Zahn, R., Comas, M.C., and Klaus, A. (Eds.), 1999
Proceedings of the Ocean Drilling Program, Scientific Results, Vol. 161

29. SOURCES, PRESERVATION, AND THERMAL MATURITY OF ORGANIC MATTER IN PLIOCENE–PLEISTOCENE ORGANIC-CARBON–RICH SEDIMENTS OF THE WESTERN MEDITERRANEAN SEA[1]

Philip A. Meyers[2] and Heidi Doose[3]

ABSTRACT

The occurrence of sapropels and sapropel-like sediments has been documented to the far western basins of the Mediterranean Sea in cores obtained by drilling during Leg 161. Multiple, dark-colored layers in which total organic-carbon (TOC) concentrations exceed 0.5% occur in the Pleistocene sedimentary sequences of the Tyrrhenian Basin, the Menorca Ridge, and the basins of the Alboran Sea. Higher Rock-Eval Hydrogen Index values and elemental C/N values in the sediments that have higher TOC concentrations indicate that variations in the production and preservation of marine organic matter are the principal factors involved in the formation of the sapropels and sapropel-like layers at these locations. TOC concentrations generally decrease from east to west as sedimentation rates increase, reflecting dilution of the organic matter. Precessional climate changes that increased delivery of land-derived nutrients and thereby enhanced paleoproductivity appear to be central to formation of the sapropels and sapropel-like layers.

INTRODUCTION

Multiple layers of dark-colored sediments rich in organic carbon have been recognized as common features of the post-Messinian sedimentary record of the Mediterranean Sea in both uplifted exposures on land and in deep-water settings (e.g., Cita and Grignani, 1982; Thunell et al., 1984; Rossignol-Strick, 1985; Fontugne and Calvert, 1992). These sequences, called rhythmites, laminites, or sapropels depending on their settings, are noteworthy because the expected fate of most organic matter in the oceans is oxidation and destruction, rather than accumulation in the seafloor. These unusual accumulations required special depositional conditions that involved both enhanced delivery of organic matter to the seabottom and improved preservation of the organic matter during and after burial.

The term “sapropel” is strictly applied to unconsolidated oozes or sludges that accumulate in shallow anaerobic environments (Bates and Jackson, 1987), although the term is commonly applied to organic-carbon–rich sedimentary layers that may have resulted from such or similar settings. We will use the “sapropel” in the more general context of a discrete layer of dark-colored, fine-grained, deep-sea sediment in which the organic-carbon concentration exceeds 0.5%. For those dark-colored intervals that are stratigraphically less well defined than sapropel layers, but in which organic-carbon concentrations still exceed 0.5%, we will use the term “sapropel-like sediments.” In this overview of the organic matter contents of sapropels and sapropel-like sediments at locations cored during Leg 161, we also consider the significance of these organic-carbon–rich deposits to paleoceanographic and paleoclimatic reconstructions of the Mediterranean Sea and its surrounding land areas.

SAMPLING AND ANALYSIS

Depositional Settings

Samples of Pliocene–Pleistocene sediments were collected for organic-matter analysis at frequencies of two to five per 9-m core at each of the six sites investigated during Leg 161 (Fig. 1). The amount and type of organic matter were determined both in the organic-carbon-lean sediments that constituted most of the sequences found at these sites and in the dark-colored, organic-carbon–rich sapropels and sapropel-like layers that were minor parts of the sequences. The six sites encompass a variety of water depths and sedimentation rates, and they represent the major depositional basins of the western Mediterranean Sea.

Site 974 is located at a water depth of 3454 m in the central Tyrrhenian Basin (Fig. 1). Pliocene–Pleistocene sediments consist of bioturbated pelagic to hemipelagic nannofossil-rich clays and nannofossil oozes that were deposited above the carbonate compensation depth (CCD). Twenty-eight sapropel layers occur in this sequence. The average sedimentation rate of Pliocene–Pleistocene sediments at this site is 5 cm/k.y.

Site 975 is situated on the Menorca Rise between the Balearic Basin to the east and the Algerian Basin to the south (Fig. 1). The water depth at this site is 2116 m, which is above the CCD. Pliocene–Pleistocene sediments consist of bioturbated pelagic to hemipelagic nannofossil clays and oozes. Thirty-eight sapropel layers occur in the upper part of this sequence. The average sedimentation rate at this site is 7 cm/k.y.

Site 976 is located on the southern Iberian continental slope at a water depth of 1108 m in the Western Alboran Basin. Pliocene–Pleistocene sediments consist of hemipelagic nannofossil-rich clay, nannofossil clay, and nannofossil silty clay and contain 28 sapropel-like layers. The average sedimentation rate at this site is 23 cm/k.y.

Sites 977 and 978 are in the Eastern Alboran Basin. Site 977 is located south of the Al-Mansour Seamount at a water depth of 1984 m, and Site 978 is north of this seamount at a depth of 1929 m (Fig. 1). Sediments at Site 978 were continuously cored below 213 mbsf (meters below seafloor), but only spot-cored at shallower depths. Pliocene–Pleistocene sediments recovered at both sites consist of bioturbated hemipelagic nannofossil clay and nannofossil-rich silty clay. Thirty-nine sapropel layers occur in the Site 977 Pliocene–Pleistocene sediments, and the sedimentation rate for this sequence is 16 cm/k.y.

Site 979 is situated on the southern margin of the Alboran Ridge in the South Alboran Basin (Fig. 1). The water depth at this site is 1062 m. Pliocene–Pleistocene sediments consist of bioturbated hemipelagic nannofossil clay, which accumulated at an average rate of 21 cm/k.y. Twenty-nine sapropel-like layers occur in the Pliocene–Pleistocene sequence at this site.

---

[1] Zahn, R., Comas, M.C., and Klaus, A. (Eds.), 1999. *Proc. ODP, Sci. Results,* 161: College Station, TX (Ocean Drilling Program).

[2] Marine Geology and Geochemistry Program, Department of Geological Sciences, The University of Michigan, Ann Arbor, MI 48109-1063, U.S.A. pameyers@umich.edu

[3] GEOMAR, Christian-Albrechts Universität zu Kiel, Wischhofstraße 1-3, 24148 Kiel, Federal Republic of Germany.

