17. THE FORMATION OF PLIOCENE MEDITERRANEAN SAPROPELS: CONSTRAINTS FROM HIGH-RESOLUTION MAJOR AND MINOR ELEMENT STUDIES[1]

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ABSTRACT

Two Pliocene Mediterranean sediment cores from Sites 964 (Pisano Plateau, Ionian Basin) and 967 (lower northern slope of Eratosthenes Seamount, south of Cyprus), which comprise a total of 428 samples, have been analyzed for major and minor elements (Si, Ti, Al, Fe, Mg, Ca, K, Ba, Cr, Ni, V, Zn, and Zr) by X-ray fluorescence analysis at a depth resolution of 3–4 cm. Core 160-964C-9H comprises five sapropels with up to 9.7% total organic carbon (TOC), one 2.5-m-thick turbidite, and a 50-cm segment of a second turbidite, whereas Core 160-967B-9H contains eight sapropels with TOC content of up to 6.7%.

Cyclic variations in carbonate content and detrital-matter composition are evident at both sites. At Site 964 (Pisano Plateau) terrigenous detrital matter chemistry reflects periods of stronger Saharan dust input alternating with fluvial input from the northern borderlands (higher K/Al and Mg/Al ratios). Cyclicity is not that well expressed at this location because turbidites or other short-term resedimentation processes occur. Site 967 (Eratosthenes Seamount) sediments are strongly influenced by discharge from the Nile River during humid periods (low K/Al and Mg/Al ratios).

At Site 967 sapropels are occurring only during periods of enhanced Nile discharge and the corresponding lower Si/Al, Ti/Al, Mg/Al, K/Al, and Zr/Al ratios. Accumulation rates of carbonate and terrigenous detrital matter were 30% lower during such episodes because of the reduction in eolian input, carbonate production, and/or carbonate dissolution. Ba enrichments, which are not only seen in the sapropels, but also very periodically in every K/Al minimum, document the triggering effect of enhanced bioproductivity on sapropel formation. As calculated from excess Ba concentrations, productivity increased by up to a factor of five during time intervals of intensified Nile runoff. Fluviatile discharge seems to be responsible for an enhanced input of nutrients and suspended matter containing low Mg/Al and K/Al ratios.

Based on organic-carbon concentrations, episodes of sapropel formation did last at least from 1000 to 4000 yr at Site 964 and from 2000 to 6000 yr at Site 967. Periods of enhanced bioproductivity, as defined by Ba enrichments, did last from 8000 to 12,000 yr at Site 967. Episodes of high river discharge and corresponding nutrient input, as well as conditions of sapropel formation, seem to have lasted longer in the eastern part of the Eastern Mediterranean (Site 967) as compared to the Pisano Plateau (Site 964).

INTRODUCTION

Pliocene to Holocene Mediterranean sediments contain numerous dark colored layers, termed sapropels, which are characterized by high total organic carbon (TOC ≥ 2%), S, and Fe content and significant enrichments in various trace elements (Calvert, 1983; Pruysers et al., 1991; Thomson et al., 1995; Nijenhuis et al., Chap. 16, this volume). Different approaches have been made to elucidate the paleoceanographic scenario that led to their formation.

The occurrence of sapropels is of cyclic nature and seems to correspond closely with minima in the precessional index when perihelion occurred in the northern hemisphere summer (Rossignol-Strick, 1983, 1985; Prell and Kutzbach, 1987; Hilgen, 1991). Rossignol-Strick (1983) demonstrated that the temporal distribution of the Eastern Mediterranean sapropels correlates with maximum potential strength of the African monsoon, a function of orbital precession, which would have resulted in maximum discharge from the Nile River. Rohling and Hilgen (1991) postulated that increased precipitation along the northern borderlands of the Eastern Mediterranean, because of increased activity of Mediterranean summer depressions, could have been an additional precession-related factor for reduced salinities at sea surface during sapropel formation. By studying the δ^{18}O signatures of planktonic foraminifers, it could be shown that surface-water salinities must have been lower during times of sapropel for-

mation (Williams and Thunell, 1979; Vergnaud-Grazzini et al., 1986).

Carbonate cycles found in Pliocene to Holocene Mediterranean sediments have been well examined by use of micropaleontological (De Visser et al., 1989; Howell et al., 1990) and magnetostratigraphical (Langereis and Hilgen, 1991; Hilgen, 1991) as well as geochemical (Van der Weijden, 1993; Van Os et al., 1994) methods. The consensus is that carbonate cycles, including intercalated sapropels, correspond closely with minima in the precessional index (e.g. Rossignol-Strick, 1983; Prell and Kutzbach, 1987; Hilgen, 1991; Lourens et al., 1992).

Only a few studies exist that deal with sources and distribution of terrigenous detrital matter in the Mediterranean Sea sediments. Investigations by Venkatarathnam and Ryan (1971) and Dominik and Stoffers (1978) are based on clay mineralogical studies of surface-sediment cores. Foucault and Mélières (1995) analyzed the mineralogy of cyclic sediments from the Narbone Formation in Sicily. They found varying amounts of eolian and fluvially derived minerals, which, according to their interpretation, were controlled by alternation of humid and dry periods on both the northern and southern borderlands of the Western Mediterranean.

In this paper, high-resolution geochemical studies of Pliocene sedimentary sequences from Ocean Drilling Program (ODP) Sites 964 and 967 in the Eastern Mediterranean are presented. This is the first attempt to investigate longer sedimentary sequences from the Eastern Mediterranean that contain several sapropels by high-resolution major- and minor-element geochemistry. The basic idea behind such an approach is that any change in paleoenvironmental or climatic conditions should be reflected in major- and minor-element abundances. In particular, the question will be addressed, if cyclic chemi-

cal changes are not only restricted to sapropel-containing intervals, but are also seen in the homogenous parts of the sedimentary sequences.

MATERIALS AND METHODS

Sampling Location and Biostratigraphy

ODP Site 964 (Fig. 1) is located in 3670-m water depth in the Ionian Basin at the foot of the Calabrian Ridge on a small bathymetric high, the Pisano Plateau. Site 967 is located south of Cyprus on the lower northern slope of Eratosthenes Seamount in 2560-m water depth.

Samples were taken from Cores 160-964C-9H and 160-967B-9H at a resolution of 3–4 cm (distance between the tops of the sampling intervals), with each sample including 2 or 1 cm of sediment, respectively. The Hole 964C core was sampled over its full length (270 samples in total). From Hole 967B, 160 samples were taken from the upper 6.4 m (Sections 1–5).

According to ODP Leg 160 shipboard biostratigraphic studies both cores are of Pliocene age and ~2.6–2.8 Ma (Emeis, Robertson, Richter, et al., 1996; see also for further information about stratigraphy and lithology).

