

Sapropel-like Pliocene sediments of Sicily deposited under oxygenated bottom water

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Key words. – Sapropels, Mediterranean, Manganese, Early diagenesis, Anoxia

Abstract. – The Pliocene Punta Piccola series, deposited on the Sicily sill at 100-400 m depths, consists of alternating whitish hemipelagic marl and carbonate-poor, organic-carbon-rich, brownish dark marl. The rhythmic bedding is interpreted to result from the precession driven alternation of more or less humid periods. In the present study, we compare the mineralogical and geochemical composition (isotope ratios of oxygen and carbon; Ca, Mn, Mg, Sr, and Fe concentrations) of the carbonate fractions of the whitish marl to those of the dark layers to evaluate the environmental changes that likely produced these alternations.

High Mn concentrations in the dark layers, and the occurrence of pseudo-kutnahorite (Mn-Ca mixed carbonate), bioturbation, ostracodes, and benthic foraminifera favour the hypothesis of the dark-layer deposition taking place under oxygen-bearing bottom waters. The original value of the concentration of the organic carbon in the dark layers of Punta Piccola, estimated from the $\delta^{13}\text{C}$ measured in the carbonate fraction, was higher than the post-diagenetic one. It may have reached 7% in the dark layer 107, which was therefore a true sapropel at the time of deposition. This result indicates that anoxic conditions are not a prerequisite for sapropelic sediment formation. However, the pristine concentration of the organic carbon in the dark layers at Punta Piccola is lower than those of coeval sapropels cored in the nearby deep settings, which were deposited under an anoxic water column. This difference may result from the effect of water column anoxia on the organic carbon content.

Diagenetic reactions took place in the dark layers through the oxidation of large amounts of organic matter. The dissolution of primary calcium carbonates (biogenic in origin) and the reduction of Fe and Mn oxyhydroxides led the interstitial solutions to be supersaturated towards Mn-rich calcite and/or pseudo-kutnahorite. The secondary carbonates are Mg-enriched and Sr and Fe-depleted. The negative shifts of the $\delta^{18}\text{O}$ signal in the carbonates of the dark layers of Punta Piccola are consistent with an increased river discharge in the Mediterranean at the time of deposition.

Sédiments pseudo-sapropéliques pliocènes de Sicile déposés sous des eaux de fond oxydantes

Mots clés. – Sapropèles, Méditerranée, Manganèse, Diagenèse précoce, Anoxie.

Résumé. – Les séries pliocènes de Punta Piccola, déposées sur le seuil de Sicile à 100-400 m de profondeur, sont des alternances de marnes blanchâtres hémipélagiques et de marnes brunâtres pauvres en carbonates et riches en carbone organique. Ces dépôts cycliques résulteraient de l'alternance de période plus ou moins humides, rythmées par les cycles de précession. Dans cette étude, nous comparons les compositions minéralogiques et chimiques (composition isotopique du carbone et de l'oxygène, concentrations en calcium, manganèse, magnésium, strontium et fer) des fractions carbonatées des marnes blanchâtres à celles des marnes sombres pour évaluer les changements environnementaux susceptibles de conduire à de telles alternances.

Les concentrations en manganèse élevées des niveaux sombres, la présence de pseudo-kutnahorite (carbonate mixte de Mn et de Ca) dans l'un de ces niveaux, ainsi que la présence de bioturbations, d'ostracodes et de foraminifères benthiques préchent en faveur d'un dépôt des niveaux sombres sous des eaux de fond oxygénées. La teneur initiale en carbone organique des niveaux sombres, estimée à partir de celle du $\delta^{13}\text{C}$ des fractions carbonatées, était plus élevée que la valeur post-diagénétique. Elle a pu atteindre 7 % dans le niveau sombre du cycle 107, qui était donc un sapropèle *sensu stricto* au moment du dépôt. Ce résultat indique que l'anoxie n'est pas une condition nécessaire pour la formation de sédiments sapropéliques. Les valeurs originelles des concentrations en carbone organique des marnes sombres de Punta Piccola sont toutefois inférieure à celles des sapropèles de même âge déposés dans des sites profonds proches. Cette différence est attribuable aux effets de l'anoxie des eaux sur la richesse en carbone organique des sédiments.

Dans les marnes sombres, les réactions diagénétiques ont été plus intenses que dans les marnes blanchâtres du fait de l'oxydation de quantités importantes de matière organique. La dissolution des carbonates de calcium primaires (d'origine biogène) et la réduction des oxyhydroxides de Fe et de Mn ont conduit à la sursaturation des solutions interstitielles vis-à-vis de la calcite magnésienne et/ou de la pseudo-kutnahorite. Les carbonates secondaires sont enrichis en magnésium et en strontium et appauvris en fer par rapport aux carbonates initiaux. Les pics négatifs du signal $\delta^{18}\text{O}$ dans les carbonates des niveaux sombres sont cohérents avec une augmentation des apports d'eau douce en Méditerranée au moment du dépôt.

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INTRODUCTION

The Mediterranean Pliocene to Holocene sedimentary record has received much attention over the last decades because these more or less marly deposits are rhythmically bedded in both uplifted exposures on land and in deep water settings. These sequences consist of couplets of dark-coloured sediments, commonly rich in organic matter and trace elements, and light-coloured marls. The darker layers are usually referred to as sapropels when the sediment contains more than 2% organic carbon by weight [Kidd *et al.*, 1978]. Their cyclic occurrence correlates closely with minima in the precessional index characterised by intensified rainfall and river runoff [e.g. Rossignol-Strick, 1983, 1985; Hilgen, 1991; Rohling, 1994; Lourens *et al.*, 1996; Wehausen and Brumsack, 1998; Foucault and Mélières, 2000]. The effects of increased freshwater supply to the Mediterranean Sea may have been: (1) development of a low-salinity surface layer resulting in reduced deep-water circulation, and (2) delivery of increased amount of nutrients from the continents, supporting increased productivity. These two conditions may explain the formation of sapropels by enhanced preservation of organic matter in anoxic bottom water [e.g. Cita *et al.*, 1977; Thunell *et al.*, 1977; Béthoux, 1993] or by high planktonic production [Pedersen and Calvert, 1990; Calvert and Pedersen, 1992]. A combination of the two processes (water stratification and high productivity) has also been considered [Howell and Thunell, 1992; Rohling, 1994; Sancetta, 1994; Thomson *et al.*, 1999].

