

## Long chain alkenones in the Early Pliocene Sicilian sediments (Trubi Formation – Punta di Maiata section): Implications for the alkenone paleothermometry

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### ABSTRACT

The  $U_{37}^k$  record and coccolithophorid remains in sediments from the early Pliocene Sicilian Trubi Formation (Punta di Maiata) have been estimated to assess the possible influence of changes in the alkenone-producing coccolithophorids on the  $U_{37}^k$ -temperature relationship. The samples were dominated by small *Reticulofenestra* (*R. minuta* and *R. minutula*) and the  $C_{37}$  and  $C_{38}$  methyl and ethyl unsaturation ratios ( $U_{37}^k$ ,  $U_{38Me}^k$  and  $U_{38Et}^k$ ) were similar to those found in modern populations (*E. huxleyi* and *G. oceanica*). Those results suggest that the Early Pliocene small Reticulofenestrids had a similar temperature sensitivity of  $U_{37}^k$  to that found in present day. These results support the application of the  $U_{37}^k$  modern calibrations to reconstruct SST at least back in the Pliocene.

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### 1. Introduction

The alkenones comprise a suite of long-chain ( $C_{37}$ – $C_{39}$ ) unsaturated ethyl and methyl ketones that are biosynthesized by a restricted group of modern haptophyte algae most notably the cosmopolitan coccolithophores *Emiliania huxleyi* and *Gephyrocapsa oceanica* (Winter et al., 1994). The alkenone unsaturation ratio ( $U_{37}^k$ ) is sensitive to temperature changes (Prah et al., 1988; Conte et al., 2006) and is now widely used in the marine sediment (Brassell, 1993) to reconstruct sea surface temperatures (SSTs).

The first appearance datum of *E. huxleyi* in sediments is a well-established biostratigraphic marker occurring around 270,000 yr B.P. (Thierstein et al., 1977). Both plankton data and the micropaleontologic record indicate that in most places throughout the late Neogene the coccolithophore assemblages are dominated by species belonging to the family of the Noelaerhabdaceae, including the genera *Emiliania*, *Gephyrocapsa* and *Reticulofenestra*. Species of this family are known or believed to be the main alkenone-producing species in the present day ocean (Marlowe et al., 1990; Volkman et al., 1995).

For studies related to climate variability during times predating the first appearance of the modern alkenone producing species, two main questions must be addressed: (1) identify the paleo-alkenone

synthesizers, and (2) ensure the applicability of modern calibrations for the reconstruction of past environments.

The focus of this study is to assess the extent to which alkenone temperature calibrations based on modern day species *E. huxleyi* and *G. oceanica* are appropriate for paleo-alkenone-synthesizing populations. This paper addresses some of these questions through the analysis of the Sicilian Lower Pliocene deposits from the Punta di Maiata section.

### 2. Geological setting

The Pliocene stratigraphy in the central Mediterranean realm has been mainly established by well-exposed South Sicilian outcrops forming the Capo Rossello composite section composed by the Eraclea Minoa section (lower part), Punta di Maiata (middle part) and Punta Grande and Punta Piccola sections (upper part). This composite section is considered as the reference for the Mediterranean Pliocene chronostratigraphy (Langereis and Hilgen, 1991). From the base to the top, two formations have been distinguished: the Trubi Formation and the Monte Narbone Formation. The Trubi Formation consists of cyclic sedimentary sequences of marls and marly limestones that, according to Cita (1975), correspond to the Zanclean (Seguenza, 1868; Cita and Gartner, 1973). The Monte Narbone Formation comprises regular alternations of gray marls and light gray marly limestones. This formation corresponds approximately to the Piacenzian and the Gelasian (i.e. Cita et al., 2000).

The sedimentary cycles expressed along the Capo Rossello composite section are known to be strongly related to precession (Rossignol-Strick,

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1985; Hilgen, 1991) and enabled the establishment of a cyclochronology of the Pliocene (Langereis and Hilgen, 1991; Lourens et al., 1996). The Capo Rossello composite section constitutes stratotypes of both the Zanclean and Piacenzian stages, having an excellent magnetostratigraphy,

calcareous nannoplankton biostratigraphy and isotope stratigraphy (Rio et al., 1984; Hilgen, 1991; Langereis and Hilgen, 1991; Lourens et al., 1996). The Punta di Maiata section crops out on a cliff along the southern coast of Sicily, 1 km East of Capo Rossello in the Caltanissetta basin. It

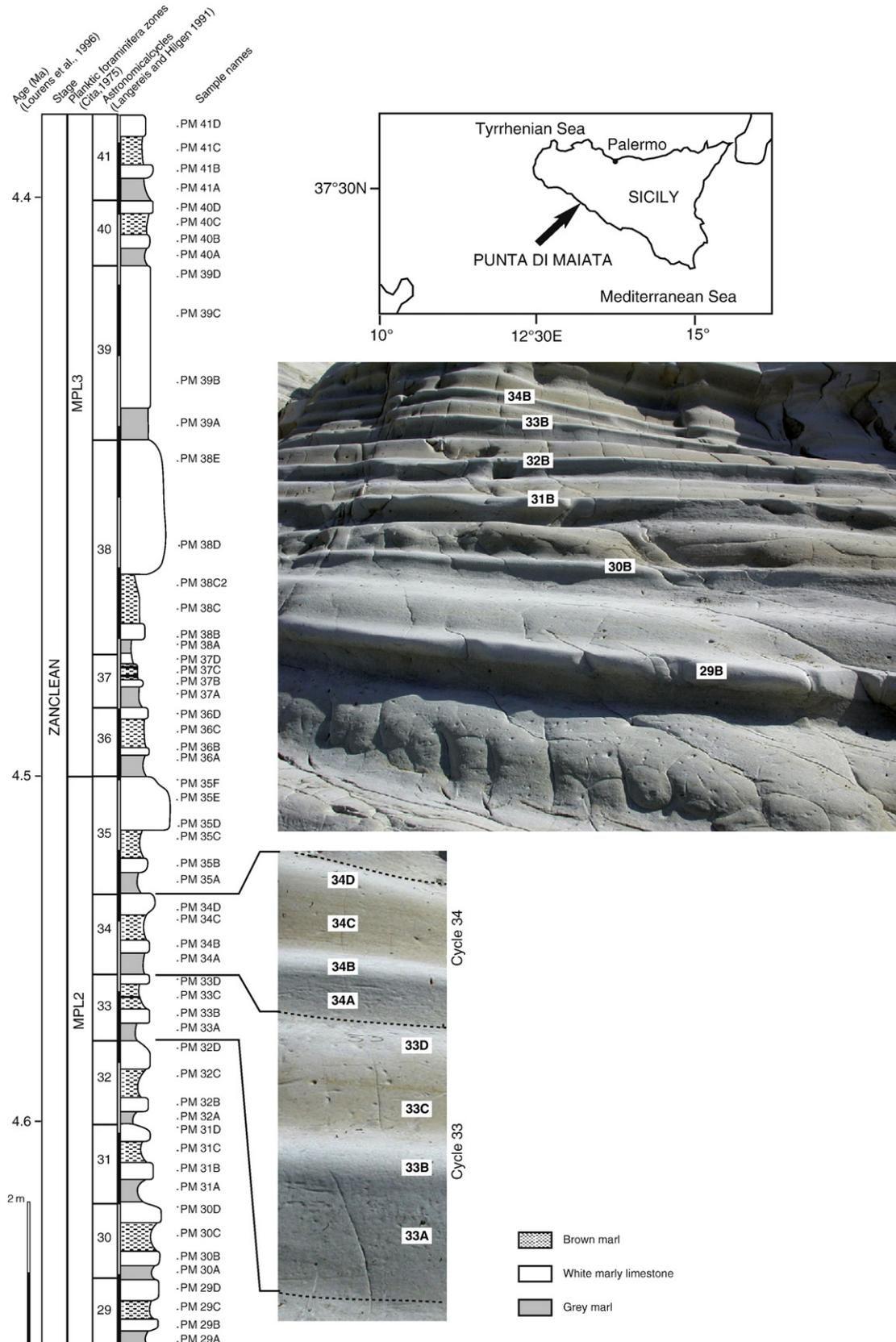


Fig. 1. Localization, picture and schematic representation of the Punta di Maiata section and of the studied sedimentary cycles.

consists of a continuous succession of ~50 rhythmites from the Trubi Formation. These sedimentary cycles correspond to a meter thick quadripartites characterized by the regular alternation of gray-white-brown-white color marly limestones (Fig. 1).