Sample Preparation and Analytical Methods

Before analysis, the samples were freeze dried and then ground and homogenized in an agate ball mill. For X-ray fluorescence analysis (XRF), 600 mg of the sample powder were mixed with 3600 mg lithium tetraborate ($Li_2B_4O_7$, Spektromelt), preoxidized at 500°C with NH_4NO_3, and fused to glass beads. The beads were analyzed by a Philips PW 2400 X-ray spectrometer. Analytical precision, as checked by parallel analysis of one international (GSR-6) and several in-house standards, was better than 1% for major (except for Na, 2%) and better than 3% for the minor elements.

TOC content of sapropel samples were determined by coulometric titration following combustion with a Ströhlein instrument after removal of the carbonates with hydrochloric acid (analytical precision was better than 4% for sapropels and better than 8% for samples with TOC <2%).

RESULTS AND DISCUSSION

Bulk Chemistry

The sediments from both sites investigated may be regarded as marls or calcareous marls with mean $CaCO_3$ content (calculated from CaO) of 62% for Site 964 and 51% for Site 967 (Table 1). In a ternary plot (Fig. 2), which shows the relative proportions of SiO_2 (representing quartz or opaline silica), Al_2O_3 (representing clay minerals), and CaO (representing carbonate), the sediments can be described as mixtures of biogenous carbonate with an aluminosilicate component that is similar in composition to "average shale" (Wedepohl, 1971). Sediments from Site 967 (Eratosthenes Seamount) display slightly higher Al_2O_3 contents than those from Site 964 (Ionian Basin), which may indicate a slightly different clay mineralogy. Some specific intervals from Site 964, which are described as "normally graded sections" (Emeis, Robertson, Richter, et al., 1996), show higher SiO_2 content. One of these "events" covers the upper 52 cm of the core, and a second one is located in the center of the core. These and some other thin layers show huge differences in their chemical composition in comparison to the surrounding sediments. The two large "events" have to be regarded as turbidites. Similar sedimentary features have already been described in earlier studies for this area of the Ionian Sea (Kastens and Cita, 1981; Blechschmidt et al., 1982). Thin intervals
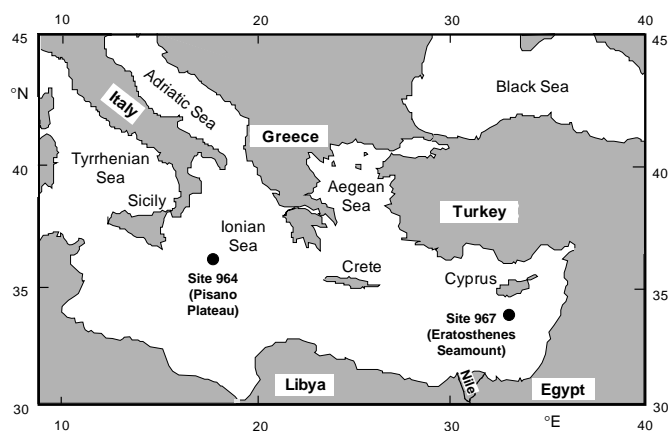

Figure 1. Locations of ODP Sites 964 (Pisano Plateau) and 967 (Eratosthenes Seamount).

rich in Si (quartz) may be caused by particle size fractionation caused by bottom-current–induced resuspension processes (winnowing).

In this contribution, the chemical composition of the sediments is discussed on the basis of element/Al ratios (Table 1). Element/Al ratios are used to compensate for carbonate dilution. Significant differences in the lithogenic sediment fraction of the two sites are evident: Ti/Al ratios are higher at Eratosthenes Seamount, whereas Si/Al, Mg/Al, and K/Al ratios are higher in the Ionian Basin. Intervals that are referred to as sapropels (Emeis, Robertson, Richter, et al., 1996) are characterized by their typical enrichment in Fe and specific trace elements, such as Ba, Co, Cr, Ni, V, and Zn (Calvert, 1983; Sutherland et al., 1984; Thomson et al., 1995; Nijenhuis et al., Chap. 16, this volume). Maximum values for those elements and higher enrichments relative to average shale (Table 1) are attained in or around sapropel layers. The core from the Ionian Basin (Site 964) contains five individual sapropels with TOC content ranging between 2.2% and 9.7%. The investigated interval of Core 160-967B-9H (Eratosthenes Seamount) comprises eight sapropels with TOC values between 1.8% and 6.7%.

Cycles and Events

The most obvious feature discernible in sediments from Site 964 (Fig. 3) are the turbidites. The one in the center of the core (78–76.5 mbsf) consists of an ~50-cm-thick basal layer and an overlying ~2-m-thick homogenous interval. The basal part is characterized by a higher content of elements that are enriched in minerals of the silt or sand fraction and in heavy minerals, e.g. Si, Ti, Mg, Ca, Ba, and Zr. The upper homogenous part of the turbidite displays a high content of Al (clay fraction). The chemical composition of these sedimentary "events" can easily be explained by a particle sorting effect. Cr and V are not enriched in either the upper or the lower parts of the turbidite. Therefore, these elements must be evenly distributed over the different particle-size fractions. The basal layer of a second turbidite, which shows the same chemical characteristics as mentioned above, is present at the top of the core (72 mbsf).

In the lower part of Core 160-964C-9H variations in Si/Al, Ti/Al, Mg/Al, Ca/Al, Cr/Al, and Zr/Al ratios display a distinct cyclicity (Figs. 3, 4). The Ti/Al and Zr/Al profiles are mirror images of Mg/Al, Ca/Al, and Cr/Al. In the upper part of the core this cyclicity is less evident, as it seems to be disrupted by short-term changes in sedimentation. Ca/Al ratios as well as $CaCO_3$ content (calculated from CaO values) show a large variability. In contrast to the relatively smooth, cyclic changes in $CaCO_3$ contents, as displayed between 78.1 and 79.5 mbsf (Fig. 3), the $CaCO_3$ content decreases drastically by as

Table 1. Element abundance and element/Al ratio of Core 160-964C-9H (turbidites excluded) and Core 160-967B-9H, Sections 1–5.

