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Alkenones in the Northwestern Mediterranean sea: interannual variability and vertical transfer

Marie-Alexandrine Sicre[1,*], Yann Ternois[1], Juan-Carlos Miquel[2], and Jean-Claude Marty[3]

Abstract. C_{37} alkenone fluxes were measured with sediment traps at 200 m depth over the years 1989/1990 and 1993/1994 to assess the interannual variability of the alkenone flux from the surface waters of the Mediterranean Sea. Fall and spring were identified as the high flux periods. SST estimates derived from the U^K_{37} index indicated 50 m and 30 m as major production depths in spring and fall, respectively. Althought interannual variation of alkenone fluxes was notable, the seasonality and depth of production appeared to be recurrent features of the coccolithophorid cycle of production. Alkenone fluxes at 1000 m measured over the year 1993/1994 were about 5 times lower than at 200 m and show no evidence of preferential preservation relative to the organic carbon between these depths. SST predicted at 200 m and 1000 m indicated a remarkably good transfer of the surface temperature signal to deeper layers.

Introduction

In the past few years, time series sediment trap experiments have produced significant data on the production and export of alkenones to the ocean floor in the Pacific Ocean [*Prahl et al.*, 1993], in the Mediterranean Sea [*Ternois et al.*, 1996, 1997], in the Indian sector of the Southern Ocean [*Ternois et al.*, 1998] and in the Norwegian Sea [*Thomsen et al.*, 1998]. Such studies aim to better constrain the use of the alkenone unsaturation index (U^K_{37}) for the reconstruction of Sea Surface Temperature (SST) in the past. In this respect, proper interpretations of the U^K_{37} requires consideration of the water depth and season at which alkenones are biosynthesized and the subsequent temperature signal is produced. While a number of unresolved problems exists in the use of U^K_{37} ratio [*Brassell*, 1993; *Volkman et al.*, 1995; *Hoefs et al.*, 1998], many studies have used alkenones in sedimentary records to monitor SST variations, from decadal scale El Niño events [*McCaffrey et al.*, 1990; *Kennedy and Brassell*, 1992] to millenial scale climate changes [*Brassell et al.*, 1986; *Prahl et al.*, 1989; *Sikes et al.*, 1991; *Eglinton et al.*, 1992; *Rostek et al.*, 1993; *Zhao et al.*, 1993; *Ohkouchi et al.*, 1994; *Schneider et al.*, 1995; *Bard et al.*, 1997; *Madureira et al.*, 1997; *Villanueva et al.*, 1998]. In most cases, paleo-SST were predicted from the original calibration published by *Prahl and Wakeham* [1987] and revised by *Prahl et al.* [1988]. These studies assume that the relationship linking U^K_{37} and production remains unaltered during sedimentation throughout the water column and with subsequent long-term burial. Several coretop statistical evaluations have led to the conclusion of the applicability of this relationship on a global scale [*Sikes et al.*, 1991; *Rosell-Melé et al.*, 1995; *Sonzogni et al.*, 1997; *Müller et al.*, 1998], although questions have been raised for environments where *Emiliana huxleyi* is a minor alkenone producer [*Sonzogni et al.*, 1997; *Pelejero and Grimalt*, 1997]. Moreover, *Ternois et al.* [1997] recently reported that SST derived from the *Prahl et al.* [1988] calibration equation for the Northwestern Mediterranean waters lead to significantly lower values than those measured *in situ*. This result motivated a new investigation to produce a calibration for this oceanic basin, using particulate material from the euphotic zone (U^K_{37} = 0.041T - 0.21, r^2 = 0.97). The determination of surface sediment U^K_{37} values at various sites of the Northwestern Mediterranean provided evidence that this calibration was most suitable for SST reconstruction [*Ternois et al.*, 1996]. In this study, we built an expanded sediment trap data base to assess the interannual variability of the production pattern of alkenones and to follow the propagation of the temperature and flux signals to deep layers. This work follows on the one year survey undertaken by *Ternois et al.* [1996].

