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# Palaeoclimatic cyclicity in central Mediterranean Pliocene sediments: the mineralogical signal

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#### Abstract

A high resolution X-ray mineralogical study of four Pliocene sediment sections from the central Mediterranean (Punta Piccola, Sicily; Monte Singa and Vrica, Calabria; ODP Hole 964 A, Ionian Sea) shows cyclic opposite abundance variations of two groups of clay minerals. The first is dominated by palygorskite and kaolinite, whose abundance maxima can be interpreted as resulting from periods of aridity on the African continent, allowing their transport as wind-blown dust. The second is dominated by smectite, whose abundance maxima can be interpreted as indicative of periods of abundant rainfall on the Mediterranean borderlands. These variations in abundance show a 22 ky cyclicity, implying a control by the precession of the Earth's orbit. Sapropels and sapropelic layers always occur in the smectite-rich beds, and therefore appear to have been deposited during the wet periods. © 2000 Elsevier Science B.V. All rights reserved.

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# 1. Introduction

In the central Mediterranean, marine Pliocene deposits unconformably overlay Miocene evaporitic formations as a result of the Messinian salinity crisis. These deposits usually show a rhythmic bedding of rather regular carbonate-rich and carbonate-poor alternations. Some layers, dark or black in colour, are rich in organic matter, up to 30% in marine sediments drilled during ODP Leg 160 (Emeis et al., 1996). According to Kidd et al. (1978), these sediments are called sapropels when their organic carbon content reaches or exceeds 2%.

Several hypotheses have been proposed to explain both the formation and repetition of these

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dark beds, requiring variations in either production or preservation of organic matter (Rohling and Gieskes, 1989; Rohling and Hilgen, 1991; Tang and Stott, 1993; Rohling, 1994). All these hypotheses imply that sedimentation of these organic matter-rich layers is controlled by climatic variations linked to the Earth's orbit, mainly to precession cycles whose duration is approximately 22,000 years (Rossignol-Strick, 1983, 1985; Hilgen, 1991). This astronomical and climatic control concerns the whole cyclic sedimentation in which the dark beds are included (Hilgen, 1987).

The aim of the present study is to analyse the mineralogical sedimentary content of some central Mediterranean Pliocene sections and to interpret these signals in terms of sedimentary and palaeoclimatic processes, including those prevailing during the time of sapropels deposition.

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The Pliocene stratigraphy in the central Mediterranean has been mainly established by studies of particularly well-exposed South Sicilian outcrops. From the base to the top, two formations have been distinguished: the Trubi Formation and the Monte Narbone Formation. The Trubi Formation consists of marls and marly limestones that, according to Cita (1975), correspond approximately to the Zanclean (Seguenza, 1868; Cita and Gartner, 1973). It shows cyclically deposited sedimentary sequences, having a thickness of approximately 1 m, each corresponding typically to four successively grey, white, beige and white marly facies (Hilgen, 1987). The Monte Narbone Formation comprises regular alternations of grey marls, sometimes very dark, and of light-grey marly limestones. In the lower part of the formation some beige layers occur in the same sequential position as in the underlying formation (Van Os et al., 1994). This formation approximately corresponds to the Piacenzian and the Gelasian (Cita et al., 2000).

Clay mineralogy of the central Mediterranean Pliocene sediments has been studied at the scale of Pliocene series in land sections as well as in marine drilled sections, and at the scale of precession related cycle on land sections. At the Pliocene series scale, the most striking feature is a decrease in palygorskite content from high values in the Trubi Formation to low values in the Monte Narbone Formation, interpreted as resulting from an uplift of Sicily in the Mid-Pliocene (Chamley, 1975, 1976; Mélières et al., 1978). At the precession related cycle scale, the clay mineral assemblage composition displays cyclic variations characterized by opposite variations of palygorskite and smectite abundances. This pattern is thought to result from the alternation of dry and humid periods on the Mediterranean Basin (De Visser et al., 1989; Foucault and Mélières, 1995; Mélières et al., 1998).

