

A window into eastern Mediterranean productivity conditions over three Pliocene precession-forced climate cycles

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Abstract

Here, we explore the importance of export productivity versus anoxia in the formation of sedimentary layers with enhanced total organic carbon (TOC) content. We use geochemical, sedimentological and micropaleontological records from two SW Sicily outcropping successions, Lido Rosello (LR) and Punta di Maiata (PM), over three mid-Pliocene precession-forced climate cycles (4.7 – 4.6 million years ago [Ma]). Grey marls, deposited during precession minima, show enhanced TOC in both records. We suggest that basin-wide, low-oxygenated bottom-waters, resulting from freshwater-induced stratification during precession minimum, was integral to preserving grey marl TOC. Furthermore, prolonged eastern Mediterranean stratification may have produced a deep chlorophyll maximum (DCM), leading to ‘shade-flora’ dominated productivity. The LR succession displays two unique laminated layers containing enhanced TOC. These laminations do not occur at specific times in the precession cycle or in time-equivalent PM samples. They are likely to have been produced by an intermittent dysoxic/anoxic pool at LR, caused by a local depression, which enhanced TOC preservation. Consequently, the laminations provide a rare window into ‘true’ eastern Mediterranean productivity conditions during precession maxima, as organic matter is typically poorly preserved during these period due to enhanced ventilation. The laminated ‘windows’ indicate that eastern Mediterranean export productivity may not have been significantly lower during precession maxima compared to precession minima, as previously thought. During these periods, productivity conditions are likely to have been comparable to the modern eastern Mediterranean, with a spring-bloom caused by enhanced winter/spring deep-water mixing preceding a summer ‘shade-flora’ bloom caused by a summer-stratification induced DCM.

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A window into eastern Mediterranean productivity conditions over three Pliocene precession-forced climate cycles

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Key Points

- The two Lido Rosello laminated layers are likely caused by an intermittently present dysoxic/anoxic pool which preserved organic material
- The laminated and grey marl layers offer rare insight into Mid-Pliocene eastern Mediterranean productivity during precession minimum/maximum
- Precession minimum, productivity dominated by shade-flora. Precession maximum, productivity composed of a spring-bloom and summer shade-flora

Abstract

Here, we explore the importance of export productivity versus anoxia in the formation of sedimentary layers with enhanced total organic carbon (TOC) content. We use geochemical, sedimentological and micropaleontological records from two SW Sicily outcropping successions, Lido Rosello (LR) and Punta di Maiata (PM), over three mid-Pliocene precession-forced climate cycles (4.7 – 4.6 million years ago [Ma]). Grey marls, deposited during precession minima, show enhanced TOC in both records. We suggest that basin-wide, low-oxygenated bottom-waters, resulting from freshwater-induced stratification during precession minimum, was integral to preserving grey marl TOC. Furthermore, prolonged eastern Mediterranean stratification may have produced a deep chlorophyll maximum (DCM), leading to ‘shade-flora’ dominated productivity. The LR succession displays two unique laminated layers containing enhanced TOC. These laminations do not occur at specific times in the precession cycle or in time-equivalent PM samples. They are likely to have been produced by an intermittent dysoxic/anoxic pool at LR, caused by a local depression, which enhanced TOC preservation. Consequently, the laminations provide a rare window into ‘true’ eastern Mediterranean productivity conditions during precession maxima, as organic matter is typically poorly preserved during these period due to enhanced ventilation. The laminated ‘windows’ indicate that eastern Mediterranean export productivity may not have been significantly lower during precession maxima compared to precession minima, as previously thought. During

these periods, productivity conditions are likely to have been comparable to the modern eastern Mediterranean, with a spring-bloom caused by enhanced winter/spring deep-water mixing preceding a summer ‘shade-flora’ bloom caused by a summer-stratification induced DCM.

Keywords

Mediterranean, Productivity, Anoxia, Preservation, Sapropel, Pliocene

1. Introduction

Periodic discrete layers of black, organic-rich material, known as sapropels, are found in eastern Mediterranean sedimentary sequences throughout the Neogene and Quaternary (Kullenberg, 1952; Olausson, 1961; Vergnaud-Grazzini, 1977; Rossignol-Strick *et al.*, 1982; Hilgen *et al.*, 2003). These layers are associated with an enhanced freshwater influx into the eastern Mediterranean, linked to precipitation intensification in circum-Mediterranean regions (Rossignol-Strick, 1983; 1985; Rohling and Hilgen, 1991; Rohling *et al.*, 2002; Scrivner *et al.*, 2004; Wu *et al.*, 2018). These climate conditions are predominately related to the Milankovitch precessional cycle, whereby perihelion occurs in Northern Hemisphere summer (every ~21 thousand years [ka]) (Rossignol-Strick, 1983; 1985; Rohling and Hilgen, 1991). This enhanced freshwater-input lowers the surface-water salinity and causes stratification in the eastern Mediterranean (Rohling and Hilgen, 1991; van der Meer *et al.*, 2007). The underlying mechanism causing sapropel formation, however, is still debated, giving rise to a contentious debate over the relative importance of export productivity (Calvert, 1963) versus stratification-driven anoxia (Olausson, 1961).

Several suggestions have been proposed for the cause of enhanced primary productivity: 1) a reversal in the vertical flow of nutrient-poor surface-waters and nutrient-enriched deep-waters (Calvert, 1983; Calvert *et al.*, 1992); 2) an increased nutrient supply from enhanced fresh-water runoff (Calvert, 1983); and 3) the development of a deep chlorophyll maximum (DCM) (Rohling and Gieskes, 1989). A DCM develops in stratified regions of the Mediterranean where the freshening of Mediterranean intermediate water at its source in the Levantine basin causes a shoaling of the pycnocline. This leads to an overlap between the pycnocline/nutricline and the base of the euphotic zone, producing a DCM (Rohling and Gieskes, 1989). The DCM scenario as locus for enhanced export production during sapropel formation has been favoured by microfossil studies of foraminifera (Rohling and Gieskes, 1989; Lourens *et al.*, 1992; Corselli *et al.*, 2002), calcareous nannofossils (Castradori, 1993; Corselli *et al.*, 2002), diatoms (Kemp *et al.*, 1999; Corselli *et al.*, 2002), and nitrogen isotope measurements of fossil chlorophyll (Sachs and Repeta, 1999).

Calculations based on a simple two-layered ocean model for the Mediterranean show that the permanent pycnocline between intermediate and surface-waters may have shoaled into the euphotic zone at times of sapropel formation resulting from reduced surface-water salinities (Rohling, 1991). This process would not only account for the incursion of nutrient-enriched intermediate water into the

photic zone to fuel new production by a deep-dwelling algal community, but also reduce ventilation of the deep-waters, thereby facilitating anoxic conditions down from a few hundred meters in the water column (Rohling, 1994). In some highly organic-rich sapropels of Pliocene age, derivatives of isorenieratene were found, indicating that anoxic conditions may have extended into the lower euphotic zone (Passier *et al.*, 1999).

Focusing on samples from a unique setting in Sicily (Fig. 1), we aim to explore preservation and productivity changes in the eastern Mediterranean over three Pliocene (5.3–1.8 Mya) precession-forced climate cycles. Using geochemical, micropaleontological and sedimentological records, we aim to i) better understand the relative role of enhanced productivity vs stratification-driven anoxia in the formation of sedimentary layers with enhanced organic carbon content, and ii) explore the contribution of a DCM to primary productivity in the eastern Mediterranean during periods of precession minima and precession maxima.

2. Environmental Setting

2.1. Geological Setting

Over four kilometres of exposed marine Pliocene sediments can be found as continuous cliff outcrops along the south Sicily coastline. These outcrops cover the lower Pliocene “Trubi” formation with these sediments formed at a 500–800 m water depth (Brolsma, 1978).

The Pliocene Trubi formation sediments show a quadripartite cycle of white limestone, grey marl, white limestone, beige marl, reflecting productivity changes resulting from changing cyclicity (Brolsma, 1978). While the grey marl sediments cannot be strictly defined as sapropels, as their total organic carbon (TOC) content does not exceed 2% (Calvert, 1983), these layers are slightly TOC-enriched (0.1–1.2%) comparative to the white and beige layers (Van Os *et al.*, 1994) and coincide with minimum precession (i.e., Northern Hemisphere summer insolation maximum). These layers are therefore useful for better understanding the processes responsible for sapropel formation.

For this study, Pliocene Trubi sediment samples were taken from two locations of this outcrop: Lido Rossello (LR) and Punta di Maiata (PM), located <2 km apart (Fig. 1). Both span carbonate cycles 29, 30 and 31 of the Trubi Formation (4.7 – 4.6 million years ago [Ma]), defined by Hilgen and Langereis (1989). The LR record contains two intercalations of brownish-rose, finely laminated diatomaceous-enriched limestone layers that are not observed in the time-equivalent PM samples (Brolsma, 1978). The laminated layers’ presence at LR and absence at PM provides the opportunity to compare differences in palaeo-oceanographic conditions and diagenetic processes between both localities in order to shed new light upon the climatic mechanisms causing the astronomically-driven carbonate cycles (Hilgen, 1991; Lourens *et al.*, 1996).

2.2. Oceanographic setting

The Mediterranean Sea has been an elongated satellite basin of the Atlantic

since at least the late Miocene (Rögl and Steininger, 1983). Today, it is one of the world’s most oligotrophic regions (Berman *et al.*, 1984a; 1984b; Azov, 1986; Krom *et al.*, 1991). The modern Mediterranean can be roughly divided into three water masses: Modified Atlantic Water (MAW), found at the surface (50–200 m); Levantine Intermediate Water (LIW) (200–800 m); and Mediterranean Deep Water (MDW), formed in both western and eastern basins (Wüst, 1960; Lacombe and Tchernia, 1972). In the eastern Mediterranean, evaporation is dominant over freshwater-input leading to high-salinity waters which contrast with the inflowing lower salinity Atlantic waters in the western basin. This forms a west to east salinity gradient, driving an anti-estuarine circulation pattern (Wüst, 1960).

