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Mid-Pliocene warm climate and annual primary productivity peaks recorded in sapropel deposition

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ABSTRACT: The Mid-Pliocene deposition in the Northern Apennines includes finely laminated sapropelitic horizons (insolation-cycles i-292 to i-282; 3.058 to 2.983 Myr) intervening within the slope-basin deposition of the foredeep, during a late highstand dated to the *Globorotalia bononiensis* zone. An integrated sedimentological, geochemical and micropaleontological study of the sapropel-bearing succession allowed the estimation of the time involved in the sapropel layer deposition, and to define the origin of the organic matter and the contribution of the primary productivity. The calculated average sedimentation rate of the section, including the intervening bioturbated beds, was about 0.4 mm yr^{-1}—similar to the rest of the pelitic deposition during the whole Pliocene. Within individual sapropels, recurrently-spaced 0.3 to 0.6 mm thick laminae consisting of calcareous and/or siliceous plankton tests, alternating with pyrite- and organic-rich mudstones, were interpreted as the record of annual variation in the supply. We could thus calculate the duration of individual sapropels by simply counting the number of couplets occurring in the layers: these spanned between 7500 and 10 000 yr. The kerogen content of the sapropels is ≥65 % marine origin, whereas the same component in the intervening bioturbated intervals is ~10 %. This supports the hypothesis that the sapropel deposition is linked to significant primary productivity peaks. In contrast, changes in the terrigenous supply or strong disoxia were not recorded at the bottom. Taking the nutrient supply as constant, productivity peaks could then be forced mainly by variations in the intensity of the insolation. The latter, is linked to the precession minima and has a wide oscillation; this oscillation occurred even at the end of the Mid-Pliocene warm climate, which was mainly characterized by a progressive climate deterioration that heralded the Northern Hemisphere glaciation.

KEY WORDS: Mid-Pliocene climate · Sapropel deposition · Sedimentation rate · Organic matter · Primary productivity

1. INTRODUCTION

Signals of abrupt climate and related ecosystems changes can be detected in the sedimentary record (e.g. Parrish 1998) and allow a better understanding of the amplitude of natural versus anthropogenic variations. Major climate oscillations, such as ice ages and interglacials, are induced by changes in the amount of seasonal and latitudinal sunlight distribution caused by perturbations in the tilt of the Earth's axis and other astronomical variations. The Pliocene period spans from 5.3 to 1.8 Myr BP, and encompasses the transition from Earth's relatively warm climate to the beginning of cyclic Northern Hemisphere glaciations. The warm Pliocene period (3.3 to 2.9 Myr BP) is particularly referred to when discussing wide climate fluctuations because, among other older periods warmer than the present that have been recognized in the geologic

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record, the palaeogeography and the plant and animal species were quite similar to the present. Moreover, high resolution stratigraphic dating is available and the estimated higher temperatures were warmer than the warmest Quaternary interglacials (Leroy et al. 1999). We chose a case study in the Northern Apennines, where marine sediments belonging to the warm Pliocene interval crop out and can be correlated with coeval stratigraphic records on land and in the Mediterranean Sea (e.g. Rio et al. 1997, Nijenhuis & De Lange 2000). The Pliocene evolution of the main depositional systems and the stratigraphic succession of the Romagna Northern Apennines foredeep have been reconstructed and biochronologically calibrated (Capozzi et al. 1992, 1998, Capozzi & Picotti 2003). During the Middle Pliocene, laminated sapropelitic horizons were deposited at the slope and basin plain of the Northern Apennine foredeep. The organic-rich deposition occurred during late sea-level high stand of a third-order sequence (sensu Van Wagoner 1995, i.e. duration of 1 to 3 Myr BP for the entire sequence), which followed a climatic optimum for the growth of a carbonate platform. The remarkable bioerosion and phosphatisation characterizing the drowning surface of the carbonate platform points to an increase in the trophic level of the surface water that triggered the shift from C_{carb} to C_{org}. In this study we focus on part of the clastic marine succession, which includes laminated dark-colored sapropels interbedded with bioturbated mudstones (Fig. 1) deposited during the high stillstand (Capozzi & Picotti 2003).

