0.02	0.2	12	81	0.7
	Co	26	8	5-32%	250	2.5	0.001	0.2	0.003	3238	30	217
	Cr	46	15	13-	445	5	0.21	1	0.54	27	10	1.8
	Cu	88	28	4-16%	845	27.5	0.25	1.5	0.64	44	13	2.9
	Mo	169	53	<11%	1614	5	10.6	0.5	27.03	2	39	0.065
	Ni	121	38	7-34%	1159	18.75	0.47	0.5	1.2	32	54	2.1
	V	603	191	4-24%	5777	9	1.8	0.77	4.59	42	176	2.7
Zn	40	13	(100%)	382	275	0.39	0.35	0.99	13	24	0.8	

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will be higher in a geological period of increased hydrothermal activity, like the Cretaceous. This mechanism can be ruled out, however, since an element such as Zn, which is typically associated with hydrothermal activity [James and Elderfield, 1996], is only slightly enriched in the sapropels, whereas non-hydrothermal elements, like Mo and V [Björnsson et al., 1972], show strong enrichments.

(4) *Aeolian input* - Estimates for the contribution of wind-derived material in Mediterranean sediments are highly variable, so aeolian input is a potentially important trace element source. Yet in the orbital forcing model sapropels are formed during wet climatic conditions, when wind input is likely to be lower rather than higher. Evidence for lower wind-borne input during sapropel formation has been reported recently [Foucault and Mélières, 1995; Wehausen and Brumsack, 1998].

(5) *Fluvial runoff* - The average trace element concentrations in river water are generally rather low (Table 6.5), and the water volumes supplied to oceans by rivers are relatively small. Consequently, a special setting and long periods of time are needed for river water to become the main source of trace elements in marine sediments.

Unfortunately, no reliable data for pristine (pre-anthropogenic) trace element input of rivers into the Mediterranean are available. Data from recent trace element studies are affected by anthropogenic contributions, whereas in older studies these elements have neither been sampled contamination-free, nor measured accurately enough. Therefore, data of the mean world river composition [Broecker and Peng, 1982; Martin and Whitfield, 1983; Brumsack, 1989] are used in the following calculations. Since climatic conditions during precession minima are more humid [Rossignol-Strick, 1983; Rohling and Hilgen, 1991], river input into the Mediterranean is likely to be significantly higher during sapropel formation than at present. Furthermore, the sharp contrast in climate during precession minima (humid) and maxima (arid) may lead to a higher trace metal load of circum-Mediterranean rivers [Wehausen and Brumsack, 1998].

Even if a 50% increase of the present-day fluvial input (including the amount coming through the Bosphorus from the Black Sea, which was a freshwater lake in the Pliocene), and the incorporation of all trace elements supplied by rivers into the sediment is assumed, long periods of fluvial input into the Mediterranean are needed to supply the amount of trace elements present in the sapropel (Table 6.5, column 10). Except for As and Sb, these values are unrealistically high if we assume a sapropel formation time of 3,000-6,000 years. Even doubling the river flux or the trace metal concentration in the fluvial input would not provide the amounts of trace metals that are actually found in the sapropel within a reasonable time period.

(6) *Seawater* - Based on mean seawater trace metal concentrations [Broecker and Peng, 1982; Brumsack, 1989], we have calculated the amount of seawater that has to be stripped of its trace element content in order to explain the composition of the sapropel (Table 6.5, column 9). Less than fifty times the amount present in the eastern Mediterranean is sufficient for most elements. Based on the current water input ($40 \cdot 10^3 \text{ km}^3 \text{ yr}^{-1}$, [Béthoux, 1980]) of western Mediterranean surface water, this means that about 4,000 years of exchange with that basin are necessary (Table 6.5, column 11).

Vanadium is a key element for this calculation because its seawater concentration is known well (1.8 ppb; [Bruland, 1983; Collier, 1984]) and its river water concentration ranges from 0.5 to 1.0 ppb [Shiller and Boyle, 1987], i.e. lower than in seawater. For the elements Cr, Cu, and Ni the time necessary for their accumulation is comparable to that of V. As, Mo, Sb and Zn can easily be supplied within the inferred sapropel formation time. This is not the case for Co, for which another source, e.g. suboxic shelf and slope sediments, has to be important. Still, seawater is the most likely source for the trace metal enrichments encountered in the sapropels.

As discussed earlier, a large part of the eastern Mediterranean water column may have been euxinic during the formation of the i-282 sapropel. Under such conditions, redox-sensitive and chalcophilic trace elements can be bound to organic matter (Cr, Mo, V, Cu, Zn), or (co)precipitated as sulphides (As, Cd, Co, Cu, Ni, Zn). Indeed, concentrations of Cd, Cu, Mo, Se, V and Zn have been reported to be considerably lower in anoxic than in oxic seawater [Pilipchuk and Volkov, 1974; Collier, 1984; Jacobs and Emerson, 1985; Takayanagi and Wong, 1985]. Through deposition of organic matter and sulphides, trace elements may be efficiently transferred from seawater to the sediment. This concept has often been proposed to explain trace element enrichments in sapropels [Nijenhuis *et al.*, 1996 (Chapter 2); Van der Weijden, 1993], and seems to be the most likely mechanism for the trace element enrichment in the Pliocene Mediterranean sapropel discussed here. The lack of a Zn enrichment in 964D10/1 and its relatively low enrichment at the other sites compared with recent sapropels and older black shales (Table 6.2, 3) is unexpected in this scenario, but might be explained by a relatively low supply of this element to the Mediterranean in the Pliocene. The strong hydrothermal input of Zn in the Cretaceous can account for its high enrichment in black shales of this period [Arthur *et al.*, 1990].

Because the concentration of trace elements in anoxic seawater is not zero, and because anoxia may have developed under stagnant conditions, when water exchange with the western Mediterranean was probably lower than at present, the calculated period of seawater exchange is too low. If the periods necessary to supply Co, Cr, Cu, Ni and V are higher than calculated, they may exceed the assumed sapropel formation period of 3,000-6,000 years. Therefore, circulation during sapropel formation was most likely not at a standstill. *Passier et al. [in press] (Chapter 5)* have shown, based on Ba contents of the sapropels, that the total amount of organic matter being produced during the formation of this Pliocene sapropel is high enough to reduce all oxygen supplied in the present circulation mode, leading to anoxia in the eastern Mediterranean. However, the concomitant high nutrient demand cannot be met by the present-day hydrography. There are three ways by which the nutrient availability can be increased: higher river influx, shoaling of the pycnocline into the photic zone, or circulation reversal.

There is no doubt that river input was higher during sapropel formation (see before). *Sarmiento et al. [1988]* have shown that 1.7 times the present river input into the eastern Mediterranean will supply enough phosphate to support a productivity that will lead to anoxia. Since the present-day eastern Mediterranean exports its nutrients with its bottom water to the western Mediterranean, this latter basin will subsequently also become anoxic. Anoxic

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events, visualized by the occurrence of sapropels, are, however, more limited both in time and space in the western Mediterranean than in the eastern Mediterranean. The western Mediterranean can remain oxic if water exchange (and thus nutrient supply) at the Strait of Sicily is reduced by at least a factor of twelve [Sarmiento *et al.*, 1988]. Such a decrease of seawater exchange at the Strait of Sicily would also drastically reduce the marine trace element input in the eastern Mediterranean. Thus, in such a stagnation scenario, a period longer than 3,000-6,000 years would be needed for supplying the observed sapropelic trace element content.

Shoaling of the pycnocline into the photic zone because of increased freshwater input will allow deep water nutrients to become available for primary productivity [Rohling and Gieskes, 1989]. However, this also invokes water column stratification and, therefore, stagnation.

Circulation reversal in the eastern Mediterranean from anti-estuarine during non-sapropel periods to estuarine during sapropelic periods would result from a decrease of surface water salinity due to increased riverine input [*e.g.* Calvert, 1983; Buckley and Johnson, 1988; Thunell and Williams, 1989]. In this case the eastern Mediterranean will change from a nutrient desert to a nutrient trap, utilizing nutrients from both the inflowing western Mediterranean deep water and the riverine input, while exporting nutrient-poor surface water to the western Mediterranean. In this case the eastern Mediterranean will inevitably become anoxic, while the western Mediterranean remains oxic [Sarmiento *et al.*, 1988]. Furthermore, since there are no circulation restraints, trace elements will be supplied by the western Mediterranean deep water, which has higher concentrations than the surface waters flowing into the eastern Mediterranean in the other scenarios. Therefore, based on nutrient and trace element demands, and on the absence of widespread anoxic events in western Mediterranean Pliocene sediments, a circulation reversal in the eastern Mediterranean seems to be the most plausible scenario.

Summarizing, early diagenesis can only account for a small fraction of the trace element enrichment in the sapropels, in other words, the largest part of the signal is primary. The contribution by shallow shelf and slope sediments is difficult to quantify, but might be significant for the elements Co, Cr and Zn. Aeolian input and hydrothermal activity are not responsible for the trace element enrichments found in the sapropels. The trace element amounts in the sediments cannot be supplied by river water in a reasonable time period. Seawater can provide enough trace elements (except for Co), except if water exchange at the Strait of Sicily was more restricted than at present.

For comparison, these calculations were also applied to sapropel i-292 at sites 964, 966 and 967. Isorenieratene derivatives have been found in this sapropel, except at Site 966 (Table 6.2). Although the time intervals calculated (Table 6.5) are shorter for i-292 than they are for i-282, the result is essentially the same: rivers cannot supply the trace elements in a reasonable time period, and several thousands of years of seawater exchange with the western Mediterranean are necessary for most trace elements. The differences in calculated time intervals between i-282 and i-292 are likely to be caused by samples originating from different

sites. In particular, those from Site 969 with well-developed sapropels being used for i-282, whereas those from Site 966 with poorly developed sapropels were used for i-292.

Comparison with black shales

Some black shales are characterized by high C_{org} and trace element contents and the presence of isorenieratene derivatives, like the Pliocene sapropels of this study. In order to assess to what extent these deposits are equivalent, we will compare the geochemistry of these sapropels with that of black shales which are also rich in C_{org} and trace elements, which have been analysed for isorenieratene, and for which trace element sources and enrichment mechanism have been inferred in the literature (Table 6.3).

Organic matter and trace element contents - Although the maximum C_{org} content in black shales can be extremely high (up to 50-65% in certain thin oil shale horizons of the Kimmeridge Clay [Van Kaam-Peters, 1997]), the average and maximum C_{org} contents of the i-282 sapropel are similar to those reported for many Mesozoic and Cenozoic black shales (Table 6.3). The trace element content of the sapropel is, however, higher than that of most black shales listed in Table 6.3, with those from the CTBE as notable exceptions. The lower trace element and C_{org} content of the Monterey Formation may be explained by a moderate level of primary productivity and the absence of free H_2S in the water column; plankton is the only source for most trace elements [Piper and Isaacs, 1995a]. For the Posidonia and CTBE black shales and the Kimmeridge Clay, anoxic bottom water conditions have been inferred from trace element enrichment patterns [Brumsack, 1980; 1991; Dypvik, 1984; Tribovillard et al., 1994]. The Posidonia Shale formed in an epicontinental sea, therefore, after a marine trace element source, fluvial input was most important for the trace element enrichment in this black shale [Brumsack, 1991]. In the CTBE black shales, trace elements must be derived from seawater, rivers, and possibly hydrothermal (Zn) input [Brumsack, 1980; Arthur et al., 1990]. The Kimmeridge Clay formed on a continental shelf where circulation may have been reduced due to shallow sills [Tribovillard et al., 1994]. The ultimate trace element source has not been reported.

Isorenieratene - On the basis of trace element data it was concluded that strong anoxic conditions were important for the trace element enrichment in the Posidonia and CTBE black shales and in the Kimmeridge Clay. In all these black shales, isorenieratene derivatives have been found [Van Kaam-Peters, 1997; Sinninghe Damsté and Köster, 1998]. Despite extensive research this is not the case for the Monterey Formation [Schouten, 1995], which is in agreement with the inferred lack of sulphate reduction in the water column during its formation. For the CTBE black shales in the southern part of the North Atlantic Ocean it was recently suggested [Sinninghe Damsté and Köster, 1998] that they were deposited under a water column that was sulphidic up into the photic zone. Thus, scavenging by sulphides could explain the high trace element contents, as suggested previously by Brumsack and Thurow [1986].

In conclusion, photic zone anoxia and high trace element fixation rates are typical for some black shales. However, the black shales discussed in this paper differ from organic matter rich Pliocene sapropels by their shallower setting and different ultimate trace element sources.

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The CTBE black shales are most similar to the i-282 sapropel in the sense that some of these are also found in abyssal sites and that trace elements are accumulated by scavenging by organic matter and sulphides in an anoxic water column. Still, the time scale of the anoxic events is quite different: several thousands of years for the sapropel versus 10^5 years or more for the CTBE. Because of this larger time scale and lateral distribution, seawater as a trace element reservoir is not large enough for the CTBE black shales and, therefore, fluvial and hydrothermal input dominate on a long term basis [Arthur *et al.*, 1990].

Water column anoxia is generally attributed to stagnant conditions. For Mediterranean sapropel formation this is not necessarily the case [Sarmiento *et al.*, 1988] and in fact our trace element data suggest that these Pliocene sapropels may have been formed under conditions of ongoing circulation. This could have been the case in the southern North Atlantic Ocean during the formation of the CTBE black shale as well [Sinninghe Damsté and Köster, 1998]. The fact that the C_{org} and trace element contents are comparable, however, seems to be coincidental. The presence of isorenieratene derivatives does not always coincide with the highest trace element contents (Table 6.3). This has two important implications. First, although the presence of isorenieratene suggests that the water column was anoxic up into the photic zone, the absence of isorenieratene only indicates that the photic zone was not euxinic; it does not provide any information on the oxygen levels of the rest of the water column. In the case of the CTBE black shale at Site 641, characterized by very high trace element contents, it is likely that a large part of the water column was anoxic during its formation, but anoxia did not extend into the photic zone. Secondly, isorenieratene-derived compounds are not a prerequisite for high trace element contents. One reason for this is that it is unknown how long the water column has been anoxic. Isorenieratene derivatives may be found in a black shale or a sapropel even if sulphidic conditions lasted only a few years. Another reason is that the trace element amount that can be precipitated is strongly dependent on the duration of sapropel/black shale formation and the local setting: sedimentation rate, the amount of trace elements already present in the basin, the potential amount supplied by rivers, wind and hydrothermal vents and the importance of diagenesis.

The Black Sea: a modern analogue?

The largest contemporary euxinic basin, the Black Sea, may be considered as a modern analogue of Pliocene sapropels and CTBE black shales. This basin has been anoxic for more than 7,000 years and currently is sulphidic up into the photic zone [Repeta *et al.*, 1989]. Isorenieratene and its derivatives are found in Black Sea sediments, indicating that similar conditions existed in the past [Repeta, 1993; Sinninghe Damsté *et al.*, 1993]. In this basin, trace metals are trapped during mixing of oxic surface water (which is a mixture of river water and eastern Mediterranean seawater) with anoxic deep water. The trace element contents of the Black Sea sediments, however, are not as high as those found in the eastern Mediterranean Pliocene sapropels and in CTBE Black Shales (Table 6.3). Still, the trace element extraction efficiency is very high, and the mechanism (scavenging by organic matter and sulphides in an

anoxic water column [Brumsack, 1989]) is the same as inferred for the Pliocene sapropels and the CTBE black shales. The trace element content in sediments of the Black Sea is lower because the exchange with the eastern Mediterranean at the Bosphorus is restricted, which limits the trace element input from seawater into the basin, and because the sedimentation rate is rather high, diluting authigenic signals from trapping processes within the anoxic water column.

Conclusions

Some eastern Mediterranean Pliocene sapropels are characterized by exceptionally high C_{org} and trace element contents and the presence of isorenieratene derivatives. The trace element enrichment is thought to be the result of efficient scavenging by sulphides and organic matter in a euxinic water column. Because seawater is the ultimate trace element source, circulation must have been relatively vigorous during sapropel formation, and may have been reversed in the eastern Mediterranean.

A comparison of the sapropel with C_{org} and trace element enriched black shales shows that the latter are not always deposited in comparable environments, and often have lower trace element contents. The CTBE black shales are an exception, but were deposited over a longer time period and in a larger area than Mediterranean sapropels. As a result, fluvial and hydrothermal input are the ultimate trace element sources in this case. Still, because the inferred trace element removal mechanism in the CTBE black shale is similar to that in the sapropels, and because the water column was also sulphidic up into the photic zone during deposition of these sediments, sapropels can be considered younger analogues of these black shales.

The Black Sea is a smaller, contemporaneous analogue of both the CTBE black shale and the sapropels investigated, because it also has a sulphidic water column, and the same efficient trace element removal mechanism is operative. Sedimentary trace element contents are lower in this basin because of a limited supply and dilution due to the high sedimentation rates.

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Chapter 7

Geochemical constraints on Pliocene sapropel formation in the eastern Mediterranean

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Abstract - Seventeen, partly coeval, sapropels recovered during ODP Leg 160 from Sites 964, 966, 967 and 969 (eastern Mediterranean) have been analysed for their geochemistry. The sapropels are characterized by high organic carbon contents, due to both increased productivity and improved preservation of organic matter. Improved preservation resulted from anoxic bottom water conditions caused by the inferred high productivity. High C/N ratios in the sapropels may indicate that productivity was N-limited; P regeneration from the anoxic sediments may have provided a positive feedback to productivity. More negative $\delta^{13}\text{C}_{\text{org}}$ values in the sapropels result from diagenesis and/or surface waters being diluted by (Nile) river water. A west-east trend of increasingly more positive $\delta^{13}\text{C}_{\text{org}}$ is ascribed to biological fractionation and may indicate that surface water circulation was not reversed during sapropel formation.

Sedimentation rates did not change dramatically during sapropel formation (they were at most 30% lower or 50% higher), which lasted between 2,000 and 10,000 years. Increased Nile discharge played an important role in sapropel formation, leading to longer sapropel duration in the eastern part of the basin.

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Introduction

Mediterranean Neogene to Quaternary marine sediments are often composed of two dramatically contrasting lithologies: light-coloured, homogeneous marls and greenish-brown to black, laminated layers. These dark layers are enriched in organic carbon (C_{org} ; up to 30%), and are called sapropels. Sapropels are typically also enriched in clays, iron, sulphur, barium and trace metals, but depleted in carbonates and manganese [e.g. Sutherland *et al.*, 1984; Pruyssers *et al.*, 1991; Thomson *et al.*, 1995; Nijenhuis *et al.*, 1996 (Chapter 2)]. The pattern in which sapropels occur is regular and basin-wide in the eastern Mediterranean, suggesting a link with Milankovitch cyclicity. Hilgen [1991a] first presented a direct correlation between Plio-Pleistocene sapropels in Sicilian and Calabrian land sections and minima in the index of the precession of the Earth's equinoxes. Later, these correlations were extended down into the Miocene [Hilgen, 1991b; Hilgen *et al.*, 1995]. Lourens *et al.* [1996a] showed that the best fit with the sedimentary record is obtained when using the 65°N summer insolation target curve. The link between astronomical variations and sapropel formation is thought to be the increase in monsoonal activity [Rossignol-Strick, 1983; Prell and Kutzbach, 1992] and Mediterranean Atlantic-born depressions [Rohling and Hilgen, 1991] at times of precession minima (Northern Hemisphere insolation maxima). This leads to an increased freshwater flux into the Mediterranean, on the one hand supplying nutrients that enhance production of organic matter, and on the other hand stabilizing the water column, facilitating oxygen depletion of deep waters, and thus promoting organic matter preservation. It has been a major issue in discussions about sapropel formation whether productivity or preservation caused the organic matter enrichment [e.g. Calvert, 1983; Calvert *et al.*, 1992; Howell and Thunell, 1992]. In addition, the marine versus terrestrial nature of organic matter in sapropels has been a matter of debate [e.g. Sigl *et al.*, 1978; Ten Haven *et al.*, 1987; Meijers, 1993]. Another uncertainty is the formation time of sapropels, except for the Holocene S1 which is young enough to be dated by AMS ^{14}C techniques. As sapropels and precession cycles correlate closely, it is clear that one cycle of sapropel-homogeneous sediment deposition must have lasted 21,000 years on average. However, it is uncertain if and how sedimentation rates changed during such a cycle, and, therefore, how long sapropel formation itself lasted [e.g. Nijenhuis *et al.*, 1996 (Chapter 2); Wehausen and Brumsack, 1998].

During ODP Leg 160 and 161 to the eastern and western Mediterranean, excellent Plio-Pleistocene sapropel-containing sedimentary records have been obtained. We have studied the geochemistry of several sapropels from four sites spanning all of the eastern Mediterranean and representing different water depths. In this paper, we will use these data to put constraints on the possible conditions under which eastern Mediterranean sapropels were formed in the Plio-Pleistocene.

Material and methods

Seventeen individual sapropels and adjacent homogeneous sediments were sampled during ODP Leg 160 to the eastern Mediterranean or later in the ODP core repository in Bremen. The sapropels were obtained from Sites 964, 966, 967 and 969 (Fig. 5.1) and range from 3.08 to 1.56 Ma in age (Table 7.1).

Slices with a thickness of 0.5 to 2 cm were cut from the split cores, using Teflon cutters. The slices were freeze-dried, after which subsamples were taken. These samples were powdered in an agate mortar, and subsequently used for all further geochemical analyses.

After removal of inorganic carbon with 1 M HCl, C_{org} and remaining nitrogen (N_{tot}) contents were measured with a Fisons NA 1500 NCS analyser. Stable carbon isotopes of organic matter ($\delta^{13}C_{\text{org}}$) were determined with a Stable Isotope Ratio Analyser (VG SIRA 24), and are reported relative to the PeeDee Belemnite (PDB) standard. For major, minor and trace element analyses, a 250 mg sample was digested in 10 ml of a 6.5 : 2.5 : 1 mixture of $HClO_4$ (60%), HNO_3 (65%) and H_2O , and 10 ml HF (40%) at 90°C. After evaporation to dryness on a sand bath at 190°C, the residue was dissolved in 50 ml 1 M HCl. The resulting solutions were analysed with a Perkin Elmer Optima 3000 inductively coupled plasma atomic emission spectrometer (ICP-AES) for Al, Ti, Ca, Ba, V, Mo and Ni. In sapropel samples, Ba was determined separately in solutions prepared by the same procedure, but using only 40 mg sample to prevent $BaSO_4$ precipitation. Opal analyses were performed on selected samples, following the method of Müller and Schneider [1993], using a Technicon TRAACS 800 auto-analyser.

All results were checked with international and house standards. For C_{org} , N_{tot} and all ICP analyses, relative standard deviations in duplicate measurements are below 4%. Absolute standard deviations in $\delta^{13}C_{\text{org}}$ analyses are below 0.2‰.

Results

The sapropels are characterized by higher C_{org} (up to almost 30%) and lower Ca contents (Fig. 7.1), higher C/N and more negative $\delta^{13}C_{\text{org}}$ values (Fig. 7.2) than the homogeneous intervals. Barium (Fig. 7.3) reaches values up to almost 5,200 ppm in the sapropels and correlates well with C_{org} contents. Opal has been analysed in three intervals and is also higher in the sapropels, especially in i-176B (up to 30%; Fig. 7.3). Aluminium contents are generally lower in the sapropels than in the homogeneous intervals (Fig. 7.4). Ti/Al profiles appear irregular in Sites 964 and 969, but are cyclic in Sites 966 and 967, with minimum values in sapropels (Fig. 7.4). Mo/Al, V/Al and Ni/Al are much higher in the sapropels than in the homogeneous intervals (Fig. 7.5).

Average sedimentation rates (Table 7.1) are determined by dividing the thickness of an astronomically calibrated cycle [taken from Emeis *et al.*, 1996] by its calculated duration [Lourens *et al.*, 1996a].

Discussion

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Based on the geochemical data of these Plio-Pleistocene sapropels, we will now discuss (1) the importance of productivity and preservation for the high sapropelic C_{org} contents, (2) the nature of the organic matter, (3) the duration of sapropel formation, and (4) the implications for sapropel formation scenarios.

Table 7.1 *Sapropels analysed: official ODP sample coding, Mediterranean Precession Related Cycle coding after Lourens et al. [1996a], age of cycle midpoints [Lourens et al., 1996a] and average sedimentation rate.*

Leg	Hole	Core	Section	Interval	Sapropel	Cycle Code	Lagged¹ age (Ma)	Average sed. rate (cm/kyr)
160	964D	5	7	1-84	19-39	i-152	1.565	2.05 ⁽²⁾
160	964D	10	1	92-133	103-110	i-282A	2.945	2.14
160	964E	6	5	55-152	87-104	i-290	3.038	2.98
160	964E	6	6	0-45	5-13	i-292A	3.060	2.98
160	966C	5	2/3	141-028	0-14	i-284	2.967	1.66
160	966C	5	3/4	135-025	147-16	i-292C	3.060	1.89
160	966C	5	4	25-65	33-52	i-294A	3.082	1.89
160	967B	6	2	95-150	115.5-134	i-156A	1.603	2.91
160	967C	6	2	17.5-61	30.2-47	i-176A	1.808	2.58 ⁽²⁾
160	967C	7	6	70-130	93-114	i-250A	2.589	2.77
160	967C	8	4	95-151	114-130	i-282B	2.945	2.09
160	967C	8	6	26-68	37-58	i-292B	3.060	2.07
160	967C	8	6	68-120	77-97	i-294B	3.082	2.07
160	969D	4	5	0-80	35-52	i-156B	1.603	2.69
160	969D	5	2	16-98	41-73	i-176B	1.808	3.68
160	969E	6	1/2	110-020	135-148	i-250B	2.589	4.23 ⁽²⁾
160	969E	6	6	19-52	26-40	i-282C	2.945	1.98

¹ "Lagged" means corrected for the time lag observed between the last precession minimum and the onset of S1 formation.

² These numbers are approximate because the total cycle thickness could not be determined exactly from *Emeis et al. [1996]*.

