



Alkenone distributions in the North Atlantic and Nordic sea surface waters

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[1] The C₃₇–C₃₉ alkenones were quantified in suspended particulate matter obtained from the surface waters of the North Atlantic, including the Nordic seas, over a temperature range of 4°–20°C. U₃₇^{K'} values were linearly correlated to temperature over the entire range covered by our data set, i.e., 4°–20°C (U₃₇^{K'} = 0.027T + 0.036, r² = 0.97). The compilation of water column data from the Atlantic, Pacific, and Southern Ocean and Mediterranean Sea suggests that the linear model may not be the best function for fitting U₃₇^{K'} and in situ temperature values. It also shows that suspended matter data from warm waters (T > 20°C) are still needed to constrain the equation of the global curve. High abundances of C_{37:4} were found in the coldest polar waters. Around 4°C, %C_{37:4} represented up to 35%, a value that dropped to zero at temperatures above 10°C. Values of %C_{37:4} were linearly correlated to temperature (%C_{37:4} = –3.7T + 43.7, r² = 0.50) and salinity (%C_{37:4} = –48.1S‰ + 1691, r² = 0.78). Further investigations from other oceanic basins are necessary to confirm these findings.

Components: 6222 words, 6 figures, 1 tables.

Keywords: Alkenones; paleotemperature; calibration; Atlantic Ocean; plankton.

Index Terms: 1050 Geochemistry: Marine geochemistry (4835, 4850); 1615 Global Change: Biogeochemical processes (4805); 4267 Oceanography: General: Paleooceanography; 9325 Information Related to Geographic Region: Atlantic Ocean.

Received 8 March 2001; **Revised** 26 November 2001; **Accepted** 26 November 2001; **Published** 16 February 2002.

Sicre, M.-A., E. Bard, U. Ezat, and F. Rostek, Alkenone distributions in the North Atlantic and Nordic sea surface waters, *Geochem. Geophys. Geosyst.*, 3(2), 10.1029/2001GC000159, 2002.

1. Introduction

[2] Over the last decade, the alkenone unsaturation index, $U_{37}^{K'}$, has become a widely used proxy by paleoceanographers to estimate past sea surface temperatures (SSTs). Alkenones were first recognized in the cosmopolitan coccolithophorid *Emiliana huxleyi* [Volkman *et al.*, 1980; Marlowe *et al.*, 1990] which is considered today as the major marine organism producing them. Culture experiments have shown that the related species *Gephyrocapsa oceanica* also contributes to their production [Volkman *et al.*, 1995; Conte *et al.*, 1998]. The $U_{37}^{K'}$ index was initially defined as follows to quantify the degree of unsaturation of C_{37} alkenones [Brassell *et al.*, 1986]:

$$U_{37}^{K'} = \frac{[C37:2] - [C37:4]}{[C37:2] + [C37:3] + [C37:4]},$$

but because the C_{37} tetraenoic alkenone is often absent or not detectable, this ratio was simplified to

$$U_{37}^{K'} = \frac{[C37:2]}{[C37:2] + [C37:3]}.$$

[3] The first calibration establishing a relationship between the $U_{37}^{K'}$ index and temperature was published by Prahl and Wakeham [1987] and then revised using batch cultures of *E. huxleyi* by Prahl *et al.* [1988] ($U_{37}^{K'} = 0.034T + 0.039$; 8° – 25° C). This linear fit is the most commonly used to derive SSTs from downcore $U_{37}^{K'}$ values. Sikes and Volkman [1993] extended this calibration to colder temperatures, down to -0.7° C. They demonstrated a change in the nature of the relationship for $T < 4^{\circ}$ C and proposed a nonlinear exponential function to better fit low temperatures of the Southern Ocean. Nevertheless, when combining their data for $T > 4^{\circ}$ C with the field data from the Pacific Ocean of Prahl and Wakeham [1987] they were able to calculate a linear equation ($U_{37}^{K'} = 0.0414T - 0.156$, 4° – 25° C) which is different from the original one. Ternois *et al.* [1997] calculated a similar slope and intercept for the NW Mediterranean Sea ($U_{37}^{K'} = 0.041T - 0.21$), though over a restricted temperature interval (13° – 19° C). Water column data were also produced by Conte and

