Available online http:/amq.aiqua.it
ISSN (print): 2279-7327, ISSN (online): 2279-7335

Alpine and Mediterranean Quaternary, 25 (2), 2012, 81-89

MEDITERRANEAN SAPROPELS: A MERE GEOLOGICAL PROBLEM OR A RESOURCE FOR THE STUDY OF A CHANGING PLANET?

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ABSTRACT: Sapropels are sediments rich in organic carbon occurring cyclically in the Mediterranean marine records and whose origin has been matter of great debate during the last decades. While the first sapropels were found in eastern Mediterranean sediments from the Miocene period, in this paper we focus on the layers that were subsequently found in sediment cores of Pliocene to Quaternary age from the eastern Mediterranean mostly. Since the very beginning of the history of studies on sapropels, authors inferred that those levels, being interbedded as dark layers in more or less normal light "open marine" sediments, formed during short-lived but catastrophic alterations in Mediterranean oceanographic conditions, probably linked to broader climate changes. In this paper, the main hypotheses regarding the origin of those sediments are described and we highlight the importance of sapropel records for the study of climatic and oceanographic variability in the Mediterranean area in the context of global climate change.

Keywords: Mediterranean Sea, Plio-Pleistocene, Sapropel, Paleoclimate.

1. INTRODUCTION

More than 477 papers have been published in the last 40 years with the keywords 'Mediterranean sapropels'. Publication frequency is plotted in Fig. 1. The number of papers published over this time interval is highly fluctuating, and this evidences periods of high interest and moments of decline in the attention to the topic.

In this paper, we will recall the main approaches to the sapropel issue and we will propose new challenges in the study of these objects that must be seen not only as a local geological problem, but as a resource for the understanding of our changing planet.

2. THE HISTORICAL RECORD

The occurrence of stagnation episodes in the Mediterranean basins during Quaternary was first predicted by Bradley (1938), who proposed that sapropels were due to low sea level in the glacial Mediterranean. Though, no marine sedimentary evidence was available at that time to strengthen his hypothesis. Later on, Kullenberg (1952) discussed the problem of sapropel formation as related to interstitial salinity variations using the cores of the Swedish Deep Sea Expedition (1948). Few years later, Olausson (1961) argued that Sapropels were deposited after cold periods of glacially lowered sea level (about 100 meters lower than at present); during these periods, communication between the western and eastern Mediterranean became restricted through the straits of Sicily, resulting in an increase of salinity in the eastern basins, notwithstanding the (eventual) increase in runoff and precipitation. At the same time, surface water temperature decreased by about four degrees centigrade, increasing the density of surface water and leading to a continual renewal of the bottom water mass (e.g. non-sapropel condition). During deglaciation, temperature and sea level rose, then water density tended to decrease near the surface, as a result of less saline water added from the Atlantic through the western Mediterranean. As this transgression persisted, sea level eventually reached the elevation of the sill at the Bosporus (40 m), causing low-density water from the Black Sea to pour out into the Aegean, further lowering the density of surface water of the eastern Mediterranean. Then, the combination of warm, low-density superficial water led to density stratification and to stagnation of bottom water and sapropel formation.

This model has been subsequently variously discussed by several authors (e.g Chamley, 1971; Miller, 1972; Ryan, 1972; Nesteroff, 1973; McCoy, 1974; Cita et al., 1973). However, Olausson's classic glacio-eustatic model was not sufficient to explain all aspects of sapropel formation.

During DSDP Legs 13 and 42A (Ryan et al., 1973; Hsu et al., 1978) in the Mediterranean Sea, many sapropels were obtained from deep sea cores and stimulated researchers to find explanations for their origin. Sigl et al. (1978) suggested that differing faunal and lithological characteristics within sapropelic layers of different ages were indicative of different mechanisms of sapropel formation. Since according to Brongersma-Sanders (1957) bituminous rocks may be formed when "either the supply of oxygen to the lower water layers is excessively low (persistent stagnation), or the supply of dead plankton and other oxidizable material is extremely high (hypertrophy)", Sigl et al.1978 proposed that both mechanisms could have helped to explain the occurrence of