Sampling and Methods

The sampling site is located in the Northwestern Mediterranean basin, at the DYFAMED (Dynamique des Flux Atmosphériques en Méditerranée) station about 50 kms, or 28 nautical miles, offshore of Nice, France (Ligurian Sea). The water depth at the site is about 2300 m. Sediment traps were deployed at 200 m from February 1989 to March 1990 and at 200 and 1000 m, from May 1993 to November 1994 (station 1, Figure 1) with an interruption from late March to early June 1994. The sediment traps used in 1989-1990 were cylindrical (Technicap model PPS3) with a height of 1.9 m, a height/width ratio of 2.5 in the cross cylindrical portion and a collection section of 0.125 m^2. In 1993-1994, a blaffled conical sediment trap (Technicap model PPS5) with a height of 2.3 m and 1 m^2 opening was used. Preliminary results from an intercomparison exercise indicate that fluxes obtained by these two trap models are comparable when currents are weak as is the case at the DYFAMED station (< 10 cm s^{-1}). Sediment traps were equipped with an automatic pre-programmed cup

[1]Laboratoire des Sciences du Climat et de l'Environnement, 91191 Gif sur Yvette Cedex, France. (e-mail: Marie-Alexandrine.Sicre@lsce.cnrs-gif.fr) (corresponding author)
[2]IAEA Marine Environment Laboratory, P.O. Box 800, MC98012 Monaco Cedex. (e-mail: J.C.Miquel@iaea.org)
[3]Laboratoire de Physique et Chimie Marines, Université Pierre et Marie Curie, CNRS/INSU, BP 8, 06230 Villefranche Sur Mer, France. (e-mail: marty@ccrv.obs-vlfr.fr)

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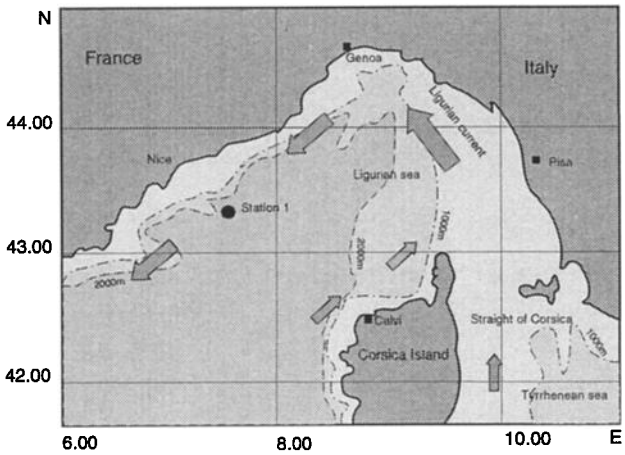

Figure 1. Map showing the sediment trap location in the Northwestern Mediterranena Sea.

collector to collect discrete samples every 10 to 15 days. Due to weather conditions and a ship delay in the redeployment of traps, the 1994 spring data are missing. Analytical methods were described in detail by *Miquel et al.* [1994] for Particulate Organic Carbon (POC) and *Ternois et al.* [1997] for alkenone determinations.

Results and Discussion

Production Pattern and Temperatures

C_{37} alkenone flux was strongly seasonal with moderate fluxes from December through March followed by a high flux pulse in spring, low fluxes in summer and a second well-pronounced high flux pulse in fall (Figure 2). In 1989, the sedimentation of alkenones was greater in fall than in spring. In 1993, these two high flux periods were of comparable intensity while POC fluxes were always more pronounced in spring. Earlier studies using pigment biomarkers have shown that highest primary production in the Northwestern Mediterranean Sea generally takes place during March/April and that it is dominated by diatoms and flagellates [*Marty et al.*, 1994]. As can be seen in Figure 2, interannual variations