Previous studies by De Visser et al. (1989) or Thunell et al. (1991) on the Trubi Formation attributed these sedimentary cycles to rapid alternations (precession cycles) between wet and dry climatic conditions leading to periods of increased dilution by river-supplied terrigenous material (gray layers) and decreased carbonate production in surface waters (white-brown layers).

### 3. Material and methods

#### 3.1. Sampling

Our study focuses on cycles 29 to 41 of Langereis and Hilgen (1991) (insolation cycles i-448 to i-420) spanning the period between 4.66 and 4.38 Ma (Hilgen et al., 2006; Fig. 1).

All sampled cycles are of about 1 m thick except the cycles 35, 38 and 39 which are two times thicker. Moreover, in the cycle 39, the quadripartite is not clearly expressed with only two layers recognized: the gray and the white ones (Fig. 1). A total of 52 levels have been studied with an average sampling spacing of 30 cm. One sample per lithology has been collected for each sedimentary cycle studied except for the cycles 35 and 38 in which 6 samples have been taken leading to a total number of 56 samples.

In order to simplify, the gray layers will be named A, the overlying white layers, B, the brown layers, C and the upper white layers, D (Fig. 1).

#### 3.2. Organic compound analyses

Total Organic Carbon (TOC) contents were determined on decarbonated samples with a LECO IR 212 by infrared detection after combustion at 1200 °C. Analytical precision is of about  $\pm 0.02\%$ . Then the TOC content has been recalculated for whole rock taking into account the dilution effect of organic compounds by carbonates.

The  $C_{37}$  and  $C_{38}$  alkenone concentrations were determined for the 56 samples of the Punta di Maiata section. About 9 g dry weight was freeze-dried, extracted with organic solvents and partitioned into compound classes following the procedure of Sicre et al. (2001). Alkenones were isolated by silica gel chromatography using solvents of increasing polarity. The fractions containing alkenones were concentrated, transferred to clean glass-vials and evaporated under nitrogen. They were then analyzed on a Varian 3400CX series equipped with a SPI (Septum Programmable Injector) injector and a flame ionization detector. Gas chromatography was performed on a fused silica capillary column (Chrompack CP Sil8, 50 m long, 0.32 mm internal diameter, 0.25  $\mu\text{m}$  film thickness). Helium was used as a carrier gas. The alkenone concentrations were calculated using  $5\alpha$ -cholestane as an external standard.

#### 3.3. Calcareous nannofossil analysis and countings

The procedure used to prepare the smear slides for the inventory of the calcareous nannofossil assemblages is detailed in Flores et al. (1995) and Flores and Sierro (1997). This procedure ensures the homogeneity of the samples and the reproducibility of the counts.

Routine countings were performed using a polarized light microscope ( $\times 1250$ ). To obtain statistically significant percentage values for all species, about 300 coccoliths were counted per sample, distributed in a variable number of viewing fields. According to Dennison and Hay (1967), this represents the 99.5% of probability to record all the specimens represented over the 1% in the assemblage. Results are presented in absolute (liths per gram of sediments) for the total assemblage and in relative (%) for the identified taxa. In addition, Scanning Electron Microscope (SEM) observations were performed in selected sample microscopy in order to identify morphological and preservational features.

## 4. Results

### 4.1. TOC and alkenone contents of the sediments

The TOC content is globally low throughout the entire section with values ranging between 0.02% and 0.18% (Table 1). In spite of those low TOC values, the gray layers (A) have a higher TOC (0.11%) while the lowest values correspond to brown layers (C) (0.04%). For each cycle, the white marls (B and D layers) have similar TOC around 0.05% (Table 1).

$C_{37}$  alkenone concentrations vary between 1.2 and 107.5 ng/g of dry sediment, slightly lower than found in the Mid-Pliocene Punta Piccola section (Beltran et al., 2007). The  $C_{38}$  alkenone concentrations vary between 1.2 and 116.1 ng/g of dry sediment (Table 1).  $C_{37}$  and  $C_{38}$  concentrations are correlated to the TOC content. The gray marls (A) yield higher alkenone concentrations ( $C_{37}$  mean value of 40.2 ng/g,  $C_{38}$  mean value of 45.2 ng/g) compared to the other lithologies. The brownish layers (C) are lowest in alkenones with mean  $C_{37}$  values of 3.7 ng/g and  $C_{38}$  values of 4.1 ng/g. The white layers (B and D) exhibit intermediate values (Table 1). In three samples (PM 32C, PM 33C and PM 33D) alkenone concentrations were not detectable (Table A1).

### 4.2. Calcareous nannofossils

About 10 nannofossil species were identified in the studied samples including *Calcidiscus macintyreii*, *Coccolithus pelagicus*, *Calcidiscus leptoporus*, *Sphenolithus abies*, *Helicosphaera carteri*, *Schypophosphaera* sp. and *Reticulofenestra* (*R. minuta*, *R. minutula*, and *R. pseudoumbilicus*). *Reticulofenestra* is the dominant genus contributing to 95% of the total assemblage. Even though liths show some dissolution traces, small forms and other easily dissolved species are still present in the samples inferring a globally good to moderate preservation of the nannofossil assemblages (Fig. 2).

Fig. 3 depicts the absolute total abundances ( $\times 10^6$  liths/g of dry sediment) and the relative abundance variations of the main calcareous nannofossil taxa along the studied cycles. The total number of coccoliths fluctuates between  $247 \cdot 10^6$  and  $2747 \cdot 10^6$  liths/g of sediment and is the higher, on average, in the B layers where carbonate is also high. Altogether the number of coccoliths is poorly correlated to the carbonate content. This setting is explained by the variable calcite volume contribution inferred to foraminifera and micarb (Beltran et al., 2009).

Small *Reticulofenestra* (<5  $\mu\text{m}$ : *R. minuta* and *R. minutula*) is the most abundant taxon in the section (Fig. 3). The relative abundance of *R. minuta* ranges from 7.5% to 90.5%. On average the highest values are reached in the gray layers (64.5%) whereas the lowest ones in the white B layers (35%). *R. minutula*, second more important specie in the samples, has relative abundances ranging between 2% and 86% (Fig. 4).

Comparison of the relative abundances of *R. minutula* and *R. minuta* species reveals a generally opposite trend through the section (Fig. 3).

The relative abundances of *R. pseudoumbilicus* (size >5  $\mu\text{m}$ ) range from 0.5% to 14%, with highest proportions in the gray layers (3.5%) and the lowest in the brown ones (2%). The three cycles at the bottom of the section display the highest proportions of *R. pseudoumbilicus*. The

**Table 1**  
Mean organic content (TOC) and  $C_{37}$  and  $C_{38}$  alkenone concentrations related to lithology. The range of values is in italic between brackets. A: gray layer, B and D respectively the first and second white layers and C the brown layer.