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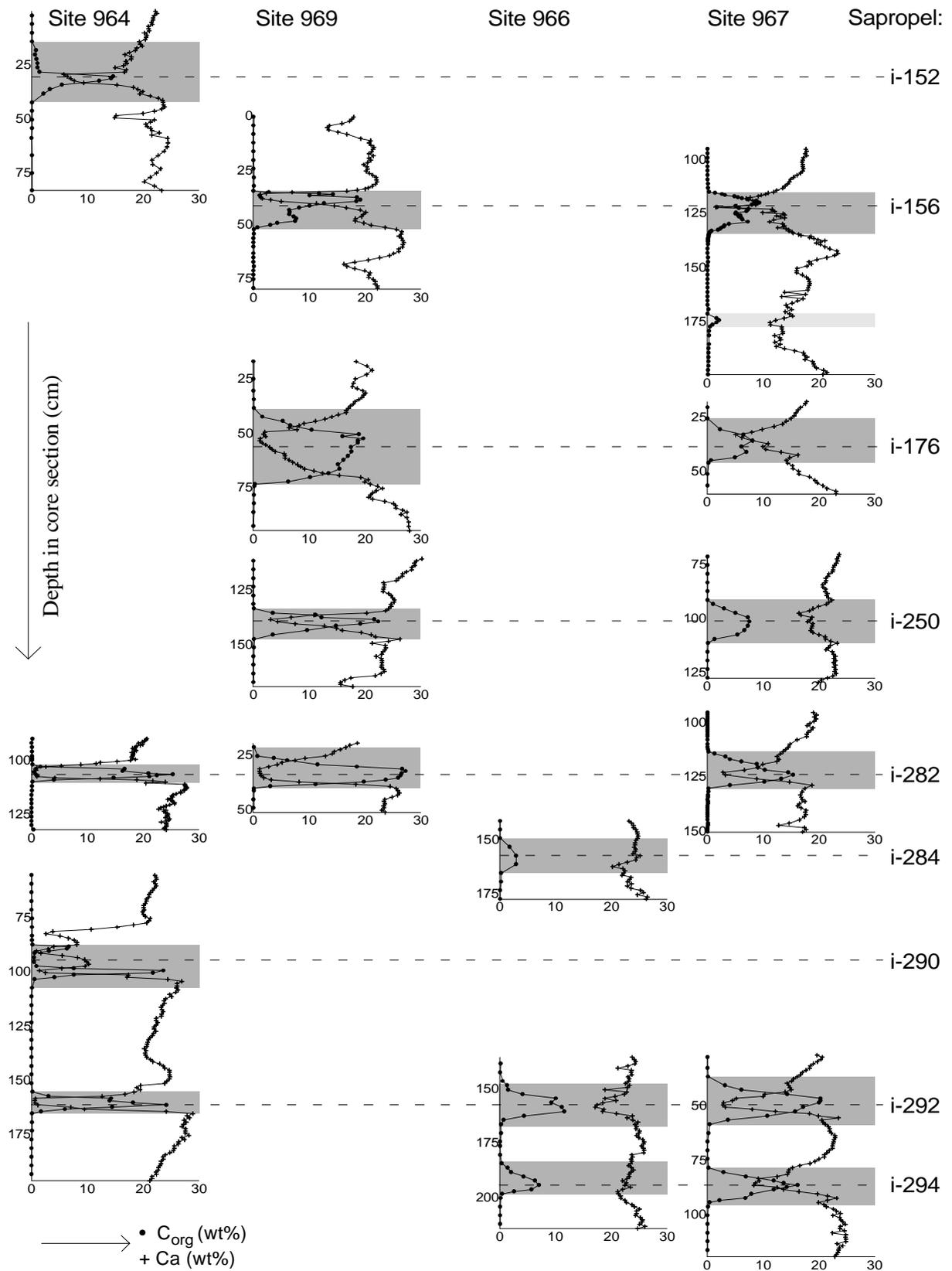


Figure 7.1 C_{org} and Ca versus depth profiles for each interval. Dotted lines connect sapropels of the same age; ODP sites are arranged from west to east.

Geochemical constraints on Pliocene sapropel formation

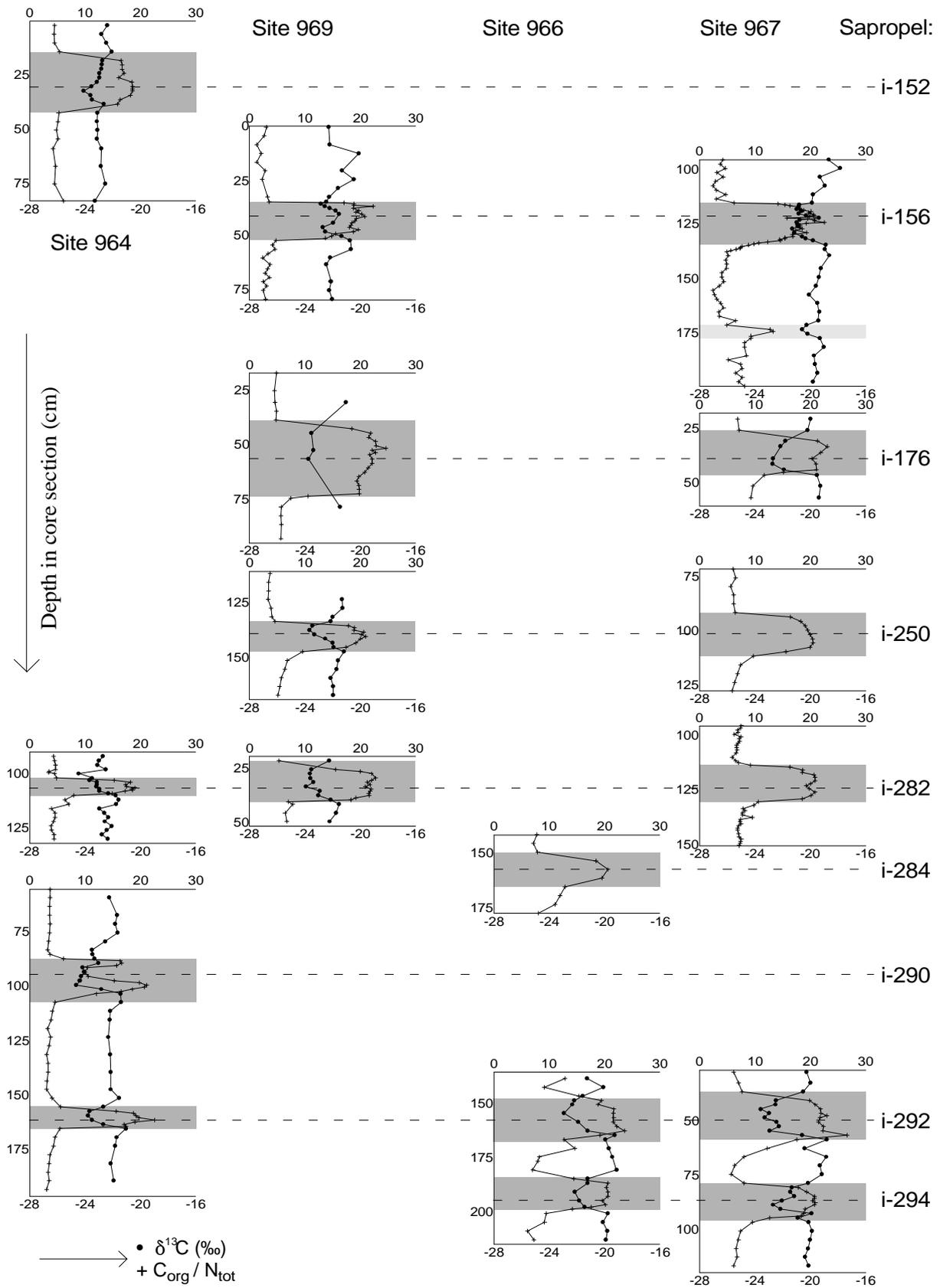


Figure 7.2 $\delta^{13}C_{org}$ (in as far analysed) and C_{org}/N_{tot} versus depth profiles for each interval.

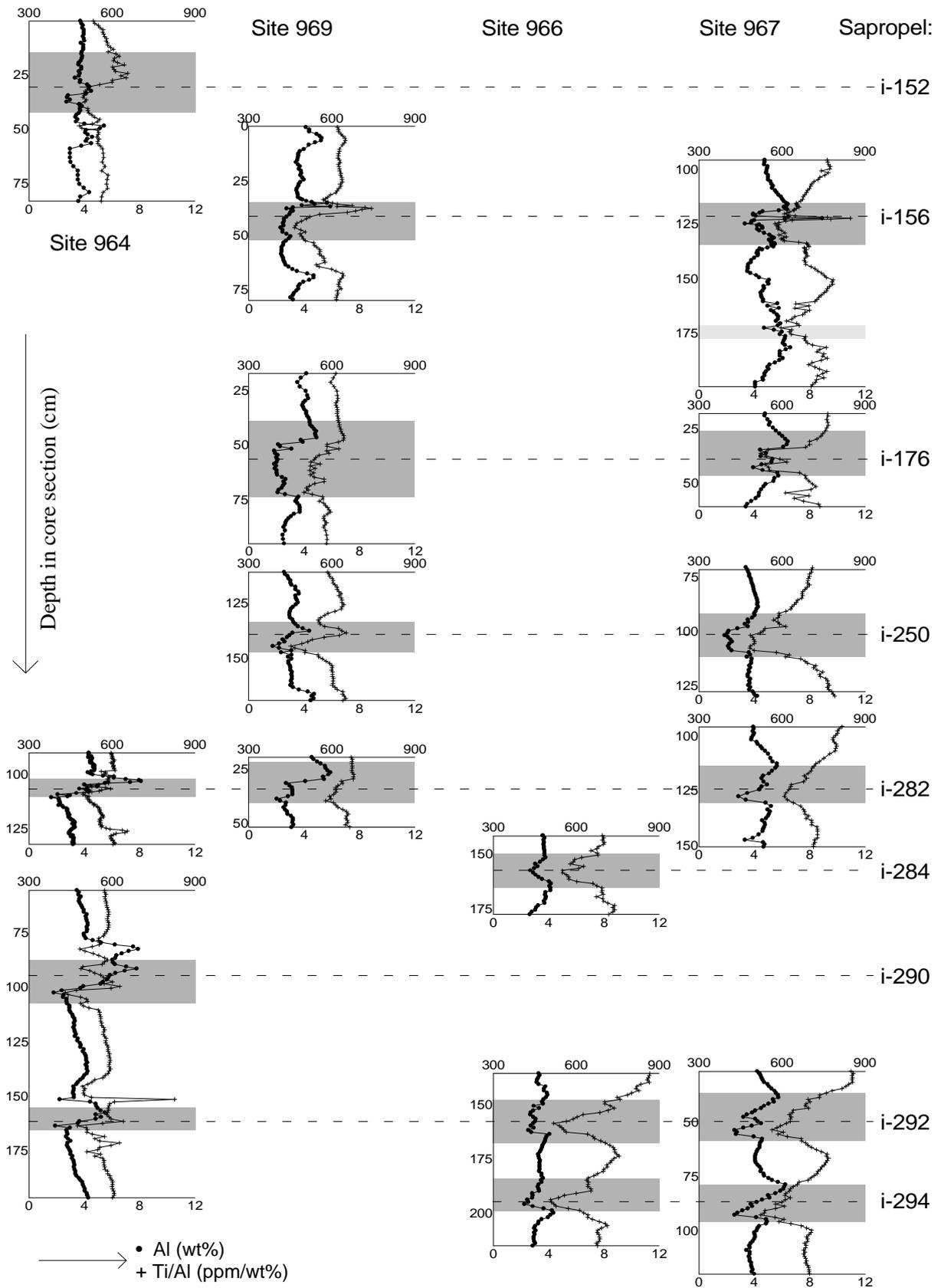


Figure 7.4 Al and Ti/Al versus depth profiles for each interval.

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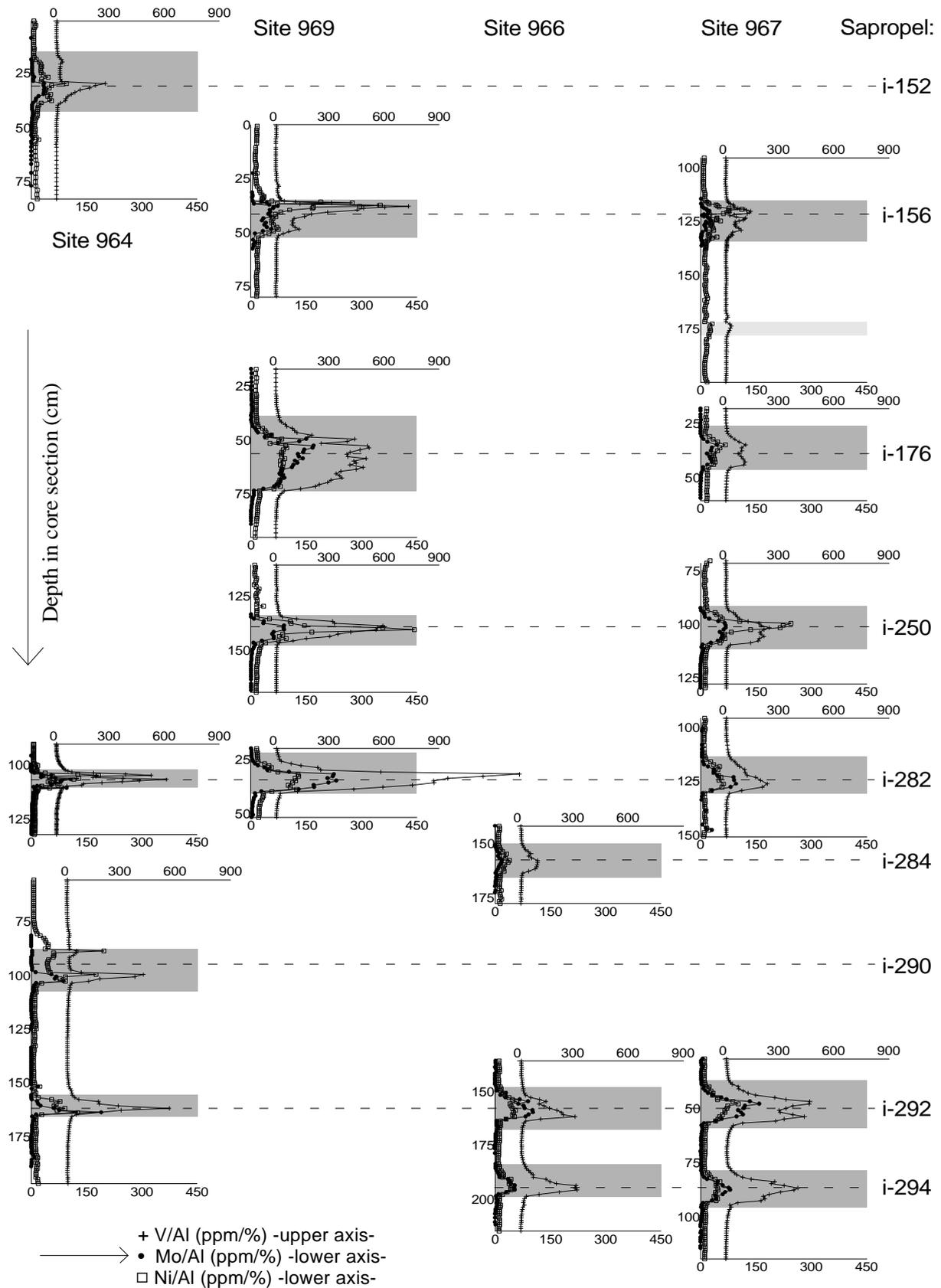


Figure 7.5 Profiles of V/Al, Mo/Al and Ni/Al versus depth for each interval.

1. Productivity and preservation

When eastern Mediterranean sapropels were first described, their high C_{org} content was mainly attributed to enhanced preservation under anoxic conditions, due to stagnation of eastern Mediterranean water masses [Olausson, 1961]. The concept of stratification resulting from increased freshwater input to the surface water during wet periods was developed by Rossignol-Strick *et al.* [1982] and Mangini and Schlosser [1986]. However, later it was argued that anoxia does not automatically enhance organic matter preservation, and that high C_{org} contents should be explained by increased primary productivity (PP) [Calvert, 1983; Pedersen and Calvert, 1990]. Canfield [1994] argued that both views are essentially correct, and that sedimentation rate determines whether bottom water oxygen levels result in increased organic matter preservation. At sediment deposition rates over $0.04 \text{ g cm}^{-2} \text{ yr}^{-1}$, little difference in preservation is found with varying bottom water O_2 content since C_{org} is mainly degraded by anaerobic pathways. At lower deposition rates, low-oxygen conditions result in better preservation of organic matter [Canfield, 1994]. Since average accumulation rates of the sediments of this study (Table 7.1) are below 0.004 cm yr^{-1} (approximately $0.005 \text{ g cm}^{-2} \text{ yr}^{-1}$), anoxic conditions could promote organic matter preservation. But is there any evidence for anoxic conditions and/or increased productivity during sapropel formation?

Barium and opal enrichments in the sapropels (Fig. 7.3) indicate that productivity was increased during sapropel formation. Sedimentary Ba content is considered a reliable indicator for palaeoproductivity because of the good correlation between C_{org} and Ba observed in sediments and sediment traps [Dymond *et al.*, 1992; De Lange *et al.*, 1994; François *et al.*, 1995]. Opal is precipitated by algae in highly productive surface waters. However, opal easily dissolves upon sedimentation, so that special conditions (a high sedimentation rate and a high opal flux) are needed for its preservation. Consequently, the presence of opal proves (but the absence of opal does not exclude) high productivity. We have analysed three sapropels for opal, and found intermediate contents (up to 4% opal) in two of them (i-176A and i-282C) and very high contents (up to 26%) in another (i-176B) (Fig. 7.3).

There is also ample evidence that at least the bottom water of the eastern Mediterranean must have been anoxic during Pliocene sapropel formation. Firstly, most sapropels are laminated, indicating the absence of benthic activity. Secondly, in all sapropels chalcophilic and redox-sensitive trace elements are strongly enriched (Mo, V and Ni shown as examples in Fig. 7.5). These trace elements may be transferred from seawater to the solid phase under reducing conditions by scavenging or (co)precipitation. Thirdly, the abundance and sulphur isotopic composition of pyrite in some of the sapropels indicates that iron sulphide formation took place in the water column [Passier *et al.*, *in press* (Chapter 5)]. Finally, the occurrence of isorenieratene-derived molecular fossils in some sapropels points to photic zone euxinia during their formation [Bosch *et al.*, 1998]. Isorenieratene is a pigment exclusively biosynthesized by the brown-coloured strain of photosynthetic green sulphur bacteria (Chlorobiaceae), which need both light and hydrogen sulphide. Consequently, these bacteria are restricted to the chemocline in the photic zone of euxinic basins. The combination of all of these factors in

sapropel i-282 in three investigated sites is the basis for the suggestion that the eastern Mediterranean was euxinic up into the photic zone for substantial periods during the formation of at least this sapropel [Passier *et al.*, *in press* (Chapter 5)]. Anoxic conditions clearly prevailed during Pliocene sapropel formation, which is likely to have resulted in enhanced preservation of organic matter [Canfield, 1994].

The very high C_{org} contents of the Pliocene sapropels cannot be achieved by increased productivity alone or just by improved preservation: both factors are imperative. This can be illustrated by a few simple calculations, clarified schematically (Fig. 7.6). In these calculations we will neglect the presence of terrestrial organic matter: most organic matter in these sapropels is of marine origin [Bosch *et al.*, 1998]. We can assume that PP during non-sapropel intervals was comparable to that of the present-day Mediterranean, because Pliocene and present-day homogeneous sediments are geochemically similar [*cf.* Sutherland *et al.*, 1984; Pruyssers *et al.*, 1991], and Mediterranean climate and hydrography have been essentially the same since the late Miocene [Schenau *et al.*, 1999 (Chapter 3)]. The average Mediterranean PP currently is $26 \text{ gC m}^{-2} \text{ yr}^{-1}$, but may have been lower in the Pliocene because of current excess

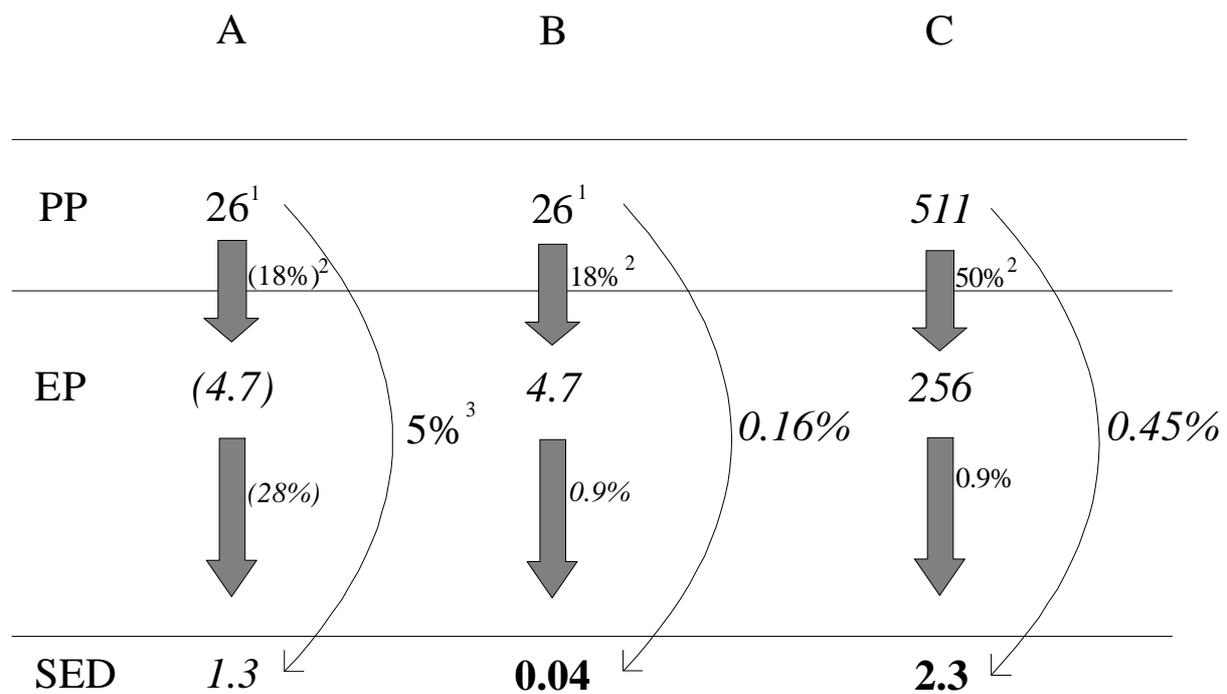


Figure 7.6 Calculations of fluxes (in $\text{gC m}^{-2} \text{ yr}^{-1}$) and preservation factors (in %),
 A: Situation during non-sapropel intervals, assuming a maximum preservation factor of 5%
 B: Situation during non-sapropel intervals.
 C: Situation during sapropel intervals, assuming no change in preservation (EP).
 Bold numbers are from this study, numbers in italics have been calculated from the other data. 1: Béthoux [1989]; 2: Eppley and Peterson [1979]; 3: Arthur *et al.* [1994].
 SED: sediment

anthropogenic nutrient (phosphate and nitrate) input into the Mediterranean [Béthoux, 1989]. If we apply the maximum preservation factor of the presently euxinic Black Sea (5%) [Arthur et al., 1994] to this value, we obtain a C_{org} accumulation rate of only $1.3 \text{ gC m}^{-2} \text{ yr}^{-1}$ (A in Fig. 7.6). Therefore, improved preservation without productivity levels higher than at present cannot account for the observed accumulation rates in sapropels of $2.3 \text{ gC m}^{-2} \text{ yr}^{-1}$ on average, or $9.5 \text{ gC m}^{-2} \text{ yr}^{-1}$ at maximum (calculated assuming a constant sedimentation rate). On the other hand, increased productivity alone is also insufficient. We can calculate that only 0.9% of the export productivity (EP), or 0.16% of the PP is preserved in non-sapropel sediments (B in Fig. 7.6). This is comparable to the preservation factor of 0.2% calculated by Howell and Thunell [1992] for oxic Holocene sediments in the Bannock Basin area (eastern Mediterranean). If we apply the preservation factor of 0.9% of the EP to the mean C_{org} accumulation rate calculated for the Plio-Pleistocene sapropels of this study, we find an EP of $256 \text{ gC m}^{-2} \text{ yr}^{-1}$ (C in Fig. 7.6). At high productivity levels, the EP asymptotically moves to 50% of the PP [Eppley and Peterson, 1979], so PP must have been in the order of $500 \text{ gC m}^{-2} \text{ yr}^{-1}$. For the highest C_{org} accumulation rate encountered in these sapropels this value would even be $2,100 \text{ gC m}^{-2} \text{ yr}^{-1}$. These calculated PP levels are far in excess of data reported for present-day open marine settings [e.g. Berger and Herguera, 1992; Sarnthein et al., 1992]. We can conclude that both productivity and preservation must have been higher during the formation of these Pliocene sapropels. Possibly, anoxia resulted from increased PP and consequent high C_{org} rain rates [Passier et al., in press (Chapter 5)], making productivity the key factor in Pliocene sapropel formation.

Can we use the Ba contents of these sediments to calculate the actual productivity levels during sapropel formation? That depends on whether the Ba enrichment mechanism in the Pliocene is comparable to that in modern settings. Barium is supposedly precipitated as barite

Table 7.2 Export productivity (EP) in $\text{gC m}^{-2} \text{ yr}^{-1}$ (calculated from sedimentary Ba contents) and the percentage of EP preserved in the sediments (PF).

	964		969		966		967	
	EP	PF	EP	PF	EP	PF	EP	PF
i-152	30	6%						
i-156			14	3%			28	5%
i-176			77	6%			13	10%
i-250			45	11%			13	9%
i-282	20	15%	16	21%			14	13%
i-284					2	21%		
i-290	20	8%						

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i-292	49	7%	9	12%	20	12%
i-294			2	25%	14	10%

in decaying organic matter in surface waters [Bishop, 1988]. During transit through the water column, C_{org}/Ba decreases because C_{org} is degraded, and additional barite may precipitate. Such a decrease is indeed observed: C_{org}/Ba is highest in Site 966 (926 m) and lowest in Site 964 (3,660 m) both in the sapropels and in the homogeneous intervals. However, the average C_{org}/Ba value in the Pliocene sapropels (59) is considerably higher than in the Holocene S1 sapropel (36:1) [Van Santvoort et al., 1996]. This is most likely the result of better C_{org} preservation in the Pliocene sapropels because a larger part of the water column may have been anoxic (this also explains why C_{org}/Ba values are higher in sapropels than in non-sapropel sediments). The relationship between Ba and C_{org} postulated by Van Santvoort et al. [1996] for the S1 is, therefore, not applicable to the sapropels of this study. The best fit to our data is $C_{org} = 0.0059 \cdot [Ba]$, but there is considerable variation per sapropel and per site. High sedimentary Ba contents indicate that anoxic water column conditions do not prevent barite precipitation: this occurs in the photic zone [Dymond et al., 1992; François et al., 1995], which remained oxic. Therefore, we can calculate EP using the equation [François et al., 1995]:

$$EP = 1.95 \cdot (F_{bioBa})^{1.41}$$

with EP in $gC\ m^{-2}\ yr^{-1}$, and in which F_{bioBa} is the biogenic barium flux (in $\mu g\ cm^{-2}\ yr^{-1}$), which can be calculated with the equation [Dymond et al., 1992]:

$$F_{bioBa} = \frac{Ba_{bio-acc}}{0.209 \log(MAR) - 0.213}$$

with the sediment mass accumulation rate (MAR) and biogenic Ba accumulation rate ($Ba_{bio-acc}$) in $\mu g\ cm^{-2}\ yr^{-1}$. Biogenic barium can be calculated assuming a detrital Ba/Al ratio of 0.0019 [Van Os et al., 1994]. In the homogeneous intervals, there is a significant (40% on average) detrital Ba fraction, but in the sapropels more than 95% of the Ba is biogenic. The thus calculated EPs (Table 7.2) vary considerably, but are clearly higher than at present ($4.7\ gC\ m^{-2}\ yr^{-1}$). Site 966 is an exception; the low Ba and C_{org} contents as well as the low sedimentation rates at this shallow site may be the result of winnowing. Using the observed sedimentary C_{org} accumulation rates (calculated assuming constant sedimentation rate; I in Table 7.3), we can determine the percentage of the EP that is preserved in the sapropels (PF in Table 7.2). These preservation factors of the EP vary between 3 and 25%, which is considerably higher than in homogeneous intervals (0.9%), but lower than inferred from maximum Black Sea preservation factors (28% of EP, Fig. 7.6). The variations per site for individual sapropels are not so large, which may indicate that these preservation factors provide a measure for the part of the water

column that is anoxic. Indeed, highest preservation factors are reached in sapropel i-282, for which a completely anoxic water column was postulated [*Passier et al., in press (Chapter 5)*].