The contemporaneous formation of sapropels over the entire eastern Mediterranean (marine and land sections) has been demonstrated [Emeis *et al.*, 2000; Nijenhuis and De Lange, 2000]. However, the facies and duration of sapropel deposition differ between sites. It was shown for instance, that Pliocene sapropels have lasted longer in the part of the basin closest to the Nile [Nijenhuis and De Lange, 2000]. The effects of water depth and diagenesis on the sedimentation and preservation of sapropels have been discussed [Emeis *et al.*, 2000]. The conditions prevailing at great depths during sapropel deposition are well documented. ODP Site 963, located in the strait of Sicily (at a depth of 470 m), is one of the rare shallow sites studied in the literature [Böttcher *et al.*, 2003]. The geochemical characteristics of the organic-rich layers occurring in the sediment at this site indicate the (perhaps temporary) presence of an anoxic water column during their deposition.

Here, we focus on the even shallower Mid-Pliocene rhythmic succession of the land site of Punta Piccola (Sicily). We investigate the nature and geochemical composition (isotope ratios of oxygen and carbon, Ca, Mn, Mg, Fe and Sr concentrations) of the carbonates of this land section and compare the features of this shallow cyclic sequence to those of deeper settings. The redox conditions in the sediment and the water column at the time of deposition of the dark layers at Punta Piccola are examined. The influence of depth on the sedimentary regime is highlighted.

GEOLOGICAL SETTING AND PREVIOUS STUDIES

The Punta Piccola outcrop is a Pliocene cliff section along the southwest coast of Sicily in the Caltanissetta basin at 13°E 37.5°N (fig. 1). It is located near the boundary between the eastern and western Mediterranean basins. A

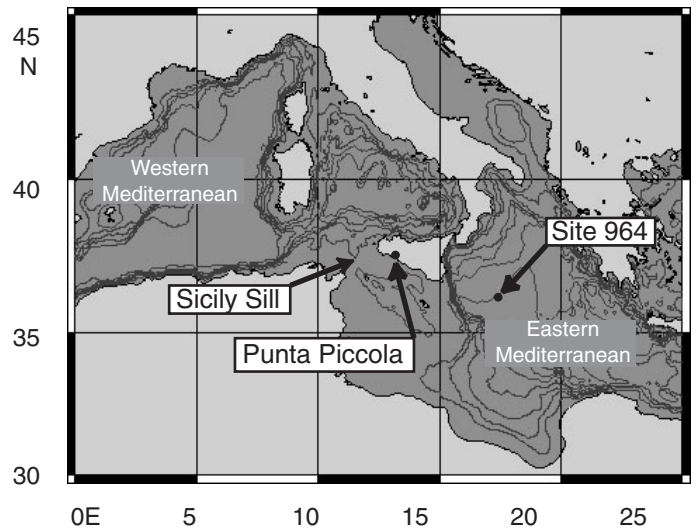


FIG. 1. – Location of Punta Piccola and ODP site 964.

FIG. 1. – Localisation de Punta Piccola et du site ODP 964.

compressional system on Sicily has resulted in a gradual uplift leading to the shallowing and emersion of the Caltanissetta basin during the Pleistocene. The fossil assemblage of this formation indicates that it was deposited at 100 to 400 m water depth [Brolsma, 1978].

The stratigraphic pattern is an alternation of whitish hemipelagic marls and carbonate-poor, brownish marls (subsequently called dark layers; fig. 2). The succession is of Piacenzian age [Cita *et al.*, 1999]. Astronomically calibrated cycles 105 to 108 (2.92 to 3 m.y.) [Langereis and Hilgen, 1991] were assigned to these cyclic sediments. The correspondence to the insolation cycles (i-cycles 280 to 286) [Lourens *et al.*, 1996] is given in figure 2. The couplet thickness averages about 160 cm. The dark colours seem to be caused by ferromanganese oxides, which are abundant in dark layers 105 to 107 [Brolsma, 1978], and by varying proportions of calcite and clay [Foucault and Mélières, 2000]. In the dark layers, the presence of burrows filled with the contrasting cream coloured overlying marls is a proof of the sedimentary nature of the Mn enrichment [Brolsma, 1978]. The dark layers are a little richer in organic carbon than the whitish marls [Combourieu-Nebout *et al.*, 2005]: the concentration of the total organic carbon (TOC; figure 2) is circa 0.2% in the whitish marls and no more than 0.46% in the dark layers. These latter layers are not, strictly speaking, sapropels. They may only have deserved this appellation at the time of their deposition (see § discussion).

X-ray mineralogical studies have demonstrated the cyclic variation of clay mineralogy throughout the section [Foucault and Mélières, 1995, 2000]. The palygorskite and kaolinite show maximum abundance in the whitish marls layers, while smectites and chlorites dominate the clay fraction in the dark ones (fig. 2). This succession is interpreted as resulting from the precession-driven alternation of more or less humid periods on the Mediterranean borderlands. During humid periods (precession minima), abundant rainfall, entailing greater river discharge, was followed by increased smectites and chlorites influx to the sedimentary basin. On the other hand, the enhanced aridity on the African continent during precession maxima resulted in an enhanced accumulation of wind-blown palygorskite and kaolinite.