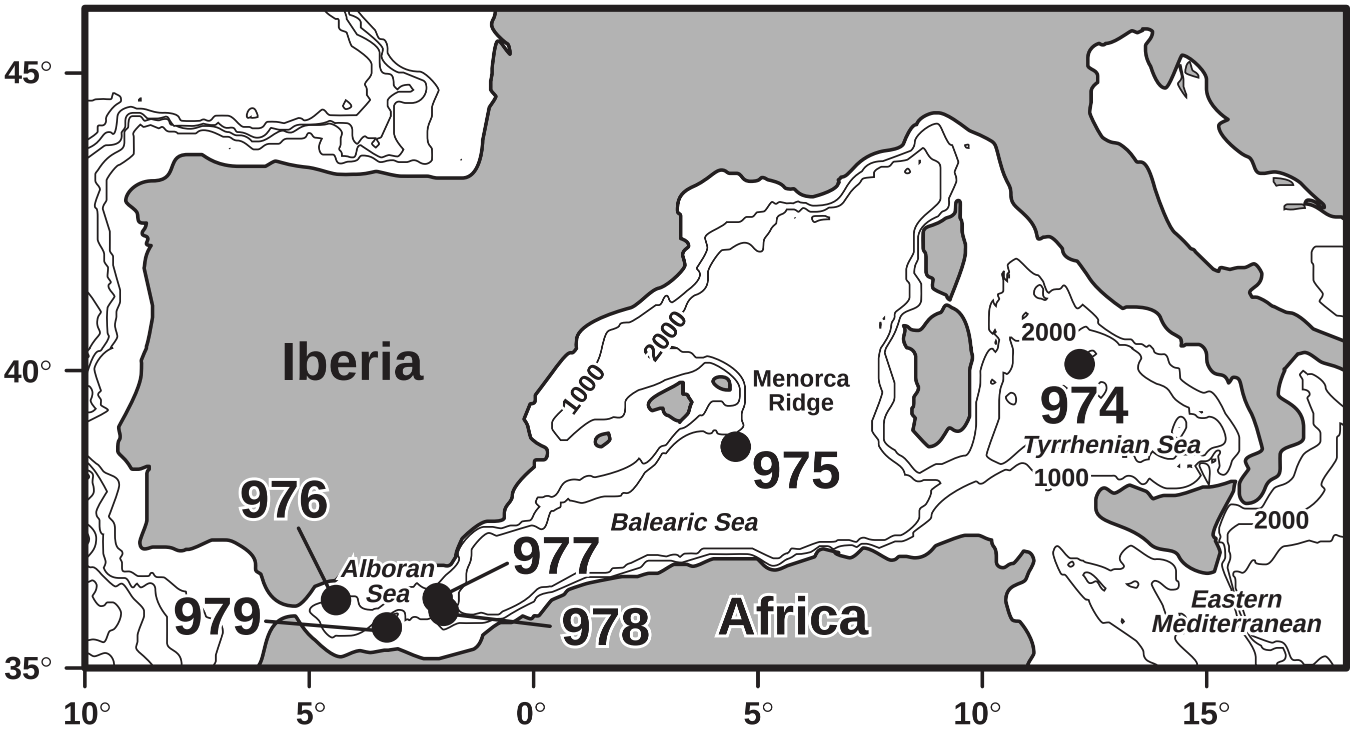

Figure 1. Locations of Site 974 in the Tyrrhenian Basin, Site 975 on the Menorca Ridge, and Sites 976, 977, 978, and 979 in the Alboran Basin. Depth contours in meters.

Organic Carbon Measurements and C/N Values

The total organic-carbon contents (TOC) of Leg 161 samples were determined by the difference between total carbon concentrations as measured by a Carlo Erba NA 1500 NCS analyzer (Verardo et al., 1990) and the carbonate-carbon concentrations as measured by a Coulometrics 5011 inorganic carbon analyzer (Engleman et al., 1985). Freeze-dried samples were combusted at 1000°C in an oxygen atmosphere in the NCS analyzer, and the resulting combustion products were chromatographically separated and quantified to yield the concentrations of total carbon and nitrogen. The TOC and total nitrogen values were used to calculate atomic C/N values of the samples. These C/N values are assumed to represent those of sediment organic matter in this report.

This procedure, in which TOC concentrations are determined from the difference between total carbon and carbonate-carbon concentrations, has been tested against the direct-determination analysis of carbonate-free sediment samples by Meyers and Silliman (1996). Agreement is good for TOC concentrations ranging between 0.2% and 2% and for C/N values between 5 and 15. Both procedures, however, cease to measure accurately TOC concentrations that are below 0.1%, and this level is considered the limit of detection in this report.

Rock-Eval Pyrolysis

Rock-Eval pyrolysis of organic matter consists of heating samples at a rate of 25°C/min between 300°C to 600°C to yield the amount of volatile hydrocarbons present in the sediment (S_1), the amount of hydrocarbons released during pyrolysis (S_2), and the amount of CO_2 released during heating to 390°C (S_3). These values are combined with TOC values to provide the information necessary to calculate the hydrogen index (HI = $100 \times S_2$/TOC, or milligrams hydrocarbons/gram organic carbon) and the oxygen index (OI = $100 \times S_3$/TOC, or milligrams CO_2/gram organic carbon). The temperature of maximum hydrocarbon release during pyrolysis (T_{max}) is also obtained and provides a measure of organic matter thermal maturity (Espitalié et al., 1977).

RESULTS AND DISCUSSION

Organic Carbon Concentrations

TOC concentrations are bulk sedimentary parameters that represent the fraction of organic matter that has survived degradation during sinking to the seafloor and early diagenesis in the sediments. TOC concentrations are influenced by both initial primary production and subsequent exposure to degradation, so they integrate the different origins of organic matter, delivery routes, depositional processes, and consequent degrees of preservation. TOC concentrations are expressed in weight/weight ratios and are therefore influenced by other components of the sediments. For example, TOC concentrations can be diluted by clastic sediment particles in some settings or concentrated by dissolution of carbonate minerals in others.

Most of the Pliocene–Pleistocene sediments sampled in the six sites cored during Leg 161 contain organic-carbon concentrations that are approximately the same as the average of 0.3% compiled by McIver (1975) from Deep Sea Drilling Project (DSDP) legs 1 through 33. The organic-carbon-poor Leg 161 sediments represent conditions of low productivity and poor preservation of organic matter that evidently typify most of the post-Messinian history of the Mediterranean Sea. The exceptions are the dark-colored sapropel layers in which TOC concentrations exceed 0.5% and reach as high as 6.3% (Comas, Zahn, Klaus, et al., 1996). Comparison of TOC concentrations at the five sites from which continuous sedimentary records were obtained shows two general patterns: (1) the differences between the TOC content of background sediments and sapropels is greatest in sediments from Site 974 in the Tyrrhenian Basin and diminishes in more westward locations, and (2) the occurrence of sapropels is limited to Pleistocene sediments (Fig. 2).

