*Instituto Andaluz de*
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# Acumulación y Preservación de Materia Orgánica en Sedimentos Marinos: Implicaciones en el Ciclo del Carbono y Nutrientes

## *Accumulation and Preservation of Organic Matter in Marine Sediments: Implications on the Carbon and Nutrients Cycle*

Memoria de Tesis presentada por el Licenciado en Ciencias Geológicas D. David Gallego Torres para optar al Grado de Doctor por la Universidad de Granada.

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*Tesis Doctoral*

# Acumulación y Preservación de Materia Orgánica en Sedimentos Marinos: Implicaciones en el Ciclo del Carbono y Nutrientes

## *Accumulation and Preservation of Organic Matter in Marine Sediments: Implications on the Carbon and Nutrients Cycle*

**David Gallego Torres**

**Chapter I: Introduction and Objectives**

**Chapter II: Materials and Methods**

The carbon cycle has become a major scientific and social issue due to its direct relation with climate change. Carbon dioxide, a key greenhouse gas, has increased its concentration in the atmosphere, partly due to fossil fuels burning, this increase having probably raised the Earth surface temperature. The oceans can behave as a sink for carbon in the forms of inorganic carbonate material and/or organic matter deposited in sediment. Due to its efficiency, the biological pump in the oceans constitutes a mechanism for carbon sequestration in the lithosphere and intense research has been devoted to the marine organic carbon cycles. As part of this study, organic matter accumulation in the geologic record constitutes a crucial topic. Organic-rich sediments have traditionally been interpreted as the response to bottom water anoxia that inhibited organic matter decomposition. However, marine productivity has proven to play a key role in the accumulation of organic matter in marine sediments. The controversy between Anoxia vs. Productivity has been the motif of extensive studies, partly based on the development of geochemical proxies.

In this Thesis, different geochemical techniques have been applied to the reconstruction of paleoceanographic conditions that leaded to organic matter accumulation in marine sediments, and its implications in the carbon cycle and climate variability. To reach this goal, different examples of organic-rich sediments were studied.

Eastern Mediterranean sapropels have been the main case of study. A transect across the basin, using four ODP Leg 160 Sites, has been analyzed for different periods of sapropel formation. Deposition of Eastern Mediterranean sapropels is related to cyclic climate variation in the Mediterranean area and the African craton, as the main source of nutrients. Paleoxygenation proxies were tested at Site 964 (Ionian Basin) using as an example a set of sapropel from different geologic periods, and provided information about the evolution of oxygenation conditions in the basin at time of sapropel formation. These organic-rich layers formed associated to periods of increased productivity in the basin, although diminished bottom water ventilation exerted an important role during the Upper Pliocene-Lower Pleistocene. From this period onward deep-water circulation and oxygenation has progressively increased during sapropel formation until the Holocene. Indeed, the Holocene sapropel shows geochemical features of normal deep-water ventilation, and suboxic conditions appear as a consequence of intense oxygen consumption due to massive export productivity. Increased productivity during sapropel formation was the consequence of higher nutrient input due to intense Nile River discharge, and a change in bacterial community to nitrogen-fixing bacteria that maintained high nutrient availability.

Another three different cases were selected in order to compare a range of oceanographic settings. Each case is representative of past or recent favo urable conditions for deposition of organic-rich sediments: The Black Sea basin, as an anoxic basin, the Northwest African upwelling system, an area of intense present-day marine productivity, and Cretaceous Black shales from the Cenomanian-Turonian Anoxic Event, sampled at two different locations; Demerara Rise and Newfoundland platform.

The Black Sea has been an anoxic basin for most of the Holocene. During the early Holocene a sapropel layer was deposited, most likely associated to a period of increased productivity,

although the geochemical signal has been altered by diagenesis. After this event no significant organic matter enrichment in the sediments has been detected, although the basin remained anoxic until present.

Studied section at Demerara Rise (ODP Site 1258) shows evidence of extreme anoxic conditions but also present high barium concentration, this indicating intense primary productivity. The second black shale example, off Newfoundland (ODP Site 1276), shows cyclic concentration of organic matter associated to increased productivity and a relatively low decrease in oxygen availability.

The Mauritanian upwelling system has functioned for at least the last 200ky, showing fluctuating intensity of organic matter productivity. Fluctuating levels of organic matter enrichment in the sediment appears associated to variations in export productivity. The high rate of organic matter “rain” developed an oxygen minimum zone (OMZ), although clear evidence for anoxic bottom waters appears rarely and punctually.

All these results suggest that organic matter accumulation in marine sediments is primarily associated to intensified primary and export productivity. Anoxic conditions favours preservation of organic matter, but they are not sufficient to produce organic-rich sediments. On the other hand, anoxia may induce nutrient recycling and thus sustain increased productivity, so a feedback between anoxia and productivity can produce organic matter accumulation in sediments. This organic carbon sequestration in the lithosphere is also related to the climate system since high $CO_2$ concentration in the atmosphere facilitates increased productivity due to carbon excess. This $CO_2$ is later fixed in the form of organic matter and removed from the atmospheric reservoir, thus promoting lower Earth surface temperature. Eastern Mediterranean sapropels constitute an excellent example of the link between climate and preferential organic matter accumulation in sediments, and similar conclusions might be extended to other past and present environments.

El ciclo del carbono se ha convertido en un asunto principal de interés científico y social debido a su relación con el cambio climático. El dióxido de carbono, uno de los principales gases de efecto invernadero, ha incrementado su concentración en la atmósfera, en parte debido a la utilización de combustibles fósiles, y este incremento ha hecho subir rápidamente la temperatura superficial de la Tierra. Los océanos pueden actuar como un sumidero de carbono en forma de carbonatos inorgánicos o como materia orgánica depositada en el sedimento. Debido a su eficacia, la bomba biológica en el océano constituye un mecanismo de secuestro de carbono en la litosfera, y una intensa actividad investigadora se ha dedicado al ciclo del carbono en el mar. Como parte de esta investigación, la acumulación de materia orgánica durante el pasado geológico constituye un tema de estudio crucial.

Los sedimentos enriquecidos en materia orgánica se han interpretado tradicionalmente como la respuesta a condiciones anóxicas de las aguas profundas, que impedían la descomposición de la materia orgánica. Sin embargo, la productividad marina ha demostrado tener un papel importante en la acumulación de materia orgánica en sedimentos marinos. De esta forma, la controversia entre Anoxia y Productividad ha sido el motivo de amplios estudios, basados en parte en el desarrollo de indicadores geoquímicos.

Para la elaboración de esta Tesis se aplicaron diferentes técnicas geoquímicas para realizar la reconstrucción de las condiciones paleoceanográficas que indujeron la acumulación de materia orgánica en sedimentos marinos y sus implicaciones en el ciclo del carbono, y por extensión, en la variabilidad climática. Para ello, se estudiaron distintos ejemplos de sedimentos enriquecidos en materia orgánica.

Los sapropeles del Este del Mediterráneo han sido el principal caso de estudio. Se analizó para diferentes periodos de formación de sapropeles un transecto a través de la cuenca, utilizando cuatro localizaciones del Leg 160 de ODP. El depósito de sapropeles del Este del Mediterráneo está relacionado don la variación climática en el área mediterránea y en el cratón Africano, como principal fuente de nutrientes. Los indicadores de oxigenación fueron evaluados en el Site 964 (Cuenca Jónica) utilizando como ejemplo una serie de sapropeles de diferentes periodos geológicos, y se obtuvo información sobre la evolución de las condiciones de oxigenación en la cuenca en el momento de formación del sapropel. Estos niveles enriquecidos en materia orgánica se formaron asociados a periodos de alta productividad en la cuenca, aunque una ventilación restringida de aguas profundas ejerció un importante papel durante el Plioceno Superior-Pleistoceno Inferior. Desde este periodo en adelante, la oxigenación y circulación profunda ha incrementado progresivamente para las fases de formación de sapropeles hasta el Holoceno. De hecho, el sapropel holoceno muestra señales geoquímicas de una normal ventilación de las aguas profundas, y las condiciones sub-óxicas aparecen como consecuencia del intenso consumo de oxígeno debido a la masiva productividad. El incremento de productividad durante la formación de los sapropeles fue consecuencia de un mayor aporte de nutrientes, debido a una intensa descarga del río Nilo, y a un cambio en la comunidad bacteriana hacia bacterias fijadoras de nitrógeno que mantuvieron una alta disponibilidad de nutrientes.

Otros tres casos fueron seleccionados con el objetivo de comparar una gama de citaciones

paleoceanográficas. Cada caso es representativo de condiciones pasadas o recientes de depósito de sedimentos ricos en materia orgánica. El Mar Negro, como cuenca anóxica, la zona de alta productividad del Noroeste africano, una región de intensa productividad marina, y pizarras negras del Cretácico correspondientes a el Evento Oceánico Anóxico del Cenomaniense-Turoniense, muestreadas en dos localizaciones; Alto de Demerara y la plataforma de Newfoundland.

El Mar Negro ha sido una cuenca anóxica durante la mayor parte del Holoceno. Durante el Holoceno Inferior un nivel de sapropel se depositó, plausiblemente asociado a un periodo de productividad intensificada, aunque la señal geoquímica ha sido distorsionada por la diagénesis. Después de este evento no aparece ningún enriquecimiento de materia orgánica en el sedimento significativo, a pesar de que las condiciones anóxicas se mantuvieron hasta hoy. La sección estudiad en el alto de Demerara (ODP Site 1258) muestra evidencias de condiciones extremadamente anóxicas pero también presenta una alta concentración den bario indicativa de una intensa productividad primaria. El segundo ejemplo de pizarras negras, en la plataforma de Newfoundland, (ODP Site 1276) muestra concentraciones cíclicas de materia orgánica asociadas a alta productividad y una deficiencia relativa de disponibilidad de oxígeno. El sistema de alta productividad de la costa Mauritana ha funcionado al menos durante los últimos 45000 años, evidenciando fluctuaciones en la intensidad de la productividad de materia orgánica. Las oscilaciones de enriquecimiento de materia orgánica en el sedimento aparecen ligadas a variaciones en la productividad. La alta tasa de caída de materia orgánica desarrolló una zona de mínima oxigenación (OMZ), aunque evidencias claras de aguas profundas anóxicas aparecen puntual y escasamente.

Todos estos resultados sugieren que la acumulación de materia orgánica en sedimentos marinos esta principalmente asociada a una intensificación de la productividad primaria. Las condiciones anóxicas favorecen la preservación de esta materia orgánica, pero no son suficientes por sí solas para producir enriquecimiento en el sedimento. Por otra parte, la anoxia provoca el reciclaje de nutrientes y así mantiene la alta productividad, de forma que la interacción de anoxia y productividad puede promover la acumulación de materia orgánica en sedimentos. Esta fijación carbono orgánico en la litosfera está relacionada además con el sistema climático, ya que altas concentraciones de $CO_2$ en la atmósfera facilita la alta productividad, debido a un exceso de carbono. Este $CO_2$ es posteriormente fijado, en forma de materia orgánica, y eliminado del reservorio atmosférico induciendo una bajada de la temperatura superficial de la Tierra. Los sapropeles del Este del Mediterráneo constituyen un ejemplo excelente de la relación entre el clima y la acumulación preferencial de materia orgánica en sedimentos, y las conclusiones que allí aplican pueden ser extendidas a otros ambientes presentes y pasados.

# CHAPTER I

# Introduction and Objectives

## 1.1. INTRODUCTION

Global climate change and human-induced global warming has become a major scientific and social issue. One of the main concerns relates to the evidence that Earth surface temperature has continuously raised an average of 0.6ºC during the last decades. Alterations in animal cycles, migration of flora and fauna to higher latitudes and altitudes, or retreat of glacial fronts evidence this instability (e.g., Anisimov et al., 2002; May, 2007; Saier, 2007).The consequences of the increase in global surface temperature appear as a menace for many different ecosystems, and directly affect human societies. The instability of the atmospheric system created by this global warming is supposed to be the cause of meteorological events previously unseen, such as intensity and frequency of tornadoes or hurricanes, intense droughts, major floods, etc. These events have alerted society and promoted international committees concerned with the effects and causes of these dramatic changes (http://www.ipcc.ch/; http://unfccc.int/home/items/993.php). Although the climate system is very complex and thus climate prediction is difficult, it is well-known that the atmospheric composition, particularly its concentration in greenhouse gases (such as $CO_2$ or methane) and aerosols, determines the absorption and/or reflection of solar radiation, and thus, the surface temperature.

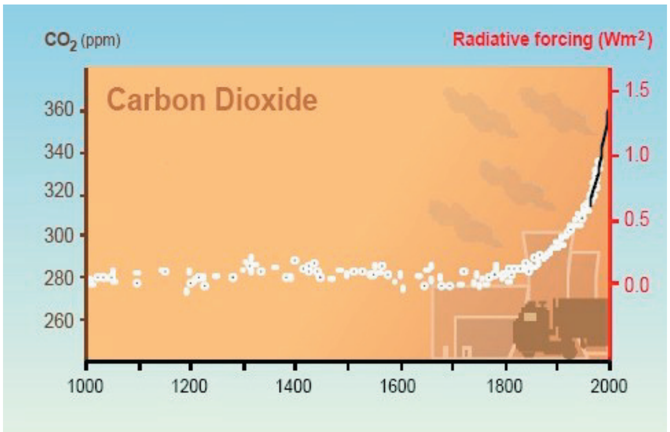


*Figure I.1. Increment of atmospheric carbon dioxide concentration during the last two centuries, modifieded from Jasen et al., 2007.*

The atmospheric concentration of $CO_2$ is assumed to exert a major control in the Earth temperature and hence in the global climate. Carbon dioxide is present on very small concentrations and minimal variations in its total content drastically affect its concentration and its behaviour. Atmospheric $CO_2$ concentration has varied through time as observed in the geologic record. Particularly the ice record provides an archive of these variations, and clearly indicates the positive correlation between $CO_2$ concentration and increasing surface temperature (e.g., Cuffey and Vimeux, 2001; Andersen et al., 2004; Cuffey, 2004) as appears clearly reflected on glacial/interglacial periods. However, these records indicate that these variations have been cyclic and progressive on the glacial/interglacial time-scales, whereas during the last centuries biomass and fossil fuel burning, associated to industrial revolution, have become a source of rapid $CO_2$ emission into the atmosphere. An increase of up to

31% in atmospheric $CO_2$ and up to 151% in methane concentration during the last three centuries manifest the anthropogenic effect on the Earth system (Andersen et al., 2004). The consequences of this abrupt (in geological time-scale) event of increased carbon dioxide and greenhouse gases in the atmosphere is still under debate, since the carbon cycle is complex, and the transits among reservoirs are not well constrained.

The carbon cycle involves atmospheric CO and $CO_2$, terrestrial and marine biomass, dissolved oceanic $CO_2$, and carbon trapped in sediments, both as inorganic phase (mainly as calcium carbonate) or organic (TOC). All these reservoirs and a wide range of interaction make the carbon cycle a complex one. (e.g., Falkowski et al., 1998; Duntas, 2007; Eliseev et al., 2007; Friend et al., 2007; Matthews and Keith, 2007; Patra et al., 2007).The oceans, due to their extension and dynamics, constitute a major carbon reservoir in the form of dissolved $CO_2$ (e.g., Bleck and Sun, 2004; Cameron et al., 2005; Gonzalez-Davila et al., 2007; Patra et al., 2007), and as inorganic and organic compounds (e.g., Falkowski et al., 1998; Bopp et al., 2001; Saliot, 2006; Tanhua et al., 2007). In this way, the oceans act as a buffer for $CO_2$ concentration in the atmosphere (e.g., Cameron et al., 2005; Saliot, 2006; Eliseev et al., 2007; Ridgwell and

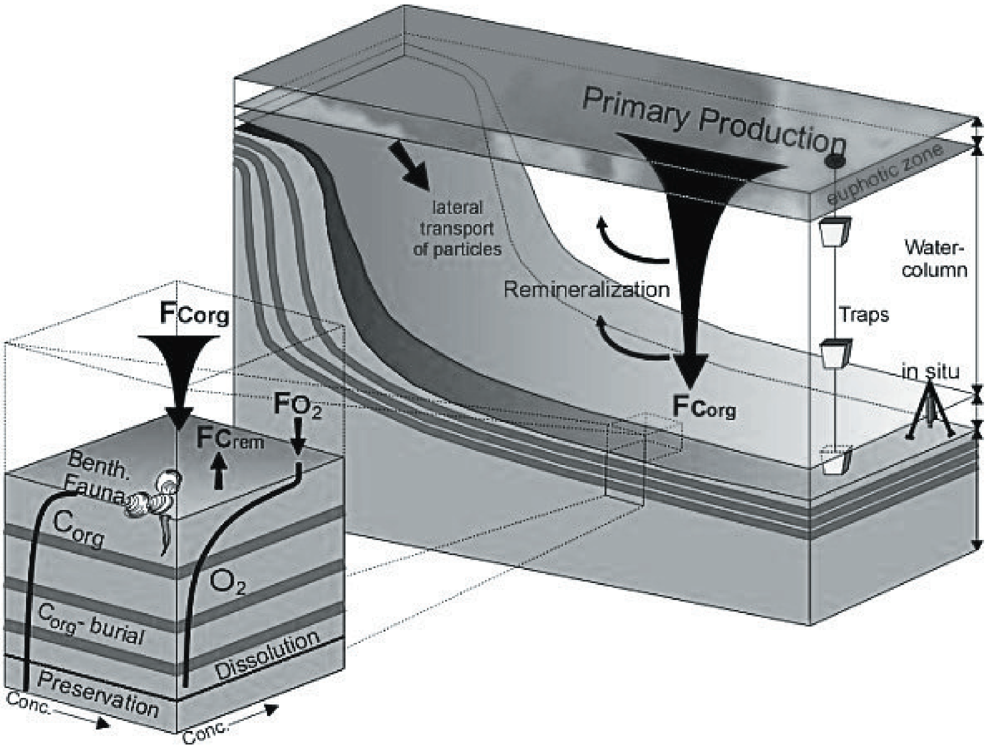


*Figure I.2. Schematic organic carbon cycle in marine system and sediments.*

Hargreaves, 2007), they being capable to storage up to 5/6 of the excess of anthropogenic $CO_2$ emissions in the form of inorganic and dissolved carbon (e.g., Maier-Reimer et al., 1996). Hence, it is obvious the necessity of improving the scientific knowledge of the marine carbon cycle in order to understand the present and future behaviour of $CO_2$ and, as an extension, that of the climate system.

Within the marine system, the biogeochemical carbon cycle is particularly important. On one side, it constitutes a major reservoir in terms of C-mass. Secondly, it is a very dynamic system that transforms enormous amount of carbon. Photosynthesis in the oceans produces up to 72 X $10^9$ t of organic carbon every year (Kuznetsov and Vinogradov, 2001), which means that 6 X $10^{12}$kg of $CO_2$ is converted into organic matter in the ocean. The efficiency of the oceanic biological pump in fixing $CO_2$ is unquestionable. However, 99% of this organic matter is consumed or recycled in the water column (Kuznetsov and Vinogradov, 2001). Only 1% is transported to the seafloor, and ca. 0.2% is accumulated in sediments, approximately half of it is transformed by diagenesis. All these processes liberate $CO_2$ as a residue of the reactions, but still 0.61 X $10^8$t of carbon, in the form of organic matter, are preserved in the sediment. Considering the data from the World Resources Institute (http://earthtrends.wri.org/index.php), more than 2% of emitted $CO_2$ is deposited on the sea floor, and more than 1% is sequestered by accumulation of organic matter in oceanic sediments every year, but rate of carbon sequestration can be as high as 20.6mg/m$^2$/d in areas of high marine productivity (e.g., Helmke et al., 2005). It is thus necessary to study the processes leading to carbon entrapment in the form of organic matter within the lithosphere, not only as a topic of scientific interest but also for its consequences for the study of the climate system and the global climate change. There is a third factor of interest; organic matter accumulated in sediments during earlier geologic periods is the origin of the main source of energy in present day society, in the form of hydrocarbons and fossil fuels. However, this carbon, accumulated during hundreds of millions of years, is rapidly being liberated back to the atmosphere, increasing $CO_2$ concentration and inducing global warming.

The *Fourth Assessment Report of the Intergovernmental Panel on Climate Change* (Solomon et al., 2007) contains a chapter on palaeoclimate (Jasen et al., 2007), and stresses the importance of the research on past trends and evolution of the climate system in order to understand the future evolution. As part of this research, carbon cycle in the past and the effect of the oceans as sink for atmospheric $CO_2$ and carbon fixation in the form of organic matter represents a major objective. Increased $CO_2$ concentration in the atmosphere increases carbon availability for biological activity, and thus, productivity blooms exert a feedback into the atmosphere and global climate. The question about this effect through the geologic history is still open for further research.

Classic interpretation of the formation of organic-rich sediments considered them as a consequence of anoxic conditions in the water column. This lack of oxygen prevented organic matter from being decomposed and became preserved in the sediment (e.g., Aller and Mackin, 1984; Thunell et al., 1984; Canfield, 1994). Black shales were the classic example of organic matter concentration in marine sediments due to *Oceanic Anoxic Events* (OAE) (e.g., Arthur and Sageman, 1994; Nijenhuis et al., 1999; Rimmer, 2003). However, the controversy arouse when Pedersen and Calvert (1990) proposed that increased marine productivity, instead of bottom water anoxia, was the key for organic matter concentration in marine sediments. This hypothesis initiated the extensive research on tracers for marine primary and export productivity (e.g., Glenn and Arthur, 1985; Dymond et al., 1992; Prahl, 1992; Meyers and Ishiwatari, 1993; Dymond and Collier, 1996; Meyers, 1997; Paytan, 1997; Fahl and Stein, 1999; Barcena et al., 2001). The study of present day regions of high productivity detected the concentration of barium in a characteristic crystal shape and size of biogenic origin (Dymond and Collier, 1996). This allowed the definition of Ba enrichment as a palaeoproductivity proxy (e.g., Dymond et al., 1992; Dymond and Collier, 1996; Paytan, 1997). This barium signature has since become a valuable geochemical tool for paleoceanographic research, tested in different environmental settings. Other inorganic and organic geochemical tracers has proven their efficiency. For example, cadmium, phosphorus, biogenic opal, organic matter isotopic composition ($\delta^{13}C$ and $\delta^{15}N$), or organic biomarkers add valuable information about paleoproductivity in marine environments. Parallel to the development of paleoproductivity proxies, the study of bottom water oxygenation and paleo-redox proxies was also improved (e.g., Thomson et al., 1993; Jones and Manning, 1994; Bertrand et al., 2003; Negri et al., 2003; Rimmer, 2003; Bond et al., 2004), providing evidence for or against the relative importance of export productivity in organic matter enriched sediments. Concentration of these elements within the sediment provides information of the re-dox state of bottom waters and sediment pore waters at the time of deposition of during early diagenesis. A third factor that is currently considered in the equation of organic matter accumulation and preservation is the sedimentation rate and *dilution factor* (e.g., Tyson, 2001; Sageman et al., 2003); at very low sedimentation rates organic carbon is decomposed, whereas if sedimentation is too intense, under normal export productivity conditions, organic carbon is diluted and present low concentration in the sediment. In any case, the debate between anoxia vs. productivity (Pedersen and Calvert, 1990) is still open and the development of more sophisticated and precise analytical methods has encouraged geochemical research providing extra information available for unresolved problems (e.g., Fossing and Jorgensen, 1989; Paytan, 1993; McManus et al., 2002; Paytan, 2004).

These unresolved problems motivated this Thesis, conceived as a multiproxy geochemical study of marine sediments particularly enriched in organic matter on recent and past oceanographic settings. The scope is to characterize these organic-rich sediments, considering as the main case of study Eastern Mediterranean sapropels. On a more global scale, four different environments were selected to carry out a reconstruction of paleoproductivity and paleoxygenation conditions of and their relevance in $C_{org}$ entrapment in marine sediments. The four selected locations represent past and present environment of favourable conditions for organic matter accumulation:

1. The Black Sea is the largest present day anoxic basin, an enclosed basin with strong vertical stratification and a shallow chemocline (e.g., Glenn and Arthur, 1985; Jorgensen et al., 1991; Glazer et al., 2006). and hence, it is a perfect natural laboratory to analyse the effect of anoxia in organic carbon sequestration in sediments.
2. Off Mauritanian upwelling system, a continental margin that has presented high productivity during the last 200ky (e.g., Helmke et al., 2005; Haslett and Smart, 2006). It thus represents the opposite scenario of prevailing increased marine productivity.
3. Eastern Mediterranean sapropels were defined by Kidd et al., (1978) and they represent climatically controlled cyclic sediments enriched in organic matter (e.g., Rossignol-Strick, 1985; Rohling and Hilgen, 1991).
4. Cretaceous black shales, traditionally interpreted as the consequence of cyclic occurrence of Oceanic Anoxic Events (e.g., Brumsack, 1980; Arthur and Sageman, 1994).

These four study cases also allow the comparison of recent and past environment and characteristic oceanographic settings, and the implications of $CO_2$ fixation on the global climate system.

With that scope, a set of geochemical proxies was applied. Barium proxies and $\delta^{13}C$ variation were used to reconstruct paleoproductivity and nutrient uptake. $\delta^{15}N$ and C:N allowed the reconstruction of nutrient recycling and palaeoecological interpretations. A wide variety of trace elements ratios served as indicators of oxygen availability and diagenetic processes. Redox proxies were first evaluated by comparing their behaviour under equal environment. Bulk and clay mineralogy, and major and trace element ratios were used to interpret sedimentological processes, such as detrital input, aeolian input or terrigenous source areas. The combination of all different proxies permits a more precise paleoceanographic reconstruction, as well as the definition of possible interaction of the different subsystems involved.

The results of this Thesis are organized in four main chapters.

Chapter III presents the Eastern Mediterranean basin and sapropel formation as a case study for organic matter accumulation. This case is particularly remarkable because it gathers many possible scenarios. The evolution of the Eastern Mediterranean basin, mainly controlled by climate cyclicity, insolation variation and changes in monsoonal activity, produced periods of reduced circulation that induced bottom water anoxia. Organic-rich levels were eventually deposited during these anoxic periods, but linked also to productivity blooms. On the other hand, recent sapropels present evidence of deposition of normally oxygenated waters, only related to productivity increase. Thus, the study of Eastern Mediterranean sapropels provides information on paleoproductivity, paleoxygenation and climate variability that makes it a particularly interesting example. Chapter III also introduces a wide vision of the evolution of the basin during the last ca. 3Ma.

Since oxygen conditions play a key role in the formation of organic-rich sediments, a profound study on paleoredox indicators was conducted. Chapter IV aims to the comparison and validation of different paleoxygenation proxies in the Eastern Mediterranean basin, and provides more detailed information of the evolution of redox conditions during sapropel deposition from Late Pliocene to Holocene.

A detailed study on paleoproductivity in the Eastern Mediterranean is exposed in Chapter V, where productivity variations and nutrients cycling are extensively discussed. This chapter presents the evolution of productivity increases in the Eastern Mediterranean at the time of sapropel formation for the last ca. 3Ma, the relationship of productivity, photic zone biota, and nutrient cycling, and the implications for sapropel formation.

The last of the results chapters is a comparison between the main case of study, Eastern Mediterranean sapropels, and different environments of preferential organic matter accumulation; one present day example of a basin governed by anoxic conditions (Black Sea), a late Quaternary example from an area controlled by intense productivity (NW Africa upwelling system), and an ancient case of organic matter accumulation during Oceanic Anoxic Events (black shales). This comparison extends the discussion of organic matter enrichment in sediments to past times and to different areas.

## 1.2. OBJECTIVES

As exposed on the previous section, social concern for the global carbon cycle and climate change, scientific interest of paleoceanographic reconstructions, in general, and organic matter accumulations interpretations, in particular, as well as the rapid advance in the development of new paleoceanographic proxies, concentrated the attention for this Thesis, and set the following general objectives:

**1.** Reconstruction of nutrient fluxes, carbon fixation in the form of organic matter and paleoproductivity variations in different paleoceanographic settings.

**2.** Comparison between present-day favourable environments for organic matter accumulation and ancient equivalents from the geologic record.

**3.** Evaluation of the role of productivity versus anoxia in the accumulation and preservation of organic matter in marine sediments from different paleoenvironmental settings and periods across the geologic record.

**4.** Establishment of relationships between variations in marine productivity and atmospheric carbon uptake, and implications for global climate evolution.

In order to accomplish these objectives, the following specific goals have also been defined:

**5.** Compilation and evaluation of a set of geochemical proxies that allow the reconstruction of paleoproductivity and deep water ventilation.

**6.** Comparison of reliability of each proxy on different paleoenvironmental conditions.

**7.** Characterization of mineralogical and geochemical sediment composition and its relationship with organic matter concentration in the sediment.

**8.** Reconstruction of oxygenation conditions in the water column, particularly in bottom waters, during $C_{org}$-rich sediments deposition and implications in deep waters circulation and main oceanographic currents distribution.

**9.** Reconstruction of eventual diagenetic processes occurring in $C_{org}$ enriched sediments, remobilization of major and trace elements, and implications in deep water ventilation and circulation.

# CHAPTER II

# Materials and Methods

## 2.1. MATERIALS

### 2.1.1 Eastern Mediterranean Sapropels

The Eastern Mediterranean basin was studied at four Sites drilled during Leg 160 of the Ocean Drilling Program (ODP) (Emeis et al., 1996). Site 964 is located on the Pisano Plateau, in the Ionian Basin, at a water depth of 3658 mbsl. This geographic position is close to the confluence of Adriatic and Western Mediterranean waters incoming into the Eastern Mediterranean Sea. Sites 966 and 967 are both on the Levantine Basin, easternmost Mediterranean, at relatively short distance from the main fresh-water source of the basin, the Nile River, but they are located at different water depths: Site 966 is on top of the Eratosthenes Seamount, at a water depth of 926 mbsl, whereas Site 967 was drilled on the deep basin at 2555 mbsl. Being on a tectonic high, Site 966 is not directly affected by the deltaic fan deposits from the Nile River, and sediments recovered at this location provide an undisturbed paleoceanographic signal. Besides, due to its shallower water depth, it is more sensitive to changes in the formation of intermediate water circulation (Levantine Intermediate Waters). Site 967, northward of Site 966, registers the influence of the Nile River influence and minor turbidites from the north. It contains the deep equivalent of the section on the Eratosthenes Seamount, and thus, provides information of the influence of water depth in sapropel formation. The last studied site, Site 969, is located on the Mediterranean Ridge, at a water depth of 2200 mbsl. It is the central position in the Eastern Mediterranean basin, and the tie point between Ionian and Levantine basins.

Sediments recovered on all four sites are very similar, mainly composed of nannofossil ooze and nannofossil clay, with cyclically interbedded sapropels layers, dark olive green to black in color, frequently laminated (Emeis et al., 1996).

On the Pisano Plateau 9 sapropels levels were studied, covering Upper Pliocene, Upper Pleistocene and Holocene ages (see Table II.1). Only Quaternary sapropels were sampled at the Eratosthenes Seamount, Holocene and Upper Pleistocene in age. Site 967, on the deep Levantine basin was sampled for latest Pliocene (from 1.872 to 1.715Ma), Upper Pleistocene and Holocene sapropels. Finally, a total of 10 sapropels from Upper Pliocene, the transit Pliocene-Pleistocene, Upper Pleistocene, and Holocene ages, were sampled in the Mediterranean Ridge.

### 2.1.2. Black Sea sapropel

Core MD04-2770 was recovered during the ASSEMBLAGE 2004 Campaign on board of the R/V Marion Dufresne, on the Bulgarian Black Sea shelf at a water depth of 358 mbsl. Recovered sequence includes a lacustrine section of dark grey to greenish grey banded calcareous clays. This is overlapped with greenish-grey mud with scarce shell debris, and a clear marine section, composed of olive green, laminated mud transitioning to dark green laminated mud. The sapropel layer appeares between 0.43 and 0.85 (mcd) within the marine sequence

### 2.1.3. Cretaceous Black Shales

Two sections of Cretaceous black shales were sampled from cores recovered during ODP Leg 207 in the Demerara Rise, and Leg 210 in the Newfoundland platform.

Leg 207 specifically goaled the recovering of black shales strata deposited during the early stages of the opening of the Atlantic Ocean that represent different Oceanic Anoxic Events (Erbarcher et al., 2004). At Site 1258, drilled at 3192 mbsl, more than 50 meters of laminated black shales and limestones were recovered, covering an age span between Late Albian to Turonian. The section includes the Cenomanian-Turonian boundary, OAE 2, and defined as Unit IV (Erbarcher et al., 2004), is dark olive-gray to black, finely laminated calcareous claystone and clayey chalk and limestones with organic matter in variable amounts.

In the Newfoundland platform, the Mesozoic sedimentary record represents the syn-rift deposits of the Northwestern margin of the early Atlantic Ocean. As part of this sequence, black shales appears as decimetre-scale layers of finely laminated claystones interbedded in calcareous claystones and marlstones (Unit 5A in Tucholke et al., 2004). These strata also correspond to OAE 2, and have similar age as the above mentioned black shales of the Demerara Rise. At Site 1276, at water depth of 4549 mbsl, black shales appears at approximately 1100 mbsf, and represent ca. 5% of the total Unit 5A.

| | | | Site 964 3658 (mbsl) Pissano Plateau | Site 969 2200 (mbsl) Mediterranean Ridge | 967 2555 (mbsl) Levantine Basin | 966 926 (mbsl) Eretosthenes Seamount |
|---|---|---|---|---|---|---|
| Sapropel | i-cycle | Age | | | | |
| S1 | 2 | 8 ky | ▨ | ▨ | ▨ | ▨ |
| S3 | 8 | 81 ky | | | ▨ | ▨ |
| S4 | 12 | 124 ky | ▨ | ▨ | ▨ | |
| S5 | 16 | 172 ky | | ▨ | | ▨ |
| S6 | 16 | 172 ky | ▨ | ▨ | | ▨ |
| S7 | 18 | 195 ky | ▨ | ▨ | ▨ | ▨ |
| S8 | 20 | 217 ky | ▨ | | | ▨ |
| ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| S27? | 152 | 1.564 Ma | | ▨ | | |
| S28? | 156 | 1.604 Ma | | ▨ | | |
| S29? | 160 | 1.643 Ma | | ▨ | | |
| ? | 168 | 1.715 Ma | | | ▨ | |
| ? | 176 | 1.808 Ma | | | ▨ | |
| ? | 178 | 1.829 Ma | | | ▨ | |
| ? | 180 | 1.851 Ma | | | ▨ | |
| ? | 182 | 1.872 Ma | | | ▨ | |
| ■ | ■ | ■ | ■ | ■ | ■ | ■ |
| S 49 | 272 | 2.828 Ma | ▨ | | | |
| S50? | 280 | 2.923 Ma | | ▨ | | |
| S 52 | 282 | 2.943 Ma | ▨ | | | |
| S 53 | 284 | 2.965 Ma | ▨ | ▨ | | |
| S 54 | 286 | 2.989 Ma | ▨ | | | |

*Table II.1. Location, ages and correlation of studied sapropels. Shaded squares correspond to sampled sapropels.*

### 2.1.4. Northwest African Upwelling System

Gravity core GeoB7926-2 was recovered at ca. 2500m water depth off Mauritania during the Meteor 53/1 cruise. This area on the Northwest African margin is an intense upwelling system that since early Quaternary times. Sediments of GeoB7926.2 are mainly composed of olive green to olive grey and light grey claystone, with a predominant mineralogical composition of clays, calcite, quartz and minor feldspars. Aragonite appears, especially in the upper part of the core, and substantial pyrite content on determined levels. This core contains a continuous high-sedimentation rate sequence, for the last ca. 50ky, with an average sedimentation rate of 95cm/ky that allows high resolution studies in an area of intense productivity and rapid variations.

## 2.2. METHODS

### 2.2.1. Sampling

*2.2.1.1. Mediterranean Sapropels:*

Eastern Mediterranean sediments were sampled at the IODP Core Repository Bremen (Germany). Selected sapropels and background sediments above and below the TOC-enriched layer were sampled every 2cm. Where possible and on the contacts between sapropels and background sediment, samples were subdivided down to 0.5cm thick sub-samples in order to obtain higher resolution.

*2.2.1.2. Black Sea Sapropel:*

Core MD04-2770 was sampled continuously every 2cm from top to 5mcd, and every 5cm from that depth onward. Only the top 3 metres (mcd) are considered on this Thesis.

*2.2.1.3. Cretaceous Black Shales:*

Black Shales samples were provide (upon request) by the IODP Core Repository Bremen (Germany). Samples were obtained continuously along requested sections every 2cm.

*2.2.1.4. GeoB 7926-2:*

This core was sampled at temporal high resolution, every 5cm continuously on selected sections. According to the age model, a 5cm interval corresponds to an age difference between 10 and 100 years in the upper section, and ~150 years in the lower section.

### 2.2.2. Analytical Methods and Sample Preparation

*2.2.2.1. Bulk and Clay Mineralogy:*

Mineralogy of the total sample and the clay fraction were determined by X-Ray diffraction (XRD) using a Phillip PW 1710 diffractometer at the Departamento de Mineralogía y Petrología, Universidad de Granada.

a) *Sample Preparation:*

For determination of bulk mineralogy, samples were dried in a ventilated heater at 50ºC for 24 hours, and homogenized on an agate mortar and/or a micromill RETSCH MM 301. The resulting powder samples were packed on aluminium holders for XRD analyses.

The clay fraction was separated following the procedure described by Kirsch (1991). Carbonate fraction was eliminated by acetic acid reaction at low concentration (0.1N) on the first step and progressively higher concentration (up to 1N), depending on carbonate content. Decarbonated samples were successively washed with demineralised water for deflocculation, adding 0.001 mo/l sodium hexametaphosphate solution. Clay fraction (<2 µm) was separated, following the application of the Stoke's law by centrifuging at 9000 rpm for 1.3 minutes, at least 4 times, on a KUBOTA KS 800 device. Extracted clay fraction was washed with pure water in order to eliminate the dispersing agent. Suspended clay fraction was smeared onto glass slides in order to allow orientation of clay minerals with crystallographic axis perpendicular to the glass slide so that (001) refractions are improved. Two glass slides were prepared for each sample. The first one was analyzed as a raw orientate aggregate (AOA) after air dried. The second was glicolated by heating at 60ºC for 48 hours in etilenglycol atmosphere (EG), in order to expand smectites and expansive clays.

*b) Analyses:*

For XRD analyses the instrument conditions were set as follows:

Radiation: Cu-Ka
Filter: Ni
Window slit: 1º
Slit counter: 0.1º
Time constant: 0.2

Exploration speed: 6º 2θ/min
Voltage; 40 Kv
Intensity: 40 mA
Sensibility: 5 X $10^{-3}$

Scan range were 2-64º 2θ for bulk and AOA samples, and 2-30º 2θ for EG samples.

*c) Phase identification and semi-quantitative analysis:*

Identification of different mineral phases was carried out using X-Powder software, (Martin-Ramos 2004). Diffraction peaks were compared to Powder Data File (PDF) from the *Joint Committee of Powder Diffraction Standards*. For clay mineralogy, identification of smectites was done by comparison between AOA and EG, since smectites expand and increase their interlaminae separation. Kaolinite and chlorite present their maximum intensity peak at very close angles (7.16Å for kaolinite, 7.10 Å for chlorite), and thus in order to discern the two phases, the (003) peak was used (3.58 Å for kaolinte and 3.55 Å for chlorite) (Moore and Reynolds, 1997).

Semiquantitative analysis was carried out using peak areas, corrected by the reflectance for each mineral phase (see Table II.2). Estimated error of semiquantitative analysis is 5% for bulk mineralogy and 5% to 10% for the clay fraction.