Table 7.3 a) Sedimentation rate (cm/kyr), b) sapropel duration (yr) and c) C_{org} accumulation rate ($gC\ m^{-2}\ yr^{-1}$) for each sapropel, assuming:

- I : constant sedimentation rate
 II : 30% lower sedimentation rate during sapropel formation than during non-sapropel periods
 III : 50% higher sedimentation rate during sapropel formation than during non-sapropel periods

wd: water depth

	964 (wd 3660 m)			969 (wd 2201 m)			966 (wd 926 m)			967 (wd 2553 m)		
	I	II	III	I	II	III	I	II	III	I	II	III
i-152 a	2.05	1.55	2.73									
b	9756	12903	7326									
c	1.8	1.4	2.4									
i-156 a				2.69	1.98	3.73				2.91	2.14	4.04
b				6324	8586	4558				6357	8645	4579
c				2.4	1.8	3.3				1.5	1.1	2.1
i-176 a				3.68	2.92	4.61				2.58	1.98	3.37
b				8691	10959	6941				6507	8485	4986
c				5.0	4.0	6.3				1.3	1.0	1.7
i-250 a				4.23	3.09	5.93				2.77	2.16	3.54
b				3075	4207	2192				7574	9722	5932
c				4.8	3.5	6.7				1.2	0.9	1.5
i-282 a	2.14	1.57	2.99	1.98	1.52	2.57				2.09	1.63	2.67
b	3277	4459	2341	6828	8882	5253				7652	9816	5993
c	3.0	2.2	4.2	3.4	2.6	4.4				1.8	1.4	2.3
i-284 a							1.66	1.31	2.09			
b							8438	10687	6699			
c							0.4	0.3	0.5			
i-290 a	2.98	2.24	3.99									
b	5710	7589	4261									
c	1.6	1.2	2.1									
i-292 a	2.98	2.17	4.19				1.89	1.53	2.31	2.07	1.68	2.52
b	2688	3687	1909				10072	12418	8225	10154	12500	8333
c	3.6	2.6	5.1				1.1	0.9	1.3	2.5	2.0	3.0
i-294 a							1.89	1.53	2.31	2.07	1.67	2.54
b							10072	12418	8225	9670	11976	7874
c							0.6	0.5	0.7	1.4	1.1	1.7

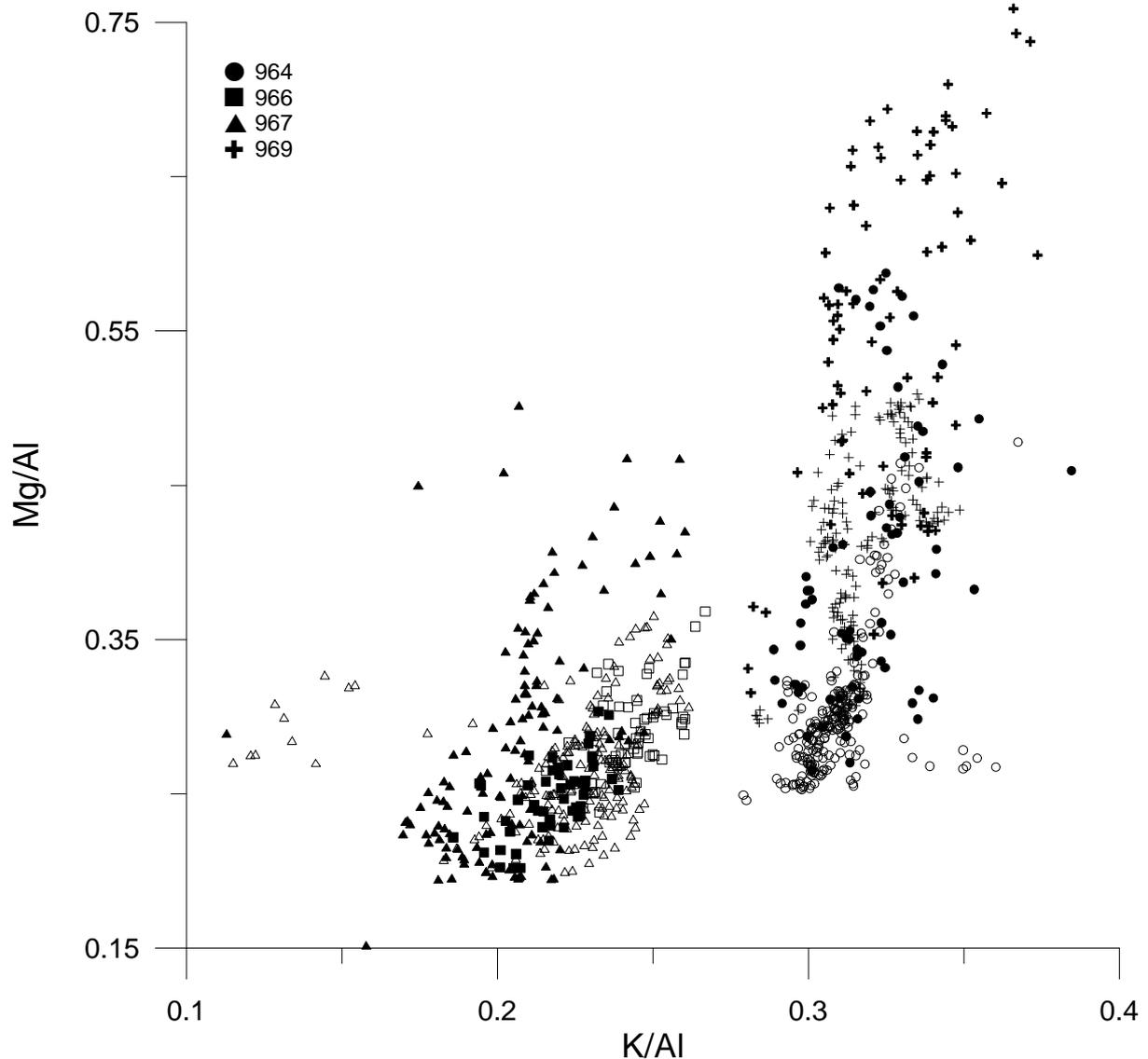


Figure 7.7 Scatter diagram of Mg/Al and K/Al for each site. Open and closed symbols (light and heavy plusses) represent, respectively, non-sapropel and sapropel intervals.

2. Nature of the organic matter

Two bulk parameters are commonly used for characterizing organic matter in sapropels: C/N ratio [e.g. Sigl et al., 1978; Calvert, 1983; Meyers, 1993] and $\delta^{13}\text{C}_{\text{org}}$ [e.g. Sutherland et al., 1984; Ten Haven et al., 1987; Fontugne and Calvert, 1992]. These are often interpreted in terms of terrestrial (with light $\delta^{13}\text{C}_{\text{org}}$ and high C/N) versus marine (with heavy $\delta^{13}\text{C}_{\text{org}}$ and low C/N) organic matter. However, the relative contribution of terrestrial organic matter to these sapropels is probably too low to have a significant influence on these parameters [Bosch et al., 1998]. Variations in $\delta^{13}\text{C}_{\text{org}}$ and C/N should, therefore, be explained by other factors.

C/N ratio - When C/N ratios are reported it is not always clear whether these refer to $C_{\text{org}}/N_{\text{org}}$ ratios, or to the more easily analysed $C_{\text{org}}/N_{\text{tot}}$ ratios. We have analysed $C_{\text{org}}/N_{\text{tot}}$ ratios. In the sapropel intervals, there will not be a marked difference between the two C/N parameters

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because C_{org} and N_{org} contents are high. In homogeneous intervals, however, a relatively large contribution of inorganic nitrogen to N_{tot} can considerably influence the $C_{\text{org}}/N_{\text{tot}}$ ratio. This problem can be solved by plotting C_{org} versus N_{tot} : if this yields a straight line, then the average $C_{\text{org}}/N_{\text{org}}$ ratio for the interval is the regression coefficient, and the contribution of inorganic N is represented by the offset on the N axis. This method works for the sapropels, where straight lines with coefficients of determination of 0.99 are obtained (0.94 for Site 969). In the homogeneous intervals $C_{\text{org}}/N_{\text{org}}$ ratios could also be obtained with this method for Sites 966 and 967 ($r^2=0.7$). In Sites 964 and 969, however, correlation between C_{org} and N_{tot} is poor ($r^2 < 0.2$), indicating admixture of variable amounts of inorganic N. This may be the result of illite being the dominant clay mineral in the Ionian Basin (Sites 964 and 969), and smectite and kaolinite in the Levantine Basin (Sites 966 and 967): compared with other clay minerals, illite contains more inorganic (fixed) N [e.g. Comans et al., 1989; De Lange, 1992b]. Illite is delivered to the Ionian Basin by bottom water currents from the Aegean and Adriatic Sea [Dominik and Stoffers, 1978], as well as by wind [Tomadin et al., 1984], whereas mainly smectite and kaolinite are transported to the Levantine Basin by the Nile [Venkatarathnam and Ryan, 1971]. The dominance of K-rich illite and Mg-rich chlorite at Site 964 and of K- and Mg-poor clay minerals at Site 967 was demonstrated by Wehausen and Brumsack [1998]. A plot of Mg/Al versus K/Al (Fig. 7.7) indicates that illite and chlorite are also dominant at Site 969 on the Mediterranean Ridge, whereas Site 966 is comparable to Site 967. Nitrogen fixed to illite, therefore, disturbs $C_{\text{org}}/N_{\text{org}}$ determination in the homogeneous intervals at Sites 964 and 969. However, it is clear that the $C_{\text{org}}/N_{\text{org}}$ values are higher than the $C_{\text{org}}/N_{\text{tot}}$ values in the homogeneous intervals, whereas only small differences between these ratios occur in the sapropel intervals (Table 7.4). A marked difference between homogeneous and sapropel $C_{\text{org}}/N_{\text{org}}$ values remains. The change in $C_{\text{org}}/N_{\text{tot}}$ from homogeneous to sapropel intervals and back is more abrupt than the changes in C_{org} content, suggesting that these C/N changes are not (only) caused by different types of organic matter being deposited. High C_{org} contents and C/N values are always correlated in the Mediterranean [Sigl et al., 1978; Calvert, 1983] and, more generally, in ancient sediments [Tyson, 1995]. The reasons for this correlation are not yet fully understood. A possible mechanism that may contribute to this relation in the Mediterranean is a change from P-limited to N-limited productivity during sapropel formation. Productivity in the present-day Mediterranean Sea is P-limited, possibly because of high N-fixation rates [Béthoux and Copin-Montégut, 1986]. Usually, however, oceans are N-limited because N-fixation is too slow to keep up with productivity: N-limited conditions are, therefore, also expected in the Mediterranean when productivity increases [Codispoti, 1989]. Additionally, supply of P may increase during sapropel formation because this nutrient is better regenerated in sediments deposited under anoxic conditions than in oxic sediments [Ingall et al., 1993]. This is reflected by $C_{\text{org}}/P_{\text{tot}}$ values [Van Cappellen and Ingall, 1994], which reach values up to 500 in the sapropels, whereas they are only ~1 in the homogeneous sediments. Phosphorus regenerated from abyssal sediments will be exported from the Mediterranean unless there was a circulation reversal, or unless there was efficient vertical transport of nutrients to the photic zone, e.g. by upwelling or eddies. Phosphorus

Table 7.4 Average C_{org}/N_{tot} and calculated C_{org}/N_{org} values in sapropels and homogeneous sediments, and detrital nitrogen (N_{detr}). $\delta^{13}C_{org}$ for sapropels and homogeneous intervals for each site, and the difference in this parameter between the two types of sediment ($\Delta\delta^{13}C_{org}$). Sites are arranged from west to east. C_{org}/N_{tot} and $\delta^{13}C_{org}$ values are averages of the mean values of each interval; values in brackets represent the standard deviation. No standard deviations are given for C_{org}/N_{org} values because only one value is obtained for each site. Homogeneous $\delta^{13}C_{org}$ for Site 966 is based on one interval. Question mark indicates poor correlation between C_{org} and N_{tot} .

ODP Site	964	969	966	967
water depth (m)	3660	2201	926	2553
C_{org}/N_{tot} homogeneous	4.3 (0.4)	4.5 (1.9)	9.8 (0.2)	6.6 (1.3)
C_{org}/N_{tot} sapropel	17.1 (1.3)	19.8 (1.4)	19.5 (1.4)	19.1 (1.6)
C_{org}/N_{org} homogeneous	?	?	16.6	11.7
C_{org}/N_{org} sapropel	18.7	21.0	20.9	21.1
N_{detr} (wt%)	0.04	0.07	0.03	0.03
$\delta^{13}C_{org}$ homogeneous (‰)	-22.4 (0.3)	-21.7 (0.4)	-20.1	-19.5 (0.4)
$\delta^{13}C_{org}$ sapropel (‰)	-23.3 (0.2)	-22.9 (0.6)	-21.5 (0.2)	-21.6 (0.7)
$\Delta \delta^{13}C_{org}$ (hom-sap) (‰)	0.9	1.2	1.4	2.1

regeneration under anoxic conditions combined with vertical transport or a circulation reversal would provide a positive feedback mechanism possibly sustaining high primary productivity during sapropel formation. In that scenario, nitrogen would most likely be the limiting nutrient, resulting in high C/N values during sapropel formation [Tyson, 1995].

$\delta^{13}C_{org}$ - In the intervals in which this parameter has been analysed, there is a consistent shift from heavier $\delta^{13}C_{org}$ values in the homogeneous intervals to lighter values in the sapropels. This shift is more gradual and less pronounced than the changes observed in the C/N-ratio (Fig. 7.2). Additionally, there is a distinct west-east trend of increasingly more positive $\delta^{13}C_{org}$ in both the homogeneous and the sapropel intervals (Table 7.4). Tyson [1995] lists several factors influencing $\delta^{13}C_{org}$ in marine sediments, which we will briefly discuss:

- C3 and C4 plants have distinctly different $\delta^{13}C_{org}$ values. However, C3 plants usually dominate, and significant contributions of C4 organic matter in marine sediments is only observed in seagrass meadows and salt marsh deposits.
- temperature: at the high temperatures in the Mediterranean, the effect of temperature on $\delta^{13}C_{org}$ is small. Moreover, Fontugne and Calvert [1992] do not find a reflection of glacial/interglacial temperature changes in $\delta^{13}C_{org}$ of Mediterranean sediments.

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- grain size: no significant changes in $\delta^{13}\text{C}_{\text{org}}$ have been reported for fine-grained pelagic sediments.
- CO_2 -recycling: will not affect $\delta^{13}\text{C}$ in the photic zone.
- productivity: isotopic fractionation by phytoplankton may decrease at high PP, resulting in less negative $\delta^{13}\text{C}$ values. Palaeoproductivity was higher in the sapropels, but $\delta^{13}\text{C}_{\text{org}}$ values in these layers are more negative.
- early diagenesis may result in negative shifts of up to 3‰. Anoxic facies have a greater potential for these changes. Furthermore, the magnitude of the change may increase with heavier initial $\delta^{13}\text{C}_{\text{org}}$.

From all these factors, a change from mainly oxic to mainly anoxic organic matter degradation is most likely to lead to heavier $\delta^{13}\text{C}_{\text{org}}$ in homogeneous sediments and lighter values in sapropels. The increase of this difference ($\Delta \delta^{13}\text{C}_{\text{org}}$) from 0.9‰ in the west to 2.1‰ in the east may result from initially heavier $\delta^{13}\text{C}_{\text{org}}$ values (which have a greater potential for diagenetic $\delta^{13}\text{C}_{\text{org}}$ reduction [Tyson, 1995]) in the east. Another factor that may contribute to the more negative $\delta^{13}\text{C}_{\text{org}}$ values in sapropels is increased river runoff [Fontugne and Calvert, 1992], which may lead to a low-salinity surface water layer all over the eastern Mediterranean [e.g. Rossignol-Strick et al., 1982]. River water usually contains more CO_2 than seawater and has, therefore, lighter $\delta^{13}\text{C}$ values of ΣCO_2 . Increased CO_2 concentrations in ocean surface water will also favour a higher degree of discrimination against ^{13}C during photosynthesis [Fontugne and Calvert, 1992]. The increasing $\Delta\delta^{13}\text{C}_{\text{org}}$ from west to east can, therefore, also be explained by a stronger increase in (Nile) freshwater input in the east.

The trend towards more positive $\delta^{13}\text{C}_{\text{org}}$ values in the east, both in sapropels and homogeneous intervals, is difficult to explain by any of the aforementioned factors. We propose that it results from biological fractionation. Surface water in the present-day Mediterranean flows from west to east and becomes depleted in ^{12}C which is preferentially taken up by plankton. Intermediate water flows from east to west, and becomes richer in ^{12}C derived from decaying organic matter. $\delta^{13}\text{C}$ of ΣCO_2 used for primary productivity will, therefore, be more positive in the east, especially when deep water is used for primary productivity, because in this case no exchange with the atmosphere is possible. If this interpretation is correct, then the circulation pattern must have been anti-estuarine during sapropel formation as well as during non-sapropel periods.

3. Sapropel formation time

The Holocene S1 sapropel can be dated by ^{14}C measurements [e.g. Troelstra et al., 1991]. Its onset may have been time-transgressive [Ströhle and Krom, 1997] and its top is often affected by oxidation [Thomson et al., 1995; Van Santvoort et al., 1996], but a duration between 3,000 and 4,000 years for this sapropel is a reasonable estimate [Rohling and Hilgen, 1991; Higgs et al., 1994]. Older sapropels cannot be dated directly, and estimates of their formation time vary from ~2,000 years for Pleistocene laminites [Nijenhuis, 1998], and 1,000 to 6,000 years for Pliocene

sapropels [Wehausen and Brumsack, 1998], to 10,000 years for Miocene sapropelites [Nijenhuis et al., 1996 (Chapter 2)].

Although the duration of one precession-related sedimentary cycle is precisely known, sapropel formation time is more difficult to determine because assuming constant sedimentation rates may not be correct. In addition, (early) diagenetic processes such as dissolution of opal and carbonates, and oxidation of organic matter may have resulted in considerable thinning of the initial sapropel intervals. Removal of organic matter from the top of a sapropel by oxic degradation, "burning down" [e.g. Higgs et al., 1994], can be recognized by a sharp and sudden instead of a gradual decrease in C_{org} content at the sapropel top, and high Ba but low C_{org} contents directly above it [Van Santvoort et al., 1996]. These characteristics are not found in any of the sapropels of this study, so we conclude that the thicknesses of the sapropels were not affected by post-depositional oxic degradation. The carbonate content of several Plio-Pleistocene sapropels is very low (down to 1%; Fig. 7.1). This is not only due to the absence of benthic foraminifera under anoxic conditions, but also to the near absence of planktonic foraminifera. In sapropel i-282C planktonic foraminifera are even completely absent [L. Lourens, pers. comm.]. This may result from a dominance of siliceous or organic-walled plankton over calcareous species at times of high productivity [e.g. Van Os et al., 1994; Nijenhuis et al., 1996 (Chapter 2)]. Additionally, carbonate dissolution may have occurred. During formation of this particular sapropel, however, a large part of the water column was euxinic, meaning that sulphate reduction took place in the water column [Passier and De Lange, 1998]. During organic matter oxidation by sulphate reduction in the absence of bioturbation, a build-up of HCO_3^- will prevent carbonate dissolution [Canfield and Raiswell, 1991]. Since the sapropels are still suboxic, or even anoxic-sulphidic [Passier and De Lange, 1998], carbonate dissolution can only have occurred before deposition. In seawater, when oxygen becomes depleted as a result of oxic organic matter degradation, calcite becomes undersaturated [Canfield and Raiswell, 1991] and may dissolve. Thus, carbonate dissolution can only have taken place in the upper part of the photic zone, and was, therefore, probably of minor importance. Opal, on the other hand, mainly dissolves at the sediment-water interface [Broecker and Peng, 1982]. This may have occurred in all sapropels, but the effect on accumulation rates of other elements is probably limited because accumulation rates of sapropel i-176B, in which 26% opal is preserved, are comparable to those of other sapropels at Site 969. In order to estimate sapropel duration, we will compare scenarios with (I) a constant sedimentation rate during each precession cycle, (II) a 30% lower sedimentation rate during sapropel formation than during deposition of homogeneous intervals, and (III) a 50% higher sapropel sedimentation rate.

Under the assumption of a constant sedimentation rate (scenario I), a sapropel formation time between 2,700 and 10,000 years can be calculated (Table 7.3). The Ti/Al curve (Fig. 7.4), which has been shown to mimic the precession index at least at Site 967 [Lourens et al., 1998], shows half-cycles that are broader than the sapropels. Therefore, sapropel formation must have been shorter than 11,000 years (half a precession cycle). Five out of the 17 individual sapropels of this study have durations close to 11,000 years if a constant sedimentation rate is assumed

(Table 7.3). For most other sapropels a 30% decrease in sedimentation rate also results in durations of this magnitude, indicating that a sedimentation rate decrease of more than 30% is not possible. Site 964 is an exception because most sapropels are relatively thin there. However, based on cyclic K/Al patterns, it has been suggested that sedimentation rates were ~30% lower at Site 964 [Wehausen and Brumsack, 1998]. Scenario III (a 50% increase in sedimentation rate during sapropel formation) implies relatively short sapropel formation times which are close to the alleged formation time of the S1 (Table 7.3). However, the resultant sapropel C_{org} accumulation rates must have been rather high because of the high C_{org} content of these Pliocene sapropels. A good modern analogue of the eastern Mediterranean at times of Pliocene sapropel formation is the Black Sea [Chapter 6]. It is deep, euxinic, and sedimentation rates are relatively low. In this basin, PP is in the order of $73 \text{ gC m}^{-2} \text{ yr}^{-1}$ (EP ~ $17 \text{ gC m}^{-2} \text{ yr}^{-1}$) and C_{org} accumulation rates are about $2.8 \text{ g m}^{-2} \text{ yr}^{-1}$ [Bralower and Thierstein, 1987]. In the Mediterranean during Pliocene sapropel formation, productivity may have been higher (Table 7.2). We will, therefore, assume an upper limit of $5 \text{ gC m}^{-2} \text{ yr}^{-1}$ for C_{org} accumulation rates in the sapropels, corresponding to an EP of ~ $30 \text{ gC m}^{-2} \text{ yr}^{-1}$. In scenario III, average C_{org} accumulation rates of five out of the seventeen sapropels approximate or exceed this value (Table 7.3). Bearing in mind that these accumulation rates are only averages, and maximum accumulation rates were considerably higher, this indicates that sedimentation rate cannot have increased to such an extent in most sapropels. In Site 966, where sapropels are characterized by low C_{org} enrichments, a higher increase in sedimentation rate is theoretically possible.

Concluding, we can state that sedimentation rates probably did not change dramatically during sapropel formation. Most sapropels must have been deposited under sedimentation rates comparable to those of homogeneous intervals. Some sapropels may have been deposited with sedimentation rates that were at most 30% lower or up to 50% higher than those during non-sapropel intervals. Sapropel formation times may have been variable, but were clearly shorter in the western part (Site 964), than in the eastern part of the eastern Mediterranean (Sites 966 and 967); at Site 969 sapropel duration was intermediate (Table 7.3).

4. Implications for sapropel formation scenarios

Ever since it was predicted that stagnation of the Mediterranean water column might lead to the deposition of organic-rich, laminated sediments [Bradley, 1938], sapropel occurrence has been linked to water column stratification. Isotopic analyses of foraminifera tests and oceanographic considerations indeed provided proof for reduced surface water salinity [Olausson, 1961; Rossignol-Strick et al., 1982; Anastasakis and Stanley, 1986] or increased surface water temperatures [Mangini and Schlosser, 1986; Emeis, et al., 1991] at times of sapropel formation, which might lead to such a stratification. The idea that sapropel formation was solely initiated by hydrographic changes leading to stagnation, bottom water oxygen depletion and improved preservation was later challenged by Calvert [1983] who showed that increased productivity must have been at least as important.

A problem associated with increased productivity in the eastern Mediterranean is the supply of nutrients: due to the anti-estuarine water circulation, most nutrients are exported with deep water and do not become available in the photic zone ("nutrient desert"). An elegant solution to this problem is the DCM (deep chlorophyll maximum) model in which deep water nutrients become available for PP because of shoaling of the pycnocline into the photic zone [Rohling and Gieskes, 1989; Castradori, 1993]. An alternative solution is a circulation reversal in the (eastern) Mediterranean, changing the basin into a nutrient trap [Calvert, 1983; Sarmiento et al., 1988; Howell and Thunell, 1992; Nijenhuis et al., 1998]. A third mechanism invokes increased seasonal contrasts at times of Northern Hemisphere insolation maxima. As a result, there may be intense mixing of the water masses during the cold winter, and a more stratified situation in the hot summer because of surface water warming. In this scenario, the supplied nutrients will be available throughout the basin for spring blooms. Next, during the summer, more oligotrophic conditions will prevail, when surface waters become isolated and nutrients are only supplied to the near-coastal areas [Nijenhuis et al., 1996 (Chapter 2); Schenau et al., 1999 (Chapter 3)].