There is a large seasonal contrast in water temperatures and vertical mixing of the surface-waters in the Mediterranean (Marullo *et al.*, 1999). During winter, (semi-) permanent eddies in the east (Levantine basin) and deep turbulent mixing or mesoscale cyclonic and anticyclonic gyres in the west (Ionian basin) fertilize surface-waters and cause a deep mixed-layer (Brenner *et al.*, 1991). This leads to enhanced productivity at the surface and a ‘spring-bloom’ (Krom *et al.*, 1992; Ziveri *et al.*, 2000). In the Ionian Basin this ‘spring-bloom’ is dominated by a high abundance of coccolithophores, diatoms and dinoflagellates (Malinverno *et al.*, 2003; 2014; Varkitzi *et al.*, 2020) and a high standing-stock of the planktonic foraminiferal species *G. bulloides*, *G. inflata*, and *G. truncatulinoides* (Pujol and Vergnaud-Grazzini, 1995), which primarily depend on deep convective overturning for their lifecycle (Reichart *et al.* 1998). In summer, the photic zone becomes well-stratified leading to highly oligotrophic conditions in the shallow mixed-layer (~25 m), and eutrophic conditions associated with a DCM at the seasonal thermocline and/or pycnocline (Roussenov *et al.*, 1995; Pujol and Vergnaud-Grazzini, 1995). Primary productivity in the eastern Mediterranean at this time is dominated by ‘shade-flora’ (primarily diatoms) which regulate their buoyancy to move between the euphotic zone and a deeper nutrient source and/or have adapted to low-light conditions (Kemp *et al.*, 1999; 2000). In autumn, the breakdown of summer-stratification causes a ‘dump’ of these shade-flora to the sea-floor (Kemp *et al.*, 2000). Although the growth rate and primary production of ‘shade-flora’ is typically lower than the spring-bloom, the total primary production of summer phytoplankton can be equal to/greater than the spring-bloom, as it occurs over several summer months (Kemp *et al.*, 2000).

3. Materials and Methods

3.1. Sampling

Samples from LR and PM were taken over three campaigns: October 1994, June 1995, and August 1996. Prior to sampling, the weathered surface was removed to expose fresh sediment. Small cores (2.47 cm diameter) were drilled and packaged in aluminium foil. During the 1994 campaign, additional samples for geochemical analysis were removed parallel to the bedding plane using a stainless-steel spatula and placed in small glass jars. All other geochemical

analysis was performed on 5 mm samples scraped off of the drilled cores.

3.2. Geochemical analyses

Freeze-dried sediments were ground in an agate mortar mill and analysed for TOC, total organic nitrogen (TON) using a ThermoScientific Flash EA Delta V Plus IRMS. Temperature for oxidation, reduction and the oven were 900°C, 680°C, and 40°C, respectively. Flow was 100 ml/min. Prior to TOC analysis, inorganic carbon was removed from the sediment using HCl (2 mol), cleaned with bi-distilled water, then freeze-dried. Opal analyses were performed on selected samples, following the method of Müller and Schneider (1993), using a Technicon TRAACS 800 auto-analyzer. A subsample (~250 mg) was digested in HF (10 ml; 40%) and a 10 ml mixture (6.5:2.5:1) of HClO₄ (60%), HNO₃ (65%) and H₂O at 90°C. After evaporation of the solutions (190°C on a sand bath), the dry residue was dissolved in 50 ml 1 M HCl. The concentration of elements Ba, Al, P, S, Fe, Mo, Ti, V, Sc and other various trace elements were measured with an inductively coupled plasma emission spectrometer (ICP-AES: Perkin Elmer Optima 3000) and are expressed in % or parts per million [ppm]. The analytical precision and accuracy were determined by replicate analyses of samples and by comparison with international (BCR-71) and in-house (F-TURB and MM-91) standards. Relative standard deviations, analytical precision, and accuracy were better than 3%. Bulk CaCO₃ content was derived from the % weight of Ca which was obtained through ICP-AES.

Biogenic barium (Ba_{bio}) is a useful proxy of export productivity, defined as the fraction of total Ba not associated with terrigenous material (Calvert, 1983; Paytan and Griffiths, 2007; Schoepfer *et al.*, 2015), calculated using the element's total flux, the sample's Al content, and the ratio of (Ba/Al)_{terrigenous}.

$$\text{Ba}_{\text{bio}} = \text{Ba}_{\text{total}} - \text{Al} * \left(\frac{\text{Ba}}{\text{Al}} \right)_{\text{terrigenous}}$$

An average (Ba/Al)_{terrigenous} value of ~0.0019 was derived from the beige intervals by assuming ~70% of the Ba within these intervals comes from Saharan dust (Van Os *et al.*, 1994).

3.3. Isotope analyses

The ¹³C and ¹⁸O of two planktonic foraminiferal species (*Globigerinoides obliquus* (Bolli) and dextrally-coiled *Neogloboquadrina acostaensis* (Blow)) and one benthic species (*Cibicidoides italicus* (di Napoli)) were measured. Approximately 60 specimens of *G. obliquus* and ~100 specimens of *N. acostaensis* were picked per sample (104 LR samples and 77 PM samples) from the 125 to 595 m fraction, with ~3 *C. italicus* specimens picked per sample (72 LR samples and 39 PM samples) in the >212 m size range. In several samples of the two sections, the size of all specimens of both planktonic species were measured to check the size variability. These measurements indicate that the average size

and standard deviation for the various samples are nearly identical, with an average size of $\sim 310 \pm 50$ μm and $\sim 205 \pm 30$ μm for *G. obliquus* and *N. acostaensis*, respectively. Consequently, we assume that the picked specimens for isotopic measurement are from the same size range.

To remove any organic remains, the picked planktonic foraminifera were heated for 30 minutes at 470°C under vacuum. Parts of the samples were transferred into glass reaction tubes and evacuated for 14 hours, followed by 6 hours of reaction with 103% phosphoric acid at 25°C under high vacuum. The released CO_2 was cryogenically separated from other gases and measured on a VG SIRA 24 mass spectrometer. The remaining planktonic samples were analysed using an ISOCARB directly coupled to the mass spectrometer, reacting with 103% phosphoric acid for 6 to 7 minutes at 90°C. Samples were run alongside 1 international (IAEA-CO-1) and 9 in-house (NAXOS) standards. During each run a linear decrease in the isotopic composition of the NAXOS standards was observed, which varied between 0.05 and 0.2, and 0.1 and 0.4‰ for ^{13}C and ^{18}O respectively. This linear trend is likely related to an increase in the phosphoric acid concentration due to water loss during the analyses, therefore a (linear) correction of the samples was applied using the NAXOS standard as reference. The analytical precision and accuracy were determined by replicate analyses of samples and by the comparison with international (IAEA-CO-1 and NBS-19) standards, with the relative standard deviations, analytical precision, and accuracy better than 0.05 and 0.1‰ for ^{13}C and ^{18}O respectively. The benthic foraminiferal specimens were ultrasonically cleaned and analysed with an automated carbonate reaction device (Kiel III) coupled to a Thermo-Finnigan MAT253. Each sample reacted with 103% phosphoric acid (H_3PO_4) for 7 minutes at 70°C. Calibration to the international carbonate standard NBS-19 revealed an analytical precision better than 0.1‰ and 0.03‰ for ^{13}C and ^{18}O , respectively. All data are reported as per mil (‰) relative to the VPDB standard.

3.4. Micropalaeontological analyses

200 – 400 planktonic foraminiferal specimens were picked from the 125 to 595 μm size fraction (101 LR samples and 49 PM samples). These were mounted on Chapman slides, identified and counted. For each slide, benthic foraminifera, siliceous organisms and palynomorphs were also counted. In some samples, organic compounds of small spherical objects (always wrinkled) were observed. Broelsma (1978) had these forms tentatively identified by G.T. Boalch (Plymouth) as possible representatives of the genus *Pachysphaera* (division Chlorophyta (green algae), class Prasinophyceae (Boalch and Parke, 1971)). In this study, these components have been combined into one category: prasinophytes.

The planktic foraminifera ratio was calculated as follows: Planktonic count/(Benthic + planktonic counts). Micropalaeontological records are presented here using mass accumulation rates ($\# \text{ cm}^{-2} \text{ yr}^{-1}$), calculated using the counts per gram of dry sediment, the sedimentation rate (ka cm^{-1}), and dry bulk density (ρ) (g cm^{-3}) of the sample.

4. Results

4.1. Astronomical tuning and phase relations

As starting point for our chronology, astronomical ages for the midpoints of the grey layers of PM have been taken from Lourens *et al.* (1996). These astronomical ages refer to 3-ka lagged ages of the correlative maxima in the La90_(1,1) summer insolation curve. Additionally, the cyclic variations in the Ti/Al ratio of marine sediments in the Mediterranean can be used to refine the astronomical age model within one cycle, due to the approximately linear response of this proxy to changes in summer insolation (Lourens *et al.*, 2001). From a detailed comparison between the Ti/Al record of ODP 967 spanning 2.4 to 2.9 Ma and the La90 solution (Laskar *et al.*, 1993), Lourens *et al.* (2001) obtained the optimum fit for all La90 solutions including values for the dynamical ellipticity and/or tidal dissipation (with respect to their present-day estimates) ranging from 1.003 and 0 to 0.9997 and 1, respectively. The observed smaller average value for the combined dissipative effects was attributed to the severe glacial cyclicity, which harassed global climate over the last 3 Ma. Presently, it is still unclear if this relationship also holds true for the early Pliocene since large ice caps were absent during that time interval. For the present study the La90_(1,1) summer insolation curve is maintained as target, because this solution yields on average the best fit with the geological record over the last 5.3 Ma (Lourens *et al.*, 1996). Subsequently, our age model is refined for LR and PM by assigning the astronomical ages for maxima and minima in the Ti/Al ratio to their corresponding minima and maxima in the 65°N summer insolation curve (Fig. 2). For ease of reference, a 3-ka time lag was not included as was proposed by Lourens *et al.* (1996).