	TOC (%)	$C_{37}$ (ng/g)	$C_{38}$ (ng/g)
A	0.11 (0.04–0.18)	40.2 (3.5–107.5)	45.2 (3.3–116.1)
B	0.05 (0.04–0.1)	6.9 (1.9–29)	6.9 (1.9–29)
C	0.04 (0.02–0.07)	3.7 (1.2–5.6)	4.1 (1.2–7)
D	0.05 (0.03–0.07)	5.5 (1.4–12)	6.3 (1.5–14)

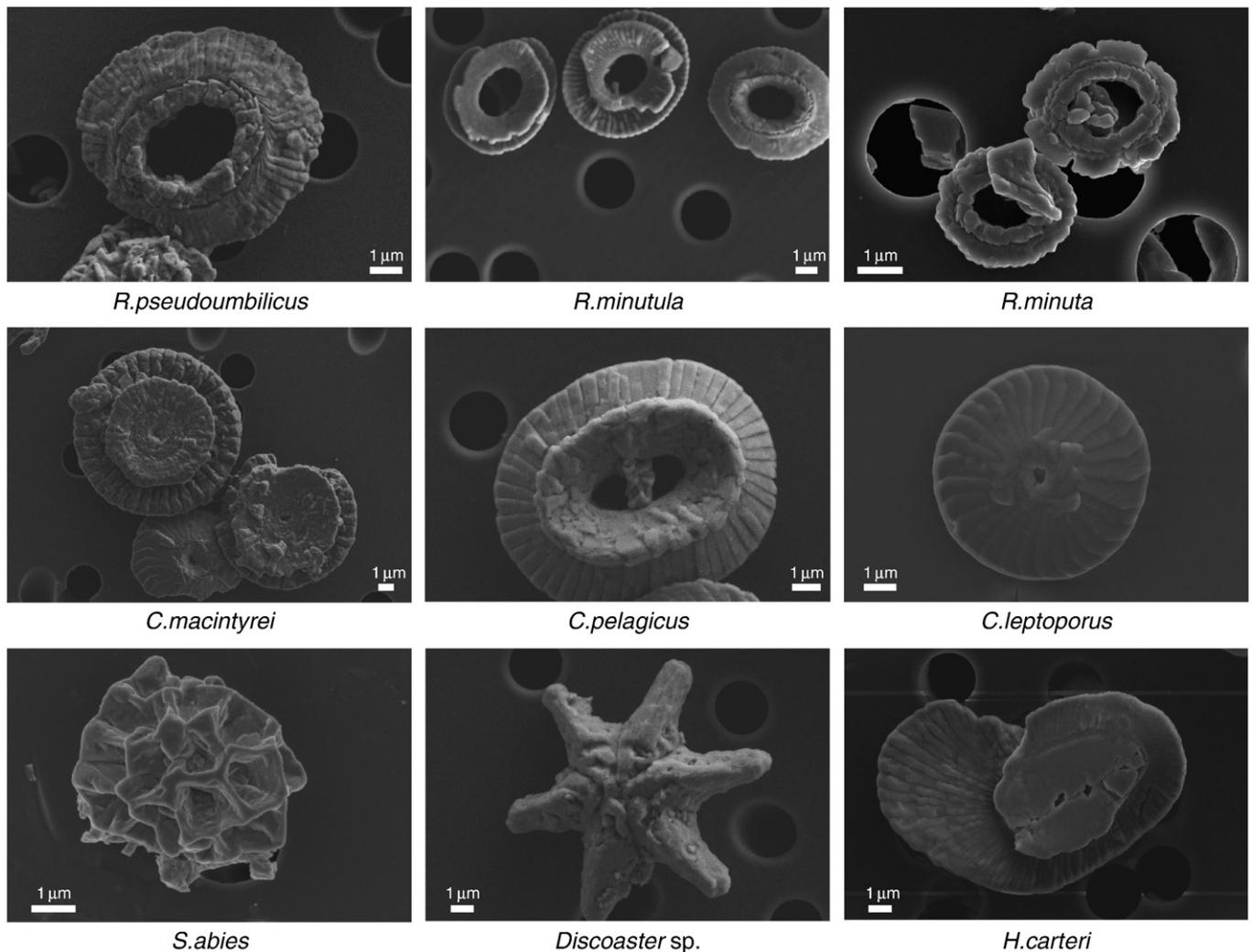


Fig. 2. SEM pictures of the main calcareous nanofossils from the Punta di Maiata samples. Those SEM observations show that most of the biogenic constituents are slightly broken or dissolved but no overgrowths are detected confirming the absence of strong diagenetic modifications in the studied section.

remaining nanofossil taxa (including *Calcidiscus macintyreii*, *Coccolithus pelagicus*, *Calcidiscus leptoporus*, *Sphenolithus abies*, *Helicosphaera carteri*, and *Schizophosphaera* sp.) have been gathered as they account for less than 10% of the assemblages (Figs. 3 and 4). Their relative abundances range from 0.7% to 45.5%, and this latter maximum value corresponds to one sample at the base of the section (PM 30B). On average, this group of nanofossils is relatively more abundant in the gray layers (10%) while a minimum is reached in the upper white marls (layers D). At last, *Discoaster* s.l. which is an important component of the Paleogene and Neogene nanofossil assemblages represent only 0.2% of the calcareous nanofossil assemblages (Fig. 4).

## 5. Discussion

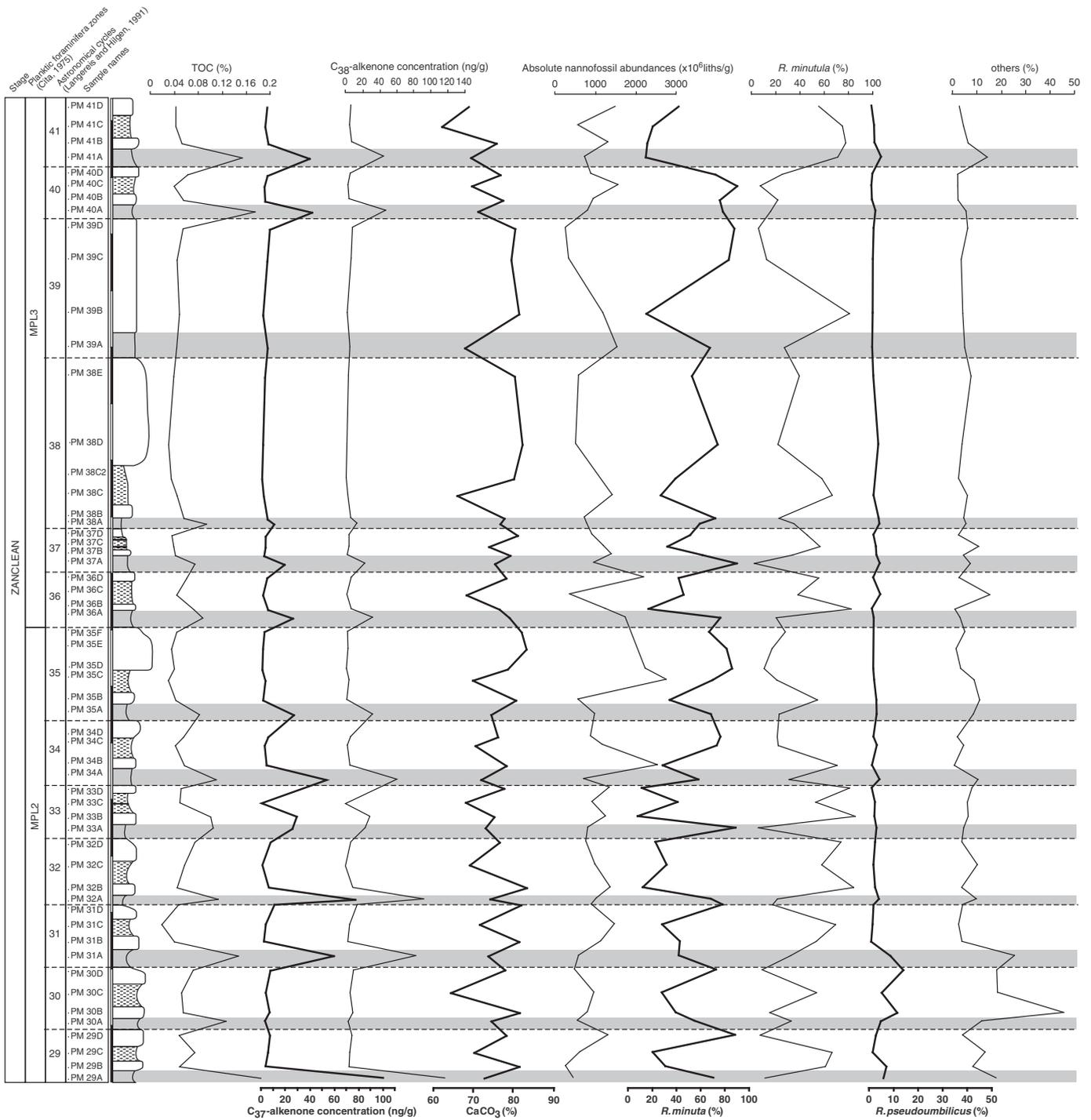
### 5.1. Alkenone production during the Early Pliocene