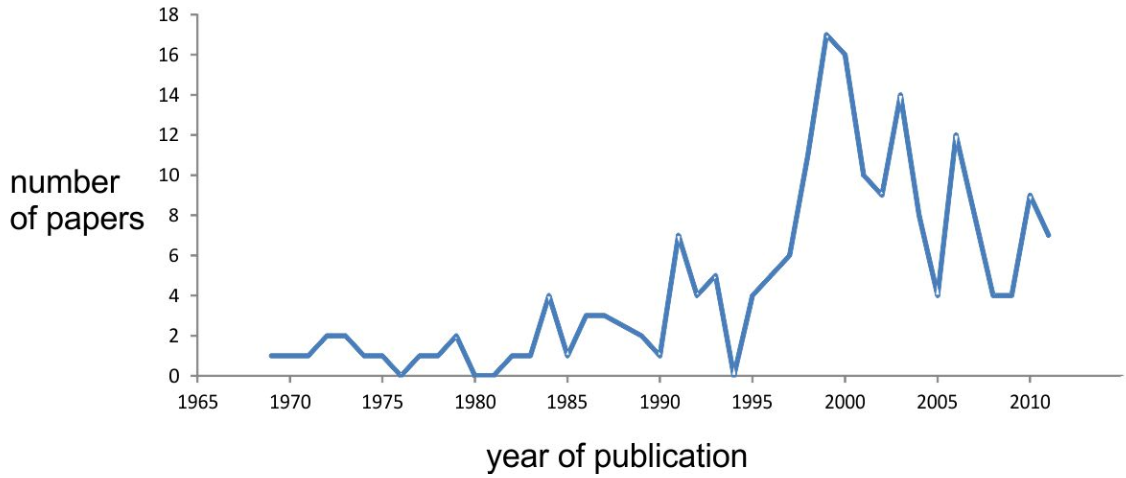

Fig. 1 - Papers published in the last 40 years having the word ‘sapropel’ in the title.

sapropelic sediments in “preglacial” lower Pleistocene and upper Pliocene sediments recovered by DSDP Leg 13 (Ryan et al., 1973; Cita et al., 1973), as well as others in Miocene cores recovered by Leg 42A (Hsu et al., 1978). During the same DSDP Leg 42A, the discovery of sapropelic sediments in the western Mediterranean (Kidd et al., 1978) proved that this phenomenon was not entirely restricted to the eastern basin as it was assumed at that time, therefore stimulating new hypothesis about the mechanisms of sapropel formation.

From that time on, two main models, encompassing the earlier hypotheses, were proposed to explain sapropel deposition: the “stagnation/anoxia” and the “increased productivity” models.

According to the stagnation/anoxia model, anoxic bottom conditions are caused by a strong stratification of the water column that prevents vertical mixing and oxygen supply to the bottom waters. The origin of this stratification was explained as being due to increased Nile river runoff linked to the periodic intensification of the African-Asian monsoons (Rossignol-Strick 1983, 1985) and, later, by increased rainfalls and river discharge along the northern part of the Eastern Mediterranean Sea (Cramp et al., 1988; Rohling & Hilgen, 1991). In this framework, Sarmiento et al. (1988) proposed a reversal in the water flow circulation as the most effective way of increasing nutrient concentrations to the point where anoxia occurs. Indeed, numerical studies on thermohaline circulation suggest that a weakening of the present-day anti-estuarine circulation can lead to the deposition of enough organic carbon to account, at least, for the formation of the youngest sapropels S5 (125 ka) to S1 (9 ka) (Myers et al., 2000; Stratford et al., 2000). In addition, more recently, Bianchi et al. (2006) suggested that a weak thermohaline circulation, supplying oxygen only to the first 500 meters of the water column can cause the development of an anoxic blanket at the seafloor, when coupled with increased productivity in the euphotic zone.

In the “increased productivity” model, sapropel deposition was linked to enhanced organic matter flux (Calvert, 1983; Calvert et al., 1992), since the present production of organic matter in the Eastern Mediterranean cannot account for the high values of organic carbon (TOC) characterizing these layers (Calvert, 1983). This view has been further supported by evidence of a significant increase of productivity at times of sapropel deposition revealed by paleo-productivity proxies, as barium and marine barite concentration (e.g., Thomson et al., 1995, 1999; Martinez-Ruiz et al., 2000, 2003; Gallego-Torres et al., 2007).