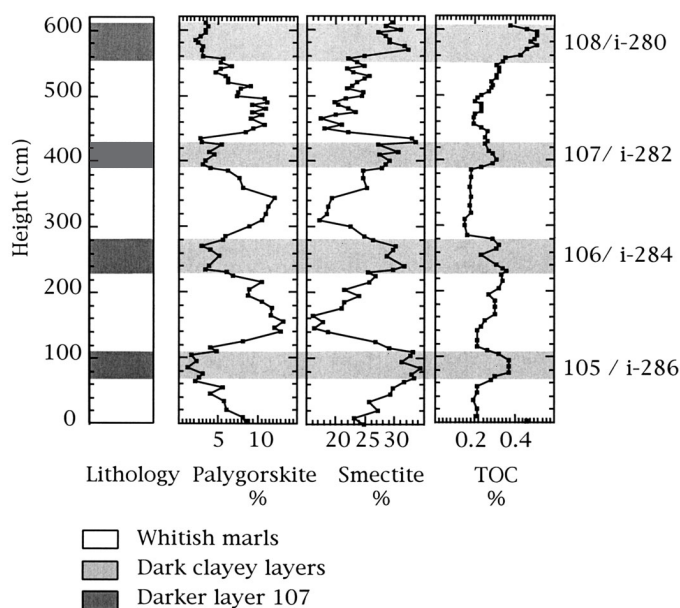


FIG. 2. – Variation with the height of sampling in the cliff section (in cm) of the relative abundance of palygorskite and smectite in the clay fraction [after Foucault and Mélières, 2000], and of the total organic content [after Combourieu-Nebout *et al.*, 2005]. The references to Langereis and Hilgen [1991] astronomical cycles 105 to 108 and to Lourens *et al.* [1996] insolation cycles (i-280 to i-286) are reported at the right of the graph.

FIG. 2. – Variation de l'abondance relative de la palygorskite et de la smectite dans la fraction argileuse [d'après Foucault et Mélières, 2000], et du carbone organique total [TOC; d'après Combourieu-Nebout *et al.*, 2005]. Les références aux cycles astronomiques 105 à 108 de Langereis and Hilgen [1991] et aux cycles d'insolation (i-280 à i-286) de Lourens *et al.* [1996] sont reportés à droite du graphique.

The benthic foraminiferal fauna of the dark layers were shown to be more abundant than those of the whitish marls and their diversity to be lower [Brolsma, 1978]. The epiphytic species *Cibicides pseudoungerianus* is the most abundant species in the whitish marls. In the dark layers, the infaunal species *Bulimina aculeata* (40% of the assemblage in the dark layer 108) or *Bulimina exilis* (50% in the dark layer 107) dominate the assemblage; *Epistominella smithi* and *Bolivina dilatata* form other abundant species in the dark layer 107 [Brolsma, 1978].

MATERIALS AND METHODS

The cliff section investigated here is 615 cm long. It was sampled every five centimetres. To avoid weathering, the samples were collected at a distance from the surface (from 50 to 100 cm), away from veins and cracks. The mineralogy of the bulk sediment was characterised by powder X-ray diffraction.

The acetic acid soluble fractions of 83 samples were analysed for Ca, Sr, Mg, Mn and Fe concentrations according to the procedure developed by Richebois [1990]. The oxygen and carbon isotopic ratios of the carbonate fraction (phosphoric-acid-soluble) of the same samples were determined.

Ca, Sr, Mg, Mn and Fe

Bulk samples were ground in an agate mortar and treated with distilled water for the removal of sea salts. The sediment was subjected to a selective chemical attack using

CH₃COOH (6%, i.e. 1N, pH = 2.4). The suspensions resulting from this digestion were filtered and the dried residues were weighted. After evaporating the filtrates to dryness, HCl (30%) was added and evaporated. The final residues were taken up in HCl 6%. The trace elements and calcium concentrations in the attack solutions were measured on different dilutions by flame AAS on a Hitachi Model Z-8100 Zeeman spectrometer. The measurements were carried out in an air/acetylene flame. Reference solutions were prepared from Titrisol® (Merck) standard solutions with different percentages of Ca, Sr, Mg, Mn and Fe. For trace element measurements, we adjusted the Ca concentrations of the sample and reference solutions to 2,500 ppm. A matching matrix is essential to compensate for the physical and spectral interferences resulting from high Ca concentration in the sample solution.

The analytical precision of the measured values was better than 3% for all elements; this was checked by making use of an in-house standard and by analysing replicate samples (20% of the samples were replicated). The carbonate concentration is calculated as the difference between the weight of the sample and the weight of the dry residues collected in the filters after acetic digestion.

The selective attack we have adopted is expected to dissolve the carbonates but partial dissolution of other phases cannot be completely ruled out. According to Ray *et al.* [1957] dilute acetic acid at low temperature does not attack the lattice structure of clay minerals. For Sutherland *et al.* [2004], the breakdown of an aluminosilicate lattice by acetic acid is limited: for instance, less than 0.2% of the total Al of a road sediment (mineral composition not given) is solubilised. Aluminium occupies the tetrahedral and octahedral sites of clays. The cations in the interlayer position may be more easily solubilised than Al. We may thus expect a slight extraction of the interlayer cations of smectites during the attack by dilute acetic acid.