Additional support for our age model comes from the good agreement between successive high and low amplitude Ti/Al maxima and the precession-obliquity interference patterns displayed in the summer insolation minima of i-cycles 443 to 447 (see also Lourens *et al.* (1996)). This interference is also clearly reflected in the lithological column of PM by a thick-thin-thick alternation of the beige layers. The good similarity between the age models of LR and PM and the quadripartite layering of the Trubi marls is corroborated by the CaCO₃ timeseries of both sections (Fig. 2).

The grey marls are marked by slightly reduced $\delta^{13}C_{org}$, probably due to the more clayey character of the sediment (Fig. 2). The two laminated beds (L5 and L6) are well expressed by very low $\delta^{13}C_{org}$ values. A thin homogeneous marly interval within L5 is indicated by a small $\delta^{13}C_{org}$ increase. From Fig. 2 it is evident that these two laminates are not related to a specific orbital configuration; L6 occurs slightly after a summer insolation minimum (i.e., transition from top beige to base white of cycle 30), while L5 coincides with the transitional interval from a summer insolation maximum to a minimum (i.e., top of grey to mid beige of cycle 29). This in contrast with the grey-coloured marls and associated minima in Ti/Al, which are ultimately-controlled by the astronomical (e.g., summer insolation maxima) perturbations (Lourens *et al.*, 1996, 2001).

4.2. CaCO_3 , TOC and TON

The characteristic quadripartite-layering of the Trubi Formation (De Visser *et al.*, 1989) is clearly indicated by the fluctuations in carbonate content of both the studied sediment records, notwithstanding the exceptional occurrence of the laminated intervals in the LR record (Fig. 2). CaCO_3 concentrations are enhanced in the white layers, have intermediate values in the grey layers and are lowest in the beige layers. The LR carbonate record does not display an aberrant pattern related to the laminated intervals L5 and L6. In both records, TOC and TON content is lowest in the white and beige layers ($\sim 0.08\%$ and $\sim 0.02\%$, respectively) and more enriched in the grey layers (up to 0.30% and 0.04% , respectively) (Fig. 2). In the LR record, the highest values of TOC and TON are found in L5 (up to 0.80% at 4658 ka, and 0.07% at 4659 ka, respectively) and L6 (up to 1.12% at 4633 ka, and 0.07 at 4632 ka, respectively); these values are comparable to those found in the sapropels of the overlying Narbonne Formation (Van Os *et al.*, 1994).

4.3. Trace elements, opal and siliceous organisms

The concentration of opal in the LR record peaks in the lower section of L5, reaching 4% at 4665 ka. Ba_{bio} records from both sites show enhanced concentrations within all grey marls (Fig. 3). In the laminated layers L5 and L6, Ba_{bio} concentrations increase. The largest Ba_{bio} increase occurs in the early part of L5, reaching ~ 800 ppm between 4665 and 4663 ka, which is coeval with a peak in the concentration of molybdenum (Mo) peaking at 33 ppm (Fig. 3). Siliceous organisms (radiolarians, diatoms and silicoflagellates) were found in the L5 interval (see also Zachariasse *et al.*, 1978), reaching a peak of 67215 organisms $\text{cm}^{-3} \text{yr}^{-1}$ at 4664 ka (Fig. 3). The vanadium to scandium ratio (V/Sc) in the LR record shows higher values in the grey marls (~ 10) and in the laminated layers (~ 10 during L6, ~ 12 in the early part of L5, lowering to ~ 9 later in L5), and lower values in the beige and white layers (~ 8). The ratio of iron to aluminium (Fe/Al) is consistently low throughout the PM record (~ 0.5), which is also seen in the LR record, with the exception of slight increases during L6 and the start of L5, with peaks of ~ 0.9 .

4.4. Prasinophytes (green algae)

In both L5 and L6, high abundances of the prasinophyte *Pachysphaera* and some large ($>125 \mu\text{m}$) phycomas of *Pterosperma* (Pouchet) spp. (also of the class Prasinophyceae) were found. Similar to *Halosphaera*, these green algae are pelagic organisms with a vegetative (motile) and an encysted (non-motile) stage (Boalch and Parke, 1971) and are very resistant to chemical or biological degradation (Wall, 1977). The few relevant literature sources on modern prasinophycean algae (*Pachysphaera*, *Halosphaera*, and *Pterosphaera*) and their fossil equivalents (*Tasmanites* and *Leiosphaeridia*) (Boalch and Parke, 1971; Guy-Ohlson, 1988) suggest they primarily occur in marine surface-waters of relatively high northern latitudes (cold) and epicontinental (fresh-water), often

near-shore environments including the Mediterranean Sea (Prauss and Riegel, 1989). The prasinophyte *Halosphaera* has, however, been recorded at depths up to 1000m in the Mediterranean Sea and found living together with diatoms in deep-water algal communities (Kimor and Wood, 1975; Sournia, 1982; Jenkinson, 1986). Their abundance at these depths is highest in autumn, with these organisms rising from deeper to surface-waters during winter and early spring (Parke and Hartog-Adams, 1965; Jenkinson, 1986).

4.5. *Calcareous organisms*

Planktonic foraminiferal shells are well preserved in both records and the identified species/groups are outlined in Supp. Table 1. The relative abundance patterns of the various species display almost identical patterns in both records (Supp. Fig. 1), with small offsets which are attributed to differences in sample resolution. *Globoturborotalita apertura*, *Globigerina falconensis*, and dextrally-coiled *N. acostaensis* are the dominant species, followed by *Globigerinita glutinata* and *G. obliquus*. The less frequently occurring species *Sphaeroidinellopsis seminulina-subdehiscens*, *Globorotalia margaritae* and *Globigerinoides trilobus* appeared to be very useful for confirming the time correlations between LR and PM. *Turborotalita quinqueloba*, *Orbulina universa* and *Globigerinella siphonifera* are reflected by very low percentages. During deposition of the grey layers, sinistrally coiled *N. acostaensis* becomes more abundant relative to its dextrally coiled counterpart. Similar patterns were previously observed within the Trubi marls (De Visser *et al.*, 1989).

The planktonic foraminiferal accumulation rate ($\# \text{ m}^{-2} \text{ ka}^{-1}$) indicates that the flux of all species declined significantly during deposition of the grey layers but remained high within the beige and white layers (Fig. 4). There is an increased accumulation rate of planktonic foraminifera in L6 and at the base of L5. The benthic foraminiferal flux is low and remained rather constant throughout the studied interval and consequently, drops in the P/P+B ratio within the grey layers must therefore be related to the significant drops in the amount of planktonic foraminiferal shells (Fig. 4).

Preliminary nannofossil counts on the samples of LR cycles 29 and 30 shows that the coccoliths are overall not well preserved and are not very diverse (L. Beaufort, pers. comm. 1996). Highest abundances were found for the white layers (not shown).

4.6. *Stable isotopes of planktonic foraminifers*

The two planktonic foraminiferal species investigated for their stable isotopic composition, *G. obliquus* and dextrally-coiled *N. acostaensis*, were present throughout both records. *G. obliquus* is a mixed-layer, oligotrophic, warm water species, and its abundance in the Mediterranean gradually declined during the

Plio/Pleistocene (Lourens *et al.*, 1992; 1996) before becoming extinct (Parker, 1973; Berggren and Amdurer, 1973). All living representatives of *Neoglobobadrina* belong to one biogeographic cline (Srinivasan and Kennett, 1976), which feed exclusively on phytoplankton (Hemleben *et al.*, 1989) near or below the (seasonal) thermocline (~25 to 100 m) in association with maximum chlorophyll concentrations (Fairbanks *et al.*, 1982; Ravelo *et al.*, 1990; Ravelo and Fairbanks, 1992; Sautter and Thunell, 1991). In the present-day eastern Mediterranean, *N. pachyderma* (dex) occurs in low abundances and in some areas it might be associated with a DCM (Dowidar, 1984). We assume that *N. acostaensis* (dex) had a similar feeding strategy as its modern representatives, inhabiting the thermocline in seasonally productive regions (Lourens *et al.*, 1992). The benthic foraminifera species investigated for its stable isotopic composition, *C. italicus*, is an epifaunal species endemic to the Mediterranean basin, living at the sediment surface (Sprovieri *et al.*, 1990).

At both sites, the ^{18}O records of both planktonic species display similar a pattern and values (Fig. 5). The ^{18}O record of both species closely follow Northern Hemisphere summer insolation (65°N): minimum ^{18}O coincide with maximum summer insolation and grey layer deposition, while maximum ^{18}O values coincide with minimum summer insolation and the beige layer deposition. While both records show similar patterns, the *G. obliquus* record shows more negative values (~1.3‰) compared to *N. acostaensis*. This is in part caused by their different depth habitats and confirms the assumed vertical distribution pattern of both species within the photic zone (Williams *et al.*, 1979). The covariation of these records suggests both species thrived at approximately the same time of the year, implying that their difference in oxygen isotope composition can be used to reconstruct variations in the thermocline structure (i.e., summer to autumn) (Ravelo and Fairbanks, 1992). The greatest oxygen isotope difference between the mixed-layer and the thermocline ($^{18}\text{O}_{\text{m-t}}$), as shown by *G. obliquus* and *N. acostaensis*, occurs in the grey layers, while the beige layers display the smallest difference (Fig. 6). Furthermore, $^{18}\text{O}_{\text{m-t}}$ is similar at PM and LR, throughout the record.