The first of these patterns is a general extension of results obtained from the eastern Mediterranean Sea during Leg 160, wherein TOC concentrations in Pleistocene sediments reach 20% on the Pisano Plateau in the Ionian Basin (Bouloubassi et al., in press). This trend may reflect significant paleoceanographic differences between the locations that roughly correspond to their distances from the Nile River and the Black Sea, the largest present-day sources of nutrient-enriched fresh- or low-salinity water to the Mediterranean Sea. The TOC concentrations in the seafloor may record geographical differences in surface paleoproductivity. It is more likely, however, that the pattern of decreasing TOC is produced by differences in sedimentation rates, which in general increase from east to west. Organic carbon concentrations are diluted more in the western locations by clastic and biogenic sediment components than in the eastern sites. If this is true, then production and subsequent burial of organic matter has been periodically elevated to the same or similar levels throughout the Mediterranean Basin since the beginning of the Pleistocene. Until sediment chronology is refined sufficiently to allow calculation of organic-carbon–mass-accumulation rates, this hypothesis remains untested.

An important difference exists between the histories of organic carbon burial in the western Mediterranean sites that were sampled during Leg 161 and those in the eastern Mediterranean sampled during Leg 160. Sapropel occurrences begin during the middle Pliocene in the eastern Mediterranean Sea (Emeis, Robertson, Richter, et al., 1996), whereas they do not start to appear in the western sites until the beginning of the Pleistocene (Fig. 2). Furthermore, TOC concentrations are higher in the Pliocene sapropels than in their Pleistocene equivalents, reaching as high as 32% at Site 969 on the Mediterranean Ridge south of Crete (Bouloubassi et al., in press). In contrast, chronologically equivalent sediments from the Leg 161 sites contain only a few tenths of a percent TOC (Fig. 2). Unlike the Pleistocene TOC concentrations, the difference in onset of sapropel deposition indicates real paleoceanographic differences between the eastern and western Mediterranean locations.

Organic Carbon/Nitrogen Values

C/N values help to distinguish between algal and land-plant origins of sedimentary organic matter. Algae typically have atomic C/N values between 4 and 10, whereas vascular land plants have C/N values of 20 and greater (Premuzic et al., 1982; Emerson and Hedges, 1988; Jasper and Gagosian, 1990; Meyers, 1994; Prahl et al., 1994). This distinction arises from the absence of cellulose in algae and its abundance in vascular plants. The difference between algal and land-plant C/N source signatures is largely preserved in sedimentary organic matter (Jasper and Gagosian, 1990; Meyers, 1994).

C/N values in Leg 161 Pliocene–Pleistocene sediments are variable (Comas, Zahn, Klaus, et al., 1996). The C/N values of some samples low in TOC are very low (<5). These values are lower than those observed in fresh algal matter. They are probably an artifact of the low carbon contents combined with the tendency of clay minerals to absorb ammonium ions generated during microbial degradation of organic matter (Müller, 1977). The C/N values in samples especially low in organic carbon consequently are not accurate indicators of organic-matter source; they instead indicate continued breakdown of organic matter after burial.

In contrast to the organic-carbon–poor background sediments, the C/N values of sapropels range between 10 and 20 (Comas, Zahn, Klaus, et al., 1996), which is intermediate between unaltered algal organic matter and fresh land-plant material. Because diagenesis rarely depresses land-plant C/N values to values as low as those found in the sapropels (Meyers et al., 1995), it is likely that the organic-carbon–rich sediments contain algal material that has been partially degraded during or soon after settling to the seafloor. Preferential loss of nitrogen-rich, proteinaceous matter can elevate the C/N values of algal organic matter by this process.

In support of the concept of diminished degradation of the organic-matter content of the sapropels, a well-developed correspondence

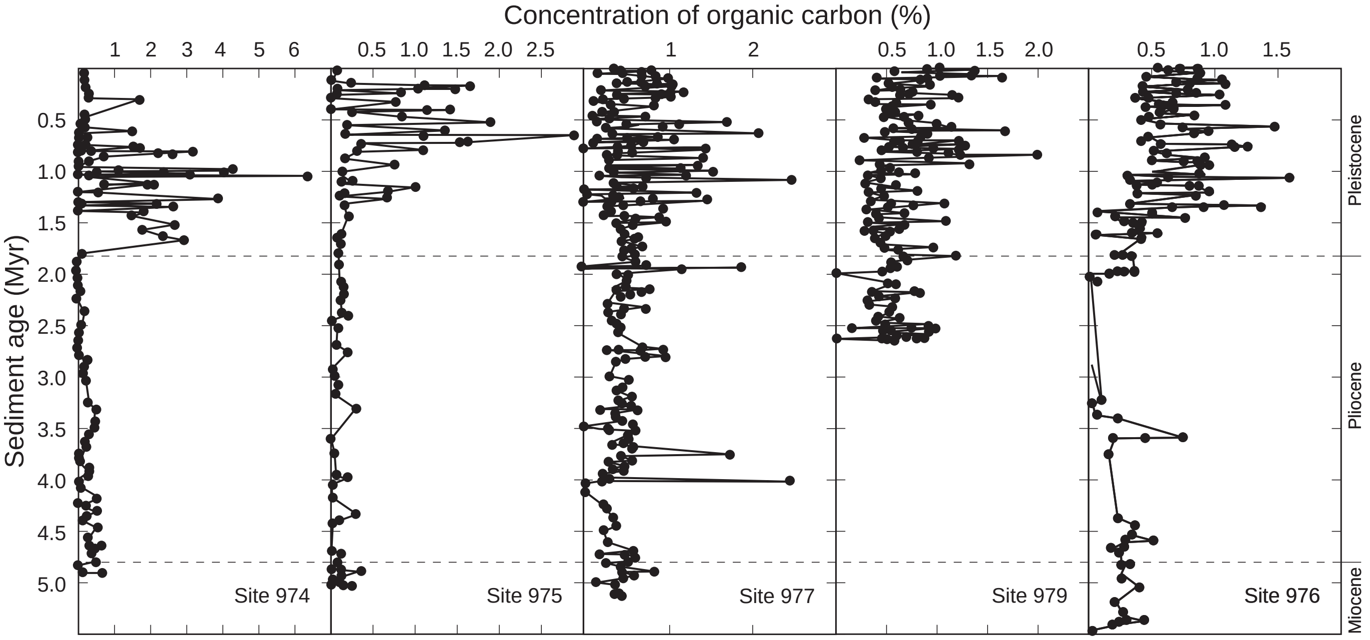

Figure 2. Concentrations of organic carbon in Miocene, Pliocene, and Pleistocene sediments from Site 974 in the Tyrrhenian Basin, Site 975 on the Menorca Ridge, and Sites 976, 977, and 979 in the Alboran Basin. Organic-carbon depth-profiles for the five sites are ordered from east to west to show geographical change in organic-carbon concentrations.