At pH 5, the acetic acid digestion of sediments does not lead to Mn and Fe oxy-hydroxides dissolution [Gompy, 1997]. The acetic digestion of pelagic sediments under more acidic conditions (25% CH₃COOH, pH = 1.7) leads to a slight dissolution of the iron and manganese crystalline oxides (0.93% of the iron oxide minerals and 1.18% of the manganese oxide minerals of a ferro-manganese nodule) [Chester and Hughes, 1967]. We can thus expect insignificant dissolution of Fe and Mn crystalline oxides during our experiments. Nevertheless, the more soluble amorphous hydrous Fe and Mn oxides may have been partially dissolved.

As the selective attack essentially dissolves the carbonate fraction of the rock, the fraction solubilised by the acetic acid is hereafter referred to as "carbonate fraction" for convenience. As shown above, the acid attack can also result in the solubilisation of a few percent of the cations of the smectites, in particular of those occupying the interlayer positions, and of some amorphous Mn and Fe oxides. Considering the relative proportions of a given cation in calcite, smectites and oxide minerals, this collateral effect may or may not significantly affect the concentration of the element in the attack solution. We thus infer that Sr concentrations cannot be affected and that Mg, Mn and Fe concentrations may be slightly modified. Smectites and Mn-oxides are more abundant in the dark layers than in the whitish marls. Therefore, Mg, Mn and Fe concentrations are

more likely biased in the carbonate fraction of the dark layers. However, the decrease of the iron concentrations in the carbonate fraction of the dark layers (see § Results) demonstrates that the dissolution of iron oxides is limited or non-existent.

Note that the Ca, Sr, Fe, Mg and Mn concentrations (% or ppm) discussed in the “Results” section and reported in figure 3 are the concentrations in the carbonate fraction rather than in the whole rock.

$\delta^{13}\text{C}$ and $\delta^{18}\text{O}$

Carbonates were converted to CO_2 according to the standard method of McCrea [1950]. The bulk powdered samples were transferred into glass reaction tubes that were evacuated for at least 5 hours. This stage was followed by 12 hours of reaction with 100% phosphoric acid at 25°C in a vacuum. The released CO_2 was cryogenically separated from the other gases and measured on a Finnigan Delta E mass spectrometer. Data are reported as per mil (‰) relative to the PDB standard. Replicate analyses and repetitive analysis of the laboratory standard showed a standard deviation of ca. 0.1‰ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$.

RESULTS

Mineral components

The sediment is made up of carbonates, clay minerals, and a few magmatic minerals (bytownite, biotite, quartz, magnetite). The carbonate phase is essentially biogenic calcite. Dolomite crystals are very scarce. The crystallinity of the calcite (deduced from the width at half height of the 104 diffraction peak) is higher in the dark layers, particularly in couplets 106, 107 and 108, than in the marls.

Pyritised burrows and pyrite and/or goethite infillings in foraminiferal tests are observed occasionally in dark layers. Goethite also appears occasionally in some whitish marl.

The X-ray powder patterns from the dark layer 107 indicate that the sediment contains a mixed (Mn, Ca)-carbonate. The interplanar spacing corresponding to the 104 peak,

obtained from X-ray powder diffraction performed on white polyhedrons hand-picked in this layer, is 2.93 \AA . Using the powder diffraction data from the International Center for Diffraction Data, we calculated that this position corresponds to 54 to 47% Mn and 46 to 48% Ca if the diffracting carbonates contain 0 to 5% Mg. The order diffraction peak 015 cannot be detected. We thus conclude that the diffracting mineral is a pseudo-kutnahorite ($\text{Ca}_x\text{Mn}_{1-x}(\text{CO}_3)$). The presence of pseudo-kutnahorite rather than kutnahorite in Punta Piccola sediments is in agreement with the more likely occurrence of the disordered than the ordered (Mn, Ca) – carbonate in the sedimentary environments [Goldsmith and Graf, 1957; Fubini and Stone, 1983; Capobianco and Navrotsky, 1987; Mucci, 1991; Böttcher, 1998].

Biogenous components

The biogenous fraction is dominated by calcareous nanofossils: *Pseudoemiliana lacunosa* and *Reticulofenestra minuta* are the most abundant, followed by *Coccolithus pelageus*; *Discoaster broweri* and *Pentosphaera spp.* are rare. The same assemblage is observed in the marls and in the dark layers [S. Gardin, pers. comm., 2003].

Benthic and planktonic foraminifera are present throughout the section in both marls and dark layers. Ostracodes appear in some whitish marl and in some dark layers. Siliceous biogenous components were not detected. The foraminifera fragmentation and corrosion is moderately to strongly (in dark layer 107) more important in the dark layers than in the whitish marls. In the dark layers, the nanofossils have obviously also suffered dissolution [S. Gardin, pers. comm., 2003].

Geochemistry

The carbonate content of the bulk samples, the concentrations of Sr, Fe, Mg and Mn, and the oxygen and carbon isotope ratios of the carbonate fraction of the samples are depicted as a function of the position of the samples in the cliff section in figure 3. The dominant features are :

– a decrease of the carbonate content from 50-60% in the whitish marls to 30-40% in the dark layers;