The ^{13}C records of both planktonic species display very similar patterns at both sites, with the exception of the laminated intervals L5 and L6 which show small negative excursions in *N. acostaensis* ^{13}C (~0.3‰). The ^{13}C of both species, however, varies between the two sites; there is a systematic shift towards more positive values in the PM record compared to LR for both species (0.25‰ and 0.15‰ for *G. obliquus* and *N. acostaensis*, respectively). *N. acostaensis* ^{13}C shows a very similar pattern to the insolation record, with minimum ^{13}C coinciding with maximum summer insolation and grey marl deposition and maximum ^{13}C coinciding with minimum summer insolation and beige layer deposition. *G. obliquus* ^{13}C shows a similar relationship with summer insolation in the early part of both records, but this breaks down after ~4.62 Ma with ^{13}C continuously declining until 4.60 Ma. Despite similar patterns in ^{13}C of both planktonic species, *G. obliquus* displays more positive values (+1.3‰) than *N. acostaensis*, which is also likely the result of their different depth habitats

(Kroopnick, 1985). The carbon isotope difference between the mixed-layer and the thermocline ($^{13}\text{C}_{\text{m-t}}$), as shown by *G. obliquus* and *N. acostaensis*, varies throughout the record (Fig. 6) with the smallest difference shown in the white layers and the largest difference occurring in L5 ($\sim 2.0\text{‰}$), although this is not shown in the time-equivalent PM samples.

At both sites, ^{13}C of benthic species *C. italicus* displays similar patterns, with a clear depletion in ^{13}C in the grey layers (-1.0‰) compared to the rest of the timeseries (Fig. 5). With regards to the stable oxygen isotope record of *C. italicus*, the two sites do not show a similar pattern. In the LR record, two carbonate cycles (30 and 31) display an increase in $^{18}\text{O}_{\text{C. italicus}}$ in the grey layers. The PM record, however, shows no distinct pattern between the layers, but does generally display lower $^{18}\text{O}_{\text{C. italicus}}$ values compared to that of the LR site (-0.3‰). The low-resolution of both the *C. italicus* ^{18}O and ^{13}C records in the laminated layers of the LR record prevent a thorough analysis of these intervals.

5. Discussion

5.1. Possible causes of the laminated intervals at the LR site

The two laminated diatomaceous-enriched limestone layers observed in the LR record are not present in the time-equivalent samples at PM. While L5 coincides with declining summer insolation (65°N) and the deposition of white and beige layers in the PM record, L6 coincides with minimum summer insolation (65°N) and the upper section of a beige layer in the PM record.

Sediments under high productivity areas are known to contain elevated concentrations of organic matter (Pederson and Calvert, 1990; Canfield, 1994), biogenic and diagenetic phosphate (e.g., Burnett, 1977; Froelich *et al.*, 1988), and barite-barium formed in micro-environments containing decaying organic matter (e.g., Bishop, 1988; Dehairs *et al.*, 1980; Dymond *et al.*, 1992). Both laminated intervals are characterised by elevated concentrations of Ba_{bio} and TOC, indicating enhanced palaeo-productivity conditions during deposition of these layers (Tribovillard *et al.*, 2006; Schoepfer *et al.*, 2015). A localised increase in primary productivity conditions may be inferred from higher ^{13}C of surface-dwelling *G. obliquus* and the enhanced carbon isotope gradient between the mixed-layer and thermocline ($^{13}\text{C}_{\text{m-t}}$) that occurred during the deposition of L5 (Fig. 6), which is suggested to indicate enhanced surface-ocean productivity and an intensified oxygen minimum zone below the surface (Shackleton, 1985; Corfield and Cartlidge, 1992).

It is possible, however, that these primary productivity conditions occurred over the wider region and were preserved only at LR because of a local depression. Such a depression may have led to the intermittent presence of a stagnant dysoxic/anoxic pool at LR which contained high levels of dissolved silica and barium (Bjorklund and De Ruiter, 1987; De Lange *et al.*, 1990; Erba, 1991). The preservation of opaline skeletons is a rare occurrence in Mediterranean sediments as these waters are highly undersaturated in silica (Kemp *et al.*, 1999),

but this dysoxic/anoxic pool may have acted as a geochemical buffer, leading to the preservation of siliceous skeletons as seen in L5 (Fig. 3), and the enhanced preservation of opal, TOC and Ba_{bio} in both laminated layers. Redox-sensitive elements in the record are consistent with this theory. The first of these is V; the ratio of V/Sc is a useful proxy for bottom-water oxygen conditions, with values <9.1 , as seen in our laminated intervals (Fig. 3) indicating dysoxia/anoxia (e.g., Emerson and Husted, 1991; Calvert and Pedersen, 1993; Gallego-Torres *et al.*, 2007). This is further supported by the presence of the redox-sensitive element Mo in L5 (Fig. 3), which is found in higher concentrations in anoxic sediments (e.g., Emerson and Husted, 1991; Calvert and Pedersen, 1993; Crusius *et al.*, 1996; Nijenhuis *et al.*, 1999; Algeo & Lyons, 2006; Scheiderich *et al.*, 2010). Finally, Fe/Al values >0.6 in the sedimentary record are interpreted as representing euxinic bottom-water conditions, whereby Fe_2^+ reacts with dissolved sulfide to form Fe sulfide minerals that are then preserved in the underlying sediments, leading to increased Fe/Al and S (Canfield *et al.*, 1996; Lyons and Severmann, 2006; Scheiderich *et al.*, 2010; Azrieli-Tala *et al.*, 2014). This pattern is seen here in our LR records, with corresponding peaks in Fe/Al and S occurring in both laminated intervals and values of the former exceeding 0.6 (Fig. 3). In the time-equivalent samples of the PM record, Fe/Al and S are significantly lower and do not show the same increase. This indicates that conditions in the LR depression may have been euxinic as well as dysoxic/anoxic during the deposition of the laminated sediments.

These dysoxic/anoxic conditions at LR may also explain the $^{13}C_{m-t}$ increase in L5 which is not present in the time-equivalent samples of the PM record. The smaller $^{13}C_{m-t}$ in the PM record may instead be an artefact of enhanced carbonate dissolution resulting from aerobic conditions (Berger and Soutar, 1970), while L5 may record the ‘true’ productivity conditions at this time. The removal of the outer layer of planktonic foraminifera shells through carbonate dissolution can increase the ^{13}C signal (Berger and Killingley, 1977), with the rate of dissolution affected by species morphology (Regenberg *et al.*, 2013). This may explain the higher *N. acostaensis* values in the time-equivalent PM samples, as this species may be more prone to dissolution, while *G. obliquus* may be more resistant to dissolution, leading to similar $^{13}C_{G. obliquus}$ values at both sites during this period.

A slump level directly below the first laminated interval (Brolsma, 1978) possibly reflects the formation of a small physical depression at the LR site. It is possible that while this depression was present at LR throughout this period, local bottom-water circulation patterns determined the oxygenation of this pool. During the deposition of the laminated layers, it is possible that localised changes led to poor ventilation in the pool, causing anoxic, sulfidic conditions, despite a well-ventilated water column above (illustrated in Fig. 7a). The absence of benthic organisms in both laminated layers of the LR record, but their presence during the same period of the PM record also indicates dysoxic/anoxic conditions at LR. At PM, bottom-waters at these times are likely to have been well-oxygenated and undersaturated with respect to barium and silica, shown

by the lower concentrations of TOC and Ba_{bio} and absence of siliceous opaline skeletons. Considering the sediment accumulation rate (SAR) at LR during these intervals, these conditions would have had to remain for decades to prevent opal removal from the top 2-3 cm of sediments and enable the deposition of sediment above.

Consequently, it is possible that export productivity was homogenous across the region during these intervals and the productivity conditions recorded in L5 and L6 did not differ from those during the deposition of the time-equivalent layers in the PM record. Instead, dysoxic/anoxic bottom-waters at LR containing high levels of dissolved silica led to the enhanced preservation of organic matter and carbonate fossil geochemical signatures, and the preservation of opaline skeletons of siliceous plankton. Consequently, the laminated layers at LR may offer rare insight into the productivity conditions that occur during insolation minimum (beige marls) and insolation maximum (grey marls).

Within the L5, there is a difference between the Ba_{bio} and TOC concentrations in the upper and lower sections. The upper (lower) section displays reduced (increased) Ba_{bio} concentrations despite a higher (lower) TOC content. L6 also demonstrates lower Ba_{bio} concentration than L5 despite a higher TOC content, and lacks diatoms (H. Schrader, pers. comm. 1995). This could have been the result of reduced SAR during the deposition of L6 and the upper section of L5 (Fig. 2), which led to longer exposure of the upper sediments and consequently the dissolution of barium (Schoepfer *et al.*, 2015) and opal. Another possibility, however, is that anaerobic degradation of organic matter took place during or soon after deposition of laminates L6 and L5. This may have led to barium mobilization and the destruction siliceous organisms in L6 and the upper section of L5 (Brumsack, 1986; Trefry and Klinkhammer, 1988; Van Os *et al.*, 1991), whilst simultaneously enriching siliceous organisms and barium within the lower section of L5.

5.2. Paleooceanographic conditions during the deposition of the beige and white layers

The background conditions (CO_2 concentrations, global ice volume, and Northern Hemispheric summer insolation) during the deposition of the beige marls of the Trubi formation ($\sim 4.7 - 4.6$ Ma) were remarkably similar to present day (Tiedemann *et al.*, 1994; Shackleton *et al.*, 1994; Pagani *et al.*, 2010). This implies comparable climatic and paleooceanographic conditions at the time of their deposition to the contemporary eastern Mediterranean.