Elemental abundance	Site 964 (Ionian Basin)			Site 967 (Eratosthenes Seamount)			Average shale
	Average	Minimum	Maximum	Average	Minimum	Maximum	
SiO_2 (%)	19.09	10.03	41.99	22.92	14.72	31.40	58.00
TiO_2 (%)	0.325	0.172	0.647	0.515	0.309	0.736	0.780
Al_2O_3 (%)	6.11	2.77	12.78	8.53	5.74	11.00	16.80
Fe_2O_3 (%)	2.81	0.97	12.59	4.27	2.86	12.90	6.90
MgO (%)	1.97	1.17	5.56	1.74	1.23	2.33	2.60
CaO (%)	34.61	8.27	44.22	28.72	16.96	36.89	2.30
K_2O (%)	1.24	0.70	2.66	1.18	0.74	1.59	3.40
Ba (µg/g)	179	55	2519	270	80	1060	650
Cr (µg/g)	58	21	281	59	39	103	90
Ni (µg/g)	55	2	649	63	25	394	68
V (µg/g)	74	22	841	105	51	568	130
Zn (µg/g)	38	14	179	52	34	99	95
Zr (µg/g)	73	33	227	95	46	152	200
$CaCO_3$ (%)*	61.8	14.7	78.9	51.3	30.3	65.8	4.1
Element/Al ratio							
Si/Al	2.75	2.46	5.83	2.38	2.10	2.69	3.00
Ti/Al	0.060	0.051	0.115	0.068	0.056	0.084	0.053
Fe/Al	0.60	0.41	2.29	0.67	0.52	2.63	0.54
Mg/Al	0.37	0.27	0.75	0.24	0.17	0.33	0.18
Ca/Al	8.55	1.07	19.17	4.66	2.63	8.25	0.18
K/Al	0.32	0.30	0.41	0.22	0.17	0.26	0.32
Ba/Al × 10⁻⁴	54	26	917	61	19	297	73
Cr/Al × 10⁻⁴	17	10	47	13	10	23	10
Ni/Al × 10⁻⁴	15	1	117	14	5	130	8
V/Al × 10⁻⁴	22	14	152	24	12	148	15
Zn/Al × 10⁻⁴	11	7	34	12	8	24	11
Zr/Al × 10⁻⁴	23	13	155	21	14	29	22
Sapropels: TOC (%)		2.2	9.7		1.8	6.7	0.2

Notes: * = calculated from CaO values. Average shale data set from Wedepohl (1971, 1991).
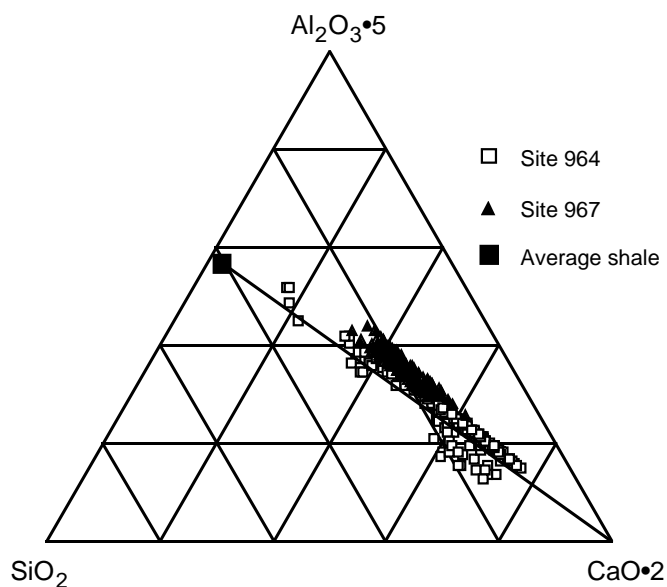

Figure 2. Ternary plot of SiO_2 (representing quartz or opaline silica), Al_2O_3 (representing clay minerals), and CaO (representing carbonate). Average shale data point from Wedepohl (1971, 1991).

much as 40% in the sapropels, which can be explained by dissolution of carbonate. The sapropel at 80.6–80.7 mbsf (Fig. 4) also shows a decrease in the Mg/Al ratio. By leaching two samples of this site with water and 1 mol/L acetic acid, respectively, and analyzing the residues by XRF, we were able to see that Mg is partly present as sea salt and partly bound to carbonate phases, which might dissolve during sapropel formation. However, most of the Mg was still present in the residue after treatment with acetic acid, and a correlation between Mg and Ca is not observed. Therefore, the major fraction of the Mg seems

to be fixed in the detrital clay mineral component of terrigenous origin.

Aside from the carbonate cycles, which are presumably resulting from orbital forcing (Hilgen, 1991), rhythmic variations in detrital-matter composition of the sediments should also have been caused by Milankovich-type cycles, because they all seem to have the same frequency pattern. This can be seen in the Si/Al, Ti/Al, Mg/Al, Ca/Al, Cr/Al, and Zr/Al ratios (Figs. 3, 4). Cyclicity in elemental ratios is often disturbed by other sedimentary features such as those found in the upper part of Core 160-964C-9H. These features are, for example, indicated by "spikes" in the Si/Al, Ti/Al, Mg/Al, and Zr/Al ratios (Fig. 3).

In Core 160-967B-9H from the Eratosthenes Seamount, cyclicity is displayed by all elements of a typical lithogenic origin. Depth profiles of Si/Al, Ti/Al, Mg/Al, K/Al, and Zr/Al ratios all show very similar shapes (Fig. 5). Ca/Al shows a similar pattern as the other elements with the exception of an interval without sapropels (76.8–74.5 mbsf). This implies that the cyclicity of all element/Al ratios is likely caused by earth precessional cycles (see above).

Every minimum in element/Al ratio is marked by an enrichment in Ba/Al. All sapropel layers are enriched in Ba, but not all Ba-enriched layers are typical sapropels. Four Ba spikes are discernible in the sapropel-free interval (76.8–74.5 mbsf) that, as far as we can notice by our sampling resolution, do not show significant trace metal enrichments like observed in oxidized ("burned-down") sapropels as described by Thomson et al. (1995). Only very slight enrichments in trace metals and Fe are apparent in the profiles (Fig.5).

From the chemical profiles (Fig. 5), it seems evident that Ba-enriched intervals, like those typically encountered in sapropels, were deposited during periods when lithogenic matter with lower Si/Al, Ti/Al, Mg/Al, K/Al, and Zr/Al ratios was introduced into the Eastern Mediterranean.

