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ENVIRONMENTAL AND CLIMATIC CHANGES IN THE BALTIC SEA
AND THE EASTERN MEDITERRANEAN SEA

AS RECORDED BY PIGMENTS AND ISOTOPES IN SEDIMENTS

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Abstract

This thesis is a study of Holocene sapropels from two semi-enclosed seas; the Baltic Sea and the Mediterranean Sea. Sapropels are sedimentary layers with organic C > 2%. The Baltic Sea and the Mediterranean Sea have a limited water exchange, and despite differences in water depth and salinity, mechanisms for fluxes and preservation of C_{org} are principally the same. Primary focus is on biomarkers for increased primary productivity and anoxic/euxinic bottom water. Pigments (primarily from cyanobacteria), $\delta^{15}\text{N}$, $\delta^{13}\text{C}$, N and C_{org} have been used for studying increased primary productivity. Presence of the pigment isorenieratene from green sulphur bacteria indicates photic zones anoxia. Zn, Mn and $\delta^{34}\text{S}$ have also been used to identify different scenarios during sapropel formation.

Pigments start to appear at the beginning of both the Baltic Sea sapropel and S1, the Holocene sapropel in the Mediterranean Sea. Cyanobacterial pigments generally increase early in the sapropel, due to fast adaptation to more P-rich conditions. Cyanobacteria are favored by low N/P-ratios and P was probably in excess during the formation of S1 and the Baltic Sea sapropel sediments. Lowering of $\delta^{15}\text{N}$ and concurrent increase in N in both the Baltic Sea and S1 sapropels is probably caused by cyanobacterial N₂-fixation. This most likely increased the N/P-ratio and enhanced overall primary productivity. Both increased primary productivity and enhanced preservation of organic carbon are important mechanisms for sapropel formation. The appearance of isorenieratene in the protosapropel is most likely the result of an environment where even moderate increases in primary productivity could create anoxic conditions. This favours an estuarine water circulation scenario with anoxic bottom waters. $\delta^{34}\text{S}$ of sulphate and sulphide confirm this scenario, which can be explained by the coexistence of sulphate reducing and sulphur disproportionating bacteria together with phototrophic purple and green sulphur bacteria.

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Cover photo (by R. Hallberg): Sapropel S1 from the eastern Mediterranean Sea

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This doctoral thesis consists of a summary and four papers. The four papers are listed below and are referred to as Paper I-IV in the text:

Paper I

Westman, P., Borgendahl, J., Bianchi, T.S. and Chen, N., 2003: Probable Causes for Cyanobacterial Blooms in the Baltic Sea: Role of Anoxia and Phosphorus Retention. *Estuaries* 26(3): 680-689. *Reprinted with permission by the Estuarine Research Federation.*

Paper II

Borgendahl, J. and Westman, P.: Cyanobacteria as a trigger for increased primary productivity during sapropel formation in the Baltic Sea – a study of the Ancyclus/Litorina transition. *Journal of Paleolimnology (in press).*

Paper III

Borgendahl, J.: Phytoplankton pigments and $\delta^{15}\text{N}$ in the eastern Mediterranean sapropel S1 and comparisons with the Holocene sapropel from the Baltic Sea. Submitted to *Marine Geology*.

Paper IV

Borgendahl, J., Hallberg, R.O. and Torssander, P.: Sapropel S1 formation from proxy signals – biomarkers and sulphur isotopes. *Manuscript.*

My contribution to the papers is:

Paper I: Participation in fieldwork, phosphorus analyses, sample preparation for C, N and isotope analyses, participation in pigment analyses, interpretation of these data and writing minor part of the text.

Paper II: Pigment analyses, sample preparation for C, N and isotope analyses, interpretation of these data and writing major part of the text.

Paper III: Participation in fieldwork, pigment analyses, sample preparation for C, N and isotope analyses, all data interpretation.

Paper IV: Participation in fieldwork, pigment analyses, interpretation of pigment data and writing major part of the text.

Stockholm, February 2006

Johanna Borgendahl

1 Introduction

In 1947 – 1948, the Swedish Deep Sea Expedition aboard the M/S Albatross sampled the seafloor of the eastern Mediterranean Sea (Kullenberg 1952). The cores contained several dark layers of unconsolidated sediment with high concentrations of organic carbon. These carbon-rich sedimentary layers are usually referred to as sapropels. A generally accepted definition of a sapropel is “ a discrete layer greater than 1 cm in thickness, set in open marine pelagic sediments and containing greater than 2% organic carbon by weight” (Kidd *et al.* 1978). Sapropels contain abundant and well-preserved calcareous microfossils of planktonic origin but are mostly devoid of benthic fossils (Thunell *et al.* 1977, Castradori 1993, Rohling 1994).

The Mediterranean sapropels are the most famous, but the definition of sapropels is true for sediments from many other areas. In Sweden, this type of sediment is traditionally called gyttja-clay. Sapropel formation in the Baltic Sea started *ca.* 8000 ¹⁴C years BP, approximately 1500 years after the onset of the latest sapropel (S1) in the Mediterranean Sea, which is dated to *ca.* 9500-6000 ¹⁴C years BP. In the Baltic Sea, sapropel sediments are still forming. Today, the Baltic Sea has an estuarine water circulation with marine water entering at depth, and relatively fresh water exiting at the surface. The present Mediterranean Sea has an anti-estuarine circulation pattern with marine water entering at the surface and dense, saline water exiting the Strait of Gibraltar at depth. The Baltic Sea and the Mediterranean Sea are however both semi-enclosed seas with limited water exchange with the open ocean. There are thus similarities between the Mediterranean and the Baltic Sea, even though the latter is much shallower and less saline than the Mediterranean Sea. The mechanisms for fluxes and preservation of organic carbon are, however, the same.

Most authors have now agreed that in order to form sapropels, both oxygen depleted bottom water conditions and increased primary production are needed (Calvert *et al.* 1992, Passier *et al.* 1999, Thomson *et al.* 1999, Cramp and O’Sullivan 1999, Hallberg 2004). Conventionally, variations in the amount of organic carbon in sediments have been used to indicate changes in primary productivity, even though the amount preserved in sediment also depends on the preservation capability. Therefore, when studying paleoenvironments, it is important to find other proxies for primary production, as a complement to organic carbon. Some plankton and bacteria live only in specific environments and under certain conditions. Many of these organisms have no

hard shell that is preserved in the sediment, but the presence of their pigments in sediments reveals their past existence. Pigments have for a long time been extensively used as biomarkers indicative of different organisms (Fox 1944, Vallentyne 1956, Eglinton *et al.* 1964, Eglinton and Calvin 1967). In order to understand the formation of sapropels, pigments are hence useful in reconstructing the paleoenvironmental conditions at the time of their formation.

The objective of this thesis is to elucidate the mechanisms that lead to sapropel formation.

2 The study areas and their sedimentary records

The Baltic Sea

The present Baltic Sea

The Baltic Sea (Fig. 1) is 377 000 km², which makes it the world’s largest semi-enclosed brackish-water body. Water depths generally vary from 25-200 m (Björck 1995, Sohlenius 1996), with several deep basins, e.g. the Bornholm Basin (105 m), the Gotland Basin (249 m) and the Landsort Deep (459 m) (Björck 1995, Sohlenius 1996). In the Baltic Proper, a halocline restricts the vertical water circulation. This, together with the shallow thresholds of the Danish Straits limits the water exchange with the North Sea, which results in only occasional inflows of saline dense water that reaches the deep basins. This leads to periods of oxygen depletion and formation of hydrogen sulfide in the bottom water of deep basins (Fonselius 1970). The Bothnian Sea and Bothnian Bay have no well developed halocline, and the bottom waters are well-mixed and oxygenated. Since the freshwater input from rivers is much larger than the input of saline water, salinity in the Baltic Sea is much lower than in the oceans. The salinity of the surface waters varies from 1‰ in the Bothnian Bay up to 6-8‰ in the central Baltic and 8-16‰ close to the inlets. The bottom waters have higher salinities, up to *ca.* 15-20‰ in the central Baltic (Nehring and Matthäus 1991, Björck 1995). The Baltic Sea has a weak anti-clockwise circulation with saline bottom water flowing north along the Finnish coasts, and less saline surface water transported south along the Swedish coast (Kullenberg 1981).

At present, the Baltic Sea has an estuarine circulation, where freshwater input exceeds evaporation. Rivers are the main input of fresh water to the Baltic Sea, and precipitation is of approximately the same order as evaporation. Surplus freshwater exits by a

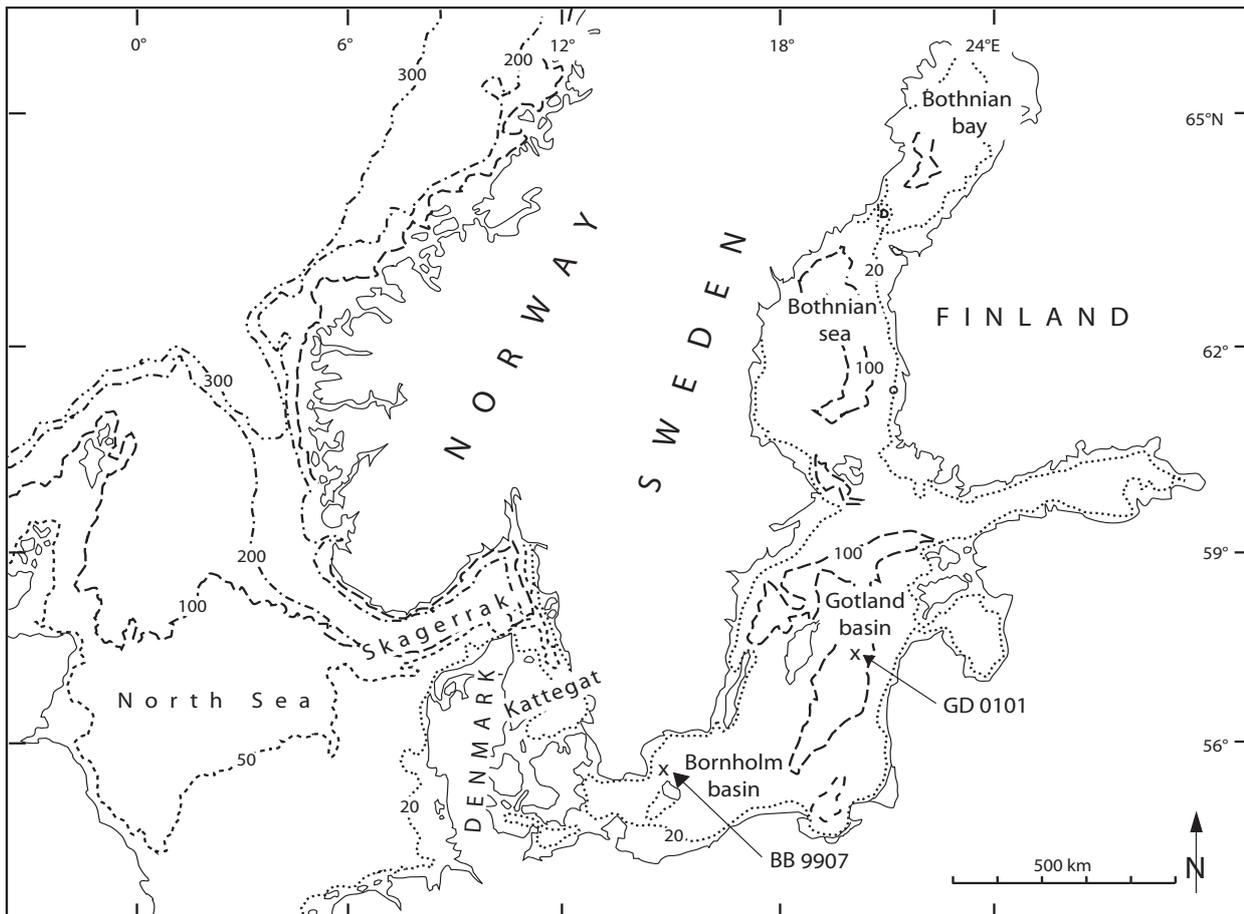


Fig. 1: Map of the Baltic Sea. Coring points in the Bornholm Basin and eastern Gotland Basin marked with an "x".

surface outflow through the Danish Straits, while a subsurface inflow of marine water flows in the opposite direction (Håkansson 1993, Hallberg 2004).