Recently, since ¹⁴C-dating of the S1 has become more advanced, it has been suggested that this sapropel was formed by deposition in a slowly to greater depths expanding oxygen minimum zone [Ströhle and Krom, 1997]. The opposite suggestion, that sapropel formation started in the deeper parts of the basin, has been suggested by Troelstra et al. [1991], and is similar to a model developed for the Black Sea [e.g. Calvert et al., 1987]. Which of these models, which were mostly developed for Quaternary sapropels can be reconciled with our data for Pliocene sapropels?

Our calculations for sapropel i-292 and i-282 show that sapropel formation time was clearly shorter at Site 964 than at the other sites. Although this might be caused by an overestimation of the average sedimentation rate at Site 964 because of possible intercalation of small turbidites or slumps in the homogeneous intervals, the lack of geochemical indications for turbidites and the necessity of systematic occurrence of this phenomenon in each cycle suggests that this is not the case. Because Site 964 is both the deepest and the most western site, there may be a geographic and a bathymetric reason for the shorter sapropel formation time. A "deepening OMZ" scenario, in which low-oxygen conditions extend to greater water depth with time, is one explanation. An ideal place to test this is at Erathostenes Seamount (Site 966 and 967). Site 966 and 967 are geographically very close to each other, but the former is at 926 m depth while the latter is at 2,553 m. It is striking that although their geochemistry is different, the calculated sapropel formation times are very similar. This suggests that sapropel formation, at least at the depth range of 1 - 2.5 km was more or less simultaneous. Obviously, this also contradicts the hypothesis developed for S1 that sapropel formation started earlier in the deeper parts of the Mediterranean [Troelstra et al., 1991]. Therefore, the lower sapropel formation times at Site 964 are more likely explained by an east-west trend, even more so because sapropel formation times at Site 969, situated between 967 and 964, but at shallower depth, are intermediate. The fact that sapropel formation lasted longer in the eastern part of the basin can be explained by a scenario in which Nile runoff is important for sapropel formation. During

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insolation maxima, precipitation increased by monsoonal activity, leading to a strong surge of freshwater from especially the Nile [Rossignol-Strick *et al.*, 1989], supplying extra nutrients to the eastern part of the basin. Therefore, productivity will increase first in this part of the basin. Similarly, when precipitation and monsoonal activity decrease, the most eastern part will keep receiving nutrients for the longest period. The importance of Nile runoff may be confirmed by the eastwards increasing $\Delta\delta^{13}\text{C}_{\text{org}}$ values.

Did the increased Nile outflow affect circulation in the Mediterranean? Evidence that bottom waters were not fully stagnant during sapropel formation comes from K/Al and Mg/Al ratios. The high amounts of K-rich illite and Mg-rich chlorite transported to the Ionian basin by bottom water currents from the Aegean and Adriatic Seas [Dominic and Stoffers, 1978] and by wind input [Tomadin *et al.*, 1984] are reflected by high values of K/Al and Mg/Al at Sites 964 and 969 (Fig. 7.7). During sapropel formation, these ratios are even higher at these sites. Since wind input was reduced during sapropel formation because of a wetter climate, this increase in illite and chlorite must be caused by bottom water currents, indicating that these were not restricted. The decrease of the K/Al and Mg/Al values at Sites 966 and 967 confirms increased deliverance of K- and Mg-poor clays to the Levantine Basin by the Nile during sapropel formation [Venkatarathnam and Ryan, 1971]. Ongoing water circulation during at least deposition of sapropels i-282 and i-292 has been inferred from trace element budgets of sapropels [Nijenhuis *et al.*, 1998; Chapter 6]. These authors suggested that water circulation may have been reversed in order to supply enough nutrients to sustain high productivity. Eastwards increasing $\delta^{13}\text{C}_{\text{org}}$ during both sapropel and homogeneous intervals (Table 7.4) may indicate that surface waters always flowed from west to east, if this pattern can indeed be explained by biological fractionation. If circulation was not reversed, but normal, nutrients may have been supplied by rivers and made available for productivity by increased seasonal contrasts and winter mixing. Additionally, P released from anoxic sediments may be transported to the photic zone, e.g. by eddies, and constitute a positive feedback mechanism to increased productivity.

Conclusions

- The high organic matter content in Pliocene Mediterranean sapropels is the result of both increased PP and improved preservation because of extensive anoxia. The anoxic conditions are most likely caused by the high productivity, not by stagnation of water circulation.
- More negative $\delta^{13}\text{C}_{\text{org}}$ values during sapropel formation and eastwards increasing $\Delta\delta^{13}\text{C}_{\text{org}}$ may result from diagenesis and/or increased river runoff.
- Sedimentation rates did not change dramatically during Pliocene sapropel formation. Sapropel sedimentation rates were at most 30% lower or 50% higher than in homogeneous intervals.
- Sapropel formation lasted 2,000-10,000 years, and was longer in the eastern than in the western part of the eastern Mediterranean Sea.
- In the depth interval between 1 and 2.5 km, sapropel formation was simultaneous.

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Caenozoic	Tertiary	Neogene	Pliocene	0.01
			Miocene	1.6
		Palaeogene	Oligocene	5.3
			Eocene	23.7
			Palaeocene	36.6
			57.8	
			66.4	

Part III: The Pleistocene

"The Mediterranean is an absurdly small sea; the length and greatness of its history makes us dream it larger than it is."

Lawrence Durrell, *Balthazar*

Chapter 8

Comparison of coeval organic carbon rich sediments in the Vrica section and in ODP Sites 967 and 969

I.A. Nijenhuis, J. Becker, G.J. de Lange

Abstract - The geochemistry of eastern Mediterranean sediments from the early Pleistocene insolation cycle i-156 was studied in the Vrica section (Calabria, Italy) and in ODP Sites 967 and 969. The ODP sediments are rich in carbonates and contain a sapropel with up to 20% organic carbon, whereas the Vrica sediments are rich in clays and contain a laminite with up to 1% organic carbon. Processes that affected the land section but not the ODP sediments can only partly account for these differences. In the land section, dessication and compaction resulted in higher dry bulk densities. Subsurface weathering caused oxidation in sediments surrounding conductive planes constituted by ash layers, resulting in lower organic carbon and total nitrogen contents, and lower C/N ratios and organic carbon isotopic values. Subaerial weathering resulted in higher Na and K contents because of evaporation at the outcrop surface.

Other geochemical differences are thought to be due to the different settings: the Vrica sediments have been deposited closer to land, in shallower water, with a higher sedimentation rate and in a more western part of the Mediterranean than the ODP sediments. This resulted in higher aluminium and organic carbon accumulation rates, lower "terrestrial" and redox-sensitive element to aluminium ratios, lower barium contents and more negative organic carbon isotopic values in the sediments of Vrica compared with those of ODP.

Formation of a laminite enriched in organic carbon at Vrica, and of laminated sapropels at the ODP sites can be explained by one model combining higher productivity and better preservation. The occurrence of an interval enriched in organic carbon immediately above and below the anoxic laminite provides evidence for the hypothesis that organic carbon production increased before anoxia developed. The inferred duration of the laminite is shorter than that of the sapropels, indicating that anoxia probably lasted longer in deep water than in shallow environments.

This chapter has been submitted for publication in *Palaeogeography, palaeoclimatology, palaeoecology*.

Introduction

In the Mediterranean area, particularly on islands like Sicily, Crete and Gavdos, outcrops of Neogene marine sediments can be found, which are characterized by an alternation of light-coloured marls and darker layers with a higher clay and organic matter content. These dark layers are occasionally called sapropels, although they generally contain less organic carbon (C_{org}) than implied by that term (at least 2% [Olausson, 1961]). Their cyclic occurrence coincides with minima in the index of the precession of the Earth's equinoxes [Hilgen, 1991a, b; Hilgen et al., 1995]. Similar layers have been recovered from the present-day Mediterranean seafloor in piston-, box- and gravity-cores. These layers generally seem to be better developed than those found in land sections, in the sense that they are more enriched in C_{org} , more depleted in carbonate, and have better developed lamination. On the other hand, they are usually thinner. Unfortunately, a direct comparison between age-equivalent sediments recovered with traditional marine coring techniques (younger than approximately 1 Ma) and astronomically tuned sapropels in land sections (older than 1.2 Ma) has not been possible until now. During ODP Leg 160 to the eastern Mediterranean, sapropel-containing sediments of a Recent to Miocene age were recovered from several sites by hydraulic coring techniques, offering the opportunity to compare abyssal, well-developed sapropels from ODP sites with shallower equivalents in land sections. We sampled the coeval sapropels of insolation cycle i-156 in ODP Sites 967 and 969 and laminite "o" [Selli et al., 1977] in the Vrica section (Calabria, Italy; Fig. 8.1) in high resolution. We show that the geochemical differences between the sapropels and the laminite are due to the dissimilarity of the settings and to the combined results of compaction,

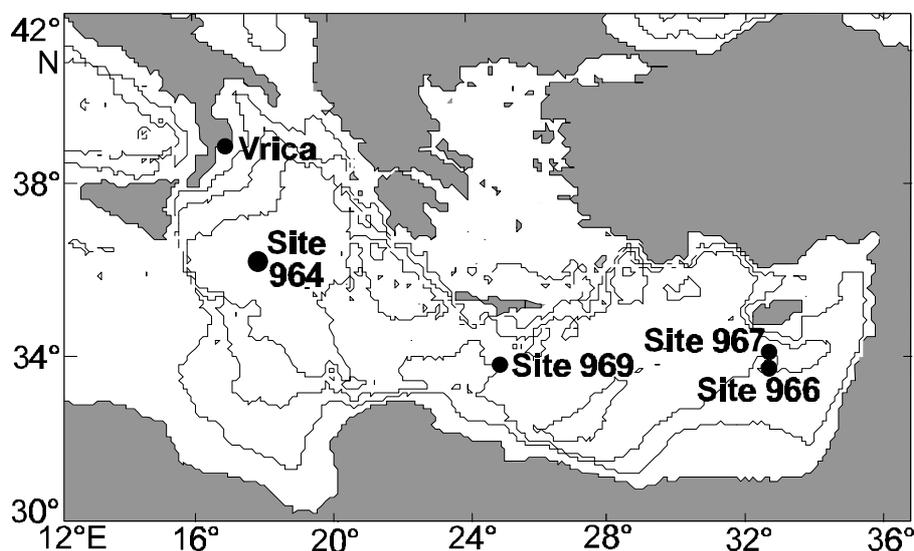


Figure 8.1 Location of the Vrica section and ODP drilling sites.

Comparison of coeval organic carbon rich sediments

⁶ ρ_{hom} , ρ_{sap} : dry bulk density of the homogeneous and sapropel (or laminated) intervals

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NCS analyser. Stable carbon isotopes of organic matter ($^{13}\text{C}_{\text{org}}$) were determined with a Stable Isotope Ratio Analyser (VG SIRA 24), and are reported relative to the PeeDee Belemnite (PDB) standard. On the Vrica samples, the carbonate content was determined gas-volumetrically. For the ODP samples, the CaCO_3 content was calculated from the amount of inorganic carbon present (determined with the NCS analyser).

For major, minor and trace element analyses, a 250 mg sample was digested in 10 ml of a 6.5 : 2.5 : 1 mixture of HClO_4 (60%), HNO_3 (65%) and H_2O , and 10 ml HF (40%) at 90°C . After evaporation to dryness on a sand bath at 190°C , the residue was dissolved in 50 ml 1 M HCl. The resulting solutions were analysed with a Perkin Elmer Optima 3000 inductively coupled plasma atomic emission spectrometer (ICP-AES) for Al, Fe, K, Na, Mg, Sr, Ba, Mn, V, Mo, Cu, Ni, Zn, Cr, Ti and Y. In the ODP sapropel samples, Ba was determined separately in solutions prepared by the same procedure, but using only 40 mg sample to prevent BaSO_4 precipitation. On selected Vrica samples, As and Se were measured with a Perkin Elmer 3100 hydride Atomic Absorption Spectrometer (AAS), and Mo with a Perkin Elmer 4100 ZL ZGFAAS (AAS with Zeeman correction). From other selected samples of the Vrica section, pyrite was extracted following the methods in *Passier et al. [1997]*, and analysed for its stable sulphur isotopic composition ($^{34}\text{S}_{\text{pyr}}$, reported relative to the Vienna-Canyon Diablo troilite) by means of combustion isotope ratio monitoring mass spectrometry (C-irmMS [*Böttcher et al., 1998*]). Opal was analysed on selected samples following the method of *Müller and Schneider [1993]*, using a Technicon TRAACS 800 auto-analyser.

All results were checked with international and house standards. Relative standard deviations in duplicate C_{org} and N_{tot} measurements are $<5\%$. The absolute standard deviation in $^{13}\text{C}_{\text{org}}$ and $^{34}\text{S}_{\text{pyr}}$ analyses are below 0.2‰ and 2‰ , respectively. Relative standard deviations in duplicate measurements are $<1\%$ for carbonate analyses. ICP duplicate measurements have relative standard deviations $<5\%$ for all elements. Molybdenum, As and Se (Vrica) were measured in triplicate with a standard deviation of, respectively, $<10\%$, $<3\%$, and $<10\%$ for samples that contain more than 1 ppm Se.

Results

Vrica

Microscopic analysis of thin sections revealed that the laminite consists of 0.2-0.5 mm thick calcareous-clayey layers separated by 0.01-0.1 mm thick organic strands. Foraminifera shells are present in the clay layers, and are sometimes filled in by pyrite. In the laminated intervals, this pyrite occurs mainly in shells as 5-10 μm large framboids composed of crystals of $\sim 0.5 \mu\text{m}$ in diameter. In more homogeneous intervals, pyrite occurs both as framboids (but unrelated to foraminifera shells), and as larger (\varnothing 5-8 μm) euhedral crystals. $^{34}\text{S}_{\text{pyr}}$ ranges from -30.2 to -39.6‰ (Table 8.2). The red-brown intervals in the laminite are located around very thin (<1 mm) layers of fine-sand-sized, angular grains of plagioclase, amphibole and quartz, which are interpreted as volcanic ash deposits. Laminae are continuous around the ash layers, but

appear darker in colour. Non-laminated intervals appear homogeneous, with some small organic strands or pyrite aggregates.

The background C_{org} content of the sediments is 0.28%. Enrichment of C_{org} in a 179 cm thick interval is indicated by a lightly shaded area (Fig. 8.2). Highest C_{org} contents (up to 1%) are reached in the 56 cm thick laminite (indicated by dark shading in Fig. 8.2), located within the C_{org} -enriched interval. In the laminite, red-brown intervals around the thin ash layers (indicated by horizontal lines in Fig. 8.2) are characterized by lower C_{org} contents. The N_{tot} profile (not shown) is virtually identical in shape to that of C_{org} ; N_{tot} values range from 0.05 to 0.1%. C_{org}/N_{tot} and $^{13}C_{org}$ profiles show the same pattern (Fig. 8.3). Barium is shown relative to aluminium (Fig. 8.2) in order to correct for relative variations in detrital input. Ba/Al values are virtually constant except for some local spikes, especially in the laminite. No opal was detected in six selected samples coming from within and around the laminite. The carbonate content of the Vrica sediments (Fig. 8.4) is relatively low compared with most Mediterranean Neogene sections, namely approximately 23%, with even lower values (~18%) in the C_{org} -enriched interval. Sr/Ca values (Fig. 8.5) are also lower in this interval, but higher again in the actual laminite. Because the carbonate content is rather low, most of the sediment consists of clays, which is confirmed by the high Al content (Fig. 8.4). The laminite contains less of other "terrestrial" elements (Fe, K, Mg, Na, Ti, Y and Zr) relative to Al than the homogeneous sediments (Table 8.3; Na/Al and K/Al shown graphically in Fig. 8.6), except for Fe/Al (Fig. 8.5), which is high in the C_{org} -enriched interval. Redox-sensitive and chalcophilic trace elements (As, Cr, Cu, Mo, Ni, Se, V) are also high in this interval (relative to Al), but especially in the laminite (Ni/Al and V/Al shown as examples; Fig. 8.7). Manganese contents, on the other hand, are lower in the C_{org} -enriched interval. Weathered samples only differ geochemically from their fresh equivalents by higher Na/Al and K/Al values (Fig. 8.6).

ODP Sites

Compared with the Vrica section, the ODP sapropels are characterized by substantially higher C_{org} and N_{tot} contents (up to 20% and 1.1%, respectively), sharper and larger changes in C_{org}/N_{tot} values, and a reversed pattern of the $^{13}C_{org}$ profile (Figs. 8.2 and 8.3; Table 8.4). Ba/Al is higher in the sapropels than in the homogeneous intervals (Fig. 8.2). Ash layers are not present except

Table 8.2 Details of samples from which pyrite was extracted, and $\delta^{34}S_{pyr}$

sample location (cm)	description	^{34}S (‰)
363	homogeneous sediment	-33.1
531	upper part laminite	-36.5
575	bottom laminite	-30.2
620	bottom C_{org} enriched interval	-31.7

Table 8.3 Average Al contents and terrestrial element to Al ratios of homogeneous and sapropel (shaded) intervals of the Vrica section and the ODP sites.

Site	Al (%)	Fe/Al (%/%)	K/Al (%/%)	Mg/Al (%/%)	Na/Al (%/%)	Ti/Al (ppm/%)	Y/Al (ppm/%)	Zr/Al (ppm/%)
Vrica	7.42	0.51	0.29	0.22	0.12	561	2.96	12.8
	7.74	0.55	0.27	0.22	0.10	528	2.70	11.5
969	3.58	0.55	0.32	0.45	0.31	609	5.04	17.6
	2.99	1.06	0.32	0.55	0.62	548	9.01	23.0
967	4.74	0.68	0.23	0.29	0.23	714	4.39	19.4
	5.08	1.27	0.21	0.32	0.29	632	4.78	19.3

at Site 967, just above the middle of the sapropel (indicated by a horizontal line in Figs. 8.2-4 and 8.7). The carbonate content varies between less than 1% in the sapropels to almost 70% in the homogeneous intervals (Fig. 8.4). The Al content of the ODP sediments varies inversely with CaCO_3 and is, with values between 2.3% and 6.5% (except for a maximum of 8.9% in the ash layer at Site 967), lower than in Vrica (Fig. 8.4; Table 8.3). With respect to Al, all terrestrial elements are higher in the sapropel (Table 8.3). Redox-sensitive trace element contents are considerably higher in the ODP sapropels than in the Vrica laminite (Fig. 8.7). The geochemistry of sapropel i-152 in ODP Site 964 is comparable to that of sapropel i-156 in Site 967 and 969 [Chapter 7]. Of the i-152 sapropel, only the $C_{\text{org}}/N_{\text{tot}}$ ratio and the $^{13}\text{C}_{\text{org}}$ values are reported (Table 8.4).

Table 8.4 Average $C_{\text{org}}/N_{\text{tot}}$ and $\delta^{13}\text{C}_{\text{org}}$ values of homogeneous and sapropel (shaded) intervals of the Vrica section and the ODP sites. C_{org} accumulation rates for these intervals calculated under the assumption that sedimentation rate did not change during deposition (not shown for Site 964). n.d.: no data

Site	$C_{\text{org}}/N_{\text{tot}}$		$^{13}\text{C}_{\text{org}}$ (‰)		acc. rate C_{org} ($\text{g m}^{-2} \text{yr}^{-1}$)	
Vrica	5.8	9.3	-23.95	-23.67	1.51	3.68
964	5.5	17.4	-22.83	-23.21	n.d.	n.d.
969	3.0	18.4	-21.64	-22.11	0.029	2.36
967	4.7	17.7	-19.02	-20.70	0.067	1.52

Comparison of coeval organic carbon rich sediments

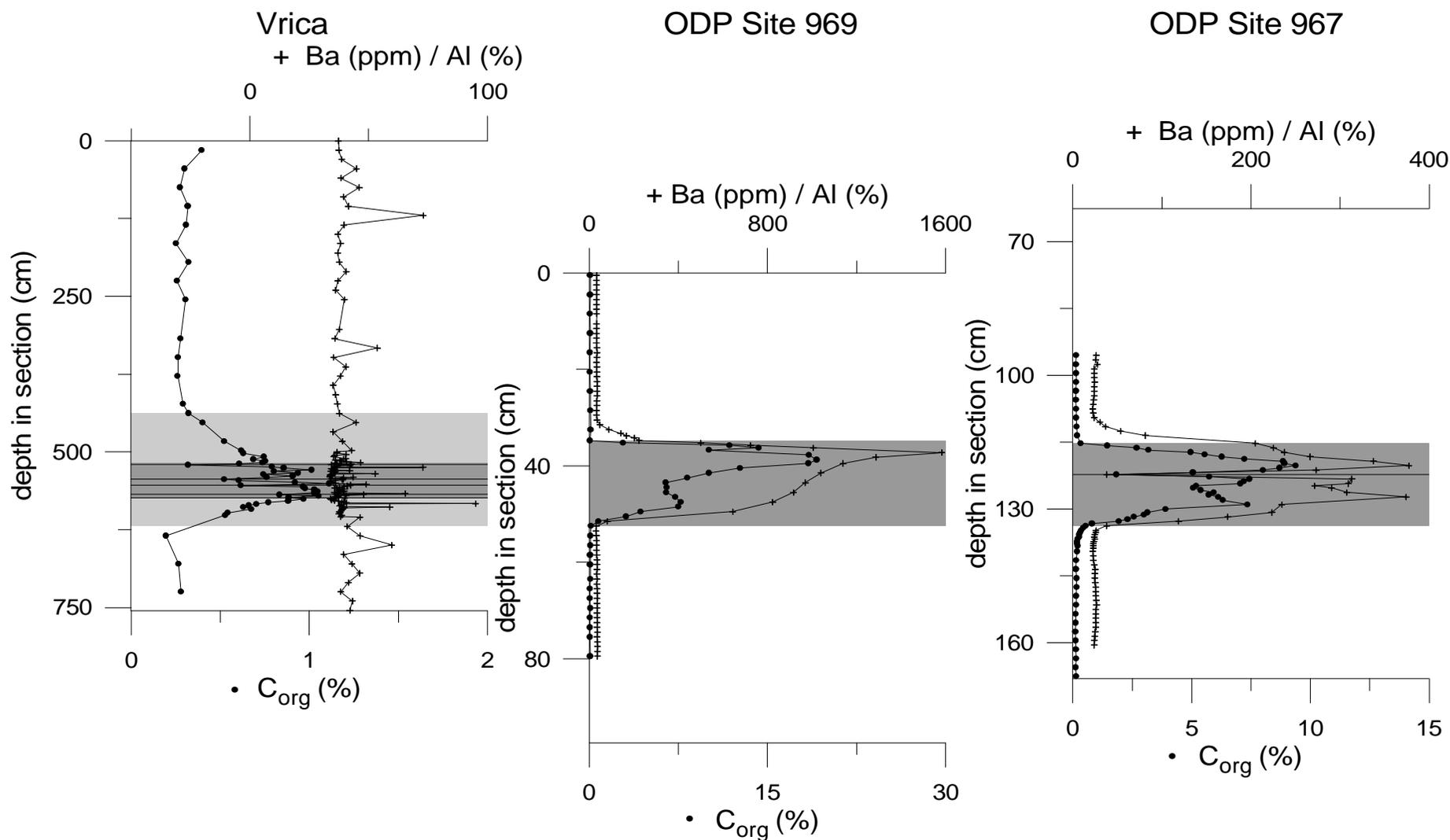


Figure 8.2 C_{org} and Ba/Al versus depth profiles in Vrica, ODP Sites 969 and 967. For Vrica, light grey denotes the area enriched in C_{org} , dark grey the laminite. For the ODP sites, dark grey denotes the sapropel. Horizontal lines in Vrica and ODP Site 967 indicate the position of ash layers. The graphs have been arranged so that the bases of the C_{org} -enriched layers are aligned. The vertical axes have been scaled according to sedimentation rate: the three axes have equal length, representing 36,000 years. Note that the scale of the horizontal axes is different.

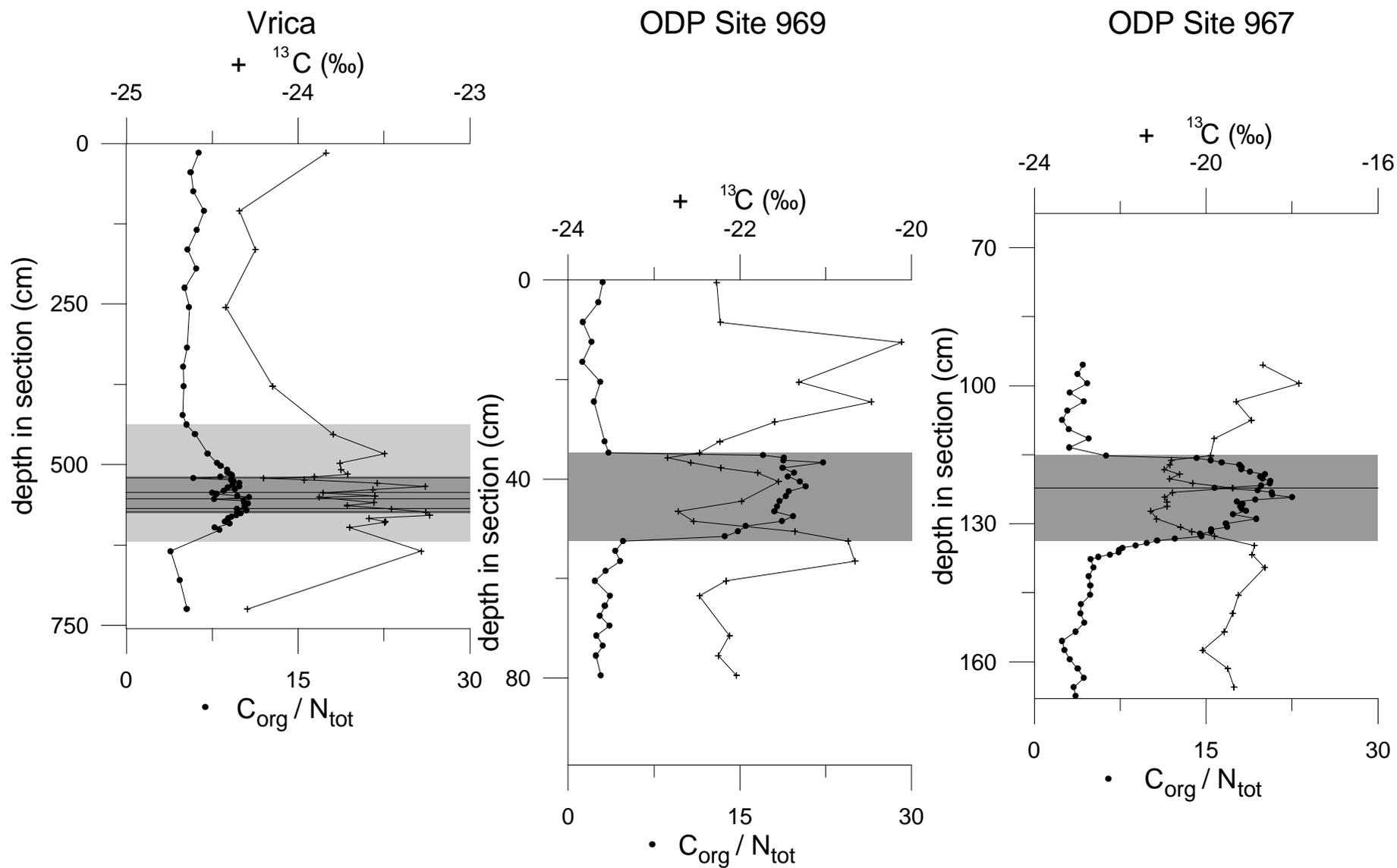


Figure 8.3 $C_{\text{org}}/N_{\text{tot}}$ and $\delta^{13}\text{C}_{\text{org}}$ versus depth profiles (like Fig. 8.2).