### *2.2.2.2. Field Emission Scanning Electronic Microscopy (FE-SEM).*

Morphological analyses of particular mineral phases were done under a Leo Gemini 1530 FE-SEM, at the *Centro de Instrumentación Científica (CIC)*. Dried samples slightly homogenized were placed on an aluminium base and fixed with carbon adhesive, then metallised in a Hitachi UHS with a thin carbon layer. FE-SEM allows higher magnification thanks to a tension range between 0.1 and 30 kv, and a zoom 20X to 5000000X that provides a maximum resolution of 1nm. A microanalysis device of backscattered electrons also allowed the determination of mineral composition

| Mineral | Reflectance | Reflection (Å) |
|---|---|---|
| Quartz | 1.43 | 3.34 |
| Calcite | 1.05 | 3.03 |
| Clay Minerals | 0.09 | 4.45 |
| Feldspars | 1.03 | 3.18 |
| Dolomite | 1.05 | 3.93 |
| Illite | 0.36 | 10 |
| Smectites | 0.98 | 17 |
| Kaolinite+Chlorite | 0.98 | 7.1 |

*Table II.2. Reflectance and maximum intensity reflection of the principal identified minerals under XRD.*

#### *2.2.2.3. High Resolution Transmission Electron Microscopy (HR-TEM).*

HR-TEM allowed the analysis of chemical composition of clay minerals. Samples were diluted on pure ethyl alcohol and prepared on a gold grid. The analyses were carried out at the CIC, with a Philips CM-20 STEM device with a $Ba_6La$ filament, and up to 200kV acceleration potential. This allows a resolution of 50 Å under STEM mode. An attached EDX detector was used for microanalyses and a CCD camera for image capturing. Analytical window used was a 1 X 1μm in order to avoid alkaline volatilization (mainly Na and K) (Nieto et al., 1996). Atomic proportions calculated from peak intensity was transformed into atomic concentrations using natural standards (albite, biotite, espesartine, muscovite, olivine, titanite, MnS and CaS) (Cliff and Lorimer, 1975).

#### *2.2.2.4. Inductively Coupled Plasma Mass-Spectrometer (ICP-MS).*

Trace elements were analyzed by ICP-MS technique at the CIC. Samples were prepared by sequential acid digestion with $NHO_3$ and HF. 100mg of powder sample was dissolved in 2ml of $HNO_3$ and after reaction, 3ml of HF. The resultant dilution was heated until total evaporation and then re-dissolved in 1ml of $HNO_3$ twice. The final residue was dissolved in 4ml of $HNO_3$+96ml of ultrapure water. 1ml of this dissolution was mixed with 0.5ml of a 200ppb Rh dilution (as internal standard) and 8.5ml of ultrapure water and injected in a Perkin Elmer-Siex ELAM 5000 ICP-MS. Natural standard prepared with the same sample procedure were intercalated to calibrate analyses. ICP-MS provided analytical results for Li, Rb, Cs, Be, Sr, Ba, V, Cr,Co,Ni, Cu,Zn,Ga,Y, Nb,Ta,Zr, Hf, Mo,Sn,Tl,Pb, U, Th, La, Ce,Pr,Nd, Sm,Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. Instrumental error is ±2% and ±5% for elemental concentrations of 50 and 5 ppm respectively (Bea, 1996).

#### *2.2.2.5. Atomic Absorption (AA).*

Major elements for Eastern Mediterranean and Black Sea samples were measured using a Perkin Elmer mod. 5100 Atomic Absorption Spectrometer with a C chamber, mod 5100 ZEEMAN and a FIAS-100 injector, at the CIC. Injected samples were the same dissolution prepared for ICP-MS analysis. Detection limit is 0.1ppm and analytical error is <2%.

#### *2.2.2.6. X-Ray Fluorescence (XRF.)*

Major elements for Cretaceous black shales were analyzed with the XRF technique, using a S4 Pioneer Bruker AXS device at the *Instituto Andaluz de Ciencias de la Tierra*, (IACT) CSIC-

Universidad de Granada. Samples were homogenized and mixed with a binder (wax) and then pressed into aluminium cups with boric acid backing to produce a 50mm homogenous equal density pellet. The S4 device is provided with a 4kW excitation source that allows higher analytical precision. Interpretation of raw data was done using Bruker-designed software SPECTRA plus.

#### *2.2.2.6. Elemental Analysis (EA).*

Total Carbon (TC), Total Organic Carbon (TOC), Total Nitrogen (TN) and Total Sulphur (TS) were measured following different procedures at different laboratories.

At Stable Isotope Lab, Geological and Environmental Sciences Department, Stanford University, Eastern Mediterranean samples were measured for TC and TOC, and TN using a using a Carlo Erba (now CE Elantech, Inc.) NA1500 Series II Elemental Analyzer. Dried samples were directly introduced in the elemental analyzer for TC and TN. For TOC measurements samples were repeatedly acidified with cold $HSO_3$ until no bubbling was visible under binocular lenses, in order to eliminate inorganic carbon.

Samples from ODP Legs 207 and 210 and from GeoB7926 core were analyzed for TC and TOC at the University of Bremen using a Heraeus CNH-O Rapid elemental analyzer by total combustion at 1050ºC. The elimination of inorganic carbon was done by repeated acidification with 1N HCl.

TN and TS analyses were performed at the Biogeochemistry Department of Max Planck Institute für Marine Mikrobiologie. Samples were prepared with $VO_6$ in order to optimize combustion, and introduced into a Carlo Erba Elemental Analyzer at 1050ºC combustion temperature.

#### *2.2.2.7. Carbon and Nitrogen isotopic composition ($\delta^{13}C$ and $\delta^{15}N$).*

Isotopic composition of the organic matter ($\delta^{13}C$ and $\delta^{15}N$) were analyzed at Stable Isotope Lab, Stanford University, following the procedure described by Mucciaroni (2003). The analytic device was a Finnigan MAT isotope ratio mass spectrometer (IRMS) connected to a Carlo Erba (now CE Elantech, Inc.) NA1500 Series II Elemental Analyzer. Analyzed samples were the same as for TOC analysis in the same lab (see 2.2.2.6) and thus the same preparation applies.

# CHAPTER III

# Spatial and temporal variability of Eastern Mediterranean sapropels: basin-wide trends of mineral and trace metal signatures

## ***Abstract***

*Eastern Mediterranean sedimentation has been characterized by the deposition of sapropel layers. The origin of these carbon-rich layers has been widely discussed. The most generally accepted scenario for sapropel deposition includes the increase in surface productivity, mostly associated to higher nutrient input from river drainage, which led to increasing oxygen consumption and finally to Corg accumulation in sediments. However, when comparing sapropels from different periods and locations, regional and temporal differences are obvious. Thus, representative settings in the basin have been analyzed within a four site transect in order to investigate the spatial and temporal evolution of sapropel formation. At these sites, sediments, covering an age span between ~2.9 Ma to recent, were recovered during ODP Leg 160 and cover the areas of preferential influence from the northern margin, the Nile River dominance, a pelagic high and almost a central location of the eastern basin. Geochemical proxies evidence that the proximity to the Nile River debaucher, to the African continent or to the northern margin exert a geographic control in sapropel expression in terms of sedimentary regime, timing of sapropel development, oxygenation and, to a lesser extend, primary productivity. Bathymetric differences are obvious for all aspects, being sapropel development more intense in deep waters. Temporal evolution in the basin evidence a progressive enhanced in deep water ventilation from Pliocene to Holocene, a parallel increase in sedimentation rate and thus detrital input, and a consistent increase in intensified productivity during sapropel formation from Pliocene to Late Pleistocene. All these evidences suggest a progressive intensification of basin circulation for the last ~2.9 Ma, primarily detected on sapropel deposition events.*

## 1. Introduction

Eastern Mediterranean sapropels have been a case study for organic matter accumulation and preservation in marine basins for the last three decades (e.g., Jenkins and Williams, 1984; Mangini and Schlosser, 1986; Rohling and Hilgen, 1991; Aksu et al., 1995; Emeis et al., 1996; Jung et al., 1997; Diester-Haass et al., 1998; Emeis et al., 2000a; Menzel et al., 2002; Negri et al., 2003). Formation of these cyclically deposited organic-enriched levels (Kidd et al., 1978) is controlled by astronomical precesional cycles (Hilgen, 1991). The oceanographic setting in which these layers formed and their cyclic deposition characteristics made them a particularly interesting topic for both paleoceanographic and climatic studies. Despite extensive research of these events, the oceanographic conditions that leaded to sapropel formation are still a matter of debate. Two distinct interpretations have been proposed for sapropel formation; the first calls for water column stratification and anoxic bottom waters resulting from sluggish circulation (e.g., Thunell et al., 1984; Rohling and Hilgen, 1991; Menzel et al., 2002; Negri et al., 2003), and on the other, invokes increased productivity and carbon burial (e.g., Diester-Haass et al., 1998; Martínez-Ruiz et al., 2000; Weldeab et al., 2003a; Slomp et al., 2004; Meyers and Arnaboldi, 2005). These scenarios are not mutually exclusive and a combined model (e.g., Calvert, 1992; Rinna et al., 2002; Filippelli et al., 2003; Gallego-Torres, 2004; Slomp et al., 2004) currently appears as the most plausible scenario. This model suggests increased export production inducing greater oxygen consumption in deep waters resulting in local anoxic environment in the sediment-water interface which further increase organic matter preservation. However, this model is not constant through time. Indeed, remarkable differences arise when Pliocene sapropels are compared with younger equivalents. These differences have been previously explored by different authors (e.g., Emeis et al., 1991; Passier et al., 1999; Rutten et al., 1999; Martinez-Ruiz et al., 2003; Menzel et al., 2003). Collectively it has been demonstrated that the Eastern Mediterranean basin has evolved from restricted circulation during the Pliocene to greater ventilation from Upper Pleistocene to Holocene. From the spatial point of view, regional variations in sapropel expression are also visible (e.g., Nijenhuis et al., 2001; Meyers and Arnaboldi, 2005). The onset of sapropel formation appears to be controlled by enhanced river discharge from the Nile manifesting itself in the Eastern basin and then spreading to more western locations. Thus, the aerial influence of the Nile, as well as water depth and other local conditions, modify the sapropel expression in different locations (e.g., Murat and Got, 2000; Nijenhuis et al., 2001; Meyers and Arnaboldi, 2005). Although sapropels are deposited both in platform environment (between Western and Eastern Mediterranean) and in deep basinal settings across the basin, depositional conditions are substantially different for each oceanographic setting. Accordingly, it is important to study the specific differences between sapropel deposition at the various settings. The differences between platform and hemipelagic sapropel deposition were highlighted by Meyers and Bernasconi (2005). However, important differences within the pelagic environment related to basin dynamics and the intensity of the main currents which induced spatial variations linked to sediments and nutrient distribution across the basin may also results in variability among deep water sapropels. With this scope, a set of 4 sites drilled during ODP Leg 160 were selected to construct a transect across the

Eastern Mediterranean basin. These four locations include the most representative settings in the basin, covering the areas of (1) influence from the northern margin, (2) Nile River dominance, (3) a pelagic high and (4) a central location within the Eastern Mediterranean basin (Fig. 1 and Table III.1). The study includes several layers from each site that represent the temporal evolution of sedimentary conditions at the time of sapropel formation. We present geochemical data that provides a reconstruction of the transition of the Eastern Mediterranean basin from late Pliocene to Holocene at the time of sapropel deposition and highlight the evolution along the basin. The aim of this multiproxy study is to characterize the local and regional climatic-oceanographic conditions that induced sapropel formation, with special emphasis on progressive changes in deep water ventilation patterns during the last ~3My.

## 2. Materials and methods

A transect across the Eastern Mediterranean has been studied using samples from cores recovered during ODP Leg 160. We selected four locations representing different paleoceanographic environments (Fig. 1). Site 964 is located in a deep marine setting (3658 mbsl) on the Pisano Plateau (Ionian Basin), and is influenced by the Adriatic Sea and currents coming from the Western Mediterranean basin through the Strait of Sicily. Site 969, located on the Mediterranean Ridge at a water depth of 2200 mbsl, represents the centermost location in the Eastern Mediterranean. Sites 966 and 967 are located on the Levantine Basin. Site 967 contains a sequence of deep pelagic sediments (2555 mbsl), although detrital influence is greater than the previously mentioned sites, since it is influenced by the Nile River plume. Site 966 is situated near Site 967 on a pelagic high on the Eratosthenes Seamount at a relatively shallow water depth of 926 mbsl. The sediments in these cores are composed mostly of nannofossil clay, clayey nannofossil ooze and nannofossil ooze with some intervals of clay and foraminifera sand, variably bioturbated (Emeis et al., 1996; Emeis et al., 2000a). Dark colored to black sapropel layers appear periodically interspersed throughout the pelagic sediments. Representative total organic carbon (TOC) enriched sediments and sections of the overlying and underlying sediments in these cores were sampled at 2 cm intervals. A finer resolution sampling was carried out close to the contacts between TOC-rich and "background" sediments. TOC measurements were made using a *Perkin-Elmer Elemental analyzer* at the Stable Isotope Laboratory (Stanford University), after progressive acidification with $H_2SO_3$, and also at Bremen University, acidifying with 1N HCl, using a TC/TOC analyzer. Major elements (Al, Ca, Mg, Fe, Mn, K) were determined by atomic absorption spectrometry at the Analytical Facilities of the University of Granada. Trace elements were measured with an ICP-MS Perkin-Elmer Sciex Elan 5000 spectrometer (CIC; Analytical Facilities of the University of Granada), using Re and Rh as internal standards. These analyses were carried out after $HNO_3$ and HF digestion. Coefficients of variation calculated by dissolution and subsequent analyses of 10 replicates of powdered samples were better than 3% and 8% for analyte concentrations of 50 and 5 ppm respectively (Bea, 1996). Bulk and clay mineralogy were determined using a Phillips PW1710 difractometer in the Mineralogy Department, University of Granada, and resulting difractograms were interpreted using XPowder software (Martin-Ramos, 2004). Samples were prepared following the recommendations by Kirsch (1991). In order to determine the chemical composition of clay minerals, selected samples were suspended in ethanol, the finest fraction recovered onto a gold grid, and analyzed under High Resolution TEM (STEM PHILIPS CM20, CIC, University of Granada). For the morphological description of marine barite, selected samples were observed under Field Emission SEM (LEO Gemini 1530, CIC, University of Granada) using Backscattered and Secondary Electrons images. Mineral phase composition was determined by an X-Ray dispersion microanalysis coupled to the device.

TOC and Ba mass accumulation rates (MAR) were calculated based on the sediment dry bulk

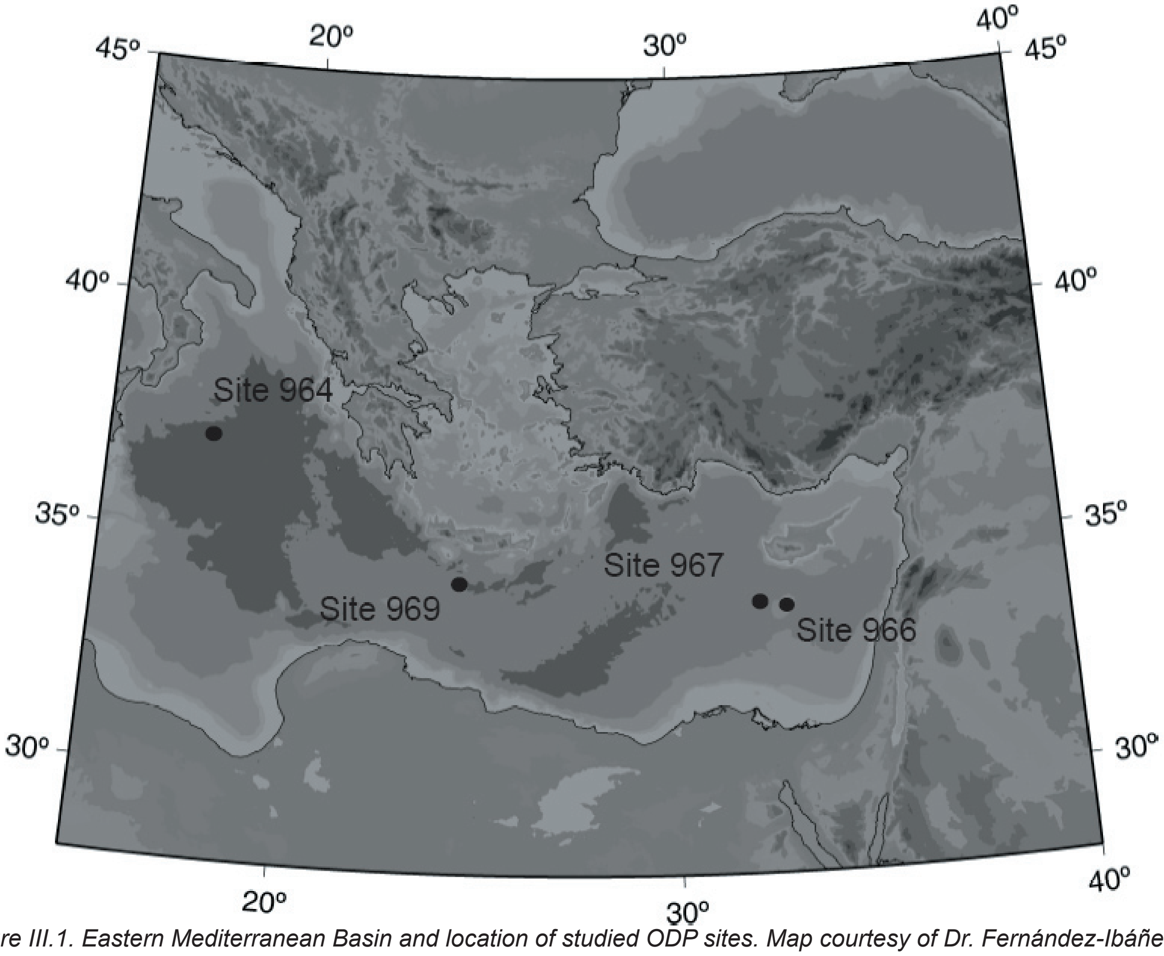


*Figure III.1. Eastern Mediterranean Basin and location of studied ODP sites. Map courtesy of Dr. Fernández-Ibáñez.*

Samples were dried and ground in an agate mortar, homogenized and prepared for geochemical and mineralogical analyses. Representative sample portions were used to determine bulk and clay mineralogy, TOC and nitrogen (N) contents as well as major and trace element concentrations. High Resolution electron microscopy (transmission and scanning) analyses were also performed on selected samples.

density (DBD) obtained from ODP Leg 160 database (available online; http://www-odp.tamu.edu/) and linear sedimentation rates (LSR) calculated for our particular sampling intervals. We based our calculation on the methodology used by Meyers and Arnaboldi (2005). According to these authors, the peak TOC concentration measured in each sapropel layer is assumed to represent the orbitally tuned age of the corresponding insolation cycle. The difference in core depths between successive sapropel layers was then divided by the ~21 ky of each precessional cycle to obtain calculated ages. Linear sedimentation rate is then calculated based on these ages.

## 3. Results on paleocenographic proxies

### 3.1. Productivity; Ba/Al and TOC.

Reconstruction of paleoproductivity based on Ba/Al ratios, Total Organic Carbon (TOC) content and their correspondent Mass Accumulation Rates (MAR).

TOC concentration in sampled sediments ranges from less than 0.05% to 28.40%, with the highest values detected in Pliocene sapropels in all studied sections (see Figures 2 to 9). The general trend consists of a progressive increase in organic carbon content within the sapropel from the Holocene through the Pleistocene and into the Pliocene sapropels, although the accumulation rate of organic carbon is generally higher during the upper Pleistocene.

Barium proxies, considered as reliable indication of paleoproductivity (e.g., Dehairs et al., 1987; Paytan, 1993; Dymond and Collier, 1996; Paytan, 1997; McManus et al., 1999; Paytan, 2004), were successfully applied in the Mediterranean Sea (e.g., Wehausen and Brumsack, 1999; Martínez-Ruiz et al., 2000; Weldeab et al., 2003b). In the analyzed sapropel intervals, Ba/Al ratios exhibit a nearly parallel trend to TOC, except for the significant difference that high Ba sections frequently extend over the top of the organic enriched layer in Quaternary sapropels. This case is especially visible in sapropels sampled in core 966A, recovered at the Eratosthenes seamount. These layers show a distinct offset between the organic carbon accumulation and the productivity signal as represented by Ba/Al. Ba and TOC show the best fit in terms of timing and extend of the event in the sections sampled in cores 967D and 967C, geographically adjacent to site 966 but in the deep basin.
Ba-MARs exhibit maxima for upper Pleistocene sapropels in all sampled sections except for section at site 967, where the Holocene sapropel 1 presents higher Ba-MARs than the older sapropels. Highest MARs coincides with maximum LSR's at all four studied locations.

Comparing different locations, the highest Ba-MARs are found at the Mediterranean Ridge, (Site 969), located in the center of the basin, although the maximum TOC-MAR corresponds to the Ionian basin (Site 964). During the Upper Pleistocene, productivity, indicated by Ba-MAR, is higher at the eastern sites in the deep basin (sites 967 and 969) and slightly lower on the westernmost East Mediterranean (site 964), whereas accumulation rate of $C_{org}$ is generally higher in the Ionian basin. The shallower site 966 systematically exhibit lower TOC/Ba-MARs. As for Pliocene and Early Pleistocene, both Ba and TOC MARs are generally lower. During this period, the Ionian basin shows the higher values for both proxies compared to other sampled sites.

For sapropels deposited during the same insolation cycle, (e.g., Figs. 1, 4 or 7) the magnitude of increase in Ba content and Ba-MAR are similar for the 3 sites located in the deeper parts of the basin, but these are notably lower for the core recovered at the Eratosthenes seamount (site 966). During the Pliocene, the deepest site (964) exhibit the maximum increases in Ba and TOC.

### 3.2. Detrital input

Fe/Al, Zr/Al, Mg/Al, Ca/Al and La/Lu ratios as well as mineral composition have been used as proxies for the reconstruction of detrital and eolian input. Total and clay mineralogy allows the reconstruction of detrital input and basic current dynamics in the Mediterranean (e.g., Maldonado and Stanley, 1981; Rossignol-Strick, 1985; Diester-Haass et al., 1998; Krom et al., 1999). Kaolinite vs. illite fraction represents the fluctuations of aeolian input from North Africa, since kaolinite in the basin arrives predominantly by wind storms from the south (Diester-Haass et al., 1998), whereas chlorite and smectite come from riverine input from the European margin, (e.g., Maldonado and Stanley, 1981; Rossignol-Strick, 1985; Martínez-Ruiz et al., 2000). Other mineralogical indicators such as presence of fibrous minerals (sepiolite and/or paligorskite) are also considered (Diester-Haass et al., 1998) as indicators of wind activity, preferentially coming from meridian latitudes. The results obtained from X-Ray diffraction show a clear relative increase of the clay mineral percentage during sapropel deposition, and within this clay fraction, a particular increase in illite, chlorite and smectite and decrease in kaolinite (e.g., Maldonado and Stanley, 1981; Ehrmann et al., 2007). TEM observations also evidence that fibrous minerals are rare or absent in sapropel layers. As for the geochemical indexes, high Zr/Al is indicative of aeolian input while lower La/Lu ratio indicates more intense drainage of the African craton through the Nile River (Hamroush and Stanley, 1990). A sharp decrease in La/Lu ratio is detected coinciding with each sampled sapropel, especially in the deep marine settings (Figures 2 to 9). Parallel to this tendency, Zr/Al content usually decreases during sapropel formation, although this trend seems to have a strong geographic control. Sites located closer in the deep basin close to the Nile river delta, 969 and 967, show a clearer tendency than sites 966, situated on a pelagic high, and 964, far from the direct Nile influence. The shift to lower values of the La/Lu ratio is notable on all sampled sapropels, independently of the age, and only punctual anomalies to this trend are visible, for example, sapropel 272 (~2.825Ma) presents

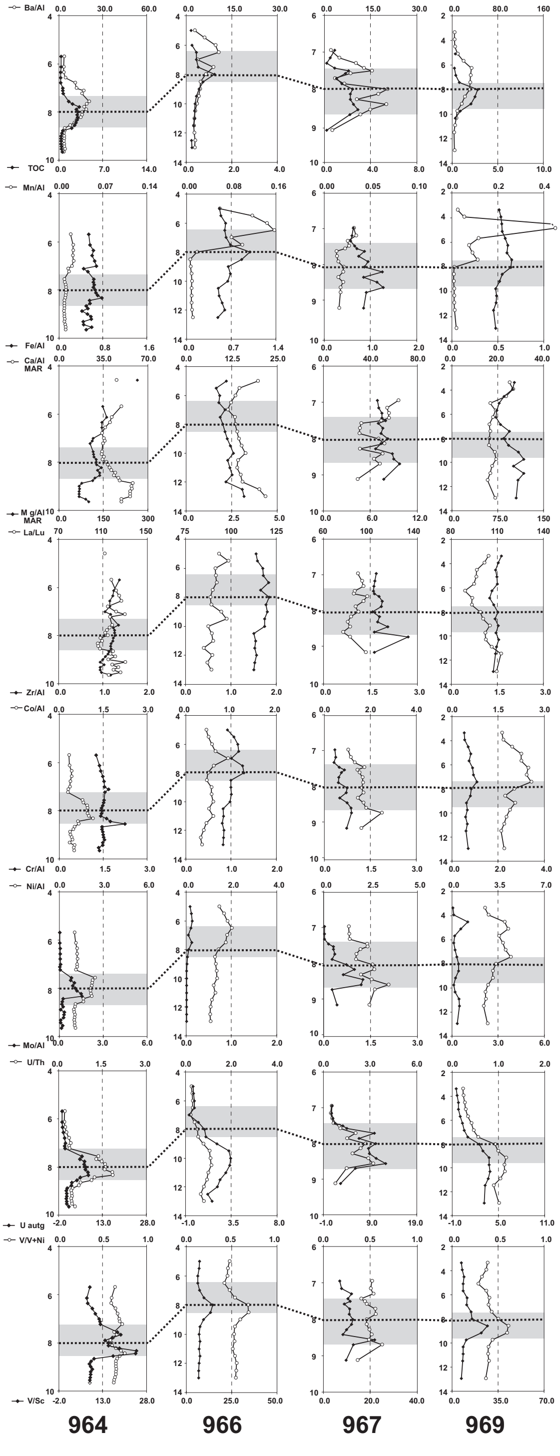


*Figure III.2. Geochemical signals for deposition of sapropel 1.*

lower La/Lu ratio above the sapropel (Fig. 9). In some other cases, such as S4 (i-cycle 10) La/Lu ratio presents a shift to lower values within the TOC-rich level, or a fluctuating trend, such as in sapropel 3 (i-cycle 8) on the Eratosthenes seamount (Figs. 3 and 4). Regionally, La/Lu values are generally higher on the Ionian basin, closer to the Western Mediterranean and the European continent, and lower values are described on the eastern part of the basin, with minima on the Mediterranean Ridge. Bathymetry does not substantially affect the signal of La/Lu, since adjacent sites 966 (Eratosthenes Seamount) and 967 (deep Levantine basin) present similar values, slightly higher on the pelagic values.

To evaluate the degree on Nile input compare to other terrestrial sources we use Mg and La/Lu to determine the dominant source of detrital material. Mg, as mentioned before, is deposited in association with chlorite, which is preferentially arriving from the European margin. La/Lu value provides information of the balance between Northern and Southern margins input. A comparison between the two proxies is plotted in figure 10.

Ca/Al MAR, shows a decrease in the sapropel layers clearly visible in cores recovered on the Ionian basin (site 964) and site at 966, on the pelagic seamount. However, this behaviour is not constant across the basin. For Pliocene intervals, the decrease in Ca/Al in sapropel levels is constant basin wide, for all sampled intervals at 3 sites (Fig. 9). On the other hand, in the Levantine basin (967) and on the centre of the Eastern Mediterranean (site 969), this ratio appears to correlate better with the Ba/Al, productivity proxy, since it increases during sapropel formation.

These two sites also show generally higher values. No significant difference of Ca-MAR is apparent between site 966, located at a water depth of 900m, and the rest of sites, all below 2000mbsl.

Although partially linked to carbonate deposition, Mg/Al MAR is interpreted as an indicator for detrital input (Wehausen and Brumsack, 1999; Nijenhuis and de Lange, 2000). Mg is assumed to be deposited in association with chlorites, and thus, as explained by the above mentioned authors, related primarily to the drainage of the European continent. However, this element may show local variation depending on the source area, such as ultramafics rocks outcropping in Crete (Wehausen and Brumsack, 1999), carbonate composition and/or marine circulation. These factors make Mg a highly variable proxy across the basin and through time. It is useful to compare Mg to Ca to evaluate contrasts between the detrital input and basin autocyclic carbonate production. Pliocene sapropels sampled on the Ionian basin show general increase in Mg/Al during sapropel formation, opposite to Ca/Al-MAR, although no significant change is detected during i-cycle 284 (Fig. 9). This increase in Mg/Al is not visible on the Mediterranean ridge (site 969). Likewise, uppermost Pliocene and lower Pleistocene sapropels do not denote a clear trend (Figs. 3 to 8). Only in the Levantine basin, a slight increase in Mg relative to carbonate production is apparent during sapropel formation. Upper Pleistocene and Holocene sapropels and background sediments show as a common feature of an increase in Mg/Al-MAR values. However, important differences are obvious comparing geographic locations. The highest values are obtained on the Ionian basin, followed by the Mediterranean Ridge, and much lower

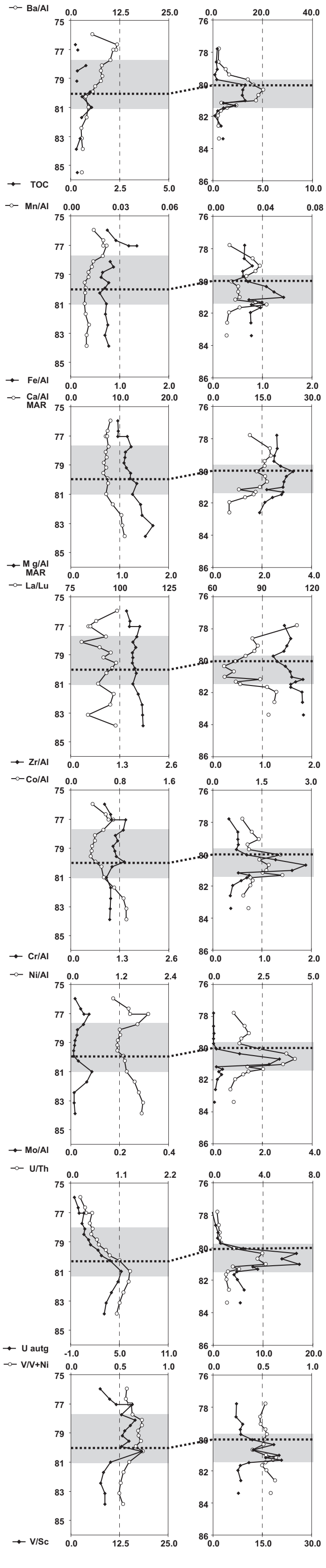


*Figure III.3. Geochemical signals for deposition of sapropel 3.*

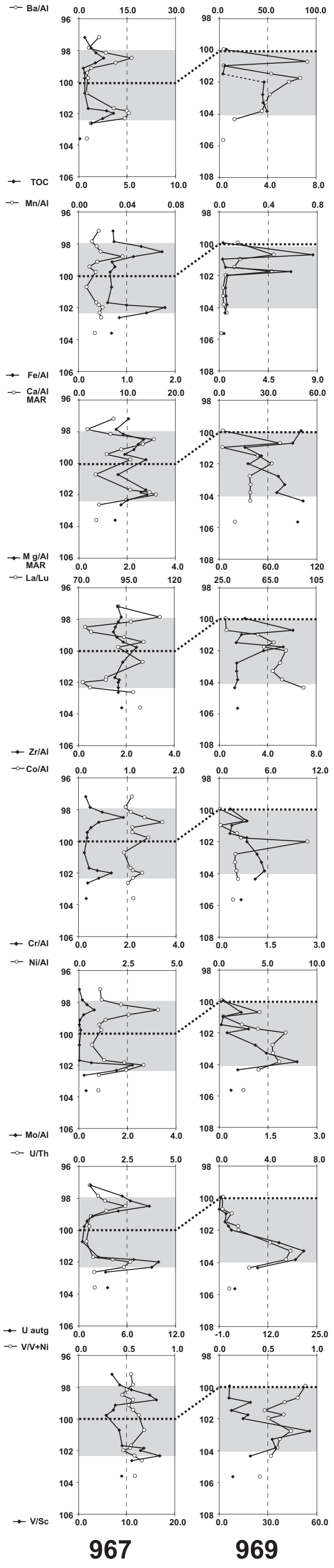


*Figure III.4. Geochemical signals for deposition of sapropel 4.*

values predominate at the deep Levantine basin and the Eratosthenes seamount. These geographic differences are also obvious in the Ca vs. Mg profiles in sapropel layers. On both sites, where Mg content is higher, there is a general inverse relation between detrital Mg and authigenic Ca, whereas on the Levantine basin the trend is unclear or even parallel between the two elements.

### 3.3. Oxygenation proxies

The study of paleo-oxygenation which is related to deep water circulation and ventilation, was carried out applying a set of proxies previously used in this and other settings (e.g., Wignall and Myers, 1988; Calvert and Pedersen, 1993; Jones and Manning, 1994; Calvert et al., 1996; Holser, 1997; Nijenhuis et al., 1999; Nijenhuis and de Lange, 2000; Schovsbo, 2001; Powell et al., 2003; Ivanochko and Pedersen, 2004; Tribovillard et al., 2006). For this study we selected 4 different proxies considered as the most informative; U/Th, $U_{authigenic}$, V/Sc and V/(V+Ni). For further discussion of the utility of these proxies in the Eastern Mediterranean see Gallego-Torres et al., (2004). The U-based indexes have been more extensively applied, and successfully calibrated previously, although some discrepancies arise in the degree of anoxia they define, as reported in Gallego-Torres et al., (2007). Vanadium-based proxies are utilized less frequently, and their calibration in terms of quantification of oxygen concentration is still under debate (Powell et al., 2003; Gallego-Torres, 2004). However, their use for qualitative reconstruction is very valuable.

Once again, there is a clearly visible systematic difference among different water depths, with the lowest anoxia seen at the shallower site, 966. In the Pliocene, the increase in redox proxies within the sapropels is clearly detectable, but this trend is more intense at the Pisano Plateau (Site 964). However, the sampled Pliocene sapropels at the different sites are not time equivalent thus the geographic comparison is not representative. At all sites the older sapropels show more anoxic conditions (Fig. 9) when compared to younger (upper Pleistocene) equivalents at each site.

In fact, in Pliocene sapropels, V/Sc, and U-based proxies invariably show values corresponding to anoxic conditions, either punctually or along the whole TOC-enriched section (Fig. 9). The evolution into upper Pleistocene sapropel layers is defined by lower values of these redox proxies, although ratios showing anoxic condition are still frequently obtained. The most oxygen depleted conditions are reached at sites 967 and 969, corresponding to deep basin settings in the Levantine basin and Mediterranean ridge, respectively (Figs. 3 to 8). Site 966, the shallowest studied location, on the Eratosthenes seamount, shows the lowest enrichment in redox sensitive elements. Finally, Holocene sapropel 1 (Fig. 2) is characterized by a relatively minor increase in anoxia proxies. Oxygen depletion is not reached at any controlled point according to $U_{authigeneic}$ or V/(V+Ni), although the other two proxies point toward oxygen absence. This discrepancy is consistent throughout the studied interval.

Apart from these proxies, we also evaluated the relative increase in redox sensitive elements, such as Ni, Cr, Mo, and Co. Their contents have been normalized to Al content in order to correct for detrital variations and used as evidence for sulphide enrichment, thus for sulfidizing conditions within the sediment (e.g., Huerta-Diaz and Morse, 1992; Morse and Luther, 1999). The trace metal enrichments should only be regarded qualitatively because these elements are easily remobilized during early diagenesis particularly in sediment which are highly enriched in organic carbon (e.g., Baturin, 2002; Kochenov and Baturin, 2002; Algeo and Lyons, 2006) The enrichment in these elements coincides with the high-TOC sections, although occasionally it extend over it, mirroring the Ba/Al ratio profile (e.g., Co/Al profile for S1, on site 969; Co/Al and Ni/Al, S3, site 967; Ni/Al, S7, on site 964). In some cases, the distribution of redox sensitive element is bimodal, with two maxima marking the top and bottom of the $C_{org}$-enriched level (e.g., Cr/Al for S1, site 964; Ni/Al and Cr/Al, sapropel 5, site 964; Cr/Al profile for i-cycle 284 on site 969).

### 3.4. Post-depositional alteration

As described by different authors, some sapropels has been proven to be oxidized either partially (e.g., Thomson et al., 1995; van Santvoort et al., 1996; Martínez-Ruiz et al., 2000) or completely erased by oxidation (e.g., Mangini and Dominik, 1982; Jung et al., 1997; Larrasoana et al., 2003). Evidences are based on Mn and/or Fe deposited as oxi-hydroxoxides, and not sulfide; thus these elements ar enriched under oxydizing conditions. High Mn concentration thus indicates the oxic front penetrating the sediments (e.g., Thomson et al., 1995; van Santvoort et al., 1996; Thomson et al., 1999; Martínez-Ruiz et al., 2000; Crusius and Thomson, 2003; Martinez-Ruiz et al., 2003; Gallego-Torres, 2004). Iron (Fe) is considered a terrestrial element, and it may be used as an indicator for detrital input, but it can also precipitates with authigenic phases, as oxide and also as sulfide in the form of pyrite. Accordingly Fe can be use to trace an oxic front when combined with other proxies (e.g. Mn), or as a redox proxy when combined with S (e.g., pyritization degree described by Canfield (1992) (see also Huerta-Diaz and Morse, 1992; see also Raiswell et al., 1994; Roychoudhury et al., 2003; Lyons and Severmann, 2006). Both elements are typically concentrated on the band between the top of the present day visible sapropel and the end of the Ba/Al enrichment event. In this study the Fe and Mn distribution indicates the advance of the "burn-down" front in several Quaternary sapropels (Figs. 2 to 8). In the Holocene sapropel (Fig. 2) the Mn peak is present on top of the TOC enriched level in all studied locations, marking the offset between the productivity increase (e.g. Ba/Al) and the $C_{org}$ defined sapropel. Upper Pleistocene sapropels (Fig. 3) show evidences of post-depositional oxidation only locally, and in selected levels. Sapropel 3 presents both Mn and Fe peaks marking oxidation at two sites in the Levantine basin (966 and 967). The two flanks of the Eastern Mediterranean, the Ionian basin and the Eratosthenes seamount, show post-depositional oxidation for sapropel 5, (Fig. 5) again coinciding with the offset between Ba/Al and $C_{org}$ but no evidence for this process is visible on the Mediterranean ridge (site 969) for the same i-cycle sapropel. Sapropel S7 (Fig. 7) shows a Mn oxidation peak at the two deepest studied sites (964 and 967). The rest of sites and/or sapropels do not show evidences of sapropel oxidation in the late Pleistocene sequence. No oxidation is visible in Pliocene sapropels (Fig. 9), where Mn concentration increases above and below the TOC-rich layer, and Fe is concentrated within the sapropel, in the form of SFe, as described by previous studies (Passier et al., 1996; Passier et al., 1999).

| Proxy | Oxic environment | Disoxia | Anoxia |
|---|---|---|---|
| **Uauthigenic** | | | ≥12 |
| **U/Th** | | 0.75 to 1.25 | ≥1.25 |
| **V/(V+Ni)** | | | ≥0.85 |
| **V/Sc** | ≤9.1 | | |

*Table III.2. Summary of applied paleo-oxygenation proxies and their significance (Gallego-Torres et al., 2007, and references within).*

## 4. Saprопel sedimentary regime

A clear increase in anoxia based on both types of proxies is visible in each sapropel. However, the degree of anoxia shows differences both aerially and temporarily. If we compare these proxies among different sites for equivalent levels (same i-cycle), generally, the highest anoxia is found at sites 967 and 969 for upper Pleistocene sapropels (Figs. 3 to 8).