The coincidence of Neogene and Quaternary Mediterranean sapropels with cyclic variations in insolation in the Northern Hemisphere has been established and related to variations in the precession index (Hilgen 1991a, Lourens et al. 1996). This conclusion allowed for calculation of several astronomical solutions to calibrate the age of deposition of each cycle, starting from the present and extended back to the Miocene period (e.g. Hilgen 1991b, Lourens et al. 1996). The formation of sapropel layers has been linked to the increase in monsoonal activity (Rossignol-Strick 1983) and Mediterranean Atlantic-born depression (Rohling & Hilgen 1991), occurring during the minima in the precession index of the Earth's equinoxes and corresponding to the periods of insolation maxima in the Northern Hemisphere (e.g. Lourens et al. 1996). This climate change appears to cyclically provide freshwater flux in the Mediterranean, supplying nutrients that enhance primary productivity and carbon flux. It can also favor a stabilization of the water column with consequent oxygen depletion in deep waters and enhanced preservation of organic matter.

Many questions remain regarding the recognition of whether preservation or productivity is the major cause of organic matter enrichment, and whether the nature of the stored organic matter essentially terrestrial or marine. Among these questions still under discussion, we addressed in this study: (1) the evolution of the organic rich depositional system in terms of sedimentary processes and sedimentation rates; (2) the duration of each individual sapropel; (3) the relationships between productivity and preservation during sapropel deposition.

2. MATERIALS AND METHODS

We performed a multiproxy study of selected Middle Pliocene sapropels, including facies analysis, organic and inorganic geochemistry and micropaleontology.

For this study, we sampled a stratigraphic section in the Romagna region (the Fiumana section in Capozzi & Picotti 2003) that includes 5 individual finely-laminated sapropels with interbedded homogeneous bioturbated mudstones (Fig. 1). The sapropel-bearing interval is 52 m thick (Fig. 2); at the top of this interval, more than 20 m of homogeneous mudstones have been measured. These mudstones prelude passage to the overlying lithostratigraphic unit consisting of turbiditic sandstones, whose deposition was forced by the onset of a low-stand period.

The upper 4 laminated/bioturbated mudstones cycles (here named Sapropel A, C, D and E, Fig. 1, for description see also Capozzi et al. 2006) have been directly measured on the outcropping section and 57 samples (each 10 cm thick) have been collected at every 20 cm of each individual sapropel. Each sample has been oriented, preserved in its original setting and stored at 4°C for all analytical purposes. Five samples were additionally collected in the bioturbated intervals and results of the analyses compared with those of the laminated layers.

The different factors controlling organic rich layers deposition and preservation have been studied by integrating information deriving from sediment texture, mineralogical composition and micropaleontological content.

2.1. Geochemistry

Organic C and N were determined on duplicate samples using a FISONS NA2000 Elemental Analyzer (EA) after removal of the carbonate fraction by dissolution in 1.5 N HCl. Stable isotopic analyses of N and organic C were carried out by using a FINNIGAN Delta Plus mass spectrometer, which was directly coupled to the FISONS NA2000 EA by means of a CONFLO interface. The IAEA standards NBS19 were used