Eglinton [1993] for the North Atlantic between 61° N and 24° N. They indicate that for $T > 16^{\circ}$ C, $U_{37}^{K'}$ and SSTs are linearly correlated ($U_{37}^{K'} = 0.056T - 0.496$), while in the colder waters north of 47° N, these parameters are uncorrelated. The authors also emphasize the absence of correlation over the entire temperature range. Although there are some differences in the various linear equations produced so far, overall, they tend to follow similar trends. Part of the variability observed between these studies may be attributed to small data sets and different temperature ranges used to establish each calibration. More field data covering the entire range of temperatures and various ecological conditions of the global ocean, in particular at high latitudes and in the equatorial regions, are still needed to establish a global water column calibration and thus improve SST prediction.

[4] Differences exist between water column and culture data. Results from culture experiments yield a nonlinear relationship between $U_{37}^{K'}$ and growth temperatures [Conte *et al.*, 1998]. This is in contrast with field calibrations established from surface water or core tops, which indicate that the linear model is the best approximation. However, few water column calibrations include temperature extremes which are driving the relationship nonlinear in cultures, except for the data produced in the Southern Ocean [Sikes and Volkman, 1993]. It is worthy of note that no water column data exists for the warm surface waters of the equatorial ocean. Core-top material has also been used to evaluate the statistical relationship of $U_{37}^{K'}$ and sea surface temperature. The most recent compilation of core-tops data from the world ocean [Müller *et al.*, 1998] has shown a strong linear correlation of $U_{37}^{K'}$ with mean annual surface temperature at 0 m from the world atlas. The resulting calibration is identical to the equation established for *E. huxleyi* in laboratory cultures by Prahl *et al.* [1988]. However, the reasons of this close agreement are not entirely clear, and thus recommendations for further concerted laboratory and field works have been made (see review paper from Prahl *et al.* [2000]).

[5] This paper reports on alkenone distributions in the suspended particles obtained in the surface

waters of the North Atlantic and Nordic Seas over a temperature range of 4°–20°C and on C_{37:4} abundances found in low temperature waters. Implications of our findings for the estimation of temperature are also discussed in relation with existing data.

2. Experimental

[6] Samples of particulate material were collected in the North Atlantic surface waters between 36°N and 77°N, during the IMAGES V cruise in June–September 1999 on the R/V *Marion Dufresne*. Samples obtained cover different provinces of the North Atlantic, a wide latitudinal range, as well as a 16°C spread of surface water temperatures (Figure 1). During the cruise the vertical distribution of temperature, salinity, and fluorescence were obtained using a CTD equipped with a Chelsea fluorimeter and water samples obtained from 12-L bottles mounted on the Rosette. The sampling depths for discrete analyses of alkenones were chosen based on the temperature and fluorescence profiles measured at each site. Samples were taken in the fluorescence maximum and sometimes other depths. Forty to sixty liters of seawater were filtered depending on the fluorescence intensity. Filtration was performed on precombusted GFF filters (Watman: 143 mm, 0.45 μm porosity) installed on a stainless steel Millipore filter holder connected to a pneumatic pump (ASTI, PFD1 210). The pump and the tubing were all teflon to avoid contamination. Sample filters were frozen on board at –80°C immediately after filtration and kept frozen until processing.

[7] In the laboratory, filters were freeze-dried then cut into small pieces and placed in a 250 mL Erlenmeyer flask for extraction in 50 mL of a mixture of 2:1 dichloromethane:methanol (v/v) in an ultrasonic bath for 15 min. Extraction was repeated twice. The three extracts were combined in a 250 mL pear-shaped flask and concentrated to ~1–2 mL by evaporation with a rotary evaporator (Laborota 4000). The concentrated extracts were then transferred in a 4 mL vial and evaporated to dryness under a nitrogen stream. Lipid were frac-

tionated into compound classes by silica gel chromatography. The fractions containing alkenones were stored in vial flasks at –18°C until gas chromatographic (GC) analyses. C_{37:2} and C_{37:3} were quantified on Varian Star 3400CX gas chromatograph equipped with a fused CP-Sil-5CB silica capillary column (50 m × 0.32 mm i.d., 0.25 μm film thickness, Chrompack), a Septum Programmable Injector (SPI) and flame ionization detector (FID). The oven temperature was programmed from 100°C to 300°C at 10°C min⁻¹. Helium was used as the carrier gas (25 mL min⁻¹). Analytical precision obtained after duplicate injections was calculated to be less than 0.01 U₃₇^K unit ratio. Quantitation of individual alkenones was achieved by comparison of chromatographic peak areas with α-cholestane added prior gas chromatography injection.