One of the greatest uncertainties of the  $U_{37}^k$  paleothermometry is linked to the knowledge of the alkenone producers. Along the studied section, three members of the family Gephyrocapsaceae (alkenone contributors in the geological past according to Marlowe et al. (1990)) are present: *R. minuta*, *R. minutula* and *R. pseudoumbilicus*. The results presented in Fig. 3 show a general scheme in which the gray layers (A) associated with high TOC, alkenone and *R. minuta* contents can be distinguished from the upper “white-brown-white” group (B, C and D

layers) in which very low alkenone concentrations are recorded and the relationship with nanofossil assemblage composition is poor. Despite none of the *Reticulofenestra* present in the Punta di Maiata sediments can clearly account for the alkenone profile, the similarities between the *R. minuta* abundances and alkenone concentrations (with some exceptions in the cycles 30, 31 and 41) strongly suggest that the dominant alkenone contributors to those sediments may be *R. minuta*. However, the lack of correlations between *R. minuta* and *R. pseudoumbilicus* and the alkenone profiles may imply but does not necessarily demonstrate that they were not sources of alkenones in the Punta di Maiata sediments.

This feature could be explained by the fact that the alkenone concentrations in the sediments are a complex function of production and of processes such as losses due to grazing or degradation during their downward transport (Malinverno et al., 2008). Thus, interpreting the sedimentary alkenone content in terms of paleoproductivity has to be done with caution. Information lack on the amount of alkenone produced per cells by the Pliocene species (see Sicre et al., 2000) and this cellular production may have varied with the oceanographic conditions as observed in the modern coccolithophore community (Epstein et al., 1998; Pancost et al., 1999; Yamamoto et al., 2000; Epstein et al., 2001; Malinverno et al., 2008).

Moreover, the mechanisms regulating the export to the seafloor and the losses during sedimentation and early diagenesis have a



**Fig. 3.** Evolution of the total organic content (TOC, %), the C<sub>37</sub> and C<sub>38</sub> alkenone concentrations (ng/g), the carbonate content (%), the total absolute nannofossil abundances ( $\times 10^6$  liths/g of dry sediment) and of the relative abundances of the main coccolith species *R. minuta*, *R. minutula*, and *R. pseudoumbilicus* in the Punta di Maiata section. The other taxa (*C. macintyreii*, *C. pelagicus*, *C. leptoporus*, *S. abies*, *H. carteri*, and *Schypophosphaera* sp.) have been gathered as each accounts for less than 10% of the assemblages. The gray bands represent the gray A levels of each sedimentary cycle.

strong influence on the sedimentary alkenone content (Conte et al., 1992). According to these authors, a significant degradation of alkenones occurs in the water column independent of water oxygenation. Then the proportion of the total production reaching the seafloor depends on the water column residence time. Alkenones incorporated into rapidly sinking material will make a proportionally greater contribution to the sedimentary input than equivalent amounts of production incorporated into slowly settling material. However, although the Punta di Maiata sedimentary cycles have been related to precession cycles (Hilgen et al., 2006), the sedimentation

rates for each individual lithology is unknown. It is then impossible to constrain the possible effect of sedimentary rate variations on the alkenone preservation in each lithology.

Because of all these uncertainties, we consider here that the alkenone production in the sediments studied is inferred to the small *Reticulofenestra* (<5  $\mu$ m) as they dominate the coccolith assemblages (Figs. 3 and 4). As for any proxy used for paleo-reconstructions, SST estimates rely on the hypothesis that the modern U<sub>37</sub><sup>S</sup>-SST calibration can be applied to Early Pliocene sediments. This can tentatively be tested through the use of alkenone indices (Table 2).

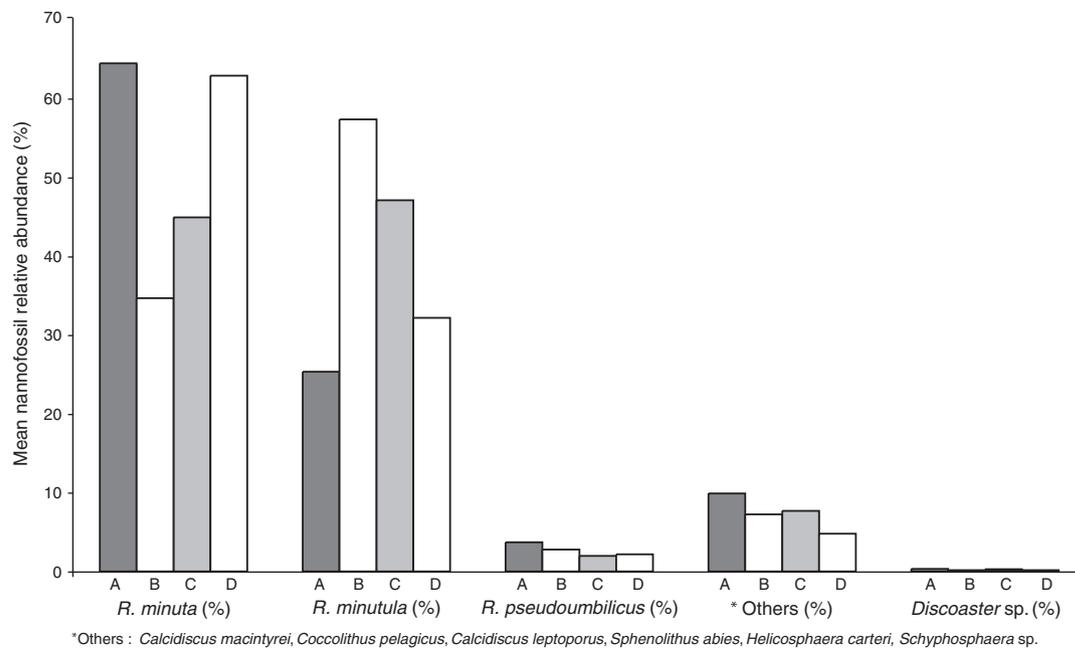


Fig. 4. Mean relative abundances of the main nannofossil species as a function of the lithology (A: gray layer, B: first white layer, C: brown layer and D: the second white layer).