At the Eratosthenes Seamount location (Site 967), cyclic sedimentary changes are more distinctive, and sapropel formation did take place more regularly than in the Ionian Basin (Site 964). Additionally, sapropels and Ba-enriched layers are more substantial than
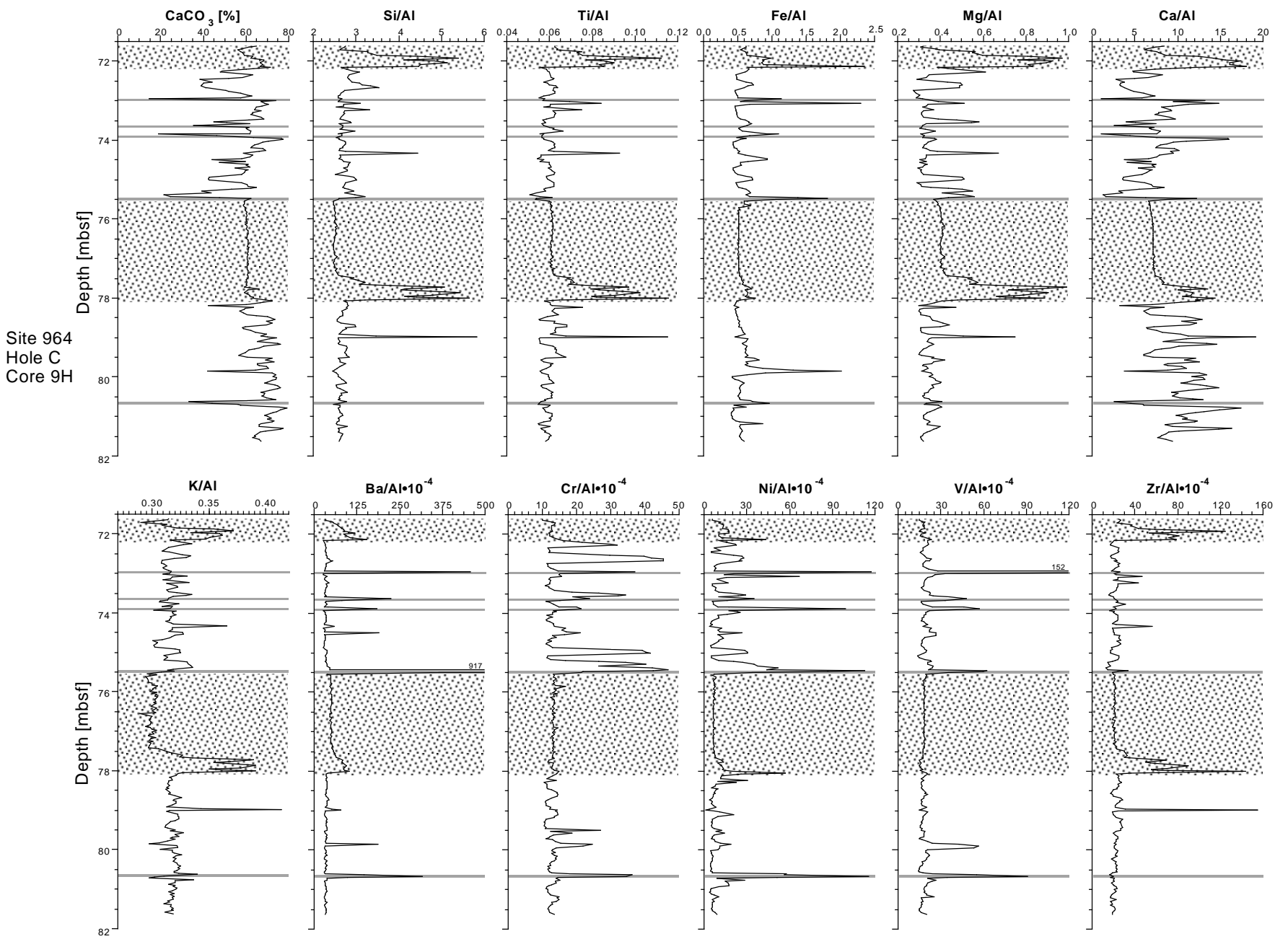
Figure 3. Carbonate content and element/Al ratio of ODP Core 160-964C-9H (Pisano Plateau, Ionian Basin). Gray bars = sapropels; hatched areas = turbidites.
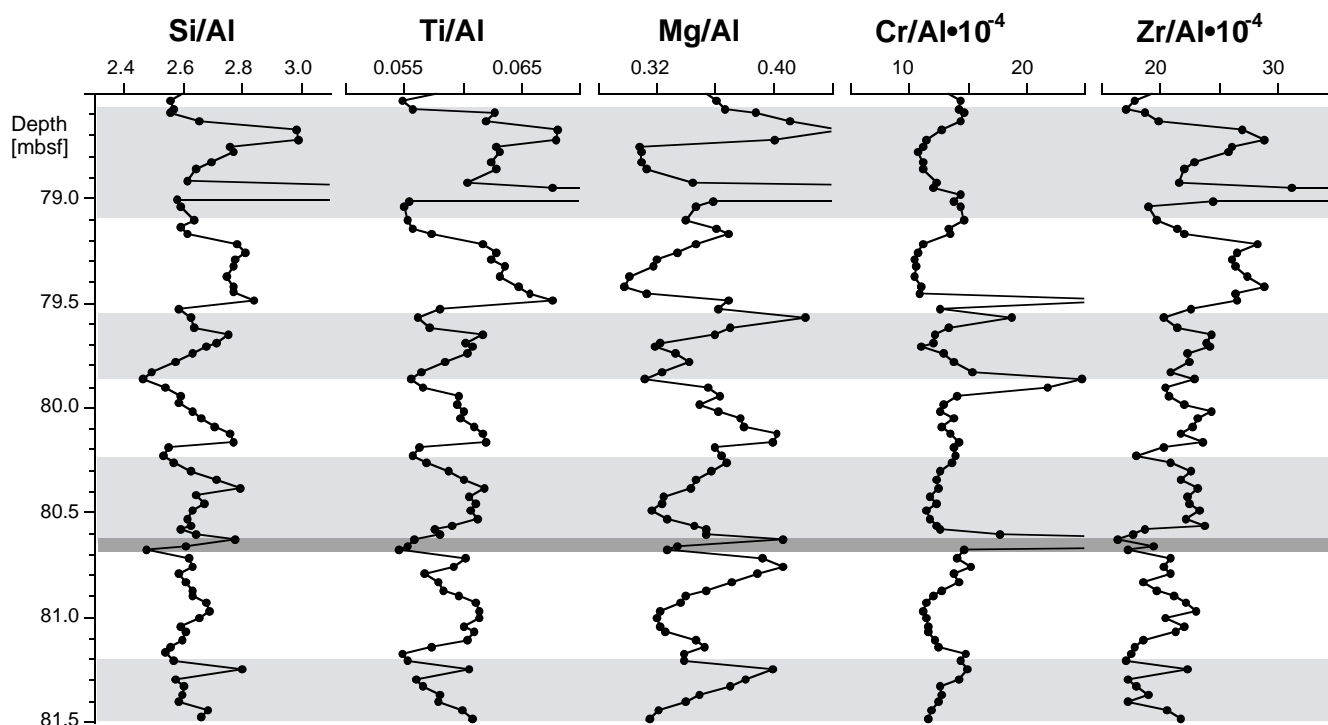
Figure 4. Depth profiles of element/Al ratios of Core 160-964C-9H, Sections 5 through CC. Dark gray bar = sapropel; light gray/white bars = precession cycles.

those encountered at Site 964. For Site 964 sapropels, it cannot be ruled out whether they occur exactly within certain minima or maxima of detrital element/Al ratios. At Site 967 (Fig. 5), carbonate concentrations do not show the extreme variations as observed at Site 964.