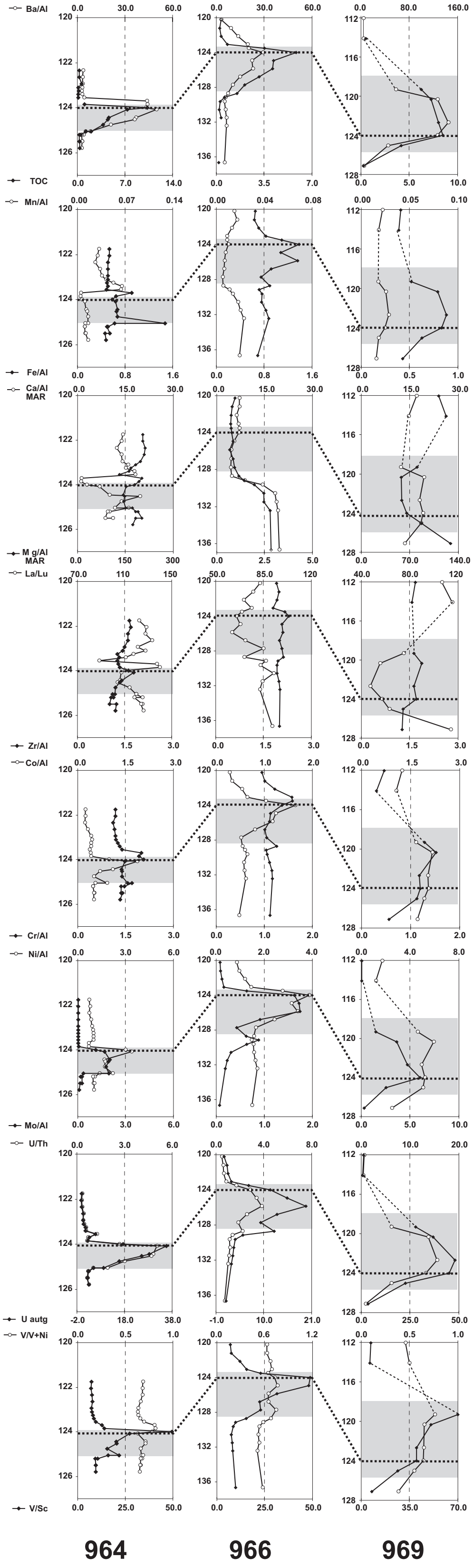


*Figure III.5. Geochemical signals for deposition of sapropel 5.*

Previous studies interpreted cyclic formation of sapropels as the response to insolation cycles coinciding with precession minima astronomical cycles (e.g., Rossignol-Strick, 1985; Hilgen, 1991; Rohling and Hilgen, 1991; Lourens et al., 1992; Aksu et al., 1995; De Lange et al., 1999; Emeis et al., 2000a; Calvert and Fontugne, 2001). These cyclic variations would effect precipitation and change the Nile flow into the Eastern Mediterranean basin, which in turn provides nutrients and freshwater to the system. The predominant inflow from the southern margin is compared to the detritan input from the European margin, Mg-enriched. On figure 10 it is clearly visible that samples of non sapropel layers have higher Mg/Al-MAR and La/Lu ratios. Although clay minerals are redistributed across the basin through the main currents, the diminished Mg concentration is detectable during sapropel formation (e.g., Wehausen and Brumsack, 1999; Emeis et al., 2000a; Warning and Brumsack, 2000).

Combined Zr/Al and La/Lu ratios show that sapropel deposition corresponds to periods in which aeolian influence from the African continent is weaker and detrital/riverine input is enhanced, (e.g., Rossignol-Strick, 1985; Hilgen, 1991; Rohling and Hilgen, 1991; Lourens et al., 1992; De Lange et al., 1999; Wehausen and Brumsack, 1999; Weldeab et al., 2003b).

The most drastic shifts in La/Lu ratio correspond to maximum contrast between the Nile river drainage and European input, such as during sapropel 7 event (Fig. 7). The variation in La/Lu between insolation cycles is minimal, and the prevailing southern margin origin of detrital material during sapropel deposition is constant through time. On the other hand, Mg

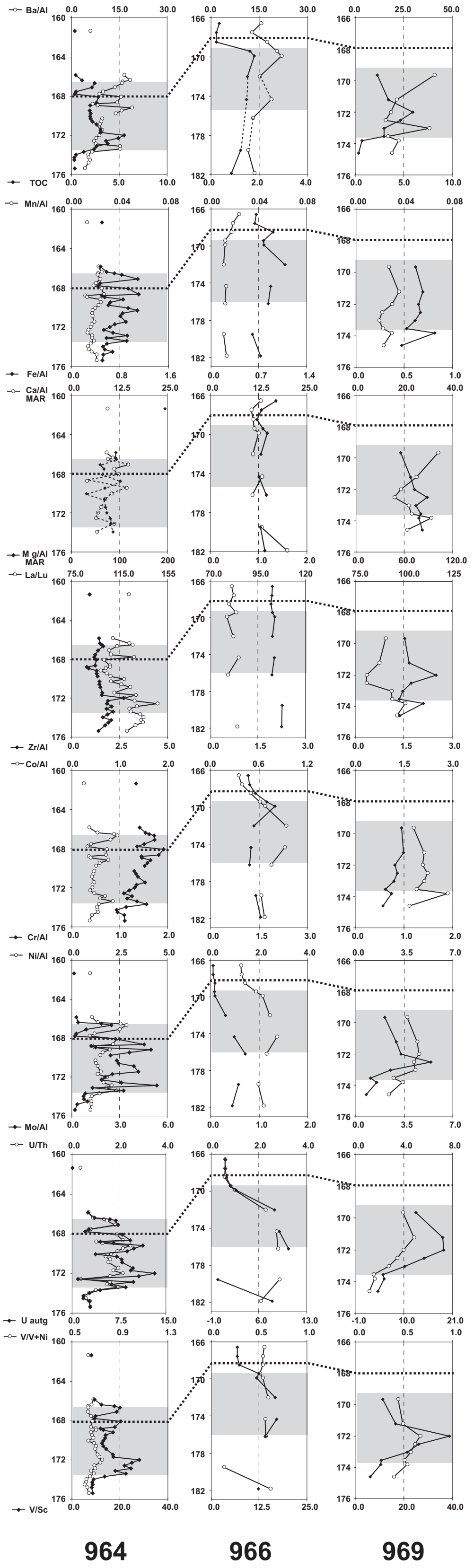


*Figure III.6. Geochemical signals for deposition of sapropel 6.*

does provide interesting evidence of increasing detrital input from the Pliocene to recent. This is particularly visible on the Ionian basin, where average values of Mg/Al-MAR of ~60 ppm/cm$^2$/ky (Fig. 9) shift to around 100ppm/cm$^2$/ky during the Upper Pleistocene and up to 150ppm/cm$^2$/ky during the Holocene at site 964 (Fig. 9). During the Pliocene, the sudden increases of Mg content visible on top of studied sapropels from the Ionian basin indicate that a renewed inflow of drainage from the European continent coincides with the end of $C_{org}$ concentration in the sediment. The opposite trend is observed during i-cycle 286 and might correspond to a stagnation event that prevented redistribution of detrital material arriving from the Adriatic Sea. The standard signal for Pliocene sapropels (low Ca and Mg content) is observe on top of the sapropel formed during i-cycle 272. Other evidence described below suggests that this is an oxidized sapropel that has been only partially preserved.

Site 964, on the Pisano plateau, typically shows a higher La/Lu ratio and Mg/Al-MAR, due to its location farther from the African craton and directly influenced by the debaucher of the Adriatic Sea into the Eastern Mediterranean and thus, the northern margin source area. It is very obvious that sapropel deposited on the Eratosthenes Seamount (Site 966) received a much lower input of detrital material, as the rate of accumulation of Mg/Al show much lower values and the trends of La/Lu are less obvious than in the rest of the analyzed sites. Since this core was recovered on a pelagic high, it is reasonable that we see lower values of detrital proxies. Site 967, due to its proximity to the Nile delta, received sediments mainly from the African craton that provided primarily smectites as the main clay mineral phase (Maldonado and

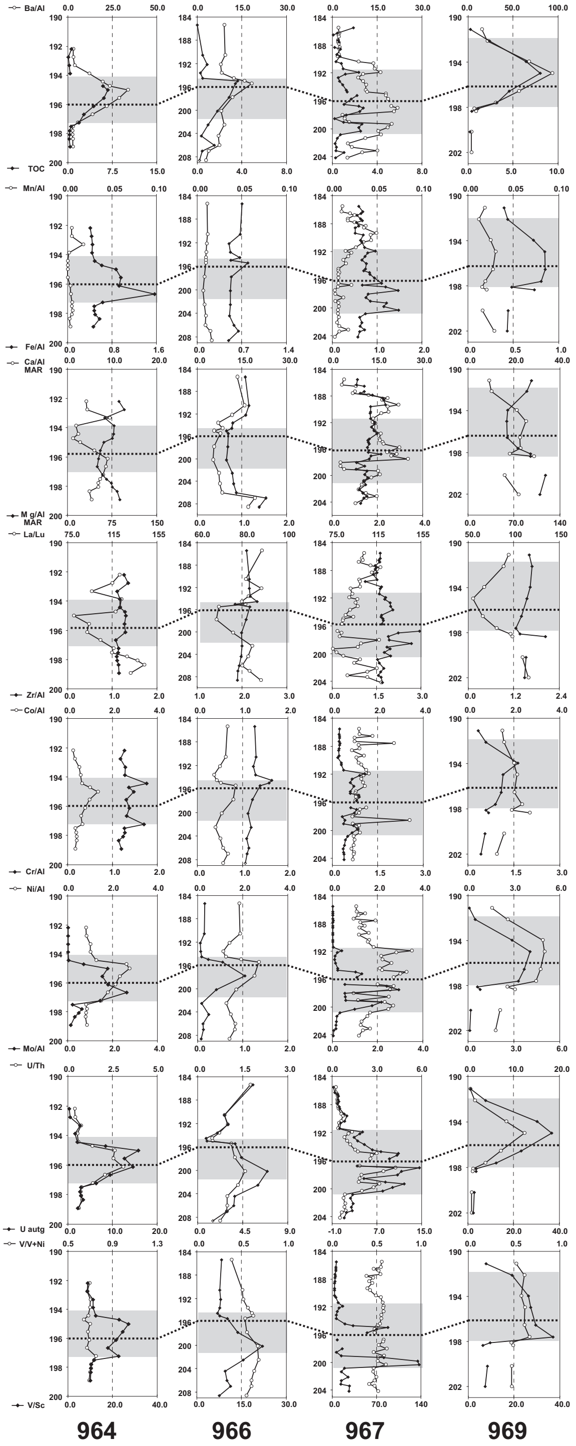


*Figure III.7. Geochemical signals for deposition of sapropel 7.*

Stanley, 1981), and thus show low Mg values. The geographic location favours a clear trend in the variations of La/Lu ratio and explains the globally low values of this proxy. At the centre of the basin, site 969 shows relatively high values of Mg/Al considering its proximity to the African margin. Wehausen and Brumsack (1999), observing similar results, proposed that this is due to the drainage of ultramafic rocks outcropping in Crete, which is the closest emerged area.

As a whole, Mg/Al distribution is not straight forward, and must be interpreted together with other proxies. Since Mg/Al MAR represents mainly northern margin origin, and La/Lu is determined by southern margin drainage a plot of the two proxies allows the comparison between the two main source areas (see Fig. 10). On the Pisano Plateau (site 964), the average La/Lu ratio in sapropel layers is <110, whereas on Mediterranean ridge (site 969) sapropels show ratios <90, and values of La/Lu <80 correspond to the Levantine basin. These plots show that globally lower values in La/Lu ratio (i.e., main source of sediments in the African craton) mainly correspond to lower Mg content.

The diminished carbonate sedimentation has been previously described by several authors (e.g.,Wehausen and Brumsack, 1999; e.g.,Emeis et al., 2000a; Martínez-Ruiz et al., 2000; Murat and Got, 2000; Gallego-Torres, 2004). The oldest sampled layers, middle Pliocene age, located on sites 964 (Ionian basin) and 969 (Mediterranean ridge), show a nearly complete absence of calcite, (Fig. 9, Table 3) observed in mineralogical analysis and by very low Ca/Al content. Although this carbonate might have been dissolved during diagenesis (Pichevin et content. Although this carbonate might have been dissolved during diagenesis (Pichevin et al., 2004), this decrease also responds to a diminished carbonate production in the basin. The decrease in Ca during sapropel formation is not constant throughout the basin. For example, a visible increase in Ca is observed during the formation of late Pleistocene sapropels on site 967. Emeis et al., (2000a) also detected that inorganic carbon sometimes appears associated to $C_{org}$ accumulation at the same site. It is thus inferred that the increase in surface productivity is variable in term of the fauna that provided organic matter to the sediment. These variations are observed in time and space, since the Ionian basin generally maintains diminished carbonate productivity in all sampled intervals.

## 5. Paleoenvironment and Paleoceanography during sapropel deposition

The paleoceanographic conditions that induced sapropel deposition have been discussed for years by different authors (e.g.,Mangini and Schlosser, 1986; Aksu et al., 1995; Strohle and Krom, 1997; De Lange et al., 1999; Passier et al., 1999; Emeis et al., 2000a; Emeis et al., 2000b; Martínez-Ruiz et al., 2000; Murat and Got, 2000; Nijenhuis and de Lange, 2000; Menzel et al., 2002; e.g.,Bottcher et al., 2003; Weldeab et al., 2003a; Weldeab et al., 2003b; Meyers and Arnaboldi, 2005). Although it has been widely demonstrated that sapropel formation appears associated to an increase in marine primary productivity (e.g., Paytan, 1997; Diester-Haass et al., 1998; Martínez-Ruiz et al., 2000; Weldeab et al., 2003a; Meyers and Arnaboldi, 2005; Paytan and Griffith, 2007), the relative importance of water column oxygenation during these periods of organic matter entrapment is still controversial, partially because it appears to be variable through time (e.g., Jung et al., 1997; Passier et al., 1999; Wehausen and Brumsack, 1999; Emeis et al., 2000a; Menzel et al., 2002; Gallego-Torres, 2004). The application of a set of paleo-redox proxies that proved their usefulness for the interpretation of deep water ventilation, at least in a qualitative mode (Gallego-Torres, 2004), allow the reconstruction of the evolution of deep water circulation and ventilation. Table 2 summarizes the average values of applied proxies and estimated conditions they represent. These proxies evidence a temporal evolution as well as regional variations in ocean circulation and implications to sapropel formation across the basin.

### 5.1. Upper Pliocene to Lower Pleistocene

The oldest sampled sapropel, deposited during i-cycle 286 (studied in the Ionian basin) shows evidences of punctual anoxia at the top of the sapropel (Fig. 9). Although U, V, Mo and Cr proxies do not indicate anoxia for the onset of the TOC-rich level, the highest Ni and Co concentrations are at the base of this sapropel. This is likely due to re-mobilization through downward diffusion of these elements under reducing conditions within the sediment, when anoxia was reached in the sediment-water interface. This is coherent with high sulfidic conditions dominating the bottom waters during the last phase of formation of this sapropel. Samples from i-cycle 284 (Fig. 9) correspond to the Ionian basin and the Mediterranean ridge (sites 964 and 969). At both locations we observe evidence for the absence of oxygen (Fig. 9), although at the Ionian Basin, these conditions are reached at the end of sapropel deposition, whereas on the Mediterranean Ridge minimum oxygen concentration occurred at the base. Calculated ages, however, show that the minimum oxygen is reached at nearly the same time in both areas. Vanadium based proxies indicates higher degree of anoxia than U-based ratios at both sites. Sapropel onset started first at site 964, with an increase in Ba/Al followed by accumulation of organic carbon and ending with low oxygen concentrations. On the other hand, at the Mediterranean Ridge, although the productivity increase and oxygenation minimum are synchronous with the Ionian Basin, $C_{org}$ enrichment occurs later (2ky approx.) under progressively higher oxygen concentrations. The ending of sapropel formation in the Ionian basin is more abrupt. As mentioned above, it coincides with a sharp increase in Mg content, and thus detrital input from the northern margins. It corresponds to a sudden renewed circulation with major influence from the European continent.

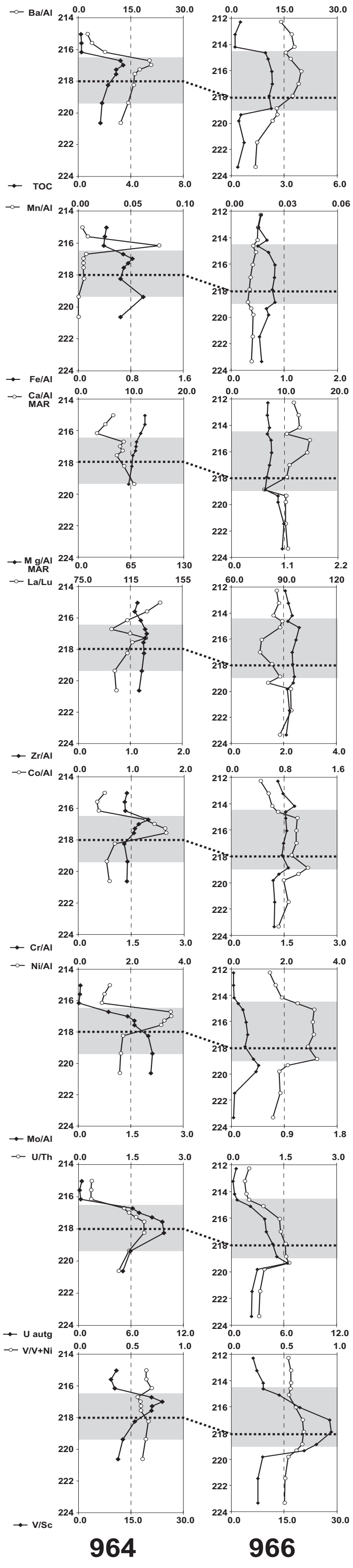


*Figure III.8. Geochemical signals for deposition of sapropel 8.*

Sapropels deposited during i-cycles 282 and 280 (sampled at sites 964 and 969 respectively) show very similar features in terms of oxygenation. The establishment of low oxygen conditions coincides with the base of the TOC-rich level, indicated by U and V indexes, as well as Mo, Ni and Cr content, although the highest level of anoxia, according to these proxies, is reached at the centre of both layers, coinciding with maximum $C_{org}$ concentration (Fig. 9). Although Ba/Al ratios indicate higher productivity at the base, the trace metal data for both layers suggest that the late stage of sapropel development is mainly controlled by the absence of deepwater ventilation, since productivity recovered background values before redox proxies do, and organic matter continued to accumulate at a high rate even under lower surface productivity.

Sapropel deposited during i-cycle 272 (Fig. 9) in the Ionian basin is a very thin one, in which the relation between increased productivity, $C_{org}$ accumulation and redox conditions is ambiguous. The Ba/Al ratio marks two maximum peaks; the first one coincides with the TOC enrichment, and associated peaks in Co/Al, Cr/Al and Ni/Al positive peaks (Fig. 9). However, V-based proxies present a decrease and no U or Mo/Al enrichment is observed. The second Ba/Al peak has very minor TOC increase associated, but Cr/Al, and V and U proxies exhibit a positive excursion. Approximately 1ky after the deposition of this sapropel (using our calculated ages), another minor increase in Ba/Al ratio with no TOC peak appears. Some redox sensitive elements, such as Mo, Cr or Co, also show a slight increase. The Mn/Al profile, which shows very high values from the end of the sapropel deposition up to 2.825Ma (calculated age), and detrital proxies (described before), all suggest that this period had a well developed deep current at this site, and TOC accumulation is directly linked to increased productivity. The absence of organic carbon in the upper productivity events responds to general oxidation, as indicated by high Mn content. Only punctual sub-oxic/anoxic conditions were reached in the upper part of the level, and this prevented the complete oxidation of the lower TOC enrichment, and remobilized redox sensitive elements, particularly Ni, Co and Cr, producing their peaks within the present visible sapropel.

The next set of sapropels studied are of latest Pliocene to early Pleistocene in age, and are sampled at the deep Levantine basin and Mediterranean ridge respectively. They all show very similar features. The TOC profile runs virtually parallel to the Ba/Al enrichment, and the maximum values of redox proxies coincide with the maximum $C_{org}$ content. However, some peculiarities appear. On sapropels corresponding to i-cycles 178, 176, 168, 160, 156 and 152, the base of the sapropel coincides both with minima in redox proxies and Ba/Al increases (Fig. 9). From that point onward, redox proxies follow a trend very similar to TOC content in the sediment, which follows the Ba/Al, with only minor deviations. This means that although accumulation of organic matter in this sapropel is controlled predominantly by productivity, the change in surface water conditions might be a response to a change in global circulation, reflected by lower deep water oxygenation (e.g., Passier et al., 1999; Nijenhuis and de Lange, 2000; Menzel et al., 2002).

Some other local differences arise, representing the differences in sapropelic events. Sapropel deposited during i-cycle 178 (site 967, Levantine basin) show maximum values of TOC and redox proxies at the base, whereas Ba is highest at the top of the layer. Restricted circulation appears to establish at the same time as the first productivity increase. This condition persisted for a short period, and then deep water ventilation returned, although higher productivity

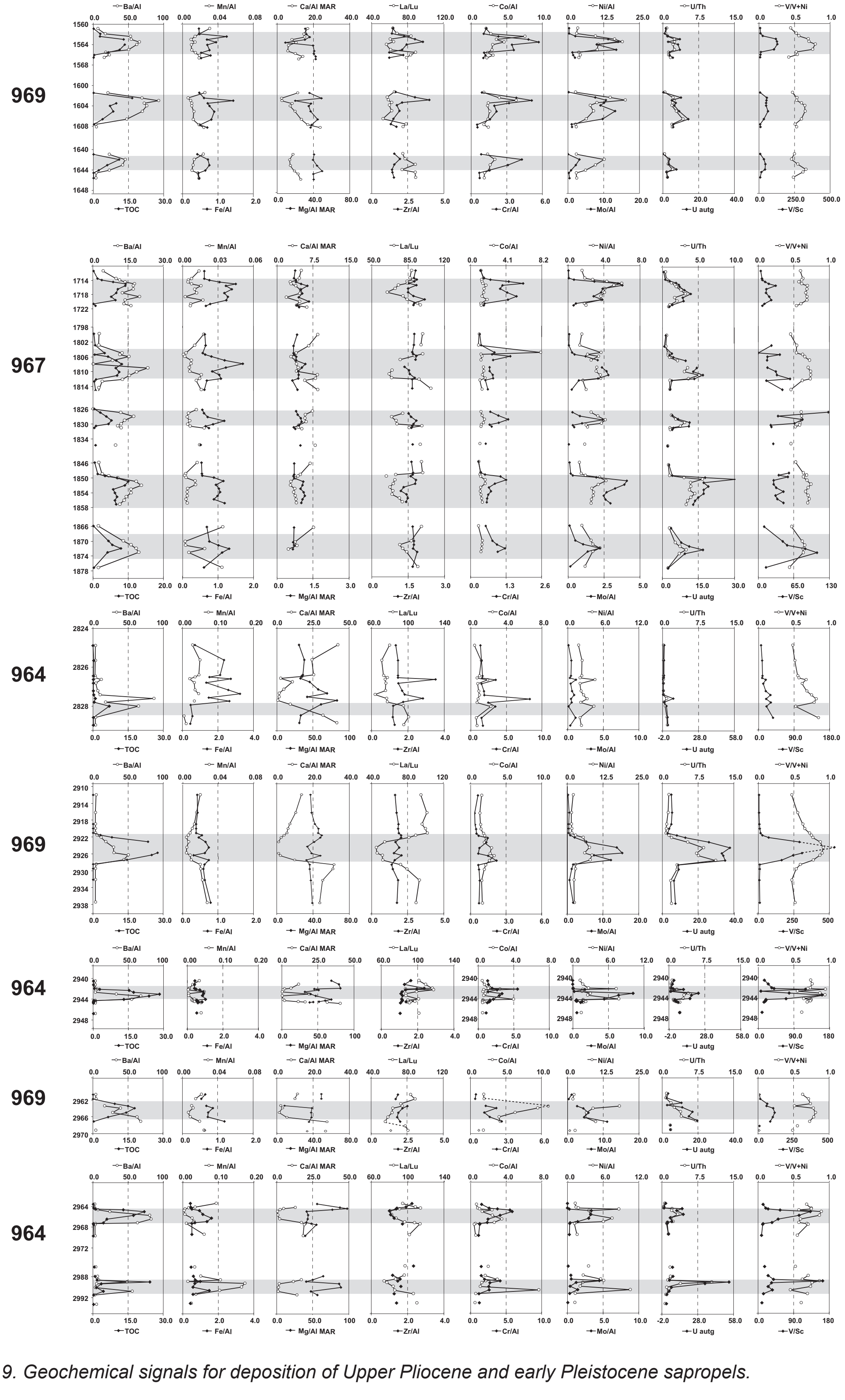


Figure III.9. Geochemical signals for deposition of Upper Pliocene and early Pleistocene sapropels.

maintained high organic carbon accumulation. In any case, this sapropel represents a minor event compared to the underlying and overlying equivalents, which are remarkably longer in time.

Globally, this set of layers corresponds to a period in which current dynamics changes resulted in more restricted bottom water ventilation and induced an increase in productivity. Organic carbon preferential accumulation is constrained to the period when surface production was high and ceased when productivity returned to "normal background" values. Although no stagnation is visible, these coincide with a period of relatively low sedimentation rate and circulation and water masses exchange was notably diminished.

## 5.2. Upper Pleistocene and Holocene

The Upper Pleistocene presents a very different scenario as determined from the paleoceanographic proxies. This period corresponds to the highest sedimentation rate in the basin. TOC and Ba values corrected to MAR show the highest values of productivity and organic carbon accumulation.

In this environment, sapropel 8 (i-cycle 20) formed when surface productivity reached a high rate. However, it is visible that redox proxies present an increase prior to the TOC enrichment (Fig. 8). Although not reaching anoxic indicative values, U and V based proxies present relatively high levels prior to the sapropel on the Ionian basin and the Levantine basin (sites 964 and 966). U/Th ratio shows evidence of anoxic conditions, although $U_{auth}$ remains within the

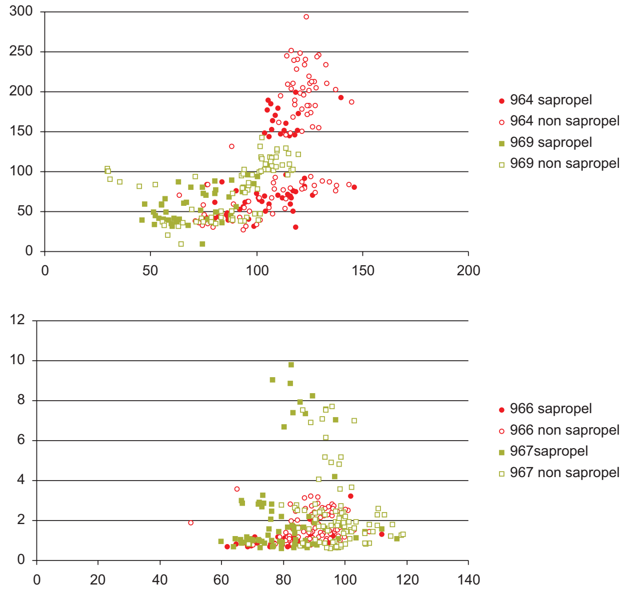


*Figure III.10. Relation between Mg content and La/Lu ratio representing period of sapropel deposition and background sedimentation* range of sub-oxic environment. The remobilization of redox sensitive elements suggests that oxygen was not completely absent in the deep basin. The neat peak in Mn on top of S8 and the sharp decrease of Ni/Al just below the Mn peak at site 964 are indicative of the oxidation process. The record for the Pisano plateau (site 964) shows a progressive increase in TOC, Ba/Al and trace metals, whereas in the Eratosthenes Seamount the onset of S8 is more abrupt. In this case, the paleoceanographic event which leaded to sapropel formation seems to spread from the debaucher of the Adriatic Sea toward the east according to calculate ages.

Sapropel S7 deposition (Fig. 7), on the other hand, is initiated first on the area of influence of the Nile river (site 966), with a progressive increase in Ba/Al. Although this increase in productivity induced a decrease in oxygen content, indicated by U and V proxies, preservation of organic matter does not occur until these conditions are maintain for some time. This is a complex sapropel, which includes several Ba/Al maxima, clearly visible at site 967 (deep Levantine basin). Only the more intense Ba/Al produced $C_{org}$ accumulation on the centre of the basin (site 969) and the Ionian basin (site 964), and for both sites a notable offset of about 1ky is observed. In all three deep basin settings, the redox response is abrupt, and proxies abruptly increase their values. Nevertheless, their maximum values are generally coinciding with Ba/Al peaks. A slight increase in Mn/Al at sites 964 and 967 on top of the TOC-rich level indicates that oxygen was immediately available on both Ionian and Levantine basins when export productivity returned to background levels. This draws a situation where increase productivity started on the eastern most part of the basin, and progressively extended across the whole region. The elevated export production exceeded the oxygen consumption rate and thus organic carbon accumulated. On the Eratosthenes seamount, at a shallower water depth (site 966) this $O_2$ consumption was slower, whereas in the deep settings this is an abrupt effect. On the other hand, return to normal oxygen concentration is equally fast, when surface production decreases.

Sapropel 6 also originated slightly earlier on the Levantine Basin (site 966), although the time offset is much smaller. However, although the increase in Ba/Al content is similar at all 3 sampled sites, it is a poorly developed sapropel on the Eratosthenes seamount, not reaching 2%TOC, (Fig. 6) whereas in deep locations (sites 964 and 969) $C_{org}$ content exceeds 5%. At site 964 S6 clearly appears as a composite sapropel, similar to S7, and in fact, the oxygenation evolution is similar to the level mentioned above.

S5 (i-cycle 12) is a well developed sapropel basin-wide and shows the same features in all sampled locations. The increase in TOC is parallel to the Ba/Al profile, (Fig. 5) progressively increasing from bottom to the top of the organic-rich level, but $C_{org}$ content decreases abruptly while Ba/Al ratio expands slightly over the top. This sapropel has been studied previously with similar results (Emeis et al., 2000b). Oxygenation proxies follow a very similar profile, increasing upwards through the sapropel, and diagenetic peaks of Ni and Co mark the top of the layer. Mn/

Al precipitation, indicative of the return to oxic conditions, marks the difference between the two records.

Sapropel 4 (i-cycle 18) is sampled on the Mediterranean ridge and the Levantine basin (sites 969 and 967). At both sites this sapropel is composed of two distinct intervals of surface productivity increase, nearly simultaneous, although at the Mediterranean Ridge the onset occurs earlier in time. Uranium based proxies suggest anoxic conditions for both sites, coinciding with the TOC peaks (Fig. 4), with a return to normal oxygenation between the two productivity events. V/Sc ratio shows a similar trend, although V/(V+Ni) shows a somewhat opposite profile. The Ni/Al content in the sediment however, also show high values coinciding with the TOC and Ba/Al maxima, thus the signal of this proxy is masked by Ni precipitation. Similar to the observation on other Upper Pleistocene sapropels, the relation between Ba, $C_{org}$ and redox conditions is very close, implying that the three processes (export production, C burial and preservation and oxygen content) are intimately linked.

Sapropel 3 is only sampled on the Levantine basin, both in the deep setting and at the shallower Eratosthenes seamount (sites 967 and 966), and in fact this event is poorly developed or absent at sites further west (Emeis et al., 2000a). S3 seems to respond to a local minor event in the Nile river discharge (Gallego-Torres et al., submitted*)*. In fact, the sapropel development is rather limited even at these two sites, (Fig. 3) particularly on the Eratosthenes seamount. The TOC enrichment is lower than in other sapropels, and particularly, at site 966, a strong oxidation is apparent based on Mn/Al and other redox sensitive elements (Mo, Ni, Co and Cr) that show the peak on top of the defined sapropel. At the deep basin, site 967, TOC reaches moderately high values and the development is more pronounced. Still, positive peaks of the above mentioned elements indicate oxidation immediately after the return to normal productivity.

The Holocene sapropel 1 has been extensively studied (e.g., Aksu et al., 1995; van Santvoort et al., 1996; Thomson et al., 1999; Martínez-Ruiz et al., 2000; Casford et al., 2003; Martinez-Ruiz et al., 2003). This study obtains similar results, with clear evidences for increased productivity and post depositional oxidation of organic matter (Fig. 2). Redox proxies indicate reduced ventilation although anoxic conditions are only locally obtained, such as at site 967. The most remarkable feature is the increase in U/Th and $U_{auth}$ prior to the TOC enrichment on site 966. No clear anoxia is visible, but the highest values precede both Ba and TOC peaks, whereas sapropel formation occurred in ventilated conditions,. This support the idea that increase productivity is the factor that ultimately determined the formation of the S1 (e.g., van Santvoort et al., 1996; Rutten et al., 1999; Thomson et al., 1999; Martínez-Ruiz et al., 2000).

## 6. Conclusions: Regional evolution across the Eastern Mediterranean basin

The observation of the diverse geochemical proxies used in this study presents a consistent picture of a progressive evolution of the Eastern Mediterranean basin towards a general increase in deepwater ventilation over time, punctuated with events of sapropel formation that also reflect this trend of increasing ventilation thus oxygen supply to depth with time.

During the Upper Pliocene, sapropel deposition occurred in a generally less dynamic basin (slower circulation and ventilation rates). Some of these sapropels appear laminated. Linear sedimentation rates during this period are lower, and formation time for TOC-rich levels is quite homogeneous across the basin (average 2.4kys, (Gallego-Torres, 2004). This is a rather short time compared to Upper Pleistocene levels. The general decrease in inorganic carbonate content during sapropel formation also suggests a drastic change in the basin dynamics and productivity. Although the increase in detrital input from the African continent is clearly visible through La/Lu ratio, the low sedimentation rate indicates a generally slower continental input. The decrease in sedimentation rat is also related to the much lower carbonate production, although lower Mg/Al-MAR values equally indicate diminished terrigenous input. Anoxic conditions in the sediment are particularly evident during this period. An increase in Fe content within the sapropel layer and the presence of pyrite (e.g., Passier et al., 1999) indicates that hydrogen sulphide formed and thus supports the idea of oxygen absence. All these evidences point to a relatively stagnant water column or, at least, diminished water circulation at depth. Nevertheless, onset of sapropel formation is linked to productivity increase (as evidenced by Ba/Al increase). The change in bacterial community indicated by N isotopic composition is a proof for the change in surface condition and the increased productivity (e.g., Struck et al., 2001; Meyers and Bernasconi, 2005; Arnaboldi and Meyers, 2006; Gallego-Torres et al., submitted).

Late Pliocene to early Pleistocene sapropels show similar depositional conditions. Formation time is slightly longer, although a cyclic alternation of longer periods of organic matter accumulation and short events of sapropel formation is apparent. Redox proxies also exhibit a progressive decrease in maximum peak values, suggesting that, although oxygen concentration reached very low values, it was relatively higher than during the formation of older sapropels. Ca/Al, and thus carbonate sedimentation, is also more constant and its decrease is less drastic. Again, Ba/Al is always linked to sapropel formation, and a more close relationship between TOC and Ba is visible. We may thus infer that basin conditions during sapropel formation have undergone important changes in productivity and circulation, but less pronounced than during the Pliocene.

During the Upper Pleistocene the regional basin dynamics present important differences. Sedimentation rates are remarkably higher, implying an increase in continental weathering and input of detrital material into the basin, supported by high values for detrital proxies. This coincides with maximum values of Ba/Al-MAR and TOC-MAR. This means that, although the final concentration of $C_{org}$ in the sediment is lower than in Pliocene sapropels, the amount of organic carbon arriving to the seafloor was greater than during Pliocene times, but it appears diluted as a result of the genarally higher sediment load. Despite this accelerated accumulation of organic matter, oxygen depletion, as indicated by redox sensitive elements, is less intense than during older equivalents, and oxidation fronts developed immediately after the period of increase productivity. It is thus possible to infer that deep water ventilation did not stop, and very high export production levels were the inductor of oxygen consumption and thus disoxic conditions at the sediment-water interface. The shift towards increased surface productivity, also associated to N-fixing bacteria, does not imply a general decrease in carbonate production, although the fluctuating Ca/Al profile indicate global readjustment in the basin. Strong differences of carbonate content between sites for the same age sapropels suggest that the change in carbonate production responds more to local variations rather than to basin wide alteration. Nevertheless, increased surface productivity and $C_{org}$ fixation is recognizable across the whole region.

Finally, the Holocene sapropel was formed under the highest sedimentation rates (up to 7 times higher than Pliocene LSR). Mg/Al ratio, as a proxy for detrital input, shows maximum values at the Ionian basin and the Mediterranean ridge, both close to Mg-rich source areas, and drainage from the African continent is also enhanced, as evident by the La/Lu decrease. This terrigenous input supported the clear increase in productivity and favoured TOC accumulation. Although this signifies a great change in the biogeochemistry, basin wide paleoceanographic perturbations are not as visible as during the deposition of older sapropels. Oxidation fronts on top of the TOC-rich layer, semi-oxidized sapropels and minor increase in redox sensitive elements, relatively low values of U and V proxies indicate that basin circulation was not greatly modified in terms of water mass ventilation rates.
As a whole, a general trend is visible from Pliocene through to Holocene in the Eastern Mediterranean basin. Present day circulation is progressively achieved, with increasing exchange between Western and Eastern Mediterranean and remarkable increase in detrital input and sedimentation rate, thus implying intensified continental erosion.

In terms of regional variation, it is evident that paleoceanographic conditions in each different sub-basin are modulated by local condition. The Adriatic Sea and the drainage of the Po River exert a major influence on the Ionian basin, whereas the Levantine basin is controlled almost exclusively by the Nile River. The end of sapropel formation in the Ionian basin generally coincides with renewed circulation from the Adriatic Sea providing Mg-rich detrital material whereas in the centre and eastern-most Eastern Mediterranean such evidence is not clearly detected. The exchange with the Adriatic sea also affected deep water ventilation, particularly during deposition of Quaternary sapropels. For this period oxygenation exhibit a notable difference to progressively lower values from the Ionian Basin to the easternmost sites. It is also remarkable that periods of sapropel formation are slightly longer in the Mediterranean Ridge and Levantine basin, where each sapropel deposition started earlier, progressively spreading toward the west. Thus, the paleoceanographic situation depicted consists of alteration in surface productivity and in the direction of the main currents, associated to the increase in Nile River inflow into the Eastern Mediterranean. This increase in productivity spread westward, and as a consequence, organic matter accumulated developing sapropel formation progressed from East to West, and oxygen consumption produced general suboxic conditions at the sediment water interface. Termination of sapropel formation is also earlier in the Ionian basin, which suggests that the area influenced by the altered surface waters conditions progressively diminished, and new influence from the Western Mediterranean and Adriatic seas prevailed earlier in the Ionian basin, and later “normal” conditions extended to the whole Eastern Mediterranean basin.