between higher TOC concentrations and greater C/N values exists in the sapropels from all five Leg 161 sites that were continuously cored (Fig. 3). This correspondence suggests two factors that are important to elevating the TOC levels of the sapropels. First, the organic matter that was delivered to the seafloor and accumulated in the sapropel layers experienced less degradation during sinking than the organic matter that was delivered during times when sapropels did not form. Nitrogenous components of biological organic matter are typically recycled more effectively than other forms of organic matter under conditions of partial degradation. The organic matter in the sapropels consequently retained a greater proportion of its carbon content, and C/N values were therefore enhanced. This process accompanies the elevated fluxes of organic matter to sediments under upwelling zones, where Suess and Müller (1980) document enhancement of C/N values in surficial bottom sediments. Second, organic carbon experienced less remineralization after being incorporated into the bottom sediments, so that organic matter retained the elevated C/N values that developed during transport to the seafloor.

Results of Rock-Eval Pyrolysis

Rock-Eval pyrolysis was originally developed to characterize the organic matter present in oil source rocks, which typically is more thermally mature and at higher concentration than commonly found in non-lithified sediments obtained by scientific ocean drilling. Rock-Eval analyses have nonetheless proved valuable in helping to determine organic matter sources in DSDP and ODP samples. The hydrogen index (HI) and the oxygen index (OI) relate to the origin of the total organic matter and are commonly plotted against each other in a Van Krevelen-type diagram in which a comparison of elemental H/C and O/C values is approximated. In the HI-OI plot, three main types of organic matter and their thermal alteration pathways are defined. Type I organic matter is especially rich in aliphatic hydrocarbons and hydrocarbon-like components and is derived from algae and microbial biomass. Type II organic matter is moderately rich in these aliphatic components and originates from the waxy coatings of land plants and from partially degraded algae. Type III organic matter is poor in hydrocarbon-like materials but rich in carbohydrates. Land-plant organic matter is usually rich in woody components and consequently has lower hydrogen indices and higher oxygen indices than found in lipid-rich and cellulose-poor algal organic matter. Type III organic matter therefore usually typifies woody land-plant matter, but it may also represent poorly preserved algal organic matter.

The source-distinction between continental and marine organic matter that can be made from the results of Rock-Eval pyrolysis becomes blurred by diagenesis. Oxidation of organic matter affects both HI values and OI values. As hydrocarbon-rich organic matter (Type I or II) is oxidized, its hydrogen content decreases while its oxygen content increases, and it takes on the HI-OI characteristics of Type III vascular plant organic matter. A further constraint on the use of Rock-Eval pyrolysis for determination of organic-matter source is that samples should contain at least 0.5% TOC to yield meaningful results (Katz, 1983; Peters, 1986).

The results of Rock-Eval analyses of Leg 161 sapropels show that their organic-matter content appears to be dominated by varying mixtures of Type II algal material and Type III land-plant-material (Fig. 4). The indication of large proportions of land-derived organic matter in many of the sapropels conflicts, however, with C/N values in these sediments (Fig. 3) that are too low (<20) for land-plant organic matter. The contradiction between the Rock-Eval source characterization and the elemental source characterization is evidence that the marine organic matter has been heavily oxidized, because well-preserved Type II organic matter has high HI values (Espitalié et al., 1977; Peters, 1986).

Comparison of TOC concentration with Rock-Eval HI values shows that sapropels with higher TOC concentration also have higher HI values (Fig. 5), which is a pattern also found in sapropels in the eastern Mediterranean (Bouloubassi et al., in press). Higher TOC concentrations also correspond to higher C/N values (Fig. 3). Sapropels having higher HI values consequently also have higher C/N values, which is an indication of partial but not extensive alteration of marine organic matter during sinking and incorporation into bottom sediments. The relationship between higher HI values and elevated TOC concentrations is therefore consistent with preservation of marine organic matter being important in elevating the organic-matter content of Mediterranean sapropels (e.g., Ten Haven et al., 1987; Calvert et al., 1992; Cheddadi and Rossignol-Strick, 1995).

Thermal Maturity of Organic Matter

Rock-Eval T_{max} values are below 425°C in most of the Pliocene–Pleistocene sediments from the locations sampled by Leg 161 (Comas, Zahn, Klaus, et al., 1996). These values indicate that the organic matter in most of the basins of the western Mediterranean is thermally immature with respect to petroleum generation (Espitalié et al, 1977; Peters, 1986). Because organic matter is sensitive to temperatures that are only slightly elevated (>60°C), the thermal immaturity of the Pliocene–Pleistocene organic matter is evidence of low heat flows in the western Mediterranean basins since the times these sediments were deposited.

Two of the Leg 161 sites, however, exhibit T_{max} values that deviate from being relatively low. The deviations suggest that local geo-

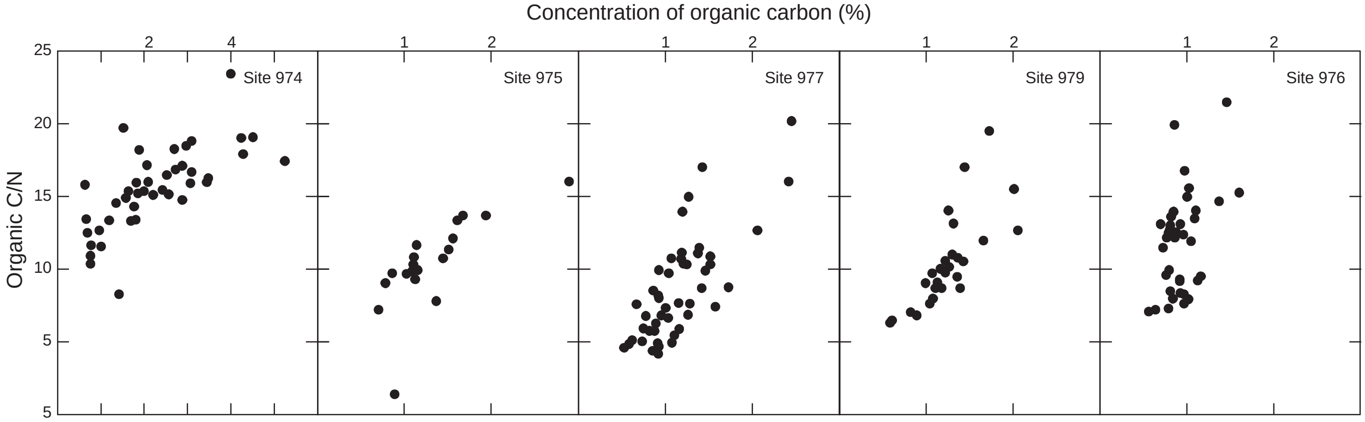

Figure 3. Comparison of organic C/total N values to organic carbon concentrations in Miocene, Pliocene, and Pleistocene sediments from Site 974 in the Tyrrhenian Basin, Site 975 on the Menorca Ridge, and Sites 976, 977, and 979 in the Alboran Basin. Data are in same east-west geographical order as in Figure 2.