The maxima in Ti/Al in the beige layers (seen in both LR and PM records) indicates that the primary source of terrigenous material in these layers is aeolian, transported from the north African continent (Wehausen and Brumsack, 1999; 2000). The relatively high ^{18}O of the surface-waters (shown by both planktonic species; Fig. 5) points to a lower influx of freshwater and/or lower surface-water temperatures compared to periods of grey marl deposition. This

indicates increased aridity, reduced soil moisture and vegetation cover in North Africa resulting from the precession maxima (Larrasoana *et al.*, 2003). The reduced oxygen isotope gradient ($^{18}\text{O}_{\text{m-t}}$) between the mixed-layer and thermocline (shown by *G. obliquus* and *N. acostaensis* ^{18}O , Fig. 6) indicates enhanced ventilation of the eastern Mediterranean compared to insolation maxima and the deposition of the grey marls (Fig. 7b and c). This is much like modern eastern Mediterranean conditions whereby vertical mixing is enhanced in the winter and surface-water stratification is confined to summer months (Krom *et al.*, 1992).

The low levels of TOC and Ba_{bio} in the beige marls may point to reduced export productivity resulting from reduced nutrient availability in the photic zone (Van Os *et al.*, 1994; Tribovillard *et al.*, 2006; Schoepfer *et al.*, 2015). The insight gained from the laminated layers, however, may challenge this interpretation. If L5 and L6 do indeed provide insight into the ‘true’ productivity conditions during the deposition of the beige marls, export productivity may actually have been higher than previously acknowledged during these periods, but this signal is not typically preserved in the sedimentary record due to oxic bottom-waters caused by enhanced winter vertical mixing. In L6 and upper L5 (which coincide with precession maxima and the deposition of beige layers at PM), organic carbon levels are relatively high, pointing to significant export productivity. The increase in $^{13}\text{C}_{\text{m-t}}$ during L5 also points to enhanced primary productivity (Shackleton, 1985; Corfield and Cartlidge, 1992). The minimum CaCO_3 values in both the beige marls and laminated layers at this time may indicate that calcareous organisms did not dominate primary productivity, but instead siliceous organisms played a significant role, as shown by the presence of siliceous skeletons and opal in the laminated layers.

Today, in addition to the ‘spring-bloom’ that results from deep turbulent mixing during winter months, a summer bloom of ‘shade-flora’ diatoms can occur in areas like the Mediterranean, which exhibit a strong seasonal thermocline and nutricline during the summer. Many diatom species are able to generate substantial production at depth beneath oligotrophic surface-waters (Kemp *et al.*, 2000). These large, relatively slow growing diatom species, including *Thalassiothrix longissima* (a mat-forming species (i.e., Bodén and Backman, 1996)) and some *Coscinodiscus* spp., may represent ‘shade-flora’ that have adapted to i) grow in symbiosis with nitrogen-fixing cyanobacteria under low-light conditions and/or ii) regulate their buoyancy to move between a deep nutrient source and the euphotic zone (Kemp *et al.*, 2000; Kemp *et al.*, 2006; Kemp and Villareal, 2013). During autumn and/or winter mixing, stratification will break down, causing as much, or in some cases even more, export production (the autumn ‘dump’) than during the spring-bloom (Kemp *et al.*, 2000). In particular, nutrients from intermediate layers can be upwelled, through isopycnal or diapycnal mixing, to the photic zone, thereby stimulating diatom production. Consequently, these laminated layers indicate that biomass blooms were not confined to late winter/early spring. Instead, these layers likely record two annual primary productivity blooms. The first of these is the winter/spring-

bloom, dominated by calcareous organisms, when vertical turbulence fertilised the surface-ocean and deepened the mixed-layer, and/or Saharan dust fertilised the surface ocean (Rutten *et al.*, 2000). The second of these is a summer bloom, dominated by siliceous ‘shade-flora’. This theory may be supported by the presence of prasinophytes in L5 and L6 which today are found living together with diatoms in these deep-water algal communities related to nutrient-rich, cold waters (Kimor and Wood, 1975; Sournia, 1982; Jenkinson, 1986; Prauss and Riegel, 1989).

Finally, the white limestone layers correspond with increasing (white to grey layers) or decreasing (white to beige layers) input of riverine terrigenous material relative to aeolian terrigenous material (as shown by the Ti/Al record). These layers occur as Northern Hemisphere summer insolation is increasing (declining) from minimum (maximum) to maximum (minimum) values. The maximum CaCO_3 content suggests that calcareous primary producers (i.e., coccolithophores) dominated primary productivity which may point to oligotrophic conditions as these organisms thrive in low-nutrient environments (Ziveri *et al.*, 2000; Malinverno *et al.*, 2003). With decreasing summer insolation at this time, summer-stratification may not have been strong enough to allow for the summer ‘shade-flora’ bloom, and therefore these layers represent transitional conditions in the eastern Mediterranean (Van Os *et al.*, 1994), where calcareous organisms were the dominant primary producers.

5.3. Formation of the grey layers: Palaeoproductivity vs. anoxia

The minimum Ti/Al values within the grey marls demonstrate a larger contribution of riverine sourced terrigenous material during these periods of maximum Northern Hemisphere summer insolation (65°N) (Van Os *et al.*, 1994; Lourens *et al.*, 1998; Wehausen and Brumsack, 1999) while the lowered oxygen isotope composition of the mixed-layer and thermocline (as record by the *G. obliquus* and *N. acostaensis*) point to an enhanced input of ^{16}O -enriched monsoonal freshwater into the eastern Mediterranean basin caused by the precession index reaching minimum values (Rossignol-Strick, 1983; 1985; Emeis *et al.*, 2003; Rohling *et al.*, 2006) and/or elevated sea-surface temperatures. Furthermore, the decline in ^{13}C of the mixed-layer and thermocline dwelling planktonic species, *G. obliquus* and *N. acostaensis*, also points to an enhanced supply of ^{12}C -enriched freshwater (Fontugne and Calvert, 1992), while the depleted ^{13}C values of the benthic species, *C. italicus*, at this time likely reflects the lighter isotopic signature of the planktonic organisms reaching the sediment from the upper water column. Our planktonic ^{18}O records show an enhanced oxygen isotope gradient between the mixed-layer and thermocline which points a strong (summer) surface-water stratification resulting from the enhanced monsoonal input of freshwater (Rossignol-Strick, 1983; 1985; Rohling and Hilgen, 1991; van der Meer *et al.*, 2007). The benthic ^{18}O shows no obvious pattern in the grey layers, although the ^{18}O values are higher than those of both planktonic species. This is not unique to the grey layers and is seen throughout the records, likely due to the lower temperatures and higher salinities that characterise deep-waters (Pierre, 1999).

Consequently, like previous sapropel research, these records show enhanced stratification during summer insolation maxima and grey marl deposition (Fig. 7c). At this time, the TOC and Ba_{bio} concentration was also enhanced, but whether this is the result of increased productivity and/or enhanced preservation caused by anoxia needs to be explored here further.

The presence of benthic foraminifera throughout the grey marls of both records indicates that bottom-waters were not completely anoxic during their deposition (Rohling *et al.*, 1993; Schmiedl *et al.*, 2003; Friedrich *et al.*, 2006). As the sediments of the Trubi formation were deposited in the mesopelagic zone (500 – 800 m), it is possible that there was still some ventilation at this depth, despite a significant reduction in vertical mixing, driven by the enhanced stratification (Fig. 7c). Conditions at these sites may have been suboxic, with these benthic organisms representing low-oxygen tolerant species (Rohling *et al.*, 1997). V/Sc ratios are also slightly higher in these layers, with values exceeding 9.1, indicating low bottom-water oxygen conditions which may have led to enhanced preservation of organic matter (e.g., Emerson and Huested, 1991; Calvert and Pedersen, 1993; Gallego-Torres *et al.*, 2007).

Based on this information, it is possible that there was significant export productivity during the deposition of the grey layers, in combination with enhanced preservation. This preservation was likely caused by suboxic bottom-waters which were generated by reduced ventilation resulting from freshwater-induced stratification. This then led to the enhanced TOC and Ba_{bio} signature of these layers. The reduced surface-water salinity will have led to the shoaling of the pycnocline into the euphotic zone leading to the formation of a DCM and oligotrophic surface-waters (Rohling, 1991). The low levels of $CaCO_3$ and reduced flux of planktonic foraminifera at this time point to a significant drop in carbonate productivity in the upper ocean (Van Os *et al.*, 1994). Consequently, primary productivity was likely dominated by siliceous ‘shade-flora’, adapted to oligotrophic conditions (Kemp *et al.*, 1999; 2000). The preservation of these opaline skeletons has been shown to be highly variable within sapropels (Van Os *et al.*, 1994; Kemp *et al.*, 1999) and the suboxic bottom-water conditions and silica undersaturation (as seen in the modern Mediterranean) at this site during the time of deposition of the grey marls may have prevented the preservation of siliceous organisms in our records. Despite the freshwater-induced stratification, some vertical mixing must have occurred during these periods to enable the survival of benthic organisms and to supply sufficient nutrients to the DCM for primary productivity. We argue, however, that without the deep winter mixing that occurs in the modern Mediterranean, two important processes which today contribute significantly to export productivity, will not have occurred: i) the annual fertilisation of the upper water column that leads to the spring-bloom, and ii) the autumn ‘dump’ of the slow-growing ‘shade-flora’ produced in the DCM. Furthermore, the reduced influx of minerals and iron to the eastern Mediterranean, supplied by Saharan dust may have also have significantly affected nutrient availability in the surface-ocean (Foucault and Mélières, 2000; Larrasoana *et al.*, 2003). As a result of this sustained stratification and olig-

otrophic surface-waters, nutrients and minerals will have been heavily recycled within the nutricline.