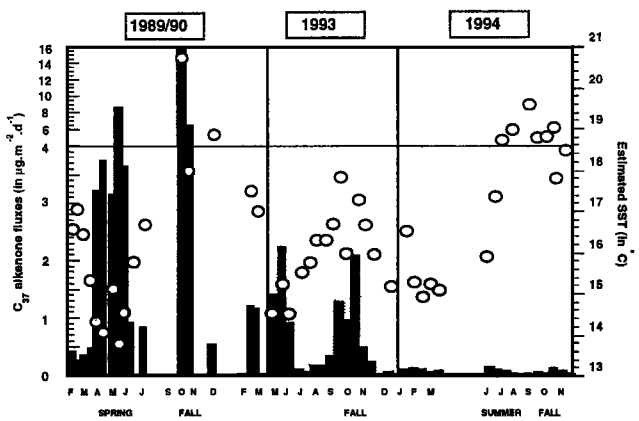

Figure 2. Temporal variations of C_{37} alkenone fluxes at 200 m from February 1989 to March 1990 and from May 1993 to December 1994. Estimated Sea Surface Temperatures (SSTs) calculated from the calibration equation: $U^K_{37} = 0.041T - 0.21$, $r^2 = 0.97$ [*Ternois et al.*, 1997] are also reported (open circles).

were also notable. However, given that the time series is not continuous because some data are missing, we did not calculate annual fluxes. Nevertheless, flux maxima of C_{37} alkenones in 1989 (8 µg/m^2/d in May; 16 µg/m^2/d in November) were undoubtedly higher than flux maxima in 1993 (2.2 µg/m^2/d in May; 2.1 µg/m^2/d in November) and 1994 (0.1 µg/m^2/d in October). Also OC fluxes were higher in 1988-1989 (annual mean flux of 6.7 to 8.5 mg/m2/d) as compared to 1993-1994 (average fluxes of 4.6 to 6.5 mg/m2/d).

SST were predicted from U^K_{37} measured at 200 m and the calibration published by *Ternois et al.* [1997]. SST ranged between 13.9°C and 20.8°C. Using the equation established by *Prahl et al.* [1988] SST varies from 9.4°C to 17.7°C, with the minimum value (9.4°C) found during the spring bloom in May/June 1989. At this time of the year *in situ* temperatures usually range from 18-19°C in the surface waters down to 13-14°C at 50 m depth (Figure 3). Below this depth the coldest *in situ* temperatures that can be found are those of deep waters which are never less than 12.5°C. Our results demonstrate quite clearly that the relationship established on cultures by *Prahl et al.* [1998] is not adequate for the Western Mediterranean Sea. Subsequently, in the following discussion SST estimates will refer to those calculated from the calibration published by *Ternois et al.* [1997].

Figure 2 shows that temporal fluctuations of SST were also highly seasonal. They displayed maxima in fall and minima in spring and late winter. Fall temperature maxima slightly differed in time and amplitude from year to year: ~ 21°C in November 1989, 18°C end of September 1993 and 19.6°C in September 1994. Spring minima were not so variable: 14°C in May 1989 and about 14.5°C in May 1993. An average temperature of 13.7°C has been reported by *Bentaleb et al.* [1999] in May 1995 using the calibration of *Ternois et al.* [1997] and U^K_{37} values measured in suspended particles collected at 30 m in the same area. These authors emphasize the good agreement between reconstructed SST and direct CTD temperature values. SST estimates from sinking particles at 200 m depict *in situ* temperatures for the upper euphotic zone. Enhanced C_{37} alkenone fluxes in fall occur between September and November, depending on the year. Production temperatures at this time of the year are those measured in the upper 30 m, while in spring they coincide with subsurface temperatures (around 50 m) below the thermocline (Figure 3) (CTD temperatures are available on the JGOFS-France database on http://www.obs-vlfr.fr/jgofs/html/bdjgofs.html). The

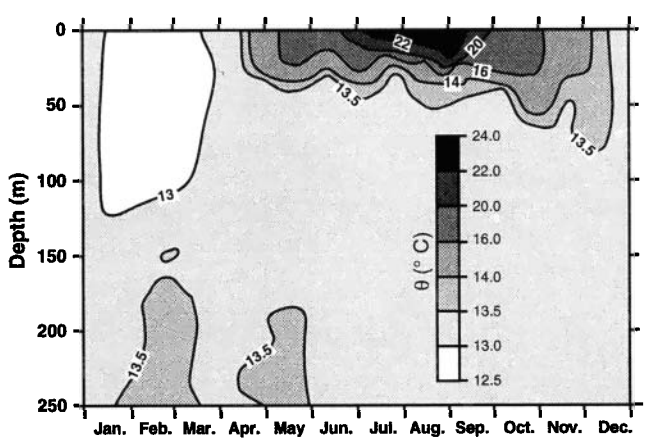

Figure 3. Composite of monthly temperatures measured at station 1 from 1991 to 1994 (see Figure 1).