The Holocene history and sedimentary record of the Baltic Sea

Since the latest deglaciation, the Baltic Sea has experienced four alternating fresh-and brackish water stages (e.g. Ignatius *et al.* 1981, Björck 1995). The first stage was the Baltic Ice Lake, an ice-dammed freshwater lake, resulting from the melt water produced by the rapidly melting ice-sheet in southern Sweden around 12 600 ^{14}C years BP. When the ice retreated from the middle part of Sweden *ca.* 10 300 ^{14}C years BP, the Baltic Ice Lake was drained and the Yoldia Sea developed. Despite the name, this was mainly a freshwater stage, with a short brackish phase *ca.* 10 000-9900 ^{14}C years BP, before the contact with the sea ended due to isostatic land uplift (Svensson 1991, Sternbeck and Sohlenius 1997). The next stage was the freshwater Ancylus Lake, which began *ca.* 9600-9500 ^{14}C BP (Svensson 1991, Björck 1995) and ended around 8500-8000 ^{14}C BP when

eustatic sea-level rise opened up the connection through the Danish Straits. Salt water then again entered the Baltic and gradually changed the fresh-water Ancylus Lake into the brackish Litorina Sea (Winterhalter 1992, Westman and Sohlenius 1999, Westman *et al.* 1999). The Ancylus/Litorina transition is believed to have been a complex period with initial, weak pulses of brackish water intruding the Baltic Sea *ca.* 8800-8900 ^{14}C BP and with fully established brackish water conditions after *ca.* 2000 years (Berglund and Sandgren 1996, Andrén *et al.* 2000b, Sohlenius *et al.* 2001). During the Litorina Sea, the salinity was higher, maybe as much as twice as high as today (Ekman 1953, Ignatius *et al.* 1981, Sjöberg *et al.* 1984). A halocline most certainly developed during the early Litorina Sea, which limited the vertical water circulation and lead to stagnant bottom waters in large areas of the Baltic Sea (Sjöberg *et al.* 1984, Westman and Sohlenius 1999, Sohlenius *et al.* 2001). This is supported by the common presence of laminated sequences in Litorina Sea sediments, which indicate periods of poorly oxygenated bottom waters (Winterhalter 1992, Sohlenius and Westman 1998, Sohlenius *et al.* 2001). Litorina Sea sediments

from the Bornholm Basin are often devoid of, or have less distinct, laminae. Therefore, the sediment-water interface in this area is thought to have been less anoxic or even oxic at times (Sohlenius *et al.* 2001). The Litorina Sea stage ended *ca.* 3000 ¹⁴C years BP and was followed by the present Baltic, or post-Litorina Sea, which has a lower salinity (Sjöberg *et al.* 1984, Sohlenius 1996).

The sediments deposited during the different post-glacial stages of the Baltic Sea are often divided into distinct deposits or units. Ignatius *et al.* (1981) constructed a general stratigraphy valid for the major part of the Baltic Sea. It can be divided into three major units: glacial clay and silt (oldest, deposited during the Baltic Ice Lake), transition clay from the Yoldia Sea and Ancylus Lake periods and on top postglacial gyttja clay and recent clay gyttja deposited since the Litorina Sea stage to present. The change from glacial clay to transition clay is diachronous as the deglaciation of the Baltic Sea took several thousand years (Sohlenius 1996).

The clays have low organic carbon content, but sediments from the Litorina Sea are characterised by relatively high organic carbon content; *ca.* 4-10 % (Ignatius *et al.* 1981, Sohlenius *et al.* 1996, Westman and Sohlenius 1999, Andrén *et al.* 2000b, Bianchi *et al.* 2000). These organic-rich sediments in the Baltic Sea are sapropels, even though the common term is gyttja in Sweden (Table 1).

Sapropel formation in the Baltic Sea

The high organic content of Litorina Sea sediments has most often been explained by increased primary production (Winterhalter 1992, Sohlenius and Westman 1998, Sohlenius *et al.* 2001). The possibility that preservation of organic matter was enhanced in the anoxic bottoms of the Litorina Sea compared to the oxic Ancylus Lake has also been discussed (Sohlenius *et al.* 1996, Sohlenius and Westman 1998). The increase in organic carbon, however, often precedes the onset of laminated sequences, which are commonly used as indicators of anoxic bottom conditions (Sohlenius and Westman 1998, Sohlenius *et al.* 2001). The increase in primary production has been suggested to be the result of more clear water,

and therefore, a deeper photic zone. The clear water was supposed to have resulted from flocculation and deposition of suspended mineral particles triggered by the increase in salinity (Winterhalter 1992). However, high organic carbon concentrations also occur during the early Litorina phase when the salinity was relatively low (Sohlenius and Westman 1998). Emelyanov (1988), argued that more nutrients reached the Baltic Sea as weathering products, resulting from the warmer climate prevalent at that time. He also suggested that nutrient-rich bottom water reached the surface by upwelling, giving rise to high primary productivity. Westman and Sohlenius (1999) also suggest upwelling as a probable explanation for the high organic carbon content in Litorina Sea sediments. Inflow of saline water will, due to its higher density, replace the bottom water, which in turn will be forced upwards and bring nutrients into the photic zone (Fonselius 1968, Shaffer 1979, Middelburg *et al.* 1991, Westman and Sohlenius 1999). Upwelling areas are often sites of extremely high primary productivity producing bottom sediments rich in organic matter; sometimes up to 20% by weight organic carbon (Reimers 1982, Höll and Kemle-von Mücke 2000). Inflowing saline water also brought nutrients into the Baltic Sea as the North Sea waters are rich in phosphorus (P) compared to the large fresh-water lakes within the Baltic Sea drainage area (Willén 1984, Persson *et al.* 1989, North Sea Task Force 1993). The inflow of water through the narrow straits probably caused erosion and land derived nutrients were added to the water (Westman *et al.* 2003).

The Mediterranean Sea

The present Mediterranean Sea

The Mediterranean Sea (Fig. 2) is a semi-enclosed sea that is separated from the North Atlantic Ocean by the narrow Strait of Gibraltar with its 284 m deep sill (Bryden and Kinder 1991). It is *ca.* 2 510 000 km² and has a general water depth of approximately 1500 m, but some areas are more than 4000 m deep. It has a distinct anti-estuarine water circulation,

*Table 1. Swedish/international terminology of sediment with varying organic carbon content (by weight) compared to sapropel terminology. 1) Karlsson and Hansbo 1992; 2) Kidd *et al.* 1978.*

Swedish/international terminology ¹⁾	Organic carbon content ¹⁾	Sapropel terminology ²⁾
Clay	< 2%	sapropelic (>0.5%)
Gyttja clay	2 - 4%	sapropel
Clay Gyttja	4 - 20%	sapropel
Gyttja	> 20%	sapropel

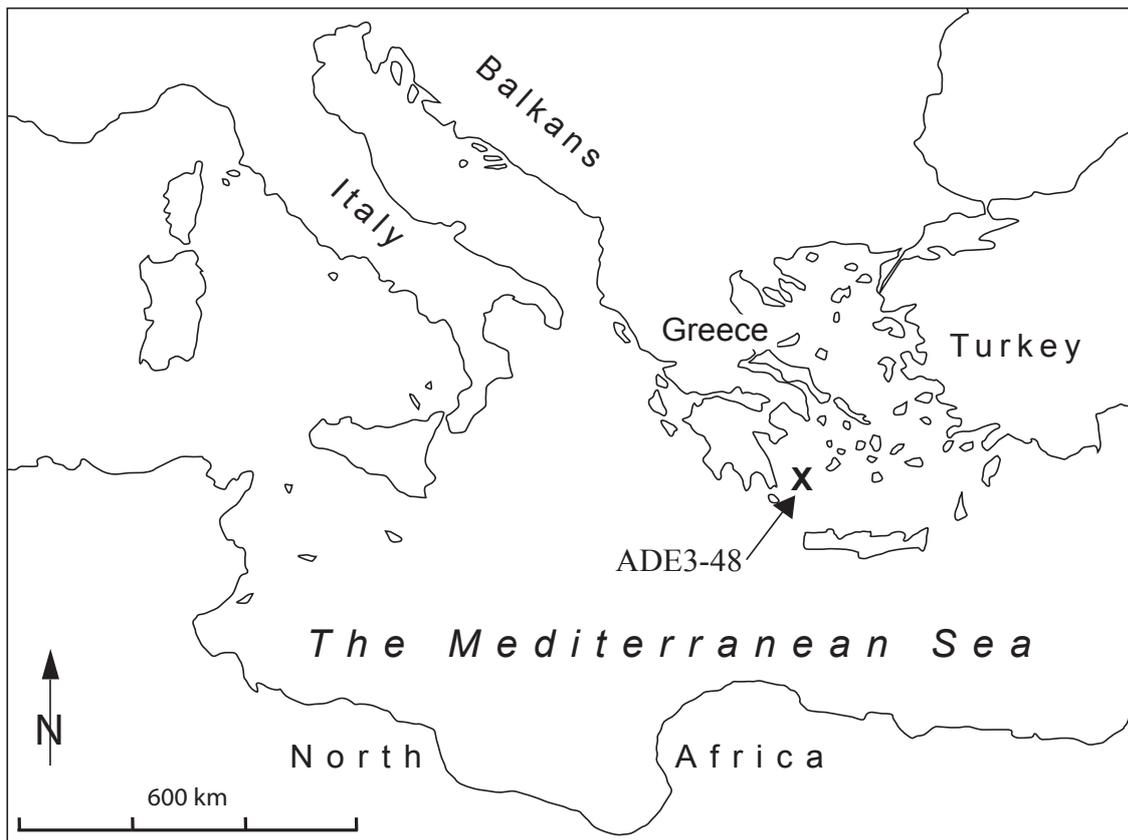


Fig. 2: Map of the eastern Mediterranean Sea. Coring point marked with an "x".

where evaporation exceeds freshwater input and a surface inflow from the Atlantic Ocean through the Strait of Gibraltar. The eastern and western sub-basins are separated by the Strait of Sicily, which has two major channels, *ca.* 365 and 430 m deep, providing the primary connections between the two sub-basins (Garzoli and Maillard 1979). The water exchange through the Strait of Gibraltar is an eastward surface flow compensated by a westward subsurface flow. The water masses are separated at a depth of *ca.* 150 m by a sharp discontinuity in the temperature and salinity profiles (Lacombe and Richez 1982, Malanotte-Rizzoli and Bergamasco 1989). The inflowing Atlantic water has a temperature around 15°C and salinity about 36.3‰ (Malanotte-Rizzoli and Bergamasco 1989). Surface water flowing eastward will, due to evaporation, become gradually more saline and dense. When it reaches the Levantine Basin, it is finally so heavy that it will sink to become Levantine Intermediate Water (LIW). This is primarily taking place during the winter, when strong winds enhance evaporation and mixing. The mixing of water masses is further improved by the absence of a thermocline, which is developed during the summer. LIW is the major constituent of the highly saline Mediterranean Intermediate Water (MIW), which is

found both in the western and eastern sub-basins (Garzoli and Maillard 1979, Malanotte-Rizzoli and Hecht 1988, Malanotte-Rizzoli and Bergamasco 1989, Rohling 1994). Similar formation of intermediate water is absent in the western part of the Mediterranean Sea. The dense, saline MIW is the major part of the subsurface water that flows westward through the Sicilian Straits and further out through the sill of Gibraltar.