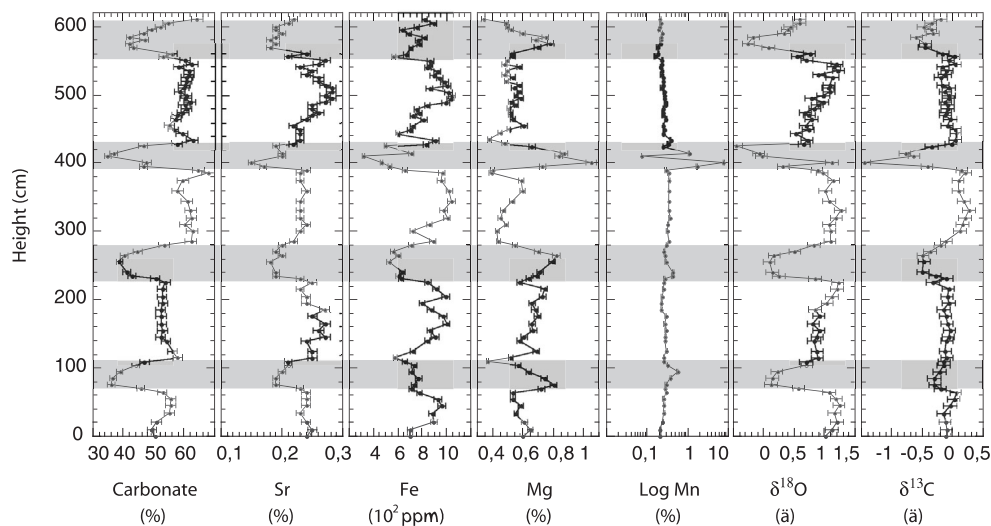


FIG. 3. – Variation with the height of sampling in the cliff section (in cm) of the carbonate content of the bulk rock, of the Sr, Fe, Mg and Mn concentrations in the carbonate fraction (error is $\pm 3\%$), and of the oxygen and carbon isotopic ratios of the carbonate fraction (error is $\pm 0.1\%$).

FIG. 3. – Variation de la teneur en carbonates de la roche totale, des concentrations en Sr, Fe, Mg et Mn de la fraction carbonatée (erreur = $\pm 3\%$), et des rapports isotopiques de l'oxygène et du carbone de la fraction carbonatée (erreur = $\pm 0.1\%$).

– a decrease of the strontium concentrations of the carbonates from 0.25% on average in the whitish marls to 0.15-0.19% in the dark layers;

– a decrease of the iron concentrations of the carbonates from around 1000 ppm in the whitish marls to 600 ppm in dark layers 105, 106 and 108 and down to 400 ppm in the dark layer 107;

– an increase of the magnesium concentrations of the carbonates from about 0.5% in the whitish marls up to 0.8% ppm in the dark layers 105, 106 and 108 and up to 1% in the black layer 107;

– an increase of the Mn concentration of the carbonates in the dark layers 105, 106 and 107; they are around 0.2-0.3% in the carbonates of the whitish marls and of the dark layers 108, and around 0.4-0.5% in those of the dark layers 105 and 106 and up to 7.65% in the carbonates of the pseudo-kutnahorite containing dark layer 107;

– a decrease of the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of the carbonates of the dark layers. The decrease of the $\delta^{13}\text{C}$ value is small in the carbonates of the dark layers 105 ($\Delta\delta^{13}\text{C} \approx -0.2\text{‰}$), 106 and 108 ($\Delta\delta^{13}\text{C} \approx -0.35\text{‰}$), and larger in those of the dark layer 107 ($\Delta\delta^{13}\text{C} \approx -1.5\text{‰}$). The $\delta^{18}\text{O}$ decreases are about 1‰.

DISCUSSION

Redox-conditions in water and sediment

At Punta Piccola, the carbonates of the dark layers (105, 106 and 107) are enriched in Mn compared to those of the whitish marls. Pseudo-kutnahorite has even been found in the dark layer of cycle 107.

Manganese may occur in seawater in three oxidation states: MnII, MnIII and MnIV. The reduced form is the most soluble, and can concentrate in oxygen-deficient water columns. The oxidized ones, less soluble, may accumulate as particulate oxyhydroxides in well-oxygenated environments. The precipitation of Mn-rich carbonates requires high Mn concentrations and high alkalinity in water. Such minerals have been observed in anoxic sediments [Calvert and Pedersen, 1996; Huckriede and Meischner, 1996; Sohlenius *et al.*, 1996; Sternbeck and Sohlenius, 1997; Heiser *et al.*, 2001; Burke and Kemp, 2002; Neumann *et al.*, 2002]. Mn-Ca carbonate precipitation is suggested to occur in anoxic bottom water of the Landsort Deep (Baltic Sea) due to high Mn (II) concentrations and unusually high alkalinity related to high organic matter content [Lepland and Stevens, 1996; 1998]. However, the Landsort Deep may represent an exception. In most cases, Mn-rich carbonate precipitation cannot occur in the water column of modern anoxic basins. Mn concentrations are indeed several fold lower than the dissolved Mn concentration required for the saturation of seawater with respect either to an ordered or disordered mixed Mn-Ca carbonate [Middelburg *et al.*, 1987; Mucci, 1991; Calvert and Pedersen, 1996]. In reference to the solubility constant proposed by Calvert and Pedersen [1996], one can calculate that the presence of Mn-rich carbonates in the dark layers at Punta Piccola implies that the concentration of Mediterranean bottom water reached several hundred μM during anoxic events. The mechanism able to deliver such an amount of Mn is not easy to identify. A more likely hypothesis is that in situ sources

of Mn supplied high Mn concentrations in the pore water of the dark layers sediments, leading to the precipitation of Mn-rich carbonates. The accumulation and burial of Mn particulate oxyhydroxides (provided by an oxygenated water column), followed by their dissolution in the anoxic sediment (in which they are instable) is a likely source of Mn.