proposed explanation for this is that over the course of the major autotrophic growth season in spring, surface waters become depleted in nutrients and alkenone producers develop preferentially in subsurface waters (~ 50 m) where nutrients are in higher concentration. This hypothesis is supported by alkenone profiles in the water column from an earlier investigation [*Ternois et al.*, 1997]. SST rises from May through fall, but summer alkenone production remains at low levels. In winter, predicted SST diverge significantly from *in situ* temperatures. For example, SST calculated from January through March range from 15°C to 17°C while *in situ* values are on the order of 13°C throughout the euphotic zone (Figures 2 and 3). This 2-4°C difference suggests that alkenones recovered in the winter season may have been produced earlier, when temperatures were warmer. This also imply that the sedimentation pattern is different: in winter, pelagic production is lower and may not be the only source of sinking matter. Alkenones produced at the end of fall would remain in surface waters till winter because grazing by herbivorous and carnivorous plankton are low [*Marty et al.*, 1994]. Dynamical factors such as wind stress or large-scale convection may then play a major part in regulating vertical particle fluxes [*Miquel et al.*, 1994]: wind-driven vertical mixing of surface waters in winter would advect particles to deeper layers.

Vertical transfer of the U^K_{37} signal

Over the year 1993/1994, sinking particles were also collected 1000 m depth. As shown in Figure 4, the strong

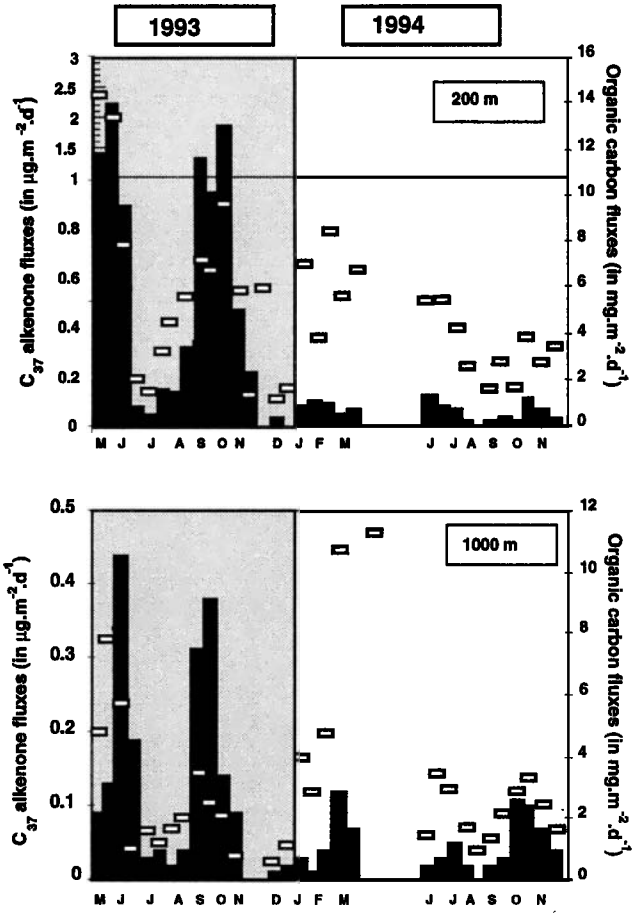

Figure 4. Temporal variations of the C_{37} alkenone (bar graph) and organic carbon fluxes (white boxes) at 200 m (upper graph) and 1000 m (lower graph).