Later on, after the pioneer phase when the scientific community argued that the above mentioned processes were mutually exclusive, another phase followed when some authors (Rohling & Gieskes, 1989, Castradori, 1993; Rohling, 1994; Emeis et al., 1996; Emeis et al., 2000a) proposed a mechanism resulting from the combination of the two processes: stratification and productivity increase could have been caused by an overall increase of nutrient input via river runoff. However, uncertainties still exist regarding the vertical extension of the anoxic/dysoxic layer in the water column and this layer has been described either as a large water mass extending below the mixed layer (Murat & Got, 2000; Stratford et al., 2000), or as an “anoxic blanket” above the sediment/water interface (Casford et al., 2003).

Regarding the increase of productivity several hypothesis have been proposed, the most intriguing being that of Kemp et al. (1999) who infer the formation of diatom mats during summer seasons of prolonged stratification (resulting from a water density contrast produced by Nile run-off). The rapid sinking of the mats at the beginning of autumn–winter wind mixing, then, is assumed to produce a massive load of organic material to the sediments that consumed the available oxygen in the water column, creating anoxic conditions. From mass-balance calculations, they argue that all of the organic carbon preserved in sapropels could have been supplied by diatoms. Although the model can apply only to sapropels containing diatoms, the authors pointed out that the silica of these diatoms is highly soluble, and therefore that sapropels lacking diatoms may have once had them.

On this basis, Sancetta (1999) argued that the mechanism invoked for modern sapropels might therefore apply, as analogues, to other carbon-rich laminated strata, such as the 120-100 million year old mid-Cretaceous black shales. A more refined hypothesis was proposed by Meyers (2006) who suggested that increased continental run-off would have delivered abundant nutri-