While previous research suggests that export productivity was significantly enhanced during precession minima compared to other periods of the precession cycle (e.g., Lourens *et al.*, 1992; Wehausen and Brumsack, 1999; Calvert and Fontugne, 2001), the laminated layers at LR contest this view. These layers may provide a ‘window’ into the ‘true’ productivity conditions during precession maxima and show that export productivity was not significantly reduced during precession maxima (the deposition of the beige marls) comparative to precession minima (i.e., the deposition of the grey marls). The enhanced organic matter content of the grey marls is influenced by both increased export productivity and enhanced preservation caused by lower bottom-water oxygenation resulting from freshwater-induced stratification.

6. Conclusions

- The laminated layers in the LR record are thought to be caused by a local depression at this site with the intermittent presence of a stagnant dysoxic/anoxic pool. The latter resulted in the preservation of organic matter and siliceous opaline skeletons.
- The productivity signal preserved in L5, L6, and the grey marls offers rare insight into productivity conditions during sediment deposition in the eastern Mediterranean during precession maximum (beige marls) and precession minimum (grey marls). The productivity signal preserved in the beige marls offer particularly valuable insight into conditions during a precession maximum, as bottom-waters are typically well-ventilated and undersaturated in silica during these periods, leading to poor preservation of organic matter and siliceous materials.
- The productivity conditions in this region during beige layer deposition are likely to be comparable to those of the modern eastern Mediterranean. The large seasonal contrast in vertical mixing of the upper water column during these periods plays an important role in export productivity. Enhanced deep-water mixing during winter and spring leads to a spring-bloom, while the summer-stratification induced DCM leads to a ‘shade-flora’ bloom which is deposited to the sea-floor in autumn during stratification break-down.
- During grey marl deposition, increased freshwater-influx into the Mediterranean (forced by precession minimum) led to enhanced, prolonged eastern Mediterranean stratification and DCM formation, resulting in export productivity dominated by ‘shade-flora’. In addition to enhanced export productivity during these intervals, suboxic bottom-water conditions, caused by freshwater-forced stratification, also played an important role in preserving the geochemical signals in these grey marls.
- While preservation in eastern Mediterranean sedimentary sequences is typ-

ically higher during precession minimum than precession maximum, the enhanced preservation in both laminated layers indicate that export productivity may not have been significantly lower during precession maximum compared to periods of precession minimum.

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Author contribution

LJL performed the sample collection of the Trubi sediments. IAN conducted the trace element analysis and produced the opal and TOC records. GJDL supervised the geochemical analyses and their interpretation. LJL provided the age model. AC produced the TON records. AC and LJL performed the overall data analysis and writing of the manuscript. All co-authors provided feedback on the manuscript.

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Figures

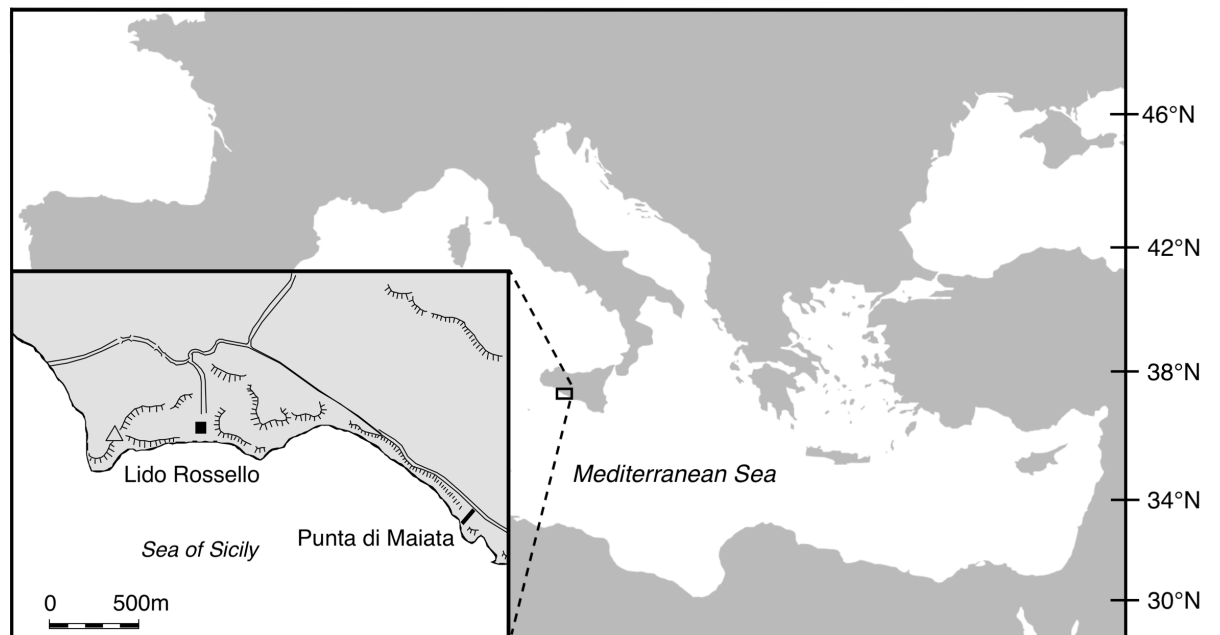


Figure 1: Map showing the two locations from which samples of the Pliocene Trubi sediments were taken: Lido Rossello (LR) and Punta di Maiata (PM). Both records span three carbonate cycles (29, 30 and 31) of the Trubi Formation

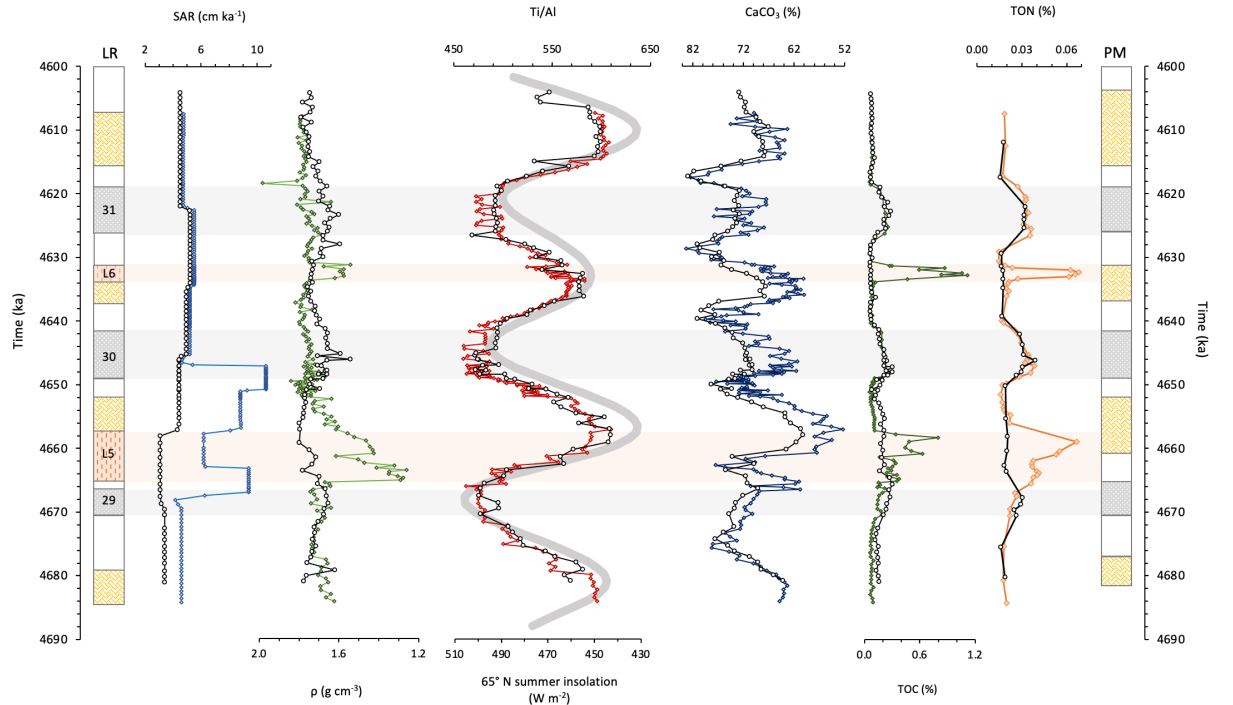


Figure 2: Changes, over three precession forced climate cycles (4690 – 4600 ka), in: sediment accumulation rate (SAR; cm ka^{-1}); dry bulk density (ρ) (g cm^{-3}); Ti/Al; CaCO_3 (%) note reverse scale; TOC (%); TON (%) in the SW Sicily records of LR (coloured lines with filled diamond markers) and PM (black lines with open circle markers). Change in summer insolation at 65°N (grey line; Berger and Loutre, 1991).