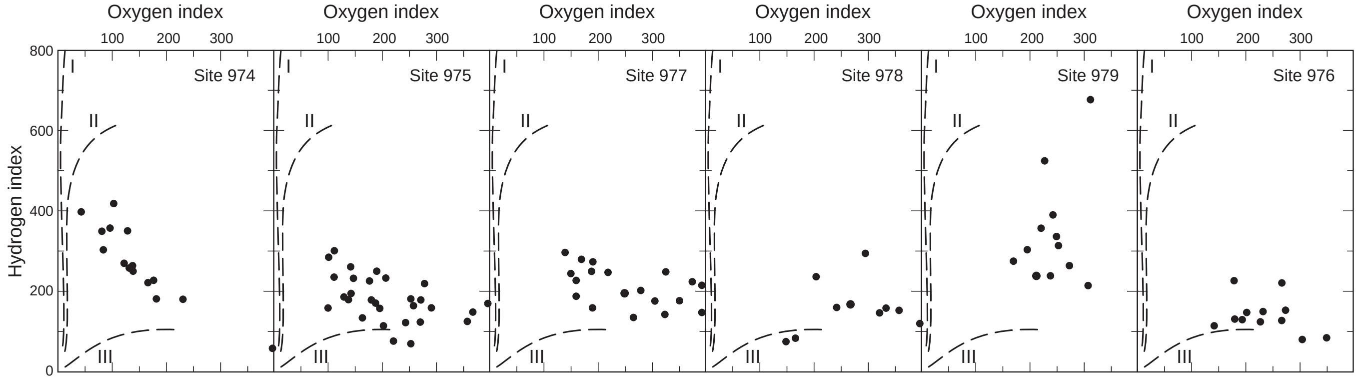

Figure 4. Rock-Eval Van Krevelen-type diagrams for organic matter in Pliocene–Pleistocene sediments from Site 974 in the Tyrrhenian Basin, Site 975 on the Menorca Ridge, and Sites 976, 977, 978, and 979 in the Alboran Basin. Units for hydrogen index are milligrams of hydrocarbons per gram TOC and for oxygen index are milligrams of CO_2 per gram TOC. Thermal alteration pathways of organic matter Types I, II, and III from source material to graphite are indicated by dashed lines.

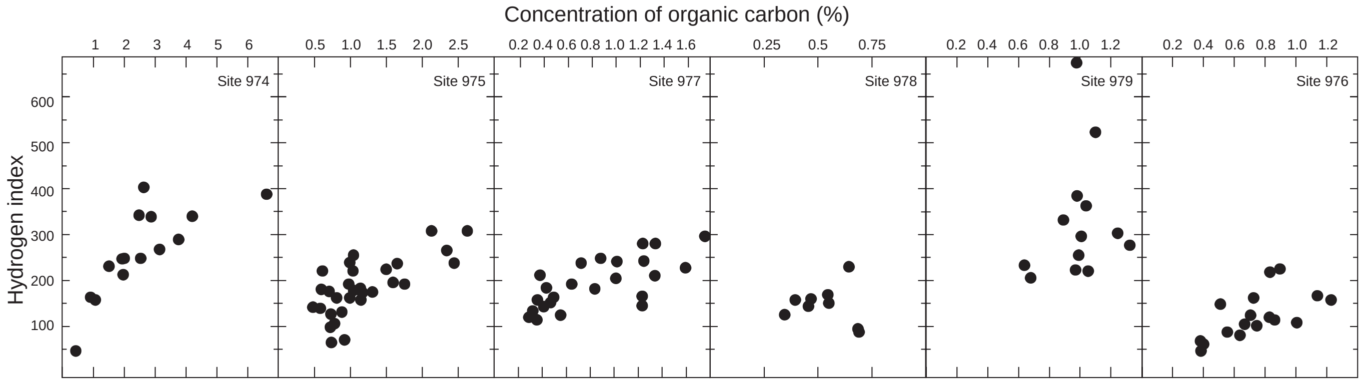

Figure 5. Relationship of Rock-Eval hydrogen index and organic carbon concentration in Pliocene–Pleistocene sediments from Site 974 in the Tyrrhenian Basin, Site 975 on the Menorca Ridge, and Sites 976, 977, 978, and 979 in the Alboran Basin.

thermal gradients may have been sufficiently elevated at some former time to have matured the organic matter buried at these locations. A well-developed pattern of increasing T_{max} values with depth is present in the upper 150 m of sediment at Site 974 in the Tyrrhenian Basin (Fig. 6). Because of the relatively shallow burial depth, the increase in thermal maturity with depth is probably a consequence of the elevated geothermal heat flow (157 mW/m^2) measured at this location (Comas, Zahn, Klaus, et al., 1996).

Rock-Eval T_{max} values are relatively low in the Pleistocene sediments of Site 977 in the eastern Alboran Basin, but they become elevated to 475°C–495°C in the deeper, Pliocene sediments (Fig. 7). The higher T_{max} values indicate that organic matter is overmature with respect to petroleum generation in the older sediments (Fig. 8). The thermal maturity indicated by the T_{max} values suggests that temperatures were between 125° and 150°C for sediments of this age, which is substantially greater than the present bottom-hole temperature that the measured heat flow (101 mW/m^2) would yield (Comas, Zahn, Klaus, et al., 1996). The thermal maturity of the organic matter in the Pliocene sediments consequently indicates that heat flows were formerly higher in the Eastern Alboran Basin, which is a tectonically active part of the greater Mediterranean Basin.