# CHAPTER IV

# Pliocoene-Holocene evolution of depositional conditions in the Eastern Mediterranean: Role of anoxia vs. productivity at time of sapropel deposition

## *Abstract*

*Sapropel deposition of in the eastern Mediterranean has been the subject of intense debate. It has been argued that increased organic carbon content is the consequence of enhanced preservation of organic material fluxes. Alternatively, marine surface productivity has also been considered the main cause of higher organic matter contents. A consensus is now emerging that both play an important role. In all of the scenarios, it is accepted that sapropels originated as a response to astronomically determined climate cycles that affected the basin by altering paleoceanographical conditions. However, the ultimate reason for the accumulation and preservation of organic matter is still a matter of debate. It has been demonstrated that major differences exist in depositional conditions through the Pliocene-Holocene interval. Both oxygenation and productivity have significantly varied during this time. On the basis of a multiproxy approach, nine sapropel layers (Hole 964A, ODP Leg 160) spanning this time interval were selected for mineralogical and geochemical analyses. Productivity (Ba), oxygen (trace metal ratios) and sedimentary regime (clay minerals, detrital elements) proxies were selected for paleoenvironmental reconstruction. Multiproxy records have evidenced the factors controlling TOC enrichment and enabled the reconstruction of the evolution of productivity and oxygenation within the basin. We have recognized a significant increase in river runoff relative to decreasing aeolian input during sapropel deposition over the whole time interval. Productivity has substantially fluctuated and was considerably higher during the Pliocene; at the same time decreasing oxygen availability parallels this fluctuation during the whole interval. When different redox proxies are compared, properly anoxic environments are recognized only in the Pliocene. Moreover, disoxic to anoxic conditions appear to coincide with maximums in marine productivity, thus suggesting that oxygen depletion may be linked to greater consumption rather than restricted circulation. This supports the hypothesis that productivity fluctuations resulting from climate oscillations were the main cause of enhanced organic matter contents and also a main controlling factor for oxygen availability.*

## 1. Introduction

Sapropel deposition of in the eastern Mediterranean has been the subject of intense debate for decades, (Kidd et al., 1978). It has been argued that increased organic carbon content is the consequence of stagnation-enhanced preservation of organic material fluxes. Evidence in favour of the stagnation model is frequently based on faunal assemblages or biomarkers (e.g., Rolhing and Hilgen, 1991; Menzel et al., 2002; Negri et al, 2003), or on the concentration of trace elements and sulphide-forming metals, (e.g., Rossignol-Strick, 1985; Nolet and Corliss, 1990). Alternatively, marine surface productivity has also been considered the main cause of higher organic matter contents. Ba excess and other productivity proxies, (e.g., Emeis et al., 1991, 2000b; Strohle and Krom, 1997; Warning and Brumsack, 2000; Martinez-Ruiz et al., 2003; Menzel et al., 2003; Paytan et al., 2004), as well as the nitrogen isotopic composition of organic matter (e.g., Meyers and Arnaboldi, 2005; Meyers and Bernasconi, 2005), indicate an increase in productivity during sapropel deposition. The combination of both processes has also been invoked and a consensus is now emerging that both productivity and preservation played an important role (e.g., Calvert and Fontugne, 2001; Rinna et al., 2002; Filippelli et al., 2003). In any of the scenarios, it is accepted that sapropels originated as a response to astronomically forced climate cycles (Hilgen, 1991) that affected the basin by altering paleoceanographic conditions. However, the ultimate reason for the accumulation and preservation of organic matter is still a matter of debate. Enhanced precipitation and wetter conditions (Rossignol-Strick, 1985) imply a higher continental runoff into the basin, thus providing the Mediterranean system with more freshwater and land-derived nutrients (e.g., Lourens et al., 1992; Aksu et al., 1995; Emeis et al., 2000a; Nijenhuis and de Lange, 2000; Casford et al., 2003; Weldeab et al., 2003a), both of which could be factors that promoted sapropel formation. On the one hand, freshwater could cause stratification of the water column, thus preventing oxygenation of the seafloor. On the other hand, nutrients would allow increased productivity and export production, which may have overwhelmed oxygenation rates and resulted in organic matter accumulation in the sediments.

These two possible explanations are at the core of a major debate understanding sapropel formation. With the aim of clarifying the main cause of TOC accumulation and preservation in the Mediterranean sedimentary record (e.g., Mangini and Schlosser, 1986; Murat and Got, 2000), and also reconstructing the conditions of the basin at the time of sapropel deposition, and the evolution of these TOC enrichment events, nine sapropel layers from ODP core 964A (Ionian Basin) spanning from the Pliocene to Holocene were analyzed at high resolution. Within this high-resolution approach, we first applied mineralogical and geochemical proxies to determine sedimentological and climatic conditions (e.g., Hamroush and Stanley, 1990; Krom et al., 1999; Frumkin and Mordechai, 2003). We then used productivity proxies, such as TOC Mass Accumulation Rates and Ba/Al and biogenic barite (e.g., Dehairs et al., 1987; Paytan et al., 2002; 2004), previously proven to be reliable in this area (e.g., Thomson et al., 1995, 1999; Passier et al, 1996; Martínez-Ruiz et al., 2000, Paytan et al., 2004). Finally, we also discuss a set of compiled redox proxies (e.g., Jones and Manning, 1994; Thomson et al., 1995; Holser, 1997; Böttcher et al., 2003; Powell et al., 2003; Rimmer, 2003) and compare their behaviour over time, bearing in mind their possible diagenetic redistribution and alteration processes (e.g., Jung et al., 1997; Crusius and Thomson, 2003).

## 2. Materials and Methods

Pelagic sediments including sapropel layers from the Pliocene-Holocene time interval were sampled in ODP cores recovered at site 964 during Leg 160. This Site is located in the Pisano Plateau near the Ionian Abyssal Plain on a small bathymetric high at a depth of 3650 m (see Fig. 1 for location). An excellent record of sapropel deposition in the Ionian Basin was obtained at this location in six drill holes. The lithostratigraphic section recovered at these holes shows little down core variations and consists predominantly of nannofossil clay, clayey nannofossil ooze and nannofossil ooze with some intervals of clay and foraminiferal sand (Emeis, Robertson, Richter et al., 1996). Within this section, numerous sapropel layers occur with variable characteristics (e.g., from massive to laminated, from sharp color boundaries to gradual contacts) and with a variable TOC content.

According to the scope of this study, we selected sapropels from different time periods in order to establish the oxygenation/productivity evolution of the eastern Mediterranean since the Early Pliocene. Sapropel layers were sampled continuously at 2cm intervals, and more detailed sampling down to mm scale was performed on selected boundaries.

Analyzed sapropel intervals are summarized below. We followed the nomenclature according to the description provided by Emeis, Robertson, Ritcher, et al. (1996) in the ODP 160 Initial Reports and Emeis et al., (2000a), eventually modified by Lourens (2004), as well as our own

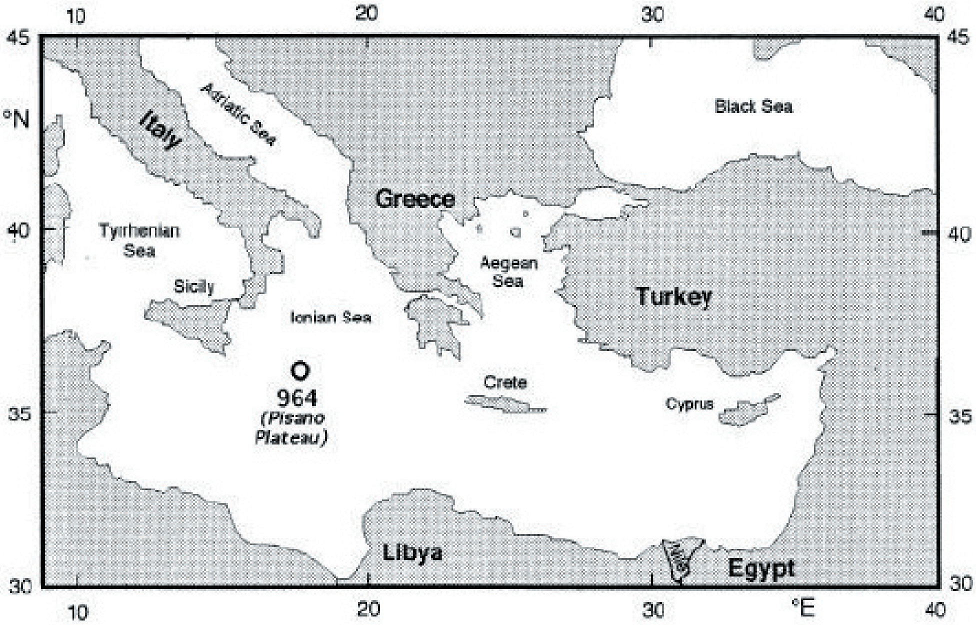


*Fig. VI.1: Location map for the studied core, ODP Leg 160, Site 964 Hole A. (Modified from Wehausen and Brumsack, 2000)* description and sampling:

- **Quaternary sapropels:** S1, S3, S5 and S6 are defined at this location as thick-bedded, greater than 5cm in thickness, dark olive gray to black in color and often laminated. S1 is the only Holocene sapropel, deposited during insolation cycle 2 (8.5kyr, Lourens, 2004). Pleistocene sapropels S3, S4, S5 and S6 correspond, respectively, to insolation cycle 12, 16, 18 and 20. The ages of these levels, following Lourens, (2004), calibration, are; S3=124kyr.; S5=195kyr.; S6=216kyr. S4 is a composite sapropel of 4 distinct dark layers separated by light-colored sediment with a total thickness of 58 cm. The calculated age at the top of this sapropel is approximately 172kyr.

-**Pliocene sapropels:** Sampled intervals are generally thinner, darker in color, with a higher TOC content, some displaying faint lamination. S49, defined as thin-bedded sapropels and thus less than 5cm thick, is dated 2.828M.a., corresponding to insolation cycle 272. Sapropel S52 (not described in the ODP Initial Reports) is defined by Emais et al (2000a), and was deposited during insolation cycle 282, with a calibrated age of 2.943M.a. S53 (according to Emeis et al, 2000a) is a composite sapropel, with 2 distinct intervals of TOC enrichment. The age for this sapropel is 2.965M.a., during insolation cycle 284. Finally, S55, described in ODP Initial Report as a sapropel, was analyzed, but it appeared to be a ghost sapropel, in agreement with Emeis et al. (2000a).

These ages are referred to the sapropels's correlative 3 kyrs lagged insolation maxima, calibrated on the sapropel mid-point, as explained on Emeis et al, 2000, and Lourens (2004) (see also Larrasoaña et al, 2003).

The samples taken from these intervals were dried and ground in an agate mortar, homogenized and prepared for geochemical and mineralogical analyses. Representative sample portions were used to determine bulk and clay mineralogy, TOC and N contents as well as major and trace element concentrations. Sr isotopic composition and detailed mineralogical analyses by High Resolution electron microscopy (transmission and scanning) were also performed on selected samples.

TOC and N measurements were made using a *Perkin-Elmer Elemental analyzer* at the Stable Isotope Laboratory (Stanford University). Samples were acidified with $H_2SO_3$ to eliminate inorganic carbon. Major elements (Al, Ca, Mg, Fe, Mn, K) were determined by atomic absorption spectrometry at the Analytical Facilities of the University of Granada. Trace elements were measured with an ICP-MS Perkin-Elmer Sciex Elan 5000 spectrometer (CIC; Analytical Facilities of the University of Granada), using Re and Rh as internal standards. These analyses were carried out after $HNO_3$ and HF digestion. Coefficients of variation calculated by dissolution and subsequent analyses of 10 replicates of powdered samples were better than 3% and 8% for analyte concentrations of 50 and 5 ppm, respectively (Bea,1996). Strontium isotope analyses were done in the CIC, University of Granada, Sr was separated using ion exchange columns (BIORAD AG 50 W8 200-400 resins). Isotopic composition was then determined with a Finnigan

MAT 262, using WSE as standard, with an estimated precision better than 0.0026% and reproducibility higher than 0.0007%. Bulk and clay mineralogy were determined using a Phillips PW1710 difractometer in the Mineralogy Department, University of Granada, and resulting difractograms were interpreted using XPowder software (Martin-Ramos, 2004). Samples were prepared following the recommendations by Kirsch (1991). In order to determine the chemical composition of clay minerals, selected samples were suspended in ethanol, the finest fraction was recovered onto a gold grid, and particles were analyzed under High Resolution TEM (STEM PHILIPS CM20, CIC, University of Granada). For the morphological description of barite, selected samples were observed under FESEM (LEO Gemini 1530, CIC, University of Granada) using Backscattered and Secondary Electrons images. Mineral phase composition was determined by an X-Ray dispersion microanalysis coupled to the device.

## 3. Paleoenvironmental conditions and detrital input

The paleoceanographic conditions leading to sapropel deposition have been a subject of debate for decades. There is now a consensus that the climate setting, humidity conditions and subsequent changes in river runoff at the time of sapropel deposition were major factors in sapropel formation. (Rossignol-Strick, 1985; Rolhing and Hilgen, 1991; Lourens et al., 1992; Aksu et al., 1995; Nijenhuis and de Lange, 2000; Casford et al., 2003) Different proxies have been used to reconstruct paleoenvironments and climate in Mediterranean regions. Mineral compositions, as well as the concentrations and ratios of detrital elements, have suggested that precipitation and runoff increased during those periods (e.g., Krom et al., 1999; Wehausen and Brumsack, 1999; Warning and Brumsack, 2000; Calvert et al., 2001; Böttcher et al., 2003). In order to validate such a scenario over the Pliocene-Holocene interval, fluctuations in kaolinite and palygorskite content, along with La/Lu, Zr/Al and $Sr^{87}/Sr^{86}$ ratios, have been used to reconstruct fluvial and aeolian input and runoff during the Pliocene and the Quaternary.

This could mean that the most intense monsoon activity (according to the above-mentioned authors) is reached during this period. The striking differences in these ratios in the Quaternary also point to a noticeable variability for the humidity (from La/Lu ratio of 80 to 148) and aeolian input in the basin (Zr/Al ranges from 0.8 to 2.7). The $Sr^{87}/Sr^{86}$ ratio is lower within the sapropel as compared to non-sapropel layers (see Table 1). Krom et al., (1999; see also Frumkin and Stein, 2003), determined the different isotopic ratios found in the material transported by Saharan winds and by the Nile river, and concluded that lower $Sr^{87}/Sr^{86}$ originates from the riverine detrital material. Thus, the interpretation of lower aeolian input is also supported by Sr-isotope data. Aeolian input fluctuations are also indicated by variations in the mineralogical composition. Fibrous minerals, as well as high kaolinite content, have been associated with aeolian input in the Mediterranean area (e.g., Diester-Hass et al., 1998), while riverine origin is indicated by increased smectite and chlorite incoming mainly from the southern and northern continents, respectively (e.g., Maldonado and Stanley, 1981; Rossignol-Strick, 1985; Hamroush and Stanley, 1990; Krom et al., 1999; Martínez-Ruiz et al., 2003). Geochemically, at Site 964, this is reflected by an increase in K/Al and Mg/Al, as interpreted by Nijenhuis et al (2001) or

Wehausen and Brumsack (2000). Both the bulk sediment and the clay fraction present higher concentrations of smectite, relative to illite and lower kaolinite content in the TOC enriched sections (see Fig. 2). The decrease in carbonate content cannot be totally accounted for calcite dissolution, as discussed by Thomson et al*.,* (2004; see also Meyers and Arnaboldi, 2005: Crudeli et al., 2004: 2006). Thus, it must be interpreted as the consequence of a global palaeoceanographic change in the basin. Furthermore, fibrous minerals (i.e., palygorskite and sepiolite, recognized and described using high resolution TEM techniques) mostly appear

| Age | | Ba/Al ($10^{-4}$) | Zr/Al ($10^{-4}$) | La/Lu | Uautg | V/Cr | V/Sc | Sr$^{87}$/Sr$^{86}$ |
|---|---|---|---|---|---|---|---|---|
| Holocene | MAXIMUM | 31.1 | 2.2 | 132.9 | 8.1 | 3.2 | 24.6 | 0.710975 |
| | AVERAGE | 20.7 | 1.2 | 118.5 | 1.8 | 1.7 | 11.3 | |
| | MINIMUN | 7.7 | 0.9 | 105.2 | -0.9 | 1.2 | 7.5 | 0.709459 |
| Pleistocene | MAXIMUM | 49.8 | 2.7 | 148.1 | 35.5 | 5.1 | 49.6 | |
| | AVERAGE | 24.7 | 1.4 | 120.6 | 4.9 | 2.0 | 13.5 | |
| | MINIMUN | 10.4 | 0.8 | 80.3 | -0.2 | 1.3 | 7.0 | |
| Pliocene | MAXIMUM | 86.5 | 3.5 | 117.2 | 54.2 | 12.2 | 163.7 | |
| | AVERAGE | 26.7 | 1.5 | 92.0 | 5.6 | 3.3 | 34.3 | |
| | MINIMUN | 16.2 | 1.0 | 63.7 | -0.6 | 1.3 | 6.3 | |

*Table IV.1. Average values of sedimentary, detrital, redox and palaeoproductivity proxies during different time periods. Complete data table is available online.*

Both the Zr/Al and La/Lu ratios have been extensively used as proxies for aeolian input in the Mediterranean area (Gallet et al., 1998; Wehausen and Brumsack, 1999; Martínez-Ruiz et al., 2000). The La/Lu ratio is used to discriminate the input from the African margin, (Hamroush and Stanley, 1990) and displays higher values when the main source of sediments is from the African craton. This ratio averages around 120 during the deposition of most of the “normal pelagic sediments”, but decreases to 115 or less within sapropel layers and can be as low as 75 in some Pliocene sapropels. Zr/Al ratios range from 1.2 to 1.8, with typically lower values within sapropels (see Table 1), indicating diminished aeolian input from the African tropical region, (e.g., Rossignol-Strick, 1985; Rolhing and Hilgen, 1991) and a general increase towards the top of the TOC enriched sediment layer. This decrease in aeolian dust is due to an increase in monsoon activity, that produces higher humidity, and thus, more abundant soil-derived detrital material and riverine denudation. During drier periods, environments similar to the present-day Sahara desert develop, and sediment can be more easily mobilized and transported by aeolian processes during wind storms. Results from both proxies indicate wetter conditions during sapropel deposition in this particular area. Average values reported for these proxies are shown in Table 1. We observed that the highest contrasts in Zr/Al between sapropel and “normal marine” layers are found in the Pliocene, when the lowest La/Lu ratio is also detected.

in "normal" pelagic sediments, and are virtually absent in sapropel layers. All of the above-mentioned observations reaffirm the idea that sapropels were deposited during a period of increased rainfall and riverine fluxes. This deduction becomes more robust when we compare our results to similar studies carried out in other Mediterranean areas, such as Eratosthenes Seamount or Mediterranean Ridge, where Wehausen and Brumsack (1999: 2000) concluded that sapropel formation depends on fluviatile input, based on Ti, Fe, Mg or K to Al ratio evolution.

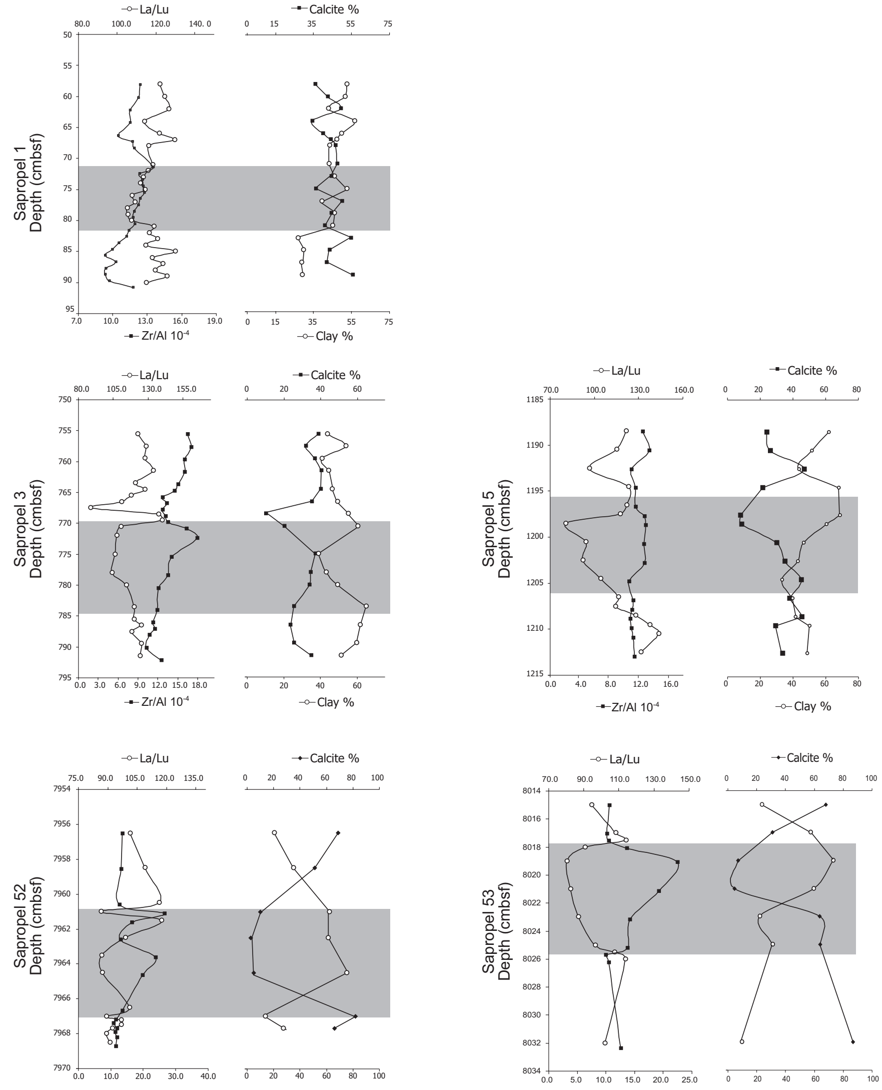


*Fig. IV.2: Trends of the mineralogical and geochemical proxies applied to the determination of the sedimentary regime and climatic implications at the time of deposition. Zr/Al ratio shows variation of aeolian input. La/Lu indicates variations in detrital input from the African craton. Shaded area corresponds to the sapropel.*

## 4. Export production fluxes during sapropel deposition

The interpretation of TOC enrichments in marine sediments raised the question of their origin in terms of enhanced export production or preservation, and put marine productivity at the center of a long debate, (e.g., Dehairs et al., 1987; Pedersen and Calvert, 1990; Calvert and Pedersen, 1993; Martinez-Ruiz et al., 2000; Filipelli et al,. 2003; Pichevin et al., 2004; Meyers and Bernasconi, 2005). Some consensus exists at present regarding the potential combination of both factors to form these TOC-rich sediments. However, productivity fluctuations through time questioned the relative importance of preservation versus export production. To further investigate productivity changes with time during sapropel deposition, marine barite and Ba/Al ratios have been used to establish export production fluxes (e.g., Thompson et al., 1995; Martinez-Ruiz et al., 2000; 2003; Rutten and De Lange, 2002). The use of Ba excess over crustal abundance as a productivity proxy is based on the correlation between the fluxes of excess Ba and organic matter in sinking particulate matter (e.g., Bishop, 1988; Dymond et al., 1992; Dymond and Collier, 1996; Paytan and Kastner, 1996: Eagle et al., 2003). This association is also supported by the observations that Ba-rich sediments usually underlie areas of high biologically productive and surface sediment barite accumulation rates correlate with upper water column productivity (Dehairs et al., 1987: Paytan, 1997; McManus et al., 1998; 1999; Eagle et al., 2003). The use of this proxy also assumes that Ba excess is related to barite crystals that originated in the water column (Paytan et al., 2002). Although Ba excess must be interpreted with care and does not allow for quantitative estimates of export production (e.g., McManus et al., 1994; 1998; Averyt and Paytan, 2004), successful paleoproductivity reconstructions using Ba excess in marine Pliocene and Pleistocene sediments from Mediterranean basins have demonstrated that widespread deposition of sapropels resulted from enhanced export production fluxes (e.g., Thomson et al., 1999; Martinez-Ruiz et al., 2000; Nijenhuis and de Lange, 2000; Weldeab et al., 2003b; Paytan et al., 2004). The reliability of this proxy to confirm enhanced productivity is additionally supported by the S isotope composition of barite crystals separated from sapropel intervals. The S isotopic composition of the sapropel barite samples is consistent with the expected water column values. This indicates that the origin of these crystals is in the water column and, consequently, that they are related to increased carbon export (Paytan et al., 2004). Barite crystals in sapropels also show sizes and morphologies similar to those described in the water column (Dehairs et al., 1987) or collected in sediments underlying areas of increased productivity (Paytan et al., 1993; 1997; Gingele and Dahmke, 1994). (See Fig.3)

Ba excess shows two distinct patterns over the time span represented by the studied samples. In Quaternary sapropels, the maximum productivity as indicated by Ba/Al ratio expands over the top of the TOC-enriched level. The offset between high organic carbon content and high Ba (thus productivity) is due to postdepositional oxidation of organic matter. The much greater stability of Ba against diagenetic remobilization makes Ba/Al ratio a more robust indicator for marine palaeoproductivity than TOC. (e.g. Thomson et al., 1999; Martinez-Ruiz et al., 2000, 2003; Nilsen et al., 2003; Powell et al., 2003). The onset of the formation of the sapropel

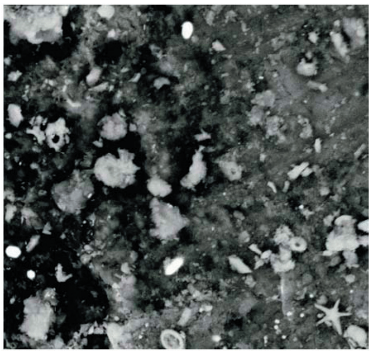


*Figure IV.3. SEM back-scattered electron image of a sediment sample from sapropel54. Light white crystals are marine barite.*

approximately coincides with the first increase in Ba excess. In contrast, in Pliocene sapropels, which have much higher Ba contents, the Ba enrichments are confined to the present day detectable black layer (Fig. 4 and 6). This reveals that Quaternary sapropel levels were more extensively altered after deposition, as further shown by the penetration of oxidation fronts marked by Mn and Fe peaks (e.g., van Santvoort et al., 1996; Thomson et al., 1999).

Although the Ba/Al ratio is not quantifiable, there are striking differences between values from Holocene to Pliocene, as we see in table 1 or figures 4 to 6. During the Early Pliocene, this ratio reaches values of up to 4 times the maximum for the Holocene. TOC and TOC-Mass Accumulation Rates (TOC-MAS) values are equally higher in the Early Pliocene, when compared to sapropel S1 (see Fig. 7). However, it is during the Pleistocene that sapropel levels show the highest Ba and $C_{org}$ MAR values. It may thus be assumed that the increase in export production during sapropel deposition was in fact much greater during the Early Pliocene and Late Pleistocene. Equally high values are described in the literature (e.g., Emeis, Robertson, Ritcher, et al. 1996; Nijenhuis and de Lange, 2000; Struck et al, 2001; Meyers and Arnaboldi, 2005; Arnaboldi and Meyers, 2006) for similar levels on different sites within the basin. After insolation cycle 12 the system suffered an abrupt change, and consequently S1 shows a relatively minor productivity increase, (e.g., Martinez-Ruiz et al, 2000; Murat and Got, 2001). This might be related to a particularly high nutrient input associated to extreme humidity in the weather system of the region, as we have detected for the same periods, and the dramatic climatic change that characterizes the Holocene. The relationship between paleoproductivity and TOC content in the sediment seems evident, although other factors, such as bottom water oxygenation, will be discussed below.

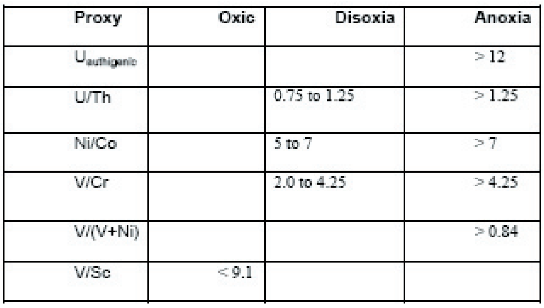
## 5. Geochemical Proxies for oxygen conditions

Increased preservation of the organic carbon due to low oxygen conditions has been used for decades as the scenario most appropriate for sapropel origin. When Calvert and co-workers (1992; 1996) proposed the alternative productivity hypothesis, the oxygen conditions at the time of sapropel deposition were further investigated on the basis of different redox proxies. A wide variety of geochemical indices and element/Al ratios have been used as indicators of the redox conditions. Those proxies include Mn, U, V, Ni, Cr and Mo contents (e.g., Calvert and Pedersen, 1993; Jones and Manning, 1994; Calvert et al., 1996; Holser, 1997; Powell et al., 2003; Nijenhuis et al., 1999; Nijenhuis and de Lange, 2000; Ivanochko and Pedersen, 2004), as well as other indices, such as $U_{authigenic}$, U/Th, Ni/Co, V/Cr, V/(V+Ni) and V/Sc (e.g., Wignall and Myers, 1988; Calvert and Pedersen, 1993; Jones and Manning, 1994; Schovsbo, 2001), summarized in Table 2.

An enrichment in redox sensitive elements is observed in all of the sampled sapropels. However, a number of clear differences appear when comparing Pliocene and Quaternary sapropels. The high concentrations of trace elements, such as V, Cr, U and Mo, are far more noticeable in Pliocene levels than in younger equivalents and thus follow a trend similar to that of Ba/Al. Most redox proxies present very similar fluctuation profiles, showing increased values within the TOC enriched sediments. The exceptions are the (V/V+Ni) and Ni/Co ratios, whose trends are unclear.

The youngest sapropel, S1, summarized in Fig. 4, presents a clear enrichment in Mo, Cr or Ni. This enrichment suggests a low oxygen concentration within the sediment, but is not diagnostic of anoxia in the water column. Of all the examined proxies, only the U/Th ratio is indicative of oxygen-depleted bottom waters (i.e., U/Th>1.25). The other selected proxies do not imply an anoxic water column during S1 sapropel formation, thus suggesting that only dysoxic conditions were reached. It is worthy of note that there is no evidence of a lack of oxygen at the onset of this sapropel (bottom of the layer).

U-based proxies suggest that the deposition conditions of sapropel S3 were slightly more anoxic than S1 (see Fig. 5). The U/Th ratio points to an intermediate dysoxic environment during deposition of the central part of the sapropel, and oxic bottom waters above and below it. However, contradictory results are obtained when using other proxies, such as Ni/Co or V/Sc. Whereas Ni/Co values are indicative of continuous oxygen availability during S3 formation, V/Sc ratios indicate reducing conditions.



| Proxy | Oxic | Disoxia | Anoxia |
|---|---|---|---|
| $U_{authigenic}$ | | | > 12 |
| U/Th | | 0.75 to 1.25 | > 1.25 |
| Ni/Co | | 5 to 7 | > 7 |
| V/Cr | | 2.0 to 4.25 | > 4.25 |
| V/(V+Ni) | | | > 0.84 |
| V/Sc | < 9.1 | | |

*Table IV.2: Summary of conditions defined by selected redox proxies, (see text for references).*

Results from Sapropel S4, which is a composite sapropel with alternating laminae of less than 1% TOC and as high as 5%, also indicate similar discrepancies among different proxies. $U_{authigenic}$ and V/Cr suggest a constant oxic environment, whereas V/Sc indicates the opposite scenario. V/(V+Ni), U/Th ratio and Ni/Co values point to reduced oxygenation, (full record is available online). The depositional environment portrayed by the redox proxies is mostly oxygenated, partly oxygen-impoverished at times. Increasing anoxia corresponds to higher organic carbon content.

Oxic conditions also prevailed during sapropel S5 deposition (see Fig. 5) according to V/(V+Ni) and Ni/Co records. Again, $U_{authigenic}$ and V/Cr display very similar behavior, suggesting normal oxygen availability on the top and bottom of the layer, and dysoxic average conditions, at points anoxic towards the middle. U/Th and V/Sc also correlate relatively well, but V/Sc is suggestive of mostly anoxic conditions, even during the onset of sapropel formation.

For sapropel S6, all proxies except the U/Th ratio indicate oxic to dysoxic conditions. U/Th points to complete anoxia during most of the deposition of this bed. In summary, most of these oxygen proxies suggest that Quaternary sapropels were deposited in generally oxygenated environments with only short-term restricted oxygenation, while only U/Th ratios seem to suggest very low oxygenation at certain times and intervals.

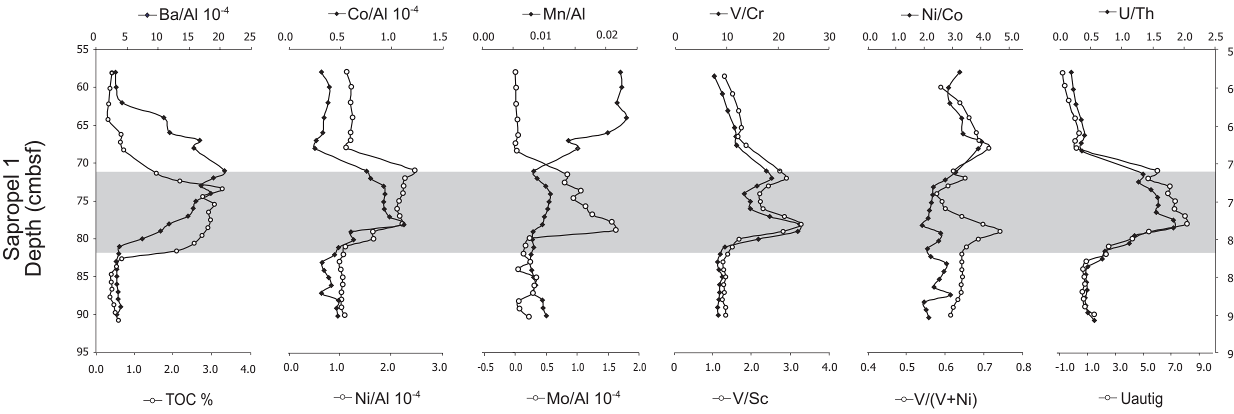


*Fig. IV.4: Geochemical proxies indicating productivity (Ba/AlX10-4), redox-sensitive elements (Ni/Al, Mo/Al, Co/Al), diagenetic remobilization of Mn and redox conditions (V/Cr, V/Sc, V/(V+Ni), U/Th and Uauthigenic) during deposition, compared to the TOC(%) content of the sediments, for Holocene sapropel S1. Shaded area corresponds to the sapropel.*

The conditions evidenced by the same set of redox proxies in Pliocene sapropels are notably different. Thus, in sapropel S49 oxygenation is clearly lower than in the Quaternary equivalents. It is worth noting that right beneath the high TOC bed, a layer of virtually no oxygenation is defined by most of the proxies used and no organic matter is preserved in the sediment at this depth.Some discrepancies also arise when using different proxies: V-based proxies indicate anoxia, the U/Th ratio mainly suggests a dysoxic environment, whereas Ni/Co and $U_{authigenic}$ values oscillate within the oxic range.

The next level within the Pliocene interval sampled downcore, S52, presents the highest organic carbon contents analyzed for this work (28% TOC, see Fig. 6). This maximum coincides with high Ba/Al ratios and all redox proxies indicating an anoxic environment, with the exception of the Ni/Co ratio, which increases but does not reach anoxic values. $U_{authigenic}$, V/(V+Ni) and V/Cr support reduced oxygen availability at the base of the sapropel layer, while oxygen would be completely consumed during the deposition of the sapropel. Of particular interest is the sudden decrease in the values of all redox proxies coinciding with a maximum in Mn.

Redox proxies indicate similar depositional conditions for sapropel S53. The onset of organic matter accumulation occurs under oxic to dysoxic conditions, and only the V/Sc ratio indicates anoxia at that level (see Fig. 6). Towards the top of the bed, all proxy values except those of Ni/Co indicates anoxia. The V/Sc values suggest that the absence of oxygen expands several centimeters over the top of the sapropel. The increase in productivity suggested by Ba/Al ends slightly before the anoxic conditions, as indicated by the redox proxies.

For the oldest sampled sapropel, S54, results are again similar: an oxic to dysoxic onset, evolving to anoxia during the later stages of formation. V/Sc situates the whole sapropel in anoxic bottom waters. Other proxies ($U_{authigenic}$, V/(V+Ni), U/Th, and V/Cr) clearly point to increasing anoxia during the deposition interval and no available oxygen at the top of the

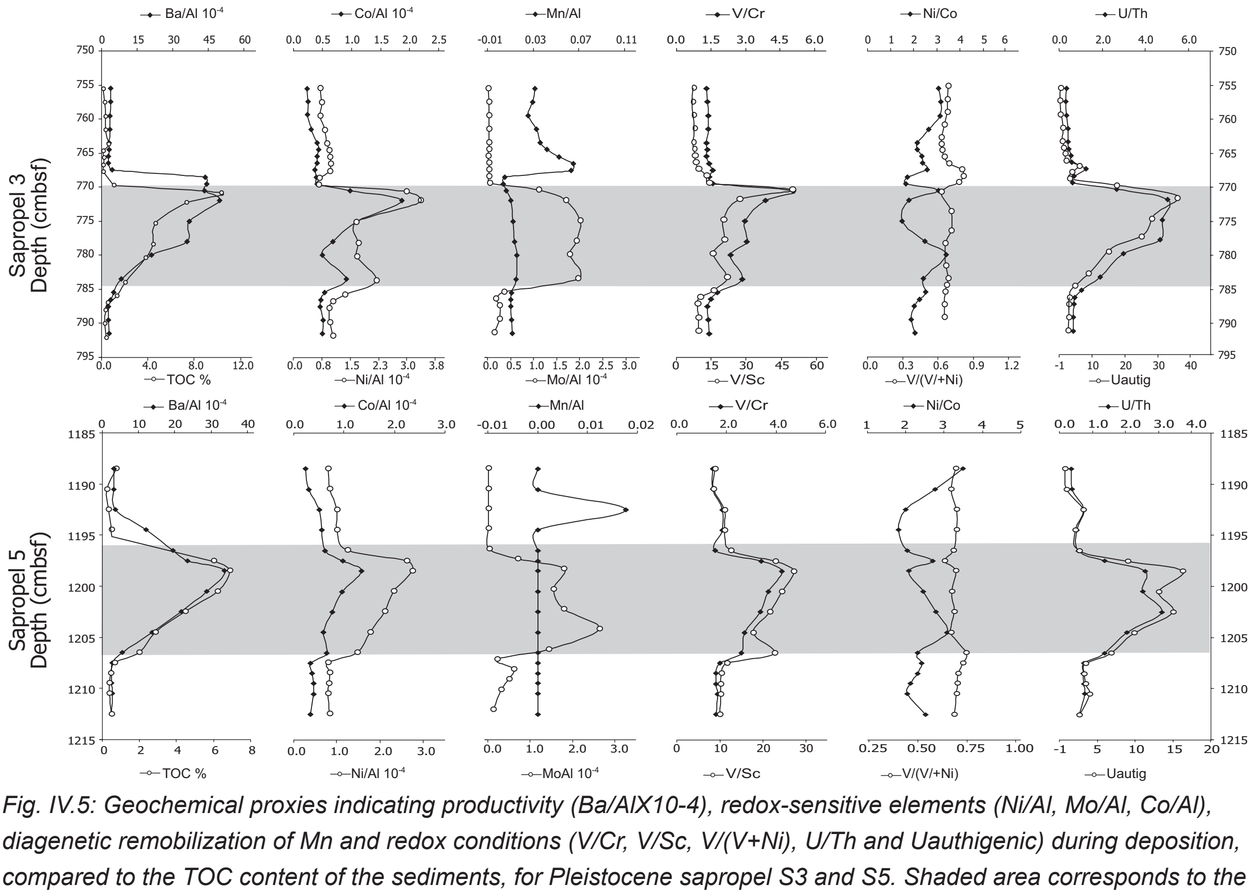


*Fig. IV.5: Geochemical proxies indicating productivity (Ba/AlX10-4), redox-sensitive elements (Ni/Al, Mo/Al, Co/Al), diagenetic remobilization of Mn and redox conditions (V/Cr, V/Sc, V/(V+Ni), U/Th and Uauthigenic) during deposition, compared to the TOC content of the sediments, for Pleistocene sapropel S3 and S5. Shaded area corresponds to the sapropel.*

layer. In general, Pliocene sapropels were deposited under low oxygenation conditions or even complete anoxia, but co-occurring increased productivity at these time intervals is also supported by Ba proxies.

In summary, Quaternary sapropels show only partial anoxic or dysoxic conditions, whereas Pliocene ones fall into more complete anoxic conditions. This is consistent with the higher export production during Pliocene sapropel deposition.

## 5. Evaluation of redox proxies

Comparison of different proxies commonly used to establish oxygen conditions (e.g., Jones and Manning, 1994; Powell, et al., 2003), has also enabled the evaluation and validation of such proxies. Certain discrepancies are evident between the various proxies with respect to the implied level of anoxia. This makes it necessary to corroborate which proxies are reliable, considering both synsedimentary and diagenetic processes that affect the distribution of redox sensitive elements (McManus et al., 2005).