[8] The relative abundance of C_{37:4} was subsequently determined on the same lipid extracts by gas chromatography/mass spectrometry (GC/MS) because of the presence of a coeluting compound under the GC conditions described above. GC/MS analyses were performed on a Fisons Instruments MD800 GC/MS system (Carlo-Erba GC8185/VG MS) operating under standard electron impact ionization (operation energy 70eV). This system includes a cold on-column injector fitted with a nonpolar fused silica capillary column DB5-MS (60 m × 0.25 mm i.d., 0.1 μm film thickness, J&W), helium being used as carrier gas. The GC oven was programmed from 45° to 200°C at 15°C/min, 200° to 250°C at 5°/min, and 250° to 300°C at 3°/min. The final temperature was then maintained for 40 min. Alkenones and alkenoates typically elute between 55 and 65 min, and the C₃₇ alkenone peaks are well separated by ~30–40 s. Fragment ion *m/z* = 109 was used to quantify the percentage of C_{37:4} as it is a major common ion in all three C₃₇ alkenone mass spectra, while it is negligible in the interfering compound. The reliability of the %C_{37:4} determinations was further checked by replicating GC/MS analyses with further refined conditions: 1/ after saponification of the lipid extracts and/or 2/ in GC/MS Selected Ion Monitoring (SIM) mode in order to quantify C₃₇ alkenones with their respective molecular ions (*m/z* = 526.5, 528.5 and 530.5 for