Other organic geochemical evidence of formerly higher geothermal gradients is present in the sediments of the eastern Alboran Basin. Higher molecular–weight thermogenic gases are present at low levels in sediments from Site 977. Concentrations of propane, *iso*-butane, and *iso*-pentane exceed those of ethane in sediments from about 200 mbsf to 450 mbsf (Comas, Zahn, Klaus et al., 1996). A general correspondence between elevated Rock-Eval T_{max} values and occurrence of these heavier gases suggests that the C_3, C_4, and C_5 gases were produced by thermal degradation of sedimentary organic matter during a period of elevated heat flow or hydrothermal activity in the Eastern Alboran Basin. Because only organic matter in sediments deeper than 200 mbsf exhibits thermal alteration, the interval of elevated heating must have occurred during the Pliocene.

Paleoceanographic Significance of Sapropels

Milankovitch-cycle changes in the earth's orbit about the sun have pervasive impacts on global climate. In particular, precessional changes, which affect summer-winter climate differences at cyclicities of 19 and 23 k.y., appear to be strongly expressed in the sapropels and their shallow-water equivalents, the laminites, of the Mediterranean Basin (Fontugne and Calvert, 1992; Berggren et al., 1995; Lourens et al., 1996; Hilgen et al., 1997). Sapropels are expressed differently at different locations and at different times of post-Messinian Mediterranean paleoclimate history. Local and regional factors evidently overprint the global Milankovitch forcing factors. Moreover, these organic-carbon–rich sediments often occur as bundles—regular successions of light/dark layers—interspersed with intervals in which the dark layers are absent. This is a common pattern and suggests repetitive variations in the intensity of precessional climate change.

Nutrient-enhanced productivity appears to be involved in the deposition of the deep-water sapropels. Upper Pliocene–lower Pleistocene sapropels from the eastern Mediterranean Sea are especially rich in organic carbon, some exceeding 30% (Bouloubassi et al., in press). Exceptionally high rates of organic-matter delivery had to

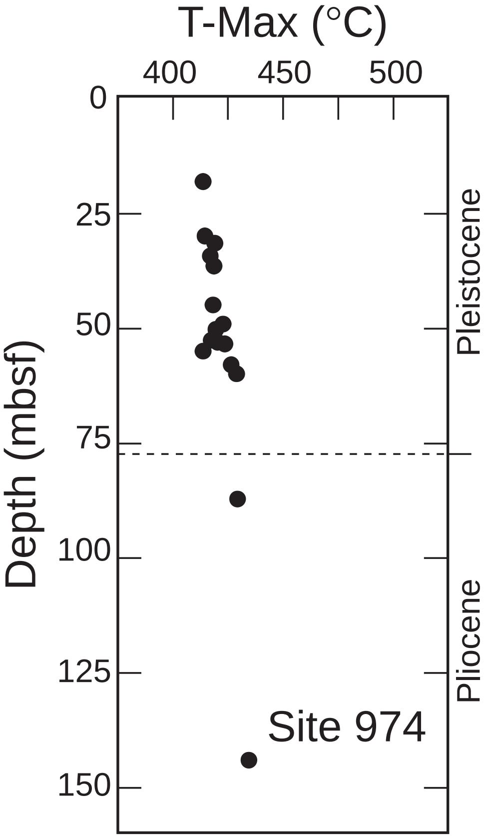

Figure 6. Increase of Rock-Eval T_{max} values with depth in Pliocene–Pleistocene sediments from Site 974 in the Tyrrhenian Basin.

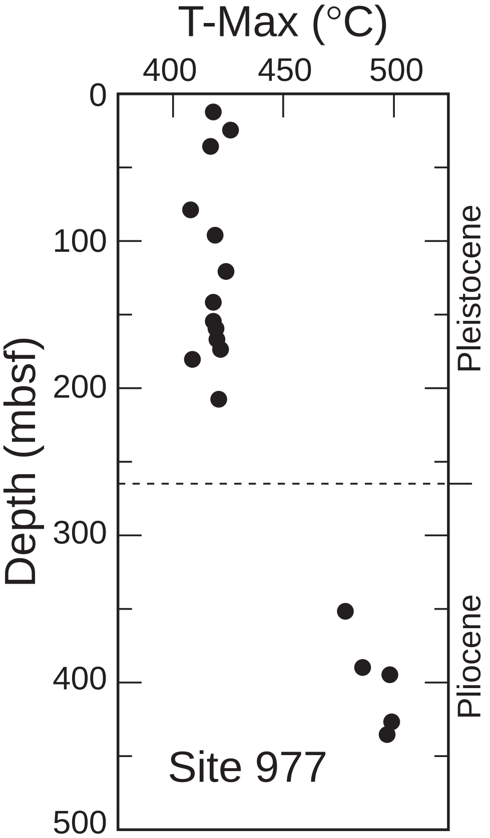

Figure 7. Difference between Rock-Eval T_{max} values of Pliocene–Pleistocene sediments from Site 977 in the Eastern Alboran Basin.

contribute to such elevated organic-carbon concentrations. Rock-Eval analyses of sapropels from Leg 161 sites indicate that variable oxidation of marine organic matter has occurred in the western Mediterranean (Figs. 4, 5). The range in degree of organic matter preservation, from good to moderate, suggests that elevated productivity ultimately contributed to improving organic matter preservation in the seafloor. When the delivery of organic matter was great enough to exhaust benthic oxygen availability, sediments rich in organic carbon accumulated. Several lines of evidence support this concept. The compositions of nannofossil assemblages in eastern Mediterranean sapropels suggest that the triggering mechanism for enhanced preservation was increased productivity (Castradori, 1993). Molecular and isotopic organic geochemical compositions confirm that the organic matter in sapropels originated from enhanced marine productivity (Ten Haven et al., 1987; Calvert et al., 1992; Rullkötter et al., in press, Bouloubassi et al., in press). These generalizations about the origin and preservation of the organic matter in the sapropels are likely to apply in the western, as well as in the eastern, Mediterranean Sea.

Fontugne and Calvert (1992) noted that the δ^{13}C values of bulk organic matter in upper Pleistocene deep-water sapropels in the eastern Mediterranean are consistently more negative than in intercalated oozes. They interpret the more negative values to reflect periodic freshwater flooding of the photic zone of the eastern Mediterranean. Enhanced delivery of soil-derived nutrients to oceanic surface waters commonly accompanies periods of increased river flow. Calvert et al. (1992) note that δ^{15}N values of the organic matter in the sapropels are exceptionally low, which is evidence that nitrogen-fixing microbes were probably important primary producers during the intervals of sapropel formation. The existence of nitrogen-fixing microbes is indirect evidence for density stratification that extended into the photic zone of the Mediterranean Sea during these intervals.