In the eastern Mediterranean Sea, MIW is found at depths between *ca.* 150 and 600 m (von Wüst 1960, Rohling 1994). The upper boundary separates the saline intermediate waters below from the less saline surface waters. This halocline also prevents substantial upward mixing of the somewhat more nutrient-rich MIW into the strongly nutrient-depleted surface waters of the euphotic zone, down to about 120 m (McGill 1961, Rohling 1994). This situation is further complicated during summer, when the surface waters overlying the halocline are sub-divided by a thermocline.

The eastern and western sub-basins have their own sources of deep water. The deep waters are found below the MIW and fill the deepest parts of the basins. The Eastern Mediterranean Deep Waters (EMDW) are formed in the Adriatic Sea, where cold

water with relatively low salinity mixes with warm and high salinity MIW. EMDW is slightly less saline than MIW, but also colder, which yields a higher density water mass (Malanotte-Rizzoli and Hecht 1988, Artegiani *et al.* 1989, POEM group 1992). The mixing also oxygenates the bottom waters in the eastern Mediterranean. In the western Mediterranean, the surface layer reaches from 0-150 m, the intermediate layer 150-400 m and the deep water is situated below 400 m (Béthoux *et al.* 1990). This Western Mediterranean Deep Water, (WMDW), is formed during the late winter in the northern part of the western Mediterranean. The surface water density is increased after intensive cooling and evaporation due to the northerly Mistral winds in the area, which permits for mixing with MIW and creation of WMDW (Leaman and Schott 1991, Rohling 1994). EMDW and WMDW are effectively separated from each other by the Sicilian sill. WMDW is also well separated from the Northern Atlantic Ocean by the sill of Gibraltar. The residence time of water in the eastern basin has been estimated as 50 years and for the western basin as 20 years (Béthoux *et al.* 1990), but Schlitzer *et al.* (1991) argued that the renewal time for the entire eastern Mediterranean Sea, including the deepest parts, is a little more than 80 years.

Today, the Mediterranean Sea is oligotrophic with oxygenated bottom waters (Krom *et al.* 1991, Bianchi *et al.* 1996, Hallberg 2004) and it has probably been so since the end of sapropel S1 deposition *ca.* 6000 ¹⁴C years BP (Hallberg 2004). Phosphorus is the limiting nutrient in the eastern Mediterranean (Berland *et al.* 1980, Krom *et al.* 1991).

The history and the sedimentary record of the Mediterranean Sea

The Swedish Deep Sea Expedition aboard the Albatross in 1947-1948 revealed 11 sapropels in eastern Mediterranean sediment cores, and later expeditions have found additional layers. The formation of the 12 latest sapropels in the eastern Mediterranean occurred during the last *ca.* 450 ka (Cheddadi and Rossignol-Strick 1995, Hallberg 2004), but sapropels have been deposited periodically in the eastern Mediterranean since Miocene times (Kidd *et al.* 1978, Rohling and Thunell 1999). Sapropels are generally more common in lower Pliocene sediments than in the upper Pliocene and Quaternary deposits where they often occur in clusters (Diester-Haass *et al.* 1998, Emeis *et al.* 2000).

Recent sediment from hemipelagic sites in the eastern Mediterranean has an organic carbon content of less than 0.5%, which is in contrast to Pliocene

to early Pleistocene sapropel sequences, where organic carbon contents often exceed 20%. Sapropel layers are often centimetres to decimetres thick, and are embedded in light brown to grey hemipelagic sediments (Passier 1998). The carbonate content in Pliocene sapropels can be up to 80%. Normal Pliocene sediments are characterized by high contents of attapulgite, which is missing or only present in very low concentrations, in the sapropels (Sigl *et al.* 1978). Late Pleistocene and Holocene sapropels contain lower concentrations of organic carbon than the Pliocene sapropels (Rullkötter *et al.* 1998). The carbonate content in Pliocene-Pleistocene sapropels varies between almost zero to *ca.* 60%. There is no significant difference in carbonate content or mineralogy between sapropels and the surrounding sediments (Sigl *et al.* 1978). Non-sapropel sediments of Pleistocene age are generally dominated by smectite clay, but the sapropel sequences contain increased amounts of irregular mixed layers of smectite-illite, smectite-chlorite and chlorite (Sigl *et al.* 1978).

Sapropel formation in the Mediterranean Sea

To explain anoxic bottom water conditions in the Mediterranean Sea, many authors (Stanley *et al.* 1975, Calvert 1983, Sarmiento *et al.* 1988, Thunell and Williams 1989, Howell and Thunell 1992) have suggested a reversal in the water circulation from today's anti-estuarine circulation to estuarine circulation (Fig. 3). This switch is thought to have been caused by increased input of freshwater. When river input and precipitation exceeds evaporation, the surface water will not be dense enough to sink and provide oxygen to the bottoms. The bottom water will then be dysoxic or even anoxic due to stratification of water masses. There is no evidence of an actual reversal of the circulation, but there are strong indications of surface waters with low salinity concentrations, a so-called "low-salinity cap", from depleted $\delta^{18}\text{O}$ values found in most sapropels. A "low-salinity cap" would have decreased, or even eliminated, the oxygen flux to the bottom waters (Cita *et al.* 1977, Thunell and Williams 1989, Tang and Stott 1993). Other authors have proposed that weakened anti-estuarine water circulation should have been enough for creating conditions that would result in formation of sapropels (Ross and Kennett 1984, Rohling 1994, Myers *et al.* 1998, Slomp *et al.* 2002).

Increased precipitation could have been imposed by intensification of the Indian Ocean summer (SW) monsoon and increased activity of the system of Mediterranean depressions (e.g. Rohling 1994). The increased precipitation over the eastern equatorial

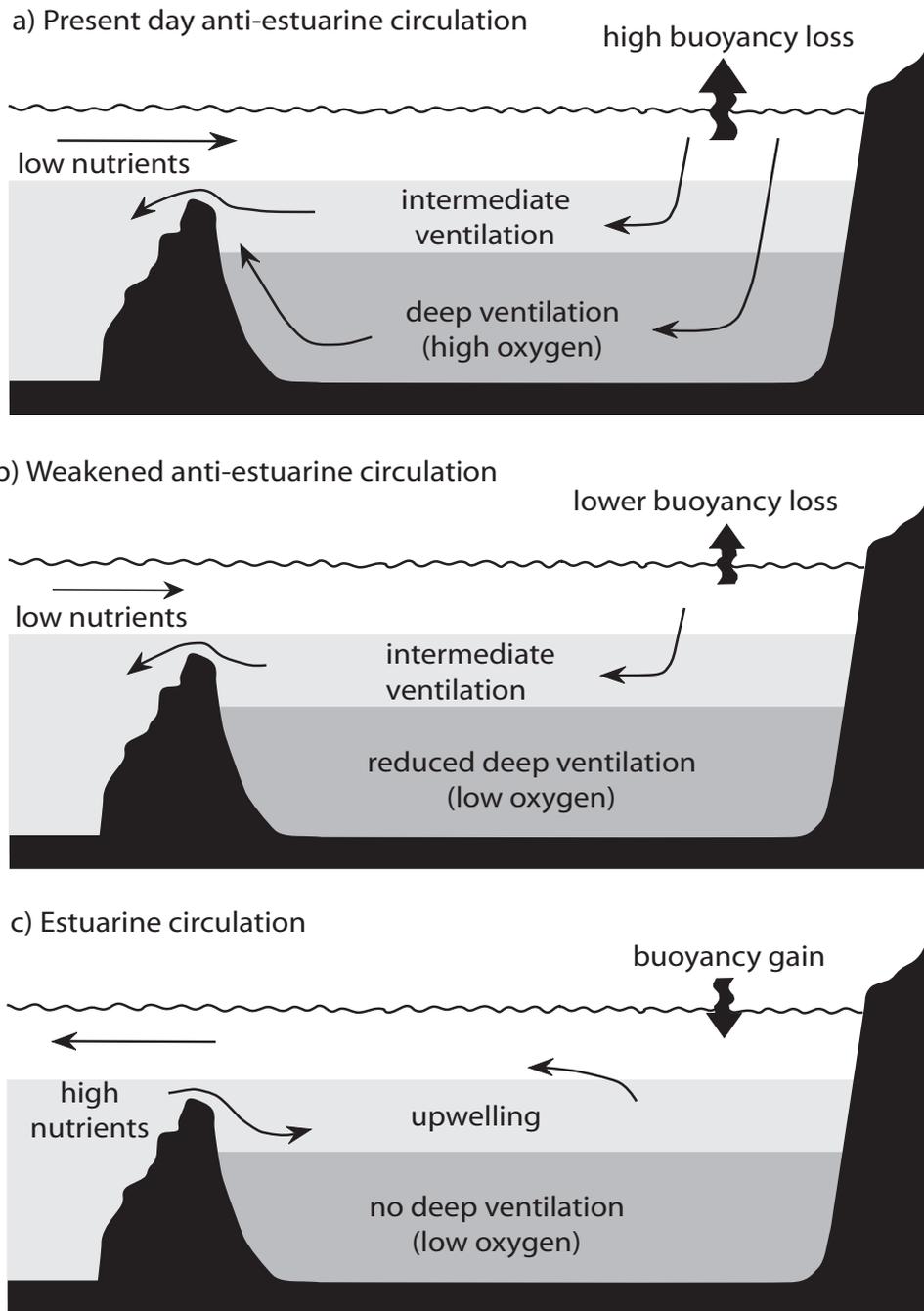


Fig. 3: Schematic figure showing the circulation in the eastern Mediterranean Sea. a) Present-day strong anti-estuarine circulation. b) Proposed weakened anti-estuarine circulation during sapropel formation. c) Proposed estuarine circulation during sapropel formation. Figure from Stratford *et al.* 2000: *Impact on circulation on sapropel formation in the eastern Mediterranean*. *Global Biogeochemical Cycles* 14(2), 683-695. Copyright 2000 by the American Geophysical Union. Reproduced with permission of American Geophysical Union.

Africa would lead to increased discharge from the Nile into the Mediterranean Sea. The intensified monsoon would be a result of a minimum in the Milankovitch precession cycle, when perihelion occurs in the Northern Hemisphere summer. This orbital configuration implies stronger insolation during Northern Hemisphere summers, and weaker insolation during winters, resulting in increased temperature contrasts between summer and winter, and also between the land and sea temperatures. This in

turn leads to an intensified monsoonal circulation and increased rainfall during the summers (Kutzback 1985, Kutzback and Guetter 1986, Rossignol-Strick *et al.* 1982, Rossignol-Strick 1985, Rohling and Hilgen 1991, van Os *et al.* 1994). The minimum in the Milankovitch precession cycle would not only increase the rainfall over Africa, but also over the northern borderlands of the eastern Mediterranean (Shaw and Evans 1984, Rossignol-Strick 1987, Rohling and Hilgen 1991). This increase in

precipitation probably can not be explained by an intensified monsoon, but instead by increased activity of the Mediterranean depressions (Rohling and Hilgen 1991). A northward shift of the westerly storm track over the Atlantic would have enhanced storm frequency across the Mediterranean Sea. This, together with increased northward heat transport in the North Atlantic led to enhanced temperature contrast across the Gulf Stream and the North Atlantic Drift, and an increased evaporation from warmer waters. The result would have been an increase in the formation of low pressure systems with improved moisture transport towards the east (Lamb 1966, 1977, Boucher 1975, McIntyre *et al.* 1989, Rohling 1994). Increased freshwater input can lead to increased productivity both by increased input of nutrients from rivers and by shoaling of the pycnocline and associated intensification of the Deep Chlorophyll Maximum (DCM) layer (Rossignol-Strick *et al.* 1982, Rohling and Gieskes 1989, Lourens *et al.* 1992). The increase in seasonal contrast due to the minimum in the Milankovitch precession cycle may also have caused intensified winter mixing of the water and concomitant nutrification of the euphotic layer. It could also lead to increased stabilization of the water column during the summer resulting in enhanced primary productivity conditions along the northern margins of the entire Mediterranean (Lourens *et al.* 1992, van Os *et al.* 1994).