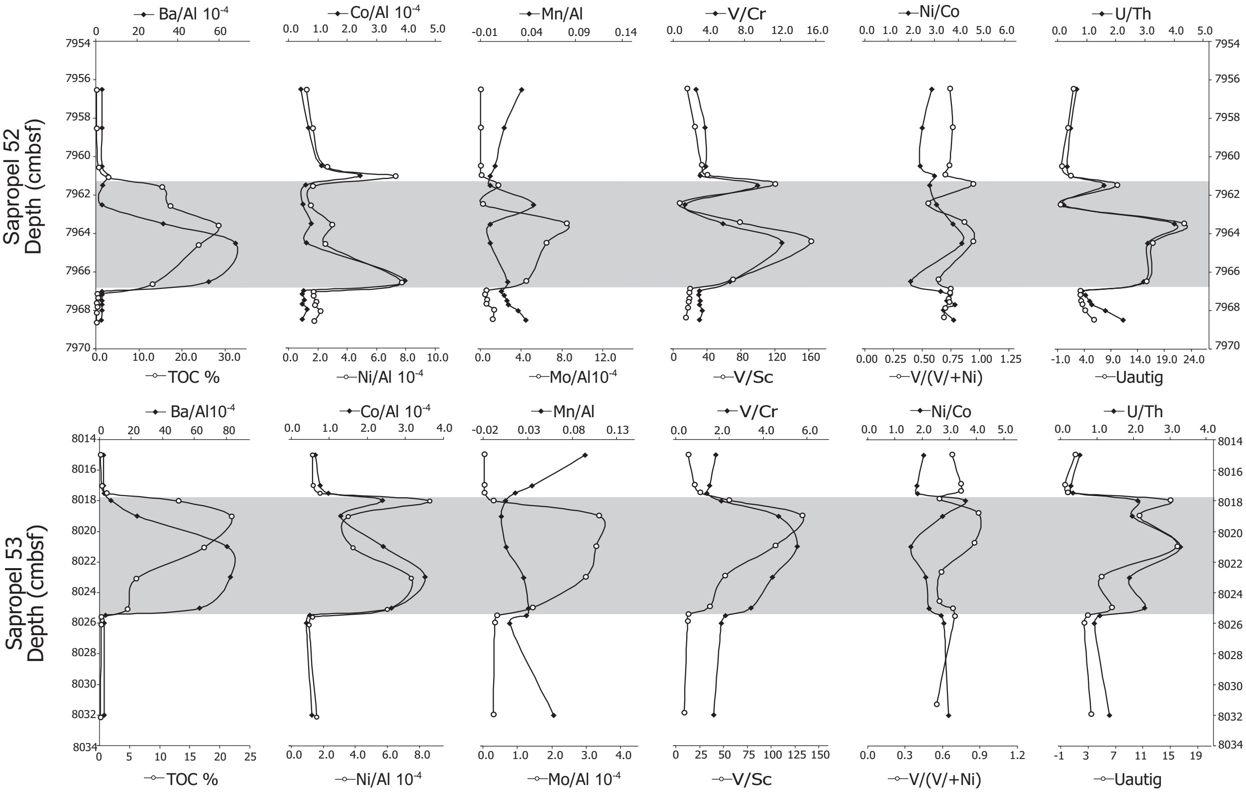


*Fig. IV.6 Geochemical proxies indicating productivity (Ba/AlX10-4), redox-sensitive elements (Ni/Al, Mo/Al, Co/Al), diagenetic remobilization of Mn and redox conditions (V/Cr, V/Sc, V/(V+Ni), U/Th and Uauthigenic) during deposition, compared to the TOC content of the sediments, for Pliocene sapropel S52 and S53. Shaded area corresponds to the sapropel.*

Most of the selected proxies follow a coherent evolution except Ni/Co, and to a lesser extent V/(V+Ni). The rest of the proxies display highly similar profiles, although very little agreement can be appreciated when they are translated into quantitative estimates for the degree of anoxia reached during sapropel deposition.

This suggests that these proxies may be used qualitatively within the same location. However, quantitative determinations are difficult. As mentioned above, the Ni/Co ratio displays a random-like pattern, always hovering in the oxic conditions field. Although no evidence of substantial sulfate reduction is found in these sapropels (Paytan et al., 2004), the evidence for reduced oxygen availability at least for the Pliocene sapropels is obvious (e.g., Passier et al, 1996; 1999). The Ni/Co ratio does not reflect these conditions. Since Ni and Co are very sensitive to diagenetic remobilization, we suggest that Ni/Co is not a very reliable proxy for determining paleo-redox conditions in the paleoceanographic context of sapropel deposition.

The rest of the selected proxies can be divided into two groups: one defines clear limits among oxic, dysoxic and anoxic fields; the other defines a limit between presence and absence of oxygen in seawater (see Table 2). U/Th and V/Cr ratios correspond to the first group. Indeed, these two proxies generally coincide in both their tendencies and the range of oxygenation defined by their values. The second group of proxies includes $U_{authigenic}$, V/(V+Ni), and V/Sc and does not define clear limits but rather general conditions. All three show very similar profiles, although V/Sc generally reaches high values, which suggest more extreme conditions compared to the other two. As proposed by Powell et al., (2003), the V/Sc ratio is not so well delimited; a reevaluation and new quantification of the behavior of this elemental ratio should be considered.

Our data suggest that a detailed and global comparison among oxygen proxies would be necessary to obtain a more accurate definition of the fields of anoxia vs. oxic conditions. It is also worth noting that very high concentrations of organic matter in the sediment are strongly associated with extreme values of certain element ratios, such as V/Sc or U/Th. This supports the link among TOC contents, redox conditions and the concentrations of certain elements. This could be the consequence of a direct association (adsorption etc.) with organic matter. In fact, uranium may complex with dissolved fulvic acid in hemipelagic sediments, as has been explained by Nagao and Nakashima (1992), and the relationship of U with organic matter in the sediment has been described in different paleoceanographic studies (e.g., Klinkhammer and Palmer, 1991; Baturin, 2002; Kochenov and Baturin, 2002). If we compare TOC-MAR and Ba/Al-MAR (see Fig. 7), for Pleistocene and for Pliocene sapropels, we observe that it was actually higher during the Pleistocene, although TOC and redox proxies values are lower. This could mean that in the Pliocene anoxia (or low dissolved oxygen concentration) was in fact a main controlling factor for sapropel formation, and that the threshold for redox proxy sensitivity should be corrected to MAR.

## 6. Preservation of the geochemical record

It is known that post-depositional processes re-distributed redox sensitive elements and thus altered the signal recorded at the time of deposition. This alteration provides information about early diagenesis in the sediment, but may also help to define sediment ventilation conditions during and immediately after deposition (e.g., Rutten et al., 1999; Gallego-Torres et al., 2004; Monford et al., 2005). Mn is frequently used as an indicator of oxidation of the sediment-water interface, since it precipitates as oxy-hydroxides when oxygen is available and constitutes a clear mark of the oxidation front (e.g., Thomson et al., 1995; 1999; Powell et al., 2003). Other redox sensitive elements, such as Ni and Co are also redistributed when oxygen levels in pore waters are low enough to reduce them. Once in solution, these elements may undergo diffusive losses through the sediment column until oxic conditions are encountered again. In Quaternary sapropels, Mn is a key element used to define the oxidation front that consumed the organic matter originally present in the sediment (e,g., Thomson et al., 1995, 1999). The Holocene sapropel shows a clear and pronounced oxidation front evidenced by a Mn peak which marks the thickness of the oxidized sapropel (e.g., Thompson et al., 1999; Martinez-Ruiz et al., 2000; Zonneveld et al., 2001; Nilsen et al., 2003; Powell et al., 2003). Also used as redox proxies, V, Cr, Mo and Co may be re-mobilized and re-precipitated with Mn oxy-hydroxides within the oxidation front, thus generating a double peak in such elements. Similar diffusion processes are expected in Pleistocene sapropels. Indeed, the oxidation front penetrates into the high productivity level, as shown by the location of the Mn peak (see Figs. 4 and 5). In Pliocene sapropels, Ni, Co, Cr and Mo show a similar distribution to that of Quaternary equivalents. In sapropel S52, as described above, redox proxies undergo a sudden decrease coinciding with the Mn maximum, thus suggesting an oxic event, although no decrease in TOC is observed. In general, during the Pliocene there are no indications of oxidation fronts that would suggest the consumption of the upper part of the sapropels, as shown in Fig. 6.

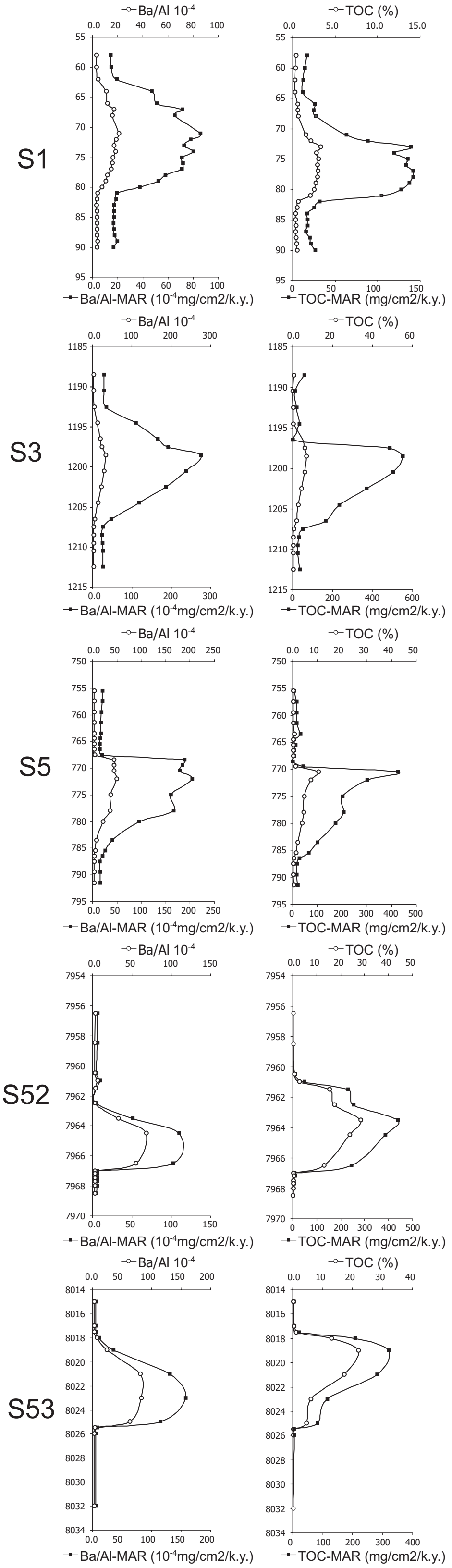


*Fig IV7: TOC (mg/cm2/k.y.) and Ba/Al (10-4mg/cm2/k.y.) Mass Accumulation Rates for selected sapropels S1, S3, S5, S52 and S53.*

## 7. Forcing mechanisms for sapropel deposition: the roles of productivity and anoxia

By comparing all of the reported sets of proxies, we can discuss the triggering mechanism for the enhanced accumulation of organic carbon in these sediments. As mentioned above, sapropels appear to be linked to cyclical variations in the climate, (e.g., Hilgen, 1991), as corroborated by detrital input. The ultimate reason for the formation of organic-enriched levels would be the effect of this climate change on the basin. With this scope in mind, we have evaluated the relations among the productivity and redox proxies, especially around the limits of the sapropel. In all the studied sections the relation between the paleoproductivity and redox proxies is clearly visible. Sampled sapropels frequently present a maximum in the value of low oxygenation proxies, such as $U_{authigenic}$, U/Th, or V/Cr, and coincide with Ba excess. This is particularly clear in Pliocene sapropels, although an offset can be seen between the two signals in certain cases, in some of which productivity typically leads to anoxia. This fact points to an anoxic environment induced by total oxygen consumption, the latter resulting from a massive input of organic matter.

If we focus on the conditions represented by the top and bottom limits of the layers studied, it can be observed that the base of the TOC-enriched level coincides with the increase in productivity in all of the sampled sapropels. As for the top of the sapropels, two distinct patterns are visible. The sapropels deposited during the Holocene and most of the Pleistocene present a peak in Ba/Al that expands over the top of the high TOC layer. Combined with the Mn peak, this provides evidence for a thicker original sapropel, later oxidized in the uppermost part. On the other hand, barium enrichment in Pliocene layers is constrained to the sapropels themselves, and in some cases TOC-enriched sediments expand after the Ba (productivity) maximum. No burn-down front is detectable.

By analyzing the redox proxies in a similar way, no clear anoxic conditions are observed at the base of the sapropels, but rather a progressive depletion of oxygen. Since maximum values of redox proxies are reached mostly coinciding with maximum productivity or with a slight offset, the range of values indicating reduced oxygen concentration (or absence) are constrained to the sapropel layer in most cases, although these conditions may sometimes extend on the top of the sapropel, mirroring the Ba/Al ratio, as seen in sapropel S1 (Fig. 4).

It can thus be inferred that productivity, which is induced by climate cycles, was the main triggering factor controlling sapropel formation. In most cases, this increase in productivity could account for oxygen depletion in bottom waters, due to exceptionally high oxygen consumption, as evidenced by “burn-down” oxidation fronts in Quaternary sapropels. In Pliocene layers, absent or limited oxygen is also linked to very high productivity, although these conditions prevail after productivity returns to normal values, thus implying either lags in the response of deep water oxygen or reduced ventilation of bottom waters.

## 8. Conclusions

The integration of multi-proxy data makes it possible to reach a set of conclusions regarding sapropel deposition in the Eastern Mediterranean within the Pliocene-Holocene time interval. Ba excess derived from marine barite supports the argument that a significant increase in export productivity is the main triggering mechanism for sapropel deposition. As regards oxygen conditions, redox proxies show that Quaternary sapropels were deposited under oxic to dysoxic bottom water conditions, while Pliocene levels display lower concentrations of oxygen, reaching anoxic environments. Post-depositional alteration mostly affected Quaternary sapropels and obliterated the TOC signal in the sediment. Thus, TOC values are not a reliable indicator for productivity variation, since organic matter is frequently oxidized at a very high rate. As geochemical redox proxies indicative of low oxygen correlate with increased marine productivity, low oxygen conditions may be a consequence of high organic matter fluxes and oxygen consumption at depth, instead of the triggering mechanism for an increased preservation due to stagnation. The use of different oxygen proxies evidenced that the results provided by U/Th, $U_{authigenic}$, V/Cr and V/(V+Ni) are relatively consistent. The V/Sc ratio displays very similar tendencies, although a re-calibration of the meaning of the values will be required in order for this proxy to be consistent with the others. The Ni/Co ratio has not been proven to be useful or reliable within the analyzed paleoceanographic setting.

# CHAPTER V

## Pliocene-Holocene Paleoproductivity Patterns Associated with Sapropel Deposition in the Eastern Mediterranean and Their Paleoceanographic Significance

## Abstract

*Temporal and spatial patterns exist in the concentrations of organic carbon in cyclically-deposited Mediterranean sapropels. Concentrations vary between 1% and 30%, with the highest values occurring in Pliocene layers in eastern basins before sapropels appeared in western basins. The elevated organic matter burial evident in sapropels has been interpreted in terms of both improved preservation due to water column anoxia and enhanced production related to increased primary productivity. Using organic and inorganic paleoproductivity proxies, we have reconstructed the paleoceanographic processes involved in Pliocene-Holocene sapropel deposition at four ODP sites in the eastern Mediterranean. Site 967 in the Levantine Basin is influenced by terrestrial input from the Nile River, whereas Site 964 in the Ionian Basin, Site 966 on the Erathosthenes Seamount, and Site 969 on the Mediterranean Ridge show minor continental influence in their organic matter compositions. Increases in Ba/Al and TOC-Ba mass accumulation rates record periods of amplified paleoproductivity associated with precessional minima and wetter climate. δ15N is interpreted as productivity proxy and as evidence of cyanobacterial activity, and organic δ13C provides information about nutrient utilization and origin of the organic matter in the sediment. Sapropels are formed principally by climatically induced increases in primary production of organic matter that lead to depletion of seafloor dissolved oxygen and consequent improved organic matter preservation. The increase in primary production was initiated and sustained by nitrogen-fixing bacteria, helped by nutrient input from continental drainage. The evolution of sapropel deposition over the past 3 My is characterized by amplified productivity and enhanced preservation of organic matter during the middle Pliocene, maxima in primary and export production and sedimentation rates during the Late Pleistocene, and a relatively weak increase in productivity during formation of the Holocene sapropel. This pattern implies that the rates of deep-water ventilation and of continental erosion generally increased in the eastern Mediterranean region as climate cooled since the mid-Pliocene.*

## 1. Introduction.

Whether improved preservation or elevated productivity is the major cause for high concentrations of organic matter in marine sediment has been a matter of debate in paleoceanographic studies for decades [e.g., *Kidd et al.*, 1978; *Jenkyns,* 1980; *Mangini and Schlosser*, 1986]. The traditional interpretation of sedimentary layers rich in organic matter as representative of anoxic events has been challenged by *Pedersen and Calvert* [1990; see also *Calvert and Pedersen*, 1993; *Calvert et al*., 1996], who argued that increased productivity, rather than absence of oxygen, was the primary factor responsible for the accumulation of organic carbon in sediments. The development in recent years of several techniques using tracers that are independent of oxygen abundance has allowed the reconstruction of palaeoproductivity in marine environments. Among these techniques, biogenic opal fraction, [e.g., *Bishop*, 1988; *Ragueneau et al*., 2000; *Romero and Hesen*, 2002; *Romero et al.,* 2002], phosphorus content, (e.g., *Slomp et al*., 2002; 2004; *Bodin et al*., 2006], barium excess and barite accumulation (Dehairs et al., 1987; Dymond and Collier, 1996; Dymond et al., 1992; McManus et al., 1998; Paytan, 1997), chlorine accumulation rates and certain biomarkers, (e.g., *Harris et al*., 1996; *Emeis et al*., 2000b*; Higginson et al*., 2003*; Menzel et al*., 2003], and nitrogen content and isotopic composition [e.g., *Peters et al*., 1978; *Calvert et al*., 1992; *Altabet and Francois*, 1994; *Meyers and Bernasconi*, 2005; *Arnaboldi and Meyers*, 2006] have been widely and successfully applied in different paleoceanographic settings.

Of particular interest to the topic of organic carbon accumulation in sediment are the multiple sapropel layers in the Mediterranean basin. Sapropels were defined by *Kidd et al*. [1978] as layers of dark colored sediment that are cyclically deposited, more than 2cm in thickness, and contain at least 2% total organic carbon (TOC). Although debate about the environmental conditions for sapropel formation is still open, sapropel deposition is usually related to an increase in marine export productivity [e.g., *Calvert et al*., 1992; *Lourens et al*., 1992; *Diester-Haass et al*., 1998; *Martinez-Ruiz et al*., 2000, 2003; *Weldeab et al*., 2003a, 2003b; *Meyers and Arnaboldi*, 2005]. Much of this work is based on Ba excess data. However, such an increase in marine productivity in a presently oligotrophic, nutrient deficient basin raises the problem of the mass balance between organic matter production and nutrient availability [e.g., *Sachs and Repeta*, 1999; *Casford et al*., 2003; *Filippelli et al*., 2003; *Menzel et al*., 2003]. The use of combined N and C stable isotopes in the organic matter, the organic matter C:N ratios, and the accumulation of reactive P should enable reconstruction of productivity and nutrient cycles in the Mediterranean basin, at the same time providing information about bacterial activity and oxygenation conditions of the water column. In recent years several papers dealt with this topic and described spatial and temporal features of sapropel deposition, [e.g., *Struck et al*., 2001; *Rinna et al*., 2002; *Meyers and Arnaboldi*, 2005; *Meyers and Bernasconi*, 2005; *Arnaboldi and Meyers*, 2006]. However, it is important to add a comparison between the previously mentioned various proxies and Ba excess, which is the most widely used paleoproductivity proxy in the Mediterranean.

One of the important outcomes of Ocean Drilling Program (ODP) Legs 160-161 has been the recognition of a time-transgressive pattern of sapropel deposition (*Bouloubassi et al.*, 1999). Sapropels containing 5% to 32% TOC exist in Pliocene sequences in the eastern Mediterranean, whereas same-age sequences in the western parts of this sea lack sapropels. In contrast, sapropels commonly are found in Pleistocene sequences across the Mediterranean Sea, although their TOC concentrations are lower and rarely exceed 10%. Moreover, Quaternary sapropels in the eastern basins typically have TOC concentrations 2-3 times larger than same-age sapropels in the western basins (*Martinez-Ruiz et al.*, 2003; *Meyers and Arnaboldi*, 2005). However, the east-west difference in TOC burial implied by concentrations typically disappears if TOC mass accumulation rates are considered because of the generally higher sedimentation rates in the western basins (e.g., *Meyers and Arnaboldi*, 2005).

In this paper, we aim first to more systematically describe the spatial and temporal patterns of sapropel deposition in the eastern Mediterranean and then to interpret such patterns in terms of their possible paleoceanographic origins. We correlate both organic and isotope signatures ($\delta^{15}$N and $\delta^{13}$C) to reinforce the information given by Ba/Al, and we employ TOC and Ba mass accumulation rates. We also consider the effect of diagenesis on the N and C isotopic composition of the organic matter, inasmuch as the organic matter is susceptible to post-depositional oxidation, [e.g., *Thomson et al*., 1995; 1999; *van Santvoort et al*., 1996; *Martinez-Ruiz et al.*, 2000]. For our purposes, we use a suite of 35 sapropels of different ages that cover the middle Pliocene to the Holocene and that originate from a four-site transect across the Eastern Mediterranean basin.

## 2. Materials and Methods.

### 2.1. Sample Settings

Samples were obtained from cores recovered at four sites during ODP Leg 160. These four sites represent a transect along the Eastern Mediterranean basin (see Fig. 1), covering the entrance area, representative of Western Mediterranean influence, the region under the effect of the Nile river discharge, and sites representing different water depths within the Eastern Mediterranean. Specifically, the sedimentary sequence deposited at Site 964, located in a deep marine setting (3658 mbsl) on the Pisano Plateau in the Ionian Basin, is influenced by the Adriatic Sea and the water masses coming from the Western Mediterranean basin through the Strait of Sicily. Site 969, also in a deep open marine setting (2200 mbsl) on the Mediterranean Ridge, represents the centermost location in Eastern Mediterranean. Cores recovered at Site 967, although containing a sequence of deep pelagic sediments (2555 mbsl), receive a stronger detrital influence from the Nile River, which drains the central African craton. Finally, Site 966 is situated on a pelagic high on the Eratosthenes Seamount at a relatively shallow water depth of 926 mbsl. At each site, high resolution sampling was carried out on selected sapropel-containing depth intervals. These sections represent Pliocene, Pleistocene and Holocene periods of sapropel deposition in Sites 964, 967 and 969, and Quaternary layers for Site 966.

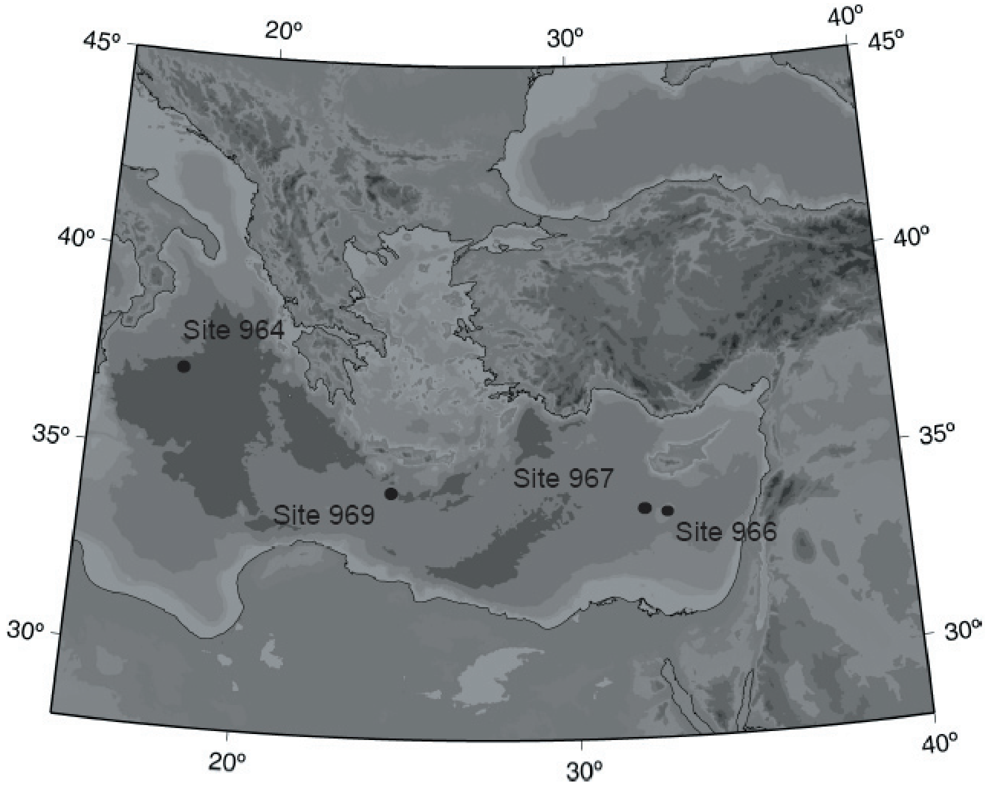


*Figure V.1. Eastern Mediterranean Basin and location of studied ODP sites.Map courtesy of Dr. Fernández-Ibáñez.*

The sediments in these cores are composed mostly of nannofossil clay, clayey nannofossil ooze and nannofossil ooze with some intervals of clay and foraminifera sand, variably bioturbated, [*Emeis, Robertson, Richter et al*., 1996]. Interspersed throughout the pelagic sediments, dark colored to black sapropel layers appear periodically. Some of these TOC-enriched sediments and sections of the overlying and underlying sediment in these cores were sampled at 2 cm intervals. Where lamination allowed a more detailed sampling, samples were collected at finer resolution down to millimeter scale.

### 2.2. Analysis

Samples were dried, homogenized in an agate mortar, and then subdivided for different analyses. TOC measurements for some samples were carried out using a Perkin-Elmer Elemental analyzer at the Stable Isotope Laboratory (Stanford University, see *Mucciarone*, [2003]). The rest of the samples were analyzed for total carbon (TC) and TOC separately at Bremen University using a TOC/TC analyzer. TOC was measured on the TOC/TC analyzer after acidification with 1N HCl to remove carbonates followed by heating to dryness. At Stanford University, parallel to TOC measurements, total N (TN), $\delta^{13}$C and $\delta^{15}$N isotopic composition were also carried out using a Finnigan MAT isotope ratio mass spectrometer (IRMS) connected to a Carlo Erba (now CE Elantech, Inc.) NA1500 Series II Elemental Analyzer. TOC/TN ratios are expressed on an atom/atom basis. $\delta^{15}N$ and $\delta^{13}C$ values are respectively expressed relative to atmospheric dinitrogen and Vienna PeeDee Belemnite (VPDB) standards. These samples were repeatedly acidified with $HSO_3$ to eliminate all inorganic carbon prior to isotope analysis.

Barium content was determined using an ICP-MS Perkin-Elmer Sciex Elan 5000 spectrometer (CIC; Analytical Facilities of the University of Granada), using Re and Rh as internal standards. Coefficients of variation calculated by dissolution and subsequent analyses of 10 replicates of powdered samples were better than 3% and 8% for analyte concentrations of 50 and 5 ppm, respectively [*Bea*,1996]. Aluminium content was analyzed by atomic absorption spectrometry at the Analytical Facilities of the University of Granada. These two analyses were carried out after $HNO_3$ and HF total digestion of the homogenized sample.

TOC and Ba mass accumulation rates (MAR) were calculated based on the sediment dry bulk density (DBD) obtained from ODP Leg 160 database (available online) and linear sedimentation rates (LSR) that we calculated for our sampling intervals. We based our calculation on the methodology used by *Meyers and Arnaboldi* [2005]. In brief, the peak TOC concentration measured in each sapropel layer was assumed to represent the orbitally tuned age of the corresponding insolation cycle. The difference in core depths between successive sapropel layers was then divided by the ~21 ky of each precessional cycle to arrive at a linear sedimentation rate for this time and place. The LSR, mean DBD, and resulting mean MAR values we employed are summarized in Table 1.

## 3. Results

### 3.1. TOC Concentrations, TOC Mass Accumulation Rates, and Depositional Durations of Sapropels

TOC concentrations in the samples range from less than 0.05% to 28.40%, (Fig. 2A to 5), with the highest values detected in the Pliocene at Sites 964 and 969. The general temporal trend is a progressive increase in organic carbon content within the sapropels from the Holocene through the Pleistocene (Fig. 2A and 2B) and into the Pliocene (Fig. 3), although the accumulation rate of organic carbon is higher during the Pleistocene at Sites 964, 966 and 967, (Fig. 4A and B and Fig 5). For sapropels deposited during the same insolation cycle, Site 966 shows the lowest TOC concentration and the lowest TOC- MAR (see Fig. 2A and B and Fig. 4A and B). The depositional durations of individual sapropels at Site 964 range between 1.3 ky to 4.5 ky within Quaternary levels and are fairly constant (aprox. 2.4 ky) for Pliocene equivalents. These episodes are notably shorter than the periods of sapropel deposition at the other three sites. Particularly, at Site 966 sapropel formation extends for up to 12.45 ky (S6, i-cycle 16). Site 967 exhibits particularly long periods of sapropel formation that reach up to 10.4 ky during i-cycle 18, and also during the Pliocene (i-cycles 168-180). Equivalent levels at Site 969 appear more similar to the ones on Site 964, always presenting shorter depositional time in the Pisano Plateau. In each site, the time span for sapropel deposition is more consistent during the

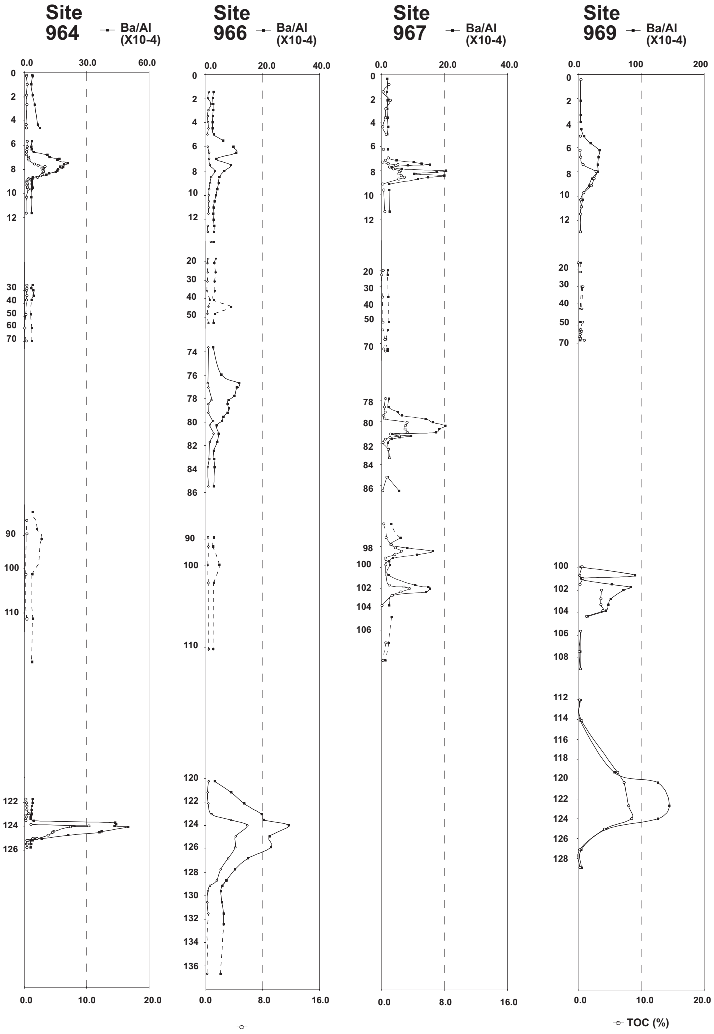


*Figure V.2A. Ba/Al (10-4mg) and TOC (mg) for Holocene and upper Pleistocene sampled sapropels.*

Pliocene, but it is highly variable during the Quaternary. Sapropel onset is always earlier on the Eratosthenes seamount, followed by formation on the nearby deep Site 967. Sites 969 and 964 display similar onset ages, although slightly earlier at Site 969, in the center of the basin.

### 3.2. Ba Concentrations and Mass Accumulation Rates

Barium concentrations vary nearly parallel with TOC concentrations (Fig. 2A to 5), although elevated Ba concentrations frequently extend above the organic enriched layer (Fig. 2A and B) in Quaternary sapropels, a feature especially visible in sapropels from Site 966. These layers show a distinct offset between the organic carbon accumulation and the productivity signal as represented by Ba/Al. Ba and TOC show the best fit in terms of timing and extend of the event in the sections sampled at Sites 967 and 967.

Ba-MARs exhibit maxima for Pleistocene sapropels in all sampled sections except for section at Site 967, where the Holocene sapropel S1 has a higher rate than the older levels, (See Fig. 4A). This Ba-MAR maximum coincides with maximum LSR's. The highest Ba-MARs values are found at Site 969, located in the center of the basin. For same-age sapropels, the amounts of

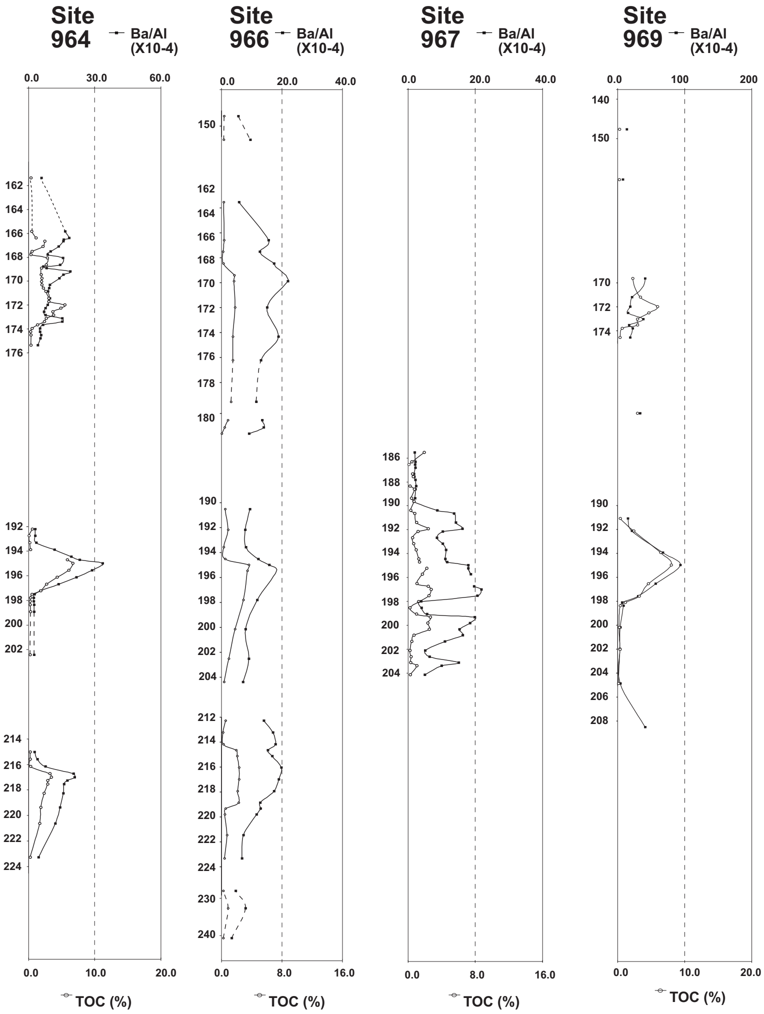


*Figure V.2B. Ba/Al (10-4mg) and TOC (mg) for upper Pleistocene sampled sapropels.*

increase in Ba content and Ba-MAR are similar for the three sites located in the deeper parts of the basin, but they are notably lower at Site 966 (Fig. 2A and B and Fig. 4A and B).

### 3.3. TOC/TN Ratios

The atomic TOC/TN ratio exhibits similar variations through time at the four locations, showing values between 5 and 10 for background “normal” pelagic sediment (carbonate ooze), and increasing up to 25 for organic rich samples (see Fig. 4A and B, and Fig. 5). Since the highest concentrations of organic matter are detected in Pliocene sediments, the TOC/TN ratio also presents maximum values for this period. This TOC/TN ratio follows an exponential correlation with the organic carbon content; the higher organic carbon content is associated with a sharp increase in TOC/TN ratio until it reaches a value ~15. Then the ratio tends to stabilize, regardless of the TOC concentration (Fig. 6). The highest TOC/TN ratios are found in Site 967, whereas the lowest are found on the bathymetric high at Site 966.

### 3.4. Nitrogen Isotopic Compositions

The $\delta^{15}N$ data show striking similarities at all four locations. The N-isotope values are significantly lower in the TOC rich sections compared to the carbonate oozes sediments. Thus, all sapropels show very low $\delta^{15}N$ values, ranging from ≈1.0-0.0‰ for the S1 sapropel to values between 0‰ and -3.0‰ for Pleistocene sapropels (see Fig. 4A and B) and down to -3.1‰, the lowest value for Pliocene sapropels (Fig. 4B). There is a detectable trend also within the successive Pleistocene sapropels with increasing average $\delta^{15}N$ value from i-cycle 10 (102 ky) to i-cycle 2 (8 ky) in the studied sections. When similar i-cycles are compared between sites, sections from Sites 966 differ from equivalent sections recovered from the deep basin, as was the case for Ba and TOC, in showing slightly higher $\delta^{15}N$ values.

### 3.5. Organic Carbon Isotopic Compositions

The $\delta^{13}C$ record is somewhat more variable and erratic (see Figs. 4A and B and Fig.5). As a whole, values range between -19.0‰ and -26.5‰, and both the highest and lowest values are found within the Pleistocene sapropels sampled from Site 967. Although there is a detectable general trend opposite to $\delta^{15}N$ in the sequences at Sites 964 and 966, this tendency is not observed for Site 967 nor in the Pliocene sequence at Site 969. There is an apparent shift towards heavier C-isotopic composition with the onset of the Quaternary sapropels or just before the increase in TOC content in the sediment. Again, this feature is not always visible in Pliocene sapropels all across the basin, where systematic variations of $\delta^{13}C$ are less discernable.

## 4. Discussion

We discuss our isotopic data in terms of what it reveals about nutrient utilization during sapropel deposition, we evaluate the records of sapropel-associated changes in marine productivity evident from the concentrations of TOC and $Ba_{excess}$ and their mass accumulation rates, we assess the origin and diagenesis of the organic matter in the sapropel sequences inferred from their TOC/TN ratios, and we consider the broader paleoceanographic implications of the patterns of sapropel deposition.

### 4.1.Paleoproductivity Proxies

#### *4.1.1. Paleoproductivity Evidence from Nitrogen Contents*

The concentration of nitrogen in sediment can be a proxy of organic matter production, provided that an insignificant amount of inorganic N is adsorbed to clay minerals [e.g., *de Lange*, 1992; *Freudenthal et al*., 2001; *Calvert*, 2004]. We verify that the percentage of inorganic N in our sediments is insignificant, and thus we may assume that $N_{tot}$=$N_{org.}$ We used the routine described by *Nijenhuis and de Lange* [2000], *Calvert* [2004], and *Arnaboldi and Meyers* [2006] in which the concentrations of TOC are plotted against those of TN. The correlation is extremely good (R>0.9 for all cores, see Fig. 6), with an intersection point at the *y* axis, even at the detection limit of the technique as is the case for Site 966 (b=0.01, see Fig. 7). The absence of a nitrogen-axis intercept indicates the absence of absorbed inorganic nitrogen. Thus, we may assume that all N in the sediment is associated with organic matter, and so our $\delta^{15}N$ analyses reflect purely $N_{org}$.