Paleoproductivity

Ba has for a long time been under discussion as an indicator element for paleoproductivity (Goldberg and Arrhenius, 1958; Dehairs et al., 1980; Schmitz, 1987; Lea and Boyle, 1990; Dymond et al., 1992). Eastern Mediterranean sapropels always show enrichments in Ba (Calvert, 1983; Sutherland et al., 1984; Higgs et al., 1994; Thomson et al., 1995). Van Os et al. (1991) stated that sedimentary barite might undergo diagenetic changes and should, therefore, be used carefully as a paleoproductivity indicator. However, Ba mobilization will only be possible under conditions of severe sulfate depletion (Brumsack and Gieskes, 1983; Brumsack, 1986; Brumsack et al., 1992). Although they could demonstrate that sediments had undergone diagenetic changes, Thomson et al. (1995) found approximately Gaussian-shaped Ba profiles in sediments in and around the most recent sapropel, S1. Our sampling resolution is not high enough to see a Gaussian-shaped Ba distribution, but the Ba peaks seem to be symmetrical (Fig. 5). Therefore, we suggest that Ba is indeed useful as a paleoproductivity indicator and that productivity increases are evident at Site 967 during those time periods when detrital matter exhibit lows in element/Al-ratios, even when sapropels were not deposited (Fig. 5). In such intervals, enrichments in Fe and trace elements are only very minor, and it is questionable whether there have formerly been real sapropels (TOC ≥ 2%) or sapropelic layers (TOC between 0.5% and 2%) that were "burned down" by an oxidation front. At Site 964 we have detected several intervals with enhanced Ba/Al ratios (see Fig.3; ~74.5 mbsf and ~79.8 mbsf), but low organic-carbon content. Since the elements Fe, Cr, Ni, and V are clearly enriched within or above these layers, this might indicate the former occurrence of sapropels, which now have been completely oxidized.

Ba content may be used to estimate paleoproductivity according to an algorithm given by Dymond et al. (1992). For performing such a calculation, the fraction of nonlithogenic Ba (Ba_{bio}) in the sediments has to be known. This fraction is easily obtained when Ba and Al concentrations are known. The biogenic Ba fraction is calculated according to

$$Ba_{bio} = Ba_{total} - [Al \times (Ba/Al)_{detrit.}],$$

where $(Ba/Al)_{detrit.}$ represents the Ba/Al ratio of the detrital fraction. For the Eastern Mediterranean Pliocene sediments from Site 967 a minimum Ba/Al ratio of 0.0019 has been analyzed for the homogenous, nonsapropel sections, which is identical to the value given by Van Os et al. (1994). The accumulation rate of biologically mediated Ba ($Ba_{bio-acc.}$) can be obtained from

$$Ba_{bio-acc.} = Ba_{bio}[ppm] \times MAR/10^6,$$

where MAR is the mass accumulation rate. The biogenic Ba flux to the seafloor is computed using the following equation of Dymond et al. (1992):

$$Ba_{bio}flux = Ba_{bio-acc.}/(0.209 \times log\ MAR - 0.213).$$

Finally, the new (or export) production (P_{new}), as defined by Sarnthein et al. (1988), is calculated according to

$$P_{new} = \{[(Ba_{bio}\ flux \times 0.171\ Ba_z^{2.218} \times z^{0.476-0.00478 \times Ba})/2056]^{1.504}\},$$

where Ba_z is the concentration of dissolved barium in the water depth z. For z, a value of 1700 m is recommended (Dymond et al., 1992), and a value of 11 µg/L dissolved Ba has been taken from Bernat et al. (1972). The new production (P_{new}) derived from this equation for the sapropels of Site 967 amounts to values from 26 to 62
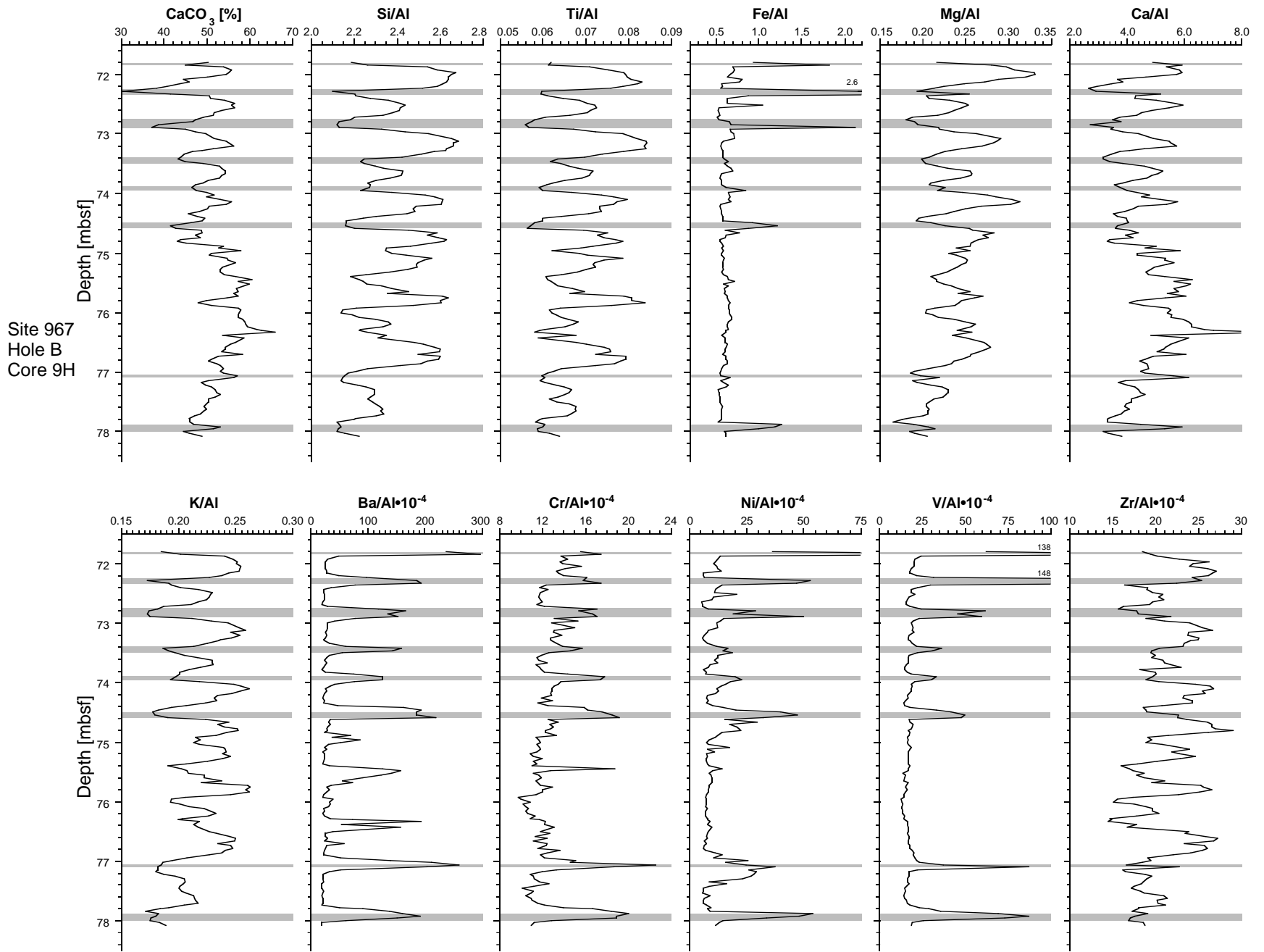
Figure 5. Carbonate content and element/Al ratio of ODP Core 160-967B-9H, Sections 1 through 5 (Eratosthenes Seamount). Gray bars = sapropels.