#### 5.1.1. The carbon chain length distribution

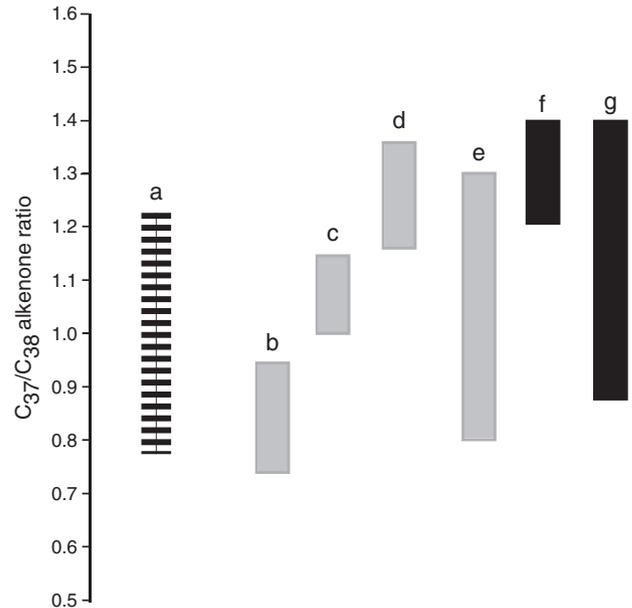
This ratio defined as the  $C_{37}/C_{38}$  reflects the relative abundances of the  $C_{37}$  and  $C_{38}$  alkenones. It is roughly constant averaging  $0.9 \pm 0.1$  (from 0.79 to 1.22; Fig. 5a). According to Conte et al. (1998) and Yamamoto et al. (2000), cultured and natural alkenone producers influence this ratio. To circumvent the effect of the growth status or physiologic differences between our sediment data and cultures, we compared the Punta di Maiata  $C_{37}/C_{38}$  ratios with published natural sample data (sediment traps, water particulate and sediments) (Fig. 5). Since SSTs could affect the  $C_{37}/C_{38}$  ratio, we restricted this comparison to tropical, subtropical and mid-latitude results to be consistent with the Pliocene mid-latitude climate (Rio et al., 1990; Thunell et al., 1990; Fauquette et al., 1998).

The  $C_{37}/C_{38}$  ratios of Punta di Maiata sediments broadly agree with those of *E. huxleyi* and *G. oceanica* dominated samples from various biogeographic settings (Fig. 5). Although the influence of genetic differences among alkenone-synthesizing populations or differences in nutrient conditions cannot be excluded (Conte et al., 1998, 2001), these results suggest that the  $C_{37}$  and  $C_{38}$  alkenone compositions in the Early Pliocene Sicilian deposits are similar to those of *E. huxleyi* and *G. oceanica*.

#### 5.1.2. The alkenone unsaturation ratios

Because of the low concentrations of alkenones found in the Punta di Maiata sediments and the strong positive correlation between TOC and alkenone concentrations (Table 1, Fig. 2), the question of the preservation of the alkenone signal during the transit of these compounds through the water column and their incorporation into the sedimentary record needs to be addressed. The accumulation of organic carbon in marine sediments

is a complex function of primary productivity and degradation processes such as grazing and sinking efficiency (Malinverno et al., 2008). Even though alkenones are among the most refractory lipid biomarkers to degradation, a significant loss of alkenones occurs in the water column and during early sediment diagenesis (Prah et al., 1989; McCaffrey et al.,

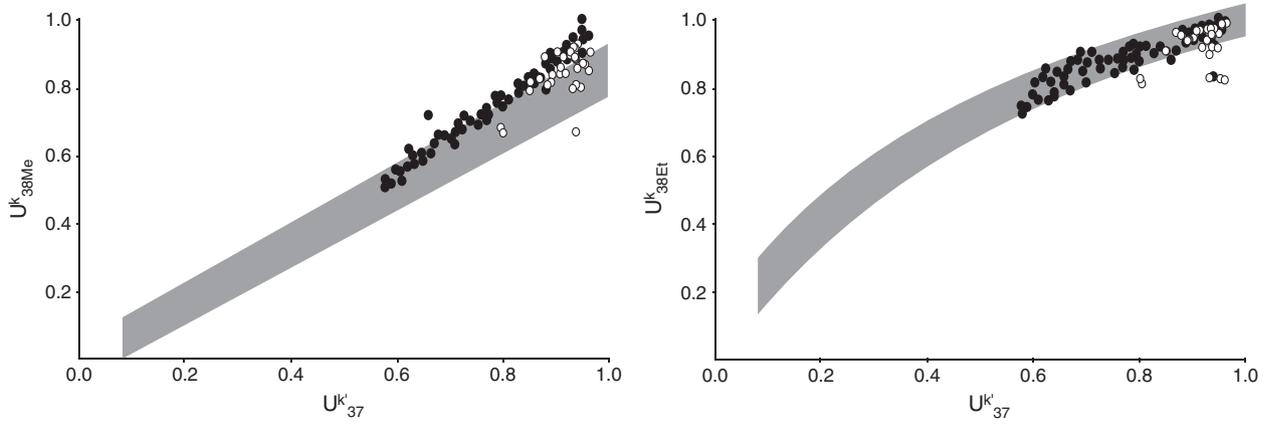


a: Punta di Maiata data set (this study)  
 b: Mediterranean sediments (Cacho et al., 1999) -  
 c: Mediterranean sediment traps (Ternois et al., 1997) -  
 d: Arabian Sea sediments (Rostek et al., 1997) -  
 e: Bermuda water particulates (Conte et al., 1998)  
 f: NE Atlantic mid latitude sediments (Rosell-Melé et al., 1994) -  
 g: Indian Ocean sediments (Sonzogni et al., 1997)

Table 2  
 Definitions of the alkenone indices used in this study.

Index	Equation	Reference
$U_{37}^k$	$(C_{37:2}Me)/(C_{37:2}Me + C_{37:3}Me)$	Prah et al. (1987)
$U_{38}^{kMe}$	$(C_{38:2}Me)/(C_{38:2}Me + C_{38:3}Me)$	Conte and Eglinton (1993)
$U_{38}^{kEt}$	$(C_{38:2}Et)/(C_{38:2}Et + C_{38:3}Et)$	Conte et al. (1998)
$C_{37}/C_{38}$	$(C_{37:2}Me + C_{37:3}Me)/(C_{38:2}Et + C_{38:3}Et + C_{38:2}Me + C_{38:3}Me)$	Prah et al. (1988)

Fig. 5. Comparison of the Punta di Maiata alkenone chain length distribution with published data from modern superficial sediments and water particulates. Gray (b to e) and black (f and g) refer respectively to *E. huxleyi* and *G. oceanica* domination in the sample compositions.