#### 2. Methods

Four sections were studied (Fig. 1) at Monte Singa, Calabria (Zanclean), Punta Piccola, Sicily and ODP Hole 964 A, Ionian Sea (Piancenzian), Vrica, Calabria (Gelasian). For all these sections, the total carbonate content was determined by manocalcimetry. Dolomite, quartz, feldspars and clay mineral contents were measured by X-ray diffractometry on a Siemens diffractometer using copper Ni-filtered radiation. The use of a highspeed rotating sample holder (Mélières, 1973), and the systematic duplication of measurements, allowed us to obtain a relative precision ranging from  $\pm 2\%$  for quartz, feldspars and dolomite, to



Fig. 1. Location (left) and stratigraphical position (right) of the studied sections. Timescale according to Lourens et al. (1996).

 $\pm$ 5% for clay minerals. As calcite and dolomite were the only carbonate minerals detected, the calcite content was calculated as the difference between the total carbonate and the dolomite contents.

# 3. Results

### 3.1. Monte Singa section

Monte Singa outcrops are located 4 km WNW from Riace Marina, Calabria (Zijderveld et al., 1986; Hilgen, 1987). We studied the basal part of the so-called Singa I section (Fig. 2), pertaining to the Zanclean, from cycle 13 to cycle 16 (Hilgen and Langereis, 1988; Langereis and Hilgen, 1991). The series mainly consists of grey marks alternating with beige and white marky limestones. In this 3.90 m-long section, 40 samples were taken every 10 cm.

Carbonate content variations are closely related to the sediment colour: the carbonate content in grey marls is always about 30%, whereas it reaches 60% or 70% in beige or white layers. Palygorskite, kaolinite and dolomite abundances show similar variations to those of carbonate content. Illite and mixed-layer do not show cyclicity, but a slightly decreasing trend upwards.

According to the chronology of Lourens et al. (1996), the age of the midpoint of the cycle 14 grey layer (at 125 cm in this section) is 5044 ky, and that of the midpoint of the cycle 16 grey layer (at 320 cm) is 4998 ky. Between these two levels the mean sedimentation rate is  $4.24 \text{ cm ky}^{-1}$ , indicating an age of 4981 ky for the top of the section and 5073 ky for the base.

#### 3.2. Punta Piccola section

The studied section (Foucault and Mélières, 1995; Mélières et al., 1998) corresponds to the Punta Piccola outcrop (Fig. 3) represented by Brolsma (1978, figs. 30 and 31) and Hilgen (1987, fig. 5B and C). It shows mainly light-coloured marls alternating with grey or brown beds, often laminated, whose colour is explained by concentrations of manganese or organic matter (Brolsma, 1978; Van Os et al., 1994). The remarkable dark

layer in the interval between 395 and 430 cm corresponds to the base of the cycle 107 of Langereis and Hilgen (1991) and to the ferromanganiferous layer G of Brolsma (1978). In the 615 cm-long section, from cycle 104 to cycle 108, 123 samples were taken, each consisting of a 5 cm-thick slice.

The calcite content shows a periodic variation which corresponds to a change in the marl colour, the lowest values characterizing the darkest beds. Light-coloured beds of cycles 105 and 106 are moderately depleted in calcite in their central parts. The same pattern was observed by Van Os et al. (1994) in cycle 102, where the decrease in calcite content corresponds to the beige-coloured parts. Optical microscopic observations show that this calcite is of a biogenic origin and consists essentially of coccoliths (80 to 90%) and foraminifers (10 to 20%).

Clay mineral abundances generally display cyclic variations corresponding to those in lithology and carbonate. Two mineral groups whose contents fluctuate in an opposite way can be distinguished. The first includes palygorskite, kaolinite and illite; their abundance maxima correspond to the lightest layers and their minima to the darkest layers. The second includes smectite and chlorite. Mixed-layer clay minerals, whose contents do not show cyclic variations but only a slightly increasing abundance towards the top of the section, cannot be included in any of the two groups.

Quartz, potassium feldspar and dolomite abundances are positively correlated with those of the palygorskite group, and therefore are related to this group.

According to the chronology of Lourens et al. (1996), the age of the midpoint of the cycle 105 dark layer (at 87.5 cm in this section) is 2989 ky, and that of the midpoint of the cycle 108 dark layer (at 582.5 cm) is 2921 ky. Between these two levels, the mean sedimentation rate is 7.3 cm ky<sup>-1</sup>, indicating an age of 2917 ky for the top of the section and 3001 ky for its base.