A pre-concentration of Mn under oxic conditions was advocated to explain the formation of ancient black shales and ore deposits [Calvert and Pedersen, 1996]. The occurrence of Mn-carbonate-rich anoxic sediments in the Baltic Sea was also related to periods of oxic bottom water conditions (in an otherwise anoxic basin) [Huckriede and Meischner, 1996; Sohlenius *et al.*, 1996; Neumann *et al.*, 1997; Sternbeck and Solenius, 1997; Heiser *et al.*, 2001; Neuman *et al.*, 2002]. The demonstration by Burke and Kemp [2002] of the existence of a causal link between kutnahorite laminae deposition and inflows of oxic saline North Sea water into the brackish Baltic Sea strongly supports this model. Therefore, the presence of pseudo-kutnahorite in dark layer 107, and possibly the high concentrations in the carbonates of the dark layers 105 and 106, must be related to Calvert and Pedersen's [1996] model of Mn oxyhydroxides accumulation. Therefore, we conclude that both the dark layers and the whitish marls were deposited under an oxic water column and that reducing conditions prevailed in the dark layer sediments at the time of their deposition. Oxic bottom water conditions are not those postulated for most of the Mediterranean C_{org} rich layers or sapropels. However, the dark layers of Punta Piccola are not the only exception to the rule. Oxic bottom water conditions have been postulated indeed for the upper part of some Pleistocene sapropels [Calvert and Fontugne, 2001].

The presence of bioturbation (also reported in Brolsma [1978]), ostracodes and benthic foraminifera throughout the Punta Piccola section corroborates the oxic water hypothesis. Ostracodes, indeed, do not suffer prolonged anoxia or even dysoxia [Geiger, 1990]. The benthic foraminifera described by Brolsma [1978] in the dark layers of the Punta Piccola belong to two groups of taxa: *Buliminata* and *Bolivina*, which have surficial infaunal microhabitat, and *Epistominella*, which is an opportunistic epifaunal species [Jorinssen, 1999]. The infaunal organisms typically occur in area with high organic matter input. They have a certain degree of resistance to low oxygen conditions [e.g. Hermelin and Shimmield, 1990; Sen Gupta and Machain-Castillo, 1993; Bernhard and Alve, 1996; Bernhard *et al.*, 1997; Jorinssen, 1999; Fontanier *et al.*, 2002]. They are adapted to the reducing conditions prevailing in the pore water in which they live and they are compatible with an oxygenated water column as shown by Fontanier *et al.* [2002]. On the contrary, the epifaunal taxa are indicative of a sufficiently high oxygen level in bottom water. The interpretation of the benthic foraminifera strongly supports the hypothesis of an anoxic sediment overlain by an oxic water column.

To our knowledge, Mn-carbonates have never been described in the sapropels of the Mediterranean deep settings. These sapropels are even Mn-depleted compared to the interbedded whitish marls [e.g. Pruyssers *et al.*, 1991; Thompson *et al.*, 1995; Nijenhuis *et al.*, 1996; Nijenhuis et De Lange, 2000; Wehausen and Brumsack, 2000; Böttcher *et al.*, 2003]. This observation is in agreement with the sedimentological, geochemical, and palynological evidence demonstrating that basin-wide water-column anoxia occurred

during the formation of Pliocene sapropels in the eastern Mediterranean Sea [Bosch *et al.*, 1998; Nijenhuis *et al.*, 1999; Passier *et al.*, 1999; Warning and Brumsack, 2000; Menzel *et al.*, 2002; Rinna *et al.*, 2002]. The discrepancy between the deep Mediterranean sites and the Punta Piccola land section can be interpreted in terms of different settings. The Punta Piccola sediments were deposited in a shallow marginal context where several processes can efficiently supply oxygen to the water column (O_2 diffusion, photosynthesis, dynamic processes). At the bottom of the oxic water column, the accumulation of particulate Mn-oxyhydroxides supplied the large amount of Mn that was further reduced, dissolved, and concentrated in the anoxic sediment, while in the anoxic water of the deep basins, the concentration of soluble MnII was not possible.

Sources of manganese

The Mn-enrichment during the deposition of the dark layers may originate from various sources : hydrothermal vents, windborne inputs, rivers or seawater. However, the first two sources are unlikely : the cyclic occurrence of the dark layers cannot be the result of hydrothermal activity and the wet climatic conditions during their deposition could not have generated increased windborne input.

The river flow into the Mediterranean is likely higher during sapropel formation and the particulate to dissolved Mn ratio in rivers from the Mediterranean area is high (22 for the Rhône river, Guieu *et al.* [1991]; 49 for the Nile river, Dekov *et al.* [1997]; 61 for the Acheloos river, Dassenakis *et al.* [1997]). Therefore, we suppose that rivers have delivered more particulate Mn to the Mediterranean during the sapropelic events. Compared to the Mn concentrations of the whitish marls, those in dark layers are equivalent in cycle 108, twice as high in cycles 105 and 106, and up to 38 times higher in cycle 107. The data necessary to calculate the Mn budget are not available. However, a 50% increase of the fluvial input [as considered by Nijenhuis *et al.*, 1998] may provide, within a reasonable time, the amount of Mn found in dark layers 105, 106, and *a fortiori* 108. On the contrary, the Mn enrichment in dark layer 107 would probably require an unrealistically long period of river input into the Mediterranean. The study of Pliocene sediments from the eastern Mediterranean led Wehausen and Brumsack [2000] to propose that an export of Mn from the eastern to the western Mediterranean may have occurred during time intervals when sapropels were deposited. This process may also account for the Mn enrichment of the dark layers of the Punta Piccola series, which was deposited in the strait of Sicily at the boundary of the western and eastern Mediterranean basins.