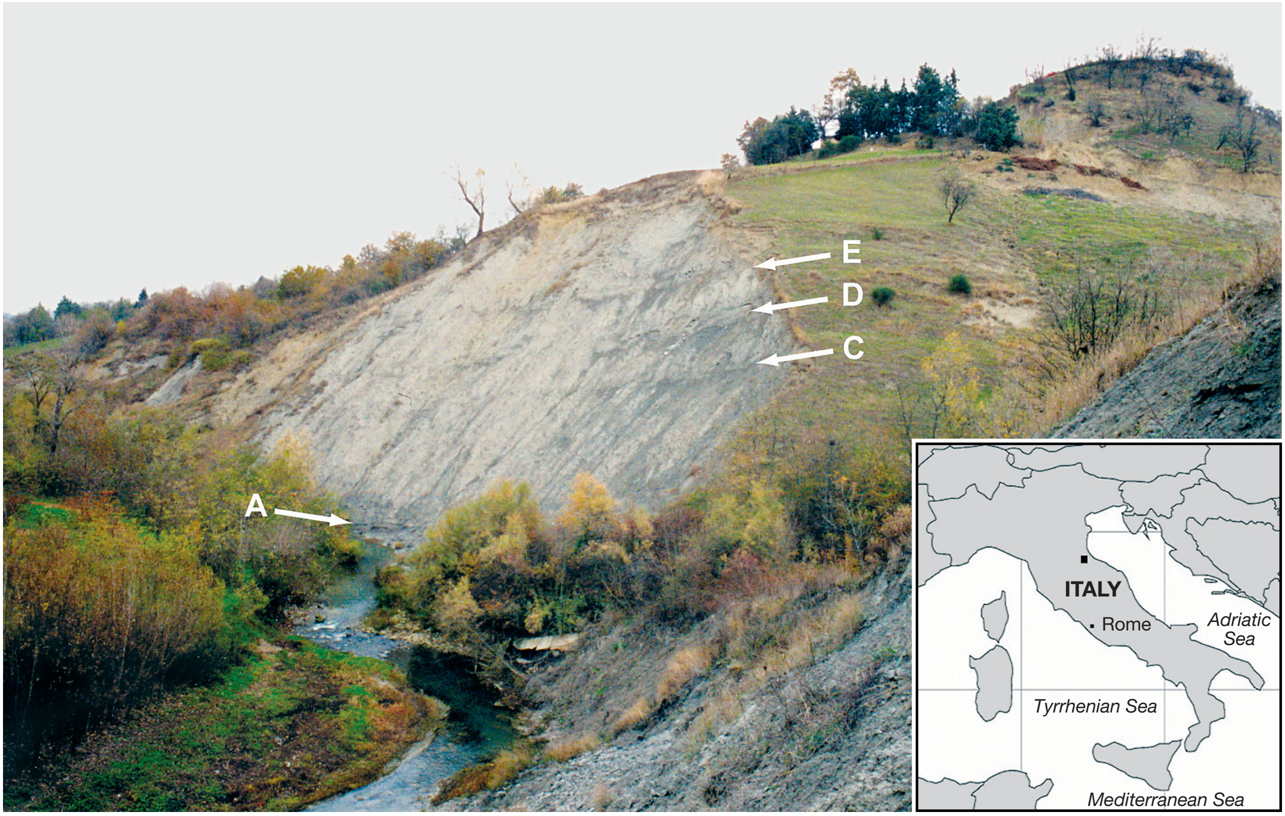

Fig. 1. Outcropping section in the Romagna region within the Northern Apennines. Notice that sapropel intervals (A, C, D and E) are characterized by dark colors and by morphologic relief

as calibration materials for C. Uncertainties are usually lower than ±0.2‰, as determined from routine replicate measurements on a reference sample. Stable isotopic data are expressed in the conventional delta (δ) notation, in which the ^{13}C:^{12}C isotopic ratios are reported relative to the international PDB standard.

Major (Si, Ti, Al, Fe, Mn, Mg, Ca, Na, K, P) and trace elements (Ni, Co, Cr, V, Sc, Ga, Cu, Zn, As, Rb, Sr, Y Zr, Nb, Mo, Ba, La, Ce, Th, Pb, S) were determined by X-ray fluorescence spectrometry on pressed powered pellets using a Philips PW 1480 automated spectrometer following the methods of Franzini et al. (1972, 1975), Leoni & Saitta (1976) and Leoni et al. (1982) for matrix corrections. Long-term reproducibility for major elements was generally better than 7%, whereas for trace elements it was on average better than 10%. Absolute accuracy relative to certified values is generally within the reproducibility range. Analytical homogeneity between batches was checked by duplicate analysis of selected samples and found to be better than 10%.

Mineralogy was investigated in selected samples by x-ray diffraction (XRD) using a Philips PW 1710 diffractometer equipped with a Cu tube. Analyses were performed by pressing powder into an alumina holder, thereby obtaining semi-quantitative information on the main mineralogy. Such a sample preparation does not enable a detailed distinction among sheet-silicates.