# 3.3. ODP Hole 964 A

Hole 964 A was drilled in 1995 during ODP Leg 160 (Emeis et al., 1996). We studied (Mélières









et al., 1998) the section between 97.585 'revised metre composite depth' (rmcd) and 102.735 rmcd (i.e. from Core 9H-2, 130.5 cm, to Core 9H-6, 45.5 cm). These sediments consist mainly of light-coloured nannofossil ooze and clayey nannofossil ooze (Fig. 4). Dark-coloured organic-rich beds (sapropels) occur about every metre. From top to bottom, six sapropels were observed, numbered from 50 to 55 (Emeis et al., 1996). In this 5.15 m-long section, 102 1 cm-thick samples were taken every 5 cm.

The carbonate content shows large cyclic variations well correlated with variations in sediment colour, with lower values occurring in darker layers. The grey bed between sapropel 51 and sapropel 52, at 99.235 rmcd, corresponds to a marked depletion in carbonate content and therefore may be interpreted as an oxidized sapropel. Palygorskite and kaolinite variations are roughly positively correlated to those of carbonate, whereas smectite and chlorite vary in an opposite way. Illite and mixed-layer mineral contents do not show cyclicity: illite displays a slight increase and mixed layers a slight decrease upwards.

In order to determine the equivalences between sapropels and precession-related sedimentary cycles as defined at Punta Piccola (Hilgen, 1991), *Discoaster tamalis* bioevents were used (Mélières et al., 1998). According to the chronology of Lourens et al. (1996), the age of the midpoint of the sapropel 50, at 98.200 rmcd, is 2792 ky, and that of the midpoint of the sapropel 55, at 102.435 rmcd, is 2989 ky. Between these two levels, the mean sedimentation rate is 2.63 cm ky<sup>-1</sup>, indicating an age of 2808 ky for the top of the section and 3003 ky for the base (the same as for the base of Punta Piccola section).

# 3.4. Vrica section

The Vrica section, 4 km south of Crotone (Calabria), was recently revised by Pasini and Colalongo (1996). It consists mainly of light grey silty marls, intercalated with dark grey layers of sapropelic laminated shales. We studied the interval including laminated shales b to e in the so-called Vrica B section (Fig. 5). In this 39.60 m-

long section, 100 5 cm-thick samples were taken every 40 cm.

The carbonate content shows cyclic variations from 15% in sapropelic beds to 25% in light grey beds. Unlike the other studied sections, palygorskite was not detected here. Kaolinite, chlorite and illite abundance variations are positively correlated with that of carbonate, whereas smectite variations are opposite. The abundances of mixed-layer clay minerals increase from the base of the section (15%) to about 28 m (25%) and then suddenly decrease to near 15%.

According to the chronology of Lourens et al. (1996), the age of the midpoint of the sapropelic bed b (at 7.15 m in this section) is 1872 ky, and that of the midpoint of the sapropelic bed e (at 36.50 m) is 1808 ky. Between these two levels the mean sedimentation rate is  $45.9 \text{ cm ky}^{-1}$ , indicating an age of 1801 ky for the top of the section and 1888 ky for the base. The Pliocene/Quaternary boundary was defined at the top of the sapropelic bed e (Aguirre and Pasini, 1985) at 1806 ky (Lourens et al., 1996).

# 4. Clay mineral origin in the central Mediterranean

In all the sections, two groups of minerals showing opposite cyclic variations can be distinguished. The first is mainly characterized by kaolinite and palygorskite whose abundance variations display the same pattern as that of carbonate content. Other minerals often show similar variations and can be related to the same group: illite in Punta Piccola and Vrica sections, dolomite in Punta Piccola and Singa sections, K feldspar in the Singa section and Hole 964 A, quartz in the Punta Piccola section and in Hole 964 A. The second group is characterized by smectite whose abundance fluctuates in the opposite way to those of kaolinite and palygorskite; it includes chlorite, except in the Vrica section.

To understand the cyclic variations of mineral abundances in these Pliocene deposits, we can compare with their present day distribution patterns (Fig. 6), although the Pliocene physiography was somewhat different from the present one.

Eolian processes play an important role in the











Fig. 6. Main present-day sources of clay minerals in the Mediterranean. Black arrows: fluvial influx; white arrows: eolian influx.