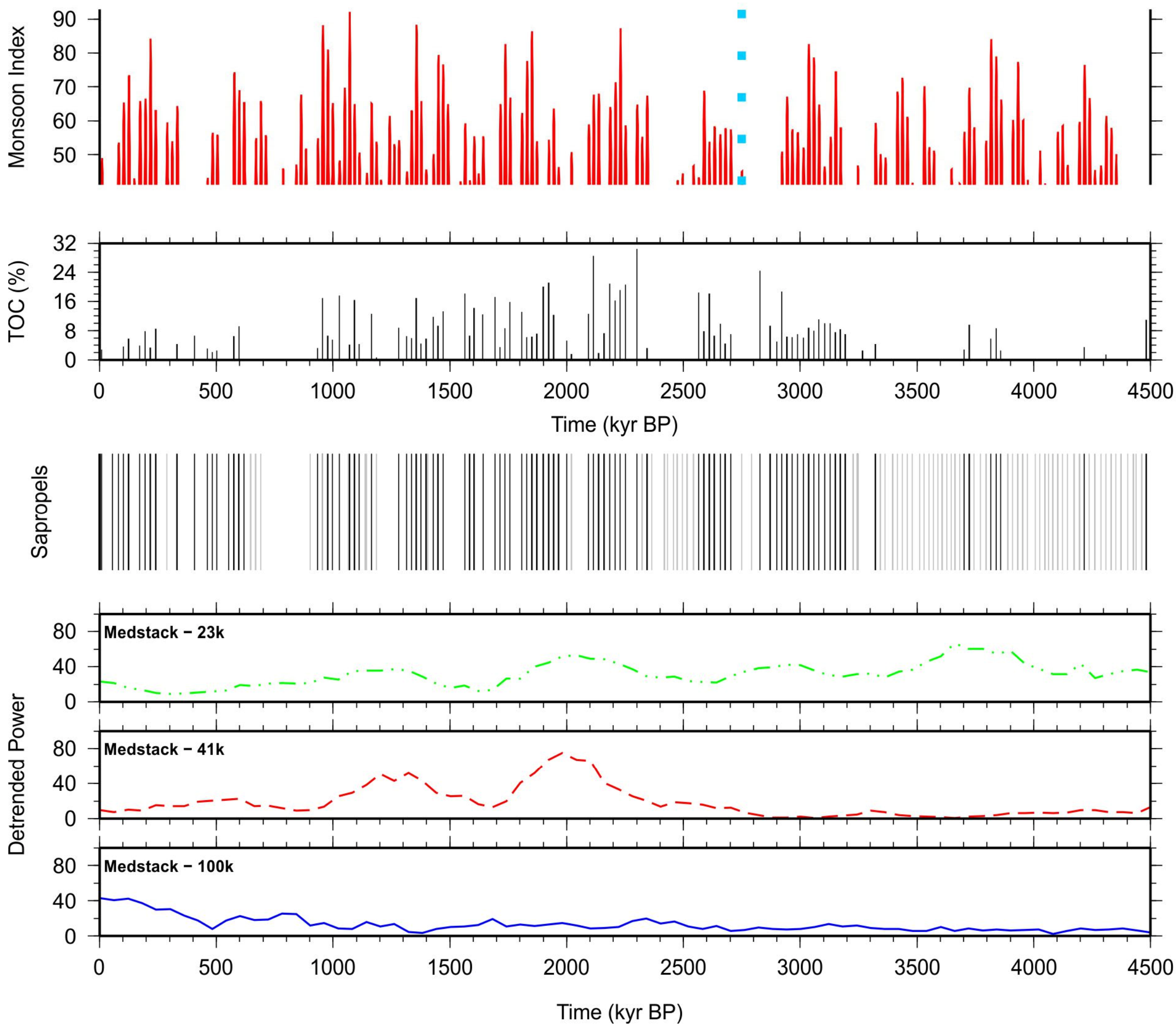

Fig. 2 - From bottom to top: Medstack detrended power in the 23k, 41k and 100k band (Colleoni et al., 2012); Sapropels (black, organic content > 2%) and grey layers succession from Emeis et al. (2000) and Lourens et al. (1996); Total Organic Content (TOC, %) of the black sapropels from the succession described above. The TOC values are from ODP 964, OPD 966, ODP 967 and ODP 969. When different TOC values were found in several cores for the same sapropel layer, the larger TOC value was selected in order to better highlight the response of the Mediterranean to the climate forcing. Some of the black sapropels from Lourens et al. (1996) does not have any TOC value assigned because no analysis have been found. African monsoon index (in Langley) based on Rossignol-Strick (1983). The vertical dotted line corresponds to the intensification of the Northern Hemisphere Glaciation (~2.75 Ma).

ents that would have first stimulated algal productivity, magnified export of organic matter, and increased mid water oxygen demand. The combination of surface water dilution, which increased salinity stratification of the upper water column and thereby discouraged mixing and mid-water ventilation, and magnified oxygen-drawdown, would have intensified and expanded the oxygen minimum zone such that anoxia intruded into the photic zone. After photosynthetic cyanobacteria, green sulfur bacteria and chemosynthetic archaea became established, their primary productivity would have first augmented and then potentially would have superseded that of algae (e.g., Kuypers et al., 2001; 2002 a,b). The shift to microbe-amplified productivity would have persisted until climate reverted to less wet conditions.

Sapropels occur all over the Mediterranean area recorded after ODP legs 160 and 161 (Emeis et al., 1996; Comas et al., 1996), which yielded the complete record of all the sapropels occurring in the last 5 million years, but they also outcrop on land sections (mainly in Greece and Italy). However, Sprovieri et al. (2012), who investigated mechanisms of sapropel deposition in the Mediterranean basin during the last 3.5 Ma, showed that the water properties and circulation of both eastern and western Mediterranean Sea during the Plio/Pleistocene appear to be conditioned by the bathymetric control at the Gibraltar and the Sicilian sills. According to these authors, climatically driven intensity and characteristics of the Western Mediterranean Deep Water formation drive timings and modes of deposition of the organic-rich layers in the Alboran Sea (ODP Sites 976 and 977). Indeed, they claim that western sapropel deposition is generally not synchronous to precession minima, contrary to sapropel deposition in the Eastern Mediterranean, and is largely related to the formation and vertical shift of oxygen minimum zones probably due to the rapid rise of the Sicilian sill in the last 2 Ma. Therefore, sapropels occur cyclically, but not in phase, in the eastern and western basin.