Physic-chemical changes were compared with the type of organic matter supply characterized for selected samples by the analysis of the kerogen and vitrinite reflectance. These analyses were performed by ENI-AGIP Division laboratories.

2.2. Biogenic content

Calcareous nannofossil and foraminifer analyses were performed on 33 samples spaced every 40 cm within the sapropels. For calcareous nannofossils sample preparation followed standard smear slide techniques, with the use of Norland Optical Adhesive for fixation of cover-glass. No centrifugation was applied to concentrate the biogenic fraction in order to retain the original composition of the nannofossil assemblage. Quantitative analyses were performed with a light microscope at 1250× by counting at least 300 specimens per sample. Additional counts in a fixed area (about 2.1 mm^2) was applied for the very rare *Braarudosphaera bigelowii*. Results were expressed as

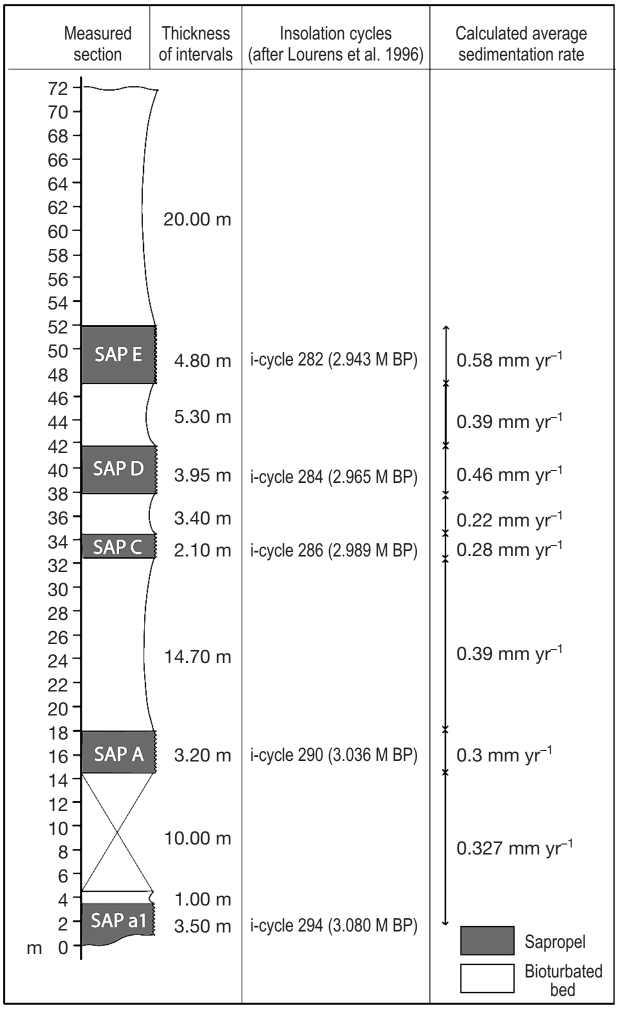

Fig. 2. Measured stratigraphic section. Sapropels labelled from SAP a1 to SAP E and correlate to i-cycles of Lourens et al. (1996). Reported average sedimentation rate of each individual sapropel was calculated by counting the number of couplets per mm in samples collected every second dm

a percent of the total assemblage. Foraminifers samples were dried and weighted. After washing the residues with a 63 µm sieve, samples were again dried and sieved with a 125 µm sieve.

Planktonic and benthic foraminiferal counts were made in the fraction coarser than 125 µm. A microsplitter was used to reduce residues into suitable aliquots of at least 200 specimens. Results are presented as percentages per total planktonic foraminiferal counts, as percentages per total benthic foraminiferal counts and as number per gram dry weight. Ostracods were counted in the same aliquots of residue and expressed as number of specimens per 100 dry g of sediment.

Based on the ecological requirements of the different species we summed warm species (*Globigerinella* spp., *Globigerinoides* spp. and *Orbulina* spp.) and cold species (*Neogloboquadrina pachyderma* sin., *Globorotalia acostaensis* sin. and *Globorotalia scitula*).