The $N_{org}$ isotopic composition can also be used as an indicator for the origin of organic matter [e.g., *Calvert et al*., 1992; *Meyers*, 1997; *Knicker and Hatcher*, 2001; *Shubert and Calvert,* 2001;

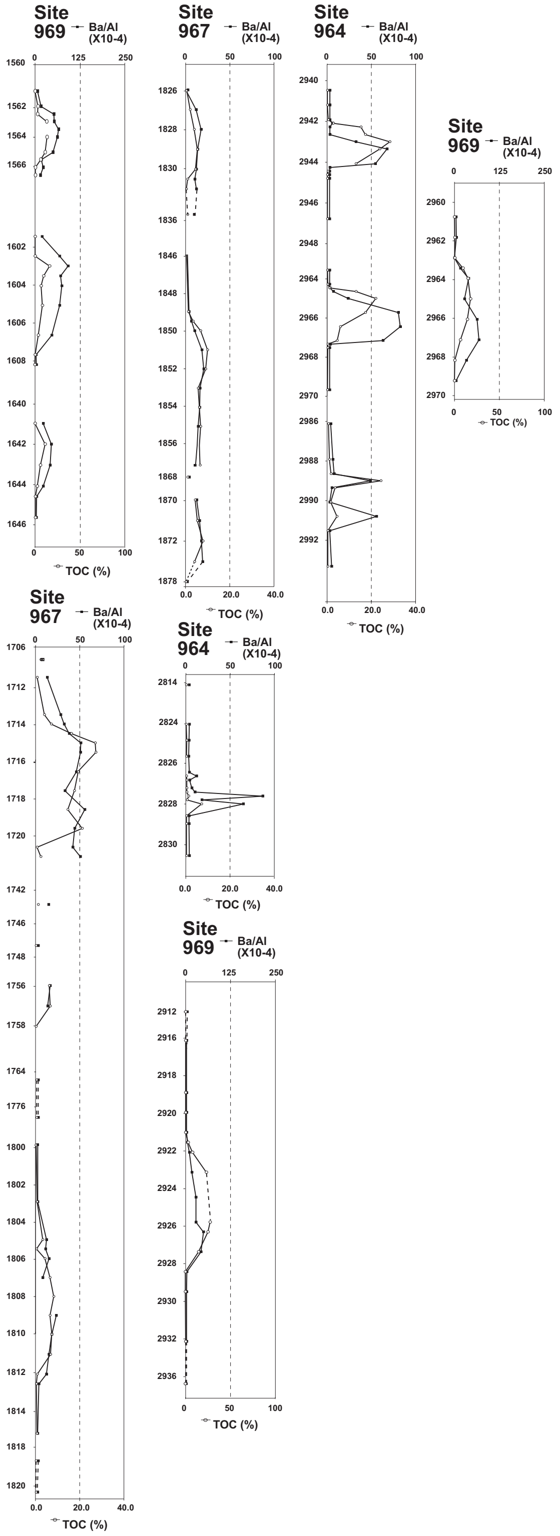


*Figure V.3. Ba/Al (10-4mg) and TOC (mg) for lower Pleistocene and upper Pliocene sampled sapropels.*

*Struck et al*., 2001; *Rinna et al*., 2002; *Meyers and Bernasconi*, 2005; *Meyers and Arnaboldi*, 2005; *Arnaboldi and Meyers,* 2006] and, what is more important, for evaluating nutrient cycles in the water column (e.g., *Altabet and Francois*, 1994: *Voss et al*., 1996; *Gruber and Sarmiento*, 1997; *Altabet et al*., 1999; *Freudenthal et al*., 2001; *Shubert and Calvert*, 2001; *Karl et al*., 2002; *Pantoja et al*., 2002]. The Mediterranean is presently an oligotrophic sea, characterized by low concentrations of macro-nutrients such as P and N in surface waters, [*Bethoux*, 1989; *Struck et al*., 2001; *Astraldi et al*., 2002; *Pantoja et al*., 2002]. This shortage of nutrients is particularly dramatic in the Eastern basin, being farther from the present day, main Atlantic Ocean source of water and nutrient to the basin. An important regional nutrient source to the Eastern Mediterranean is the Nile River [e.g., *Jenkins and Williams*, 1984; *Rossignol-Strick*, 1985; *Diester-Haass et al*., 1998; *Weldeab et al*., 2003b]. This riverine input and its significance as nutrient source has fluctuated over time as cyclic variations in the monsoon system influenced runoff from the Nile. Specifically, increased nutrients and fresh water supply from the Nile have coincided in time with precessional minima associated with sapropel formation [*Rossignol-Strick*, 1985; *Hilgen*, 1991; *Rohling and Hilgen*, 1991].

### 4.1.2. δ$^{13}$C Patterns and Paleoceanographic Significance

The $C_{org}$-isotopic compositions of the sapropel sequences differ spatially and temporally. Important conclusions about paleoproductivity can be inferred from the δ$^{13}$C values, although a wide variety of factors can affect the isotope signal for $C_{org}$, such as surface temperature, vital effects, nutrient uptake [e.g., *Meyers*, 1997; *Kump and Arthur*, 1999], nutrient recycling [e.g., *van Breugel et al*., 2005], or even massive biomass burning [*Finkelstein et al*., 2006]. Organic $\delta^{13}C$ values in our samples, ranging from -26‰ and -19‰, (Figs. 4A and B), mostly correspond to organic matter of marine origin, although some terrestrial influence could be argued from the more negative values. This land-derived influence is potentially particularly applicable for samples from Site 967, located in the distal plume of the Nile River discharge that could provide large amounts of detrital material during intensified monsoon periods [*Rossignol-Strick*, 1985]. All across the Eastern Mediterranean basin, $\delta^{13}C$ values lower than -23‰ are frequent, especially in low TOC sections. The low values are consistent with an oligotrophic setting in which C availability does not limit algal vital fractionation. On the other hand, periods of higher productivity result in greater $^{12}C$ uptake and lead to higher $^{13}C/^{12}C$ ratios in the remaining dissolved inorganic carbon available to primary producers and, thus, to less negative $\delta^{13}C_{org}$ values. This pattern of a slight increase in $\delta^{13}C_{org}$ values is the general response detected in the analyzed sections and is particularly evident at the base of the sapropel layers. However, this classic high-productivity isotopic trend is not evident at Site 967. In fact, cores recovered in the deep Levantine sub-basin exhibit the most negative $\delta^{13}C_{org}$ values and the most erratic trends in our sample suite. A possible explanation for the absence of a shift to less negative $\delta^{13}C$ values in the Site 967 sapropel layers is that near-surface recycling of organic matter lightened the isotopic composition of the carbon available to photoautotrophs [*Struck et al*., 2001; *Menzel et al*., 2003; *Arnaboldi and Meyers*, 2006]. In this scenario, increased continental runoff diluted the surface ocean and created a strongly stratified water column that impeded sinking of organic matter and discouraged vertical mixing. Oxidation of the isotopically light organic carbon could then occur within the lower part of the photic zone, where it would be assimilated by photosythesizers. The near-surface recycling of organic carbon during times of fluvial dilution of the surface ocean would potentially be augmented by terrestrial organic matter. Significantly, a shift toward heavier isotopic composition is visible at the base of the TOC-enriched layers at Site 967. We assume this shift is an indication of general increases in nutrient uptake and carbon fixation in the form of organic matter during times of sapropel deposition.

### 4.1.3. $\delta^{15}N$ Patterns in Sapropel Sequences

All the sapropels exhibit low values of $\delta^{15}N$ (Figs. 4A and B). This signature is unlikely a result of diagenesis as the decrease in $\delta^{15}N$ values is opposite to the clear increase in TOC/TN, while under suboxic-anoxic water column conditions the expected trend of organic matter degradation is an increase in $\delta^{15}N$ due to remineralization with increasing TOC/TN ratios (Nakatsuka et al., 1997; Karl et al., 2002; Lehmann et al., 2002; Arnaboldi and Meyers, 2006). Instead, the possible explanations for the dramatic decrease in $^{15}\delta N$ values in the sapropels are: (a) incomplete nutrient utilization under nutrient excess conditions [e.g., *Calvert et al.*, 1992] and (b) an ecosystem change in which a bloom of nitrogen-fixing primary producers occurs [e.g., *Sachs and Repeta*, 1999; *Milder et al*., 1999; *Struck et al*., 2001; *Pantoja et al*., 2002; *Meyers and Bernasconi*, 2005; *Arnaboldi and Meyers*, 2006].

The evidence for increased productivity based on the high TOC and Ba contents of the sapropels is strong. We may therefore reject the hypothesis of incomplete nitrogen utilization. Furthermore, fluvial delivery of an extraordinary excess of nutrients would be required to lower δ$^{15}$N values, particularly considering the amount of organic carbon accumulated in the sapropels. As discussed by *Sachs and Repeta* [1999], it is not coherent for such an input of nutrient from river discharge in the Eastern Mediterranean. On the other hand, nitrogen fixation can be the main source of bioavailable nitrogen in surface waters [e.g., *Altabet and Francois*, 1994; *Kuypers et al*., 2004]. This process would incorporate atmospheric dinitrogen (δ$^{15}$N = 0‰) into the marine system, lowering the isotopic composition [e.g., *Meyers*, 1997; *Altabet et al*., 1999; *Karl et al*., 2002; *Pantoja et al*., 2002]. Although *Krom et al.,* [2004] invoke other processes for the low δ$^{15}$N found in sapropel layers, the remarkably lighter N isotopic composition clearly points toward periods of nitrogen fixation and therefore a change

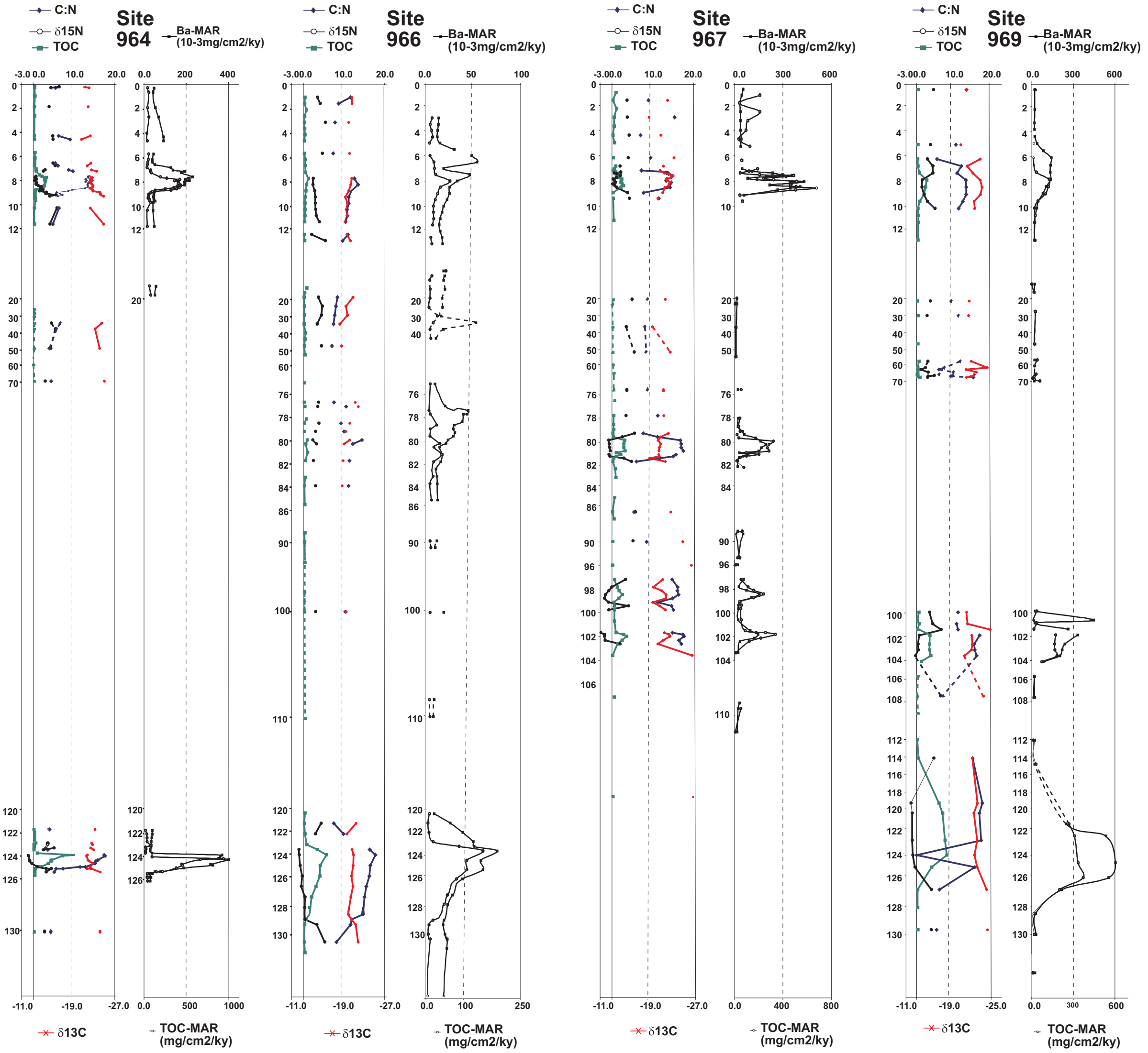


*Figure V.4A. Productivity (Ba/Al-MAR and TOC-MAR) and nutrient uptake (N and C isotopic composition) and TOC: TN ratios for Quaternary sampled sapropels.*

in the bacterial community to a primarily N-fixing biota, probably associated with a decrease in phytoplankton activity [e.g., *Sachs and Repeta*, 1999; *Pantoja et al*., 2002], is the most reasonable explanation. Nitrogen fixing cyanobacteria, such as *Trichodesmium*, see review by *Karl et al*. [2002], produce organic matter that is isotopically very light in nitrogen. This phenomenon would favor low $\delta^{15}N$ values, and at the same time, it would provide extra bioavailable nitrogen for other primary producers. Nitrogen fixation is often limited by Fe, Mo and/or P concentrations [*Karl et al*., 2002]. However, although river runoff would not be able to supply enough N to support the observed increase in productivity, it was likely capable of supplying Fe and P in excess to induce N-fixation by cyanobacteria and archaea. This extra input of freshwater would decrease salinity in the upper part of the water column. Lower salinity is known to enhance Mo reactivity and availability, [e.g., *Karl et al*., 2002] in the form of $MoO_4^{-2}$, whereas P can easily be recycled by reductive scavenging [*Karl et al*., 2002; *Slomp et al*., 2004]. All these factors, added to an increase in sea surface temperature [e.g., *Lourens et al*., 1992; *Emeis et al*., 2000b], allowed the maintenance of blooms in N-fixing community and associated biota.

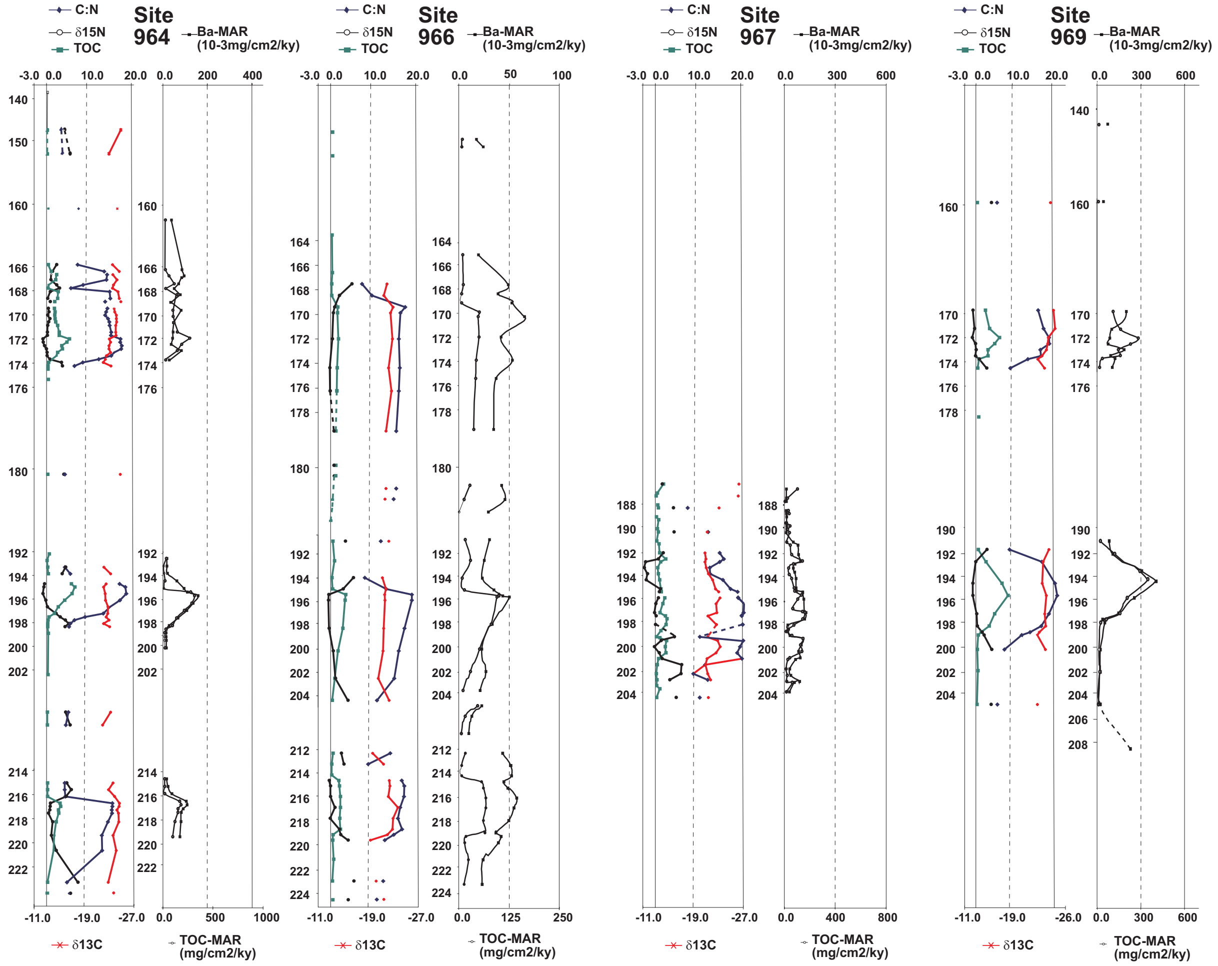


*Figure V.4B. Productivity (Ba/Al-MAR and TOC-MAR) and nutrient uptake (N and C isotopic composition) and TOC: TN ratios for Quaternary sampled sapropels.*

The multiple sapropel layers in all four locations consistently exhibit the marked change to lighter N-isotopic composition. The shift in $\delta^{15}N$ at Site 966 is slightly less intense, especially for i-cycles 2 and 8, and coincides with generally lower TOC concentrations for the respective sapropels than at other locations. This difference could reflect deposition of organic matter that experienced less reworking in the water column due to shallower water depth, or it could

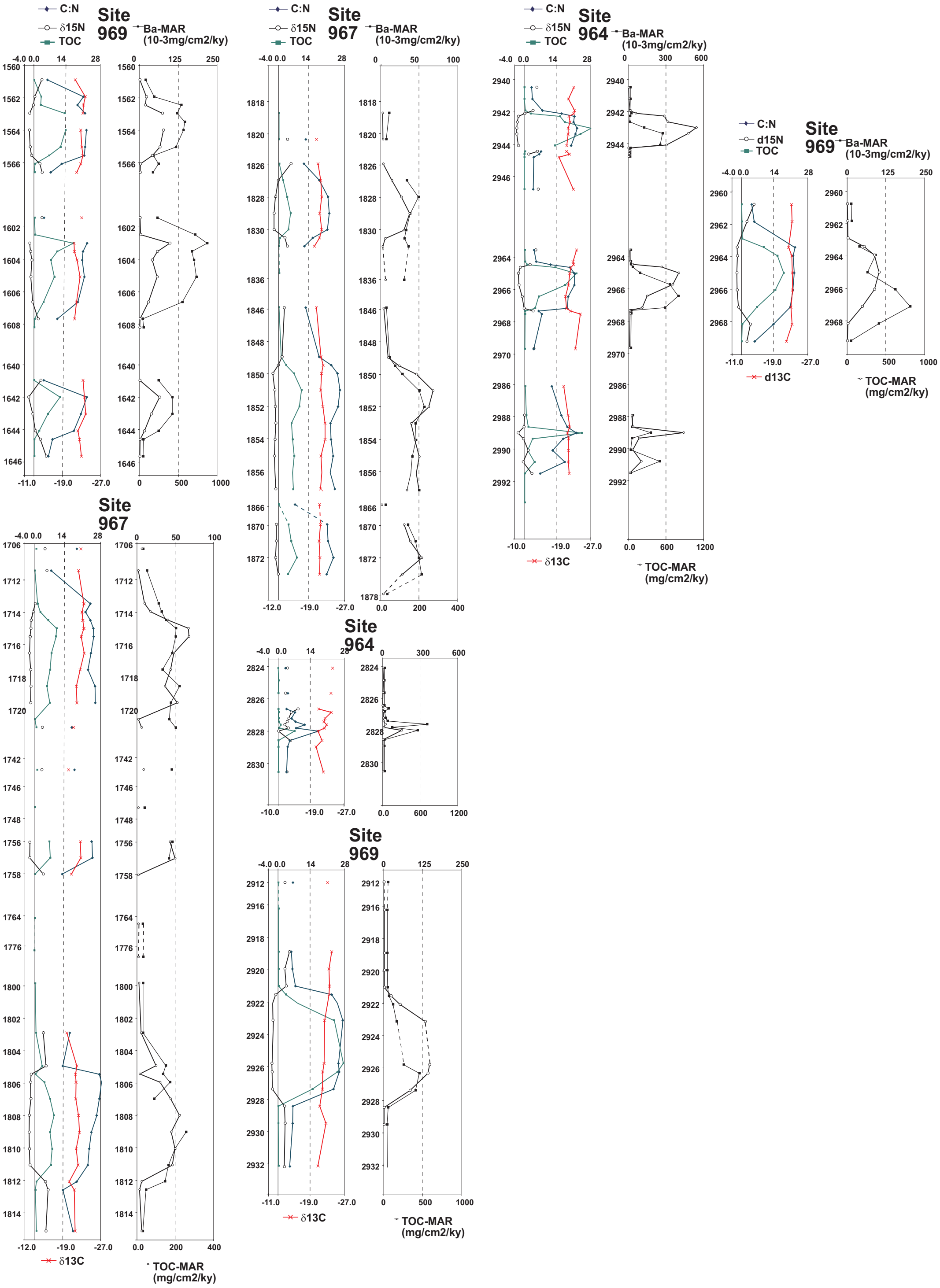


*Figure V.5. Productivity (Ba/Al-MAR and TOC-MAR) and nutrient uptake (N and C isotopic composition) and TOC:TN ratios for Pliocene sampled sapropels.*

record more intense degradation of the organic matter after deposition within the sediments [e.g., *Freudenthal et al*., 2001; *Lehmann et al*., 2002; *Kienast et al*., 2005]. In the other three sites, the shift towards very low δ$^{15}$N values is very evident in the Quaternary deposits and parallels or precedes the increase in export production indicated by Ba accumulation. The Pliocene sapropels show mutually similar trends across the basin. δ$^{15}$N values exhibit a progressive decrease from the onset of sapropel formation upwards, but not always parallel to Ba/Al enrichment. In fact, it is common to find the lighter N-isotopic composition preceding the productivity maxima, indicating that maximum N fixation was followed by an increase in total export production. As a whole, low δ$^{15}$N values coincide well with increased organic carbon concentrations, in agreement with other sapropel studies [*Calvert et al*., 1992; *Milder et al*., 1999; *Meyers and Bernasconi*, 2005*; Meyers and Arnaboldi*, 2005*; Arnaboldi and Meyers*, 2006]. We thus infer that blooms of nitrogen-fixing biota are a central factor in creating the higher surface productivity that led to sapropel formation.

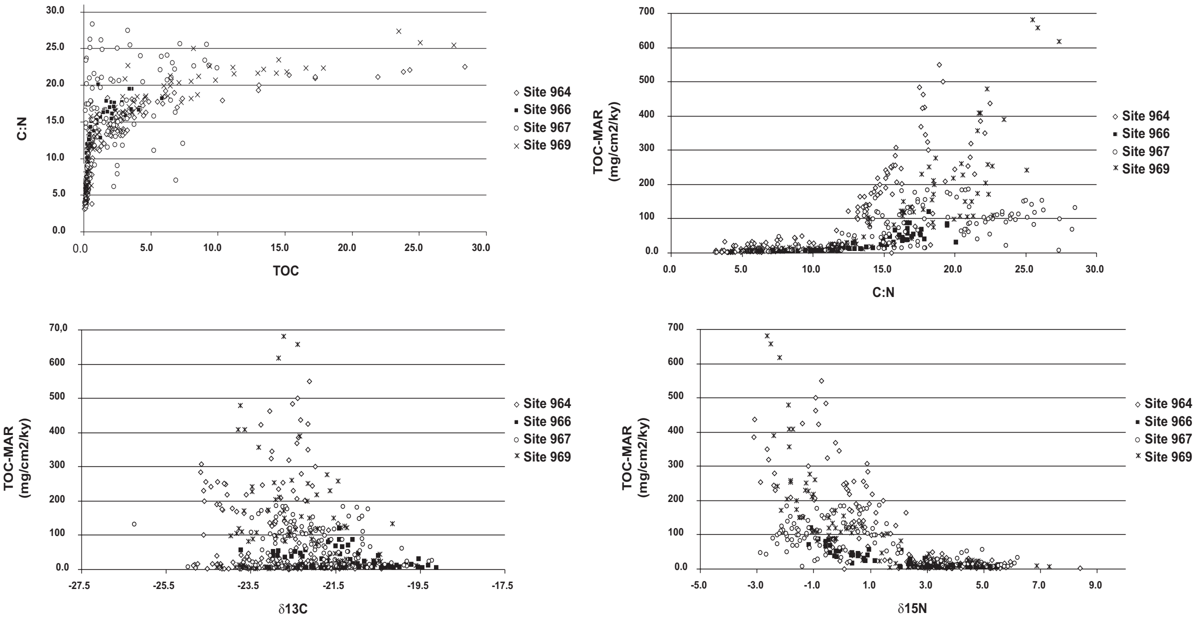


*Figure V.6. C:N, TOC, δ15N and δ13C relationships in the studied sections.*

Combining all the information on the C and N isotopic composition of the organic matter, we observe that sapropel deposition is characterized by higher nutrient utilization, indicated by increase C uptake (increase in δ$^{13}$C) and higher TOC-MAR. At the same time, the decrease in δ$^{15}$N indicates a shift to a major contribution of N-fixing cyanobacteria to the total marine productivity. The triggering factor for this situation seems to be associated to climatic conditions - higher sea-surface temperatures, lower sea-surface salinities and extra inputs of P from increased continental runoff. In marked contrast to present day Mediterranean conditions, sapropels represent former periods during which nitrogen fixation was linked to an increase in primary productivity.

#### *4.1.4. Paleoproductivity Patterns Based on Ba concentration.*

Ba concentrations and Ba/Al ratios have been used for paleoproductivity reconstructions in a wide variety of marine environments [e.g., *Dymond et al*., 1992; *Francois et al*., 1995; *Paytan*, 1997; *McManus et al*., 1999; *Kasten et al*., 2001; *Eagle et al*., 2003; *Weldeab et al*., 2003; *Paytan et al*., 2004]. Greater TOC concentration in our sapropel sequences is always linked to an increase in excess Ba. Although $Ba_{excess}$ cannot be used to quantitatively determine export productivity, [e.g., *Ginsele and Dahnke*, 1994; *McManus et al*., 1994; 1998; *Averyt and Paytan*, 2004], it has been widely and successfully applied as a semi-quantitative indicator for variations in marine productivity in the Mediterranean basin [*Dehairs et al*., 1987; *Diester-Haass et al*., 1998*; Martinez-Ruiz et al*., 2000; 2003; *Emeis et al*., 2000a; *Weldeab et al.*, 2003a]. Furthermore, it has been shown that Ba content permits a better reconstruction of paleoproductivity than TOC, because barite is less sensitive to oxidative destruction [*Thomson et al*., 1995; 1998; *Paytan and Kastner*, 1996]. In Mediterranean sapropels, the TOC destruction is evidenced by oxidation fronts in the form of high Fe and Mn concentrations above sapropel layers and low TOC concentrations in the upper parts of the sapropel, whereas high Ba concentrations remain preserved [e.g., *Thomson et al*., 1995; 1999; *Larrasoaña et al*., 2003b; *Martinez-Ruiz et al*., 2000; *Gallego-Torres et al*., 2007].

An increase in Ba/Al concentration appears in all the sapropel layers. Although these increases in concentration and Ba-MAR may vary, they always accompany the shift to higher TOC content and TOC-MAR, at least at the base of the sapropels. However, we clearly observe the disconnect between concentrations of Ba and TOC at the top of the Quaternary $S_1$ sapropel at the four study locations (Fig.2A and Fig. 4A), indicating that the increased productivity event actually persisted longer in time than evident in the more easily oxidized organic matter.

Although similar conditions also exist in the Pleistocene sapropels, the offset between TOC and the productivity signal is less striking and sometimes not even detected. Site 966, situated at a much shallower depth, is evidently more sensitive to the active post-burial “burn-down” oxidation and shows more offset between Ba and TOC than age-equivalent sapropels at the other sites that are in deep basin settings. As a whole, the sampled Pleistocene sapropels, ranging from 81 ky to 217 ky, exhibit the highest export production of the studied sections, represented by the highest Ba and TOC-MAR, although TOC concentrations are lower than during the Pliocene.

The Pliocene sapropels at Sites 964 and 969 differ in important ways from the Quaternary sapropels in the eastern Mediterranean transect. The increase in productivity is again indicated by increases in Ba/Al ratios, Ba-MARs, and TOC-MARs, but the oxidation fronts that are common in the Quaternary sapropels are generally absent. In fact the opposite offset between TOC and Ba/Al might be seen in i-cycles 282 and 284 (Site 964, see Fig. 3 and 5). These sapropels appear to have originally developed with an increase in export production but continued to accumulate after the return to normal productivity conditions, probably due to the presence of anoxic bottom waters that favored organic matter preservation. This difference suggests that deep-water circulation during the middle Pliocene was slower than in the Quaternary in the eastern Mediterranean.

A particularly interesting feature in the sapropel layers is that their lighter N-isotopic composition of organic matter mirrors organic-rich levels, but it does not extend above oxidized sapropels to parallel to the increase in productivity. Based on the evidence of the importance of nitrogen fixation to sapropel formation, increases in the productivity proxy (excess Ba) that records the change in export production should be mimicked by changes in the $\delta^{15}N$ record as this also reflects surface water processes related to primary production. However, the post burial burn-down oxidation may affect this signal. Specifically, oxidation eliminates organic matter and preferentially consumes $^{14}N$, so that the remaining organic matter in the sediment becomes enriched in $^{15}N$. Opposite to this process, suboxic degradation tends to remineralize amino-acids, which are isotopically heavier, and so, $\delta^{15}N$ would slightly decrease [e.g., *Lehmann et al.*, 2002; *van Mooy et al.*, 2002; *Meyers and Bernasconi*, 2005].

It is thus possible to combine the conclusions obtained using C and N isotopic composition, TOC-MAR and the barium proxy. A bloom in nitrogen-fixing biota provided bio-available N to other primary producers. This resulted in an increase in $CO_2$ uptake and fixation into organic carbon, which, in turns, increased export productivity. The final result is the accumulation of organic matter at a rate higher than the rate of oxidation within the sediment, and thus, sapropel generation.

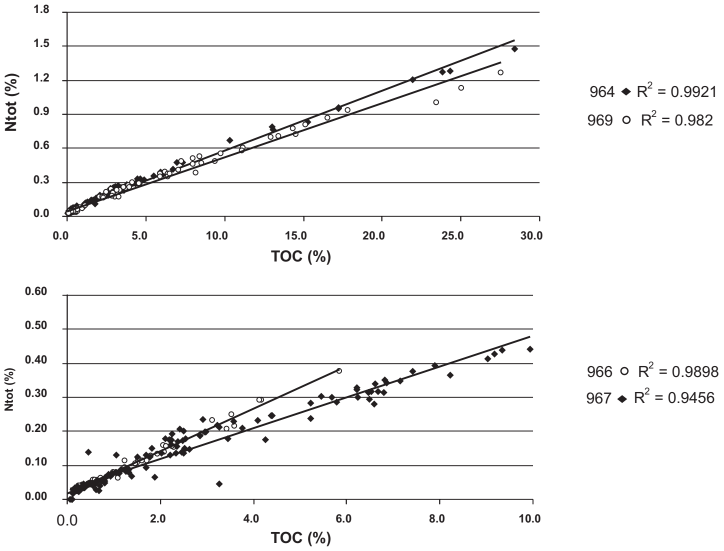


*Fig. V.7. Total Nitrogen to TOC correlation. Very high correlation rate indicates that we may consider Ntot=Norg.*

### 4.2. Sapropel Expression Across the Basin Through Time

Basin-wide patterns, temporal variations, and spatial differences exist in the history of sapropel deposition in the eastern Mediterranean Sea over the past 3 My. The general trend to lighter N-isotopic composition in the sapropel layers is clear but not particularly strong during the deposition of the Holocene S1 sapropel (i-cycle 2). The most plausible explanation is a minor increase in nitrogen-fixing cyanobacteria population and productivity. We find an important offset between deep-water Site 967 and shallow-water Site 966 for i-cycle 8. At Site 967, a well developed sapropel was deposited during that time span, with TOC values reaching up to 3.26%, and high productivity marked by a distinct peak in Ba and Ba-MAR. This level also shows an oxidation front, indicated by the sharp decrease in TOC while increased productivity is still evident from the Ba/Al peak. A minimum in $^{15}\delta$N coincides with the TOC peak. At the same time, deposition on the top of the Eratosthenes seamount (Site 966) produced a poorly developed sapropel that is now described as a Ghost Sapropel [*Emeis et al*., 2000a]. Although the Ba/Al peak indicates a period of increased productivity, TOC reaches a maximum of only 1.1%, which according to *Kidd et al*. [1978] is not even a sapropel. N isotopic composition decreases slightly, but remains over 2‰. However, if we compare same-age sapropel development in other locations [see *Emeis et al*., 2000a], it is weak or absent. We propose that the i-cycle 8 sapropel is localized to the easternmost Mediterranean, most likely due to the regional influence of the Nile River (see Fig. 1). The areally limited development of the i-cycle 8 sapropel implies that the shift to wetter climate that is associated with periods of sapropel deposition was not basin-wide during this time (81 ka) and instead must have been localized to the east African extent of the Nile drainage.

The remaining Pleistocene and Pliocene sapropels show similar and essentially concordant trends across the basin. $\delta^{15}$N values exhibit a progressive decrease from the onset of sapropel formation upwards, although not always parallel to Ba/Al enrichment. In fact, it is common to find the lighter isotopic composition preceding the maximum of productivity, suggesting that maximum nutrient availability through N fixation was followed by an increase in total export production. $\delta\ ^{15}$N correlation with TOC is typically better than with Ba/Al, and so $\delta\ ^{15}$N and TOC are clearly offset from $Ba_{excess}$ at the top of the Holocene S1 sapropel in the four study locations (Fig. 2A and 4A). The Ba-MARs during $S_1$ deposition are equivalent for Sites 964 and 969, whereas at Site 966 the MAR is considerably lower and at Site it 967 it is relatively higher. The same pattern is seen in TOC-MARs. Sites 966 and 967 are geographically proximate to each other, but they are located in very different water depths (926 mbsl vs 2555 mbsl). Export production, which is a surface ocean process, would probably be similar at these sites. The difference in Ba MARs may be instead related to the degree of barite saturation and thus its preservation in the water column, which is depth dependent [*Paytan and Griffith,* in press; *van Beek et al.*, 2007].

An attractive pattern that emerges from our calculated ages is that sapropel formation is first recorded on the Eratosthenes seamount and thus in relatively shallow waters, and later spreads to the deep basin and progressively toward the center and western part of the eastern basin. In addition, the duration of sapropel formation is minimum at Site 964 in the Ionian basin and maximum at Site 966 within each i-cycle. Also, for the same insolation cycle, the relatively shallow Site 966 exhibits the lowest TOC and Ba MARs of the four sites (Fig. 3). Therefore, it appears that water depth influences the ultimate amount of organic matter buried/preserved as proposed by *Murat and Got*, [2000], although it is not a factor influencing the mechanism of sapropel formation itself. Sapropels occur on the top of Eratosthenes Seamount, even with lower TOC values, but for a longer time and are characterized by all of the same features as those in the deep basin (increase in Ba/Al and Ba-MAR, lower $\delta^{15}N$, higher TOC/TN). These proxies point toward a progressive onset of sapropel development from the top to the bottom of the water column and are thus induced by surface productivity, at least during the period between i-cycles 20 and 2, where we are able to compare similar layers across the basin. Sapropel formation also seems to spread from the region of the Nile plume to radiate around the Eastern Mediterranean basin. This pattern allows us to conclude that the same change to wetter climate that favored the establishment of N-fixing bacteria is also responsible for an increase in Nile discharge, nutrient input and, ultimately, sapropel formation.

### 4.3. Diagenesis

The TOC/TN ratio has been used to determine the origin of the organic matter in marine sediments [*Meyers*, 1994, 1997; *Bouloubassi et al.*, 1999; *Oldenburg et al.*, 2000; *Rullkötter*, 2000]. Organic matter in sediments with a TOC/TN around 10 is considered to be of marine origin, whereas values over 20 represent terrestrial sources. By plotting TOC/TN vs. $\delta^{13}C$, it is possible to distinguish between marine,-lacustrine, and continental $C_3$-$C_4$ plants, as shown by *Meyers* [1997]. In Fig. 8, we show the TOC/TN and $\delta^{13}C$ data for the 35 sapropels we analyzed, separating the data set for different ages. The distribution of data-points is similar for all the four sites. Holocene sediments clearly plot close to the marine algae end member, with minor deviations coinciding with the highest TOC values. Pleistocene samples show a nearly bimodal distribution on the TOC/TN-$\delta^{13}C$ plot. The great majority of low TOC samples fall in the marine domain, whereas samples from within the sapropel shift towards composition that emulates $C_4$ terrestrial plants. A similar trend is observed for Pliocene levels, with a marked bimodal distribution for samples taken from Sites 964 and 969, and a somehow more scattered plot for Site 967.

Although these TOC/TN ratios and their plot could be interpreted as resulting from an influence of detrital input from the continent, $\delta^{13}C$ data, as interpreted above, and other evidence do not support this interpretation. A marine origin of the organic matter in sapropels has been previously concluded from evidence such as large values of the Rock-Eval Hydrogen Index [*Emeis et al.,* 1996; *Bouloubassi et al.*, 1999] and an abundance of marine biomarker molecules [*Bouloubassi et al.*, 1999; *Rinna et al.*, 2002]. Our data point instead toward a diagenetic impact on the elemental composition of the marine organic matter, supported by the fact that pelagic and deepwater environments show a stronger degradation signature [*Rullkötter*, 2000]. In fact, under conditions of high surface productivity, the typical TOC/TN value of the exported organic matter is higher than the typical algal signal, partly due to higher remineralization of N and N-rich molecules below the euphotic zone and/or in the sediment surface [e.g., *Freudenthal et al.*, 2001]. According to *Freudenthal et al*. [2001; see also *Macko*, 1994], TOC/TN ratios would increase when remineralization and preferential degradation of amino acids (isotopically heavy) occurs. Similar results were obtained in sediment traps by *van Mooy et al.* [2002]. In this way, the low $\delta^{15}$N values would maintain within the range of negative values, but a higher TOC/TN ratio would be detected. The increase in TOC/TN can also partly be caused by denitrification under suboxic environment that is easily achieved under highly productive waters. These diagenetic changes support the conclusions made by *Arnaboldi and Meyers* [2006] on similar sediments in the eastern Mediterranean. We observed that this increase in TOC/TN ratio is more extreme during the Pliocene, in agreement with a highly restricted water column oxygenation for this period as postulated by *Passier et al.*, [1996; 1999], *Böttcher et al.* [2003], *Warning and Brumsack* [2000], *Larrasoaña et al*. [2003a], *Weldeab et al*. [2003a; b] and *Gallego-Torres et al*. [2007].

### 4.4. Paleoceanographic and Paleoclimatic Implications

The similar patterns of the multiple paleoproductivity proxies in the multiple sapropel levels across the western basin are evidence that the periods of massive $C_{org}$ accumulation in the sapropels are the results of region-wide, repetitive variations. We observe that the low $\delta^{15}$N, the shift in $\delta^{13}$C, the increase in $C_{org}$ concentration and MAR, and the maximum values in Ba/Al and MAR detected in sapropels of different ages are all evidence of a broad change in surface biota and productivity.