Pristine organic content of the dark layers

The $\delta^{13}C$ values of the carbonates ($\delta^{13}C_{carb}$) derive from the $\delta^{13}C$ of the dissolved inorganic carbon ($\delta^{13}C_{DIC}$) of the surface waters and may be modified during diagenetic processes. Increased input of freshwater, having a relatively light $\delta^{13}C$ signature may lower the $\delta^{13}C_{DIC}$ of Mediterranean seawater [Vergnaud-Grazzini, 1983; Fontugne and Calvert, 1992]. On the contrary, the increase of productivity in surface water, during which ^{12}C extraction by plankton is high, tends to increase the $\delta^{13}C_{DIC}$. Lastly, the decomposition of organic matter (which is $\delta^{13}C$ depleted) in the sediment

lowers the carbon isotopic ratio of dissolved carbon in the porewater. As a result diagenesis tends to lower the $\delta^{13}C$ of marine carbonates [e.g. Nijenhuis and de Lange, 2000].

At Punta Piccola, the $\delta^{13}C$ values of the carbonates are depleted over the dark layers, in particular across layer 107. The analyses were performed on the whole carbonate fraction (see § Method), which makes the interpretation delicate. Few $\delta^{13}C$ analyses of foraminifera are available in the literature for this area and this period. They indicate that the effects of the two first processes (freshwater input and productivity) may not be balanced : (1) the $\delta^{13}C$ values of *G. ruber* show a decrease of 0.5‰ in the dark layer 102 of the Punta Piccola section [Van Os *et al.*, 1994], (2) in Pliocene sapropels of the near deep ODP site 964, 2.9 to 3 my old (i.e. coeval to the dark layers studied here), the values of *G. bulloides* show the same 0.5‰ depletion [Howell *et al.*, 1998].

In Mediterranean sapropels and sapropel-like sediments, the organic matter is mainly of marine origin [e.g. Bouloubassi *et al.*, 1999; Nijenhuis et de Lange, 2000; Böttcher *et al.*, 2003]. Therefore, the $\delta^{13}C_{org}$ of these layers derives from the $\delta^{13}C_{DIC}$. Increased input of freshwater into the Mediterranean should then lower the $\delta^{13}C_{org}$. However, if this were the case, the $\delta^{13}C_{org}$ in Mediterranean sapropelic sediments would be lighter towards the Nile, which is the most important freshwater source in the Mediterranean. Analyses performed on Pliocene sapropels [Nijenhuis and de Lange, 2000], and on the Quaternary sapropel S1 [Ten Haven *et al.*, 1987], show the opposite trend. The eastward tendency towards less negative values may indicate that the light land-derived CO_2 inputs are counterbalanced by gradual ^{12}C depletion, supported by a high productivity, in the west-east Mediterranean surface flow. The depletion of the $\delta^{13}C_{org}$ in the sapropels may therefore be purely diagenetic [Nijenhuis and de Lange, 2000].

By analogy, the $\delta^{13}C$ depletion in the carbonate fraction of the dark layers at Punta Piccola may reflect the incorporation of carbon from decomposed organic tissue in secondary carbonates. In this case, a simple mass balance allows estimation of the proportion of carbon of organic origin in the calcium carbonates as follows :

$$\delta^{13}C_{carb} = \delta^{13}C_{org} \times x_{org} + \delta^{13}C_{ndc} \times (1 - x_{org})$$

Here $\delta^{13}C_{carb}$, $\delta^{13}C_{org}$ and $\delta^{13}C_{ndc}$ denote the carbon isotopic composition measured in the carbonates of the dark layer, that inferred for an organic matter of marine origin, and that inferred for the non diagenetised carbonates, respectively.

If we consider a value of -21‰ for the $\delta^{13}C$ of the organic matter (typical of marine algae) and 0‰ for the non-diagenetised carbonates (identical to the mean ratio of the whitish marls), the peak value at $\delta^{13}C_{carb} = -1.45‰$ (dark layer 107) corresponds to 7% carbon of organic origin in the carbonates. In the dark layers 105 and 108, the $\delta^{13}C_{carb} = -0.35‰$ corresponds to a proportion of 2% of carbon of organic origin.

This result is a rough estimate. As shown above, during the Pliocene sapropelic events, in the Punta Piccola area, the effects of freshwater input on the $\delta^{13}C_{DIC}$ (deduced from foraminifera) tend to dominate those of productivity. Therefore, ascribing the whole deviation of the $\delta^{13}C_{carb}$ to diagenetic processes may lead to overestimating the pristine organic carbon content. Nevertheless, the mineralogical and

geochemical parameters considered in this study are consistent with an enhancement of the diagenetic reactions in the dark layers, likely through the oxidation of large amounts of organic matter (see the following section). The pristine organic contents in the dark layers were most probably higher than the post-diagenetic measured content. Originally, at the time of deposition, the dark layer 107 (and maybe also the dark layers 105 and 108) was a true sapropel. Besides, its C_{org} content is far lower than the contents in sapropels of deep settings. As an example, at the next ODP site 964 (fig. 1), the C_{org} content of sapropel i-282, which is coeval to the dark layer 107, is up to 25% by weight [Nijenhuis *et al.*, 1999].

A trend of increasing C_{org} content with increasing depth has been clearly demonstrated for the Holocene sapropel S1. It reflects the increasing preservation of organic matter due to the decreasing availability of oxygen with depth [Murat and Got, 2000]. Our observations are consistent with this model. It seems that, in the absence of anoxia, sapropels can only be moderately rich in organic carbon.

Early diagenesis in an anoxic sediment and precipitation of Mn-Ca mixed carbonates

In the dark layers, the increased fragmentation and corrosion of foraminifers and nanoplankton, and the improvement of calcite crystallinity (characterized by the width of 104 peak) attest to the dissolution of $CaCO_3$. This feature indicates the enhancement of diagenetic reactions in the dark layers, likely through the oxidation of a large amount of organic matter. The oxidative decomposition of organic matter indeed generates carbonic, nitric and phosphoric acids that titrate CO_3^{2-} [Emerson and Bender, 1981]. This process causes pore waters to be undersaturated with respect to $CaCO_3$, thereby driving the dissolution of the biogenous calcite and supplying Ca^{2+} and alkalinity to the porewater.