3. RESULTS AND DISCUSSION

3.1. Sedimentary processes and sedimentation rates

In this study a depositional environment of slope-basin transition was indicated, recording quite a high terrigenous supply consisting of prevailing pelites deriving from the adjacent uplifting Apennine chain. We observed that the terrigenous supply does not change in composition from bioturbated beds to sapropel layers. The 2 different alternating intervals also experienced the same diagenetic processes due to burial.

The studied sapropels are in the range of 2 to 4 m in thickness (Fig. 2) whereas the coeval layers recovered in the eastern Mediterranean basin are some tens of cm in thickness (i-282 and i-292 Mediterranean precession related cycles in Nijenhuis & De Lange 2000).

Each individual sapropel has been dated via correlation with precessional cycles calibrated by Hilgen (1991b) and reported by Nijenhuis & De Lange (2000) in the eastern Mediterranean, as they show the same pattern of Cluster 'O' (Verhallen 1987) and belong to the same Pliocene time interval (within the *Globorotalia bononiensis* zone, Colalongo et al. 1984). A further correlation can be made with the lower part of the adjacent Northern Apennine sapropel-bearing section along the Marecchia Valley (Rio et al. 1997). In Fig. 2 we correlated each cycle with the i-cycles (Lourens et al. 1996, Nijenhuis & De Lange 2000) and dated them starting from i-cycle 294 (Sapropel a1 in Fig. 2; 3.080 Myr BP) and ending at i-cycle 282 (2.943 Myr BP), corresponding to the deposition of the individual Sapropel E in Fig. 2. This calibration allowed us to calculate an average depositional rate for the entire section, and also to define the specific depositional interval and the related variation in the depositional rate. Like the rest of the pelitic deposition during the whole Pliocene period in the studied Northern Apennine area (Capozzi & Picotti 2003), the calculated average sedimentation rate for the sapropel-bearing section was about 0.4 mm yr^{-1}. However, in the central part of each individual sapropel, recurrently-spaced laminae (0.3 to 1 mm thickness) occur. Optical and scanning electron microscopic (SEM) observation of these laminae indicated that they could represent seasonal variation in supply because different components characterize each couplet of laminae, which are (respectively) almost exclusively calcareous or siliceous plankton tests in the light laminae, at the base of which