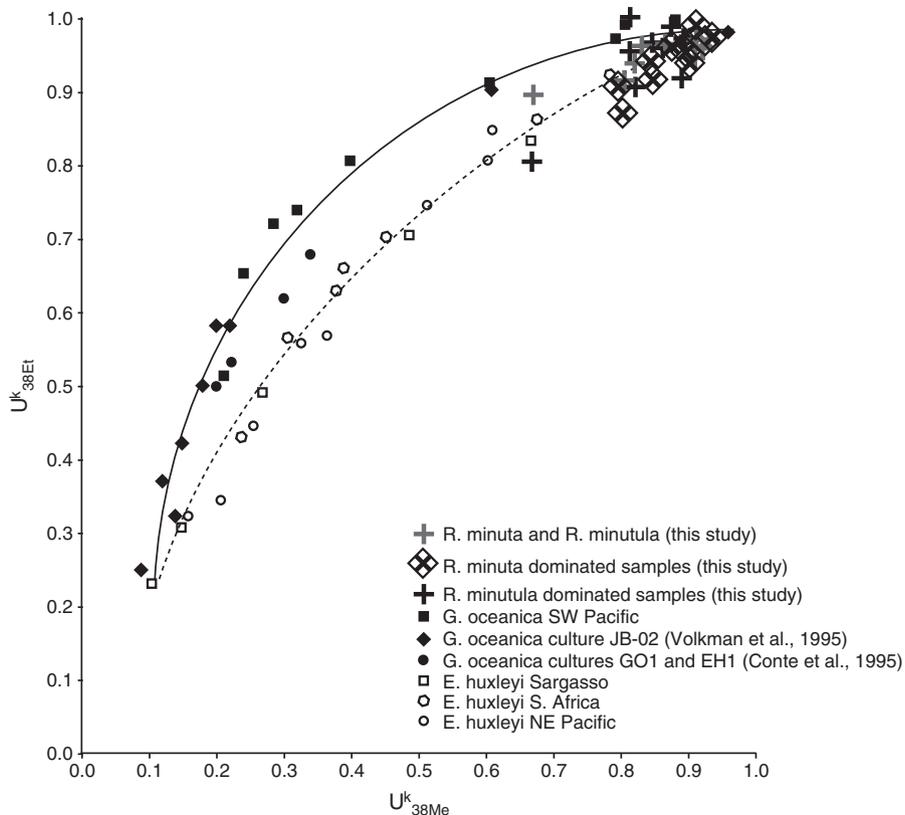


**Fig. 6.** Covariance of the  $U^k_{37}$  with  $C_{38}$  unsaturation ratios. The shaded area represents a compilation of the data from euphotic zone particulates collected in the North Atlantic (Conte and Eglinton, 1993), Norwegian fjords (Conte et al., 1994) and Mediterranean (Ternois et al., 1997), and culture data for *E. huxleyi* and *G. oceanica* strains (Conte et al., 1995, 1998). The black circles correspond to the Conte et al. (2001) Bermuda samples and the white circles, the values obtained in the present study for the Early Pliocene Sicilian deposits.

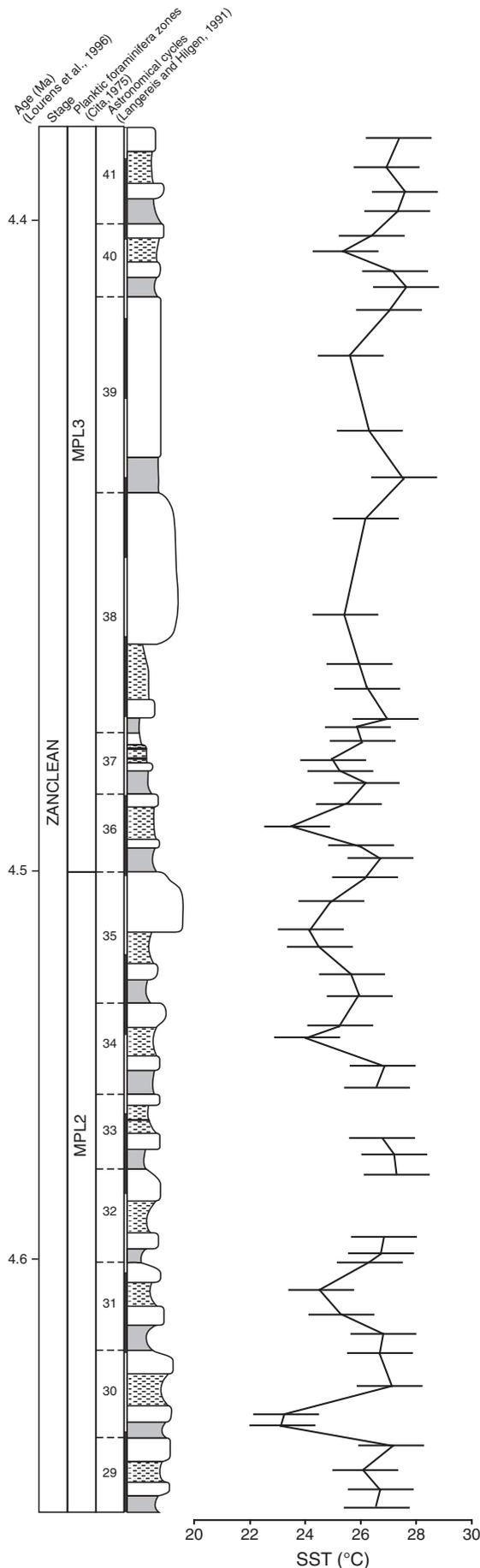
1990; Conte et al., 1992; Prah1 et al., 1993; Madureira et al., 1995). The oxygen content of the bottom water is often mentioned as the determining factor for organic matter preservation (Demaison and Moore, 1980; Pratt, 1984; Canfield, 1993). However, according to Van der Zwaan (1983) and De Visser et al. (1989), the Punta di Maiata Trubi Formation is characterized by stable bottom conditions with stable salinity and optimum oxygenation, suggesting that alternating lithologic layers are unlikely to reflect periods of strong aerobic/anaerobic variations. Therefore, the sedimentary TOC and alkenone concentrations record could be a function of production and water column residence time. Despite global losses of these organic compounds, it has been showed that the original  $U^k_{37}$  remains unaltered (Prah1 et al., 1989; Conte et al., 1992; Madureira, 1994; Madureira et al., 1995). Moreover, Cleaveland and Herbert (2009) show that alkenones in continental outcrops of marine sequences are quite well preserved. We can then

reasonably assume that the alkenone unsaturation indices in the present study provide a record of marine production.

To further characterize the alkenone composition in the early Pliocene sediments, we compared, several  $U^k$  indices with field data from the Bermuda (Conte et al., 2001), North Atlantic (Conte and Eglinton, 1993), the Mediterranean (Ternois et al., 1997), Norwegian fjord (Conte et al., 1994) and for the *E. huxleyi* and *G. oceanica* cultures (Conte et al., 1995; Yamamoto et al., 2000) (Fig. 6). The unsaturation index for the  $C_{37}$  methyl ( $U^k_{37}$ ) and  $C_{38}$  ethyl and methyl alkenones (respectively  $U^k_{38Et}$  and  $U^k_{38Me}$ ) are listed in Table A1. The  $U^k_{37}$  values range from 0.723 to 0.967, and the  $U^k_{38Me}$  and  $U^k_{38Et}$  from 0.670 to 0.933 and from 0.804 to 0.989, respectively. These ratios are consistent with those found for the *E. huxleyi* dominated field samples from Bermuda (Conte et al., 2001), suggesting that *R. minuta* and *R. minutula* have a genetic relationship with modern *E. huxleyi* and *G. oceanica* (Figs. 4 to 6).



**Fig. 7.** Comparison of the  $U^k_{38Me}$  vs  $U^k_{38Et}$  relationship for the Punta di Maiata samples with *E. huxleyi* and *G. oceanica* culture data from Conte et al. (1998).