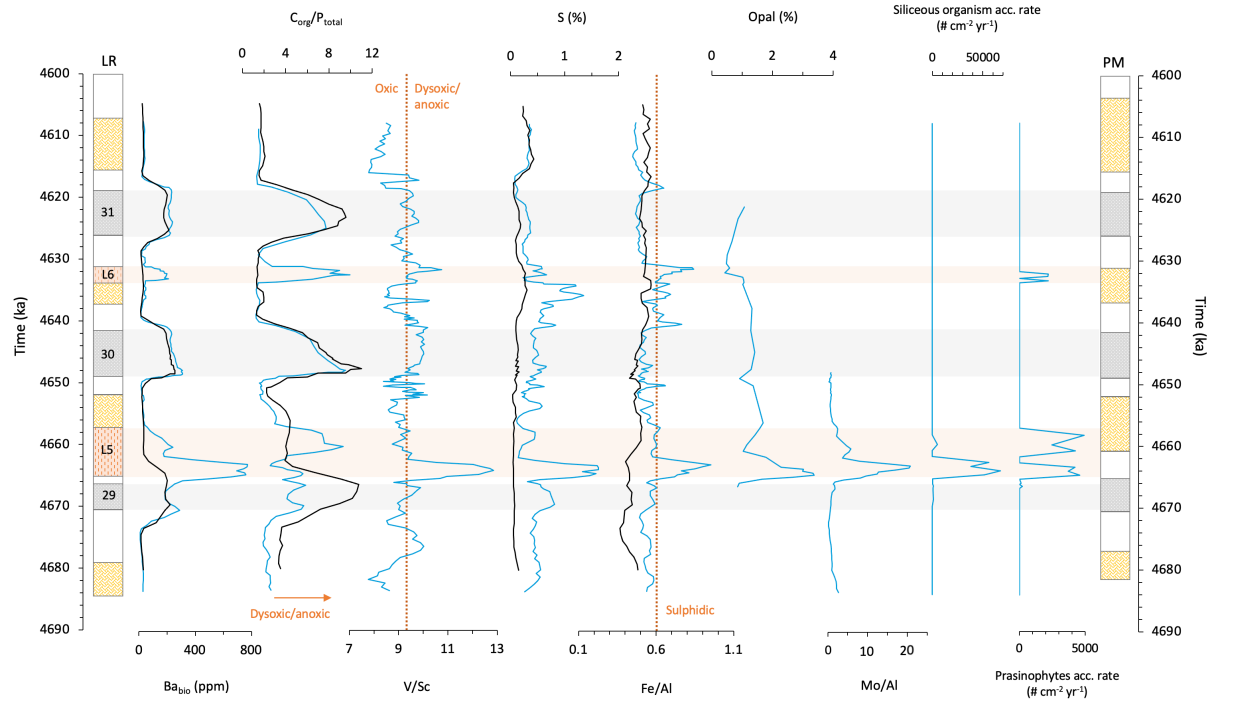


Figure 3: Changes, over three precession forced climate cycles (4690 – 4600 ka), in: Ba_{bio} (ppm); C_{org}/P_{total} ; V/Sc; Sulphur (%); Fe/Al; Opal (%); Molybdenum (ppm); Siliceous organism acc. rate ($\# \text{ cm}^{-2} \text{ yr}^{-1}$); Prasinophyte acc. rate ($\# \text{ cm}^{-2} \text{ yr}^{-1}$); in the SW Sicily records of LR (blue lines) and PM (black lines). All elements and ratios are displayed using a 3-point moving average.

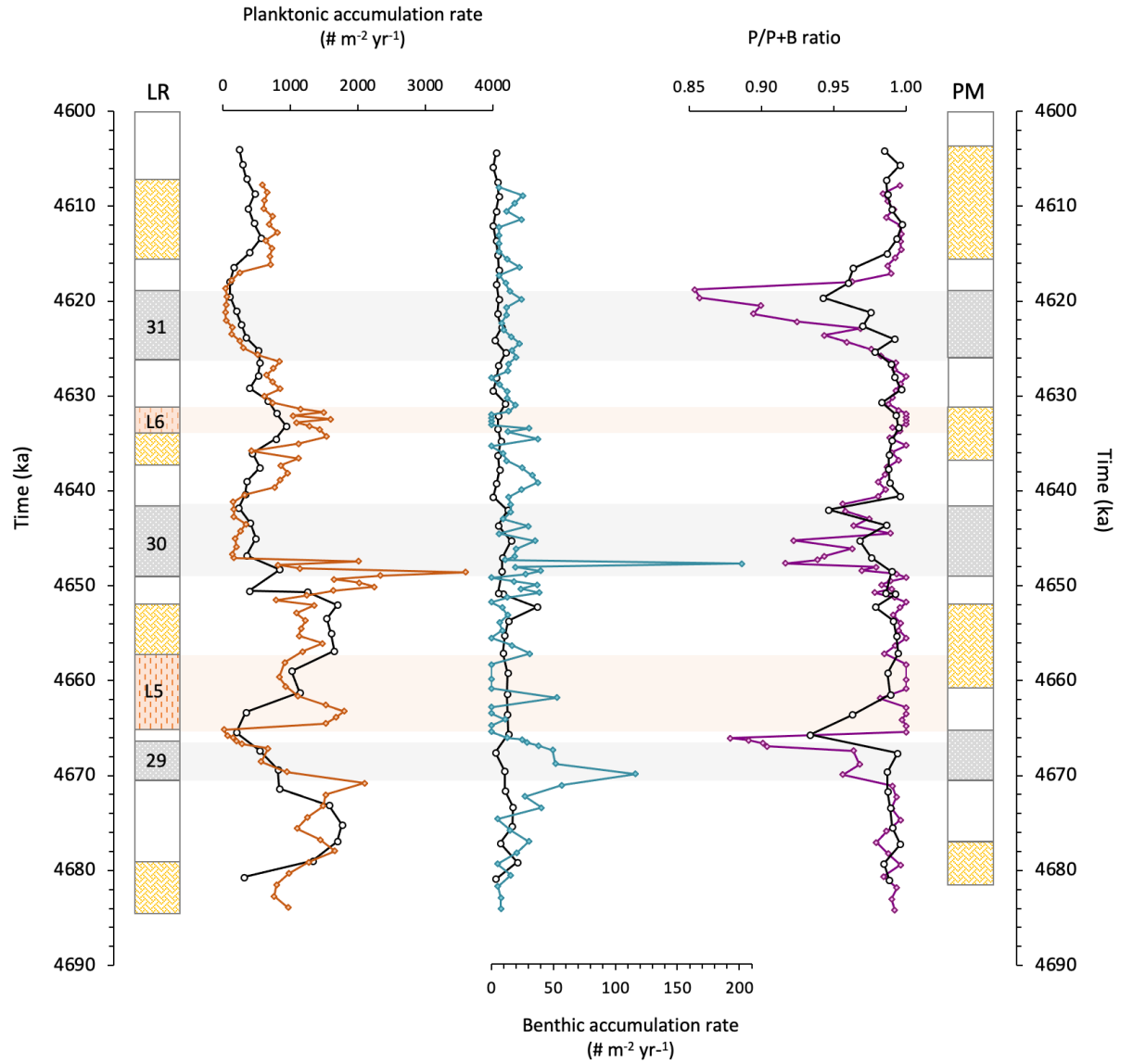


Figure 4: Changes, over three precession forced climate cycles (4690 – 4600 ka), in: planktonic foraminifera accumulation rate ($\# \text{ m}^{-2} \text{ yr}^{-1}$); benthic foraminifera accumulation rate ($\# \text{ m}^{-2} \text{ yr}^{-1}$); and P/P+B ratio; in the SW Sicily records of LR (coloured lines with filled diamond markers) and PM (black lines with open circle markers).

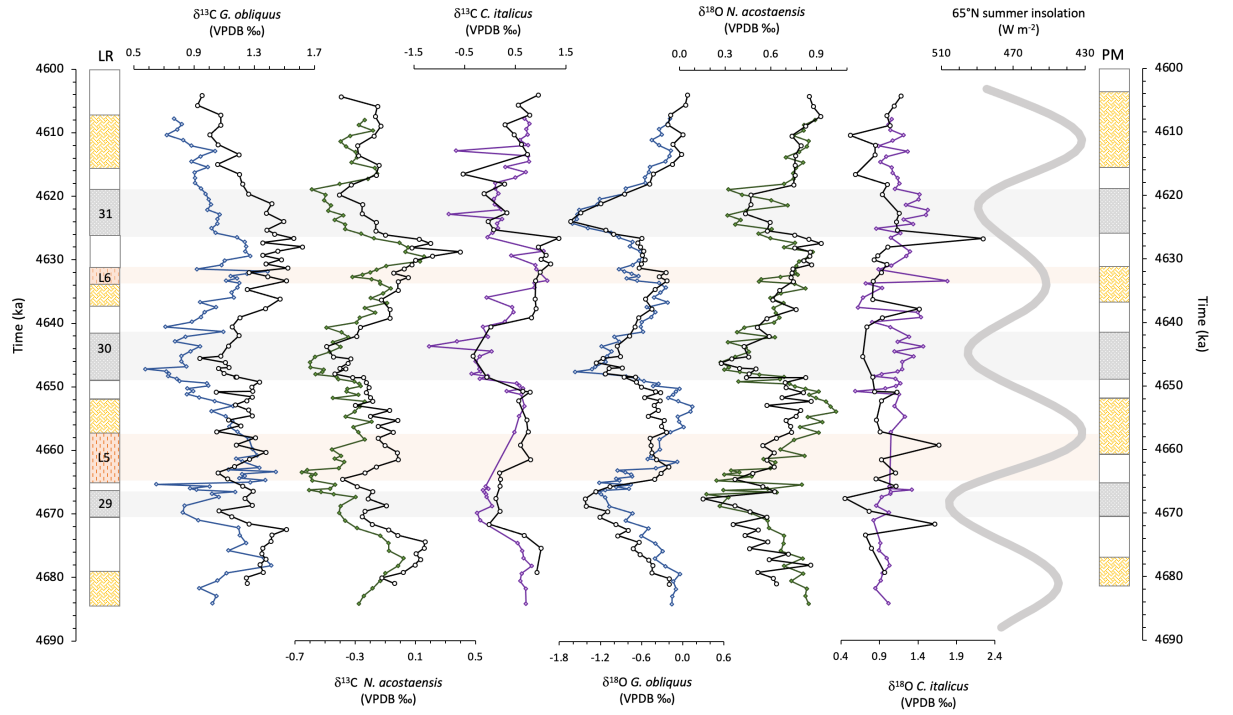


Figure 5: Changes, over three precession forced climate cycles (4690 – 4600 ka), in: ^{13}C *G. obliquus* (VPDB ‰); ^{13}C *N. acostaensis* (VPDB ‰); ^{13}C *C. italicus* (VPDB ‰); ^{18}O *G. obliquus* (VPDB ‰); ^{18}O *N. acostaensis* (VPDB ‰); ^{18}O *C. italicus* (VPDB ‰) in the SW Sicily records of LR (coloured lines with filled diamond markers) and PM (black lines with open circle markers).