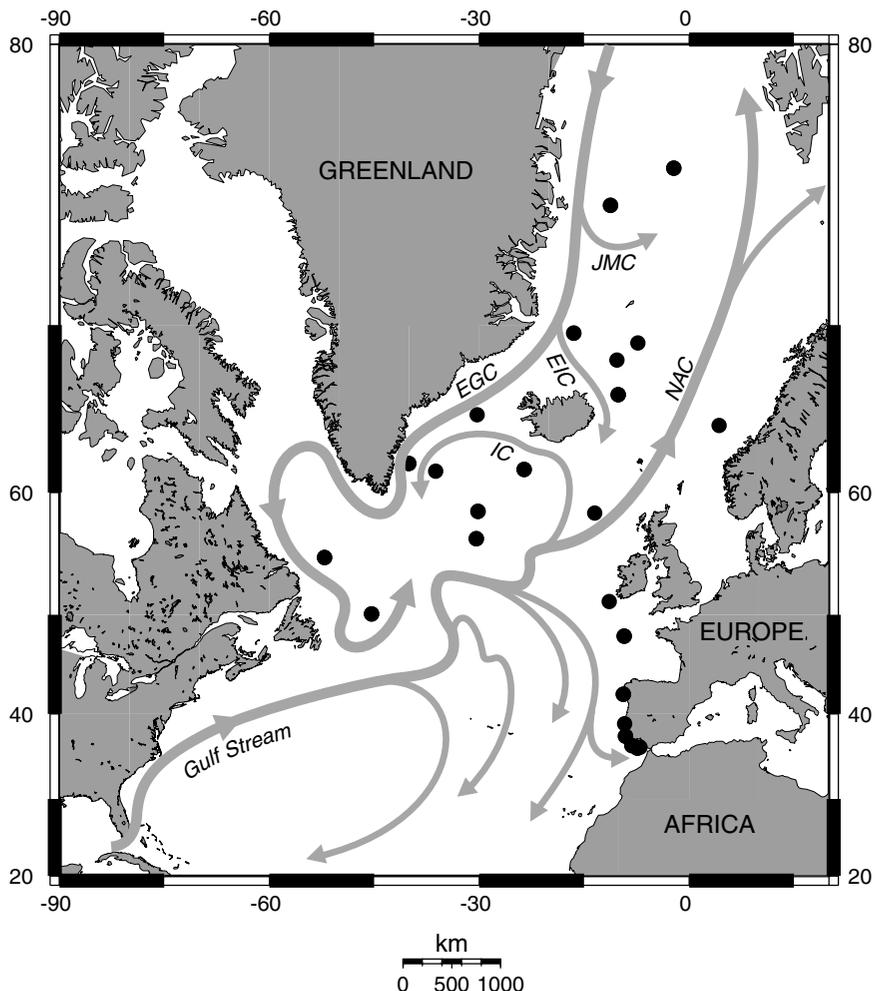


Figure 1. Map showing the sampling site locations during the IMAGES V cruise on the R/V *Marion Dufresne* from June to September 1999. EGC, East Greenland Current; EIC, East Iceland Current; NAC, North Atlantic Current; IC, Irmingier Current; JMC, Jan Mayen Current.

$C_{37:4}$, $C_{37:3}$ and $C_{37:2}$, respectively). Abundances of C_{37} alkenones measured by GC/MS were corrected for relative response factors in a similar way as in Versteegh *et al.* [2001]. Analytical precision of the % $C_{37:4}$ values has been evaluated by replicating analyses of the order of 10–20% in relative terms. Our GC/MS methods will be described in details in a separate paper (E. Bard, C. Sonzogni, F. Rostek, manuscript in preparation, 2002).

3. Results

3.1. Alkenone Distributions

[9] Alkenones were detected in waters within the temperature range 4°–20°C. They were absent or

not detectable in samples collected at temperatures comprised between –1°C and 4°C that were also collected during the cruise. Prominent abundances of $C_{37:4}$ were found at water temperatures between 4° and 10°C. The occurrence of this compound has also been reported in the surface waters of the Southern Ocean [Sikes and Volkman, 1993]. Figure 2 shows the results of GC and GC/MS analyses performed on sample IMV 24b collected at a water temperature of almost 8°C. Methyl and ethyl C_{38} ketones with two to four double bonds were also present. As can be seen in Table 1, % $C_{37:4}$ values increase from 2% at $T \sim 10^\circ\text{--}12^\circ\text{C}$ to 35% around 5°–6°C. In the coldest water sample SG29b (4°C), alkenone concentrations were too low to allow accurate estimate of $C_{37:4}$.