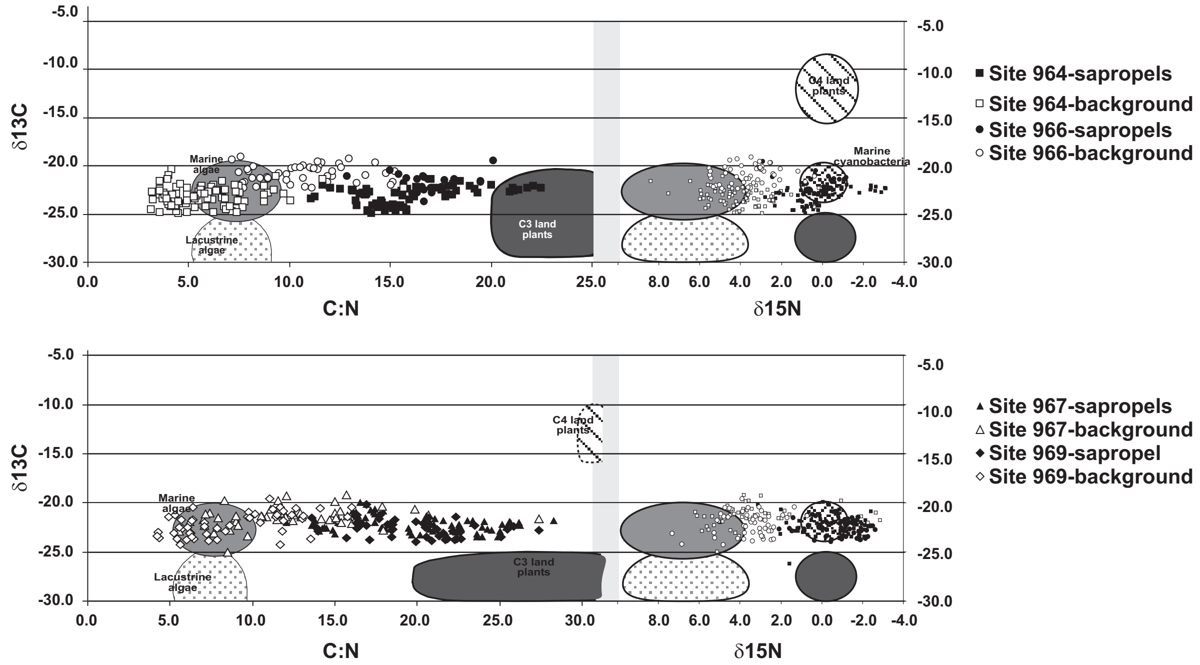


*Fig. V.8. Origin of the organic matter contained in the sampled sapropels as a funtion of δ15N, δ13C and C:N ratios.*

Based on those premises, we may establish the following paleoceanographic reconstruction. The remarkably lighter N isotopic composition indicates periods of nitrogen fixation and, thus, amplified cyanobacterial productivity in the water column. This increase in N-fixing biota and bacterial primary productivity induced an excess in export production, reflected in major increases in TOC and Ba/Al MARs. This change in mode of productivity would be favored by oligo-nutrient input, most likely through the Nile river discharge.

At the same time, it is also possible to distinguish between the importance of organic matter production and its preservation in forming the sapropel layers. TOC-MAR and Ba/Al-MAR do not show a direct correlation with $C_{org}$ concentration and Ba/Al ratio, respectively. Upper Pleistocene sapropels have lower TOC concentrations but higher TOC MARs than older equivalents, indicating that both marine productivity and detrital sedimentation dramatically increased during the later Pleistocene. Opposite to this trend, lower Pleistocene and Pliocene sapropels accumulated under markedly lower sedimentation rates and therfore exhibit higher concentrations but lower MARs than upper Pleistocene equivalents. Because the two major sources of nutrients in the Mediterranean are the Nile River and the surface inflow from the Atlantic, the smaller lower Pleistocene and upper Pliocene increases in productivity correspond to a limited water mass circulation due to a more restricted surface water inflow from the Atlantic than in late Pleistocene times; water mass circulation may have even reversed (Rinna et al., 2002; Wehausen and Brumsack, 1999). Restricted oceanic water inflow implies a lower nutrient supply and, thus, a limited productivity increase, and at the same time, a diminished bottom water ventilation, particularly in the deep basin. This interpretation supports the hypothesis that organic carbon concentration in these layers is influenced by both preservation and productivity.

Humidity maxima also contribute to the intensity of productivity increase by increasing fluvial nutrient input in the basin - primarily P, which is the most limited and whose source is primarily detrital material. A climate extreme with a more pronounced humidity maximum would enhance fluvial nutrient input to the basin. Higher humidity signifies stronger river runoff, higher nutrient supply from the continent and, at the same time, increased detrital input that would increase sedimentation rates. In fact, if we consider that the increase in African derived nutrient input is climatically controlled, which is in turn defined by insolation cycles, the maximum increase in fluvial input should correspond to i-cycles 12 to 20, which show the extreme maximum summer insolation (500 to 520 W/m$^2$) according to *Emeis et al.* [1996] and *Lourens et al.* [2004]. Sampled sapropels from i-cycles 152 to 182 correspond to insolation peaks that remain around 500 W/m$^2$ [*Larrasoaña et al.*, 2003b] or below, for i-cycles 270 to 286. Thus, detrital and nutrient input would be the highest at maximum insolation (i.e., upper Pleistocene). This notion is supported by our results that reveal relatively low TOC concentration compared to older equivalents and, at the same time, the very high TOC-MARs found at all four sites. The relative sizes of the increases in sedimentation rates and productivity rates are evidently related to the amplitudes of the precessional humidity maxima.

Combining all of the paleoceanographic and paleoenvironmental observations, we conclude that our set of data reflects a scenario in which sapropels formed under a tropical to subtropical environment, with higher SST and lower SSS [*Emeis et al*., 2000b] due to higher humidity and greater river runoff. These factors supported N-fixing communities, primarily cyanobacteria such as *Trichodesmium*. The increases in P and other available nutrients (such as Fe, Mo) that were delivered through river runoff, plus the establishment of the nitrogen-fixing biota, induced an increase in primary and export production that is indicated by higher $\delta^{13}C$ values and increases in marine biogenic barite and $Ba_{excess}$. Scavenging and recycling of organic matter and nutrients, particularly P, must have been important to sustain high levels of primary productivity. The intensity of the climate variation related to insolation maxima controlled the intensity of the productivity variations by regulating the riverine nutrient input, whereas circulation patterns of western water masses inflow partially controlled the degree of organic matter preservation by altering bottom water oxygenation. This scenario is consistent with the conclusions published by *Struck et al*. [2001]; *Rinna et al*. [2002]; *Meyers and Arnaboldi* [2005], and *Arnaboldi and Meyers* [2006].

## 5. Conclusion

A clear increase in productivity and N fixation is detected basin-wide during sapropel deposition in the eastern Mediterranean. Productivity increases are evident from Ba/Al and Ba MAR maxima, from $N_{org}$ increase and through a decrease in $\delta^{13}C_{org}$ that collectively indicate higher nutrient uptake and $CO_2$ fixation. Nitrogen fixation is deduced from the extremely low $\delta^{15}N$ values. Although N-fixation is frequently associated with oligotrophic basins, in the case of Mediterranean sapropels fixation occurred in a highly productive environment. This increase in productivity was climatically controlled and thus, it affected the whole of the Eastern Mediterranean basin. Productivity maxima are particularly pronounced during the mid-Pleistocene and then they gradually decrease in intensity through the late-Pleistocene and into the Holocene. The consequence of this cyclic climatic oscillation in productivity is the concordant deposition of TOC-rich sediment across the Eastern Mediterranean basin. Water depth seems to partly control the degree of organic matter enrichment but not sapropel occurrence itself, which is controlled by basin-wide dynamics. Sapropels deposited during the Pliocene have the highest TOC concentrations and, although they show evidence for very high productivity, they do not reach Pleistocene levels of productivity. While Pleistocene sapropels appear to be controlled mainly by extremely high productivity (maxima TOC-MAR and Ba-MAR), Pliocene equivalents, showing lower accumulation rates, partly reflect the influence of better preservation of organic matter that is related to diminished water inflow from Atlantic waters and restricted bottom water circulation. A remarkable increase in TOC/TN ratio, related to denitrification processes, suggests reduced deep water ventilation. The $\delta^{15}N$ signal, although mostly representing a primary signal, might be partially altered by diagenetic oxidation similar to TOC.

# CHAPTER VI

# Produtivity vs. Anoxia Control of Organic Matter Deposition in Marine Sediments: A Comparative Approach of Corg-Rich Paleoenvironments

## *Abstract*

*Accumulation of organic matter in open marine environments occurs at a very low rate. However, preferential accumulation and preservation of organic carbon have occurred during particular periods in distinct oceanographic settings. Although classical hypotheses attribute organic carbon enrichments to anoxic events, productivity has also revealed to play a key control for organic matter accumulation. In order to further understand both productivity and preservation roles, four characteristic environments where organic matter has been preserved have been compared to analyze the paleocenaographic conditions in which organic carbon is preferentially sequestrated: Cretaceous black shales, Eastern Mediterranean sapropels, the anoxic Black Sea, and the Mauritanian upwelling system. The first one represents periods of carbon entrapment in wide continental margins during Oceanic Anoxic Events. Mediterranean sapropels occur in a semi-enclosed basin as a response to climate changes. The Black Sea, the largest present-day anoxic basin, has been studied comparing nowadays oceanographic conditions and those leading to the Holocene sapropel formation. The Northwest African margin exhibist a long-time active fluctuating upwelling system.*

*Geochemical proxies have been used for paleoproductivity and paleoxygenation reconstructions (Ba proxies, trace metal ratios and enrichment factors, stable isotope discrimination). Accumulations of organic carbon in marine sediments are linked to periods of increased export productivity, while anoxia on its own does not appear to be enough to significantly increase TOC in sediments. Complex interactions control the relationship between increased productivity and anoxia, since the first one might force the former and vice-versa. Climate cycles are also a determining factor in preferential accumulation of organic matter as evidenced by sapropel deposition. In fact, increasing continental rainfall leads to higher nutrient input and in turn to enhanced productivity. Fresh-water input may also alter the intensity of marine circulation, thus influencing not only productivity but also ventilation. All these interactions constitute a complex system that links atmosphere, water masses, biosphere and continental areas.*

## 1. Introduction

Deposition of organic matter in marine sediments has been the subject of an intense research for years (e.g., Mangini and Schlosser, 1986; Stein, 1991; Calvert and Pedersen, 1993; Ingall et al., 1993; e.g., Arthur and Sageman, 1994; Rohling, 1994; Vancappellen and Ingall, 1994; Hedges and Keil, 1995; Kristensen et al., 1995; Nijenhuis et al., 1999b), not only from a scientific point of view but also from an economic point of view due to the potential of these sediments as petroleum source rock (e.g., Tissot et al., 1980; Stow et al., 2001; e.g., Stein, 2007). In recent years interest also increased due to the particular attention paid to climate effects and the relationship of the global change and the carbon cycle (e.g., Rohling and Hilgen, 1991; e.g., Hedges et al., 1997; Herbert, 1997; Hofmann et al., 2001; Loubere et al., 2007; Ridgwell et al., 2007). The clasical interpretations of organic-rich sediments invoked stagnation of the water column and deep water anoxia (e.g., Canfield, 1994). These mostly based on trace metal enrichments (e.g., Warning and Brumsack, 2000; Rimmer, 2003; Algeo and Lyons, 2006) or on micropaleontological and biomarkers evidences (e.g., Menzel et al., 2003; Negri et al., 2003; Erba, 2004). Since Pedersen and Calvert (1990) proposed that the increase in marine productivity was a determining factor for organic carbon accumulation, a new scenario was also considered for TOC-rich sediments (e.g., Calvert and Pedersen, 1993; Kuypers et al., 2002; Weldeab et al., 2003).

The development of new paleoceanographic proxies for reconstruction of paleoredox conditions (e.g., Wignall and Myers, 1988; Jones and Manning, 1994; Powell et al., 2003; Tribovillard et al., 2006) and paleoproductivity (e.g., Dymond et al., 1992; Paytan, 1993; Ginsele and Dahmke, 1994; Dymond and Collier, 1996; Meyers, 1997; Eagle et al., 2003) provides an excellent tool for reinterpreting previous unresolved problems related to organic carbon accumulation in marine sediments.Nowadays the interconnections between anoxia and productivity constitute an exciting research topic (Calvert and Pedersen, 1993; Calvert and Fontugne, 2001; Kuypers et al., 2002; Filippelli et al., 2003; Slomp et al., 2004; Meyers and Arnaboldi, 2005). In order to further investigate the role of anoxia and productivity and their relationships, four different oceanographic settings that cover the different settings for TOC enrichments have been analyzed in this work.

Starting with the geologically older example, two sections of Cretaceous Black Shales have been investigated. Cretaceous black shales constitute an example of thick sequences of TOC rich sediments. Sediments from the studied sections deposited during the classical Oceanic Anoxic Event (OAE) and formed on extensive platforms bordering the proto-Atlantic ocean. The first example is the Demerara Rise Cretaceous-Turonian OAE, a rifted oceanic-deep plateau that contains a thick sequence of deep marine sediments including several black shale strata (Erbarcher et al., 2004). The second studied case corresponds to the cyclically-deposited decimetre-scale black shales from the Newfoundland margin (Northwest Atlantic). The latter paleogeographic context is similar to the Demerara Rise, except that the Northwest

Atlantic platform is connected to the continent and on a shallower setting and deposited on an extensional regime of rifting development.

The second studied scenario corresponds to Eastern Mediterranean sapropels. These cyclically deposited layers of TOC-rich sediments have been long interpreted as the response of climatic changes in the region and the African craton (e.g., Thunell et al., 1984; Rossignol-Strick, 1985; Mangini and Schlosser, 1986; Rohling and Hilgen, 1991; De Lange et al., 1999). The Eastern Mediterranean region is currently an oligotrophic basin, although the geological record presents evidences of increased productivity during sapropel formation (e.g., Emeis et al., 2000; Martínez-Ruiz et al., 2000; Weldeab et al., 2003; Meyers and Arnaboldi, 2005; Gallego-Torres et al., submitted-a). Nevertheless, distinct geochemical and micropaleontological signals differentiate sapropels from different ages, as the predominance of productivity or anoxia in sapropel deposition has change through time (e.g., Thomson et al., 1999; Martínez-Ruiz et al., 2000; Warning and Brumsack, 2000; Menzel et al., 2003; Negri et al., 2003; Gallego-Torres et al., submitted-b). Thus, this paleoceanographic setting is particularly interesting for the study of the importance of anoxia vs. productivity in $C_{org}$ entrapment.

Two present-day situations representing the two above mentioned variables are the other two selected scenarios: the Northwest African margin upwelling system off Mauritania), and the larges present day anoxic basin, the Black Sea.

Presently, the Black Sea is a marginal sea with strong salinity stratification and a shallow chemocline (~175 m or less) (e.g., Glenn and Arthur, 1985; Jorgensen et al., 1991; Damste et al., 1993; Glazer et al., 2006). However, under these highly-anoxic environment the accumulation of organic carbon in the sediment is not particularly high compared to other well oxygenated basins (e.g., Calvert et al., 1991; Sun and Wakeham, 1994). This basin presented a period of lacustrine sedimentation, followed by a first pulse of marine invasion at ~9.4 ky BP (Major et al., 2006). At ~7.6 ky BP according to Ross and Degens (1974), the Black Sea presented a period of preferential organic matter sedimentation, namely the formation of the sapropel. It has been proposed that this sapropel was formed under normal oxygen conditions (e.g., Calvert et al., 1991) but very low sediment accumulation rates (e.g., Calvert and Karlin, 1998), although Glenn and Arthur (1985) assume anoxic bottom waters for sapropel formation (see also Ross and Degens, 1974). In any case, this basin represents the present-day example for the behaviour of an anoxic environment in terms of $C_{org}$ accumulation. For the Black Sea scenario, the set of data presented in this paper comes from the core MD04-2770, recovered during the ASSEMBLAGE campaign on the shallow platform (358 mbsl). This adds evidence that sapropel is not restricted to the deep basin (e.g., Ross and Degens, 1974; Glenn and Arthur, 1985).

The last studied setting corresponds to an area of high productivity due to coastal upwelling, the Northwest African margin. This region has functioned as an upwelling system for at least 200ky, and its location on a tropical region, close to the main ocean currents in the North Atlantic, make this site very sensitive to climatic and oceanographic changes (e.g., deMenocal, 2004; Haslett and Smart, 2006; Plewa et al., 2006). The Oxygen Minimum Zone (OMZ) created on the platform has been subjected to these changes, as well as the intensity of the upwelling and rate of primary productivity. Thus, this area provide recent example of the importance of primary and export productivity in TOC content in marine sediments.

These four selected scenarios are compared in terms of productivity and deep water-ventilation. This way it is possible to contrast present to ancient environments and its correspondence two extreme conditions, anoxic basins vs. upwelling systems.

## 2. Site settings, materials and methods

### 2.1. Materials

### 2.1.1. Mediterranean sapropels

A transect along the Eastern Mediterranean basin has been studied analyzing sediments recovered at four ODP sites, (Fig. 1A). Each site is representative of a particular environment within this basin (Gallego-Torres et al., submitted-b). Site 964, located in the Pisano Plateau (Ionian Basin) is a deep setting in the area of confluence of the Eastern Mediterranean, Western Mediterranean and Adriatic Seas. Site 969 is located in the centre of the Eastern Mediterranean (Mediterranean Ridge) also in the deep basin. Sites 966 and 967 are both in the Levantine Basin: 966, on top of a pelagic high, the Eratosthenes Seamount, and 967 is the equivalent in the deep basin. Sapropel layers and normal pelagic sediments were sampled in cores spanning the Pliocene-Holocene time interval.

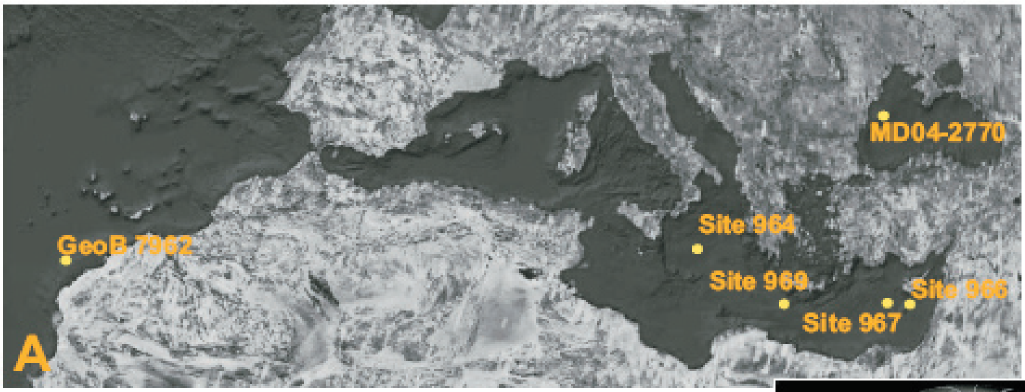
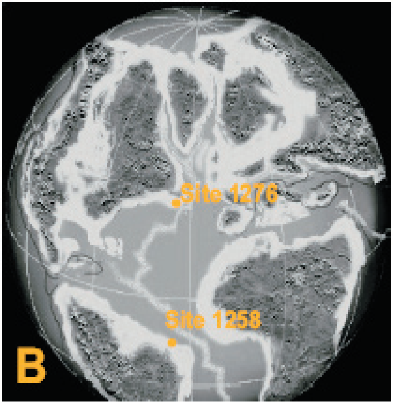


*Figure VI.1. Location maps for studied cores. A) Mediterranean, Black Sea and North African regions. Sites 964, 966, 967 and 969 correspond to studied sapropels sections. MD04-2770 is the studied core from the Black Sea. GeoB7926-2 corresponds to the Mauritanian upwelling system.*
*B) Cretaceous Atlantic paleogeographic map, indicating black shales studied sections. Site 1258 is on the Demerara Rise. Site 1276 corresponds to Newfoundland platform.*



### 2.1.2. Black Sea Sapropels

The Black Sea is largest anoxic marine basin, and thus, a perfect natural environment for the study of the influence of anoxia in organic carbon entrapment. Analyzed Black Sea sediments correspond to core MD04-2770 that was recovered on the deep platform offshore Bulgaria (Fig. 1A) at a water depth of 358 mbsl during the campaign ASSEMBLAGE MD-2004 on board the R/V Marion Dufresne and within the frame of the European Project ASSEMBLAGE. Recovered sequence includes the classical lacustrine and marine Black Sea Units (e.g., Ryan et al., 1997; Major et al., 2002 and references therein) . Sediments are mostly dark olive green muds finely laminated from the top to 85 cm (composite depth), followed by white to gray and olive green clays frequently laminated. The sapropel layer is localized between 0.43 and 0.85 (mcd) within the marine sequence (Unit II).

### 2.1.3. Cretaceous Black Shales

Analyzed Cretaceous Black Shales were recovered during ODP Legs 207 and 210.One of the sites is at Demerara Rise, ODP Site 1258. The present day geographic location is off-Suriname, at a water depth of 3192mbsl. This area corresponds to the Mesozoic Equatorial Atlantic paleomargin (Fig. 1B). Cores recovered on this site contain an extensive record of the Cretaceous sequence, including several black shales series. For this study, black shales of mid Albian to Turonian age were selected and sampled. Sediment composition of these intervals, corresponding to Unit IV as defined in Erbarcher et al., (2004) consists on calcareous claystone, cyclically alternating colours dark olive-gray to black, frequently finely laminated, with variable content in clays and calcite.

The second Black Shales studied section is located on the Newfoundland margin (Fig. 1B), at 4549 mbsl (ODP Site 1276). Recovered section at this site includes a sequence of Cretaceous black shales of different ages, defined as Unit 5A in Tucholke et al. (2004). $C_{org}$-rich shales, particularly the Cenomanian-Turonian boundary (CTB) and the CTB Oceanic Anoxic Event (OAE), are the target of this study. Tucholke et al. (2004) described this sequence as laminated calcareous claystones to marlstones, dark gray to greenish gray in colour.

### 2.1.4. Off North-west Africa upwelling system

Core GeoB7926 was recovered off Mauritania at 2500 m water depth, during the campaign R/V Meteor 53/1. This North-west African platform (Fig. 1A) is an intense upwelling system that has functioned at least for the last 200ky BP. The sequence obtained is composed of olive to olive grey and light grey claystone. Apart from minor turbidites, this core contains a continuous and unusually extended sequence, with an average sedimentation rate of 96cm/ky, which provides a very high resolution for geochemical studies in an area of intense productivity.

This core was sampled along two different intervals.The upper section (19ky to 10ky BP) and the second studied section covers the 42.5-30ky BP time span

### 2.2. Methods

Samples were dried and ground in an agate mortar, homogenized and prepared for geochemical and mineralogical analyses. Representative sample portions were used to determine bulk and clay mineralogy, TOC content as well as major and trace element concentrations.

TOC measurements were made at Bremen University and Stanford University (Stable Isotope Lab), after acidification of the samples. Major elements (Al, Ca, Mg, Fe, Mn, K) from Mediterranean and Black Sea sediments were determined by Atomic Absorption spectrometry at the Analytical Facilities of the University of Granada (CIC). Major element concentrations of Cretaceous black shales samples were determined by X-Ray Fluorescence technique, using a Brucker S4 Explorer device, at the Instituto Andaluz de Ciencias de la Tierra (CSIC-Ugr). For all samples, trace elements were measured with an ICP-MS Perkin-Elmer Sciex Elan 5000 spectrometer (CIC), following the standard procedures for these samples already described in Gallego-Torres et al., (2007). Bulk and clay mineralogy were determined using a Phillips PW1710 difractometer in the Mineralogy Department, University of Granada, and resulting difractograms were interpreted using XPowder software (Martin-Ramos, 2004). Morphological description of marine barite was obtained on selected samples under Field Emission scanning electron microscopy, SEM (LEO Gemini 1530, CIC, University of Granada) using Backscattered and Secondary Electrons images. Mineral phase composition was determined by an X-Ray dispersion microanalysis coupled to the device.

For black shales, TOC and Ba mass accumulation rates (MAR) were calculated based on the sediment dry bulk density (DBD) and linear sedimentation rates (LSR) obtained from ODP Legs 207 and 210 database (available online; http://www-odp.tamu.edu/). Enrichment Factors (EF) for different elements are always referred to Upper Crustal Abundance according to the average values from Taylor and McLennan (1985).

The age model for GeoB7926-2 is based on 16 Accelerator Mass Spectrometry (AMS) $^{14}$C dates determined on the test of the planktonic foraminifera *Globigerina inflata* at the Leibniz Laboratory for Age Determinations and Isotope Research at the University of Kiel (Nadeau et al., 1997). The $^{14}$C ages were converted into calendar years using Calib Execute Version 5.0.2 (http://calib.qub.ac.uk/). All ages were corrected for $^{14}$C and for a reservoir age of 400 yr. The entire age model will be published elsewhere (Romero et al., unpublished data).

## 3. Results

### 3.1. Sapropels:

Previous results obtained from the analysis of the selected sapropel cores are available on Gallego-Torres, et al. (2007, submitted-a).

### 3.1.1. Holocene sapropels

#### 3.1.1.1. Eastern Mediterranean

The Holocene Mediterranean sapropel presents a consistent geochemical signature across the Eastern Mediterranean Basin. This bed with $C_{org}$≥2% is also marked by a significant Ba enrichment and a progressive increase in redox sensitive elements (Mo and V) and in redox proxies values (Fig. 5). Mo and V EF increase variably depending on the area; values higher than $30X10^{-2}$ are frequent on the deep basinal settings, whereas on the Eratosthenes seamount Mo and V EF remains around $10X10^{-}2$. Ba EF and Ba/Al-MAR clear increase along the sapropel layer, reaching values up to $50X10^{-2}$, and extending over the top of the TOC rich layer. The offset between $C_{org}$ and Ba enrichments evidences an oxidation front that is marked by a Mn peak and enhanced concentrations of associated elements such as Fe.

#### 3.1.1.2. Black Sea

The geochemical and mineralogical profiles obtained from core MD04-2770 clearly mark the classical Black Sea sedimentary units (e.g., Ryan et al., 1997; Major et al., 2002). The sediments from the lacustrine unit (Unit III), lower part of the studied section from 8 mcd up to 1.15 mcd, are characterized by very uniform profiles, with no significant fluctuations. Because of the interest of sapropel unit, only the top 3 mcd have been plotted on Fig. 6 instead of the whole analyzed lacustrine interval. At 1.15 mcd the first increase in redox sensitive elements occurs. V-based proxies, U/Th and $U_{aut}$ present a continuous linear increase, whereas Mo EF variation is quite low. This increase corresponds to Unit II that contains the organic-rich interval (sapropel unit) dated at 7.16ky BP (Major et al., 2002). This organic-rich interval, between 1.0 mcd and 0.45 mcd, exhibits the highest values of all these proxies, reaching up to Mo EF>600 $X10^{-2}$ or $U_{aut}$ up to 25. However, Ba/Al ratio and EF have a very limited increase, maintaining rather low values, and present minor increases at 0.55 mcd. Unit I, the cocoolith ooze, is the uppermost section. The most intense increase in Ba/Al EF is contained within this section, from 0.35 mcd to 0.1 mcd, which is on top of the C-rich level. This level was analyzed and barite crystal were separated and observed under FESEM. These analyses provided images of large slivery aggregate of diagenetic barite. This maximum coincides with a minor positive peak in U-based redox proxies but no shift in V/Sc or V/Cr is visible. In any case, from this depth upwards all redox proxies maintain higher values than the bottom section of the core.

### 3.1.2. Pleistocene Sapropels

Pleistocene sapropels in the Eastern Mediterranean basin are characterized by the highest values of TOC and Ba/Al MAR at all studied sites. BaEF also shows higher values than the Holocene S1, reaching values ≥$100X10^{-2}$. Redox proxies increase, generally higher than during the formation of S1, and EF are frequently double than during the Holocene (Fig. 5B). This increase in redox sensitive elements extends along the TOC rich layer. The offset between TOC and Ba enrichments is smaller compared to the Holocene sapropel, or even absent.

### 3.1.3. Pliocene Sapropels

Sampled Pliocene sapropel layers present the highest values in redox proxies and trace element concentrations, as well as the maximum concentrations of organic carbon and very high Ba EF. However, both Ba/Al and TOC MAR are lower than during the Upper Pleistocene. The relation between the Ba/Al ratio and the oxygenation indicators is frequently reverse with respect to the more recent equivalents. This means that Ba/Al increase is restricted to the TOC rich sediments and eventually $C_{org}$ enrichment expands on top of the Ba/Al maximum, whereas redox sensitive elements run parallel to organic carbon increase. EF for Mo and V are relatively low for the late Pliocene sapropel (Mo EF~15X$10^{-2}$ on the Levantine basin, Fig. 5C) but present very high values during the rest of the Upper Pliocene (Mo EF~130X$10^{-2}$ on the Pisano plateau and Mediterranean ridge, Fig. 5D).

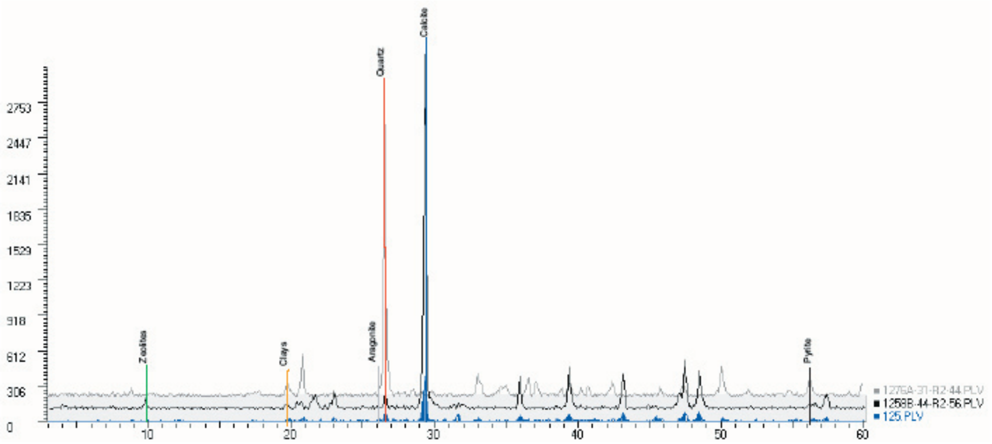


*Figure VI.2. X-Ray difractograms representing characteristic mineralogical composition of Demerara Rise black shales (1258-44R2-56), Newfoundland platform (1276-33R2-44), and Mauritanian upwelling system (125).*

### 3.2. Black Shales

Although sapropels have been considered the recent equivalents of Mesozoic Black Shales, (e.g., Nijenhuis et al., 1999a; Brumsack, 2006; Meyers, 2006) the paleogeographic setting and the time scale for Black Shale formation are significantly different. Although the two studied sections represent examples of Cretaceous OAE, important differences are observed. Whereas sediments in the Demerara Rise are basically composed of carbonate, the Newfoundland sediments are primarily detrital, with high clay and quartz content. Both have considerable amounts of zeolites, result of diagenetic remobilization of opal (Erbarcher et al., 2004; Tucholke et al., 2004).

The selected section at Site 1258 (Demerara Rise) is a minor portion of the more than 50 meters-thick Black Shale sequence. This section presents TOC values up to 15% on a continuous 0.5 m-thick bed of organic rich shales (Fig. 3). Ba/Al ratio shows a fluctuating trend but maintains very high values along the whole C-rich level and above. Barium EF is very high ~200X$10^{-2}$, as well as those of V and Mo. Both increase and decrease in TOC content are very abrupt, whereas redox-sensitive elements and redox proxies generally follow more transitional changes. For example, Mo/Al-MAR and EF show a progressive decrease from bottom to top of the C-rich bed. In any case, all these redox proxies exhibit an important enrichment in organic carbon rich sediments.

The second studied Black Shale section, recovered in the Newfoundland platform (site 1276), represents a fragment of the Cenomanian-Turonian Oceanic Anoxic Event (C-T OAE). These Black Shale layers are less developed than the Demerara Rise sequence since they only represent a 5% of the aprox. 60 meters thick sub-unit 5A (Tucholke et al., 2004). Observing the profile of $C_{org}$ content is clear that these beds developed in relatively thin centimetre-scale (3cm to 10cm thick) alternating with very thin laminae (frequently ≤1cm thick) of calcareous claystone with no organic carbon. Ba MAR and EF fluctuate but always maintaining high levels (~$140X10^{-2}$), with maximum values mostly coinciding with the TOC peaks. Mo, V content and EF as well as U and V redox proxies show a very obvious cyclicity (Fig. 4). It is particularly remarkable that the section between 1079.7 mbsf and 1079.0 mbsf has a clear tendency of progressively less intense peaks, visible for TOC, Mo, and V. Maximum Mo EF values of around $50X10^{-2}$ are notably lower than similar beds in the Demerara Rise. The same is true for other redox proxies such as U/Th, $U_{aut}$, or V/Sc, although high values are detected coinciding with TOC peak or immediately preceding the shift to high organic carbon content.

### 3.3. NW Africa Upwelling system

Sediments from the core recovered off Mauritanian upwelling zone consist mainly on green to gray claystone. These sediments are composed of clays, calcite, quartz and minor amounts of feldspars. Aragonite is also present, especially in the upper part of the core, and substantial pyrite content is detected in some levels. Observation under FESEM revealed that these sediments contains a large amount of diatoms and biogenic opal, as well as marine barite crystals (Fig. 7B). The upper section of this core (19ky to 10ky BP) presents a phase of very variable and moderately high TOC content (<2%) followed by a long period of higher content in organic carbon (≥2%). On the top of this layer lays a series of rapid $C_{org}$ fluctuations around 2% TOC, decreasing upwards. Ba/Th ratio follows a very similar trend: relatively high values from 19ky thorough 17ky BP, a clear increase up to 14ky BP, and rapid variations followed by a slow decrease to the core top.

Mo EF presents two distinct increases (Fig. 8). The first one coincides with the Ba/Th and TOC increase around 16ky BP. The second phase of Mo entrapment draws a very spiky profile and extends from 13ky to 11ky BP, coinciding with the rapid fluctuation in TOC and the first part of the progressive decrease. U-based redox proxies present rapid variation on the bottom part of this section (around 19-18ky BP). The first Ba/Th maximum is accompanied by a slight increase in U/Th and $U_{aut}$ that reach values around 1.0 and 3.5-4 respectively. These two ratios fluctuate around those values up to 13ky BP, when they experience a notable increase, similar to the one described for Mo. V/Sc and V/Cr ratios have a different trend, particularly for the bottom part of this section. The first major increase in TOC and Ba/Th coincides with a marked decrease in V/Cr and a minor decrease in the case of V/Sc, instead of the increase detected in other redox proxies. Another decrease in both ratios mark the relative maximum in $C_{org}$ at ~12.2ky BP, followed by a minor increase approximately coincident with the maximum peaks in U-based proxies.

The second studied section covering the 42.5-30ky BP time span (MIS 3) shows a clear cyclicity. A cycle of maximum-minimum in $C_{org}$ is approximately 2ky. These cycles are also visible in the BaEF. V EF follows a partially similar trend, but these periodic cycles are not clearly visible. Maxima and minima of V EF coincides with TOC variations between 37ky and 34ky BP, but above and below this layer fluctuations of TOC and V are displaced or even opposite. On the other hand, Mo EF variations approximately coincide with $C_{org}$ peaks, but the intensity of the changes in the enrichment factor is very different. From 42ky to 35.5ky BP only minor increases in Mo EF coincides with marked shifts in $C_{org}$. The last 3 cycles observed have a much more intense variation of Mo EF, reaching values of up to $11X10^{-2}$. No visible cyclic tendency appears in U and V redox proxies. U/Th and $U_{aut}$ have a wavy behaviour from 43ky to 36ky BP maintaining quite constant values between 0.7 and 1.1 in the case of U/Th and between 2 and 4 for $U_{aut}$. A second period, from 36ky to 32.5ky BP, is characterized by generally higher values, between 0.9 and 1.3 and between 3 and 6 for U/Th and $U_{aut}$ respectively. In the case of V-based proxies the trends are very different. The bottom part of this section (up to 40ky BP aprox) is a progressively step decrease in values, coincident with the trend defined by $C_{org}$. From 40ky to 34ky BP values are generally high values, with minor fluctuation and no cyclicity defined. From 34ky BP upwards V-based proxies increase slow, very constant in the case of V/Cr and V/Sc, and with significant rapid decreases in the case of V/(V+Ni).

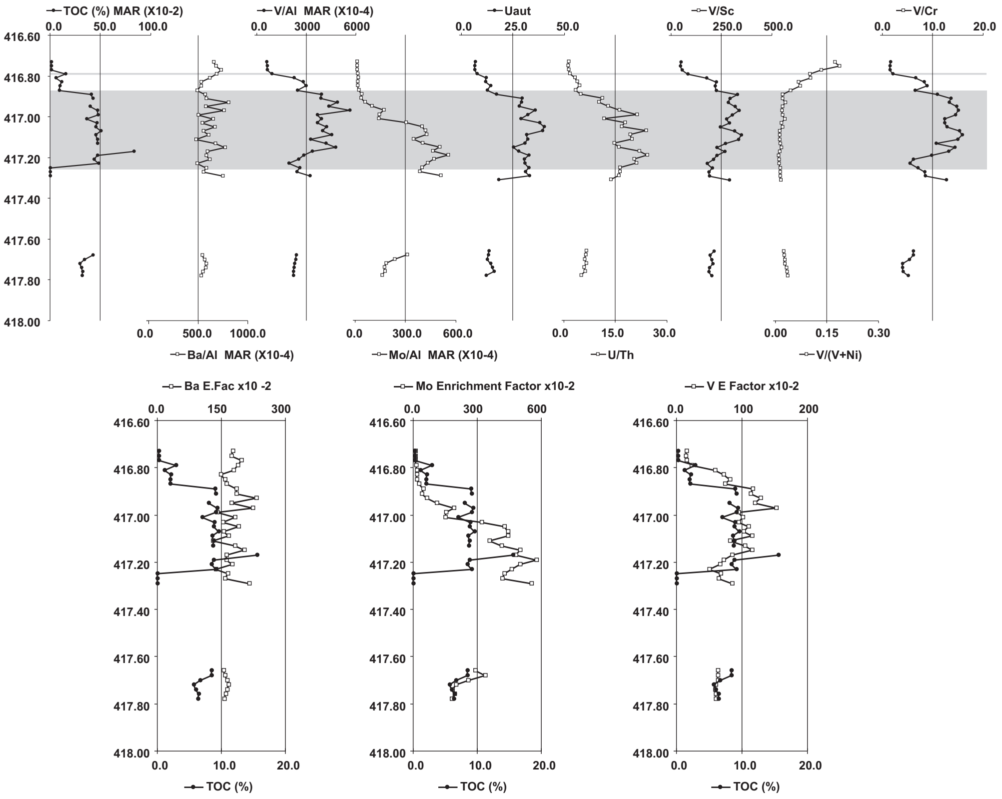


*Figure VI.3. Geochemichal signature for Cretaceous Black Shales recovered on the Demerara Rise, ODP Site 1258. Vertical scale in metres composite depth.*

## 4. Primary productivity and organic matter accumulation

In recent years, paleoproductivity reconstructions have been mostly based on Barium proxies since Ba excess in sediment, when associated with marine barite, is considered as a reliable indication of marine productivity (e.g., Dehairs et al., 1987; Paytan, 1993; Ginsele and Dahmke, 1994; Dymond and Collier, 1996; Paytan, 1997; McManus et al., 1998; Eagle et al., 2003). Although some caution is adviced using Ba as a productivity proxy (e.g., McManus et al., 1994; McManus et al., 1999; Eagle et al., 2003; Averyt, 2004), its application both in the Mediterranean area and in certain Black Shale environments has proven to be very useful for paleoproductivity reconstruction (e.g., Dehairs et al., 1987; Calvert and Karlin, 1998; De Lange et al., 1999; Emeis et al., 2000; Martínez-Ruiz et al., 2000; Paytan, 2002b; Meyers and Arnaboldi, 2005; Brumsack, 2006). Thus, the comparison between TOC and Ba EF in the sediments is a powerful tool for the study of primary and export production in marine basins.