3 Sapropels and sapropel formation

Definition

A generally accepted definition of a sapropel (Fig. 4) is “a discrete layer more than 1 cm thick containing more than 2% by weight organic carbon”. A sapropelic layer is similarly defined, but contains more than 0.5% by weight organic carbon (Kidd *et al.* 1978). Calvert (1983) modified this definition to exclude the thickness criteria and defined sapropels and sapropelic sediments simply on the basis of organic carbon content. For example, sapropel layers from the Mediterranean Sea range from a few millimetres to more than 50 cm thick (Stanley 1978), so the thickness is not a very characteristic feature. The original definition of a sapropel also included a genetic and environmental aspect. Wasmund (1930) and Potoniè (1937) define a sapropel as “a sediment rich in organic matter (>2% organic C) formed under reducing conditions in a stagnant water body”. This definition was however questioned by Calvert (1983) and Sutherland *et al.* (1984) as they argued against this prerequisite for sapropel formation. Se-

diment rich in organic matter (>20% organic C) can also be named gyttja (Karlsson and Hansbo 1992). de Lange and ten Haven (1983) stated that as the origin and environment of formation of organic-rich sediment are not always traceable, any sediment containing over 2% organic C can be considered a sapropel.

Mechanisms

Over the years, the mechanisms behind the formation of sapropel sediments have been much debated. Some authors (e.g. Cita *et al.* 1977, Thunell *et al.* 1977, Rossignol-Strick *et al.* 1982, Rossignol-Strick 1985, Stanley 1978) have proposed anoxic bottom waters to be the dominant mechanism leading to enhanced preservation of organic carbon. They argue that anoxia can be produced by water column stratification due to the inflow of less saline surficial waters. Others propose an increase in primary productivity, and thus, an increase of carbon flux to the seafloor as the primary mechanism. This theory can be further divided into:

- a) Models suggesting increased primary production as the main cause leading to sapropel formation (e.g. de Lange and ten Haven 1983, Howell and Thunell 1992).
- b) Models in which increased primary production is believed to be the only cause of the formation of all sapropel layers. Oxygen depleted bottom waters and anoxic sediments are due to the large fluxes of

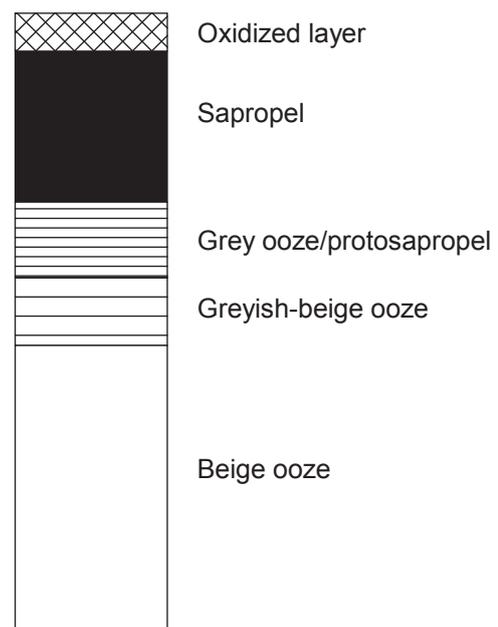


Fig. 4: Schematic figure of sapropel buildup.

organic carbon to the sea floor, the carbon is hence not preserved because of stagnation (Calvert 1983, Sutherland *et al.* 1984, Pedersen and Calvert 1990). Nowadays, most authors agree that formation of sapropels most likely is due to the combined effect of increased primary productivity and improved preservation of organic matter under anoxic bottom-water conditions (Calvert *et al.* 1992, Passier *et al.* 1999, Thomson *et al.* 1999, Cramp and O'Sullivan 1999, Hallberg 2004, Borgendahl and Westman in press).

Sapropels in the eastern Mediterranean are enriched in organic carbon (C_{org}), iron (Fe) and sulphur (S). S and Fe are generally enriched in a zone immediately below the sapropels. This zone, commonly named the protosapropel (Fig. 4), is usually grey and visibly discernible from the overlying darker sapropel and the underlying beige to grey oxidized ooze (Maldonado and Stanley 1976, Muerdter *et al.* 1984, Passier *et al.* 1996).

After a sapropel has been deposited, and the sediment-water interface turns oxic again, a downward oxidation front develops. This results in oxidation of reduced C and S species in the uppermost part of the sapropel and produces a sharp colour boundary at the top of the sapropel (de Lange *et al.* 1989, van Os *et al.* 1991, Pruyers *et al.* 1991, 1993, Thomson *et al.* 1995, Passier *et al.* 1996).

Cyanobacteria, nitrogen fixation and eutrophication

Some pigments, like zeaxanthin and myxoxanthophyll produced by cyanobacteria (Matsuno and Hirao 1989, Lotocka 1998, Bianchi *et al.* 2000, Poutanen and Nikkilä 2001), can indicate an increase in primary production, as high amounts of cyanobacteria often are observed in eutrophic environments (Züllig 1981, van Geel *et al.* 1996, Elmgren 1989, Bianchi *et al.* 2000, Codd 2000, Pitois *et al.* 2001). Cyanobacteria can also act as a trigger for increased primary production as many species are nitrogen-fixers. Import of nitrogen by cyanobacteria has been shown to make up a considerable part of the input of nitrogen (Larsson *et al.* 1985, Howarth *et al.* 1988, Glibert and Bronk 1994, Larsson *et al.* 2001, Wasmund *et al.* 2001, Struck *et al.* 2004, Voss *et al.* 2005). N_2 fixed by cyanobacteria is released as dissolved nitrogen (NO_3 -N, NO_2 -N, NH_4 -N) primarily by lysis of decaying cyanobacteria cells, grazing by heterotrophs or exudation of dissolved nitrogen and amino acids, which adds new nitrogen to the system (Gabrielson and Hamel 1985, Bronk and Glibert 1993a, b, Capone *et al.* 1994, Ohlendieck *et al.* 2000). These processes increase the N/P-ratio and intensify total primary production.

Increased primary production will provide a high flux of organic matter sinking to the sea floor. This may result in oxygen deficiency in the bottom water and the release of redox-sensitive compounds containing P, which can act as a fertilizer after being brought to the photic zone by upwelling. The high concentrations of P create the opportunity for new cyanobacterial blooms and additional N input (Larsson *et al.* 1985, Elmgren and Larsson 2001, Westman *et al.* 2003).

Nitrogen isotope values in eastern Mediterranean sapropels are generally low, 0 to +2‰ (e.g. Calvert *et al.* 1992, Borgendahl submitted). Calvert *et al.* (1992) explained this as the result of isotopic fractionation during nitrate uptake, where assimilation of nitrate and ammonium by biota yield depleted sedimentary $\delta^{15}N$ due to the biotic preference for the lighter isotope (Wada and Hattori 1976, 1978, Cifuentes *et al.* 1989, Altabet and Francois 1994, Francois *et al.* 1992, Kendall and Caldwell 1998). The prerequisite for biotic fractionation during nitrate uptake is a surplus of nitrate, so that plankton can choose the lighter isotope. However, during the formation of both S1 and Baltic Sea sapropels, N/P-ratios were probably low. The lowest $\delta^{15}N$ values measured by Francois *et al.* (1992) in surface sediments of the Southern Ocean were *ca.* +5‰ at times of high nitrate concentrations. Depletion of $\delta^{15}N$ in Baltic and S1 sapropels is more likely caused by nitrogen fixation by cyanobacteria (Rau *et al.* 1987, Struck *et al.* 2001, Kuypers *et al.* 2004, Borgendahl submitted).

Chlorobiaceae, euxinia and upwelling

Another strong indicator pigment is isorenieratene. It is a characteristic pigment biosynthesized by the brown strain of anaerobic, photolithotropic *Chlorobiaceae* (Pfenning 1978). These green sulphur bacteria live at the redoxcline where they perform anoxygenic photosynthesis, which requires H_2S and light. The presence of isorenieratene hence indicates that sulphide-containing bottom water has reached the photic zone (Repeta 1993, Kenig *et al.* 1995, Sinninghe Damsté *et al.* 1995, Menzel *et al.* 2002).

At times of increased primary productivity, the high loads of organic matter sinking down to the sea floor will consume oxygen during breakdown. In a stratified water column, this will result in oxygen deficiency in the bottom water and release of compounds such as P, which can fertilize the photic zone if upwelling occurs. This will in turn lead to enhanced primary production and anoxic bottom water conditions that gradually expand upwards in the water column. During strongly eutrophic conditions,

anoxic water can reach as high up as the photic zone, which typically reaches down to *ca.* 150 m. The presence of isorenieratene in sapropel S1 indicates that anoxic and sulphidic conditions existed in the photic zone. This is a strong evidence for enhanced preservation of organic carbon as an important mechanism for sapropel formation.

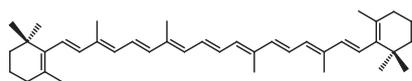
Proxies for studying paleoenvironments

Pigments

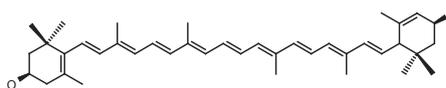
Biological markers or biomarkers (Eglinton *et al.* 1964, Eglinton and Calvin 1967) can be described as “molecular fossils” (Peters and Moldowan 1993). Many marine phytoplankton, as well as large numbers of bacteria, zooplankton and benthic organisms, synthesise characteristic pigment structures (Matsuno and Hirao 1989), which have a great paleoecological

and paleolimnological value as biomarkers. Among the most widespread and important natural pigments are the carotenoids (Fig. 5), which are yellow to red pigments found in microorganisms, plants and animals (Matsuno and Hirao 1989, Strube and Dragsted 1999). Carotenoid pigments have often been used as biomarkers for different organisms (e.g. Sanger 1988, Leavitt 1993). In living tissue, the major role of carotenoids is related to their light absorption functions. During photosynthesis they serve as accessory pigments, which function both to pass light energy during photosynthesis and to protect the photosynthetic tissue against photosensitized oxidation (Goodwin 1980, Matsuno and Hirao 1989). Pigments contain chromophore groups, often conjugated C=C bonds in a polyene chain, which can absorb light in the visible spectrum and that also give the molecule its characteristic colour (Meyers and Ishiwatari 1993, Meyers 1997). Carotenoids occur in free forms as well as glycosides, esters, sulphates