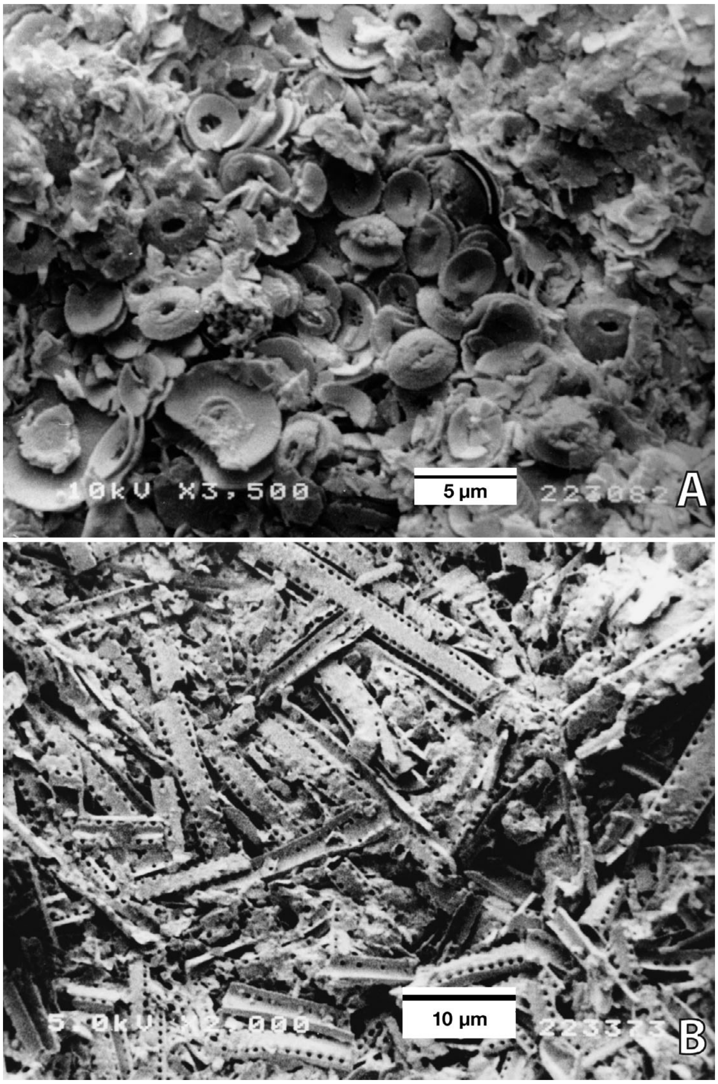

Fig. 3. SEM micrographs of light-colored laminae. (A) Coccoliths in monospecific assemblage (lamina of central part of the SAP C); (B) diatoms in monospecific assemblage (lamina of central part of the SAP D)

pyrite-rich mudstones characterize thinner (0.1 mm) dark laminae (Figs. 3 & 4). This record appears to be very similar to recent deposition observed in anoxic environments such as in the Black Sea (e.g. Calvert et al. 1991, Wignall 1994). An interesting peculiarity is that the occurrence of biogenic siliceous laminae is concentrated in the middle part of sapropels, and that they are replaced by calcareous microlaminae toward the top and the base of the sapropels.

Even if the discussion on whether laminites do or do not record seasonal variations remains open, we speculate that each couplet of <mm-scale lamina can reflect annual deposition due to 2 reasons: (1) light laminae consist almost exclusively of fossil tests (diatoms or calcareous nannofossils) — the dominant monospecific assemblages (described below) were identified as deriving from seasonal blooming events (see also Capozzi et al. 2006); and (2) the thickness of each couplet closely corresponds to the average sedimentation rate calculated for the entire section.

The duration of each sapropel can thus be calculated simply by counting the number of couplets occurring in the studied layers. The resulting sedimentation rate shows a moderate variability within each sapropel (Fig. 2) and massive beds. Subsequently, we can state that the duration of the sapropel deposition was in the range of 7500 to 10 000 yr, which is exactly the same calculated for coeval sapropels in the eastern Mediterranean (Nijenhuis & De Lange 2000). The increased thickness of the youngest sapropel layer (Sapropel E) is related to the progressive increase of sand supply owing to the maximum shelfal progradation during the late highstand, which in turn is the cause of the increased terrigenous organic C storage within the sediments; if we do not consider the thickness of sandstone layers, the duration of Sapropel E is comparable to that of other sapropels.

The kerogen analysis, conducted on Sapropel A, has revealed that 65% of total organic C (average total organic C content of Sapropel A was 1%) is of marine origin, which is comprised of amorphous organic matter and marine phytoplankton components. On the contrary, in the interbedded bioturbated beds, the amount of total organic C drops to about 0.35%, and only about the 11% of organic C is of marine origin. The $\delta^{13}C$ values of organic C that corresponded to kerogen of marine origin ranged between –23.53 and –24.94‰ PDB. These values are comparable to those measured in all samples of sapropel intervals, which fluctuated from –21.97 to –24.74‰. The $\delta^{13}C$ measured on bioturbated mudstones shows similar values, ranging from –23.39 to –24.73‰, even in the presence of (mainly) terrigenous organic C. These results indicate that caution must be taken when interpreting the origin of organic matter by simply measuring isotopic values. For instance, we think that the contribution to variations in the characteristics of organic matter may also depend on microbial activity, which, under sub-oxic conditions, becomes predominant and remineralizes both marine and terrestrial organic matter. Furthermore, bacterial mats also exert a fundamental influence on sedimentation by trapping sediment and preventing sea floor erosion. Conditions that favour oxygen depletion were recorded at the base of each light lamina, as documented by the occurrence of pyrite framboids derived from the activity of sulphate-reducing bacteria (Fig. 4).