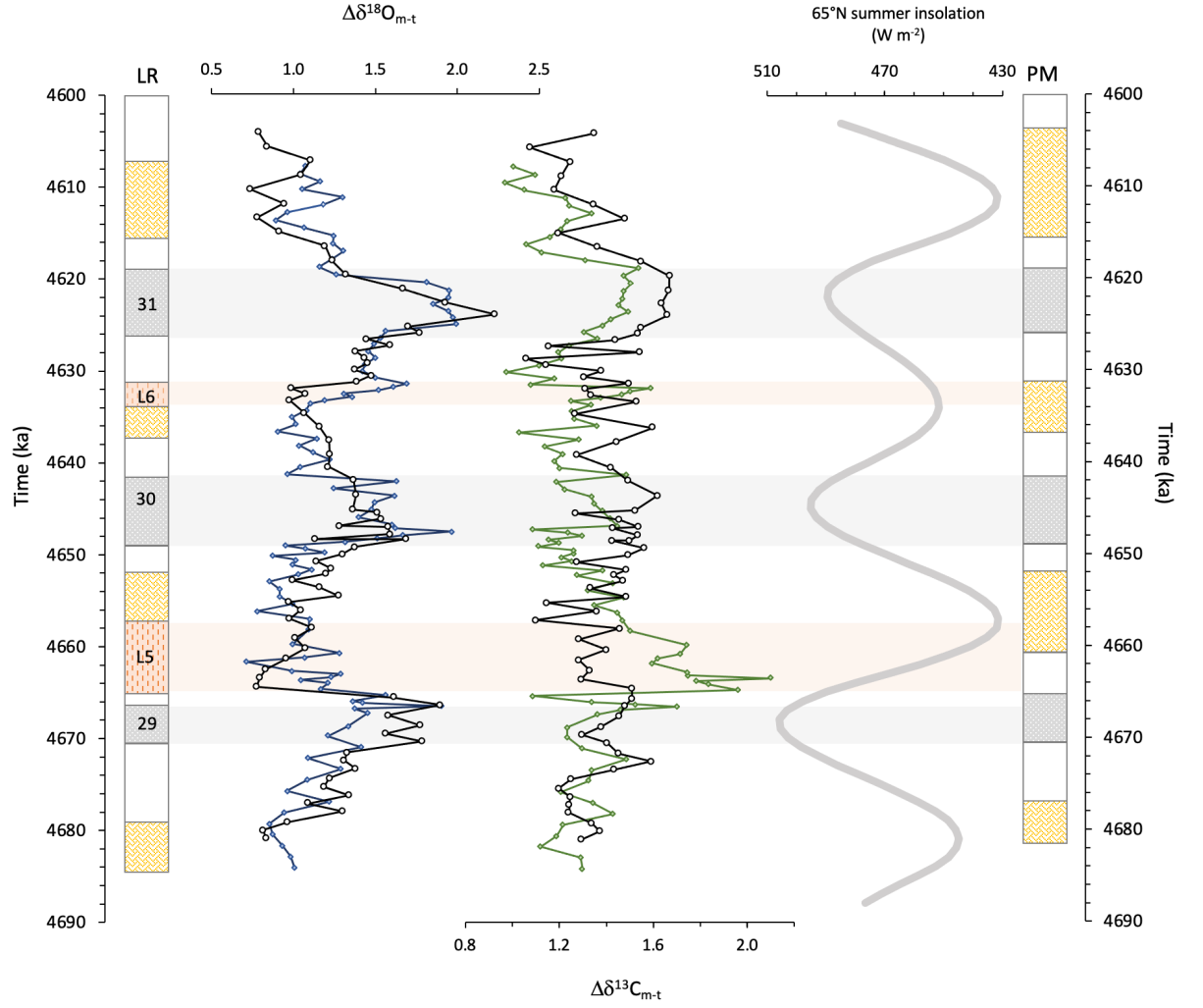
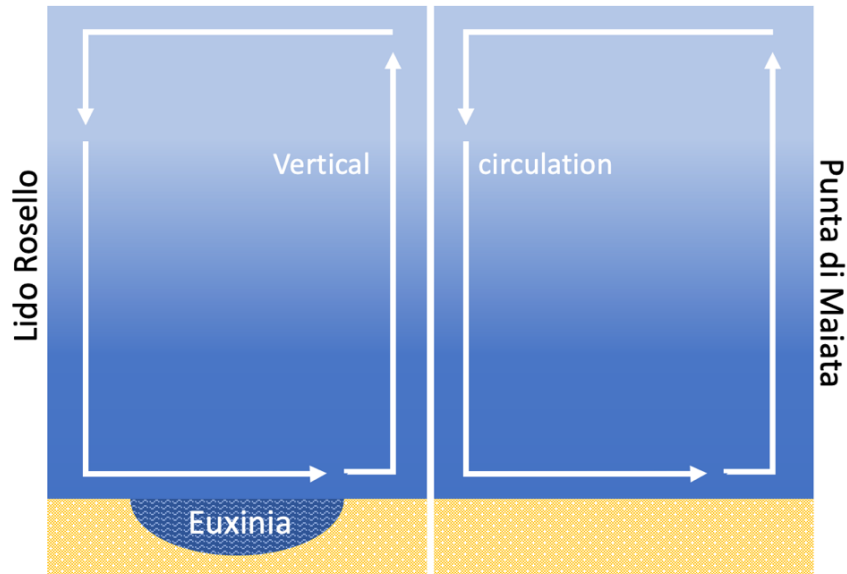


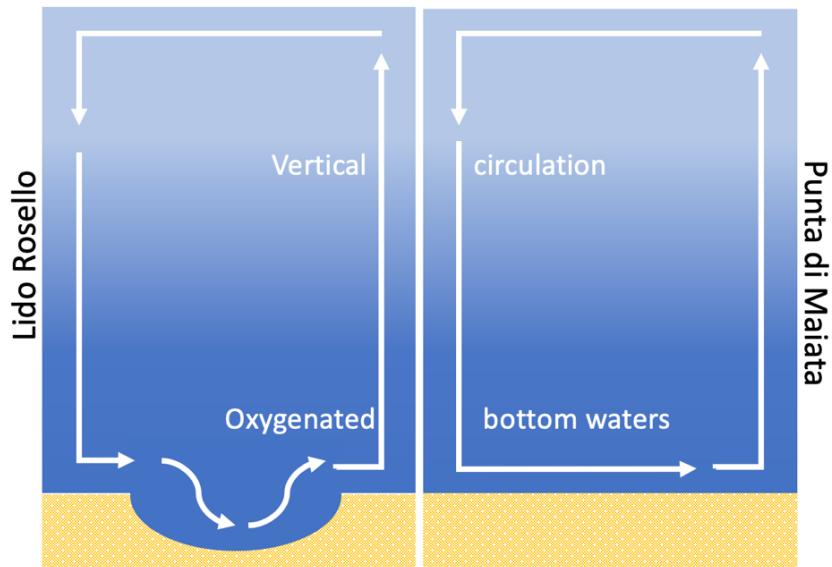
Figure 6: Changes, over three precession forced climate cycles (4690 – 4600 ka), in: $^{18}\text{O}_{m-t}$

(VPDB ‰); $^{13}\text{C}_{m-t}$ (VPDB ‰); in the SW Sicily records of LR (coloured lines with filled diamond markers) and PM (black lines with open circle markers). Change in summer insolation at 65°N (grey line; Berger and Loutre, 1991).

a. Circulation during laminated layer deposition



b. Circulation during white and beige marl deposition



c. Circulation during grey marl deposition

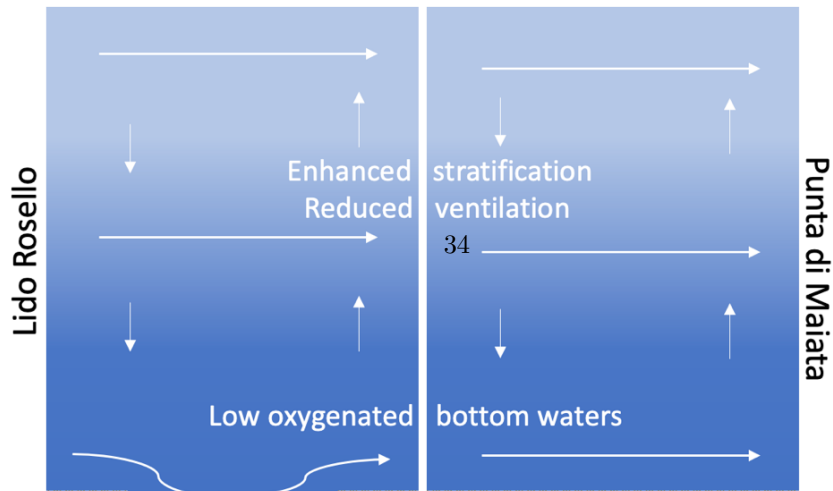


Figure 7: Illustration of the circulation changes during the deposition of different layers in both records, and the geological differences in the seafloor topography at the LR and PM sites.