At Punta Piccola, the secondary carbonates are Mn and Mg enriched and Sr and Fe depleted. Manganese and iron reduction takes place in organic-rich sediments when oxygen has been consumed. This reaction favours the precipitation of secondary carbonates by the increase of pH and alkalinity [Wilson and Thompson, 1998]. It also provides the large amount of Mn necessary to reach supersaturation with respect to (Mn, Ca) carbonates. Obviously, supersaturation with respect to (Fe, Ca) carbonates was not reached in the pore water of dark layers. The presence of pyrite in the samples favours the hypothesis of rapid precipitation of iron sulphides preventing iron carbonates from reaching saturation. The Mg enrichment of the carbonate fraction of dark layers may have two causes. It can be partly an artefact due to the leaching of smectites during the acetic attack (see "Material and method" section). It may also represent a true Mg enrichment of the secondary carbonates. Such enrichment was also observed for the Mn-rich carbonates of the anoxic sediments of the Baltic Sea and of the Panama basin [Pedersen and Price, 1981; Carman and Rahm, 1997]. The decrease of the Sr concentration in the dark layers is consistent with the classical scheme of Sr-rich biogenic calcite dissolution followed by Sr-poor inorganic calcium carbonate precipitation [e.g. Andreasen and Delaney, 2000].

$\delta^{18}O$ of the carbonate fraction: evidences of fresh water input ?

$\delta^{18}O$ values decrease in the dark layers (fig. 3). However, the Mn peak in layer 107 is associated with a sharp drop of the $\delta^{18}O$ signal towards higher values. MnO_2 are generally enriched in ^{18}O compared to the water in which they form [e.g. Mandernack *et al.*, 1995]. Therefore, their reduction in the anoxic sediment leads logically to ^{18}O enrichment of the porewater. To our knowledge, no appropriate factor for oxygen isotopic fractionation for the kutnahorite-water system is described in the current literature. Golyshev *et al.* [1981] showed that the cationic radius determines the isotopic properties of carbonates and that the mass effect is substantial only for ions with large masses. Basing their argument on Goyshev's demonstration, Neumann *et al.* [2002] assumed only small differences of oxygen fractionation between the calcite-water system and the rhodochrosite-water system. The same reasoning can logically be applied to the Mn-carbonate-water system. The positive $\delta^{18}O$ shift in the carbonates of layer 107 can thus be related to a supply of heavy oxygen from manganese oxyhydroxides.

In the other dark layers, the effect of Mn-oxyhydroxide reduction on the $\delta^{18}O$ signal, if any, is not visible.

The postdepositional diagenetic reactions involving the dissolution of biogenous carbonates and the precipitation of secondary carbonates have likely modified the $\delta^{18}O$ signature of the bulk carbonate. However, recrystallisation causes $\delta^{18}O$ values of bulk carbonate to increase because $\delta^{18}O$ values of biogenous carbonates formed in warm surficial water are lower than the value in equilibrium with the cold pore water. Therefore the negative 1.2‰ shifts of $\delta^{18}O$ in the dark layers cannot be ascribed to early diagenetic reactions.

As sea-surface salinity and $\delta^{18}O$ are correlated at local scale [e.g. Duplessy *et al.*, 1991; Wang *et al.*, 1995; Kallel *et al.*, 1997], the composition of the $\delta^{18}O$ records from planktonic foraminiferal carbonate can be used to determine paleo-sea surface salinity. However, Rohling [1999] demonstrated that in the Mediterranean the temporal salinity/ $\delta^{18}O$ gradients are significantly different from the spatial gradients, which seriously limits the relevance of Mediterranean paleosalinity reconstructions based on oxygen isotope in carbonates. Due to this limitation and to the fact that the $\delta^{18}O$ reported in this study was measured in bulk carbonates, quantitative interpretation of the $\delta^{18}O$ signal cannot be made at Punta Piccola. Qualitatively, however, the $\delta^{18}O$ depletion is consistent with the palynological data of Combourieu-Nebout *et al.* [2005], who observed Prasynophyceae (fresh water algae), an undisputable sign of enhanced terrestrial runoff, in the dark layers of Punta Piccola. More generally, it is coherent with the hypothesis of enhanced freshwater inputs during sapropelic events in the Mediterranean [Rossignol-Strick, 1983, 1985; Hilgen, 1991; Rohling, 1994; Wehausen and Brumsack, 1998; Ariztegui *et al.*, 2000; Foucault and Mélières, 2000; Bar-Matthews *et al.*, 2000; Combourieu-Nebout *et al.*, 2005].

CONCLUDING REMARKS

During the Pliocene, the site of Punta Piccola was situated in a shallow, marginal setting on the Sicily sill. This situation

may explain why our conclusions are different from those obtained by authors who investigated sapropels deposited in deep Mediterranean basins. Whereas numerous studies have concluded to the existence of an anoxic water column during the time of deposition of sapropels, our results indicate that organic carbon-rich sediments can be deposited under oxygenated bottom waters. Therefore, the process responsible for the high pristine C_{org} in the dark layer 107 of Punta Piccola (as calculated from the $\delta^{13}C$) is the increase of organic production resulting from an increased supply of continental nutrients by runoff. Anoxia is not a prerequisite for sapropel formation.

However, the pristine value of C_{org} in this layer is far lower than those of the sapropels cored in deep settings : this difference may illustrate the effect of water column anoxia on the C_{org} richness. Our data tend to indicate that in the absence of anoxia only moderately C_{org} rich sapropels are formed.

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