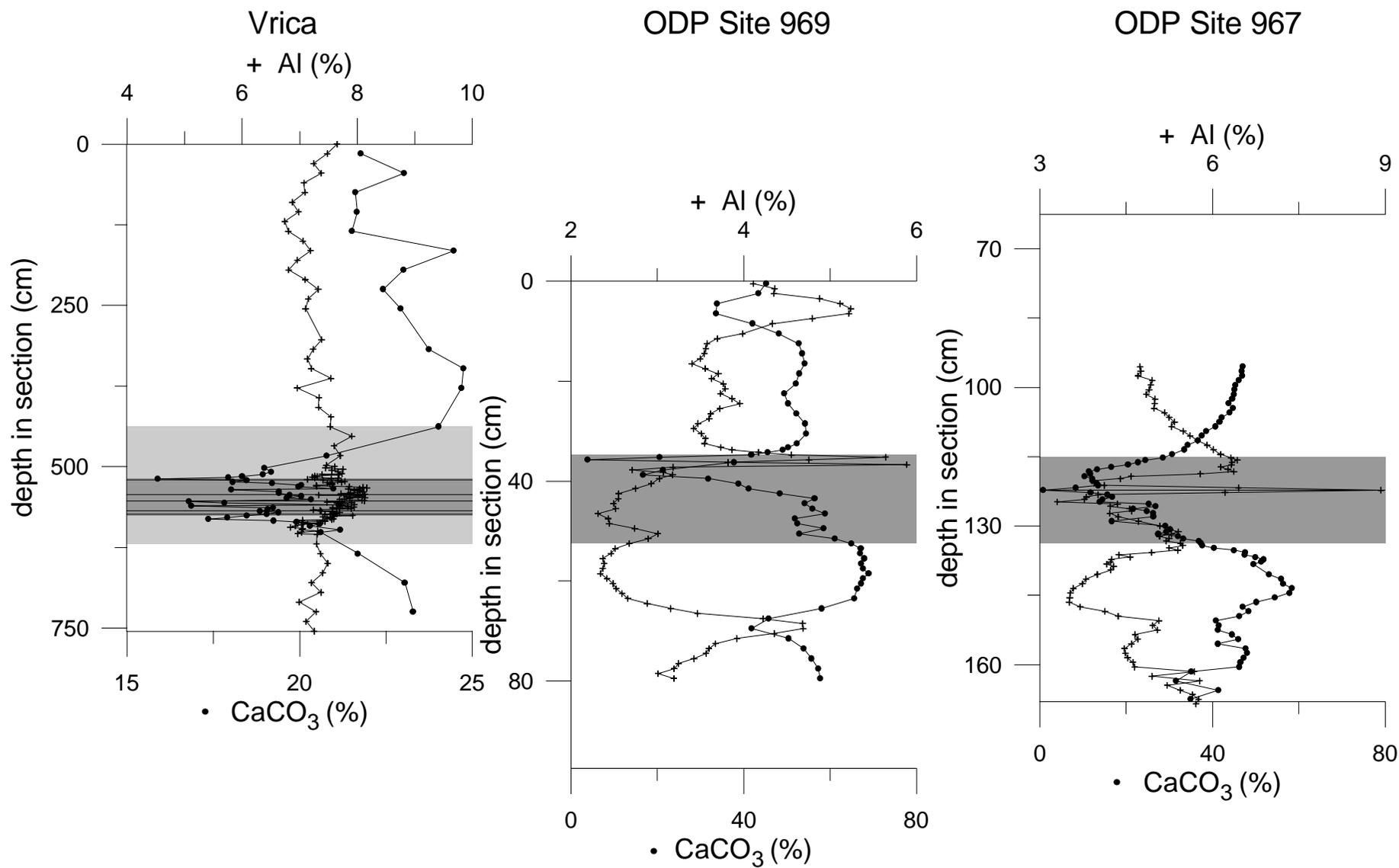


Figure 8.4 CaCO_3 and Al versus depth profiles (like Fig. 8.2).

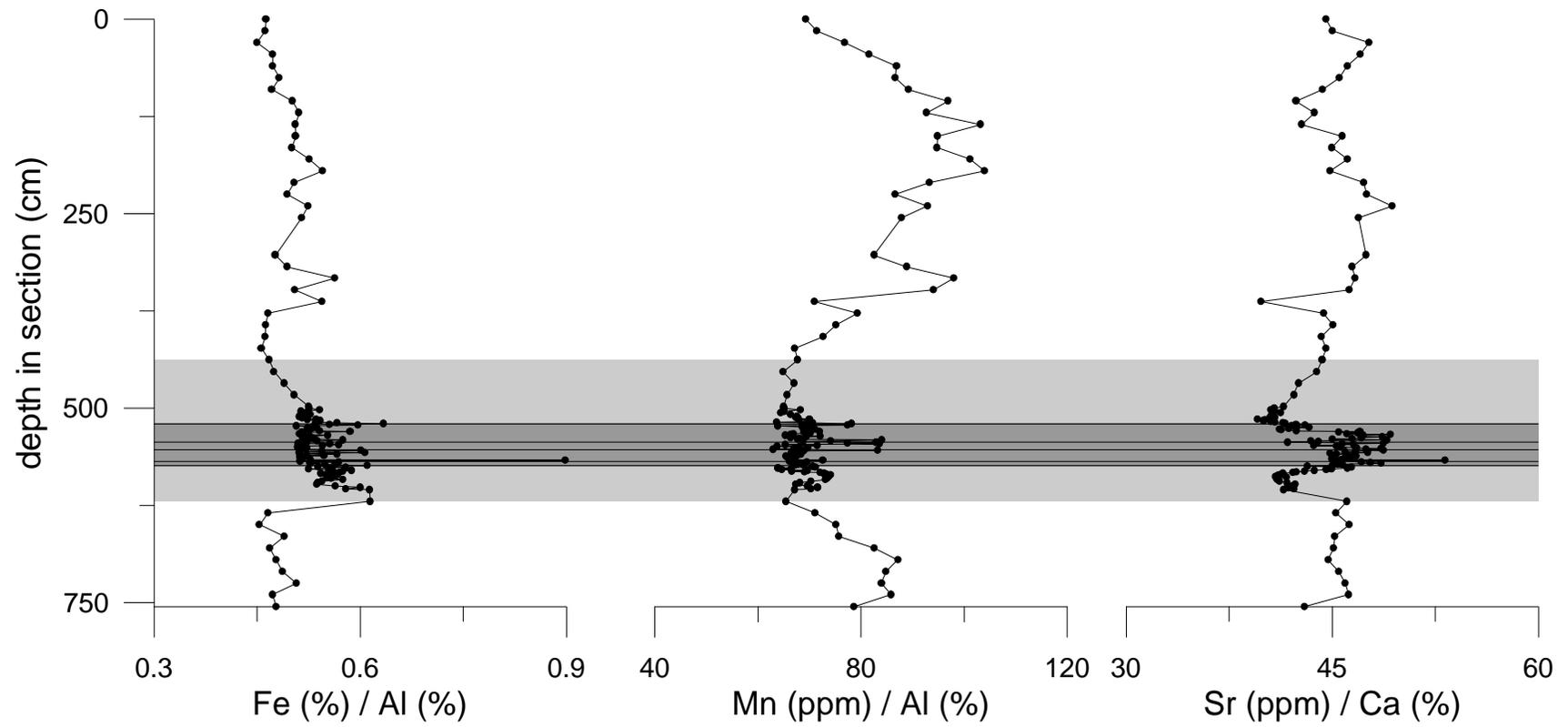


Figure 8.5 *Fe/Al, Mn/Al and Sr/Ca versus depth profiles in the Vrica section.*

Discussion

Marine sediments in a land section have been subject to a series of events that may have changed their initial composition with respect to their counterparts that have remained subaqueous. The processes involved are (1) uplift, dessication and compaction, (2) subsurface weathering and oxidation, and (3) erosion and subaerial weathering. These processes might be responsible for the differences observed between the Vrica and the ODP sediments. Alternatively, these differences may be original and result from dissimilar palaeoceanographic settings. This discussion will first deal with these aspects, and subsequently focus on implications for sapropel formation models.

Land section versus marine cores

1. *Uplift, dessication and compaction* - Marine sediments are compacted during the deposition of younger strata on the seafloor. During this process, marine pore waters are squeezed out of the sediment. When sediments are uplifted above sea level, original pore waters may be retained or exchanged for groundwater. The major element chemistry of the sediments will not change much as a direct result of such an exchange, but a change in pore water pH and Eh may affect the chemical reactions taking place during weathering. Uplift of sediments above groundwater level may result in further dessication and compaction. This is probably the reason for the observed dry bulk density difference between the ODP and Vrica sediments (Table 8.1).

2. *Subsurface weathering and oxidation* - Subsurface weathering can affect sediments deep in sections by percolation of oxidizing fluids along fault planes or other conductive areas. Studies investigating subsurface weathering mainly focussed on changes that may occur in the organic matter fraction [e.g. Leythaeuser, 1973], but other changes, such as the dissolution of carbonates and oxidation of pyrites [e.g. Littke et al., 1991], and leaching and precipitation of iron/manganese oxides and associated trace elements [e.g. Van Os et al., 1996] have also been reported.

The laminite has a blue colour, except for the red-brown sediments a few centimetres directly above and below the ash-layers. This difference in colour suggests that oxidation of reduced iron (presumably as pyrite) to iron (hydr)oxides has taken place around the ash layers. Oxidation of organic matter is likely to have occurred as well. Indeed, the red-brown sediments around the ash layers have lower C_{org} , N_{tot} , $^{13}C_{org}$ and C_{org}/N_{tot} values (Figs. 8.2,3), apparently resulting from subsurface weathering. The nature of these changes in C_{org} , N_{tot} , and $^{13}C_{org}$ values is consistent with data reported for subsurface weathering in a laminated interval in the Sicilian marls of the Narbone formation [Van Os et al., 1996], whereas the observed decrease in C_{org}/N_{tot} ratio can also be expected upon organic matter oxidation because of the relative increase of inorganic N. Except for these differences, the bulk geochemistry of the red-brown sediments around the ash layers cannot be distinguished from the rest of the laminite.

Subsurface weathering probably occurred around the ash layers because they are relatively course-grained and, therefore, more permeable for fluids. Laminated intervals may also provide a pathway for fluids, but the blue colour of the Vrica laminite indicates that the sediments still are in a reduced state. *Littke et al. [1991]* report that perhaps the most reliable indicator of weathering is the microscopic appearance of pyrite, since pyrites are easily oxidized and subsequently show dull, red-brown rims of iron(hydr)oxide. Our microscopic studies revealed that the pyrites in the laminated interval appear fresh, and are perfectly shaped cubes and framboids. Therefore, if oxidation of organic matter occurred in the laminite with respect to the homogeneous interval, it must have been by means of sulphate reduction (the sulphate being supplied by other fluids and in an earlier phase compared with oxidation around the ash layers). As a result of such subsurface weathering, C_{org} , N_{tot} , $^{13}C_{org}$ and C_{org}/N_{tot} may have decreased in the laminite if the effect of oxidation is similar as observed in the red-brown sediments around the ash layers. Such changes cannot be inferred from a comparison with the homogeneous intervals, because these have been deposited under conditions dissimilar to those during laminite formation, and which may have led to very different (initial) values for these parameters. Therefore, a comparison is made with the ODP sapropels, which were not affected by subsurface weathering. The accumulation rates of C_{org} (Table 8.4) and N_{tot} in the Vrica laminite are higher than those in the ODP sapropels. $^{13}C_{org}$ values of the Vrica laminite are lighter than in the ODP sapropels (Table 8.4). However, in ODP

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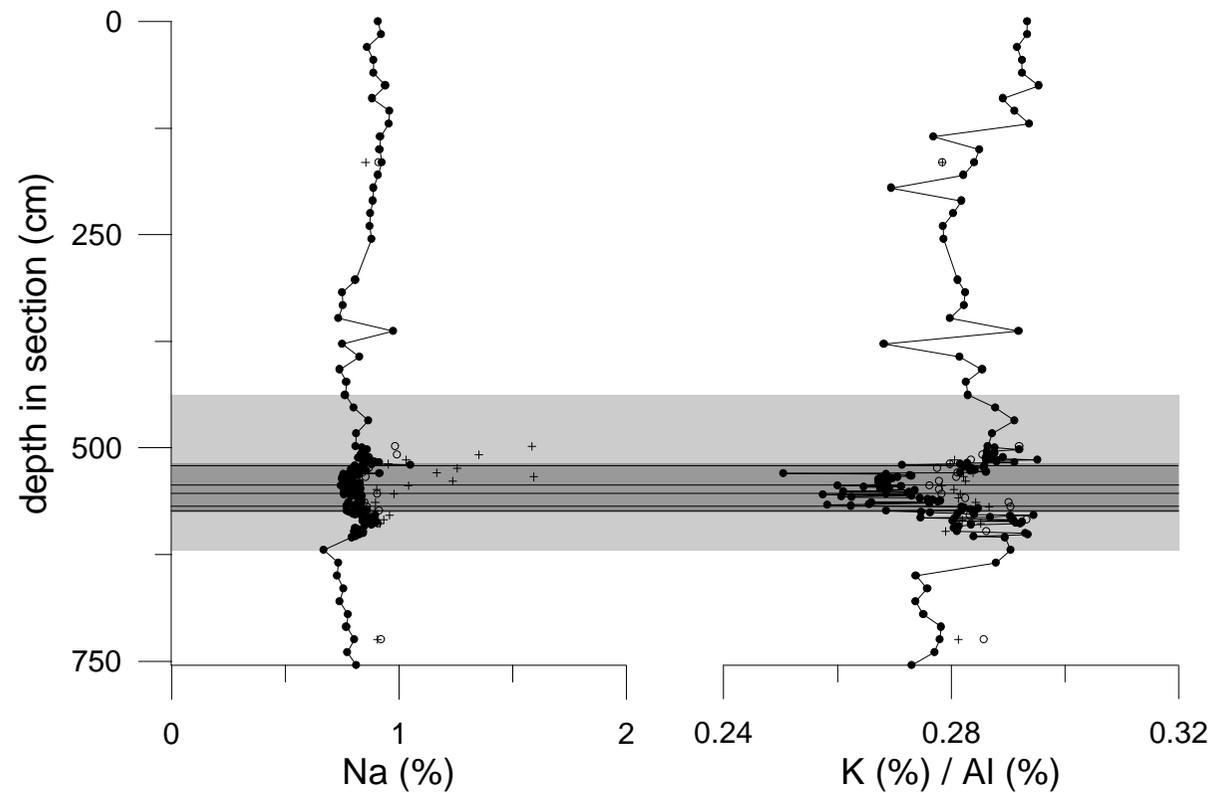


Figure 8.6 *Na and K/Al versus depth profiles in the Vrica section. "Fresh" samples (80 cm into the section) are indicated by solid dots, "slightly weathered" samples (40 cm from the edge of the outcrop) by open dots, and "strongly weathered" samples (edge of outcrop) by crosshairs.*

Comparison of coeval organic carbon rich sediments

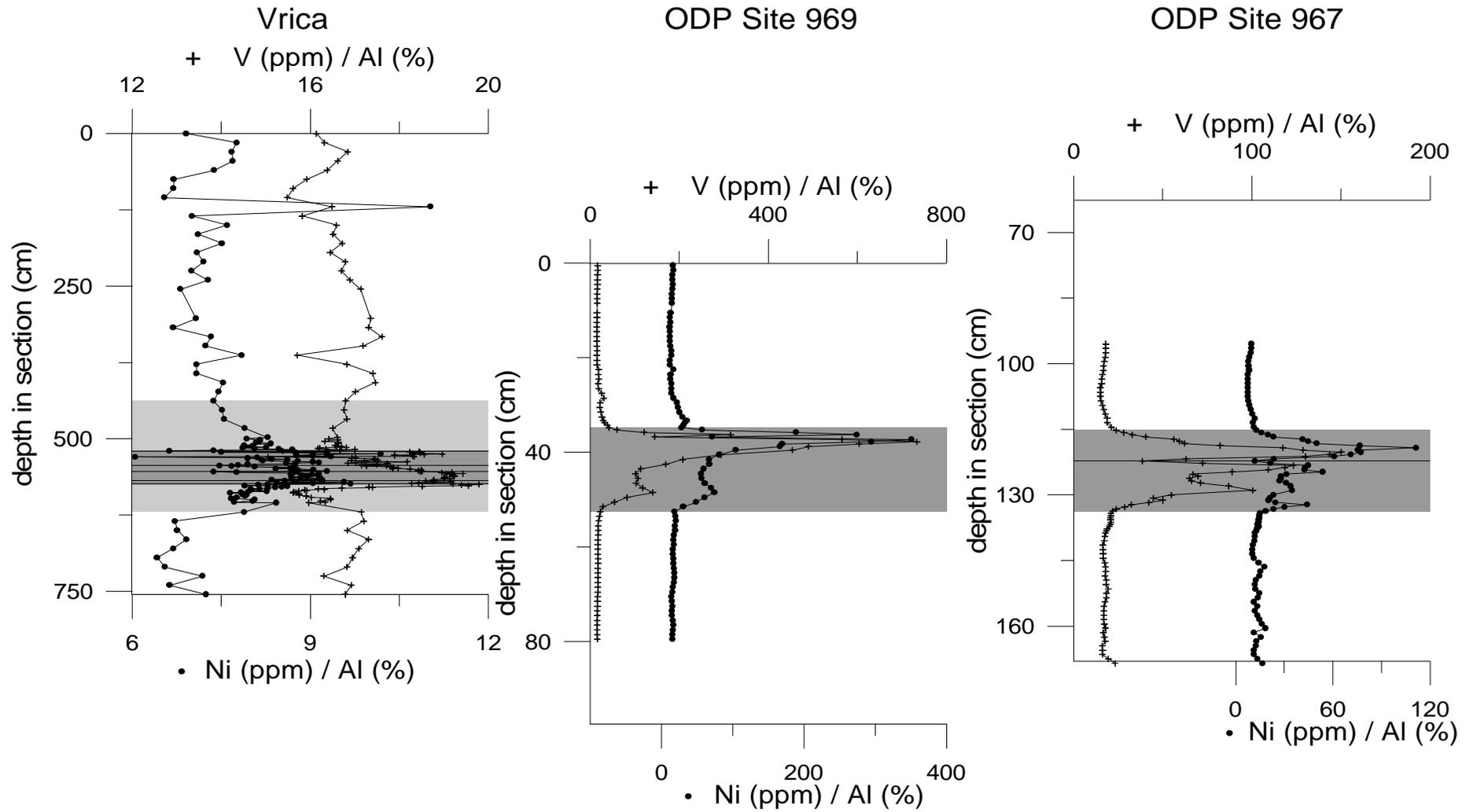


Figure 8.7 Profiles of Ni/Al and V/Al versus depth (like Fig. 8.2).

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$^{13}\text{C}_{\text{org}}$ values are more negative than in the over- and underlying homogeneous sediments (Fig. 8.3; Table 8.4), whereas in cycle i-152 in Vrica, the laminite has less negative $^{13}\text{C}_{\text{org}}$ values than the adjacent homogeneous intervals. If these $^{13}\text{C}_{\text{org}}$ values of the laminite in Vrica have decreased because of subsurface weathering, then the initial values would have been even less negative than they are now. This would contrast strongly with the shift to more negative values not only observed in the ODP sapropels, but also in the older laminite "h" of the Vrica section [Howell *et al.*, 1988; Meyers, 1993]. Therefore, it is not likely that oxidation of organic matter in the Vrica laminite did occur with respect to the homogeneous intervals.

There are no indications that leaching and precipitation of iron/manganese oxides has occurred in the Vrica section: no fronts of these elements such as observed in the Narbone marls [Van Os *et al.*, 1996] have been found in the laminite. The one iron peak in the laminite (Fig. 8.5) correlates with sulphur and can be ascribed to iron sulphide occurrences. Although manganese contents are higher in the laminite (Fig. 8.5), no localized fronts are observed. The Sr content is higher in the laminite with respect to the sediments around it, even relative to Ca (Fig. 8.5) and Al. This is remarkable, since in the ODP cores Sr contents are lower in the sapropels than in the homogeneous sediments. Van Os *et al.* [1996] attribute high Sr contents in the Narbone marls to precipitation of celestite that formed as a result of oxidation of pyrite. In the Vrica sediments of this study, there are no indications for pyrite oxidation, and the Sr enrichment is cooccurring with Ca enrichments. This may indicate a relative increase in Sr-containing carbonates (such as aragonite).

We conclude that there is no evidence for substantial subsurface weathering in the Vrica section except around some thin ash layers in the laminite.

3. *Erosion and subaerial weathering* - Outcropping sediments are exposed to subaerial weathering, which may be effective up to a few metres into a section. Littke *et al.* [1991] did not find geochemical (organic matter content and composition; silicate, carbonate and sulphide content) differences between outcrop surface samples and samples taken 30 cm into the rock. Clayton and Swetland [1978] did find lower C_{org} contents near the outcrop surface of the Phosphoria Formation, but no such change for the Pierre Shale.

The bulk geochemistry of the weathered samples from the Vrica laminite is not different from that of the fresh samples. The only exceptions are Na and K/Al (Fig. 8.6), which are higher in samples closer to the edge of the outcrop. Similar observations have been made by Van der Weijden [1993], also in the Vrica section, and by Nijenhuis and Schenau [1994] for the Miocene Faneromeni section on Crete (Greece). This phenomenon can be explained by evaporation of water at the outcrop surface drawing pore fluids to the surface. When this water evaporates, the salt remains, enriching the sediment in Na, K, Mg, SO_4 and Cl. This is most clearly visible in the K and Na profiles, because the background content of the sediment is lowest for these elements. The strong visual difference between fresh (blue, immature clays) and weathered samples (grey/beige, dry and hard sediments) is not reflected by other changes in bulk geochemistry. This is probably best explained by the relatively short aerial exposure of the sediments after the recent excavation of the building site. The short-term effect of

subaerial weathering is apparently limited to physical changes (mainly further dessication of the sediments).

Near-coastal versus abyssal sites

Now that we have established that most differences between the ODP sapropels and the Vrica laminite are not due to uplift and weathering of the land section, we can explain them in terms of different environments and palaeoceanographic settings. There are four main differences: the Vrica section has been deposited (1) closer to land, (2) in shallower waters, (3) with a higher sedimentation rate, and (4) in a more western part of the eastern Mediterranean than the ODP sites (Table 8.1). We will discuss these four factors in relation to the observed geochemical differences.

The Al content (which is representative of the clay fraction) of the Vrica sediments is 150-250% higher than that of the ODP sediments (Table 8.3). A higher clay input is expected in a setting closer to land, but the difference in Al content between Vrica and the ODP sites is relatively small because the accumulation rate of carbonates is also higher than at ODP Sites 967 and 969. Ratios of "terrestrial" elements to Al are higher in ODP than in Vrica (Table 8.3). For Ti/Al and Zr/Al, this can be explained by a relatively higher fluvial contribution in Vrica, and a more dominant aeolian input in the ODP sediments. The heavy mineral fraction, of which Ti and Zr are representative, is thought to be predominantly transported to marine sediments by wind [Boyle, 1983; Shimmield, 1992]. The higher Fe/Al values in the ODP sediments, especially in the laminite, are most likely explained by the presence of more pyrite in the latter. For other terrestrial elements, the lower abundance relative to Al in Vrica is remarkable. For example, sediments at Sites 964 (Fig. 8.1; western part of the eastern Mediterranean) and 969 are characterized by high K/Al and Mg/Al values (resulting from supply of illite by bottom currents from the Aegean and Adriatic Seas), whereas sediments at Sites 966 and 967 are more influenced by the Nile (supply of kaolinite and smectite), resulting in low K/Al and Mg/Al values [Wehausen and Brumsack, 1998; Chapter 7]. This east-west trend also applies to sapropel i-156 in ODP Sites 967 and 969, but the Vrica sediments do not show the expected higher K/Al and Mg/Al values. This is probably best explained by a different, local terrestrial source that influenced the Vrica sediments.

In the homogeneous intervals of the Vrica sediments, the Ba contents (Fig. 8.2) are about twice as high as in the ODP cores. In the laminite, however, the Ba content does not increase, whereas very high values (almost 2,200 ppm in Site 969) are reached in the ODP sapropels. Since Ba can be used as a palaeoproductivity indicator [Dehairs et al., 1980; Dymond et al., 1992], this suggests that productivity increased during sapropel formation at the ODP sites, but not during deposition of the laminite in the Vrica section. Bishop [1988] proposed a model in which barite precipitates in microenvironments containing decaying organic matter during transit from surface waters to the seafloor. As a result, barite may not be enriched in shallow highly productive areas, whereas it is increased in deeper sites with similar productivity [Von Breyman et al., 1992]. This may explain the contrasting Ba contents in the

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ODP sapropels and the Vrica laminite. Alternatively, the low Ba contents in Vrica may indicate that productivity was never high, or that barite was present but dissolved under conditions of sulphate reduction. Evidence that sulphate reduction did occur in the laminite comes from microtextures and sulphur isotopic values of pyrite, which are very similar to those reported by *Passier et al. [1997]* for the eastern Mediterranean Holocene S1 sapropel. This is indicative for pyrite forming during sulphate reduction in sediments still in contact with oxic or dysoxic seawater ("open system"). Under such conditions, barite may become undersaturated. Thus, Ba may become mobilized, and precipitate outside the zone of sulphate reduction [*e.g. De Lange et al., 1994*]. Such "mobilization peaks" may have escaped detection because they can be thinner than the sample resolution of 1-15 cm.