Precessional (19 to 23 k.y.) regional changes in climate have been postulated to be central to formation of the Mediterranean laminated sediments (Hilgen et al., 1997). The basic premise is that summer-winter differences greater than at the present (the Earth is now farthest from the sun at northern summer solstice, and modern laminites/sapropels are not being deposited) increased precipitation in the Mediterranean region (Rossignol-Strick, 1985). The periods of increased seasonal differences correspond to Milankovitch-cycle precessional minima. During the intervals of greater summer-winter contrast, increased continental runoff delivers more nutrients to seawater, thereby enhancing algal and microbial production and the delivery of marine organic matter to the seafloor. Benthic oxidation of the increased flux of organic matter overwhelms the supply of dissolved oxygen at the seabottom, and preservation of subsequently delivered organic matter is enhanced. In this scenario, deep waters need not stagnate to become anoxic, even though the increased continental runoff would probably dilute surface waters and create salinity stratification in large areas of the Mediterranean Sea.

SUMMARY

Sapropels occurrences are well-known in deep-water sediments from locations in the eastern Mediterranean extending from the Ionian Basin to the Levantine Basin. Drilling of deep-water post-Messinian sedimentary sequences by ODP Leg 161 has shown that occurrences of organic-carbon–rich sapropels and sapropel-like sediments continue westward into the Alboran Basin (Comas et al.,

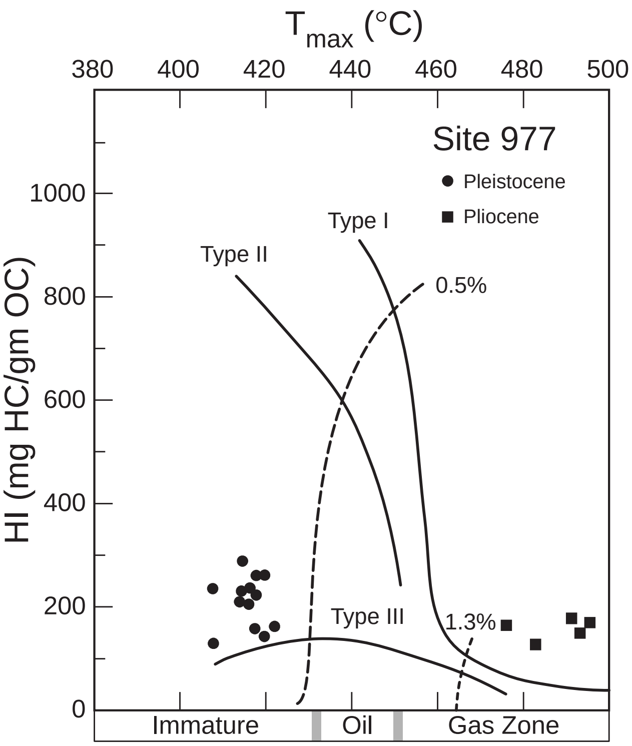

Figure 8. Relationship between Rock-Eval hydrogen index and T_{max} values in Pliocene–Pleistocene sediments from Site 977 in the Eastern Alboran Basin. Thermal alteration pathways of organic matter Types I, II, and III are indicated by solid lines. Dashed lines indicate approximate vitrinite reflectance values (not measured) that define the “oil window.” Organic matter in Pleistocene sediments is immature with respect to petroleum generation, whereas it is overmature in Pliocene sediments.

1996). Pliocene–Pleistocene sediments in the western Mediterranean typically contain little organic carbon (<0.2%), but multiple dark-colored layers in which TOC concentrations exceed 0.5% exist in Pleistocene parts of the sedimentary sequences in the Tyrrhenian Basin, on the Menorca Ridge, and in the basins of the Alboran Sea. A combination of Rock-Eval and C/N characterizations of the organic matter in these sapropels and sapropel-like layers shows that it is comprised of partially preserved marine material.

A feature common to the organic-carbon–rich sediments is that groups of these layers will occur at intervals of ~20 k.y. in parts of the sequences, but they will be absent in other parts. This characteristic indicates that the organic-carbon–rich layers represent a paleoceanographic setting different from today that recurred regularly in the past, yet one that depended on a complicated interplay of multiple factors and that may have been strongly influenced by local or regional paleoenvironments. The observed 20-k.y. spacing of the dark layers suggests that Milankovitch precessional cycles control the timing of their deposition. Precession of the Earth in its elliptical orbit around the sun causes the Earth-sun distance at summer and winter solstice—the times of greatest seasonal expression—to cycle between maxima and minima every 21 k.y. The Earth is now farthest from the sun at northern summer solstice, making northern hemisphere summers cooler than during the precessional minima when laminites/sapropels were often deposited.

Precessional climate changes that freshened the surface waters of the Mediterranean have been invoked as the underlying cause of the sapropels (Rossignol-Strick, 1985; Fontugne and Calvert, 1992; Sancetta, 1994). The basic premise is that summer-winter differences greater than at the present increased seasonality in the past, thereby causing greater precipitation and stronger winds in the Mediterranean region. These cyclic paleoclimatic changes evidently enhanced paleoproductivity, but to a different degree at each precessional minimum and at each location studied during Leg 161. When greatly enhanced, the delivery of marine organic matter to the seabottom was sufficiently large to exhaust the availability of dissolved oxygen in bottom waters, thereby temporarily establishing anoxic conditions at the seafloor and improving preservation of the magnified flux of organic matter to the sediments. A sapropel layer was deposited under these conditions. When not so greatly enhanced, the delivery of organic matter was not sufficient to create drawdown of bottom-water oxygen during the precessional minimum, and organic carbon was oxidized before or soon after incorporation into the sediment. No sapropel layer survived in the sedimentary record under the conditions of lesser productivity. The magnitude of paleoproduction of organic matter, therefore, was the primary factor involved in determining whether or not sapropels were deposited at the times of each precessional minima in the post-Messinian record of the Mediterranean, and local factors influenced the paleoclimate expressions of the Pliocene–Pleistocene precessional minima at the Leg 161 sites.

ACKNOWLEDGMENTS

Comments from Barry Katz and Ralf Littke helped to improve this contribution. We deeply appreciate the experience, knowledge, and good humor of Phil Rumford, Chieh Peng, and Eric Meissner in producing the organic carbon and Rock-Eval analytical results. The graphical skills of Dale Austin converted our crude figures into scientific art. We thank the Ocean Drilling Program, funded by the National Science Foundation and IPOD countries, for providing us with the special and oddly enjoyable opportunity to spend two months at sea. Postcruise studies of PAM were supported by a grant from JOI-USSSP.

REFERENCES

Bates, R.L., and Jackson, J.A. (Eds.), 1987. *Glossary of Geology* (3rd ed.): Alexandria, VA (Am. Geol. Inst.).