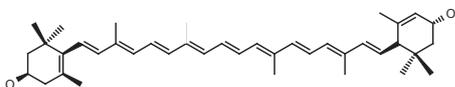
BB-carotene, C₄₀H₅₆, MW=536.89



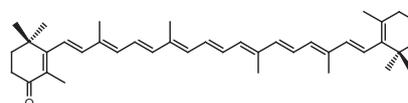
Zeaxanthin, C₄₀H₅₆O₂, MW= 568,89



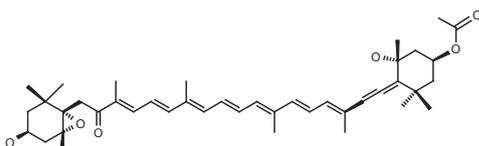
Lutein, C₄₀H₅₆O₂, MW= 568.89



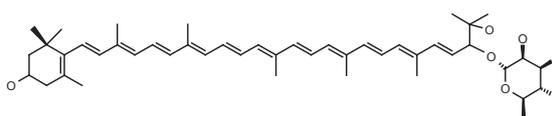
Echinenone, C₄₀H₅₄O, MW=550.88



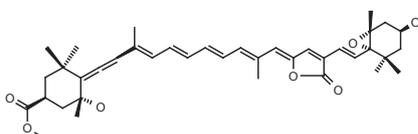
Fucoxanthin C₄₂H₅₈O₆, MW=658.92



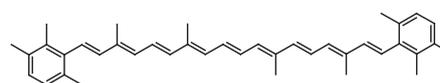
Myxoxanthophyll C₄₆H₆₆O₇, MW= 731.03



Peridinin C₃₉H₅₀O₇, MW=630.82



Isorenieratene, C₄₀H₄₈, MW=528.83



Alloxanthin, C₄₀H₅₂O₂, MW=564.85

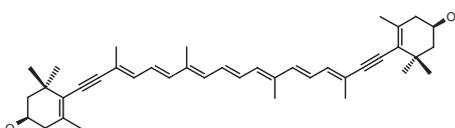


Fig. 5: Chemical structures of the analyzed pigments.

and carotenoproteins (Matsuno and Hirao 1989). They are tetraterpenoids (C_{40}), consisting of eight isoprene (C_5) units, which arise through “tail-to-tail” condensation of two identical C_{20} units (Davies 1965, Strube and Dragsted 1999). Carotenoids can be divided into carotenes, consisting of the eight isoprenoid units, and xanthophylls, which are their oxygenated derivatives (Goodwin 1980, Matsuno and Hirao 1989).

Generally, the information gained from sedimentary pigments has paralleled developments in analytical techniques. In early studies of pigments, spectrophotometric and alumina column chromatography methods were used (Vallentyne 1956, Gorham 1961). Paper chromatography (Vallentyne 1956) and later thin-layer chromatography (Züllig 1981) have also been used to separate different carotenoids and their derivatives. Today, reverse-phase HPLC and GC are the most common analytical methods for carotenoids (Lami *et al.* 1994, Sinnighe Damsté *et al.* 1995, Koopmans *et al.* 1996, Bianchi *et al.* 2000, Schmidt *et al.* 2002, Hopmans *et al.* 2005). The improved separation and detection compared to the early techniques have resulted in an increased number of known pigments.

Degradation/preservation of pigments

Many carotenoids are rather labile organic compounds, starting to break down in the water column. Carotenoid preservation depends both on chemical stability and the depositional environment. The oxygen-containing functional groups of xanthophylls together with the double bonds of xanthophylls and carotenes provide sites for microbial attack making these compounds relatively sensitive to diagenetic alteration (Meyers and Ishiwatari 1993, Meyers 1997). There are, however, disagreements about the extent of pigment degradation. Some researchers have found correlations between sedimentary plant pigment concentrations and contemporary algal abundance in the water column (Guilizzoni *et al.* 1983). Other authors show that more than 99% of the autochthonous production of some pigments is lost both in the water column during sinking and after deposition in bioturbated, oxic surface sediments (Furlong and Carpenter 1988, Hurley and Armstrong 1990, 1991). Substantial degradation also occurs by plankton grazing (Leavitt and Brown 1988). In sediment, concentrations of intact carotenoids generally decrease with depth, but Furlong and Carpenter (1988) found that below the bioturbated surface layer of oxic sediments, pigment concentrations were relatively constant. In fact, degradation of pigments

continues even after sediment burial, but at much lower rates (Leavitt 1993). Degradation can generally be divided into three phases: rapid oxidation in the water column ($T_{1/2}$ = days), a slow post-depositional degradation in surface sediment ($T_{1/2}$ = years) and much slower loss of double bonds after burial in the sediment ($T_{1/2}$ = centuries) (Leavitt 1993). Differences in the ability of different carotenoids to be preserved are observed and the time scale for degradation depends on the structure of the particular carotenoid. Some early work on pigment degradation was done by Fox (1944), who estimated that 33% of the carotenes and as much as 97% of the xanthophylls were lost prior to deposition in marine environments. This selective preservation continued after burial, with carotenes becoming the predominant fraction with depth (Fox 1944, Vallentyne 1960). This is mainly because of the preferential loss of those containing hydroxyl-, oxo- and epoxy-groups. Carotenoids containing 5,6-epoxides decompose rapidly through cleavage of the polyene, degrading to low molecular weight colourless products (Repeta and Gagosian 1987, Repeta 1989, Hurley and Armstrong 1990, 1991). Watts and Maxwell (1977) detected reduction of two double bonds in canthaxin (a diketone) in 56 000-year-old sediments. Reduction of double bonds in zeaxanthin (a diol) was found only in *ca.* 340 000-year-old sediments, whereas β,β -carotene still was unaltered. The oldest reported intact carotenoid is isorenieratene found in a marl of Miocene age (Messinian, 6 Ma) (Keely *et al.* 1995) and an unspecified diaromatic carotenoid from a Lower Miocene (*ca.* 20 Ma) clay from a deep basin in the Western North Atlantic Ocean (Cardoso *et al.* 1978). The carotenes do however also undergo extensive degradation and a number of reactions occur with the polyene chain i.e., expulsion of toluene and xylene, cyclisation, aromatisation, hydrogenation, C-C bond cleavage and reaction with inorganic sulphur species (Sinnighe Damsté and Kopmans 1997). The assumed low preservation potential has resulted in relatively few studies of these compounds. Recent results describing remnants of carotenoids in rocks and crude oils as old as 450 Ma has lead to renewed interest in these compounds as paleoenvironmental proxies. Despite the amount and complexity of carotenoid breakdown products, they will probably be increasingly more important in paleoenvironmental studies (Sinnighe Damsté and Kopmans 1997).

Generally, pigments are better preserved in eutrophic compared to oligotrophic environments, because the overall accumulation rate is higher, resulting in a rapid burial in the sediments. Preservation is further enhanced by low oxygen content and

reduced penetration of light (Leavitt 1988, Sanger 1988, Hurley and Armstrong 1990). The specific carotenoid content of sediments often increases with water depth as deep-water sediments generally receive less light and oxygen than shallow deposits (Moss 1968, Gorham and Sanger 1972). In addition, cold water, especially in the deeper bottoms, tends to preserve pigments better than warmer water (Sanger 1988). Many authors have shown that preservation of organic matter is enhanced during anoxic conditions (Sanger and Crowl 1979, Leavitt 1988, Sanger 1988, Hurley and Armstrong 1990, Sun *et al.* 1993, Sun and Wakeham 1998). Oxygen may promote loss of carotenoids either by direct oxidation (El-Tinay and Chicester 1970) or by stimulation of microbial activity (Leavitt 1988). Calvert (1983) pointed out, however, that sulphate reducing bacteria degrade organic material under anoxic conditions.

Pigments as proxies of specific environments

Many pigments can serve as indicators of specific environments and can be used in reconstructing historical environmental changes. The use of a pigment as a biomarker is dependent on the specificity of the pigment to the organism of interest. Some pigments are rather widely distributed between different classes (Table 2) and in other cases the pigment is not present within all species of a class (Matsuno and Hirao 1989, Everitt *et al.* 1990). The reliability of the interpretation also depends on the pigment's resistance to degradation. If pigments with different stabilities are analysed, the relative abundances of fossil pigments in the sediment are not totally reliable as a measurement of changes in phytoplankton community composition. Instead, fossil profiles of individual pigments should preferably be independently interpreted with each pigment scaled in context to its historical maximum to avoid misinterpretations due to differences in preservation (Leavitt 1993).

Isotopes

Stable isotopes are chemical markers that provide an integrated history of sources and pathways (Robinson 2001) and the isotopic composition of an element or compound can be changed by a number of processes. Isotopic fractionation can arise from two processes; equilibrium fractionation and kinetic fractionation. Equilibrium fractionation takes place in closed and well-mixed systems at chemical equilibrium and is reversible. At isotopic equilibrium, the forward and backward reactions are identical and the ratios of the different isotopes in each compound are constant for a particular temperature (Kendall and Caldwell 1998). One process typically viewed as an equilibrium process is the condensation of water vapor in rain clouds (Kendall and Caldwell 1998). Kinetic fractionation is most common in natural processes, and is not reversible (Hoefs 1997). Kinetic fractionation is the most common isotopic fractionation. Biological fractionation is an example of kinetic fractionation. If the isotope of interest is present in sufficient amounts, organisms will generally prefer the lighter isotope, due to the lower energy required to break the weaker bonds in these molecules (Kendall and Caldwell 1998). Therefore, the resulting isotopic signal in the biological product will be isotopically lighter than in the original material (Wada and Hattori 1976, 1978, Cifuentes *et al.* 1989, Altabet and Francois 1994, Francois *et al.* 1992, Kendall and Caldwell 1998).

Stable isotopes are reported as δ -notation (‰) = $[(R_{\text{sample}}/R_{\text{standard}} - 1)] \times 1000$, where R is the ratio heavy/light isotope, i.e., $^{15}\text{N}/^{14}\text{N}$, $^{13}\text{C}/^{12}\text{C}$ and $^{34}\text{S}/^{32}\text{S}$.

$\delta^{15}\text{N}$

Stable nitrogen isotopes have often been used to study nitrogen sources and processes (Savage *et al.* 2004, Bohlin 2005, Voss *et al.* 2005). Since nitrogen occurs in several oxidation states and mainly

Table 2: Phytoplankton pigments analysed and their potential origins. 1) Matsuno and Hirao 1989; 2) Leavitt and Hodgson 2001; 3) Goodwin 1965; 4) Pfenning 1978.

Pigment	Origin	reference
Zeaxanthin	Cyanobacteria (almost in all species)	1,2
Lutein	Green algae	1,2,3
BB-carotene	Almost all primary producers	1,2,3
Alloxanthin	Cryptophytes	2
Echinenone	Mainly Cyanobacteria (almost in all species)	1,2,3
Fucoxanthin	Bacillariophyceae, Dinoflagellates	2,3
Myxoxanthophyll	Only Cyanobacteria (almost in all species)	1,2,3
Peridinin	Dinophycean algae, Dinoflagellates	1,2,3
Isorenieratene	Brown strain of green sulphur bacteria (<i>Chlorobiaceae</i>)	4

in gaseous and liquid forms, nitrogen isotopes are suitable for studies of natural systems (Hoefs 1997). Three processes of importance for the $\delta^{15}\text{N}$ -signal in organic-rich sediments are a) nitrogen fixation b) assimilation and c) diagenesis.

a) Nitrogen fixation is a direct biological uptake of nitrogen from air ($\delta^{15}\text{N} = 0\text{‰}$) and will result in $\delta^{15}\text{N}$ of *ca.* -2 to 0‰ in the biomass (Wada and Hattori 1976, Struck *et al.* 2001). Nitrogen fixation converts inert N_2 to forms that are more reactive i.e., NO_x , NH_y , and organic N (Kendall 1998).

b) Assimilation is incorporation of dissolved inorganic matter, DIN; (ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-)) into organic matter (OM) (Kendall 1998). The average $\delta^{15}\text{N}$ -value of DIN is *ca.* +5 to +10‰ in marine oxygenated environments (Peters *et al.* 1978, Altabet 1988, Meyers 1997). It is higher in anoxic water masses where denitrification can occur, resulting in nitrate enriched in ^{15}N (Liu and Kaplan 1989). This is a process that can give the biomass an isotopic signal of *ca.* +5‰ if N is in abundance, since biological uptake favors the lighter isotope (Kendall 1998).

c) Extensive diagenesis during oxygenated conditions has been suggested to result in relatively high (+5 to +7‰) sedimentary $\delta^{15}\text{N}$ -values (Sachs and Repeta 1999).