$gC/m^2 \cdot yr$, and for the nonsapropelic, but Ba-enriched layers, to values ranging from 2 to 29 $gC/m^2 \cdot yr$. Compared with data given by Béthoux (1989; P_{new} = 12 $gC/m^2 \cdot yr$) or Krom et al. (1992; P_{new} = 16.7 $gC/m^2 \cdot yr$) for the modern Eastern Mediterranean, the export production during times of sapropel formation amounts to five times the present value. Time intervals of increased productivity without corresponding sapropel formation are characterized by a new production of up to two or three times the modern values. Unrealistically small values of 2 $gC/m^2 \cdot yr$ or less, calculated for the intervals between the Ba spikes, show that the productivity determination using the Dymond et al. (1992) algorithm is not very accurate in our case. Dymond et al. (1992) established and tested their equations on samples from the western Atlantic, equatorial Pacific, and California current.

Howell and Thunell (1992) found, based on organic-carbon accumulation rates, a 10-fold increase in primary productivity for time of sapropel formation. Our calculated productivity values are at least suitable to recognize differences between individual productivity events within one site. New production did not reach such high values during productivity events without the presence of sapropels compared to those intervals where sapropels are present. Furthermore, it must be noted that K/Al ratios on average do not show such extreme minima in the nonsapropelic productivity events as they do in the sapropelic ones (Fig. 5).

Origin and Transport Paths of Detrital Matter

Sediments of the Eratosthenes Seamount are deposited relatively close to the Nile Cone. Therefore, a strong influence of Nile-derived suspended matter can be expected for this location. According to Venkatarathnam and Ryan (1971), Nile suspended matter, which is characterized by high smectite contents, presently is dispersed mainly in the eastern Levantine Basin. It is transported by the easterly directed surface-water currents that form part of a counter-clockwise gyre, whereas the deep parts of the Ionian Basin are fed by deep water and particularly bottom currents from the Aegean and Adriatic Seas, which contain high illite and chlorite contents. These hypotheses are supported by other authors. Dominik and Stoffers (1978), for example, identified high abundances of illite and chlorite in the clay fraction of the Ionian Basin sediments. Adjacent to the Nile Cone, the samples are dominated by smectite. Illite and kaolinite have a minor role with each contributing about 10% of the clay fraction.

Aside from fluvial sources (e.g., the Nile, rivers entering the Black Sea, the Po, and other rivers of the northern borderlands), there exists an important eolian contribution to the detrital matter that is deposited in the Eastern Mediterranean (Ganor and Mamane, 1982).

The high K/Al and Mg/Al ratios we observed in the Ionian Basin sediments correspond well with the regionally higher input of illite (K-rich) and chlorite (Mg-rich) by fluvial (Dominik and Stoffers, 1978) or eolian (Tomadin et al., 1984) sources. Levantine Sea sediments, like those from Site 967, are influenced by the Nile River, and therefore contain higher abundances of clay minerals that have lower K/Al and Mg/Al ratios, like smectite and kaolinite (Venkatarathnam and Ryan, 1971).

During times of sapropel deposition at the Eratosthenes Seamount, K/Al and Mg/Al ratios were lower (Fig. 5). This could have been caused by an intensification of Nile suspended-matter delivery (Rossignol-Strick, 1983, 1985), a decreasing influence of fluvial or eolian detrital-matter contribution from the northern borderlands, or restricted easterly directed currents, which may carry more illite-rich clay minerals from the west. A plot of Mg/Al vs. K/Al (Site 964 turbidites are excluded) shows a correlation for each of the two sample sets (Fig. 6). This correlation implies that Mg/Al and K/Al ratios are controlled at both sites by two end members. For Site 967, one end member is represented by a data point for Nile suspended matter as described by Martin and Meybeck (1979), whereas the other end

member is possibly an eolian component represented by Saharan dust (Rachold, 1991) or Damascus dust (Cornille et al., 1990). For Site 964, a similar eolian component may be important as one end member, and a component with higher Mg/Al and slightly higher K/Al ratios, probably fluvial material from the northern borderlands with higher chlorite contents, is the second end member.

The elements Si (representing quartz) and Zr (representing the heavy mineral zircon) are enriched in desert sands, because their host minerals are extremely resistant against weathering (Wedepohl, 1967; Matthes, 1993). Quartz has been investigated in eolian dust from southern provenances by several authors (Chester et al., 1977; Ganor and Mamane, 1982; Tomadin et al., 1984). The Element Zr is enriched in loess, an eolian deposit (Schnetger, 1992), and Saharan dust (Rachold, 1991). The fact that Site 967 sapropels generally exhibit lower Zr/Al and Si/Al ratios further supports the assumption that the sediments have received lower proportions of eolian dust during time intervals when sapropels were formed. Rhythmic fluctuations in Si/Al and Zr/Al, which are possibly caused by variations in the eolian contribution to sedimentation, have also been found in sediments from Site 964 (Fig. 4).

Further evidence for higher Nile discharge and lower eolian input during times of sapropel formation is given by Sr-isotope investigations. Nonsapropel samples from the Eastern Mediterranean and Saharan dust samples have higher $^{87}Sr/^{86}Sr$ ratios than sapropels and Nile sediments, because Nile suspended matter largely originates from the erosion of relatively young Ethiopian volcanics with low $^{87}Sr/^{86}Sr$ ratios (Michard et al., 1995; Ströhle et al., 1996). Saharan dust particles, by contrast, are formed by erosion of old Archaean strata with more radiogenic $^{87}Sr/^{86}Sr$ ratios. First $^{87}Sr/^{86}Sr$ measurements on the noncarbonate fraction of our samples from Site 967 reveal values of 0.7086 and 0.7094 for K/Al minima (humid periods) in contrast to 0.7092 and 0.7103 for K/Al maxima (arid periods), which correspond with the findings of others (Michard et al., 1995; Ströhle et al., 1996).