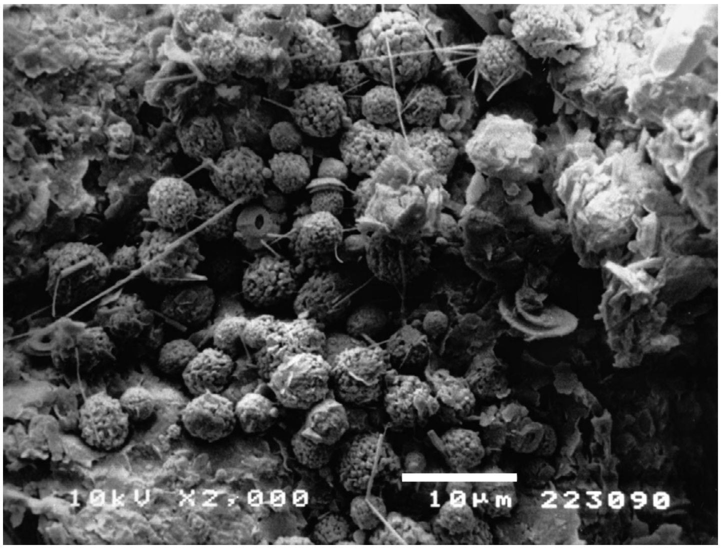

Fig. 4. SEM image of dark-colored laminae. View of pyrite framboids, which are the dominant filling of pores in mudstone laminae at the base of light laminae. Image corresponds to the dark lamina coupled to the coccolith-rich light lamina in Fig. 3A

The above observations imply that the recurrence of laminae that are rich in fossil tests, alternating with kerogen- and pyrite-rich mudstones, essentially signify enhanced export from the water column associated with increases in bacterial activity.

3.2. Geochemistry

The amount of organic C preserved after diagenetic processes and surface exposition in outcrops was ~1%. Geochemical analysis indicates some similarities with sapropel layers described in the eastern Mediterranean (Nijenhuis et al. 1999) and also with the on-land Vrica section in the southern Italy (Nijenhuis et al. 2001). The increase in marine organic C in sapropels does not correspond to values of Ni, Cr, V, and As that are higher than those in bioturbated mudstones; in contrast, enrichment in Mo, in the central part of each individual sapropel, can indicate enhanced reducing conditions on the sea bed, which can be confirmed by the presence of pyrite. Higher Si:Al ratio values were also recorded in sapropel intervals (Capozzi et al. 2006).

3.3. Biogenic content

Benthic foraminifera identified in 4 sapropels (A, C, D and E) revealed that: (1) Sapropel E had the lowest diversity (23 species) whereas Sapropel D had the highest (29 species), with the diversity of Sapropels A and C being intermediate (25 species); and (2) dysoxic species (*Bolivina alata*, *Bulimina costata* and *Bulimina exilis*, *Cassidulinoides* spp., *Globobulimina* spp., *Virgulina* spp.) are present in high abundance (10%) in Sapropel E and in 1 sample of each of the other 3 sapropels.

The youngest sapropel (Sapropel E) comprised less diverse microfauna. Furthermore, the residues in this sapropel are extremely rich in gypsum and vegetal remains. The continuous presence of benthic foraminifera and ostracods in the sapropels indicates that the bottom oxygen concentration never fell under critical values required to sustain benthic fauna, even though in Sapropel E the ostracods disappears. This event, together with the presence of benthic foraminifera specimens and presence of gypsum, indicate that during deposition of Sapropel E the sea bottom was influenced by strong dysoxia, whereas during periods of deposition of other sapropels the bottom environmental conditions were less influenced by low oxygen concentration.

Calcareous nannofossil assemblage consists of dominant *Reticulofenestra* spp. (mean 41.6%) and subordinate *Pseudoemiliania lacunosa*, *Calcidiscus leptoporus*, *Coccolithus pelagicus*, *Helicosphaera carteri*, *Helicosphaera sellii*, *Sphenolithus abies*, *Florisphaera profunda*. Other nannofossils (*C. macintyrei*, *Umbilicosphaera* spp., *Rhabdosphaera* spp., *Coronosphaera* spp. and *Braarudosphaera bigelowii*) are rare and scattered along the section.