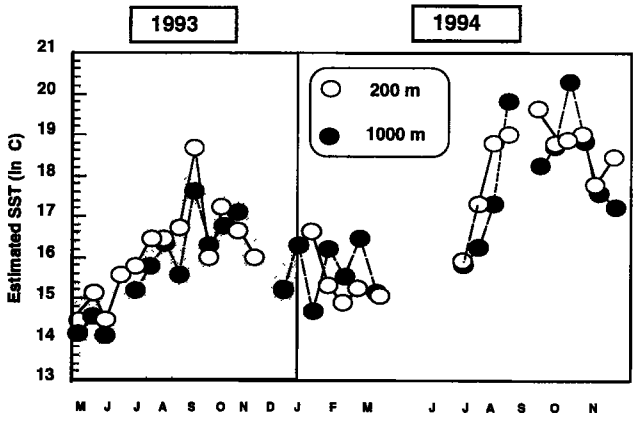

Figure 5. Temporal variations of SST (Sea Surface Temperature) estimates at 200 m (open circles) and 1000 m depth (solid circles), calculated from the calibration equation: U^K_{37} = 0.041T - 0.21, r^2 = 0.97 [*Ternois et al.*, 1997].

seasonality of alkenone fluxes in the shallow traps was also observed at 1000 m depth, althought the timing of alkenone peaks at 200 and 1000 m was not always synchronous. C_{37} alkenone fluxes were on average 5 times higher at 200 m than at 1000 m. The C_{37}/OC ratios do not indicate a preferential preservation of alkenones relative to the bulk organic carbon matter during sedimentation. The values of this ratio at 200 m range from 0.01 to 0.2, while at 1000 m depth they fluctuate between 0.01 and 0.15. OC flux at 200 m followed roughly similar trends as alkenones, except for high OC fluxes in late winter 1993/1994 (February/March), which are not so well seen in the alkenone record. The same observations can be made at 1000 m. This result suggests that coccolithophorid production is not a subtantial source of exported material in winter. Enhanced mass and OC fluxes at this time of the year have been reported in earlier investigations as a peculiar feature of this region [*Marty et al.*, 1994; *Miquel et al.*, 1994]. They coincide with the discrepancies between *in situ* temperatures and SST derived from alkenones observed during the winter season, earlier discussed. Fatty acids and *n*-alkanes data indicated that the organic material was more refractory [*Marty et al.*, 1994] which further supports the idea that this material may have remained in the euphotic zone and later exported by winter vertical mixing.

Figure 5 shows the temporal fluctuations of SST at each depth. The close similarity between SST values at 200 m and 1000 m indicate that U^K_{37} is not sensitive to degradation despite substantial diagenetic losses during sedimentation processes. As previously observed for C_{37} alkenone fluxes, surface and deep SSTs appear slightly shifted in time. This is not unexpected given the fact that sediment trap cups discretly sample a continuous flow of sinking particles. Assuming a sedimentation velocity of 100 m d^{-1}, 8 days would be necessary for particles to reach the depth of 1000 m, while our sampling interval is, on average, 15 days. However, the regression line obtained from the least square fit of the two sets of data was highly significant (r^2=0.87) and not very much different from the 1:1 fit. The average difference between estimated SST at 200 and 1000 m, around 0.7°C, is comparabe to SST accuracy calculated from this method (± 0.4°C). Higher offset was found when concentrations and fluxes of alkenones were low and SST less accurate, mainly in 1994, or during winter mixing. From these results we can conclude that the temperature signal produced in surface waters is well preserved during

sedimentation, a pre-requiste condition to the applicability of alkenones as climatic indicators.

Conclusions

Vertical fluxes of C_{37} alkenones and SST predicted from the U^K_{37} index indicate that the coccolithophorid production in the Northwestern Mediterranean is seasonal and depth variable. Two main flux phases are clearly identifiable: one in spring associated with low SST (around 14°C), a second one in fall associated with warmer SST (18-21°C). This pattern appears to be recurrent in the coccolithophorid production of the Western Mediterranean Sea. Contrary to previous conclusions based on a one year record [*Ternois et al.,* 1996], this extanded database show that coccolithophorid production in fall is not systematically higher than in spring, but can be of comparable levels. The good correspondence between algal growth SST predicted from alkenones at 200 m and *in situ* temperatures given by CTD measurements in the euphotic zone reinforce the idea that the calibration established by *Ternois et al.* [1997] provides a consistent and coherent relationship to water temperatures for the Mediterranean Sea. Flux and SST data suggest that during winter dynamycal factors have a strong influence on sedimentation. The seasonaly-varying sedimentation pattern observed at 200 m was also seen at 1000 m depth, but with some delay time. The records of SST values at 200 m and 1000 m indicate that the U^K_{37} index is remarkably well preserved during sedimentation.

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