Previous work demonstrated that the contribution of *E. huxleyi* and *G. oceanica* to sedimentary alkenone in the modern ocean can be distinguished using  $U_{38Et}^k$  vs  $U_{38Me}^k$  (Conte et al., 1998). The  $U_{38}^k$  ratios for this study fall into the range of those obtained for modern *E. huxleyi* and *G. oceanica* in cultures and sediments (Fig. 7). Yet, there is no difference between *R. minuta* and *R. minutula* dominated samples (Fig. 7). This result suggests that as in the modern subtropical and tropical waters, where *E. huxleyi* and *G. oceanica* co-exist, both *R. minuta* and *R. minutula* may have contributed to the sedimentary alkenones found in the lower Pliocene sediments from Capo Rossello.

## 5.2. SST reconstructions

We can reasonably assume that the Early Pliocene *Reticulofenestra*  $<5\ \mu\text{m}$  are genetically related to modern alkenone producers. Although some genetic differences are expected between modern and fossil alkenone producers (Conte et al., 1995; Volkman et al., 1995; Sawada et al., 1996; Conte et al., 1998; Epstein et al., 1998) previous work showed that potential bias on the temperature estimates are of second order (Conte et al., 2006). In this study we converted  $U_{37}^k$  to SST using the Conte et al. (2006) global calibration (1) because of its wide coverage of world ocean, the physiological and ecological conditions of the population collected in surface waters (approx. 700 samples) and the better adjustment of the relationship for warmer SSTs. The mean standard error of the estimated temperature is  $\pm 1.2\ ^\circ\text{C}$  (Conte et al., 2006).

$$T = -0.957 + 54.293U_{37}^{k'} - 52.894(U_{37}^{k'})^2 + 28.321(U_{37}^{k'})^3 \quad (1)$$

Estimated SSTs lie between  $23\ ^\circ\text{C}$  and  $27.5\ ^\circ\text{C}$  (Fig. 8). These relatively stable warm SSTs are consistent with the climatic conditions referred for the Early Pliocene (Keigwin, 1982; Hodell and Kennett, 1986; Keigwin, 1987). Zachariasse and Spaak (1983) reported that the Lower Pliocene intervals of the Sicilian and the Crete sections were dominated by subtropical planktonic foraminifera indicating that the Mediterranean was connected to the warm waters from the tropical–subtropical Eastern North Atlantic Ocean. This setting is confirmed by the similarity between the Punta di Maiata  $U_{37}^k$  values and the ones obtained by Herbert and Schuffert (1998) for the early Pliocene subtropical ODP Atlantic site 958 ( $23^\circ 59.94'\text{N}$ ,  $20^\circ 00.05'\text{W}$ ). Moreover, our mean SST value ( $26\ ^\circ\text{C}$ ) is consistent with Thunell's (1979a,b) summer SSTs derived from foraminifera transfer functions in the Tyrrhenian basin.

Alkenone-derived SST estimates reflect the temperature of the alkenone production season, and the depth at which this production occurs (Okada and Honjo, 1973; Okada and McIntyre, 1979; Conte et al., 1994; Ternois et al., 1997). Previous work by Ternois et al. (1997) showed that high alkenone fluxes in the modern Mediterranean occur at subsurface depths in spring and in the surface mixed-layer during fall. Therefore to properly interpret sedimentary  $U_{37}^k$  records, it is essential to know the major seasons and depth ranges in which the haptophytes biosynthesize alkenones. The depth of alkenone production is mainly controlled by the nutrient supply (Ternois et al., 1997; Ohkouchi et al., 1999). When the surface mixed layer is nutrient depleted, the alkenone synthesis can take place in colder thermocline waters. In the Punta di Maiata sediments, the overall dominance of small *Reticulofenestra* indicates that those sediments were deposited under global mesotrophic conditions (Flores et al., 2005). This is confirmed by the extremely low abundances of *Discoaster* traditionally considered to be a warm oligotrophic genus (Lohmann and Carlson, 1981; Flores and Sierro, 1987; Chepstow-Lusty et al., 1989, 1992; Flores et al., 1992, 1995; Vázquez et al., 2000). Flores et al. (2005) show that *Discoaster* may have

Fig. 8. Alkenone based sea-surface temperature (SST) variations recorded for the Zanclean period in Punta di Maiata. The mean standard error of the estimated temperature ( $\pm 1.2\ ^\circ\text{C}$ ; Conte et al., 2006) is reported (black bars).

lived in the lower photic zone under deep nutricline conditions. Thus globally, the nutricline was shallow during the deposition of these sediments, implying that the small *Reticulofenestra* (<5 µm) mainly produced alkenones in warm mixed layer as in the modern Mediterranean (Ternois et al., 1997).

## 6. Conclusion

Alkenone production in the Sicilian Early Pliocene Trubi Formation from Punta di Maiata section is due to the small *Reticulofenestra* (*R. minuta* and *R. minutula*). A strong correlation is observed among the C<sub>37</sub> and C<sub>38</sub> alkenone unsaturation ratios in the Pliocene sediments which is consistent with the culture and modern particulate results. Previous studies from McClymont et al. (2005) and Villanueva et al. (2002) showed that some of the major Pleistocene alkenone producing species turnovers (from small *Gephyrocapsa* to *G. oceanica*–*P. lacunosa* assemblage to *G. caribbeanica* to *G. aperta*–*G. ericsonii* assemblage to *G. muelleriae* to *E. huxleyi*) did not result in significant U<sup>k</sup><sub>37</sub> changes. This implies that during the Pleistocene, those coccolithophorid assemblage variations seemed to have no influence on the alkenone synthesis. The present study indicates that the cellular regulation of alkenone

unsaturation operated similarly in the Early Pliocene alkenone synthesizer and that the identified *Reticulofenestra* had an alkenone composition close to that of the present *E. huxleyi* and *G. oceanica*.

These results provide further evidence that, in spite of some expected genetic differences between fossil and modern producers, the regression of alkenone unsaturation vs temperature seems to be similar and that the modern calibrations could be confidently applied in the study of Lower Pliocene sediments. These preliminary results suggest that similar studies could be extended to longer and older geological time intervals to evidence the possible effect of alkenone producing species turnover on the alkenone based temperature estimates.

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## Appendix A

**Table A1**

Carbonate and total organic contents (%) in the Punta di Maiata early Pliocene samples. Absolute nannofossil abundances and relative abundances of the main nannofossil taxa and alkenone results in the samples studied.