Berggren, W.A., Hilgen, F.J., Langereis, C.G., Kent, D.V., Obradovich, J.D., Raffi, I., Raymo, M.E., and Shackleton, N.J., 1995. Late Neogene chronology: new perspectives in high-resolution stratigraphy. *Geol. Soc. Am. Bull.,* 107:1272–1287.

Bouloubassi, I., Rullkötter, J., and Meyers, P.A., in press. Origin and transformation of organic matter in Pliocene-Pleistocene Mediterranean sapropels: organic geochemical evidence. *Mar. Geol.*

Calvert, S.E., Nielsen, B., and Fontugne, M.R., 1992. Evidence from nitrogen isotope ratios for enhanced productivity during the formation of eastern Mediterranean sapropels. *Nature,* 359:223–225.

Castradori, D., 1993. Calcareous nannofossils and the origin of eastern Mediterranean sapropels. *Paleoceanography,* 8:459–471.

Cheddadi, R., and Rossignol-Strick, M., 1995. Improved preservation of organic matter and pollen in Eastern Mediterranean sapropels. *Paleoceanography,* 10:301–309.

Cita, M.B., and Grignani, D., 1982. Nature and origin of Late Neogene Mediterranean sapropels. *In* Schlanger, S.O., and Cita, M.B. (Eds.), *Nature and Origin of Cretaceous Carbon-rich Facies:* London (Academic Press), 165–196.

Comas, M.C., Zahn, R., Klaus, A., et al., 1996. *Proc. ODP, Init. Repts.,* 161: College Station, TX (Ocean Drilling Program).

Emeis, K.-C., Robertson, A.H.F., Richter, C., et al., 1996. *Proc. ODP, Init. Repts.,* 160: College Station, TX (Ocean Drilling Program).

Emerson, S., and Hedges, J.I., 1988. Processes controlling the organic carbon content of open ocean sediments. *Paleoceanography,* 3:621–634.

Engleman, E.E., Jackson, L.L., and Norton, D.R., 1985. Determination of carbonate carbon in geological materials by coulometric titration. *Chem. Geol.,* 53:125–128.

Espitalié, J., Laporte, J.L., Leplat, P., Madec, M., Marquis, F., Paulet, J., and Boutefeu, A., 1977. Méthode rapide de caractérisation des roches mères, de leur potentiel pétrolier et de leur degré d'évolution. *Rev. Inst. Fr. Pet.,* 32:23–42.

Fontugne, M.R., and 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 CO_2 levels. *Paleoceanography,* 7:1–20.

Hilgen, F.J., Krijgsman, W., Langereis, C.G., and Lourens, L.J., 1997. Breakthrough made in dating of the geological record. *Eos,* 78:285–289.

Jasper, J.P., and 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.

Katz, B.J., 1983. Limitations of "Rock-Eval" pyrolysis for typing organic matter. *Org. Geochem.,* 4:195–199.

Lourens, L.J., Antonarakou, A., Hilgen, F.J., Van Hoof, A.A.M., Vergnaud-Grazzini, C., and Zachariasse, W.J., 1996. Evaluation of the Plio-Pleistocene astronomical timescale. *Paleoceanography,* 11:391–413.

McIver, R.D., 1975. Hydrocarbon occurrences from JOIDES Deep Sea Drilling Project. *Proc. Ninth Petrol. Congr.,* 269–280.

Meyers, P.A., 1994. Preservation of elemental and isotopic source identification of sedimentary organic matter. *Chem. Geol.,* 144:289–302.

Meyers, P.A., Leenheer, M.J., and Bourbonniere, R.A., 1995. Diagenesis of vascular plant organic matter components during burial in lake sediments. *Aquatic Geochem.,* 1:35–42.

Meyers, P.A., and Silliman, J.E., 1996. Organic matter in Pleistocene to Quaternary turbidites from Site 897, 898, 899, and 900, Iberia Abyssal Plain. In Whitmarsh, R.B., Sawyer, D.S., Klaus, A., and Masson, D.G. (Eds.), *Proc. ODP, Sci. Results,* 149: College Station, TX (Ocean Drilling Program), 305–313.

Müller, P.J., 1977. C/N ratios in Pacific deep sea sediments: effect of inorganic ammonium and organic nitrogen compounds sorbed by clays. *Geochim. Cosmochim. Acta,* 41:765–776.

Peters, K.E., 1986. Guidelines for evaluating petroleum source rock using programmed pyrolysis. *AAPG Bull.,* 70:318–329.

Prahl, F.G., Ertel, J.R., Goñi, M.A., Sparrow, M.A., and Eversmeyer, B., 1994. Terrestrial organic carbon contributions to sediments on the Washington margin. *Geochim. Cosmochim. Acta,* 58:3035–3048.

Premuzic, E.T., Benkovitz, C.M., Gaffney, J.S., and Walsh, J.J., 1982. The nature and distribution of organic matter in the surface sediments of world oceans and seas. *Org. Geochem.,* 4:63–77.

Rossignol-Strick, M., 1985. Mediterranean Quaternary sapropels, an immediate response of the African Monsoon to variation of insolation. *Palaeogeogr., Palaeoclimatol., Palaeoecol.,* 49:237–263.

Rullkötter, J., Rinna, J., Bouloubassi, I., Scholz-Boettcher, B., Meyers, P.A., Johns, L., and Rowland, S.J., 1998. Biological marker significance of organic matter origin and transformation in sapropels from the Pisano Plateau, Site 964. *In* Robertson, A.H.F., Emeis, K.-C., Richter, C. (Eds.), *Proc. ODP, Sci. Results,* 160: College Station, TX (Ocean Drilling Program), 271–283.

Sancetta, C., 1994. Mediterranean sapropels: Seasonal stratification yields high production and carbon flux. *Paleoceanography,* 9:195–196.

Suess, E., and Müller, P.J., 1980. Productivity, sedimentation rate and sedimentary organic matter in the oceans, II. Elemental fractionation. *Coll. Int. CNRS,* 293:17–26.

ten Haven, H.L., Baas, M., Kroot, M., de Leeuw, J.W., Schenck, P.A., and 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.

Thunell, R.C., Williams, D.F., and Belyea, P.R., 1984. Anoxic events in the Mediterranean Sea in relation to the evolution of late Neogene climates. *Mar. Geol.,* 59:105–134.

Verardo, D.J., Froelich, P.N., and McIntyre, A., 1990. Determination of organic carbon and nitrogen in marine sediments using the Carlo Erba NA-1500 Analyzer. *Deep-Sea Res. Part A,* 37:157–165.

Date of initial receipt: 6 May 1997
Date of acceptance: 16 December 1997
Ms 161SR-235