C_{org} accumulation rates are higher in Vrica than in the ODP sediments (Table 8.4). The flux of C_{org} to the sediment is influenced by factors such as detrital (terrestrial) organic matter input, export productivity, water depth, sedimentation rate, and oxygen conditions of the water column. Both in Vrica and in the ODP cores, the homogeneous sediments were probably deposited under oxic conditions. This can be inferred from the absence of laminae and the low redox-sensitive and chalcophilic trace element contents. Therefore, we can use an equation relating C_{org} flux to productivity, water depth and sedimentation rate to estimate the effects of these factors on the differences in sedimentary C_{org} content between Vrica and the ODP sediments. The basic formula of *Sarnthein et al. [1992]* will serve for the calculations:

$$P_{\text{exp}} = 9.354 C_A^{0.493} S_{B-C}^{-0.105} Z^{0.300}$$

in which P_{exp} is the export productivity in $\text{gC m}^{-2} \text{yr}^{-1}$, C_A the C_{org} accumulation rate ($\text{g m}^{-2} \text{yr}^{-1}$), S_{B-C} the C_{org} free sedimentation rate (in $\text{g m}^{-2} \text{yr}^{-1}$), and z the water depth in metres. For the homogeneous ODP sediments this gives an export productivity of $19.3 \text{ gC m}^{-2} \text{yr}^{-1}$ (average of both sites). If we assume that the export productivity for the Vrica sediments was comparable, we obtain an accumulation rate of $0.16 \text{ gC m}^{-2} \text{yr}^{-1}$ for these sediments, whereas the actual value is $1.51 \text{ gC m}^{-2} \text{yr}^{-1}$ (Table 8.4). Thus, the fact that C_{org} accumulation rates are higher in the Vrica sediments than in the ODP cores can only for a small part be attributed to the differences in water depth¹ and sedimentation rate. The largest part of the difference must be due to higher productivity and/or higher terrestrial organic matter input at Vrica. The latter factor is often constrained by using $^{13}\text{C}_{\text{org}}$ and C/N values as indicators for terrestrial/marine

¹There is no systematic change with depth in the C_{org} content of ODP Sites 964, 966, 967 and 969 which vary in present-day water depth between 926 and 3,660 metres, neither in the sapropels nor in the homogeneous intervals [*Chapter 7*]. For Holocene sapropels, C_{org} contents have been observed to increase with depth [*Murat, 1991*]. This may indicate that the palaeodepth of the ODP Sites has been different from today, complicating a comparison with the Vrica section.

organic matter [e.g. Jasper and Gagosian, 1990; Tyson, 1995]. However, a simple two end-member mixing model with terrestrial organic matter characterized by high C/N and light $^{13}\text{C}_{\text{org}}$ values, and marine organic matter characterized by low C/N and heavy $^{13}\text{C}_{\text{org}}$ values, does not seem to apply in the eastern Mediterranean [Chapter 7]. There is, however, a distinct east-west trend in $^{13}\text{C}_{\text{org}}$ values in the eastern Mediterranean, with lighter values in the west and heavier values in the east [Chapter 7]. This may explain why $^{13}\text{C}_{\text{org}}$ values are lower in Vrica than in the more eastern ODP cores. Consequently, we cannot determine the relative proportions of terrestrial and marine organic matter in Vrica and in ODP Sites 967/969 using these parameters. Organic geochemical research, however, indicates that in both settings the major portion of organic matter is of marine origin [Meyers, 1993; Bosch et al., 1998].

The high contents of redox-sensitive trace elements in the abyssal ODP sapropels have been explained by effective scavenging from an anoxic water column by sulphides and organic matter [Nijenhuis et al., 1998]. Trace element accumulation rates in Vrica are higher, but the trace element to Al ratios are lower, especially in the sapropels. This may be the result of the shallower water depth, because higher amounts of trace elements can be scavenged from a larger water column. Alternatively, anoxic conditions were more restricted at Vrica than at the ODP sites. In addition, a signal of trace elements scavenged from the water column will be more diluted in the Vrica section because of the higher sedimentation rate.

Concluding, the differences in the geochemistry of cycle i-156 in Vrica and ODP Site 967/969 can partly be explained by the different settings. In Vrica, both the clay and carbonate input are higher than at the ODP sites. The clay fraction is more dominant in the near-coastal Vrica sediments, resulting in higher Al contents than in the open marine ODP sediments of this study. Lower Ti/Al and Zr/Al ratios indicate a stronger fluvial relative to aeolian input throughout the Vrica section compared with the ODP sediments. The shallower water depth may partly explain the lower trace element to aluminium ratios and higher homogeneous C_{org} accumulation rates in the Vrica section, but factors like water column oxygen level and productivity are thought to have been more important.

Palaeoceanographic implications

Productivity versus preservation - Since the Crotona-Spartivento Basin in which the Vrica section was deposited had an open connection with the Ionian Sea in the early Pleistocene [e.g. Moretti, 1993], laminite deposition in this basin and sapropel deposition in the eastern Mediterranean should be explained in one model. Schenau et al. [1999] (Chapter 3) suggest one basic model for eastern Mediterranean sapropel formation since the middle Miocene: at times of precession minima (Northern Hemisphere insolation maxima) enhanced continental runoff and Atlantic-born depression activity lead to increased productivity and reduced water circulation, the combination of the latter two resulting in reduced bottom water oxygen levels. The intensity of productivity, dilution and diagenesis will vary with time and place, depending on factors like proximity to land, depositional environment, intensity of the astronomical forcing, etc. For the Plio-Pleistocene sapropels recovered by ODP, it was shown that both productivity and

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preservation were strongly enhanced [Chapter 7]. In contrast, the Vrica laminites were thought to have formed as a result of improved preservation, not of increased productivity [Howell et al., 1988; Meyers, 1993; Van der Weijden, 1993]. However, the planktonic fauna of Vrica laminite "o" is characterized by an increase in *Neogloboquadrina* sp. [Spaak, 1983; Howell et al., 1990; Lourens, 1994]. This foraminifera species is often linked to eutrophic conditions [Tolderlund and Bé, 1971; Howell et al., 1990; Thunell and Sautter, 1992]. The uniform occurrence of increased *Neogloboquadrina* abundance in Miocene to Pliocene sapropels is, therefore, interpreted as an indication of higher productivity during their formation [Schenau et al., 1999 (Chapter 3)]. Thus, productivity may have been an important factor in the formation of the Vrica laminite as well. Evidence for higher productivity in the ODP sapropels comes from the very high C_{org} accumulation rates, Ba contents, and the presence of opal in some sapropels [Chapter 7]. Opal is not found in all sapropels: it is prone to dissolution since both seawater and sedimentary pore waters are usually undersaturated with respect to silica. Barium is a useful palaeoproductivity indicator, but as we have indicated before it may not be enriched in shallow sediments. The absence of opal and Ba enrichments in the Vrica laminite, therefore, does not exclude high productivity during its formation. There is no direct evidence that palaeoproductivity was *not* increased during the formation of laminite "o" in Vrica, so the model proposed for the abyssal sapropels can be extended to the shallower environments. The observed enrichment in redox-sensitive and chalcophilic trace elements, the absence of benthic foraminifera [Howell et al., 1990; Lourens, 1994], the indications for sulphate reduction and the presence of pyrite in the laminite, added to the preservation of the laminae themselves, confirm that the oxic-anoxic interface was located at a shallower depth in the sediment, or perhaps even in the water column during formation of laminite "o" and of the ODP sapropels [Chapter 7]. Preservation of laminae and high redox-sensitive trace element contents do not occur outside the laminite. The C_{org} -rich interval around the laminite, then, may have resulted mainly from increased productivity, whereas anoxic (bottom) water conditions and associated improved preservation of organic matter resulted in laminite deposition. This seems to support the idea that anoxia developed as a result of increased productivity in the Plio-Pleistocene sapropels [Passier et al., *in press* (Chapter 5); Chapter 7].

Duration of sapropel and laminite formation - Is the period of sapropel formation comparable to laminite duration? It has been suggested that sedimentation rates did not change much during Plio-Pleistocene sapropel formation [Chapter 7]. An indication that this might also be the case in the Vrica section comes from the thickness of the laminae (0.2-0.5 mm). If we assume that each lamina represents a year (varve-like sedimentation), the 56 cm thick laminite would have been deposited in 1,100 to 2,800 years. The 2,700 years obtained by simply dividing the laminite thickness by the average sedimentation rate of one precession cycle is within this range. Both ODP sapropels were formed in about 6,300 years [Chapter 7], i.e. a considerably longer period. However, the C_{org} enriched interval in the Vrica section represents 8,700 years. Thus, the laminite was deposited in a considerably shorter period than the sapropels, but the

C_{org} enriched interval lasted longer, if indeed sedimentation rate did not change during sapropel and laminite formation.

The discrepancy between the abyssal and near-coastal sites may indicate that anoxia was limited to deep water most of the time, and only reached the shallow areas of Vrica part of the time (namely in the period of laminite deposition). However, the decrease of the terrestrial element to Al ratios in the laminite, which do not occur in the sapropels, suggests an additional change, namely that in terrestrial influence. This may be a local variation in the Crotono-Spartivento basin. Indeed, the large and frequent variations of many parameters in the laminite indicate that the Vrica section was deposited in a dynamic environment that changed from year to year, whereas the abyssal sapropels formed in a more constant, stable environment.

Conclusions

The insolation maximum of cycle i-156 is expressed by a sapropel in ODP Sites 967 and 969, and by a laminite in the Vrica section. There is a strong difference in the geochemistry of the land section on the one hand, and the marine sediments on the other hand. Uplift, dessication, weathering and erosion of the marine sediments in the Vrica section resulted in a higher dry bulk density, oxidation of C_{org} and an associated decrease in N_{tot} , C_{org}/N_{tot} and $^{13}C_{org}$ values in intervals along conductive planes, and in salt precipitation near the outcrop surface. Other differences between the Vrica section and the ODP sites are the result of different palaeoceanographic settings. A relatively stronger river input in the Vrica section resulted in higher clay content and lower Ti/Al and Zr/Al values. Shallower water depth may account for the low Ba/Al values in Vrica, and partly for the lower trace element to Al ratios and higher C_{org} accumulation rates. Lower $^{13}C_{org}$ values in Vrica than in the ODP sediments are coherent with the east-west trend of this parameter in the eastern Mediterranean. The formation of laminite "o" in the Vrica section is thought to be not only a preservation event, but also the result of increased productivity. Therefore, our results for the Vrica section fit in the general model for sapropel formation in the eastern Mediterranean.

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References

- Aksu A.E., Yasar D., Mudie P.J., 1995. Paleoclimatic and paleoceanographic conditions leading to development of sapropel layer S1 in the Aegean Sea. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 116: 71-101.
- Anastasakis G.C., Stanley D.J., 1986. Uppermost sapropel, eastern Mediterranean: Paleoceanography and stagnation. *Nat. Geogr. Res.* 2: 179-197.
- Arthur M.A., Brumsack H.-J., Jenkyns H.C., Schlanger S.O., 1990. Stratigraphy, geochemistry, and paleoceanography of organic carbon-rich Cretaceous sequences. In *Cretaceous resources, events and rhythms* (editors: Ginsburg R.N., Beaudoin B.), pp. 75-119, Kluwer Academic Publishers, Dordrecht.
- Arthur M.A., Dean W.E., Neff E.D., Hay B.J., King J., Jones G., 1994. Varve calibrated records of carbonate and organic carbon accumulation over the last 2000 years in the Black Sea. *Global Biogeochem. Cycles* 8: 195-217.
- Baker P.A., Bloomer S.H., 1988. The origin of celestite in deep-sea carbonate sediments. *Geochim. Cosmochim. Acta* 52: 335-339.
- Barber P.M., 1981. Messinian subaerial erosion of the proto-Nile delta. *Mar. Geol.* 44: 253-272.
- Bé A.W.H., Hutson W.H., 1977. Ecology of planktonic foraminifera and biogeographic patterns of life and fossil assemblages in the Indian Ocean. *Micropaleontology* 23: 369-414.
- Berger W. H., Herguera J.C., 1992. Reading the sedimentary record of the ocean's productivity. In *Primary productivity and biogeochemical cycles in the sea* (editors: Falkowski P.G., Woodhead A.D.), pp. 455-485, Plenum Press, New York.
- Béthoux J.-P., 1980. Mean water fluxes across sections in the Mediterranean Sea, evaluated on the basis of water and salt budgets and of observed salinities. *Oceanol. Acta* 3: 79-88.
- Béthoux J.-P., 1989. Oxygen consumption, new production, vertical advection and environmental evolution in the Mediterranean Sea. *Deep-Sea Res.* 36: 769-781.
- Béthoux J.-P., Copin-Montégut G., 1986. Biological fixation of atmospheric nitrogen in the Mediterranean Sea. *Limnol. Oceanogr.* 31: 1353-1358.
- Bigg G.R., 1995. Aridity of the Mediterranean Sea at the last glacial maximum: A reinterpretation of the $\delta^{18}\text{O}$ record. *Paleoceanography* 10: 283-290.
- Bishop J.K.B., 1988. The barite-opal-organic carbon association in oceanic particulate matter. *Nature* 332: 341-343.
- Björnsson S., Arnorsson S., Tómasson J., 1972. Economic evaluation of Reykjanes thermal brine area, Iceland. *Am. Assoc. Petroleum Geologists Bull.* 56: 2380-2391.
- Blenkinsop J., Patterson R.T., Reinhardt E., Cavazza W., 1994. Observed $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic variation in pelagic mudrocks of Pliocene age are the result of orbitally forced periodic variation in continental runoff. *U.S. Geol. Soc. circular* 1107: 31, Proc. 8th international conference on geochronology and isotope geology.
- Bonelli P., Braga Marcazzan G.M., Cereda E., 1996. Elemental composition and air trajectories of African dust transported in Northern Italy. In *The impact of desert dust across the*

References

- Mediterranean* (editors: Guerzoni S., Chester R.), pp. 275-283, Kluwer Academic Publishers, Dordrecht.
- Bosch H.-J., Sinninghe Damsté J.S., De Leeuw J.W., 1998. Molecular palaeontology of Eastern Mediterranean sapropels: evidence for photic zone euxinia. In *Proc. ODP, Sci. Results*, 160 (editors: Robertson A.H.F., Emeis K.-C., Richter C., Camerlenghi A.) pp. 285-295, Ocean Drilling Program, College Station, TX.
- Böttcher M.E., Brumsack H.-J., De Lange G.J., 1998. Sulfate reduction and related stable isotope (^{34}S , ^{18}O) variations in interstitial waters from the eastern Mediterranean (Leg 160). In *Proc. ODP, Sci. Results*, 160 (editors: Robertson A.H.F., Emeis K.-C., Richter C., Camerlenghi A.), pp. 365-373, Ocean Drilling Program, College Station, TX.
- Boyle E.A., 1983. Chemical accumulation variations under the Peru Current during the past 130,000 years. *J. Geophys. Res.* 88: 7667-7680.
- Bradley W.H., 1938. Mediterranean sediments and Pleistocene sea levels. *Science* 88: 376-379.
- Bralower T.J., Thierstein H.R., 1987. Organic carbon and metal accumulation rates in Holocene and mid-Cretaceous sediments: palaeoceanographic significance. In *Marine petroleum source rocks* (editors: Brooks J., Fleet A.J.), pp. 345-369. (Geol. Soc. Spec. Publ. 26)
- Breit G.N., Wanty R.B., 1991. Vanadium accumulation in carbonaceous rocks: A review of geochemical controls during deposition and diagenesis. *Chem. Geol.* 91: 83-97.
- Broecker W.S., Peng T.-H., 1982. *Tracers in the Sea*, 690 pp., Lamont-Doherty geological observatory, Palisades, New York.
- Brolsma M.J., 1978. Quantitative foraminiferal analysis and environmental interpretation of the Pliocene and topmost Miocene on the south coast of Sicily. *Utr. Micropal. Bull.* 18: 159 pp.
- Bruland K.W., 1983. Trace elements in sea-water. In *Chemical oceanography*, vol. 8 (editors Riley J.P., Chester R.), pp. 157-220, Academic Press, London.
- Brumsack H.-J., 1980. Geochemistry of Cretaceous black shales from the Atlantic Ocean (DSDP Legs 11, 14, 36 and 41). *Chem. Geol.* 31: 1-25.
- Brumsack H.-J., 1989. Geochemistry of recent TOC-rich sediments from the Gulf of California and the Black Sea. *Geol. Rundschau* 78: 851-882.
- Brumsack H.-J., 1991. Inorganic geochemistry of the German 'Posidonia Shale': palaeo-environmental consequences. In *Modern and ancient continental shelf anoxia* (editors: Tyson R.V., Pearson T.H.), pp. 353-362. (Geol. Soc. Spec. Publ. 58)
- Brumsack H.-J. and Thurow J., 1986. The geochemical facies of black shales from the Cenomanian/Turonian Boundary Event (CTBE). *Mitt. Geol.-Paläont. Inst. Univ. Hamburg* 60: 247-265.
- Buckley H.A., Johnson L.R., 1988. Late Pleistocene to Recent sediment deposition in the central and western Mediterranean. *Deep-Sea Res.* 35: 749-766.
- Calvert S.E., 1983. Geochemistry of Pleistocene sapropels and associated sediments from the Eastern Mediterranean. *Oceanol. Acta* 6: 255-267.

- Calvert S.E., Pedersen T.F., 1993. Geochemistry of Recent oxic and anoxic marine sediments: Implications for the geological record. *Mar. Geol.* 113: 67-88.
- Calvert S.E., Vogel J.S., Southon J.R., 1987. Carbon accumulation rates and the origin of the Holocene sapropel in the Black Sea. *Geology* 15: 918-921.
- Calvert S.E., Nielsen B., Fontugne M.R., 1992. Evidence from nitrogen isotope ratios for enhanced productivity during formation of eastern Mediterranean sapropels. *Nature* 359: 223-225.
- Canfield D.E., 1993. Organic matter oxidation in marine sediments. In *Interactions of C, N, P and S Biogeochemical cycles and global change* (editors Wollast R., Mackenzie F.T., Chou L.), pp. 333-363, Springer-Verlag, Berlin. (NATO ASI Ser. I, vol. 14)
- Canfield D.E., 1994. Factors influencing organic carbon preservation in marine sediments. *Chem. Geol.* 114: 315-329.
- Canfield D.E., Raiswell R., 1991. Carbonate precipitation and dissolution. Its relevance to fossil preservation. In *Taphonomy: Releasing the data locked in the fossil record* (editors Allison P.A., Briggs D.E.G.), pp. 411-453, Plenum Press, New York. (Topics in geobiology, vol. 9)
- Canfield D.E., Thamdrup B., 1994. The production of ³⁴S-depleted sulfide during bacterial disproportionation of elemental sulfur. *Science* 266: 1973-1975.
- Canfield D.E., Lyons T.W., Raiswell, R., 1996. A model for iron deposition to euxinic Black Sea sediments. *Am. J. Sci.* 296: 818-834.
- Castradori D., 1993. Calcareous nannofossils and the origin of eastern Mediterranean sapropels. *Paleoceanography* 8: 459-471.
- Chepstow-Lusty A., Backman J., Shackleton N.J., 1989. Comparison of upper Pliocene *Discoaster* abundance variations from North Atlantic Sites 552, 607, 658, 659, and 662: Further evidence for marine plankton responding to orbital forcing. In *Proc. ODP, Sci. Results* (editors: Baldauf J., Ross Heath G., Ruddiman W.F., Sarnthein M.), pp. 121-141, Ocean Drilling Program, College Station, TX.
- Chester R., 1965. Elemental geochemistry of marine sediments. In *Chemical Oceanography*, vol. 2 (editors Riley J.P., Skirrow G.), pp. 23-80, Academic Press, London.
- Cita M.B., 1991. Anoxic basins of the eastern Mediterranean: An overview. *Paleoceanography* 6: 133-141.
- Cita M.B., Grignani D., 1982. Nature and origin of late Neogene Mediterranean sapropels. In *Nature and origin of Cretaceous carbon-rich facies* (editors Schlanger S.O., Cita M.B.), pp. 165-196, Academic Press, London.
- Cita M.B., Vergnaud-Grazzini C., Robert C., Chamley H., Ciaranfi N., D'Onofrio S., 1977. Paleoclimatic record of a long deep sea core from the eastern Mediterranean. *Quat. Res.* 8: 205-235.
- Clayton J.L., Swetland P.J., 1978. Subaerial weathering of sedimentary organic matter. *Geochim. Cosmochim. Acta* 42: 305-312.

References

- Codispoti L.A., 1989. Phosphorus vs. nitrogen limitation of new and export production. In *Productivity of the ocean: Present and past* (editors: Berger W.H., Smetacek V.S., Wefer G.), pp. 377-394, John Wiley & Sons, Chichester.
- Colalongo M.L., Pasini G., Sartoni S., 1981. Remarks on the Neogene/Quaternary boundary and the Vrica section (Calabria, Italy). *Boll. Soc. Pal. Ital.* 20: 99-120.
- Collier R.W., 1984. Particulate and dissolved vanadium in the North Pacific Ocean. *Nature* 309: 441-444.
- Comans R.N.J., Middelburg J.J., Zonderhuis J., Woittiez J.R.W., De Lange G.J., Das H.A., Van der Weijden C.H., 1989. Mobilization of radiocaesium in pore water of lake sediments. *Nature* 339: 367-369.
- Comas M.C., Zahn R., Klaus A., et al., 1996. *Proc. ODP., Init. Repts.* 161, 1023 pp., College Station, TX (Ocean Drilling Program).
- Dean W.E., Gardner J.V., Piper D.Z., 1997. Inorganic geochemical indicators of glacial-interglacial changes in productivity and anoxia on the California continental margin. *Geochim. Cosmochim. Acta* 61: 4507-4518.
- De Boer P.L., 1991. Pelagic black shale-carbonate rhythms: Orbital forcing and oceanographic response. In *Cycles and events in stratigraphy* (editors: Einsele G., Ricken W., Seilacher A.), pp. 63-78, Springer-Verlag, Berlin.
- Dehairs F., Chesselet R., Jedwab J., 1980. Discrete suspended particles of barite and the barium cycle in the open ocean. *Earth Planet. Sci. Lett.* 49: 528-550.
- De Lange G.J., 1992a. Distribution of various extracted phosphorus compounds in the interbedded turbiditic pelagic sediments of the Madeira Abyssal Plain, eastern North Atlantic. *Mar. Geol.* 109: 115-139.
- De Lange G.J., 1992b. Distribution of exchangeable, fixed, organic and total nitrogen in interbedded turbiditic/pelagic sediments of the Madeira Abyssal Plain, eastern North Atlantic. *Mar. Geol.* 109: 95-114.
- De Lange G.J., Ten Haven H.L., 1983. Recent sapropel formation in the eastern Mediterranean. *Nature* 305: 797-798.
- De Lange G.J., Middelburg J.J., Pruyssers P.A., 1989. Middle and Late Quaternary depositional sequences and cycles in the eastern Mediterranean. *Sedimentology* 36: 151-158.
- De Lange G.J., Middelburg J.J., Van der Weijden C.H., Catalano G., Luther III G.W., Hydes D.J., Woittiez J.R.W., Klinkhammer G.P., 1990. Composition of anoxic hypersaline brines in the Tyro and Bannock Basins, eastern Mediterranean. *Mar. Chem.* 31: 63-88.
- De Lange G.J., Van Os B.J.H., Pruyssers P.A., Middelburg J.J., Castradori D., Van Santvoort P., Müller P.J., Eggenkamp H., Prahl F.G., 1994. Possible early diagenetic alteration of palaeo proxies. In *Carbon cycling in the glacial ocean: Constraints on the ocean's role in global change* (editors: Zahn R., Pedersen T.F., Kaminski M.A., Labeyrie L.), pp. 225-258, Springer-Verlag, Berlin. (NATO ASI Ser. I vol. 17)

- Demaison G.J., Moore G.T., 1980. Anoxic environments and oil source bed genesis. *Org. Geochem.* 2: 9-31.
- De Visser J.P., 1991. *Clay mineral stratigraphy of Miocene to recent marine sediments in the central Mediterranean*. Ph.D. dissertation Univ. Utrecht, 244 pp.
- De Visser J.P., Ebbing J.H.J., Gudjonsson L., Hilgen F.J., Jorissen F.J., Verhallen P.J.J.M., Zevenboom D., 1989. The origin of rhythmic bedding in the Pliocene Trubi Formation of Sicily, southern Italy. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 69: 45-66.
- Dominik J., Stoffers P., 1978. The influence of Late Quaternary stagnations on clay sedimentation in the eastern Mediterranean Sea. *Geol. Rundschau* 68: 302-317.
- Dymond J., Suess E., Lyle M., 1992. Barium in deep-sea sediment: A geochemical proxy for paleoproductivity. *Paleoceanography* 7: 163-181.
- Dypvik H., 1984. Geochemical compositions and depositional conditions of Upper Jurassic and Lower Cretaceous Yorkshire clays, England. *Geol. Mag.* 121: 489-504.
- Einsele G., 1982. Limestone-marl cycles (periodites): Diagnosis, significance, causes - a review. In *Cyclic and event stratification* (editors: Einsele G., Seilacher A.), pp. 8-53, Springer-Verlag, Berlin.
- Einsele G., Seilacher, A., 1982. *Cyclic and event stratification*, 536 pp., Springer-Verlag, Berlin.
- Emeis K.-C., Camerlenghi A., McKenzie J.A., Rio D., Sprovieri R., 1991. The occurrence and significance of Pleistocene and Upper Pliocene sapropels in the Tyrrhenian Sea. *Mar. Geol.* 100: 155-182.
- Emeis K.-C., Robertson A.H.F., Richter C., et al., 1996. *Proc. ODP, Init. Repts.* 160, 972 pp., Ocean Drilling Program, College Station, TX.
- Eppley R.W., Peterson B.J., 1979. Particulate organic matter flux and planktonic new production in the deep ocean. *Nature* 282: 677-680.
- Erba E., 1991. Deep mid-water bacterial mats from anoxic basins of the Eastern Mediterranean. *Mar. Geol.* 100: 83-101.
- Esteban M., 1979. Significance of the upper Miocene coral reefs of the western Mediterranean. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 29: 169-188.
- Fairbanks R.G., Sverdlow M., Free R., Wiebe P.H., Bé A.W.H., 1982. Vertical distribution and isotopic fractionation of living planktonic foraminifera from the Panama Basin. *Nature* 298: 841-844.
- Falkner K.K., Klinkhammer G.P., Bowers T.S., Todd J.F., Lewis B.L., Landing W.M, Edmond J.M., 1993. The behavior of barium in anoxic marine waters. *Geochim. Cosmochim. Acta* 57: 537-554.
- Fischer A.G., 1980. Gilbert-bedding rhythms and geochronology. In *The scientific ideas of G.K. Gilbert* (editor: Yochelson E.L.), pp. 93-104. (Spec. Pap. Geol. Soc. Am. 183)
- Fontugne M.R., Calvert S.E., 1992. Late Pleistocene variability of the carbon isotopic composition of organic matter in the eastern Mediterranean: Monitor of changes in carbon sources and atmospheric CO₂ concentrations. *Paleoceanography* 7: 1-20.