This hypothesis agrees with that proposed by Rogerson et al. (2008) who demonstrated the older age (4-5 ky) of the most recent Organic rich layers (ORL) occurring in the western Mediterranean, and hypothesized that it might be instead related more to the global sea level changes and resulted from a strong reduction in surface water density and shoaling of the interface between the Intermediate and Deep Waters during the deglaciations.

We can therefore see the deposition of Eastern Mediterranean sapropels in a framework of a reversed circulation. In fact, the present day circulation between the Mediterranean Sea and the Atlantic Ocean depend on the fact that evaporation exceeds precipitation. This way Atlantic surface water, less saline and hence less dense, flows into the Mediterranean. Conversely, Mediterranean salty waters flow at intermediate deep out of the basin. This type of circulation pattern is often referred to as anti-estuarine and is the opposite to the Black Sea circulation where fresh surface water flow out of the Black Sea to the Mediterranean Sea and salty Mediterranean Sea water flows through the Bosphrous into the Black Sea. Then, the Black Sea acts as a nutrient trap and is anoxic.

In this view, Trabucho-Alexandre et al. (2012), argued that oceanic basins at the senile stadium of the Wilson cycle (i.e. the cycle of opening and closing of an ocean basin due to plate tectonics) as presently the Mediterranean is, can respond with black shales (sapropels) only if the circulation is estuarine, like in the Black Sea. Then, the combination of Sprovieri (2012) results and Trabucho-Alexandre (2012) hypothesis suggest that the Eastern basin could be seen as a restricted basin due to the Sicilian sill that hampers the flow of the Levantine Intermediate Water and turns the eastern basin in a euxinic environment at the time of sapropel deposition. This somehow agrees with the hypothesis postulated by Sarmiento et al. (1988), but overall, it suggests that, at least for the past 2 Ma, Western Mediterranean ORL and Eastern Mediterranean Sapropels respond to different triggering mechanisms. This means that whatever is the mechanism triggering the sapropel deposition, those objects represent an important record to be studied in detail not only at regional scale, to understand which can be the relationship with the Global ocean dynamic processes.

3. NEW CLUES

Only few attempts have been made to link what happened in the Mediterranean region over the last 5 Myr to coeval global climate change during that time period. Sapropels or ORL need not to be seen simply as regional geological problems. Instead they are a precious source of information useful for understanding the evolution of our planet. In particular, The message contained within Eastern Mediterranean sapropels has to be interpreted in a global context: they are the consequence of extreme but episodic climate changes due to particular monsoonal and oceanic conditions that have favoured a very large production and deposition of organic carbon.

The recent paper by Colleoni et al. (2012) attempted to interpret the Mediterranean oceanic changes as seen from the Eastern Mediterranean planktonic $\delta^{18}O$ stack (hereafter Medstack, Lourens, 2004, Wang et al., 2010) in a global context. The global and Mediterranean climate changes over the last 5 Ma are compared and linked through the spectral analysis of various marine records performed over the three orbital bands (100-kyr, 41-kyr related to obliquity and, 23+19-kyr related to precession). In the Mediterranean planktonic signal, three periods were identified: until ~ 2.2 Ma the signal is dominated by the 23+19-kyr frequency which is linked to the African monsoon influence in Colleoni et al. (2012); from 2.2 Ma to ~ 1.2 Ma the signal is dominated by the 41-kyr frequency which is interpreted as the incursion of the polar influence into low latitudes; and finally, after the Mid-Pleistocene transition the signal is dominated by the 100-kyr frequency (Fig. 6 in Colleoni et al. 2012).