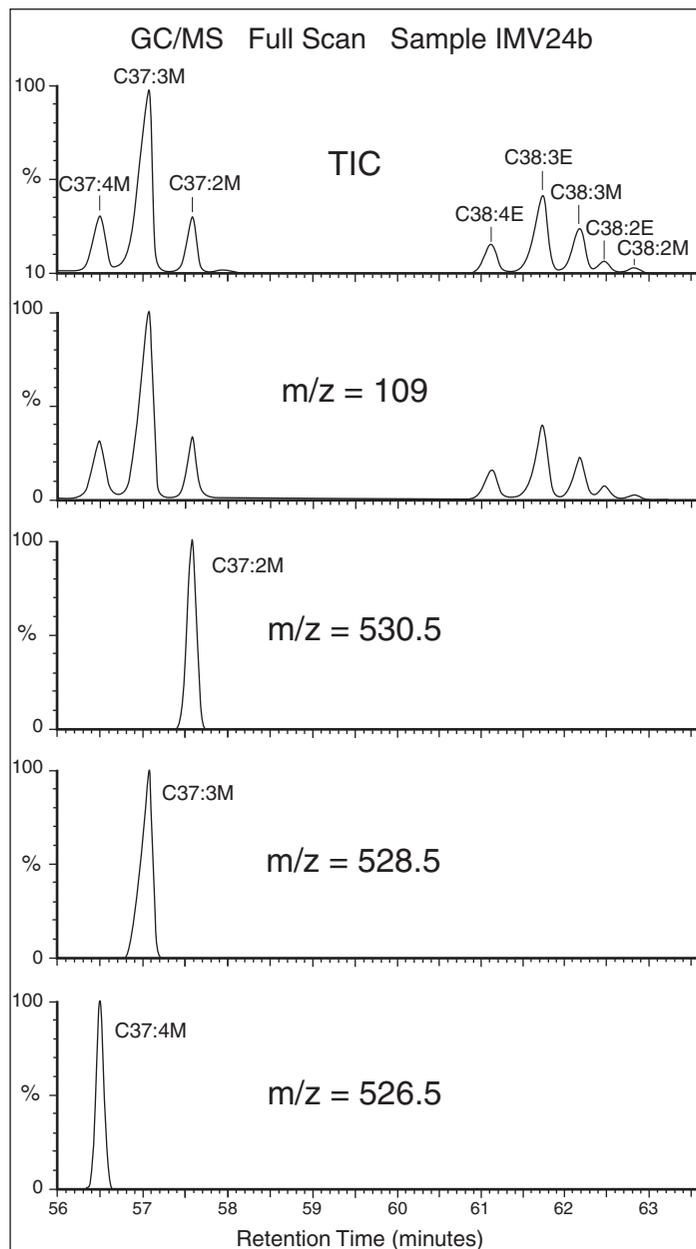


Figure 2. GC/MS chromatograms of C_{37} and C_{38} alkenones in sample IMV 24b. (a) Total ion current (TIC). (b) Mass chromatogram of fragment ion $m/z = 109$. (c) Mass chromatogram of $C_{37:2}$ molecular ion, $m/z = 530.5$. (d) Mass chromatogram of $C_{37:3}$ molecular ion, $m/z = 528.5$. (e) Mass chromatogram of $C_{37:4}$ molecular ion $m/z = 526.5$. Note that the abundance of $C_{38:4E}$ relative to the sum of $C_{38:3E}$ and $C_{38:2E}$ is similar to that for C_{37} alkenones ($\%C_{38:4E}$ is on the same order as $\%C_{37:4}$).

Figure 3 shows histograms of the C_{37} alkenone abundances at all sites where $C_{37:4}$ is present in detectable amounts. $C_{37:4}$ levels are highest ($\sim 35\%$) in the coldest (4° – 6°C) and less saline waters (~ 34.5 PSU) of two distinct oceanic regions: in the Jan Mayen Current, a branch of

the East Greenland Current (SG23b), and in the Labrador Sea (sample 1). They show intermediate values (around 25%) in water samples from the slightly warmer (6° – 8°C) and equally low salinity waters (~ 34.5 PSU) of the East Greenland Current and Iceland Current (SG42, 21c and 24). Only a