Sedimentation and Accumulation Rates

At Site 964 the Cr/Al ratio profile displays the most regular cyclicity record and is used to determine the sedimentation rate. Assuming a Milankovitch periodicity of 21 k.y. (Fischer and Bottjer, 1991),
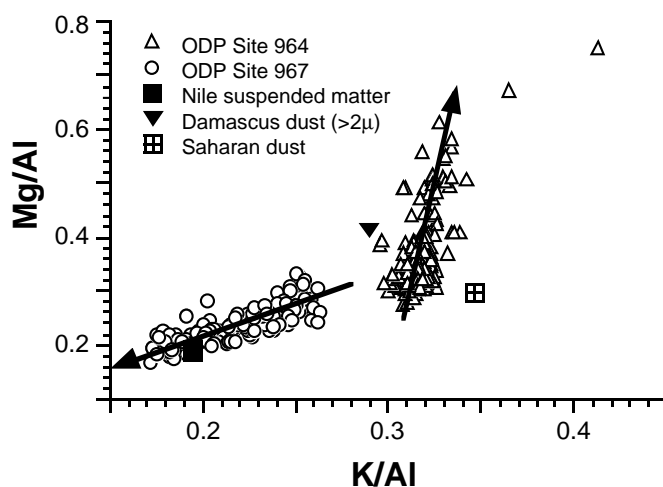

Figure 6. Plot of Mg/Al vs. K/Al ratios. Arrows indicate changes in sediment composition during times of sapropel formation. Turbidites are excluded from the Site 964 data set. Damascus dust data from Cornille et al. (1990); Saharan dust data from Rachold (1991).
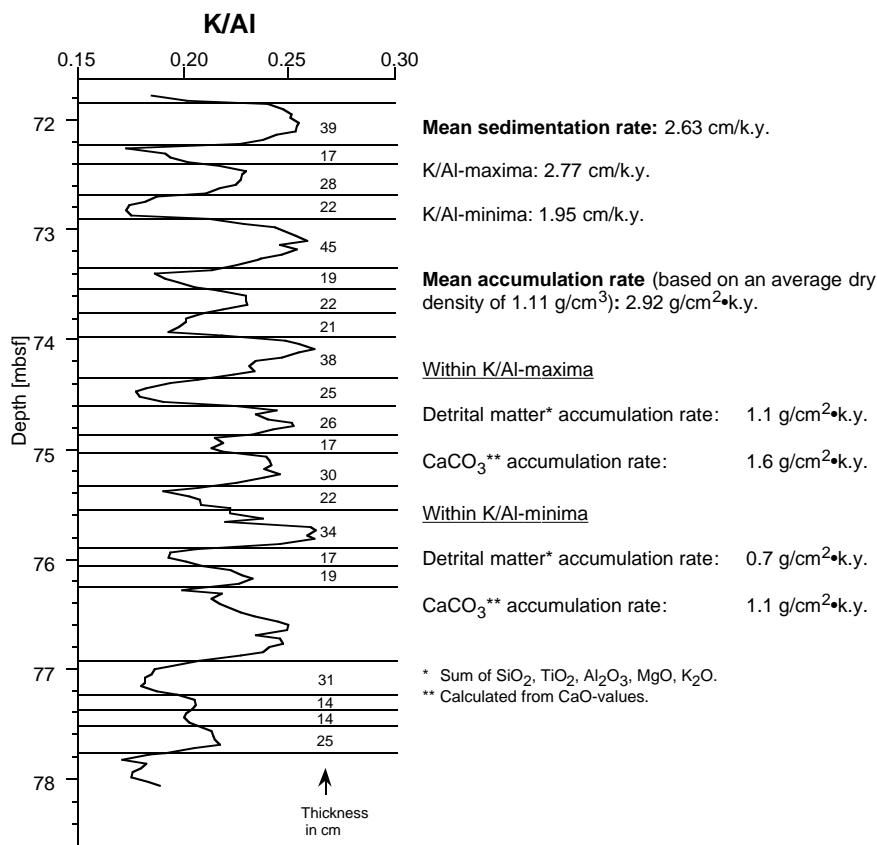
Figure 7. Calculation of sedimentation rates at Core 160-967B-9H. It is assumed that the K/Al curve represents a 21-k.y. precessional cyclicity. The curve is divided into time slices of ~10.5 k.y. (based on the assumption that 21 k.y. = one full precessional cycle). Boundaries between these zones of minima and maxima of the K/Al curve are the points of inflection.

Mean sedimentation rate: 2.63 cm/k.y.

K/Al-maxima: 2.77 cm/k.y.

K/Al-minima: 1.95 cm/k.y.

Mean accumulation rate (based on an average dry density of 1.11 g/cm^3)**:** 2.92 g/cm^2•k.y.

<u>Within K/Al-maxima</u>

Detrital matter* accumulation rate: 1.1 g/cm^2•k.y.

$CaCO_3$** accumulation rate: 1.6 g/cm^2•k.y.

<u>Within K/Al-minima</u>

Detrital matter* accumulation rate: 0.7 g/cm^2•k.y.

$CaCO_3$** accumulation rate: 1.1 g/cm^2•k.y.

* Sum of SiO_2, TiO_2, Al_2O_3, MgO, K_2O.
** Calculated from CaO-values.

the resulting sedimentation rate equals 2.38 cm/k.y. This value seems to be low in comparison to ODP Leg 160 shipboard biostratigraphical studies (Emeis et al., 1996), where a higher value of 2.7 cm/k.y. was determined. This high value is possibly caused by enhanced sediment accumulation because of turbidite deposition, which is not considered in our cyclochemostratigraphic approach.

In sediments from Site 967, Si/Al, Ti/Al, Mg/Al, K/Al, and Zr/Al do not display regular sinusoidal curves. The profiles look compressed in the sapropel intervals. One reason for this could be a decrease in the supply of carbonate during sapropel deposition or carbonate dissolution, which would lead to lower sedimentation rates. But, it should be noted that intervals without sapropels do also show an asymmetric pattern (Fig. 5).

With our data set we are able to give an estimate of the total amount of carbonate and terrigenous detrital matter accumulation per time interval. The sedimentary cycles, which are best seen in the K/Al record, are divided into minima and maxima. Boundaries between highs and lows are the points of inflection of the K/Al curve (Fig. 7). From the part of the core investigated, the average mass accumulation rate (MAR) is calculated. The mean sedimentation rate, based on a 21 k.y. periodicity of the cycles (Fischer and Bottjer, 1991), is 2.63 cm/k.y. For the K/Al maxima and minima, mean sedimentation rates of 2.77 cm/k.y. and 1.95 cm/k.y., respectively, were calculated (Fig. 7). Considering dry bulk densities from ODP Leg 160 shipboard measurements (Emeis, Robertson, Richter, et al., 1996), a mean MAR of 2.92 g/cm^2·k.y. is obtained. Furthermore, the accumulation rates of detrital matter and carbonate may be calculated for K/Al minima and maxima respectively (Fig. 7). The overall result of the calculations is that the accumulation of terrigenous detrital matter and carbonate was reduced by 30% during intervals with low K/Al ratios (i.e., during times of sapropel formation).

Mangini and Dominik (1979) determined the sedimentation rates of Eastern Mediterranean sediments by [230]Th budget calculations. According to their measurements, sedimentation rates in the

sapropels were lower than in the surrounding sediments. Dominik and Stoffers (1978) found a different clay-mineral assemblage in the sapropels as compared to adjacent intervals. We assume that the sedimentation rate decreased because of a lower carbonate productivity and partial dissolution of carbonate, and additionally, by simultaneous and rapid changes in supply of terrigenous detrital matter. According to Van Os et al. (1994), Pliocene and Pleistocene carbonate cycles are caused by variations in productivity. Carbonate production collapsed during high-productivity episodes because of a faster growth of more opportunistic organisms, which probably were more tolerant against rapidly changing oceanographic conditions. Van Os et al. (1994) showed by calculations that the decrease in carbonate could not be explained by dissolution or dilution alone.