All sapropels show a positive peak in the abundance of the species *Helicosphaera carteri*. This is a feature already recognized in other sapropels from the Neogene (Negri et al. 1999b) and the Quaternary (Castradori 1993, Negri et al. 1999a). *H. carteri* is a species generally thought to indicate moderate turbidity and nutrients level (Ziveri et al. 1995); thus, its abundance suggests that these conditions occurred during the deposition of sapropels.

Placoliths are the other significant component of sapropel nannoflora, particularly the Reticulofenestra 'group'. According to Young (1994), placolith-bearing species dominate in coastal and upwelling areas. Furthermore, this is a feature already observed in the late Pliocene Sapropel C of the Vrica section (Negri et al. 2003), and it thus appears to recur in sapropels and indicate moderate productivity in superficial waters. Finally, *Braarudosphaera bigelowii*—a species found in the recent Sapropel S1—is probably related to surface salinities; however, as for other species, its exact ecological requirements are not yet clear (see Negri & Giunta 2001). Although rare, this species peaks in abundance at the beginning and end of each sapropel.

In Sapropel D, this species abundance also oscillates in the central part of the interval. This is noteworthy in that Sapropel E individuals are smaller.

Although the ecological requirements of cited species are not yet fully understood (see Negri et al. 1999a,b, Negri & Villa 2000, Negri & Giunta 2001), these species are superficial dwellers whose frequency fluctuations suggest slightly increased nannofossil productivity in coastal areas.

As for the climatic conditions during which sapropels were deposited, we could again observe that each sapropel has its own history, and that each has its own unique characteristics. For example, planktic forams (besides the dominant *Globorotalia bononienis*) show that colder species are abundant in Sapropels A, C and E (~10% of the total assemblage) whereas in Sapropel D these species represent <5% of the entire community. Instead, warm taxa are particularly abundant in Sapropel D (>15%) and are present only in small percentage in other sapropels. Although the percentage of cold and warm species is similar in Sapropels A and C, the type of association is slightly different: higher abundance of *Neogloboquadrina pachyderma* sin. and lower abundance of *Globigerinoides ruber* in Sapropel C compared to those in Sapropel A. An increase in water temperature is recorded by planktic microfauna during Sapropel D deposition, whereas an abrupt decrease is evident during deposition of Sapropel E.

All these observations again suggest that climate was different during each sapropel deposition, but not to the extent that an increased burial of C_{org}, which characterizes these layers, was impacted.

4. CONCLUSIONS

The main results deriving from the multidisciplinary analysis of the Fiumana section concern:

(1) The duration of each individual sapropelitic layer that can be estimated by counting the laminae, because each couplet of light- plus dark-lamina can be interpreted as a record of annual productivity peaks. This count indicates a duration of individual sapropels in the range 7500 to 10 000 yr, corresponding to that calculated for coeval sapropels of the Eastern Mediterranean (Nijenhuis & De Lange 2000);

(2) The deposition of each sapropel, which was characterized by a sedimentation rate equivalent to that of the intervening bioturbated interval. Individual laminae in sapropel intervals consist of quite exclusive organism tests, marine organic C and bacterial byproducts. Laminae preservation was enhanced by the presence of microbial mats that prevented reworking of the sea floor;

(3) The preservation of sapropels, which does not strictly depend on anoxic conditions (never persisting on the sea floor), but is linked instead to higher organic matter supply of marine origin, with resulting partial oxygen depletion.

Although identification of the mechanism responsible for productivity peaks is difficult, our study suggests that variation in the terrigenous and, consequently, nutrient supply (as postulated by Rossignol-Strick 1983, 1985) is unlikely, because sediment supply is quite constant throughout the section. Increased primary production and associated enhanced export from the water column were therefore the consequence of other forcing mechanisms. Relative enhancement of insolation intensity (as calculated by Lourens et al. 1996) during the precession minima increased phytoplankton production, and thus caused the increase in C_{org} export. We document that these events occurred at the end of the Mid-Pliocene warm climate. This warm climate was favorable for a temperate carbonate platform, whereas the subsequent sapropel interval was deposited during a progressive climate deterioration—clearly evident in planktic assemblages and facies associations. A glacio-eustatic lowering of sea-level abruptly stopped sapropel deposition.

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