Table 1. Sample Information: Name, Position, Temperature and Salinity

Sample Code	Latitude	Longitude	In situ Temperature, °C	Salinity, PSU	$U_{37}^{K'}$	% $C_{37:4}$	ΣC_{37} , ng/L
IMV SG23b	76°44.02 N	2°19'88 W	4.6	34.7	0.18	35	11.6
IMV..21c	69°07.13 N	7°29'75 W	5.5	34.8	0.19	21	11.3
SG42	69°59.93 N	16°52'61 W	5.9	34.6	0.22	21	9.3
IMV 24b	66°33.20 N	10°06'69 W	7.8	34.7	0.25	26	11.1
IMV 18d	65°09.94 N	30°30'24 W	9.6	35.1	0.30	3	23.2
IMV..18c	65°09.94 N	30°30'24 W	9.6	35.1	0.28	1	11.6
IMV..13a	58°57.23 N	30°23'13 W	10.4	35.0	0.28	0	23.1
IMV..14a	56°47.87 N	30°40'00 W	10.5	35.0	0.31	0	20.2
IMV..14c	56°47.87 N	30°40'00 W	10.5	35.0	0.29	0	30.1
IMV 26b	59°26.46 N	10°35'58 W	12.8	35.0	0.35	0	23.7
IMV 30c	64°45.01 N	4°30'81 E	13.0	34.9	0.39	2	4.3
SG-HC83c	58°48.03 N	13°53'33 W	14.9	35.3	0.45	0	49.1
SG-HC83b	58°48.03 N	13°53'33 W	14.9	35.3	0.43	0	67.1
SG-HC 84b	51°24.00 N	11°39'33 W	16.3	35.4	0.44	0	72.3
SG-HC85b	48°04.65 N	9°30'36 W	17.0	35.5	0.51	0	79.5
SG-HC85d	48°04.65 N	9°30'36 W	17.0	35.5	0.52	0	155.5
SG-HC84c	51°24.00 N	11°39'33 W	17.0	35.4	0.46	0	76.3
Station 89a	37°50.07 N	9°06.04 W	18.5	35.9	0.55	0	109.1
Station 87a	38°83.52 N	9°21.89 W	18.7	35.9	0.54	0	112.2
Station 87b	38°83.52 N	9°21.89 W	18.7	35.9	0.53	0	135.0
Station 91a	36°43.03 N	8°15.54 W	18.7	36.1	0.58	0	41.4
SG29b	75°06.93 N	11°20'17 W	4.0	34.2	0.23	n.d.	3.4
IMV..1	55°02.00 N	52°08.38 W	6.0	34.4	0.25	34	0.8
IMV..12a	61°54.74 N	36°21'29 W	6.9	35.0	0.24	3	4.4
IMV..7a	50°11.55 N	45°40'62 W	7.5	35.0	0.29	2	14.6
IMV..10	62°04.37 N	40°11'57 W	7.6	35.0	0.18	5	6.4
IMV 24f	66°33.20 N	10°06'69 W	8.1	34.6	0.18	25	4.4
IMV 24d	66°33.20 N	10°06'69 W	8.5	34.6	0.21	15	8.1
IMV..12c	61°54.74 N	36°21'29 W	9.2	34.9	0.34	0	9.5
SGHC35c	68°19.47 N	10°30'34	10.0	35.1	0.32	1	14.8
IMV..13b	58°57.23 N	30°23'13 W	10.4	35.0	0.27	6	20.7
SGN57b	61°59.37 N	23°59'38 W	11.9	35.1	0.43	2	4.4
Sation 95a	36°23.61 N	7°03.75 W	16.3	36.4	0.48	0	7.0
Sation 93a	36°16.56 N	7°44.48 W	17.7	36.2	0.51	0	41.6
Station 86b	42°08.21 N	9°40.99 W	20.1	35.7	0.67	0	4.1

Abbreviations are as follows: % $C_{37:4}$, percentage of $C_{37:4}$ alkenone relative to the total of C_{37} alkenones; ΣC_{37} , sum of the C_{37} alkenones; $U_{37}^{K'} = [C_{37:2}]/[C_{37:2}] + [C_{37:3}]$; n.d., not determined.

few percent of $C_{37:4}$ was found in warmer (8°–10°C) and saltier waters (35 PSU) water samples from the Irminger current (samples 10 and 12).

[10] High occurrences of $C_{37:4}$ alkenones have been previously observed in lacustrine sediments of East Anglia [Cranwell, 1985] and in the highly alkaline Lake Van, Turkey [Thiel *et al.*, 1997]. The C_{37} tetraenoic alkenone was also described, but in lower proportions, in the sediments of Qinghai Lake and the saline Lake of Gahai (33‰) [Li *et al.*, 1996], and more recently in the Baltic Sea [Schulz *et al.*, 2000]. To our knowledge there has been no previous report of

enhanced levels of $C_{37:4}$ in the Northern Hemisphere oceanic waters such as those observed here. $C_{37:4}$ was found in minor amounts in marine particles of the Black Sea [Freeman and Wakeham, 1992]. It was also a trace constituent in samples collected during winter in the Southern Ocean even at the coldest temperatures south of the Polar Front [Sikes and Volkman, 1993]. However, up to 30% of $C_{37:4}$ was measured in spring water samples [Sikes *et al.*, 1997]. In the underlying austral surficial sediments, $C_{37:4}$ accounts for up to 40%, consistently with spring-summer being the period of highest alkenone production in this region [Sikes *et al.*, 1997]. The analyses of