Mediterranean fine-grained sedimentation (Tomadin and Lenaz, 1989; Guerzoni and Chester, 1996): the present eolian influx is estimated to be  $3.9 \times 10^6$  t y<sup>-1</sup> in the whole basin (Bergametti et al., 1989). Nevertheless, the major part of the clays is supplied by fluvial processes: the most important source of terrigenous supply is the Nile River whose suspended load was estimated to be about  $120 \times 10^6$  t y<sup>-1</sup> before the closure of the Aswan High Dam in 1964 (Holeman, 1968; Stanley et al., 1992, Milliman and Syvitski, 1992), the solid contribution of the Rhone River is evaluated to be  $31 \times 10^6$  t y<sup>-1</sup>, that of the Ebro River to be  $18 \times 10^6$  t y<sup>-1</sup>, and that of the Po River to be  $13 \times 10^6$  t y<sup>-1</sup> (Dal Cin, 1983; Milliman and Syvitski, 1992).

Smectite is mainly provided by the Nile River (Venkatarathnam and Ryan, 1971; Maldonado and Stanley, 1981; Stanley and Maldonado, 1983; Emelyanov and Shimkus, 1986). A counterclockwise current gyre carries suspensions to the northeast along the Levantine coast, then to the north along the south Turkey coast, then to the west and southwest to the south of Crete. We have no data, however, to attest that, even during periods of maximum supply by the Nile River, smectite suspensions reached the Ionian Sea. Coastal rivers of the Italian Peninsula yield smectite to the Thyrrenian and Adriatic Seas (Chamley, 1971; Emelyanov, 1972), whose recent sediments are rich in this mineral up to the southern Italian coast (Emelyanov and Shimkus, 1986). Although these sources appear to be weaker than that of the Nile River, they may play a major role in the Ionian Sea sedimentation because of their proximity.

The most important sources of illite and chlorite are the Rhone River (Chamley, 1971; Emelyanov and Shimkus, 1986) and the Po River (Tomadin, 1979), both carrying the erosional products of the alpine chain. The Rhone mineral supply is transported by the currents over the western Mediterranean basin, and part of it reaches the central basin via the Siculo-Tunisian strait current (Blanc-Vernet et al., 1975). Part of the Po supply is carried by Adriatic deep water to the Ionian Sea (Venkatarathnam et al., 1971). Chlorite, probably derived from metamorphic terranes of Dinarides, is moderately abundant in marine sediments south of the Peloponnese Peninsula (Emelyanov and Shimkus, 1986).

Palygorskite is of special interest because the only significant source area for this mineral, in this part of the Mediterranean region, is Africa. On this continent, Palaeogene sediments are known to

be palygorskite-rich. This mineral is commonly found in Senegal. Ivory Coast. Dahomey. Sudan. Morocco (Millot, 1964; Chamley, 1989), Algeria, Tunisia as well as in the southern Saharan Atlas (Chamley, 1971; Sassi, 1974; Coudé-Gaussen, 1991). Along the Algerian–Tunisian coast, the North Africa continent supplies palygorskite into marine sediments, with a seaward decreasing abundance (Blanc-Vernet et al., 1975; Burollet et al., 1979). However, marine transportation of palygorskite from Africa to Site 964 or to the Calabrian and the Sicilian coasts is unlikely because of the strong surface current flowing through the Siculo-Tunisian strait from the northwest to the southeast. acting as a hydrodynamic barrier. Because of the generally oxygenated sedimentary environment prevailing during the Pliocene, except during the sapropel events, the current pattern would not significantly differ from the present one (Béthoux and Gentili, 1994; Rohling, 1994). Consequently, a wind transportation process seems to be a better explanation of palygorskite presence north of the Siculo-Tunisian strait. In the western Mediterranean area, some Quaternary continental formations document this mechanism: in South Tunisia, thick peri-desertic, loess-like, palygorskite-rich formations resting on the Matmata plateau have an eolian origin from the Sahara (Coudé-Gaussen, 1990); the occurrence of palygorskite in Corsican Holocene lake deposits can be explained only by a wind contribution from the African continent (Robert et al., 1984).