Sample	Position (m)	TOC (%)	CaCO <sub>3</sub> (%)	Nannofossil abundances (×10 <sup>6</sup> liths/g)	<i>R. minuta</i> (%)	<i>R. minutula</i> (%)	<i>R. pseudo</i> (%)	<i>Discoaster</i> sp. (%)	*Others (%)	C <sub>37</sub> conc. (ng/g)	U <sup>k</sup> <sub>37</sub>	U <sup>k</sup> <sub>38Me</sub>	U <sup>k</sup> <sub>38Et</sub>
PM 29A	0.05	72.9	0.18	439	70.6	11.2	5.5	0.4	17.8	101.1	0.929	0.900	0.938
PM 29B	0.25	81.6	0.05	251	30.6	61.1	6.7	0.1	8.3	4	0.934	n.d.	0.827
PM 29C	0.5	70.3	0.07	604	19.9	66.6	1.1	0.2	13.3	6	0.912	n.d.	n.d.
PM 29D	0.8	78.4	0.05	1305	88.7	7.1	2.4	0.2	4	7.7	0.950	n.d.	n.d.
PM 30A	1.05	74.6	0.13	542	54.8	32.9	4.4	0.4	12	3.5	0.798	0.811	0.869
PM 30B	1.2	81.7	0.05	793	39.2	15.1	11.2	0.2	45.6	7.4	0.803	0.469	0.848
PM 30C	1.55	64.6	0.05	952	27.6	53.9	4.8	0.1	18.4	4.2	0.949	0.804	0.915
PM 30D	1.95	78.1	0.07	472	72.8	8.7	13.7	0.3	18.1	8	0.934	0.800	0.870
PM 31A	2.2	73.8	0.15	574	41.7	32.4	8.4	0.6	25.3	61.1	0.938	0.919	0.958
PM 31B	2.45	81.6	0.04	1125	42.7	53.5	0.5	0.1	3.8	2.7	0.883	0.165	0.840
PM 31C	2.75	71.7	0.02	1463	27.8	69.6	1	0.2	2.4	4.2	0.854	0.820	0.905
PM 31D	3.1	82.1	0.05	888	78.3	17.4	1.4	0.2	4.1	11.5	0.920	0.846	0.916
PM 32A	3.2	74.3	0.11	1012	68.5	21.4	3.6	0.4	9.7	78.9	0.935	0.921	0.964
PM 32B	3.4	83.5	0.04	1358	11.7	84.5	2.1	0.1	3.7	6.7	0.939	0.889	0.917
PM 32C	3.8	69.2	0.06	978	31.7	58.1	1.4	0.1	10.1	0	n.d.	n.d.	n.d.
PM 32D	4.2	76.7	0.07	754	22.2	74	2.1	0.1	3.7	8.2	0.955	0.581	0.823
PM 33A	4.45	73.2	0.10	802	89.2	5.6	2.6	0.7	4.5	26.4	0.952	0.876	0.957
PM 33B	4.65	75.4	0.10	1242	7.5	85.9	1.8	0.3	6.3	30.1	0.937	0.893	0.971
PM 33C	4.9	68.3	0.05	905	40.8	53.1	2	0.1	6	0.7	n.d.	n.d.	n.d.
PM 33D	5.15	77.8	0.05	1337	10.8	81.2	0.7	0.1	7.9	0	n.d.	n.d.	n.d.
PM 34A	5.3	72.1	0.11	695	58.1	31	3.9	0.5	10.4	55	0.930	0.911	0.969
PM 34B	5.55	78.4	0.06	2528	28.4	70.9	0.8	0.1	0.7	5	0.940	0.812	0.953
PM 34C	5.9	70.7	0.04	1163	73.4	22	2.8	0.1	4.5	3.3	0.834	n.d.	n.d.
PM 34D	6.05	76.3	0.05	869	76.5	21.3	1.4	0.3	1.9	6.3	0.881	0.894	0.952
PM 35A	6.45	74.6	0.08	974	68.5	22.8	2.7	0.2	8.5	27.7	0.907	0.856	0.962
PM 35B	6.7	80.8	0.04	557	34.2	54.6	2.6	0.1	11.1	2	0.897	n.d.	n.d.
PM 35C	7.05	70	0.03	2747	70	21	1.7	0.2	8.8	4	0.852	0.794	0.906
PM 35D	7.25	78.7	0.04	2225	86.3	10.4	1.3	0.1	3.3	1.4	0.840	n.d.	n.d.
PM 35E	7.6	83.3	0.03	2566	81.7	16.9	1.2	0	1.4	1.9	0.868	n.d.	n.d.
PM 35F	7.9	82.1	0.04	2474	67	27.9	0.5	0	5	3.1	0.914	n.d.	n.d.
PM 36A	8.15	79.1	0.09	1729	76.5	20.4	1.5	0.1	3	26.9	0.935	0.925	0.965
PM 36B	8.3	76.7	0.07	1232	16.5	82.5	0.7	0	0.9	6.2	0.910	0.844	0.965
PM 36C	8.55	68.5	0.04	348	45.8	38.3	4.2	0.7	15.2	2	0.813	n.d.	n.d.
PM 36D	8.85	78.3	0.06	2185	41.6	55.6	1.3	0.2	2.6	5.5	0.893	0.819	0.938
PM 37A	9.1	75.5	0.07	946	90.2	2.3	3.9	0.3	7.2	19.9	0.916	0.895	0.967
PM 37B	9.25	79.4	0.04	1387	61.4	34.1	2.6	0.1	4.4	2.9	0.881	n.d.	n.d.
PM 37C	9.4	74	0.04	1183	32.3	56.8	2.4	0.3	10.6	4	0.871	0.830	0.961
PM 37D	9.6	81.2	0.04	904	51.2	46.1	1.4	0.3	2.4	4.1	0.911	0.864	0.964
PM 38A	9.8	76.8	0.09	773	59.4	35	3.8	0.1	5.5	11.3	0.904	0.908	0.945
PM 38B	9.9	77.9	0.06	717	72.3	22.6	3.5	0.7	4.5	5.8	0.943	0.933	0.972
PM 38C	10.3	66.2	0.04	1409	26.8	66.9	1.5	0.3	6	2.6	0.917	n.d.	n.d.
PM 38C2	10.6	80.2	0.03	1807	39	58.1	1.3	0.5	2.4	1.2	0.907	n.d.	n.d.
PM 38D	11.2	82.4	0.03	501	74.3	21.8	3.4	0.1	3.8	2	0.888	n.d.	n.d.

(continued on next page)

Table A1 (continued)

Sample	Position (m)	TOC (%)	CaCO <sub>3</sub> (%)	Nannofossil abundances (×10 <sup>6</sup> liths/g)	<i>R. minuta</i> (%)	<i>R. minutula</i> (%)	<i>R. pseudo</i> (%)	<i>Discoaster</i> sp. (%)	*Others (%)	C <sub>37</sub> conc. (ng/g)	U <sub>37</sub> <sup>k</sup>	U <sub>38Me</sub> <sup>k</sup>	U <sub>38Et</sub> <sup>k</sup>
PM 38E	12.4	80.4	0.04	574	52.7	39.6	1.3	0.2	7.5	3.6	0.915	n.d.	0.967
PM 39A	12.9	68.1	0.04	1527	67.8	27.1	0.9	0.1	5	5.8	0.963	0.854	0.820
PM 39B	13.5	81.5	0.05	1179	14.7	81.1	1.1	0	4.1	2	0.920	n.d.	n.d.
PM 39C	14.45	79.6	0.04	328	83.5	12.5	1.2	0.5	3.5	5.5	0.895	0.842	0.939
PM 39D	15	80.5	0.05	247	88.1	5.7	1.5	0	6.1	7.7	0.945	n.d.	n.d.
PM 40A	15.3	71.3	0.17	796	78.6	15.7	2.2	0.2	5.5	42.9	0.967	0.909	0.989
PM 40B	15.5	77.6	0.05	941	76	21.7	0.8	0.1	2.2	3.8	0.950	n.d.	n.d.
PM 40C	15.75	69.8	0.04	1554	90.6	7.2	0.6	0.1	2.1	3.2	0.886	0.811	n.d.
PM 40D	15.95	76.9	0.06	879	72.5	25.4	1.0	0.1	2	5.7	0.924	n.d.	n.d.
PM 41A	16.25	69.6	0.15	723	14.3	71.4	4.5	0.1	14.2	40.9	0.956	0.873	0.987
PM 41B	16.5	75.9	0.05	1304	15.6	78	1.8	0.1	6.3	6.5	0.965	n.d.	n.d.
PM 41C	16.8	62.4	0.04	556	20.1	75.3	1.6	0.2	4.4	3.8	0.942	0.860	0.958
PM 41D	17.15	69	0.04	1482	41.7	55.5	0.6	0.1	2.7	5.4	0.957	n.d.	0.983

\* Others: *Calcidiscus macintyreii*, *Coccolithus pelagicus*, *Calcidiscus leptoporus*, *Sphenolithus abies*, *Helicosphaera cartieri*, *Schizophosphaera* sp.  
n.d.: not determined.

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