One might expect a higher accumulation rate of terrigenous detrital matter at Site 967 during time intervals of high Nile discharge. As shown, this is not the case and even a reduction by 30% during these time periods did occur. Therefore, we propose that the input of eolian matter must have decreased dramatically during times of enhanced Nile discharge. Ganor and Mamane (1982) estimated that 20–40 million tons of dust annually reach the Eastern Mediterranean. Dispersed over an area of ~1 million km^2 this would result in an accumulation rate of 20 to 40 g/m^2·yr, which is of the same order of magnitude as the calculated MAR (2.92 g/cm^2·k.y. = 29.2 g/m^2·yr), and therefore, possibly a gross overestimation. Loÿe-Pilot et al. (1986) computed a mass accumulation of 14 g/m^2·yr of Saharan dust in the northwestern Mediterranean. Such enormous amounts of dust, which are presumably transported into the Mediterranean at present, must have a drastic influence on variations of sediment accumulation rates, particularly during more humid climates.

Duration of Sapropel Events

It is not easy to give an accurate estimate for the duration of a sapropel event, because reliable criteria for the onset and end of such

events have to be established. A sapropel layer is defined by sedimentological parameters, like color, thickness, and TOC content (Kidd et al., 1978). It is difficult to determine how far diagenetic processes, such as oxidation of organic matter, might have reduced the thickness of the original sapropel. Fe/Al and Ni/Al ratios of Site 967 samples give an idea about diagenetic influences. Below sapropel layers, the Fe- and Ni-contents are elevated, which, according to Passier et al. (1996), is caused by downward migration of HS$^-$ and precipitation of sulfides. Upward-migration effects, similar to the ones described by Pruysers et al. (1991) or Thomson et al. (1995), can be seen in the Fe/Al or Ni/Al profile of Site 964 (Fig. 3). Based on the thickness of the dark-colored intervals and the sedimentation rates calculated above, values of 1000–4000 yr (Site 964) or 2000–6000 yr (Site 967) are obtained for the duration of a sapropel event.

If Ba serves as a reliable productivity indicator and if horizons with increased amounts of bio-barite have not been altered too much by diagenesis, we can use the thickness of the Ba spikes to evaluate the duration of periods with enhanced productivity, if sedimentation rates are known. At Site 964 the duration of these productivity events varies between 1000 and 4000 yr. For Site 967, values of 8000–12,000 yr are obtained; here the Ba peaks are wider than the sapropel layers. It must be noted that Ba peaks seem to indicate periods of enhanced productivity, but they do not inevitably indicate the original thickness of a sapropel.

Scenario of Sapropel Formation

We suggest that the flux of eolian dust simultaneously decreased when Nile discharge and fluvial input from the northern borderlands increased periodically (Fig. 6). When perihelion occurs during the northern hemisphere summer, monsoonal influence on equatorial Africa becomes more intense (Prell and Kutzbach, 1987). Large parts of the Sahara and important draining areas of the Nile (e.g., the Ethiopian highlands) may be under the influence of tropical monsoon rains when the trade-wind zone is shifting northwards, which is the case when sun insolation in the northern hemisphere reaches maximum value (Fairbridge, 1964). Evidence for increased humidity in the Sahara is, for example, given by the occurrence of fossil groundwaters (Sonntag et al., 1980), variations in Saharan vegetation (Lauer and Frankenberg, 1980), and the presence of Pleistocene lakes (Petit-Maire et al., 1980). Furthermore, eolian sedimentation of Saharan dust in the Atlantic has also varied periodically (Sarnthein and Koopmann, 1980; Tiedemann et al., 1989). Sediments with the lowest content of Saharan dust coincide with minima in the precessional index.

Monsoon-related increases in Nile discharge, as described by Rossignol-Strick (1983), are documented by sea-level stands in northeast Africa (Rognon and Williams, 1977; Street and Grove, 1979), as well as flood-plain deposits of the Nile (Adamson et al., 1980). Investigations by Rossignol-Strick (1987), Wijmstra et al. (1990), and Rohling and Hilgen (1991) support the idea that the northern borderlands of the Mediterranean went through periods of increased humidity when perihelion occurred in the northern hemisphere summer, and enhanced Mediterranean summer depressions provided higher precipitation rates. Additionally, Jenkins and Williams (1983/84) calculated that Nile discharge alone cannot be high enough to explain the surface-water freshening found by $\delta^{18}O$ measurements of planktonic foraminifers.

According to our results, sapropel formation seems to depend predominantly on the strength of fluviatile input or, generally speaking, on humidity in the circum-Mediterranean. This would provide the necessary nutrients for the observed productivity increase, and lead to a lower ratio of evaporation vs. runoff, plus precipitation. As we have already shown, Site 967 sapropels were formed at times of high discharge of the Nile River, as seen in the specific terrigenous detrital-matter contributions. When runoff (humidity) and productivity signals (K/Al and Ba/Al) were too weak, sapropels did not form or were easily oxidized during early diagenesis.

At Site 964, sapropel formation does not clearly correspond with changes in detrital matter input. One possible reason might be that sapropel-forming conditions did develop first in the most eastern part of the Eastern Mediterranean in close vicinity to the Nile cone. Subsequently those conditions were established in the deep Ionian basin.

CONCLUSIONS

The chemical composition of the terrigenous detrital component of Pliocene sediments from the Eastern Mediterranean (Sites 964 and 967) exhibits cyclic changes, which are caused by precession-induced climatic variations. Periodicity in major element abundances reflects episodes of either enhanced eolian or fluviatile input.

At Site 964 (Pisano Plateau), terrigenous detrital matter chemistry reflects periods of stronger Saharan dust input alternating with fluvial input from the northern borderlands. Site 967 (Eratosthenes Seamount) sediments are strongly influenced by discharge from the Nile River during humid periods (low K/Al ratio).

At Site 967, sapropels are occurring only during periods of enhanced Nile discharge. Accumulation rates of carbonate and terrigenous detrital matter were 30% lower during such episodes because of the reduction in eolian input and carbonate production and/or dissolution.

Bioproductivity, as calculated from excess Ba concentrations, increased by a factor of up to 5 during time intervals of enhanced freshwater discharge. Not every productivity event is manifested in a sapropel layer.

Based on organic-carbon concentrations, episodes of sapropel formation did at least last from 1000 to 4000 yr at Site 964 and from 2000 to 6000 yr at Site 967. Periods of enhanced bio-productivity, as defined by Ba enrichments, did last from 8000 to 12,000 yr at Site 967.

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