References

- Foucault A., Mélières F., 1995. Nature et origine des cycles sédimentaires métriques du Pliocène de l'Ouest méditerranéen d'après l'étude du contenu terrigène de la Formation Narbone (Punta Piccola, Sicile, Italie), *C.R. Acad. Sci. Paris, Ila* 321: 869-876.
- François R., Honjo S., Manganini S.J., Ravizza G.E., 1995. Biogenic barium fluxes to the deep sea: Implications for paleoproductivity reconstruction. *Global Biogeochem. Cycles* 9: 289-303.
- Fry B., Jannasch H.W., Molyneaux S.J., Wirsén C.O., Muramoto J.A., King S., 1991. Stable isotope studies of the carbon, nitrogen and sulfur cycles in the Black Sea and the Cariaco Trench. *Deep-Sea Res.* 38: S1003-S1019.
- Goldberg E.D., Arrhenius G.O.S., 1958. Chemistry of Pacific pelagic sediments. *Geochim. Cosmochim. Acta* 13: 153-212.
- Gordeyev V.V., Lisitsyn A.P., 1978. Sredniy khimicheskiy sostav vzvesey rek mira i pitaniye okeanov rechnym osadochnym materialom, *Dokl. Akad. Nauk SSSR* 238, 225-228.
- Govindaraju K., 1989. Compilation of working values and sample description for 272 geostandards. *Geostand. Newsl. special issue* 13: 1-113.
- Gudjonsson L., 1987. Local and global effects on the Early Pliocene Mediterranean stable isotope records. *Mar. Micropaleontol.* 12: 241-253.
- Gudjonsson L., Van der Zwaan G.J., 1985. Anoxic events in the Pliocene Mediterranean: Stable isotope evidence of run-off. *Proc. K. Ned. Akad. Wet. B* 88: 69-82.
- Güllü G.H., Ölmez I., Tuncel G., 1996. Chemical concentrations and elements size distributions of aerosols in the eastern Mediterranean during strong dust storms, In *The impact of desert dust across the Mediterranean* (editors: Guerzoni S., Chester R.), pp. 339-347, Kluwer Academic Publishers, Dordrecht.
- Hartgers W.A., Sinninghe Damsté J.S., Requejo A.G., Allan J., Hayes J.M., De Leeuw J.W., 1994. Evidence for only minor contributions from bacteria to sedimentary organic carbon. *Nature* 369: 224-227.
- Hartmann M., Müller P.J., Suess E., Van der Weijden C.H., 1976. Chemistry of Later Quaternary sediments and their interstitial waters from the NW African continental margin. *Meteor. Forschungsergeb. C* 24: 1-67.
- Hayes J.M., 1993. Factors controlling ¹³C contents of sedimentary organic compounds: Principles and evidence. *Mar. Geol.* 113: 111-125.
- Hemleben C., Spindler M., Anderson O.R., 1989. *Modern planktonic foraminifera*, 363 pp, Springer-Verlag, New York.
- Henrichs S.M., Reeburgh W.S., 1987. Anaerobic mineralization of marine sediment organic matter; Rates and the role of anaerobic processes in the oceanic carbon economy. *Geomicrobiol. J.* 5: 191-237.
- Higgs N.C., Thomson J., Wilson T.R.S., Croudace I.W., 1994. Modification and complete removal of eastern Mediterranean sapropels by postdepositional oxidation. *Geology* 22: 423-426.

- Hilgen F.J., 1991a. Astronomical calibration of Gauss to Matuyama sapropels in the Mediterranean and implication for the Geomagnetic Polarity Time Scale. *Earth Planet. Sci. Lett.* 104: 226-244.
- Hilgen F.J., 1991b. Extension of the astronomically calibrated (polarity) time scale to the Miocene/Pliocene boundary. *Earth Planet. Sci. Lett.* 107: 349-368.
- Hilgen F.J., Lourens L.J., Berger A., Loutre M.F., 1993. Evaluation of the astronomically calibrated time scale for the late Pliocene and earliest Pleistocene. *Paleoceanography* 8: 549-565.
- Hilgen F.J., Krijgsman W., Langereis C.G., Lourens L.J., Santarelli A., Zachariasse W.J., 1995. Extending the astronomical (polarity) time scale into the Miocene. *Earth Planet. Sci. Lett.* 136: 495-510.
- Hoefs M.J.L., Schouten S., De Leeuw J.W., King L.L., Wakeham S.G., Sinninghe Damsté J.S., 1997. Ether lipids of planktonic archaea in the marine water column. *Appl. Environ. Microbiol.* 63: 3090-3095.
- Howell M.W., Thunell R.C., 1992. Organic carbon accumulation in Bannock Basin: Evaluating the role of productivity in the formation of eastern Mediterranean sapropels. *Mar. Geol.* 103: 461-471.
- Howell M.W., Thunell R., Tappa E., Rio D., Sprovieri R., 1988. Late Neogene laminated and opal-rich facies from the Mediterranean region: Geochemical evidence for mechanisms of formation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 64: 265-286.
- Howell M.W., Rio D., Thunell R.C., 1990. Laminated sediments from the Vrica section (Calabria, S. Italy): Evidence for Plio-Pleistocene climatic change in the Mediterranean region. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 78: 195-216.
- Ingall E.D., Jahnke R.A., 1994. Evidence for enhanced phosphorus regeneration from marine sediments overlain by oxygen depleted waters. *Geochim. Cosmochim. Acta* 58: 2571-2575.
- Ingall E.D., Bustin R.M., Van Cappellen P., 1993. Influence of water column anoxia on the burial and preservation of carbon and phosphorus in marine shales. *Geochim. Cosmochim. Acta* 57: 303-316.
- Jacobs L., Emerson S., 1985. Partitioning and transport of metals across the O₂/H₂S interface in a permanently anoxic basin: Framvaren Fjord, Norway. *Geochim. Cosmochim. Acta* 49: 1433-1444.
- James R.H., Elderfield H., 1996. Chemistry of ore-forming fluids and mineral formation rates in an active hydrothermal sulfide deposit on the Mid-Atlantic Ridge. *Geology* 24: 1147-1150.
- Jasper J.P., Gagosian R.B., 1990. The sources and deposition of organic matter in the Late Quaternary Pigmy Basin, Gulf of Mexico. *Geochim. Cosmochim. Acta* 54: 1117-1132.
- Jonkers H.A., 1984. Pliocene benthonic foraminifera from homogeneous and laminated marls on Crete. *Utrecht Micropal. Bull.* 31, 179 pp.

References

- Katz M.E., Thunell R.C., 1984. Benthic foraminiferal biofacies associated with middle Miocene to early Pliocene oxygen-deficient conditions in the eastern Mediterranean. *J. Foraminiferal Res.* 14: 187-202.
- Kempe S., Diercks A.-R., Liebezeit G., Prange A., 1991. Geochemical and structural aspects of the pycnocline in the Black Sea (R/V Knorr 134-8 Leg 1, 1988). In *Black Sea oceanography* (editors: Izdar E., Murray J.W.), pp. 89-110, Kluwer Academic Publishers, Dordrecht. (NATO ASI Ser. C vol. 351)
- Kidd R.B., Cita M.B., Ryan W.B.F., 1978. Stratigraphy of eastern Mediterranean sapropel sequences recovered during DSDP Leg 42A and their paleoenvironmental significance. In *Init. Repts. DSDP. 42A* (editors Hsü K.J., Montadert L., et al.), 412-443, U.S. Govt. Printing Office, Washington.
- Kohnen M.E.L., Schouten S., Sinninghe Damsté J.S., De Leeuw J.W., Merritt D.A., Hayes J.M., 1992. Recognition of paleobiochemicals by a combined molecular sulfur and isotope geochemical approach. *Science* 256: 358-362.
- Koopmann B., 1981. Sedimentation von Saharastaub im subtropischen Nordatlantik während der letzten 25.000 Jahre. *Meteor Forschungsergeb. C* 35: 23-59.
- Koopmans M.P., Köster J., Van Kaam-Peters H.M.E., Kenig F., Schouten S., Hartgers W.A., De Leeuw J.W., Sinninghe Damsté J.S., 1996. Diagenetic and catagenetic products of isorenieratene: Molecular indicators for photic zone anoxia. *Geochim. Cosmochim. Acta* 60: 4467-4496.
- Kullenberg B., 1952. On the salinity of water contained in marine sediments. *Medd. Oceanogr. Inst. Goteborg* 21: 1-38.
- Lacombe H., Tchernia P., 1972. Caractères hydrologiques et circulation des eaux en Méditerranée. In *The Mediterranean Sea: A natural sedimentation laboratory* (editor: Stanley D.J.), pp. 25-36, Dowden, Hutchinson & Ross, Stroudsburg.
- Langereis C.G., Hilgen F.J., 1991. The Rossello composite: A Mediterranean and global reference section for the Early to early Late Pliocene. *Earth Planet. Sci. Lett.* 104: 211-225.
- Leythaeuser D., 1973. Effects of weathering on organic matter in shales. *Geochim. Cosmochim. Acta* 37: 113-120.
- Liaaen-Jensen S., 1978. Chemistry of carotenoid pigments. In *The photosynthetic bacteria* (editors: Clayton R.K., Sistrom W.R.), pp. 233-247, Plenum Press, New York.
- Littke R., Klusmann U., Krooss B., Leythaeuser D., 1991. Quantification of loss of calcite, pyrite, and organic matter due to weathering of Toarcian black shales and effects on kerogen and bitumen characteristics. *Geochim. Cosmochim. Acta* 55: 3369-3378.
- Lourens L.J., 1994. *Astronomical forcing of Mediterranean climate during the last 5.3 million years*. Ph.D. dissertation, Univ. Utrecht, 247 pp.
- Lourens L.J., Hilgen F.J., Gudjonsson L., Zachariasse W.J., 1992. Late Pliocene to early Pleistocene astronomically-forced sea surface productivity and temperature variations in the Mediterranean. *Mar. Micropaleontol.* 19: 49-78.

- Lourens L.J., Antonarakou A., Hilgen F.J., Van Hoof A.A.M., Vergnaud-Grazzini C., Zachariasse W.J., 1996a. Evaluation of the Plio-Pleistocene astronomical timescale. *Paleoceanography* 11: 391-413.
- Lourens L.J., Hilgen F.J., Raffi I., Vergnaud-Grazzini C., 1996b. Early Pleistocene chronology of the Vrica section (Calabria, Italy). *Paleoceanography* 11: 797-812.
- Lourens L.J., Wehausen R., Brumsack H.-J., 1998. Orbital variability in the Ti/Al ratio of ODP Site 967 (eastern Mediterranean): A direct response to changes in the summer monsoon. In *Reconstructing ocean history - A window into the future* (editor: Abrantes F.), Proc. 6th International Conference on Paleoceanography, pp. 154.
- Lourens L.J., Nijenhuis I.A., et al., in prep. Non-precessional driven palaeoproductivity changes in the eastern Mediterranean: a case study from the Lido Rossello section (Sicily).
- Mangini A., Schlosser P., 1986. The formation of eastern Mediterranean sapropels. *Mar. Geol.* 72: 115-124.
- Martin J.-M., Meybeck M., 1979. Elemental mass-balance of material carried by major world rivers. *Mar. Chem.* 7: 173-206.
- Martin J.-M., Whitfield M., 1983. The significance of the river input of chemical elements to the ocean. In *Trace metals in sea water* (editors: Wong C.S., Boyle E., Bruland K.W., Burton J.D., Goldberg E.D.), pp. 265-296, Plenum Press, New York.
- Meyers P.A., 1993. Origin of the Plio-Pleistocene Vrica laminites: Organic geochemical evidence. *Mar. Geol.* 115: 117-127.
- Milliman J.D., 1974. *Recent sedimentary carbonates*, 375 pp., Springer-Verlag, Berlin.
- Milliman J.D., Müller J., 1973. Precipitation and lithification of magnesian calcite in the deep-sea sediments of the eastern Mediterranean Sea. *Sedimentology* 20: 29-45.
- Moretti A., 1993. Note sull'evoluzione tettono-stratigrafica del bacino Crotonese dopo la fine del Miocene. *Boll. Soc. Geol. It.* 112: 845-867.
- Morse J.W., Mackenzie F.T., 1990. *Geochemistry of sedimentary carbonates*, 707 pp., Elsevier, Amsterdam. (Developments in sedimentology vol. 48)
- Müller P.J., Schneider R., 1993. An automated leaching method for the determination of opal in sediments and particulate matter. *Deep-Sea Res.* 40: 425-444.
- Müller P.J., Suess E., 1979. Productivity, sedimentation rate, and sedimentary organic matter in the oceans - I. Organic carbon preservation. *Deep-Sea Res.* 26A: 1347-1362.
- Murat A., 1991. *Enregistrement sédimentaire des paléoenvironnements quaternaires en Méditerranée orientale*. Ph.D. dissertation Univ. Perpignan, 280 pp.
- Nijenhuis I.A., 1998. Comparison of single sapropels in ODP Sites and land sections. *Mineral. Mag.* 62A, 1089-1090, Proc. 8th annual Goldschmidt Conference.
- Nijenhuis I.A., Schenau S.J., 1994. *On the origin of some Miocene sapropelites of Faneromeni, Crete. A geochemical survey*. M.Sc. dissertation, Univ. Utrecht, 25pp.

References

- Nijenhuis I.A., Schenau S.J., Van der Weijden C.H., Hilgen F.J., Lourens L.J., Zachariasse W.J., 1996. On the origin of upper Miocene sapropelites: A case study from the Faneromeni section, Crete (Greece). *Paleoceanography* 11: 633-645.
- Nijenhuis I.A., Brumsack H.-J., De Lange G.J., 1998. The trace element budget of the eastern Mediterranean during Pliocene sapropel formation. In: *Proc. ODP, Sci. Results* 160 (editors: Robertson A.H.F., Emeis K.-C., Richter C., Camerlenghi A.), pp. 199-206, Ocean Drilling Program, College Station, TX.
- Nolet G.J., Corliss B.H., 1990. Benthic foraminiferal evidence for reduced deep-water circulation during sapropel deposition in the eastern Mediterranean. *Mar. Geol.* 94: 109-130.
- Olausson E., 1954. Description of sediment cores from the Central and Western Pacific with the adjacent Indonesian region. *Rep. Swed. Deep-Sea Exped. 1947-1948* 6(8), 163-214.
- Olausson E., 1961. Studies of deep sea cores. *Rep. Swed. Deep-Sea Exped. 1947-1948* 8(6), 336-391.
- Orszag-Sperber F., Butterlin J., Clermonte J., Colchen H., Guiraud R., Poisson A., Ricou L.E., 1993. Tortonian paleoenvironments (11.5-6 Ma). In *Atlas Tethys palaeoenvironmental maps* (editors: Dercourt J., Ricou L.E., Vrielynck B.), pp. 243-258, Gauthier-Villars, Paris.
- Passier H.F., De Lange G.J., 1998. Sedimentary sulfur and iron chemistry in relation to the formation of Eastern Mediterranean sapropels. In *Proc. ODP, Sci. Results* 160 (editors: Robertson A.H.F., Emeis K.-C., Richter C., Camerlenghi A.), pp. 249-259, Ocean Drilling Program, College Station, TX.
- Passier H.F., Middelburg J.J., van Os B.J.H., De Lange G.J., 1996. Diagenetic pyritisation under eastern Mediterranean sapropels caused by downward sulphide diffusion. *Geochim. Cosmochim. Acta* 60: 751-763.
- Passier H.F., Middelburg J.J., De Lange G.J., Böttcher M.E., 1997. Pyrite contents, microtextures, and sulfur isotopes in relation to formation of the youngest eastern Mediterranean sapropel. *Geology* 25: 519-522.
- Passier H.F., Bosch H.-J., Nijenhuis I.A., Lourens L.J., Böttcher M.E., Leenders A., Sinninghe Damsté J.S., De Lange G.J., De Leeuw J.W., in press. Sulphidic Mediterranean surface waters during Pliocene sapropel formation. *Nature*.
- Passier H.F., Middelburg J.J., De Lange G.J., Böttcher M.E., 1999. Modes of sapropel formation in the eastern Mediterranean: some constraints based on pyrite properties. *Mar. Geol.* 153: 199-219.
- Pedersen T.F., Calvert S.E., 1990. Anoxia vs. productivity: What controls the formation of organic-carbon-rich sediments and sedimentary rocks? *Am. Assoc. Petroleum Geologists Bull.* 74: 454-466.
- Perissoratis C., Piper D.J.W., 1992. Age, regional variation, and shallowest occurrence of S1 sapropel in the northern Aegean Sea. *Geo-Mar. Lett.* 12: 49-53.
- Pilipchuk M.F., Volkov I.I., 1974. Behavior of molybdenum in processes of sediment formation and diagenesis in Black Sea. In *The Black Sea - Geology, chemistry, and biology* (editors: Degens E.T., Ross D.A.), pp. 542-553. (Am. Assoc. Petroleum Geologists Memoir 20)

- Piper D.Z., Isaacs C.M., 1995a. Geochemistry of minor elements in the Monterey Formation, California: Seawater chemistry of deposition. *U.S. Geol. Surv. Prof. Paper* 1566, 41pp.
- Piper D.Z., Isaacs C.M., 1995b. Minor elements in Quaternary sediment from the Sea of Japan: A record of surface-water productivity and intermediate-water redox conditions. *GSA Bulletin* 107: 54-67.
- Postma G., Hilgen F.J., Zachariasse W.J., 1993. Precession-punctuated growth of a late Miocene submarine-fan lobe on Gavdos (Greece). *Terra Nova* 5: 438-444.
- Potonié H., 1904. Über Faulschlamm-(Sapropel)-Gesteine. *Sitz. Gesell. nat. F. Berlin*, 243-245.
- Potonié H., 1907. Zur Frage nach der Ur-Materialien der Petrolea. *Jahrb. k. Pr. Geol. Landesanst. Bergak.* 25: 342-368.
- Pratt L.M., 1984. Influence of paleoenvironmental factors on preservation of organic matter in Middle Cretaceous Greenhorn formation, Pueblo, Colorado. *Am. Assoc. Petroleum Geologists Bull.* 68: 1146-1159.
- Prauss M., Riegel W., 1989. Evidence from phytoplankton associations for causes of black shale formation in epicontinental seas. *N. Jb. Geol. Paläont. Mh.* 11: 671-682.
- Prell W.L., Kutzbach J.E., 1987. Monsoon variability over the past 150,000 years. *J. Geophys. Res.* 92: 8411-8425.
- Prell W.L., Kutzbach J.E., 1992. Sensitivity of the Indian monsoon to forcing parameters and implications for its evolution. *Nature* 360: 647-652.
- Pruysers P.A., De Lange G.J., Middelburg J.J., 1991. Geochemistry of eastern Mediterranean sediments: Primary sediment composition and diagenetic alterations. *Mar. Geol.* 100: 137-154.
- Pujol C., Vergnaud-Grazzini C., 1995. Distribution patterns of live planktic foraminifers as related to regional hydrography and productive systems of the Mediterranean Sea. *Mar. Micropaleontol.* 25: 187-217.
- Quade J., Solounias N., Cerling T.E., 1994. Stable isotopic evidence from paleosol carbonates and fossil teeth in Greece for forest or woodlands over the past 11 Ma. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 108: 41-53.
- Quandt I., Gottschalk G., Ziegler H., Stichler W., 1977. Isotope discrimination by photosynthetic bacteria. *FEMS Microbiol. Lett.* 1: 125-128.
- Ravelo A.C., Fairbanks R.G., Philander S.G.H., 1990. Reconstructing tropical Atlantic hydrography using planktonic foraminifera and an ocean model. *Paleoceanography* 5: 409-431.
- Repeta D.J., 1993. A high resolution historical record of Holocene anoxygenic primary production in the Black Sea. *Geochim. Cosmochim. Acta* 57: 4337-4342.
- Repeta D.J., Simpson D.J., Jørgensen B.B., Janasch H.W., 1989. Evidence for anoxygenic photosynthesis from the distribution of bacteriochlorophylls in the Black Sea. *Nature* 342: 69-72.

References

- Reynolds L.A., Thunell R.C., 1986. Seasonal production and morphologic variation of *Neoglobobulimina pachyderma* (Ehrenberg) in the northeast Pacific. *Micropal.* 32: 1-18.
- Reynolds Sautter L., Thunell R.C., 1991. Planktonic foraminiferal response to upwelling and seasonal hydrographic conditions: Sediment trap results from San Pedro Basin, Southern California Bight. *J. Foraminiferal Res.* 21: 347-363.
- Rio D., Sprovieri R., Thunell R., 1991. Pliocene-lower Pleistocene chronostratigraphy: A re-evaluation of Mediterranean type sections. *Geol. Soc. Am. Bull.* 103: 1049-1058.
- Rögl F., Steininger F.F., 1983. Vom Zerfall der Tethys zu Mediterran und Paratethys. *Ann. Naturhist. Mus. Wien A* 85: 135-163.
- Rohling E.J., 1994. Review and new aspects concerning the formation of eastern Mediterranean sapropels. *Mar. Geol.* 122: 1-28.
- Rohling E.J., Gieskes W.W.C., 1989. Late Quaternary changes in Mediterranean Intermediate Water density and formation rate. *Paleoceanography* 4: 531-545.
- Rohling E.J., Hilgen F.J., 1991. The eastern Mediterranean climate at times of sapropel formation: A review. *Geol. Mijnbouw* 70: 253-264.
- Rohling E.J., De Stigter H.C., Vergnaud-Grazzini C., Zaalberg R., 1993. Temporary repopulation by low-oxygen tolerant benthic foraminifera within an Upper Pliocene sapropel: Evidence for the role of oxygen depletion in the formation of sapropels. *Mar. Micropaleontol.* 22: 207-219.
- Ross D.A., Uchupi E., 1977. Structure and sedimentary history of Southeastern Mediterranean Sea-Nile Cone area. *Am. Assoc. Petroleum Geologists Bull.* 61: 872-902.
- Rossignol-Strick M., 1983. African monsoons, an immediate climate response to orbital insolation. *Nature* 304: 46-49.
- Rossignol-Strick M., 1985. Mediterranean Quaternary sapropels, an immediate response of the African monsoon to variation of insolation. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 49: 237-263.
- Rossignol-Strick M., 1987. Rainy periods and bottom water stagnation initiating brine accumulation and metal concentrations: 1. The late Quaternary. *Paleoceanography* 2: 333-360.
- Rossignol-Strick M., Nesteroff W., Olive P., Vergnaud-Grazzini C., 1982. After the deluge: Mediterranean stagnation and sapropel formation. *Nature* 295: 105-110.
- Rutten A., De Lange G.J., Ziveri P., Thomson J., Colley S., Corselli C., submitted. Recent terrestrial and carbonate fluxes in the pelagic eastern Mediterranean: A comparison between sediment trap and seafloor sediment. *Palaeogeogr. Palaeoclimatol. Palaeoecol.*
- Sachse M., Mohr B.A.R., 1996. Eine obermiozäne Makro- und Mikroflora aus Südkreta (Griechenland), und deren paläoklimatische Interpretation. - Vorläufige Betrachtungen. *N. Jb. Geol. Paläont. Abh.* 200: 149-182.
- Sarmiento J.L., Herbert T., Toggweiler J.R., 1988. Mediterranean nutrient balance and episodes of anoxia. *Global Biogeochem. Cycles* 2: 427-444.

- Sarnthein M., Tetzlaff G., Koopmann B., Wolter K., Pflaumann U., 1981. Glacial and interglacial wind regimes over the eastern subtropical Atlantic and North-West Africa. *Nature* 293: 193-196.
- Sarnthein M., Pflaumann U., Ross R., Tiedemann R., Winn K., 1992. Transfer functions to reconstruct ocean palaeoproductivity: A comparison. In *Upwelling systems: Evolution since the Early Miocene* (editors: Summerhayes C.P., Prell W.L., Emeis K.-C.), pp. 411-427. (Geol. Soc. Spec. Publ. 64)
- Schenau S. J., Antonarakou A., Hilgen F.J., Lourens L.J., Nijenhuis I.A., Van der Weijden C.H., Zachariasse W.J., 1999. Organic-rich layers in the Metochia section (Gavdos, Greece): Evidence for a single mechanism of sapropel formation during the past 10 Myr. *Mar. Geol* 153: 117-135.
- Schouten S., 1995. *Structural and stable carbon isotope studies of lipids in immature sulphur-rich sediments*. Ph.D. dissertation Univ. Groningen, 306 pp.
- Selli R., Accorsi C.A., Bandini Mazzanti M., Bertolani Marchetti D., Bigazzi G., Bonadonna F.P., Borsetti A.M., Cati F., Colalongo M.L., D'Onofrio S., Landini W., Menesini E., Mezzetti R., Pasini G., Savelli C., Tampieri R., 1977. The Vrica section (Calabria, Italy). A potential Neogene/Quaternary boundary stratotype. *Giorn. Geol.* 142: 181-201.
- Shaw T.J., Gieskes J.M., Jahnke R.A., 1990. Early diagenesis in differing depositional environments: The response of transition metals in pore water. *Geochim. Cosmochim. Acta* 54: 1233-1246.
- Shiller A.M., Boyle E.A., 1987. Dissolved vanadium in rivers and estuaries. *Earth Planet. Sci. Lett.* 86: 214-224.
- Shimmiel G.B., 1992. Can sediment geochemistry record changes in coastal upwelling palaeoproductivity? Evidence from northwest Africa and the Arabian sea. In *Upwelling systems: Evolution since the Early Miocene* (editors: Summerhayes C.P., Prell W.L., Emeis K.-C.), pp. 29-46. (Geol. Soc. Spec. Publ. 64)
- Sigl W., Chamley H., Fabricius F., D'Argoud G.G., Müller J., 1978. Sedimentology and environmental conditions of sapropels. In *Init. Repts. DSDP 42A* (editors Hsü K.J., Montadert L., et al.), pp. 445-465, U.S. Govt. Printing Office, Washington.
- Sinninghe Damsté J.S., Köster J., 1998. A euxinic southern North Atlantic Ocean during the Cenomanian/Turonian oceanic anoxic event. *Earth Planet. Sci. Lett.* 158: 165-173.
- Sinninghe Damsté J.S., Rijpstra W.I.C., De Leeuw J.W., Schenck P.A., 1988. Origin of organic sulphur compounds and sulphur-containing high molecular weight substances in sediments and immature crude oils. *Org. Geochem.* 13: 593-606.
- Sinninghe Damsté J.S., Wakeham S.G., Kohnen M.E.L., Hayes J.M., De Leeuw J.W., 1993. A 6,000-year sedimentary molecular record of chemocline excursions in the Black Sea. *Nature* 362: 827-829.
- Spaak P., 1983. Accuracy in correlation and ecological aspects of the planktonic foraminiferal zonation of the Mediterranean Pliocene. *Utrecht Micropal. Bull.* 28, 160pp.