How do the sapropels fit in the story? The Plio-Pleistocene Eastern Mediterranean succession of organic-rich layers (Emeis et al., 2000a, Lourens et al. 1996, Fig. 2) is based on ODP sites 964, 966, 967 and 969 and on the Capo Rossello land section. This sapropel time-series is almost continuous and shows that, even if after 2.2 Ma the Medstack variability is driven by the 41-kyr frequency, the Eastern Mediterranean remains, however, paced by the African monsoon influence since the variance in the 23+19-kyr band remains strong all along the last 5 Ma. Nevertheless, some interruptions of the cyclical deposition of sapropels are observed and the longest one occurred during the so-called Middle Pleistocene Revolution (MPT) at ~0.7 Ma when the dominant frequency of the global climate variability changes from 41-kyr to 100-kyr. The interruptions are interpreted by Colleoni et al, 2012 as an intrusion of the Northern high-latitudes cooling signal into the low latitudes and therefore would have perturbed the periodic deposition of sapropels. In addition, in the first part of the Pliocene, before the Northern Hemisphere Glaciation (NHG) intensification, the occurrence of gray intervals (roughly: not well developed sapropels) suggests that the monsoon intensity was reduced during the Early Pliocene compared to the Late Pleistocene and that the monsoon was able to penetrate further into North in Africa (Larrasoana et al., 2003) only during strong precession minima.

In the sapropel succession of Fig. 2, we implemented the work of Colleoni et al. (2012) which made a distinction between black sapropels, (organic carbon > 2% in weight following the convention of Kidd et al., 1978) and grey layers showing a lower content of organic carbon. Black sapropels seem to be quite scarce until ~3.4 Ma, while after this time, grey layers (organic content < 2%) disappear almost completely (Fig. 2). This suggests that marine productivity (or organic matter preservation) increased after 3.4 Ma, this fact supported by the total carbon content (TOC) values from the black sapropels succession described previously and reported in Fig. 2. It shows that after 3.4 Ma, the TOC increased