$\delta^{13}\text{C}$

Stable carbon isotopes are primarily used for estimating the proportion between C_3 and C_4 terrestrial plants and marine/terrestrial material (Table 3), respectively (Meyers 1997, Struck *et al.* 2000, Meyers 2003). Biological uptake of carbon has two different photosynthetic pathways C_3 and C_4 . C_3 plants are most common today; more than 90% of all plants use the C_3 -pathway.

An increase in sedimentary $\delta^{13}\text{C}_{\text{org}}$ can also indicate increased primary productivity (Arthur *et al.* 1988, Hodell and Schelske 1998, Brenner *et al.* 1999, Struck *et al.* 2000). This is probably because of decreasing carbon isotope fractionation when CO_2 (aq) have been depleted during massive plankton blooms

(Hodell and Schelske 1998, Struck *et al.* 2000). An increased primary production where CO_2 (aq) is not limited will also result in increasing $\delta^{13}\text{C}_{\text{org}}$ in the sediment, as ^{12}C is preferentially removed to be recycled in the biological web (Hodell and Schelske 1998), leaving an isotopically heavier material to be incorporated in the sediment.

$\delta^{34}\text{S}$

Stable sulphur isotopes can be used to deduce paleoenvironmental changes in aquatic environments. Sulphur is present in nearly all natural environments. In marine sediments it is present as both sulphide and sulphate and in ocean waters it occurs primarily as sulphate. Its isotopic values cover more than 180‰; from the heaviest sulphates around +120‰ to the lightest sulphides at *ca.* -65‰ (Hoefs 1997). If SO_4^{2-} is present in large amounts, sulphate reducing bacteria will have the possibility to choose the lighter isotope, and hence a large fractionation will occur, resulting in lighter $\delta^{34}\text{S}$ values in the sulphide. If SO_4^{2-} is limiting, relatively little fractionation takes place and $\delta^{34}\text{S}$ in the sulphide will be heavier (Passier *et al.* 1996). During sapropel formation, five processes are of primary importance: a) bacterial reduction of SO_4^{2-} to S^{2-} b) oxidation of S^{2-} to intracellular sulphur c) oxidation of S^{2-} to extracellular sulphur d) disproportionation of elemental S e) re-oxidation of S^{2-} to elemental sulphur by ferric iron.

a) Reduction of sulphate to sulphide by sulphate reducing bacteria (SRB). Isotopic fractionation from -40 to -45 ‰ between SO_4^{2-} and reduced S has been observed (Goldhaber and Kaplan 1974, Chambers and Trudinger 1979).

b) Recycling of S by stepwise oxidation of sulphide by phototrophic purple sulphur bacteria (*Chromatiaceae*). In the first step intracellular sulphur is formed. In the next step the intracellular sulphur is further oxidized to sulphate and expelled from the cell. No fractionation occurs, but this sulphate will have a low isotopic signal because sulphide is the sulphur source (Hallberg 1985).

c) Recycling of S by oxidation of sulphide by

Table 3: Isotopic signals of different carbon sources. 1) Hoefs 1997; 2) Meyers 1997; 3) Wang *et al.* 1998; 4) Kendall *et al.* 2001.

Source	Isotopic values	References
C_3 land plants	-20 to -35‰	1,2,3
C_4 land plants	-17 to -9‰	1,2,3
freshwater organic matter	-28 to -18‰	2,4
marine organic matter	-20 to -25‰	2,4

green sulphur bacteria (*Chlorobiaceae*) to form extracellular sulphur. No or minor fractionation occurs, but this sulphur will have a low isotopic signal. This elemental sulphur can be used by SDB (Hallberg 1985).

d) Disproportionation of elemental sulphur to SO_4^{2-} and H_2S by sulphur disproportionating bacteria (SDB). The resulting fractionation is 4‰ to 9‰ (Canfield and Thamdrup 1994, Habicht and Canfield 1997, Canfield *et al.* 1998, Böttcher *et al.* 2001).

e) Re-oxidation of sulphides to elemental sulphur by ferric iron. No fractionation occurs.

Carbon, nitrogen and metals

Carbon is an important element in the biosphere. Living tissue is composed primarily of carbon and estimates of production are often made by measurements of organic carbon (Schlesinger 1997, Wang *et al.* 1998). Organic matter is, however, exposed to degradation by both biological and chemical processes. Decomposition takes place both in the water column and in the sediment, even though the latter is slower (Suess 1980, Routh *et al.* 2004). Therefore, only a small fraction of the initially produced organic matter becomes buried in the sediment (Suess 1980, Leavitt 1993). The decomposition process consumes electron acceptors, e.g. oxygen, and is slower during anoxic conditions (Sun and Wakeham 1998, Meyers and Teranes 2001, Lehmann *et al.* 2002).

Nitrogen is essential for life and is the chemical element that occurs in greatest abundance in the Earth's atmosphere. It is also abundant in soils, fresh water and oceans. More than 99% of this N occurs as N_2 , which is biologically available only for organisms that can perform nitrogen fixation (Galloway *et al.* 2003). The C/N-ratio identifies the proportion of algal and terrestrial organic matter (Sigl *et al.* 1978, Meyers 1997, 2003).

Many sapropels have a high trace-metal content, probably due to the efficient scavenging of these metals by precipitating sulphides in a euxinic water column (Passier *et al.* 1999).

Zn and Mn have been used as proxies of boundaries between protosapropel, sapropel and discontinuities in sapropel formation (Hallberg 2004). Mn is a redox-sensitive element, while Zn is not. Zn concentrations merely reflect the overall mobilization and accumulation of trace metals. It has, however, higher concentrations in the sapropel than in the surrounding sediment. Mn, on the contrary, is commonly depleted in sapropel layers, indicating bottom water anoxia (Sutherland *et al.* 1984, Hallberg 2004). Enrichment of Mn has been used as an indicator of

bottom water oxygenation (Calvert and Pedersen 1993).

Diatoms

Diatoms are siliceous microfossils of diatom algae, and their shells are often well preserved in sediments. They consist of a large number of genera which live in different and sometimes relatively specific environments. Many of them are sensitive to changes in habitat and therefore, they can be used to detect environmental changes e.g. salinity, temperature and nutrient concentration (Andrén *et al.* 1999, Westman and Sohlenius 1999). In this study they have primarily been used as indicators of salinity changes in the Baltic Sea (Westman *et al.* 2003, Borgendahl and Westman in press).

Radiocarbon dating

All samples were dated with AMS (accelerator mass spectrometry) at the Ångström Laboratory, Uppsala University, Sweden. Several age models have been presented regarding the reservoir age and resuspension effects on the apparent age of sediments in the Baltic Sea (Berglund 1971, Königson and Possnert 1988, Westman *et al.* 1999, Andrén *et al.* 2000a, b). There are however uncertainties regarding a general agreement (Westman *et al.* 2003), and therefore the dates from the Baltic Sea are given as uncorrected ^{14}C years BP.

The S1 sapropel in the Mediterranean Sea is well dated. Therefore, only one sample was dated to verify that the sapropel was an S1. This date is also given as uncorrected ^{14}C years BP.

4 Summary of papers

Paper I

This study is primarily focused on evaluating the role of anoxia and phosphorus retention in sediments and on the occurrence of past cyanobacterial blooms. The paper corroborates that the first occurrence of cyanobacterial pigment in Baltic Sea sediments date back to the early Litorina period (Bianchi *et al.* 2000), which clearly implies that cyanobacterial blooms are not solely the result of human impact. This study of a sediment core from the Bornholm Basin also investigated the reasons behind the increase of cyanobacteria during the Litorina Sea. The ability for many cyanobacteria species, among them some of today's common species e.g. *Nodularia* and *Aphanizomenon* to utilise atmospheric nitrogen

(N₂) makes them competitive at times of low nitrogen concentrations in the water. Therefore, they are probably more affected by the supply of P, and a low N/P-ratio in the water mass is often favourable for cyanobacteria (van Geel *et al.* 1996, Bürgi and Stadelmann 2002, Falcón *et al.* 2002). The intrusion of oceanic water with high P concentrations compared to the freshwater Ancylus Lake was probably a crucial factor for the increase in primary production seen as increased organic carbon concentrations in sediments beginning at the Ancylus/Litorina (A/L) transition. Cyanobacteria most likely adapted well in the early Litorina Sea phytoplankton community, maybe as a result of the low N/P ratio. This can be seen in the zeaxanthin to β,β -carotene ratio used as a measure of the amount of cyanobacteria of the total phytoplankton biomass, which has its highest value in the lowest part of the Litorina sequence (Bianchi *et al.* 2000). It is further supported by low $\delta^{15}\text{N}$ values (see Fig. 6a), indicating N-fixing cyanobacteria (Bianchi *et al.* 2000, Struck *et al.* 2000). The dysoxic to anoxic bottom conditions during the Litorina Sea may have resulted in reduction of the sediments. Phosphate is known to be released from reduced sediments (e.g. Holm 1978). Bianchi *et al.* (2000) found a small increase in total P in the Litorina sediments, which was mainly due to increasing organic P. Inorganic P generally had its lowest concentrations in these sequences. The low concentration of inorganic P is suggested to be due to release of ferric iron-bound P from the anoxic sediments of the Litorina Sea, which in turn could help trigger cyanobacterial blooms. Ruttenberg (1992) defines this Fe-bound P as reactive Fe minerals (ferrihydrite, goethite, lepidocrocite and hematite) with absorbed or coprecipitated P. However, vivianite ($\text{Fe}_3(\text{PO}_4)_2 \times (\text{H}_2\text{O})_8$) is a phosphate mineral found in reduced Baltic Sea sediments (Hallberg pers. comm.). Hence, some phosphate can bind to iron in sediments even during anoxic conditions.

No evidence was found to verify that Fe-bound P contributed or triggered the initial growth of cyanobacteria in the Baltic around 8000 ¹⁴C BP as Fe-bound P increases instead of decreases in the sediment during this period. This increase may reflect the overall increase in phosphorus in the Litorina Sea, as it can be retained in the sediment due to incomplete equilibrium reactions at the sediment-water interface. Exposure to oxygen during subsampling and analytical errors might be some of the reasons for the high Fe-bound P results. The anaerobic Fe-bound phosphorus pool could have been altered, and hence it gives misleading P concentrations (Kersten and Förstner 1987). It could also be that the Bornholm

Basin was not the ideal sampling station for such a study, as Andrén *et al.* (2000b) argued that its bottom waters were oxic after the Ancylus/Litorina transition.