References

- Sprovieri R., 1993. Pliocene-Early Pleistocene astronomically forced planktonic foraminifera abundance fluctuations and chronology of Mediterranean calcareous plankton bio-events. *Riv. It. Paleont. Strat.* 99: 371-414.
- Sprovieri R., Thunell R., Howell M., 1986. Paleontological and geochemical analyses of three laminated sedimentary units of late Pliocene-Early Pleistocene age from the Monte San Nicola section in Sicily. *Riv. It. Paleont. Strat.* 92: 401-434.
- Sprovieri R., Di Stefano E., Sprovieri M., 1996. High resolution chronology for Late Miocene Mediterranean stratigraphic events. *Riv. It. Paleont. Strat.* 102: 77-104.
- Ströhle K., Krom M.D., 1997. Evidence for the evolution of an oxygen minimum layer at the beginning of S-1 sapropel deposition in the eastern Mediterranean. *Mar. Geol.* 140: 231-236.
- Suc J.-P., Bessais E., 1990. Pérennité d'un climat thermo-xérique en Sicile avant, pendant, après la crise de salinité messinienne. *C. R. Acad. Sci. Paris II* 310: 1701-1707.
- Summons R.E., Powell T.G., 1986. *Chlorobiaceae* in Palaeozoic seas revealed by biological markers, isotopes and geology. *Nature* 319: 763-765.
- Sutherland H.E., Calvert S.E., Morris R.J., 1984. Geochemical studies of the recent sapropel and associated sediment from the Hellenic outer ridge, eastern Mediterranean Sea. I: Mineralogy and chemical composition. *Mar. Geol.* 56: 79-92.
- Takahashi K., 1986. Seasonal fluxes of pelagic diatoms in the subarctic Pacific, 1982-1983. *Deep-Sea Res.* 33: 1225-1251.
- Takayanagi K., Wong G.T.F., 1985. Dissolved inorganic and organic selenium in the Orca Basin. *Geochim. Cosmochim. Acta* 49: 539-546.
- Tang C.M., Stott L.D., 1993. Seasonal salinity changes during Mediterranean sapropel deposition 9000 B.P.: Evidence from isotopic analyses of individual planktonic foraminifera. *Paleoceanography* 8: 473-493.
- Ten Haven H.L., Baas M., Kroot M., De Leeuw J.W., Schenk P.A., Ebbing J., 1987. Late Quaternary Mediterranean sapropels. III: Assessment of source of input and palaeotemperature as derived from biological markers. *Geochim. Cosmochim. Acta* 51: 803-810.
- Thomson J., Higgs N.C., Wilson T.R.S., Croudace I.W., De Lange G.J., Van Santvoort P.J.M., 1995. Redistribution and geochemical behaviour of redox-sensitive elements around S1, the most recent eastern Mediterranean sapropel. *Geochim. Cosmochim. Acta* 59: 3487-3501.
- Thunell R.C., Reynolds L.A., 1984. Sedimentation of planktonic foraminifera: Seasonal changes in species flux in the Panama Basin. *Micropaleontol.* 30: 243-262.
- Thunell R., Sautter L.R., 1992. Planktonic foraminiferal faunal and stable isotopic indices of upwelling: A sediment trap study in the San Pedro Basin, Southern California Bight. In *Upwelling systems: Evolution since the Early Miocene* (editors: Summerhayes C.P., Prell W.L., Emeis K.-C.), pp. 77-91. (Geol. Soc. Spec. Publ. 64)

- Thunell R.C., Williams D.F., 1989. Glacial-Holocene salinity changes in the Mediterranean Sea: Hydrographic and depositional effects. *Nature* 338: 493-496.
- Thunell R.C., Williams D.F., Belyea P.R., 1984. Anoxic events in the Mediterranean Sea in relation to the evolution of late Neogene climates. *Mar. Geol.* 59: 105-134.
- Thunell R.C., Williams D.F., Tappa E., Rio D., Raffi I., 1990. Pliocene-Pleistocene stable isotope record for Ocean Drilling Program Site 653, Tyrrhenian Basin: Implications for the paleoenvironmental history of the Mediterranean Sea. *Proc. ODP. Sci. Results* 107 (editors: Kastens K.A., Mascle J., et al.), pp. 387-399, Ocean Drilling Program, College Station, TX.
- Thunell R. C., Rio D., Sprovieri R., Raffi I., 1991. Limestone-marl couplets: Origin of the early Pliocene Trubi marls in Calabria, southern Italy. *J. Sediment. Petrol.* 61: 1109-1122.
- Thurrow J., Moullade M., Brumsack H.-J., Masure E., Taugourdeau-Lantz J., Dunham K.W., 1988. The Cenomanian/Turonian boundary event (CTBE) at Hole 641A, ODP Leg 103 (compared with the CTBE interval at Site 398). In *Proc. ODP, Sci. Results* 103 (editors: Boillot G., Winterer E.L., et al.), pp. 587-634, Ocean Drilling Program, College Station, TX.
- Tibbets P.J.C., 1980. *The analysis of carotenoids and their use as environmental and palaeoenvironmental indicators*. Ph.D. dissertation, Univ. Bristol.
- Tolderlund D.S., Bé A.W.H., 1971. Seasonal distribution of planktonic foraminifera in the western North Atlantic. *Micropal.* 17: 297-329.
- Tomadin L., Lenaz R., Landuzzi V., Mazzucotelli A., Vannucci R., 1984. Wind-blown dusts over the Central Mediterranean. *Oceanol. Acta* 7: 13-23.
- Tribovillard N.-P., Desprairies A., Lallier-Vergès E., Bertrand P., Moureau N., Ramdani A., Ramanampisoa L., 1994. Geochemical study of organic-matter rich cycles from the Kimmeridge Clay Formation of Yorkshire (UK): Productivity versus anoxia. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 108: 165-181.
- Troelstra S.R., Ganssen G.M., Van der Borg K., De Jong A.F.M., 1991. A late Quaternary stratigraphic framework for eastern Mediterranean Sapropel S1 based on AMS ¹⁴C dates and stable oxygen isotopes. *Radiocarbon* 33: 15-21.
- Twenhofel W.H., 1926. *Treatise on sedimentation*, 661 pp., Baillière, Tindal & Cox, London.
- Tyson R.V., 1995. *Sedimentary organic matter*, 615 pp., Chapman & Hall, London.
- Van Cappellen P., Ingall E.D., 1994. Benthic phosphorus regeneration, net primary production, and ocean anoxia: A model of the coupled marine biogeochemical cycles of carbon and phosphorus. *Paleoceanography* 9: 677-692.
- Van der Weijden C. H., 1993. Geochemical signatures preserved in sediments of the Semaforo and Vrica sections (Calabria, Italy) and their relations with variations of the sedimentary regime. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* 103: 203-221.
- Van der Zwaan G.J., 1982. Paleoecology of late Miocene Mediterranean foraminifera. *Utrecht Micropal. Bull.* 25, 202 pp.

References

- Van der Zwaan G. J., Gudjonsson L., 1986. Middle Miocene-Pliocene stable isotope stratigraphy and paleoceanography of the Mediterranean. *Mar. Micropaleontol.* 10: 71-90.
- Van der Zwaan G.J., Jorissen F.J., De Stigter H.C., 1990. The depth dependency of planktonic/benthic foraminiferal ratios: Constraints and applications. *Mar. Geol.* 95: 1-16.
- Van Kaam-Peters H.M.E., 1997. *The depositional environment of Jurassic organic-rich sedimentary rocks in NW Europe. A biomarker approach.* Ph.D. dissertation, Univ. Utrecht, 247 pp.
- Van Kaam-Peters H.M.E., Schouten S., De Leeuw J.W., Sinninghe Damsté J.S., 1997. A molecular and carbon isotope biogeochemical study of biomarkers and kerogen pyrolysates of the Kimmeridge Clay Facies: Palaeoenvironmental implications. *Org. Geochem.* 27: 399-422.
- Van Os B.J.H., Rohling E.J., 1993. Oxygen isotope depletions in eastern Mediterranean sapropels exclude estuarine circulation. In *Primary and diagenetic signals in Mediterranean sapropels and North Atlantic turbidites; Origin and fate of trace metals and palaeo-proxies*, Ph.D. dissertation Univ. Utrecht, pp. 3-12.
- Van Os B.J.H., Middelburg J.J., De Lange G.J., 1991. Possible diagenetic mobilization of barium in sapropelic sediment from the eastern Mediterranean. *Mar. Geol.* 100: 125-136.
- Van Os B.J.H., Lourens L.J., Hilgen F.J., De Lange G.J., Beaufort L., 1994. The formation of Pliocene sapropels and carbonate cycles in the Mediterranean: Diagenesis, dilution, and productivity. *Paleoceanography* 9: 601-617.
- Van Os B.J.H., Middelburg J.J., De Lange G.J., 1996. Extensive degradation and fractionation of organic matter during subsurface weathering. *Aquatic Geochemistry* 1: 303-312.
- Van Santvoort P.J.M., De Lange G.J., Thomson J., Cussen H., Wilson T.R.S., Krom M.D., Ströhle K., 1996. Active post-depositional oxidation of the most recent sapropel (S1) in sediments of the eastern Mediterranean Sea. *Geochim. Cosmochim. Acta* 60: 4007-4024.
- Venkatarathnam K., Ryan W.B.F., 1971. Dispersal patterns of clay minerals in the sediments of the eastern Mediterranean Sea. *Mar. Geol.* 11: 261-282.
- Vergnaud-Grazzini C., Ryan W.B.F., Cita M.B., 1977. Stable isotopic fractionation, climatic change and episodic stagnation in the eastern Mediterranean during the Late Quaternary. *Mar. Micropaleontol.* 2: 353-370.
- Verhallen P.J.J.M., 1991. Late Pliocene to early Pleistocene Mediterranean mud-dwelling foraminifera; Influence of a changing environment on community structure and evolution. *Utrecht Micropal. Bull.* 40, 220 pp.
- Versteegh G.J.M., 1994. Recognition of cyclic and non-cyclic environmental changes in the Mediterranean Pliocene: A palynological approach. *Mar. Micropaleontol.* 23: 147-183.
- Vine J.D., Tourtelot E.B., 1970. Geochemistry of black shale deposits - A summary report. *Econ.geol.* 65: 253-272.
- Von Breyman M.T., Emeis K.-C., Suess E., 1992. Water depth and diagenetic constraints on the use of barium as a palaeoproductivity indicator. In *Upwelling systems: Evolution since*

- the Early Miocene* (editors: Summerhayes C.P., Prell W.L., Emeis K.-C.), pp. 273-284. (Geol. Soc. Spec. Publ. 64)
- Wallace H.E., Thomson J., Wilson T.R.S., Weaver P.P.E., Higgs N.C., Hydes D.J., 1988. Active diagenetic formation of metal-rich layers in N.E. Atlantic sediments. *Geochim. Cosmochim. Acta* 52: 1557-1569.
- Wehausen R., Brumsack H.-J., 1998. The formation of Pliocene Mediterranean sapropels: Constraints from high-resolution major and minor element studies. In *Proc. ODP, Sci. Results* 160 (editors: Robertson A.H.F., Emeis K.-C., Richter C., Camerlenghi A.), pp. 207-217, Ocean Drilling Program, College Station, TX.
- Weltje G., De Boer P.L., 1993. Astronomically induced paleoclimatic oscillations reflected in Pliocene turbidite deposits on Corfu (Greece): Implications for the interpretation of higher order cyclicity in ancient turbidite systems. *Geology* 21: 307-310.
- Wetzel A., 1991. Stratification in black shales: Depositional Models and Timing - An Overview. In *Cycles and events in stratigraphy* (editors: Einsele G., Ricken W., Seilacher A.), pp. 508-523, Springer-Verlag, Berlin.
- Wignall P.B., 1994. *Black Shales*, 127 pp., Clarendon Press, Oxford.
- Williams D.F., Thunell R.C., Kennett J.P., 1978. Periodic freshwater flooding and stagnation of the eastern Mediterranean Sea during the late Quaternary. *Science* 201: 252-254.
- Zachariasse W.J., Riedel W.R., Sanfilippo A., Schmidt R.R., Brolsma M.J., Schrader H.J., Gersonde R., Drooger M.M., Broekman J.A., 1978. Micropaleontological counting methods and techniques - an exercise on an eight metres section of the lower Pliocene of Capo Rossello, Sicily. *Utr. Micropal. Bull.* 17, 265 pp.
- Zachariasse W.J., Jorissen F.J., Perissoratis C., Rohling E.J., Tsapralis V., 1997. Late Quaternary foraminiferal changes and the nature of sapropel S1 in Skopelos Basin. *Proc. 5th Hellenic symposium on Oceanography and Fisheries, Kavalla, Greece* 1: 391-394.

Samenvatting in het Nederlands

Deze samenvatting is bedoeld voor "niet-ingewijden".

Voor een meer geologische en completere samenvatting van het onderzoek wordt de lezer verwezen naar hoofdstuk 1, "Introduction and summary".

Als je met de ferry naar Engeland gaat en in Dover aankomt, is het spectaculaire aanzicht van de Seven Sisters altijd weer adembenemend. Deze krijtwitte rotsen zijn gevormd door opheffing van zeebodem en uitdroging en verharding van het daar afgezette materiaal (sediment). Marien sediment bestaat in het algemeen uit de schelpjes en het organisch materiaal van organismen die in zee leefden, en uit klei en zand dat is aangevoerd door rivieren en wind. Het is moeilijk te bevatten dat de Seven Sisters opgebouwd zijn uit de kalkskeletjes van ontelbare piepkleine, eencellige organismen (voornamelijk foraminiferen) die miljoenen jaren geleden in zee leefden.

Ook in het Middellandse Zeegebied vind je, bijvoorbeeld op eilanden als Sicilië en Kreta, prachtige kalkrotsen. Deze mariene sedimenten zijn geologisch gezien recentelijk opgeheven doordat Afrika tegen Europa aanbotst en de Middellandse Zee als het ware dichtdrukt. Sommige lagen, die middenin de Middellandse Zee onder vier kilometer water en tientallen meters jonger sediment liggen, zijn hierdoor eenvoudigweg op land te bestuderen.

De 'landsecties' in het Middellandse Zeegebied zijn niet helemaal gelijk aan de kalkrotsen aan de Engelse zuidkust. Het meest opvallende verschil is de kleurvariatie: vaak zie je een afwisseling van lichte en donkere lagen. Die donkere lagen bevatten naast kalk en klei ook veel organisch materiaal, en heten sapropelen (van het Oudgriekse 'sapos' en 'pèlos', voor verrotting en modder). Op Sicilië zie je zelfs een continue herhaling van het kleurpatroon grijs-wit-beige-wit. De patronen van deze sedimentaire cycli zijn bijzonder regelmatig en over het hele Middellandse Zeegebied hetzelfde. Ze zijn veroorzaakt door systematische schommelingen in de stand van de aardas en de baan van de aarde. Deze variaties bepalen de hoeveelheid en verdeling van het zonlicht dat de aarde ontvangt, en daardoor het klimaat. Het klimaat bepaalt weer de temperatuur en de hoeveelheid neerslag in het Middellandse Zeegebied en daardoor het soort sediment dat wordt afgezet. Tijdens droge perioden is er weinig aanvoer van voedingsstoffen door rivieren, waardoor er maar weinig organisch materiaal kan worden geproduceerd in zee. Dit is de situatie zoals die nu is, en dat resulteert in afzetting van witte, kalkrijke lagen. Het organisch materiaal in de sapropelen is in zee gevormd gedurende natte perioden waarin rivieren veel voedingsstoffen (en ook organisch materiaal van land) aanvoerden. De aanvoer van veel zoet water bovenop het zoute water van de Middellandse Zee kan daarnaast leiden tot een stabiele waterkolom waarin weinig verticaal watertransport optreedt. Dit resulteert in zuurstofgebrek in het diepe water, hetgeen de preservatie van organisch materiaal kan bevorderen.

Ik begon met de studie van sapropelen tijdens mijn afstudeeronderzoek, waarin ik geochemisch onderzoek zou doen naar sapropelen uit het Mioceen (de periode van 24 tot 5 miljoen jaar geleden) op Gavdos, een klein eilandje onder Kreta (en daarmee het zuidelijkste

puntje van Europa). Doordat het echter slecht weer was in de periode dat we monsters wilden nemen, kon de boot naar Gavdos niet vertrekken en besloten we op Kreta zelf Mioceen sapropelen te bemonsteren. Dit gebeurde bij Faneromeni, en de resultaten van dit onderzoek leidden tot hoofdstuk 2 van dit proefschrift. Gavdos kwam later alsnog aan de beurt door een monsternamen van de palaeontologen waarmee we samenwerkten (hoofdstuk 3), maar ik heb het eiland zelf nog steeds niet gezien. De belangrijkste boodschap van deze twee hoofdstukken is, dat de vorming van sapropelen in de Middellandse Zee gedurende de laatste tien miljoen jaar het gevolg is van één mechanisme: een regelmatige afwisseling van natte en droge perioden bepaald door de variaties in de stand van de aardas.

Mijn daadwerkelijke promotieonderzoek begon met monsternamen op Sicilië en in Calabrië (Italië). Dit keer was het wel mooi weer, waardoor de schitterende kustsecties met hun grijs-wit-beige-wit afwisseling goed tot hun recht kwamen. Op Sicilië bevindt zich in de Lido Rossello sectie tussen deze 'normale' sedimenten een aantal diatomieten, die in de nabijgelegen Punta di Maiata sectie afwezig zijn. Diatomieten zijn sedimenten waarin organismen voorkomen die een skelet van silica hebben (diatomeeën en radiolariën). De grijze lagen in deze secties bevatten relatief weinig kalk, hetgeen in het verleden wel verklaard is door aan te nemen dat diatomeeën en radiolariën de foraminiferen in het oppervlaktewater verdrongen hadden. De silicaskelletjes van deze organismen zouden daarna in het zeewater opgelost zijn. In hoofdstuk 4 wordt aangetoond dat deze verklaring niet waarschijnlijk is, omdat in Lido Rossello wel degelijk diatomeeën bewaard zijn, maar er geen silica in de grijze lagen gevonden wordt. Het lage kalkgehalte in die lagen wordt daarentegen verklaard door een combinatie van oplossing van kalk door zuren die geproduceerd zijn bij de afbraak van organisch materiaal, en verdunning van kalk met klei.

Uiteraard komen er ook sapropelen voor in de sedimenten die zich nog op de bodem van de Middellandse Zee bevinden. Om echter door te dringen tot de lagen die eenzelfde ouderdom hebben als de landsecties, moet er door tientallen meters sediment geboord worden. Dit soort werk wordt gedaan door het internationale Ocean Drilling Program, waaraan ook Nederland deelneemt. In 1995 voer het schip "Joides Resolution" naar de westelijke en oostelijke Middellandse Zee om een flink aantal gaten te boren. Zelf was ik helaas niet mee aan boord, maar mijn begeleider, Gert de Lange, wel. Hij nam een aantal sapropelen voor me mee van het schip; andere heb ik later zelf bemonsterd in een ODP magazijn in Bremen. Deze sapropelen zijn zeer goed ontwikkeld: ze zijn zwart, gelamineerd, rijk aan organisch materiaal (soms meer dan 50%), en scherp begrensd. Voor twee van die sapropelen hebben wij aangetoond dat ze gevormd zijn in een periode waarin de Middellandse Zee afgezien van de bovenste ~100 meter, geen zuurstof bevatte (hoofdstuk 5). Deze situatie is vergelijkbaar met de huidige Zwarte Zee, en sommige 'zwarte schalies', organisch-rijke mariene sedimenten die in de open oceaan zijn afgezet (hoofdstuk 6). Lage zuurstofconcentraties in diep zeewater worden meestal gekoppeld aan een stagnerende watercirculatie; tijdens de vorming van deze sapropelen was er echter wel degelijk circulatie (anders kunnen de hoge gehalten aan sporenelementen niet verklaard worden), maar werd het aanwezige zuurstof steeds opgebruikt door de afbraak van organisch materiaal. Data van alle ODP monsters worden in hoofdstuk

7 gecombineerd om de processen die hebben geleid tot sapropeelvorming te herleiden. Sapropeelvorming duurde zo'n 2.000 tot 10.000 jaar, afhankelijk van de plaats in de Middellandse Zee.

In hoofdstuk 8 tenslotte wordt een vergelijking gemaakt tussen één en dezelfde sapropeel in twee ODP kernen en in de Vrica landsectie in Calabrië. De ODP sapropelen zijn rijk aan organisch materiaal en kalk, en zijn zo'n 20 cm dik, terwijl de Vrica sapropeel veel minder organisch materiaal en kalk bevat, rijk is aan kleien, en 56 cm dik is (eigenlijk is dit geen sapropeel, maar een 'laminiet'). Deze verschillen zouden gedeeltelijk veroorzaakt kunnen zijn doordat de sedimenten in de landsectie veranderd zijn als gevolg van processen die optraden tijdens opheffing, verwerking en erosie. Dit blijkt echter niet het geval; de verschillen worden daarom verklaard doordat de Vrica sectie ten opzichte van de ODP sapropelen dichter bij de kust is afgezet, in ondieper water, waar veel klei werd aangevoerd door rivieren.

Al met al worden er in dit proefschrift veel verschillende organisch-rijke sedimenten uit mariene kernen en landsecties in het Middellandse Zeegebied besproken. Ondanks verschillen in leeftijd, plaats en duur van afzetting, en samenstelling, blijkt er één mechanisme verantwoordelijk voor hun vorming: een door variaties in de stand van de aardas veroorzaakte afwisseling van natte en droge perioden. Dezelfde processen spelen een rol in de vorming van elke sapropeel: productie van organisch materiaal, kalk en silica, aanvoer van klei, en diagenetische processen zoals het oplossen van kalk en de afbraak van organisch materiaal. Toch is iedere sapropeel weer anders omdat het moment en de plaats van afzetting de intensiteit van die verschillende processen beïnvloeden. Dit proefschrift is een stap op weg naar een model waarin sapropeelvorming over de gehele Middellandse Zee van het Mioceen tot het heden verklaard kan worden. Om dat te bereiken zullen we echter een nog beter beeld moeten krijgen van wat de verschillende chemische parameters ons kunnen vertellen. Bovendien zal er een nog hechtere samenwerking moeten ontstaan tussen de verschillende disciplines binnen de palaeoceanografie: stratigrafie, sedimentologie, (micro-)palaeontologie, anorganische en organische geochemie, palynologie en oceanografie. In 2004 is het precies 100 jaar geleden dat het woord "sapropel" voor het eerst gepubliceerd werd. Het zou mooi zijn als we in dat jaar begrijpen waar deze term precies voor staat.

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*"I thank you most sincerely for all your assistance;
& whether or no my Book may be wretched
you have done your best to make it less wretched."*

Charles Darwin (*in a letter to John Hooper*)

During the four years in which I did research at Utrecht University, many people contributed in some way to the realization of this thesis. I would like to thank them all for their support and cooperation.

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Ivar Nijenhuis

Curriculum Vitae

Ivar Anders Nijenhuis werd op 25 mei 1972 in Ede geboren. In 1984 begon hij zijn middelbare school opleiding aan het zelfstandig gymnasium van het Marnix College in Ede. Na het behalen van het gymnasium diploma in 1990, begon hij in datzelfde jaar aan de studies geologie en geochemie aan de Universiteit Utrecht. Na het propaedeutisch examen geologie in 1991 behaald te hebben, legde hij zich primair toe op de exogene geochemie. De studies werden in 1994 afgesloten met het doctoraal examen geochemie (*cum laude*). Aansluitend werd hij door de Nederlandse Organisatie voor Wetenschappelijk onderzoek bij de Universiteit Utrecht aangesteld als Onderzoeker in Opleiding. In deze functie verrichtte hij geochemisch onderzoek aan Middellandse Zee sedimenten. Na beëindiging van het formele dienstverband in september 1998 werd het onderzoek afgerond, resulterend in deze dissertatie. Vanaf juli 1999 werkt hij als geoloog bij Shell International Exploration and Production (SIEP).

*"Tripsels, allemaal tripsels!
Van de Griemel weet jij niets, geen sniezel."
Korilu*

Stellingen

behorende bij het proefschrift

"Geochemistry of eastern Mediterranean sedimentary cycles"

1.

Stellingen behoren bij het proefschrift zoals het rokkostuum bij de promotie.

2.

Gezien de vermoedelijke uitspraak van het Oudgriekse woord $\pi\eta\lambda\acute{o}\varsigma$, en de internationaal geaccepteerde schrijfwijze, had in de nieuwe spelling het Nederlandse woord "sapropeel" veranderd moeten worden in "sapropel".

3.

The official definition of a sapropel as "a discrete layer (...) containing greater than 2.0% organic carbon by weight" is impractical in the field, and wrongfully suggests that a layer containing 1.9% organic carbon is fundamentally different from a 'true' sapropel.

Kidd et al. [1978]

4.

All sapropels are different, but some are more different than others.

5.

The automatic coupling of sapropel occurrences to bottom water stagnation is contestable.
e.g. Olausson [1961]; Rossignol-Strick et al. [1982]; Béthoux [1984]; this thesis

6.

It is unlikely that Miocene sapropels have been formed by another mechanism than precession-induced dry-wet oscillations in Mediterranean climate.

*Cita and Grignani [1982]; Thunell et al. [1984];
Van der Zwaan and Gudjonsson [1986]; this thesis*

7.

The eastern Mediterranean Sea was euxinic from the bottom water up into the lower photic zone during formation of sapropels i-282 and i-292.

8.

"Give me a half-tanker of iron, and I'll give you an ice age." (J.H. Martin).
Send the tanker to the Mediterranean, and I'll give you a sapropel as well.

9.

The interpretation of Pliocene carbonate cycles as resulting mostly from variations in productivity is too simple.

Van Os et al. [1991]; this thesis

10.

Establishing a Body Shop within a 2 km radius of a mortuary is unethical.

11.

Bill Gates: "Het is niet in het belang van de consument dat wij kreupele produkten op de markt brengen" (*NRC Handelsblad, 06-02-1998*). Microsoft heeft tot nu toe kennelijk niet in het belang van de consument willen werken.

12.

Iemand die beweert theeliefhebber te zijn, maar deze drank met suiker nuttigt, is eigenlijk een suikerliefhebber.

13.

Aangezien menging van blauw en rood volstaat voor het maken van paars, vormt de geringe bijdrage van het groene D'66 aan Paars II geen bedreiging voor het voortbestaan van deze coalitie.

14.

Wie naast zijn schoenen loopt, is snel op zijn teentjes getrapt.

15.

In tegenstelling tot de Messiah, die zowel in zeer grote als in kleine bezetting kan worden uitgevoerd, komen de Matthäus en Johannes Passionen het beste tot hun recht indien uitgevoerd door een klein koor en orkest.

Ivar A. Nijenhuis

18-01-1999