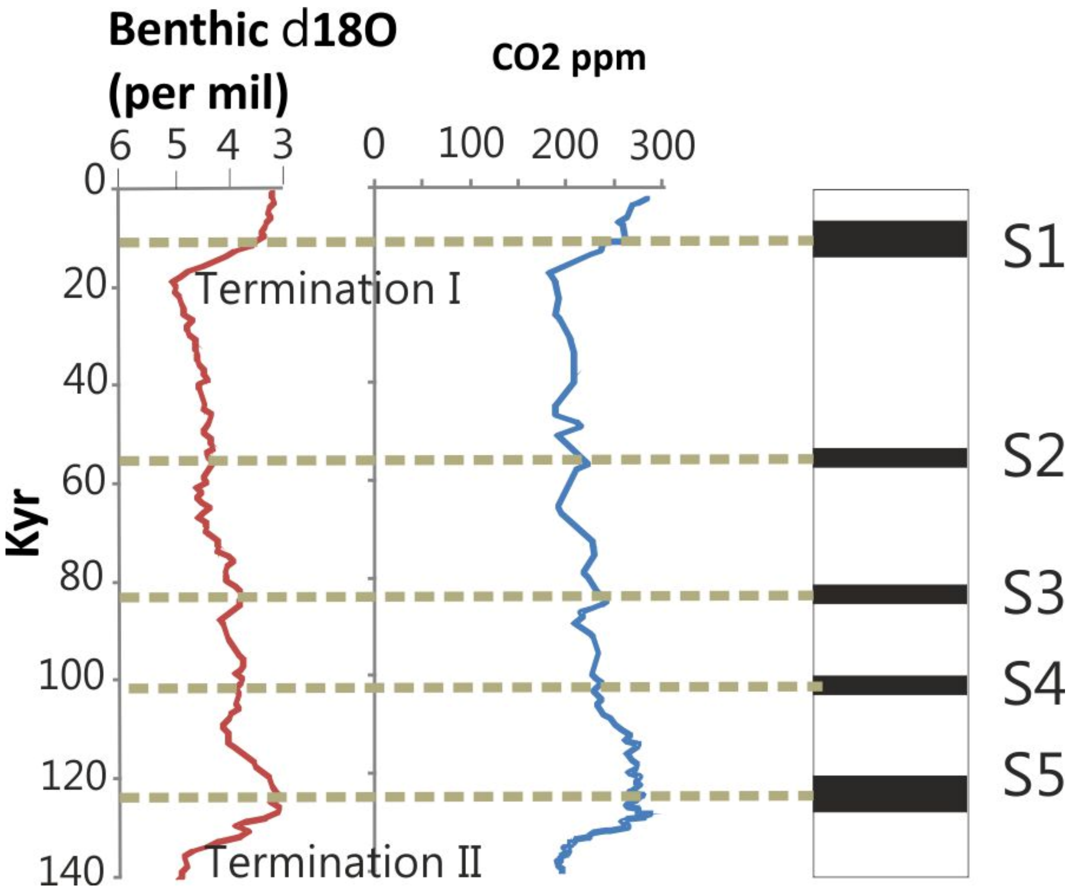

Fig. 3 - Time series of the Benthic stack Lysieki and Raymo (2005), CO2 concentration in the Vostock Ice core (Petit et al 2000) and occurrence of sapropels in the Mediterranean Sea. It is evident that the occurrence of sapropels corresponds to increases in CO2 concentration.
Thickness of sapropel does not correspond to time duration. S1 and S5 are thicker to highlight the correspondence to the sharper CO2 increase (circa 100 ppm) recorded after terminations II and I, respectively.

until reaching ~ 32% in weight during the intensification of NHG (~2.75 Ma) and then gradually decreased until present-day. What caused such a TOC increase ?

As previously described, sapropels are assumed to form under particular oceanic temperature, salinity and productivity conditions, when a significant fresh water run-off reaches the Mediterranean waters. Whatever was the cause of sapropel deposition (either anoxia or productivity), based on that information, the issue is if we can directly relate the variations in TOC to variations in continental run-off quantity and then to fluctuations in monsoon intensity alone. Rossignol-Strick (1983) tried to establish such a link by calculating an "African Monsoon Index" (Fig. 2) for the last four glacial cycles based on the summer insolation anomaly between the Equator and 23°N. They postulated that each sapropel layer corresponded to high monsoon index value (≥ 41 Ly). To check whether this hypothesis was valid also for the oldest sapropels, we expanded their calculation for the entire Plio-Pleistocene period, and we point out if each large monsoon index value is associated with a grey layer or a black sapropel (Fig. 2). Nevertheless, each sapropel or grey layer does not always correspond to a high monsoon index value as calculated by Rossignol-Strick (1983). Indeed, with this monsoon index, Rossignol-Strick (1983) assumed that a larger insolation input always triggered higher monsoon precipitation. But monsoon could be intense in terms of winds and/or precipitation. This implies that if sapropels were deposited under weak monsoon precipitation regimes, the Mediterranean oceanic conditions (temperatures, salinity, oxygen) compensated somehow for the lower (but still higher than during "non sapropel" sedimentation) fresh water input.

We can thus conclude that fluctuations in TOC suggest that (i) either the monsoon precipitation started intensifying toward 3.4 Ma and then weakened after ~2 Ma, (ii) or that since 3.4 Ma the sensitivity of the Mediterranean waters (in terms of temperature, salinity and oxygen) to sudden warm climate fluctuations increased, and then decreased after 2 Ma. This is consistent with the concomitant global climate cooling (Lisiecki and Raymo, 2005) which could have enhanced the sensitivity of the extra-tropical regions to brief and warm climate fluctuations. As a result, it is possible that this gradual global cooling increased the sensitivity of the Mediterranean waters and of the monsoon system to large insolation peaks towards the NHG (~2.75 Ma), allowing for particularly concentrated black sapropel deposition. In addition, Khelifi et al. (2009) showed that the Mediterranean outflow intensified toward ~3.4 Ma suggesting that changes in oceanic circulation occurred at this time. The relatively low value in TOC during the Pliocene could be due to the fact that the mean global climate state was warmer at this time and that consequently the monsoon intensity was almost constant and had only a limited impact on the stable Mediterranean circulation. Similarly, during the Early Pleistocene period, the mean global climate state evolved towards cooler temperatures. In that new climate context, all the system readjusted and despite the larger amplitude between glacial/interglacial periods that occurred at the end of the Quaternary, the Mediterranean became again less sensitive to the monsoon fluctuations as during the Early Pliocene period, or only during particularly warm interglacials (e.g. MIS 11 and MIS 5).