Paper II

A high-resolution pigment and isotope study of the Ancylus/Litorina transition in a sediment core from the eastern Gotland Basin investigates the role of cyanobacteria in the formation of the Baltic Sea sapropel. The focus is to determine how these organic-rich sediments were formed, and this article primarily evaluates the role of primary production. The increased carbon content in Litorina Sea sediments can be the result of increased biomass, enhanced preservation of organic carbon in the low-oxygen environment of the Litorina Sea, or most likely a combination of both. The presence of zeaxanthin strengthens the idea that increased primary production contributed to the high concentrations of organic carbon in the early Litorina sediments. Because the bottom waters most likely were poor in oxygen during the Litorina Sea stage this would have enhanced the preservation of the organic carbon. Zeaxanthin is, however, a stable pigment, which most likely should persist even under oxygenated conditions (Bianchi *et al.* 2000). Its virtual absence in Ancylus Lake sediments is more likely the result of an absence or little input, rather than of more efficient degradation pathways during oxygenated conditions. As cyanobacteria are known to flourish in eutrophic waters (Züllig 1981, van Geel *et al.* 1996, Codd 2000, Pitois *et al.* 2001), they can be used as indicators of increased primary production. This information cannot be obtained when using only organic carbon as proxy for increased primary productivity, because it can also reflect the preservation status of the organic matter.

The study further corroborates the hypothesis that cyanobacteria in early Litorina Sea were nitrogen-fixers, as the low $\delta^{15}\text{N}$ -values correlate well with increasing zeaxanthin concentrations (see Fig. 6b). Cyanobacteria could have acted as a trigger for eutrophication during the Litorina Sea stage of the Baltic Sea by fixing nitrogen. This is also supported by high zeaxanthin concentrations seen prior to sharp increases in carbon.

Paper III

This paper is a high-resolution pigment and isotope study of the Holocene sapropel S1 from the eastern Mediterranean Sea. Comparisons are also made with the Baltic Sea sapropel. Focus is set on evaluating

the role of increased primary production by studying several phytoplankton pigments. To my best knowledge, there are no reports on pigments in S1. Stable carbon and nitrogen isotopes were analysed to evaluate nitrogen fixation by cyanobacteria and terrestrial input of vascular plant material.

Cyanobacterial pigments demonstrate that cyanobacteria were part of the phytoplankton community in the Mediterranean Sea during the formation of sapropel S1. The pigment concentrations in S1 are slightly higher than previously published data for recent surface sediments from the eastern Mediterranean Sea (Bianchi *et al.* 1996). Because pigments to some extent break down during sedimentation and diagenesis, this implies that during the formation of S1, cyanobacteria were present in larger numbers than today. Since cyanobacterial growth is favoured at low N/P-ratios, this indicates that the N/P-ratio in the Mediterranean Sea was probably lower at the time of the formation of S1 than it is today. This is further supported by earlier studies demonstrating higher phosphorus concentrations during the formation of S1 (Saramiento *et al.* 1988, Slomp *et al.* 2002).

The presence of several phytoplankton pigments in S1 further corroborate that the eastern Mediterranean Sea was nutrient-rich and underwent increased primary production at the time of S1 formation. This is also supported by the total absence of pigments below and above the sapropel, as well as in the light coloured, nutrient-poor section in the middle. The lack of pigments in the middle section indicates a temporary decrease in primary productivity.

Similar to the Baltic Sea, cyanobacteria most likely increased eutrophication by fixation of atmospheric nitrogen. This is supported by the simultaneous decreasing $\delta^{15}\text{N}$ and increasing N concentrations after the initial preservation of cyanobacterial pigments (see Fig. 6c). Other processes such as isotope fractionation during nitrate uptake can also contribute to the low $\delta^{15}\text{N}$ values. Nitrogen fixation is, however, probably the only process that can account for such low values, down to 1.5‰ in the sapropel sequence. This lowering of $\delta^{15}\text{N}$ values is also found in the Baltic Sea sapropel sediments containing cyanobacterial pigments (Bianchi *et al.* 2000, Westman *et al.* 2003, Borgendahl and Westman in press (Paper II)).

The release of dissolved nitrogen from cyanobacteria could have increased the N/P-ratio in the photic zone and further stimulated primary production at the time of sapropel formation. The increases in pigments from green algae, cryptophytes, and the overall increase in organic C, which occur shortly after cyanobacterial pigments are detected, support

this assertion.

Paper IV

This is a high-resolution study of the bacterial pigment isorenieratene and stable sulphur isotopes, primarily investigating the initialization of sapropel conditions in the protosapropel and S1a. The boundary between S1a and the discontinuity has been slightly adjusted downwards compared to Paper III, due to geochemical parameters. The very stable di-aromatic carotenoid isorenieratene is a marker for the brown strain of green sulphur bacteria, *Chlorobiaceae*. These bacteria are both anaerobic and photolithotropic and live at the redoxcline where they perform anoxygenic photosynthesis, which requires sulphide and light. The presence of isorenieratene hence indicates that sulphide-containing bottom water has reached the photic zone (Repeta 1993, Kenig *et al.* 1995, Sinninghe Damsté *et al.* 1995, Menzel *et al.* 2002).

The presence of isorenieratene in sapropel S1 indicate photic zone anoxia at the time of sapropel formation. The presence of isorenieratene suggests a stratified water column, where increased organic matter flux to the bottom resulted in oxygen deficiency and reducing conditions, that lead to release of fertilizing compounds such as P, which can be brought to the photic zone by upwelling. Additional input of nutrients will in turn result in further enhancement of primary production and anoxic or euxinic bottom water conditions that gradually expand upwards in the water column. Because anoxic water conditions are known to improve preservation of organic matter (e.g. Passier *et al.* 1999, Thomson *et al.* 1999, van Mooy *et al.* 2002, Hallberg 2004), the presence of isorenieratene in S1 provides strong evidence for enhanced preservation of organic carbon as an important mechanism for sapropel formation. The presence of isorenieratene also favours an estuarine circulation during the formation of S1.

The stable sulphur isotopes show a complex pattern, which can not be explained by a direct coupling between sulphide formation and sulphate reduction. Instead of the common scenario with increasing $\delta^{34}\text{S}$ -sulphate followed by increasing $\delta^{34}\text{S}$ -sulphide as the available ^{32}S in the sulphate will decrease with time, the $\delta^{34}\text{S}$ data for S1 show a completely different pattern. A decrease $\delta^{34}\text{S}$ -sulphate is accompanied by an increase in $\delta^{34}\text{S}$ -sulphide from the beginning of the protosapropel to the middle of S1a. This can only be explained by coexistence of sulphate reducing and sulphur disproportionating bacteria together with phototrophic purple and green sulphur bacteria. The

observed low initial $\delta^{34}\text{S}$ -sulphide values (*ca.* -45%) can be explained by repetitive backward and forward fluxes of sulphur species within the SRB (sulphate reducing bacteria) cell. This is however somewhat contradicted by the $\delta^{34}\text{S}$ -sulphate data. These values (5%) are much lower than what would be expected if there was a direct coupling between sulphide formation and sulphate reduction (20%). To explain this discrepancy the presence of the phototrophic purple sulphur bacteria *Chromatiaceae* must be taken into account. These bacteria will recycle the sulphide and oxidize it to form intracellular sulphur, which in the next step is oxidized to sulphate and expelled from the cell, producing a sulphate isotopic signature lowered by *ca.* 17% (Hallberg 1985). We have no data on *Chromatiaceae* pigment, but these bacteria are known to always coexist with *Chlorobiaceae* (Sørensen 1988). *Chlorobiaceae* will oxidize sulphide to form extracellular sulphur. This elemental sulphur cannot be further oxidized by the bacterium to sulphate but can serve as a sulphur source for the sulphur disproportionating bacteria (SDB). Data on the fractionation for sulphide during the reduction of elemental sulphur by SDB is reported to be 4% to 9% (Canfield and Thamdrup 1994, Habicht and Canfield 1997, Canfield *et al.* 1998, Böttcher *et al.* 2001), which can explain the high apparent fractionation between sulphate and sulphide. The positive excursion of the $\delta^{34}\text{S}$ -sulphide can be explained by a mixture of the sulphides created by SDB in the water column and upward diffusion of sulphides from the sediment. The sulphides formed in the water column will have an isotopic signal close to -41.5% (Fry *et al.* 1991). These will mix with light $\delta^{34}\text{S}$ -sulphide diffusing from the sediment to form the observed positive trend of the $\delta^{34}\text{S}$ -sulphide. With time, the diffusion of hydrogen sulphide from the sediment will probably becoming less pronounced due to sedimentary growth and increased sulphide concentrations in the water column, restricting the diffusion. This will lead to increasing influence of $\delta^{34}\text{S}$ -sulphide from the water column, and hence increasing $\delta^{34}\text{S}$ -sulphide values. The upper part of S1 exhibits increasing $\delta^{34}\text{S}$ -sulphate data and decreasing $\delta^{34}\text{S}$ -sulphide data, which is interpreted as a progressive intrusion of oxic seawater sulphate.

Two metals (Zn and Mn) have been chosen as proxies of sapropel formation. Zn in contrast to Mn is not a redox sensitive element and therefore its concentrations merely reflect the overall mobilization and accumulation of trace metals. A ratio, $\text{Mn}/10 \cdot \text{Zn}$, mirrors the sapropel formation to a rather high degree. It decreases very sharply from 2.2 at the beginning of the protosapropel to 0.9 at

the beginning of the sapropel. The metal ratio then stays between 1 and 0.8 during the “true” sapropel formation.

5 Discussion

The use of certain carotenoid pigments together with stable isotopes, carbon, nitrogen and metals provide a good picture of the paleoenvironment at the time of sapropel formation. A comparison of sapropel sediments in two semi-enclosed seas also brings a broader understanding to how sapropels are formed.

Increased primary productivity is supported by increases of several phytoplankton pigments in sapropel sediments (Paper I-III), especially presence of the pigment markers for cyanobacteria i.e. zeaxanthin, myxoxanthophyll and echinenone. These pigments often appear very early in the sapropels (Fig. 6a-c), which indicates that cyanobacteria adapt rather fast to more nutrient-rich conditions (Paper I and II). Cyanobacteria are favored by low N/P-ratios, and during the formation of both S1 and the Baltic Sea sapropel sediments, P concentration was probably high (Paper I-III). In the Baltic Sea, the N/P-ratio in the sediment increased from around 4 to *ca.* 6 after the *Ancylus/Litorina* transition (Paper I) but it was still below the Redfield weight ratio (*ca.* 7). This increase is probably because of the increase in N and P after the transition, and may reflect a less efficient retention of P in sediments. P should instead be released to the water column due to the reducing conditions. The N/P-ratio in the water was probably lowered during the *Litorina* Sea. The general increase in sedimentary P probably reflects the inflow of phosphorus-rich water from the North Sea. This effect is most likely more pronounced than the expected release of Fe-bound P from the sediments (Paper I). The lowering of $\delta^{15}\text{N}$ contemporary with increasing cyanobacterial pigments (Fig. 6) suggests cyanobacterial fixation of atmospheric nitrogen (Paper I-III). In sapropel sediments, $\delta^{15}\text{N}$ is usually lower than the surrounding sediments. These very low values (0 to 2%) are probably the result of nitrogen fixation (Rau *et al.* 1987, Bianchi *et al.* 2000, Struck *et al.* 2001, Kuypers *et al.* 2004). Assimilation of nitrogen can also contribute to the low $\delta^{15}\text{N}$ values if nitrogen is abundant, but generally will fractionation during assimilation yield a $\delta^{15}\text{N}$ signal around 5% (Francois *et al.* 1992). Nitrogen fixation has been shown to make up a considerable part of the input of nitrogen (Larsson *et al.* 1985, Howarth *et al.* 1988, Glibert and Bronk 1994, Larsson *et al.* 2001, Wasmund *et al.* 2001, Struck *et al.* 2004, Voss *et al.* 2005). This is indicated by the simultaneous decrease of $\delta^{15}\text{N}$

and increase in N concentrations (Paper I-III). The release of dissolved N from cyanobacteria could further have stimulated primary production at the time of sapropel formation as indicated by the increase in pigments from green algae and cryptophytes, and

the overall increase in organic C, which are slightly delayed compared to cyanobacterial pigments (Paper I-III).