Eolian transportation of palygorskite across the Mediterranean has been observed: this mineral, as well as kaolinite, illite, calcite, quartz and felspars, was found in wind-blown dust coming from south Mediterranean areas (Tomadin et al., 1984; Robert et al., 1984; Bergametti et al., 1989; Tomadin and Lenaz, 1989; Coudé-Gaussen, 1991; Molinaroli, 1996).

Kaolinite occurs in all the eastern Mediterranean Basin sediments in rather moderate amounts (Chamley et al., 1962; Venkatarathnam and Ryan, 1971; Emelyanov and Shimkus, 1986). Its northwards decreasing abundance gradient in marine sediments indicates an African origin.

#### 5. Discussion and interpretation

Because of their African eolian origin and their eolian transportation, the distribution of palygorskite and kaolinite is vital for the interpretation of our data. It has been shown, particularly around the African continent, that the rate of dust flux and accumulation is positively correlated with the degree of aridity of source areas (Prospero, 1985; Middelton, 1985; Tiedemann et al., 1989, 1994). We know for instance that during recent periods, about 9 to 6 ky B.P., an increase in rainfall on the Sahara and peri-Saharan areas resulted in a spreading of vegetation (Street-Perrott and Perrott, 1993). This vegetation may have completely stopped the wind erosion processes and the export of eolian palygorskite, kaolinite and related minerals out of Africa.

We suggest that the cyclic variations of the mineral content observed in the four studied sections result from the alternation of weak and strong rainfall periods on both southern and northern Mediterranean sides as follows.

# 5.1. Periods of minimum rainfall

On the southern side of the Mediterranean, a weakening of rainfall increased the aridity of the Sahara, resulting in a reduced and scattered vegetation in peri-Saharan areas. Consequently, soils and outcropping rocks were far more vulnerable to wind erosion, which led to an increased wind transportation of minerals (palygorskite, kaolinite, quartz, potassium feldspar, dolomite, etc.) from these areas into the Mediterranean. On the northern side of the Mediterranean, a decrease in rainfall probably resulted in a decrease not only in the river discharge, but also in the sediment load, because fluvial erosion lost its efficiency. Consequently, the detrital material supply of rivers to the sea would have decreased, increasing the concentration of wind-transported material in the sediment. During these periods, sediments show the highest contents in palygorskite and related minerals (kaolinite, dolomite, quartz, and feldspar) and the lowest in smectite and chlorite.

## 5.2. Periods of maximum rainfall

On the southern side of the Mediterranean, an increase in rainfall allowed the vegetation to extend over the Saharan and peri-Saharan areas, protecting soils and significantly reducing, or even preventing eolian erosion. On the northern margin of the Mediterranean, an increase in rainfall would not have notably modified the density of a preexistent vegetation, but it would probably have resulted in an increase in fluvial erosion, providing an increased terrigenous supply to marine sedimentation. During these periods, sediments show the highest content in smectite and chlorite. Sapropels or grey beds deposition occurred during these humid periods.

Studies of the Pliocene section from ODP Hole 964 C (Ionian Basin) showed that terrigenous detrital matter geochemistry reflects periods of stronger Saharan dust input alternating with fluvial input from northern borderlands (Wehausen and Brumsack, 1998). These results are in good agreement with our conclusions (see also Foucault and Mélières, 1995).

#### 6. Conclusions

The Pliocene sedimentation in the four studied sections (Monte Singa, Punta Piccola, ODP Hole 964 A, Vrica) shows outstanding similarities. At each location, cyclic sedimentation is characterized by variations of abundance in most mineral constituents. These variations are interpreted as the result of cyclic climatic changes that controlled the eolian and fluvial sedimentation processes.

During periods of accumulation of sediments rich in palygorskite and kaolinite, these clay minerals, African in origin, were removed from vegetation depleted soils and outcropping rocks through eolian processes and dispersed across the central Mediterranean. Thus we conclude that these periods were characterized by arid conditions.

During periods of deposition of sediments poor in palygorskite and kaolinite, these clay minerals were not available to eolian erosion-transportation processes, probably because of the presence of a vegetal cover on the Saharan and peri-Saharan source areas. Therefore these periods appear to have been characterized by humid climatic conditions. Such conditions would have enhanced the northern terrigenous contribution characterized by chlorite and smectite, because of a stronger fluvial erosion. Sapropels and sapropelic layers were formed during these periods.

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