4. CONCLUDING REMARKS AND PERSPECTIVES

There is still much to do in the study of sapropels. The relationship between TOC, sapropels and the monsoon index of Rossignol-Strick (1983) is a further example that the Mediterranean Sea is adequate to study the high/low-latitude climate interplay, reflecting the dual response of the monsoon system to the mean global climate state and to regional climate constraints. The paper by Colleoni et al. (2012) shows that after the intensification of the NHG (~2.75 Ma), sapropel formation was influenced the waxing and waning of ice sheets in the Northern high latitudes and therefore was sensitive to a North-South influence of climate, whereas the Mediterranean dynamics were controlled by a East-West water mass exchange (discrepancies in the sapropels distribution between East and West). Moreover, the Medstack planktonic signal variability during the Late Pleistocene exhibits a sawtooth shape, as observed in many other records such as the benthic oceanic records or the speleothems timeseries, and is interpreted as a signature of the glacials/interglacials alternation.

Those observations raise several questions: (i) how can the global climate signal affect the Mediterranean and how much does the flow exchange with the North Atlantic at the Gibraltar Strait influence the Mediterranean? (ii) what is the interplay between the monsoon signal and the Mediterranean mean climate state?

The need of exploring these questions also arises from other proxies that could be related to sapropel deposition such as, for example, the time-evolution of atmospheric CO_2 over the last 800 kyr.

Fig. 3 shows a detail of the last two glacial terminations (I and II, 18-8 and 140-126 ka respectively) that correspond to abrupt increase of 100 ppm in the CO_2 atmospheric concentration in few thousands of years (Vostok ice core, Petit et al. 2000). At the end of the terminations, CO_2 reaches the maximum concentration, and simultaneously in the Mediterranean sapropels S1 (9-6 ka) and S5 (midpoint age 124 ka) deposited. In addition, other minor interstadial fluctuations of atmospheric CO_2 are associated to sapropel deposition as well (Fig. 3). Is there a direct correlation between the large release of CO_2 in the atmosphere after a glaciation and the almost simultaneous production of organic carbon in the Mediterranean? If yes, this could be seen as a local response of the systems to carbon removal from the oceanic water masses during the interglacial periods (CO_2 uptake in ocean increases during glacial periods).

The large increase in atmospheric CO_2 is affecting the present-day world climate and there are few doubts that the temperature increase is related to this fact even if a direct correlation has not been demonstrated. Understanding how the system reacts to CO_2 increase and, in the case of the Mediterranean Sea, tends to respond by taking up carbon that goes buried in marine sediments is an important issue that deserves an in-depth exploration by the scientific community. It is important to understand and investigate whether sapropels are part of a process that triggers CO_2 burial from global to regional scales and from millennial to decadal timescales.

Examples from the Mesozoic Era, when carbonate platforms were widespread, show that those platforms demise slightly preceded the deposition of black shales (Cobianchi & Picotti, 2001, Chiari et al. 2007) evidencing a sort of balance in the carbon pump shifting from a carbonate system to a siliciclastic organic carbon-rich system in which the organic carbon content is due to primary producers that remove carbon either as organic carbon (C_{org}) in the cells and also in the carbonate tests. In the Mediterranean basin, carbonate platforms survived until the Pliocene and the demise of some of them has been proven to occur, again, slightly before the deposition of sapropels (Capozzi & Picotti, 2003). Numerical modeling of the biotic response under different atmospheric and oceanic scenarios can help to understand how quick the system responds, but so far only few models have been proposed (Bianchi et al. 2006, Meijer & Tuenter, 2007) and their aim was restricted to analyze the phenomena at the regional scale, in order to explain the deposition of particular sapropels. Instead, the exploration of the relationships among these sedimentary systems and the climate (primarily the monsoon influence) should be explored also at a global scale in order to understand the interplays between different regions in the world and the teleconnections between low and high latitudes.

In conclusion, with this short review, we aim to stimulate the (paleo) climate community to expand the view of the Mediterranean sapropels record as a product of the interplay of different global and regional processes and variability. The connections between all those processes have to be taken in consideration for understanding how the Earth responds to climate changes at different timescales, to predict which changes can occur in a near future and how societies can adapt.

ACKNOWLEDGEMENTS

The authors warmly thank J. Trabucho-Alexandre and N. Ciaranfi for the careful revisions and important suggestions. We also acknowledge F. Falcieri and A. Sabbatini for useful comments on a early draft of the manuscript and Alessio Rovere for improving the English spelling.

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Ms. received: April 24, 2012
Final text received: Jun 8, 2012