High sedimentary $\delta^{13}\text{C}$ can be indicative of increased primary production (Arthur *et al.* 1988,

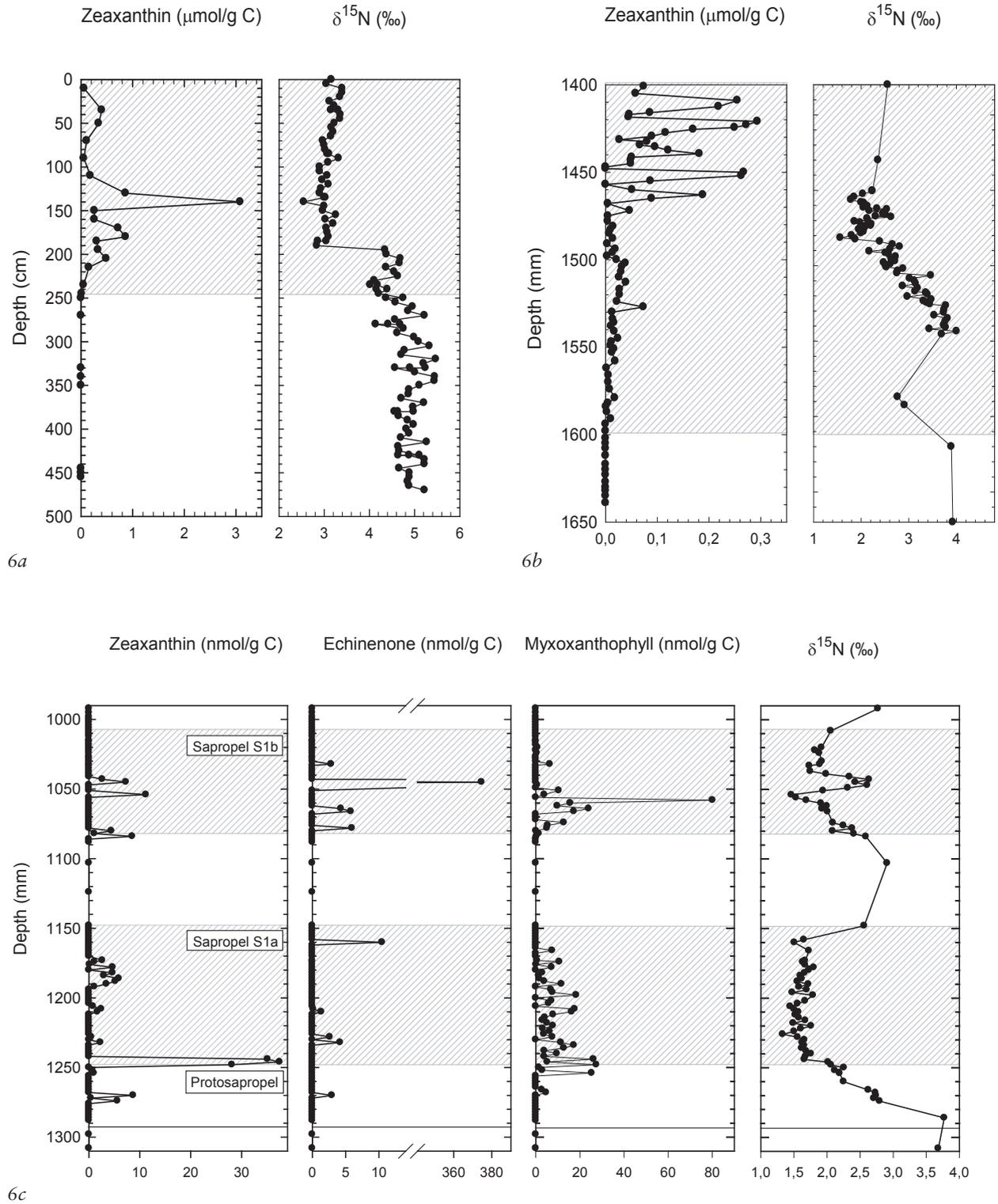


Fig. 6: Cyanobacterial pigments and $\delta^{15}\text{N}$ -values for three sediment cores from the Baltic Sea (a: BB9906 and b: GD0101) and the Mediterranean Sea (c: ADE3-48). Sapropel sediments are shaded.

Hodell and Schelske 1998, Brenner *et al.* 1999, Struck *et al.* 2000), and in sapropel S1, $\delta^{13}\text{C}$ is higher compared to the adjacent sediments (Paper III). In Baltic Sea sapropel sediments, $\delta^{13}\text{C}$ also increases, but this has been interpreted as a change to more saline water or increased input of terrestrial material (Paper I and II). In S1, the C/N-ratio shows no signs of input of terrestrial material (Paper III). Preliminary lignin analysis on this core also indicated very little terrestrial material in S1 at this location (Bianchi *et al.* unpublished results).

The presence of isorenieratene in S1 indicate that euxinic water reached the photic zone during sapropel formation (Paper IV). This suggests that the preservation of organic matter was enhanced during sapropel formation, contributing to the high organic carbon content. Hence, both increased primary production and enhanced preservation of organic carbon are important mechanisms for sapropel formation. Two metals (Zn and Mn), have been used as proxies of sapropel formation. The ratio Mn/10·Zn, mirrors the sapropel formation to a rather high degree.

The appearance of isorenieratene as early as in the protosapropel points toward conditions that responded very rapidly to a change in primary productivity (Paper IV). An anti-estuarine circulation with oxygenated bottom waters would, even if it was weakened, not develop photic zone euxinia with the small increase in primary productivity that probably was the case during the S1 protosapropel formation (C_{org} 1.5%). Pliocene-Pleistocene sapropels with high organic carbon content have been suggested to have been formed during an estuarine circulation (Sarmiento *et al.* 1988, Thunell and Williams 1989). Sapropels with relatively low organic carbon content, e.g. S1, have instead been connected to a weakened anti-estuarine circulation (Rohling and Gieskes 1989, Rohling 1994). Circulation models performed by Stratford *et al.* (2000), suggested that a weakened anti-estuarine circulation is sufficient to provide deposition of enough carbon to form a sapropel with organic carbon content between ca. 2-4%, like the S1. A weakened anti-estuarine circulation would however not result in anoxia in the water column above 500 m depth, in contrast to an estuarine circulation which would result in anoxic or euxinic near-surface waters. The presence of isorenieratene hence favours an estuarine circulation also during the formation of S1.

An oxygen minimum zone can develop in the mid water beneath the photic zone due to the degradation of the flux of organic matter sinking to the bottom. In an anti-estuarine circulation this oxygen depleted water would spread downwards in the water

column as the driving mechanism is the downward flux of organic matter (Sinninghe Damsté and Köster 1998). Even a weakened deep water circulation will, however, supply new oxygen to the bottom water, which promotes oxic degradation of organic matter. This will most likely mean that for photic zone euxinia to develop, a very large increase of primary productivity would probably be needed as euxinic conditions are prevented if there still is oxygen available in the bottom water. Photic zone anoxia can not develop in the upper part of the water column, as the transformation from SO_4^{2-} to H_2S requires the presence of Sulphate Reducing Bacteria (SBR), which are present only at the bottoms (Deuser 1970). In an estuarine circulation scenario, the water column is stratified, bottom water circulation has ceased, and oxygen is gradually depleted in the bottom water due to breakdown of organic matter from the photic zone. If primary production would increase, as during sapropel formation, the increased flux of organic matter would rapidly enhance oxygen depletion. This results in reducing bottom water conditions and anoxic water that gradually rises in the water column.

The stable sulphur isotopes show a complex pattern, which can be explained by the coexistence of sulphate reducing and sulphur disproportionating bacteria together with phototrophic purple (*Chromatiaceae*) and green (*Chlorobiaceae*) sulphur bacteria. The low initial $\delta^{34}\text{S}$ -sulphide values can be explained by repetitive backward and forward fluxes of sulphur species within the SRB (sulphate reducing bacteria) cell. The initial $\delta^{34}\text{S}$ -sulphate values are also very low, which can be explained by recycling of sulphide by *Chromatiaceae* (Hallberg 1985). These bacteria will oxidize the sulphide stepwise to form sulphate with a depleted isotopic signature, which is expelled from the cell. *Chlorobiaceae* will oxidize sulphide to form extracellular elemental sulphur. This isotopically depleted elemental sulphur can serve as a sulphur source for the sulphur disproportionating bacteria (SDB) (Canfield and Thamdrup 1994, Habicht and Canfield 1997, Canfield *et al.* 1998). The positive excursion of the $\delta^{34}\text{S}$ -sulphide can be explained by a mixture of the sulphides created by SDB in the water column and upward diffusion of isotopically lighter sulphides from the sediment. The upper part of S1 exhibits increasing $\delta^{34}\text{S}$ -sulphate data and decreasing $\delta^{34}\text{S}$ -sulphide data, interpreted as a progressive intrusion of ordinary seawater sulphate.

6 Conclusions

Sapropels are formed as a result of increased primary production and anoxic or euxinic bottom waters.

Cyanobacteria were an important part of the phytoplankton community in the Baltic Sea during post-glacial sapropel formation and in the Mediterranean Sea during the formation of sapropel S1.

The N/P-ratio in the photic zone in the Mediterranean Sea at the time of S1 formation and in the Baltic Sea during postglacial sapropel formation was probably below the Redfield weight ratio (*ca.* 7), because cyanobacterial growth is promoted by low N/P-ratios.

In the Baltic Sea and the Mediterranean Sea, $\delta^{15}\text{N}$ decreases from *ca.* 3 to 5‰ in sediments beneath sapropels to *ca.* 1 to 2.5‰ in the sapropel, indicating input of atmospheric nitrogen. This decrease coincides with the appearance of cyanobacterial pigments, which also indicates that these cyanobacteria were most likely nitrogen-fixers.

In the sapropels, concurrent decrease of $\delta^{15}\text{N}$ and increase of N concentration indicates cyanobacterial import of atmospheric N. The release of dissolved N from cyanobacteria could have increased the N/P-ratio in the photic zone and further increased eutrophication and stimulated primary productivity at the time of sapropel formation. This is indicated by the increases in pigments from green algae and cryptophytes and the overall increase in organic C, which occur slightly after the appearance of cyanobacterial pigments.

The presence of isorenieratene show that photic zone anoxia prevailed during the formation of S1. This indicates that enhanced preservation of organic carbon is an important mechanism for sapropel formation.

Photic zone anoxia favours a scenario with a reversal of the water circulation during the formation of S1. An estuarine circulation with a stratified water column and following gradual oxygen depletion in the bottom water is a sensitive system, which will respond quickly to increased primary production. That photic zone euxinia developed as early as during the S1 protosapropel is indicative of such an environment.

The stable sulphur isotopes in S1 show a complex pattern, which can be explained by the coexistence of sulphate reducing and sulphur disproportionating bacteria together with phototrophic purple (*Chromatiaceae*) and green (*Chlorobiaceae*) sulphur bacteria.

The observed low initial $\delta^{34}\text{S}$ -sulphide values (*ca.* -45‰) can be explained by repetitive backward and forward fluxes of sulphur species within the SRB cell.

The initial $\delta^{34}\text{S}$ -sulphate values (-5‰) are probably the result of recycling of sulphur by *Chromatiaceae*.

The increase in $\delta^{34}\text{S}$ -sulphate and decrease $\delta^{34}\text{S}$ -sulphide in the upper part of the sapropel is interpreted as a progressive intrusion of ordinary seawater sulphate.

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