### 4. 1. Sapropels

The case of Mediterranean sapropel productivity is extensively discussed in Gallego-Torres et al (submitted-a). In good agreement with previous studies (e.g., Emeis et al., 1991; Martínez-Ruiz et al., 2000; Struck et al., 2001; Menzel et al., 2003; Meyers and Arnaboldi, 2005) these authors have shown that increasing $C_{org}$ concentration is always associated to enhanced productivity as evidenced by Ba/Al increases. In both upper Pleistocene and Holocene sapropels, the enhanced productivity phase is generally longer than detected with $C_{org}$ content because of oxidation and burn-down of these sapropel layers. The Barium enrichment factor in sapropel is highest during Upper Pliocene-Early Pleistocene (Fig. 5) and decreases upwards through Pleistocene and Holocene. However, productivity calculated as Mass Accumulation Rates is highest during the Upper Pleistocene, coinciding with maximum detrital input (Gallego-Torres et al., submitted-a).

The Holocene aged sapropel in the Black Sea was previously described as a consequence of reduced sedimentation rate and, thus, lesser dilution (Calvert et al., 1987; Calvert and Karlin, 1998). However, although the Holocene sapropel in the Black Sea is not recognized by the Ba/Al ratio due to diagenetic remobilization, the Ba increase on the upper centimetres of the TOC-rich layer and the Be peak that appears several centimetres above the sapropel suggest initial high Ba concentration in the sapropel layer. Comparing the SEM image of samples from Eastern Mediterranean sapropels and the Black Sea equivalents (Fig. 6)., it is clearly visible that barite crystals in the latter correspond to diagenetic precipitation. Considering that no significant change in detrital input is detected for this period and that a Ba EF~700X10$^{-2}$ does not correspond to a sensible increase in fluvial input, as mentioned above, we assume that this large amount of barite has been remobilized from underlying sediments, which evidence initial high Ba content. Only under highly sulphidic conditions sulphate reduction occurs (Holmer and Storkholm, 2001; Wijsman et al., 2002). Under this situation barite becomes soluble and, thus, easy to remobilize. The most plausible source for the Ba peak above the sapropel is the original sapropel, assuming that theincrease in surface productivity induced TOC enrichment.

Considering that the anoxic bottom water in the Black Sea added to the increase in organic matter deposition during sapropel formation and a slower sedimentation rate, bacterial activity produced extreme sulphidic condition that dissolved the biogenic barite after deposition. This Ba was then remobilized upwards and precipitated when the fluids encountered less sulphidic conditions (Fig. 7C). In summary, the Holocene sapropel in the Black Sea formed also as a consequence of an increase in primary productivity, which is coherent with its Mediterranean equivalent. However, extreme suphidic conditions remobilized barite, and thus Ba peaks are found above the TOC-rich level.

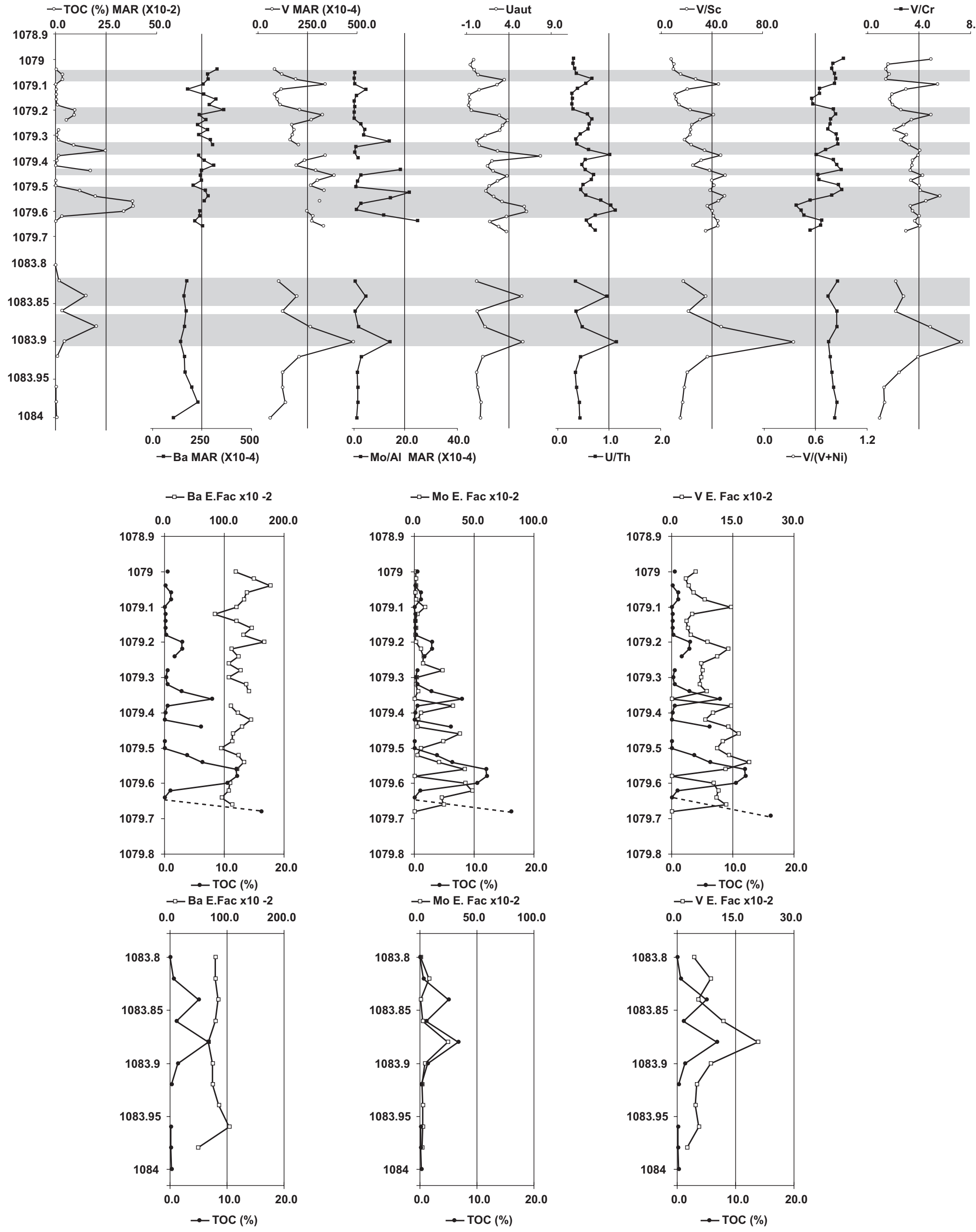


*Figure VI.4. Geochemichal signature for Cretaceous Black Shales recovered on the Newfoundland platform, ODP Site 1276. Vertical scale in metres composite depth.*

### 4.2. Black shales

Ba proxies have been widely used as paleoproductivity indicators in black shales. However, Ba-based proxies are strongly affected by diagenetic processes in some black shales, and thus Ba profiles must be interpreted with care (e.g., Paytan, 2002a; Brumsack, 2006).

In the two studied section of this Ba-EF and Ba/Al-MAR present high values associated to organic carbon accumulations. On the Demerara Rise (ODP Site 1258) Ba-MAR are continuously high thoroughout the sampled interval (Fig. 3). However, considering the wavy trend and high level of anoxia, the possibility of minor remobilization of barium it cannot be disregarded. It is clearer that the uppermost pulse of $C_{org}$ entrapment coincides with a relative maximum in Ba/Al-MAR and, thus, we conclude that the major period of TOC accumulation was also sustained by increased productivity. The black shale examplefrom the Newfoundland platform, shows a clearly visible relationship between $C_{org}$ and Ba/Al (Fig. 4). Cyclic deposition of TOC is coincident with fluctuation in Ba-EF, thus suggesting that increased productivity controlled the deposition and organic carbon and the formation of black shale levels. This periodic TOC entrapment is interpreted as orbital forcing cycles by Kuypers et al. (2004a). Further evidence for increased productivity during sapropel formation are found in recent literature (e.g., Hofmann et al., 2001; Kuypers et al., 2002; Kuypers et al., 2004b; Junium and Arthur, 2007; Mort et al., 2007).

### 4.3. Coastal upwelling

The North-west African margin has functioned as aen characterized by coastal upwelling system for at least the last 200ky. Productivity is predominantly due to diatom blooms, and a large amount of biogenic opal and diatoms are found in the sediment. Marine biogenic barite is also visible under SEM image, and Be increases cyclically along the studied core. In fact, although this area is a generally downcore highly productive, there are clear periods of increase primary production and $C_{org}$ accumulation in sediments. The Ba/Th-EF and TOC profiles run virtually parallel across the whole studied section showing a cyclic pattern (Fig. 8). Although Plewa et al. (2006) considered that Ba in this area is the response of meltwater pulses, the obtained results s suggest that Ba remains a reliable proxy for productivity. Climatic and hidrographic variations control the upwelling intensity of the system, although a high rate of primary productivity is maintained. The intensity of the deep water currents rising toward the platform, supply the necessary nutrients. TOC increases are closely related to these variations in productivity. Although biogenic barite accumulation in platform and coastal areas has been questioned (e.g., McManus et al., 1994; Plewa et al., 2006), these data support the use of barium increase as a paleoproductivity proxy in this region.

## 5. Role of anoxia and preservation

The study of redox conditions in the water column and, particularly, in bottom waters has been addressed using the enrichment in redox sensitive elements, such as Mo, Ni, V, U or Cr, and different trace elements ratios used as redox proxies (see Table 1) (e.g., Wignall and Myers, 1988; Calvert and Pedersen, 1993; Jones and Manning, 1994; Powell et al., 2003; Rimmer, 2003; Siebert et al., 2003; Siebert et al., 2006; Tribovillard et al., 2006). In this work, the application of selected proxies allow the comparison of oxygenation conditions on the different studied and environments of the world ocean.

### 5.1. Sapropel and black shales

Oxygenation conditions during the formation of the studied sapropels section on the Pisano Plateau (Ionian Basin) is extensively discussed in Gallego-Torres et al. (2007) and a regional and temporal reconstruction of these conditions is exposed in Gallego-Torres et al. (submitted-b). Both studies conclude that Upper Pliocene sapropels evidence anoxic conditions in bottom waters whereas Upper Pleistocene equivalents, were generally deposited under sub-oxic/disoxic conditions, and appear partially oxydized on the top. The Holocene sapropel formed in the Eastern Mediterranean under sub-oxic conditions. This sapropel have been also affected by an important postdepositional alteration and the top centimetres have been erased by an oxidation front. In the case of Holocene and Upper Pleistocene sapropels, the degree of oxygen depletion is primarily related to $O_2$ consumption due to increase productivity whereas early Pleistocene to Pliocene sapropel formation is controlled to a higher extend by diminished deep water ventilation.

In the case of the Black Sea, a strong water stratification and a shallow chemocline, occurred during the whole Holocene. Thus, the Holocene sapropel in this basin deposited under anoxic bottom waters. The profile of redox proxies draws a scenario of normal ventilation and very stable conditions up to 1.0 mcd, where redox conditions change to progressively more reducing environment. Here all redox proxies agree in the fact that anoxic conditions were reached before the onset of sapropel formation. According to V/Sc or V/Cr, anoxia was prevailing some significant time before organic carbon started to accumulate significantly in the sediment (Fig. 6), whereas $U_{aut}$ or U/Th mark the onset of anoxic conditions slightly later, always before TOC entrapment. High values of redox proxies, with a maximum at 0.55 mcd, indicate that anoxic/sulphidic conditions prevailed during the whole period of sapropel formation. Although these values present an important decrease after sapropel formation, they remain within the range of low oxygen concentration (e.g. V/Cr) or even absence of dissolved $O_2$ ($U_{aut}$, U/Th or V/Sc), and these conditions persist to present day, with no $C_{org}$ accumulation associated. These data suggest that stratification of the Black Sea basin started quite soon in its period as a marine basin but oligotrophic conditions allowed bacterial disoxic activity to decompose organic matter at a proper rate. However, an increase in productivity produced an overload in export production so that $C_{org}$ started to accumulate and strong sulphidic conditions established, inducing sulphate reduction and remobilizing barite. When productivity returned to normal levels deep water conditions went back to a situation similar to the pre-sapropel period, a slight increase in $O_2$ induced precipitation of diagenetic barite and decomposition of organic matter reaching the seafloor.

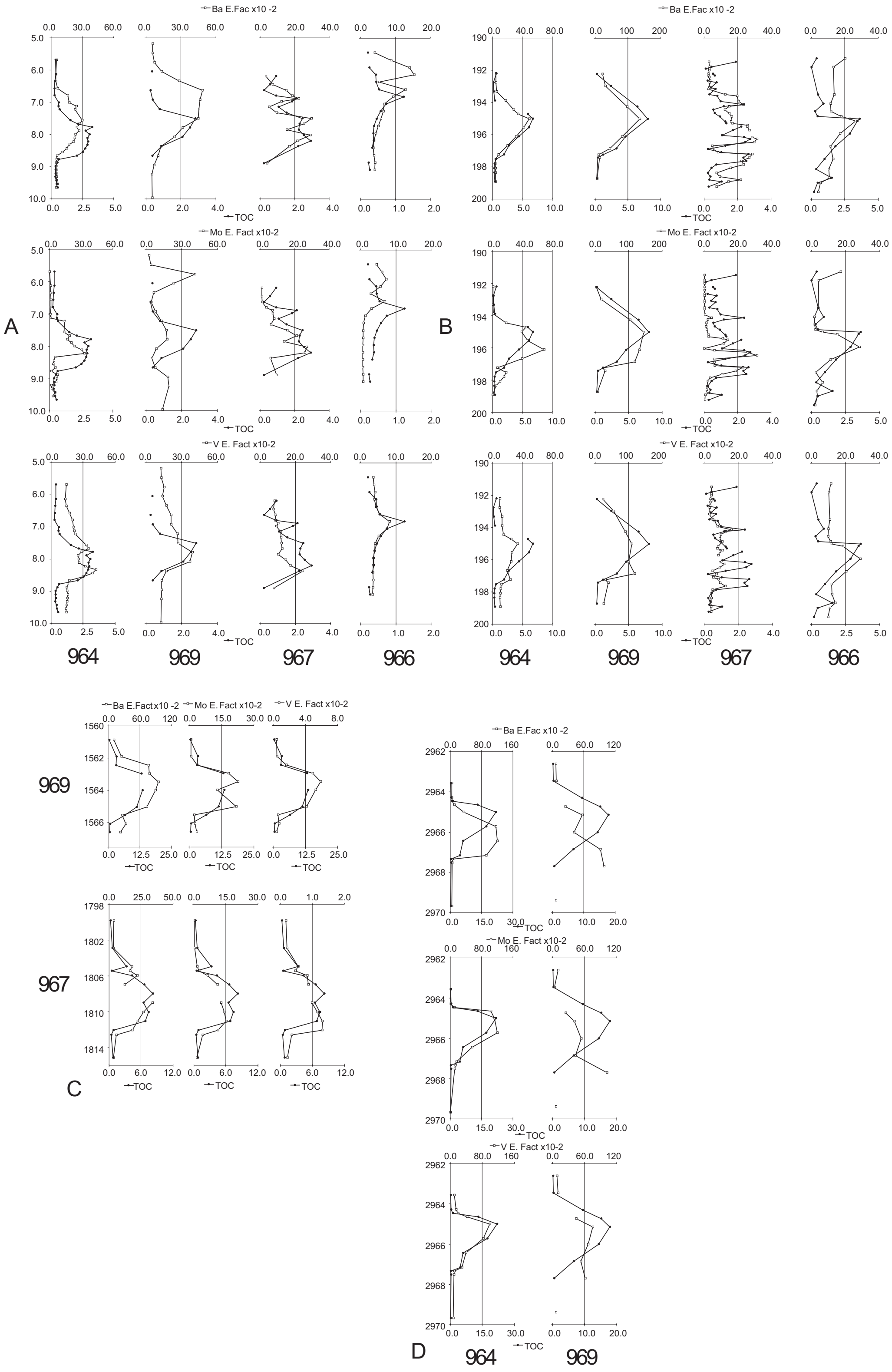


Figure VI.5. TOC vs. Enrichment Factors for selected sapropels layers. A) Holocene sapropel (S1); B) Example of Upper Pleistocene sapropel (S7); C) Example of Late Pliocene-Early Pleistocene sapropels; D) Example of Upper Pliocene sapropels. Vertical scal in (calculated) kiloyears BP. Extended representation of geochemical signature of Mediterranean sapropels on (Gallego-Torres et al., submitted-b).

The Black shales formation is also coupled to a decrease in oxygen concentration in the deep water column at the studied sites. On the Demerara Rise redox proxies evidence anoxic condition across the whole TOC-rich sequence, although in very different degrees. V/Sc exhibit extremely high values across the whole sequence and, since V/Sc≥9 is supposed to represent anoxia, it suggests highly sulphidic environment even for the low TOC sequence Fig. 3). This usefulness of this proxy in quantitative terms is still not calibrated (e.g., Powell et al., 2003; Gallego-Torres et al., 2007) and thus these high values must be compared to other proxies. For example, U/Th and $U_{aut}$ evidence strong anoxic conditions in the sedimentary interval with TOC≥5%, and disoxic/suboxic conditions in the upper centimetres of the sampled section. Similar conclusions are obtained applying V/Cr ratio. Very high Mo-EF and Mo/Al-MAR equally indicates that reducing conditions prevailed. It is worth mentioning that the minor positive peak of $C_{org}$ coinciding with a small increase in Ba/Al-MAR in the uppermost part of the section does not occur under anoxic conditions, according to U/Th, $U_{aut}$, or V/Cr. V/(V+Ni) is not applied for interpretation in this section since the profile suggest Ni remobilization, coherent with the anoxic environment.

The off Newfoundland black shale sequence is characterized by much lower values of redox proxies. This cyclic deposited of $C_{org}$ shales present values of Mo-EF comparable to the one obtained in Mediterranean sapropel. Redox proxies also show similar values to sapropels, suggesting levels of oxygen concentration much higher than at the Demerara Rise. In fact, only V/Sc ratio suggests complete anoxia for all TOC-rich intervals. $U_{aut}$ does not show evidence of anoxia for any event of $C_{org}$ entrapment and U/Th reach maximum values within the range of disoxia, always below the threshold of U/Th≥1.25. V/Cr ratio shows evidence of suboxic/anoxic condition only for the lowermost sampled level. In this case, the profile of V/(V+Ni) seems mostly as representative of the original signal, not remobilized, and the results are congruent with the V/Cr profile (Fig. 4). Punctually (e.g., 1079.58 mbsl) the variations of this proxy is inverse, suggesting remobilization on Ni. The uppermost of the sampled TOC-rich layers presents the peculiarity that maxima of redox proxies associated occur below or on the base of the TOC-rich level. In this particular case, a brief anoxic event might have triggered the onset of higher productivity due to P released to the water column (Mort et al., 2007).

The comparison between our two black shale sections offers some remarkable differences. Iit is possible to conclude that both levels of $C_{org}$ rich shales developed associated to enhanced primary productivity, the Demerara Rise section is characterized by a long period of TOC entrapment under highly anoxic waters. This anoxia might have recycled nutrients (particularly P) in a way that in sustained high surface productivity. On the other hand, Northwest Atlantic black shales resemble the Mediterranean sapropels. The former also followed a marked cyclicity and periodicity, formed during shorter pulses, productivity is intimately related to $C_{org}$ entrapment, and oxygen levels detected by redox proxies are on the limits between oxic to disoxic conditions and only punctual anoxia might have been reached on the deep waters.

## 5.2 Oxygen minimum zone (upwelling system)

The upwelling system off Mauritanian presents generally low/medium values of redox proxies, related to the development of an Oxygen Minimum Zone (OMZ). However, significant contradictions arise between U/Th ratio and the rest of proxies. Whereas U/Th ratio suggests that deep-water anoxic conditions dominated long periods, in varying degrees, $U_{aut}$ only reach values corresponding to anoxic environment in the upper part of the section. V-based proxies do not show evidence of anoxia, and only V/(V+Ni) indicates certain degree of important oxygen depletion, not reaching euxinic conditions. As a whole, maximum values of U/Th and $U_{aut}$ correspond to maxima in TOC and Ba/Th, suggesting the development of an OMZ in the platform. The important exception is the period between 35ky and 34ky BP (Fig. 8), where these proxies show relatively high values but productivity is on a relative minimum. This can be interpreted as a period of relatively slower circulation in the region, during which upwelling currents were slower, productivity is thus partially prevented, and the OMZ developed during the previous productivity maximum is maintained for some time before normal circulation patterns re-established. Our observations are consistent with Zhao et al. (2000) who proposed a similar weakening of the winds and upwelling currents in the area coinciding with Last Glacial Maximum. Despite this phase, generally cyclic pattern is also perceptible in the intensity and/or extension of the OMZ across the platform, similar to the pattern described for paleoproductivity. This cyclicity is apparently controlled by major climate cycles, and related to wind intensity and eolian input from the Saharan desert (e.g., Moreno et al., 2001), the African Humid Periods (e.g., Haslett and Smart, 2006), or variations in Central Atlantic currents that supports upwelling (e.g., Zhao et al., 2000).

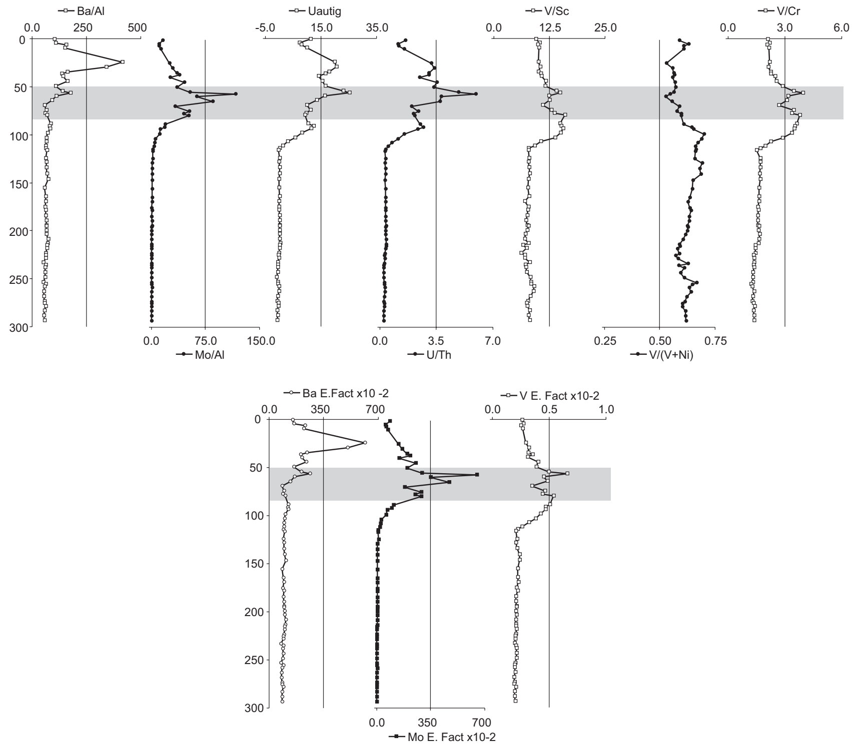


*Figure VI.6. Geochemichal signature for Black Sea sediments sampled from core MD04-2770. Vertical scale in centimetres composite depth.*

## 6. Paleoenvironmental consideration for $C_{org}$-rich sediments: spatial and temporal comparison.

Sediments with high TOC content appear associated to increased marine productivity and reduced oxygen availability on all studied environments.

The oldest studied sections, Demerara Rise and NW Atlantic black shales, are examples of Cretaceous OAE's, although sedimentological expression and geochemical signal are diverse. The Demerara Rise (Site 1258) black shales present a geochemical and mineralogical signal with an extensive deep platform, mostly disconnected from continental input (Fig.2). In this setting anoxic events have a stronger expression, as deduced from redox proxies, and longer. Although the paleoproductivity signal is not perfectly clear, our high Ba-EF values suggest that productivity exerted was also determining for black shale formation. Although highly anoxic conditions are inferred, TOC content is not remarkably higher than in Newfoundland sediments (Site 1276). This Site received primarily detrital material, (Fig. 2) and C-rich levels developed in cyclic pulses, detected both in productivity and redox proxies. In this case $C_{org}$ accumulation appears clearly associated to periods of enhanced productivity, although oxygen-depleted conditions frequently preceded TOC and Ba maxima. This is interpreted by Mort et al. (2007) as phosphorus regeneration connected to reducing conditions that provided extra nutrient to maintain higher productivity.

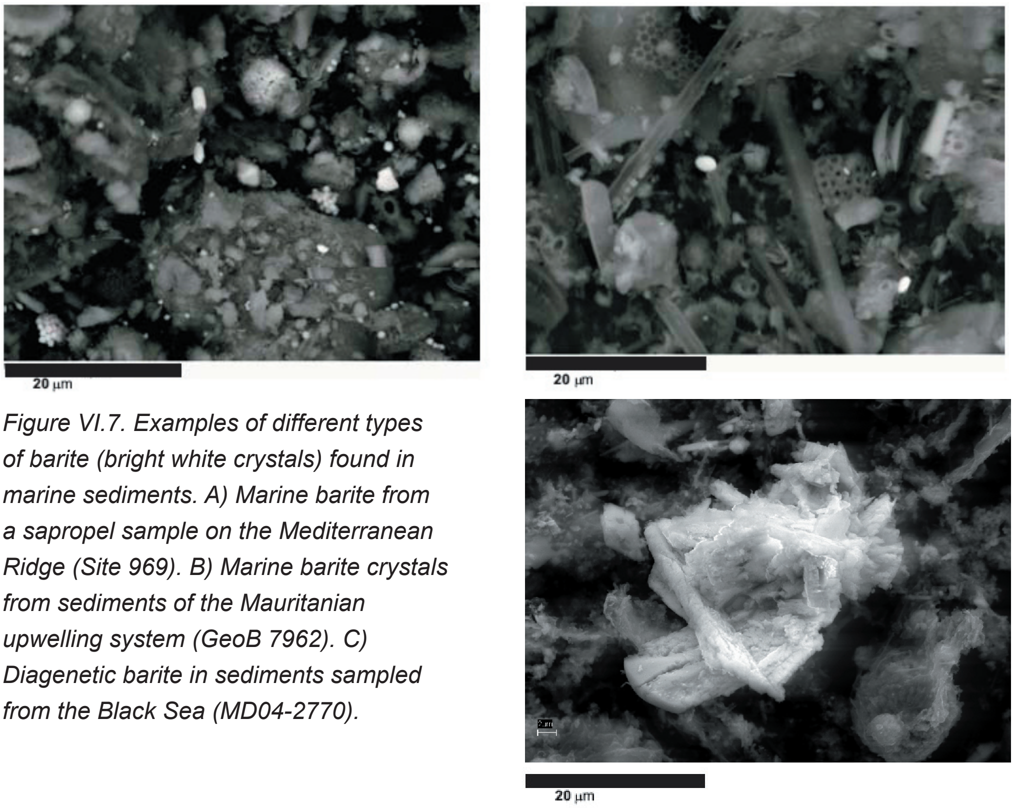


*Figure VI.7. Examples of different types of barite (bright white crystals) found in marine sediments. A) Marine barite from a sapropel sample on the Mediterranean Ridge (Site 969). B) Marine barite crystals from sediments of the Mauritanian upwelling system (GeoB 7962). C) Diagenetic barite in sediments sampled from the Black Sea (MD04-2770).*

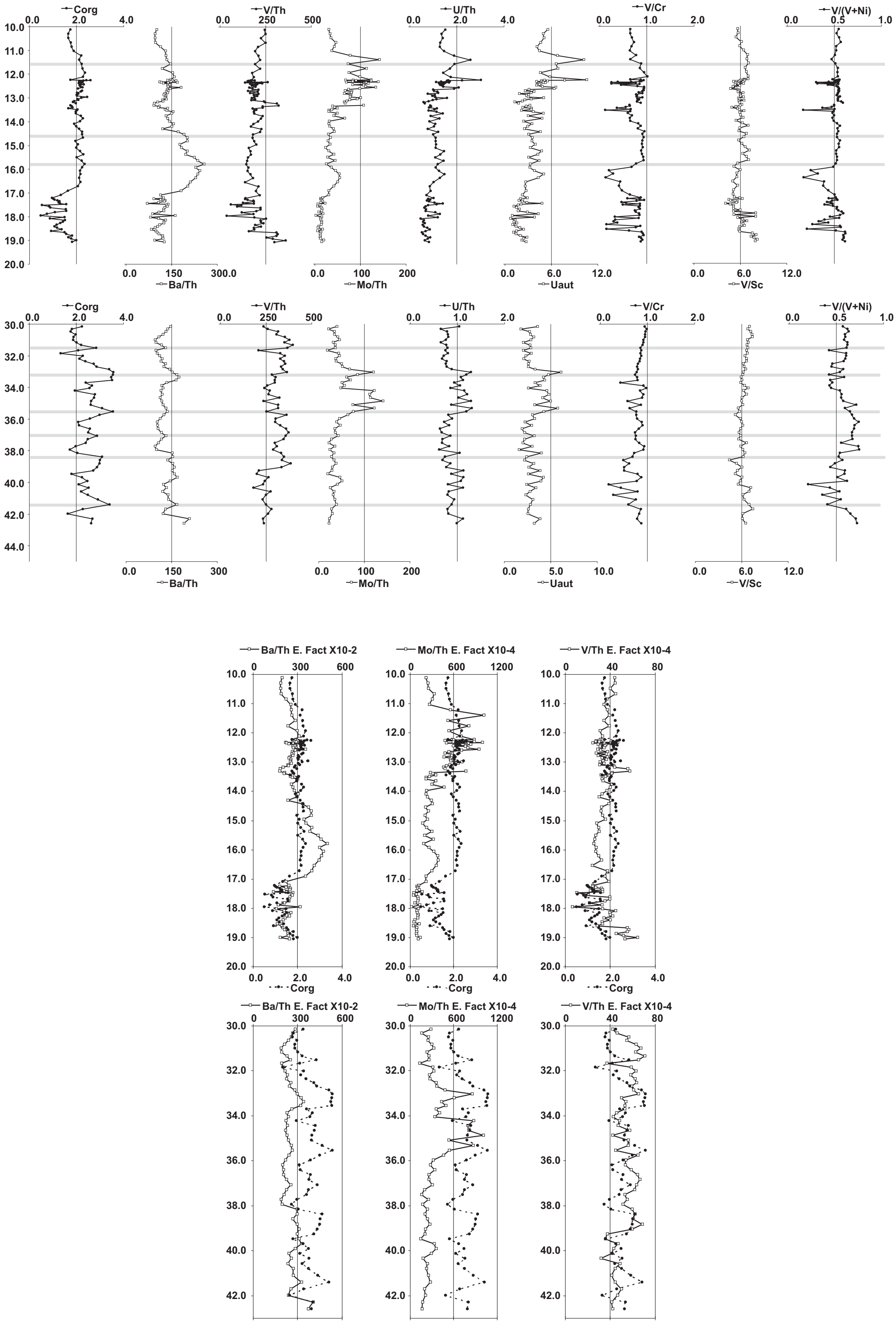


*Figure VI.8. Geochemichal signature for core GeoB7962, recovered on the Northwest African margin uwelling system. Vertical scale in kiloyears BP.*

The interpretation of Eastern Mediterranean sapropels as periods of intensified marine productivity is documented through Ba/Al ratio (e.g., Dehairs et al., 1987; Emeis et al., 2000; Martínez-Ruiz et al., 2000; Weldeab et al., 2003; Meyers and Arnaboldi, 2005; Gallego-Torres et al., 2007). All sampled sapropels corespond to increased marine productivity although two different situations are defined: Pliocene levels exhibit higher degree of anoxia that eventually precede the productivity increase, in a similar scenario as described for black shales. Upper Pleistocene to Holocene sapropels originated from a high productivity event that induced oxygen consumption and created local anoxic conditions, more similar to the Mauritanian margin (see below).

The Black Sea basin, although currently anoxic, is not characterized by TOC enrichment in recent sediments under normal productivity conditions. On the other hand, Holocene Black Sea sapropel is very likely the consequence of higher productivity, deduced by the remarkable concentration of diagenetic barite on top of the TOC-rich layer (Figs. 6 and 7C).

In the upwelling system offshore Mauritania (North-west African margin), variations of productivity respond to these climatic factors, induced by global climate change. This, in turns, produce higher rate of organic carbon rain into the sediment, higher oxygen consumption and thus stronger development of the OMZ. Thus, productivity is the major responsible for the fluctuations between oxic-disoxic-anoxic environments. Nevertheless, eventual weakening of Atlantic currents may alone alter deep water oxygenation without TOC or Ba variations.

Of all eight studied sites, there are two cases that are contradictory in terms of the influence of deepwater ventilation for $C_{org}$ accumulation and preservation. The first one corresponds to black shales. As mentioned above, there are major differences in deepwater oxygen levels (as detected by redox proxies) between Demerara Rise and off Newfoundland black shales. However, TOC enrichment does not differ significantly in both basins and the main difference lays in TOC-MAR, and thus, in linear sedimentation rate (LSR). LSR at the Demerara Rise is half of that off Nefoundland, which means that, for similar productivity levels, the concentration of organic matter in the sediment would be twice at Demerara Rise. This corresponds to a stagnation scenario which implies highly anoxic bottom waters, whereas at Site 1276 TOC is more diluted in the sediment due to higher sedimentation rate.

A similar situation is described for the Black Sea (Calvert et al., 1987; Calvert and Karlin, 1998). Present-day basin, though anoxic, does not accumulate organic carbon whereas an increase in productivity coupled to lower sedimentation rates produces $C_{org}$ enrichment during sapropel formation. This corroborates the hypothesis by Pedersen and Calvert (1990) (see also Calvert and Pedersen, 1993;Calvert and Karlin, 1998) that anoxia does not imply organic carbon preservation, since this also depends on the rate of $C_{org}$ input to the sediment.

Deposition of $C_{org}$-enriched sediments frequently appears as cyclic deposits, e.g., Eastern

Mediterranean sapropels, Newfoundland black shales or TOC maxima in the Mauritanian upwelling system. Offshore Newfoundland black shales have a very marked pattern of periodicity that has been more extensively discussed by Wagner et al. ( 2004), (see also Kuypers et al., 2004a; Kolonic et al., 2005). In the case of Eastern Mediterranean sapropel, cyclicity and orbital tuning was described by Hilgen (1991) and Rohling and Hilgen, (1991). Sapropel deposition corresponds to insolation maxima (precession minima of the Milankovich astronomical cycles). Finally, the Northwest African margin upwelling system presents a clear cyclicity that coupld to known variations in the global climate system, based on correlations with Last Glacial Maximum and other climatic events such as Heinrich Events and Younger Dryas (e.g., Zhao et al., 2000; deMenocal, 2004; Haslett and Smart, 2006). Thus, the strong control of global climate changes and TOC entrapment in marine sediments suggests a direct link between the two factors and an intense feedback between the ocean system, marine productivity and climate regulation, via atmospheric $CO_2$ sequestration cycles on the oceans.

## 7. Summary and conclusions

The comparison of different scenarios of organic matter accumulation in marine sediments allows the following conclusions:
Marine primary and export productivity appears linked to $C_{org}$ accumulations in sediments. High values of Ba-proxies generally coincide with maximum TOC content in the sediment. The only exception is the Black Sea Holocene sapropel, where sulphidic conditions lead to sulphate reduction and barite remobilization to upward levels of the sediment column.

Anoxic conditions do not imply invariably $C_{org}$ accumulation and preservation in marine basins. Present-day Black Sea, although strongly stratified and under deep-waters suphidic conditions, does not show significant TOC enrichment. In fact, compared to present-day upwelling areas, such as Mauritanian margin, organic carbon content in Black Sea sediments is considerably lower.

The relationship between anoxia and increased productivity is not always straightforward In some cases, such as Quaternary Eastern Mediterranean sapropels, increased productivity clearly leads to accelerated oxygen consumption and, thus, dysoxic to anoxic conditions. However, in the case of Pliocene equivalents or Cretaceous black shales, anoxia apparently precedes the productivity increase. Reduced ventilation may favour nutrient recycling, and, thus, feedback results between anoxia and productivity.

Accumulation of organic carbon in marine sediments is the response significant oceanographic changes. These in turn, are frequently the response to variation in global climate and thus organic-rich sediments appear cyclically deposited. Significant interactions control this complex system; marine circulation affects global climate and vice versa, and both control oceanographic conditions for productivity and deep water ventilation, and thus, $C_{org}$ accumulation in sediments. This accumulation acts as an atmospheric $CO_2$ sink, and thus, impact global climate.

# CHAPTER VII

# Conclusions

Under the light of all exposed evidence, based on different geochemical and proxies, we conclude:

- Barium has proven to be a reliable indicator of paleoproductivity in all studied environments. Observations under SEM prove that this barium is related to biogenic barite. Barite as a paleoproductivity proxy is more reliable than total organic carbon content since it is only remobilized under highly suphidic conditions.

- An increase in marine productivity is evident during the deposition of all studied Eastern Mediterranean sapropels. The maximum organic matter accumulation rate coincides with maximum productivity during the Upper Pleistocene, which is also the period of highest sedimentation rate. In the case of the Holocene Black Sea sapropel, an increase in productivity was inferred as the most plausible explanation, although the barium productivity signal is altered by diagenesis under highly sufphidic conditions. Cretaceous black shales equally present evidence for increased productivity. In the case of Newfoundland platform, positive correlation between cyclic black shale formation and increase productivity is evident. Black shales on Demerara Rise are also highly enriched in barium that indicates increased productivity. Off Mauritania, although is an area of permanent upwelling, presents fluctuations in productivity that implies increased organic matter accumulation in the sediments.

- In the case of Eastern Mediterranean sapropels, increased productivity appears related to a change in marine biota, namely nitrogen-fixing bacteria that sustained high-nitrogen availability. This biota was favoured by relatively higher sea surface temperature, lower surface water salinity, and increased nutrient input (such as P or Fe) from the Nile River discharge.

- Redox proxies were evaluated in order to select the more reliable ones. The application of multiproxy studies has revealed as a powerful tool for interpretation of paleoxygenation conditions in the studied sections.

- Anoxic conditions do not appear ubiquitously during organic matter accumulation. Eastern Mediterranean basin follows an evolution from the Upper Pliocene to Holocene exhibiting progressively more oxygenated conditions during sapropel formation, from dysoxic/anoxic in the Upper Pliocene to normal oxygenation in the Holocene. Off Newfoundland black shales show similar oxygenation conditions to Pleistocene sapropels, whereas Demerara Rise equivalents are, in terms of oxygenation, rather similar to Pliocene sapropels although more extreme anoxia is detected. The Black Sea basin presented anoxic conditions from the moment of Holocene sapropel deposition onward, although after the sapropel event no substantial increase in organic matter enrichment is visible. The Mauritanian upwelling system shows fluctuating suboxic conditions related to the Oxygen Minimum Zone, but total anoxia was not accomplished.

The combination of above exposed conclusions obtained at four particular oceanographic settings allows the extension to a more global view:

- Accumulation of organic matter in marine sediments preferentially appears associated to events of increased primary productivity. This productivity increase needs to be sustained by an extra input, fixation, and/or recycling of nutrients.

- Overload of organic carbon rain might lead to higher oxygen consumption and thus, reduced oxygen availability in bottom waters.

- Anoxia does not appear to be a sufficient factor to accumulate organic matter in sediments. However, anoxic conditions can, on one hand, favour nutrient recycling that sustains high productivity required to increase organic matter “rain” to the seafloor, and on the other hand, facilitates preservation of exported organic matter.

- Periods of preferential organic matter accumulation in marine sediments have fixed important amounts of atmospheric $CO_2$ in the lithosphere, thus regulating greenhouse gasses concentration and earth surface temperature. The relationship between global climate, marine productivity, and organic matter accumulation is clearly apparent in the case of Eastern Mediterranean sapropels, and can be extended to other recent (upwelling systems) or past (black shales) environments.

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