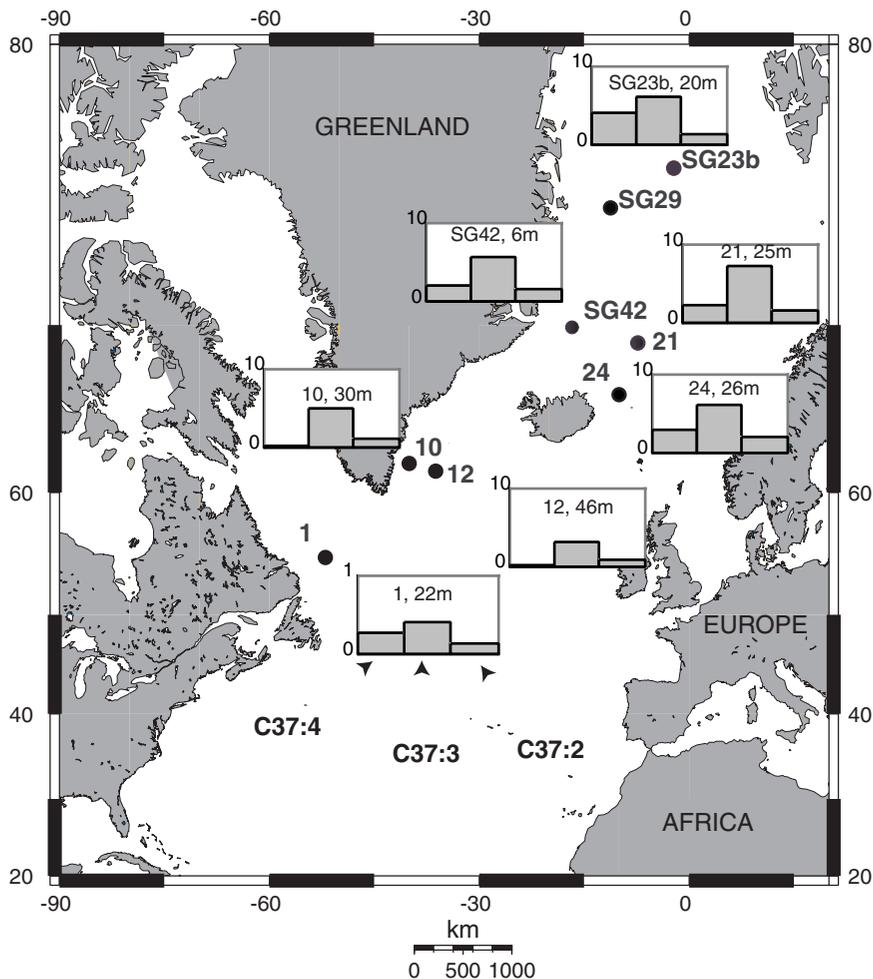


Figure 3. Histograms of the spatial distribution of $C_{37:2}$, $C_{37:3}$ and $C_{37:4}$ alkenones. Individual alkenone concentrations are expressed in ng/L.

sinking particles from the Indian sector of the Southern Ocean collected over 1 year off Kerguelen Island did not reveal detectable amounts of $C_{37:4}$ [Ternois *et al.*, 1998].

[11] $C_{37:4}$ has also been documented in surface sediments at high latitudes in the North Atlantic. Values of % $C_{37:4}$ do not exceed 20% in sediments deposited below the East Greenland Current waters and are less than 10% in the Norwegian Sea sediments for overlying water temperatures lower than 10°C [Rosell-Melé *et al.*, 1998; Rosell-Melé, 1998]. These sediment values are lower than those measured between June and September in suspended particles from this study. In summary, the occurrence of the tetraenoic alkenone has been reported in marine and lacustrine systems where temperature,

salinity, or alkalinity conditions were quite different and where alkenone precursor organisms may not be the same. Data from marine settings indicate that this compound is produced essentially in cold waters.

3.2. Calibration of $U_{37}^{K'}$ Against Temperature

[12] In this section we investigate the relationship between the unsaturation pattern of C_{37} alkenones and in situ T obtained from the CTD casts. The entire data set covers a temperature range from 4° to 20°C (Table 1). Figure 4 shows the plot of $U_{37}^{K'}$ against in situ T values. All samples were taken in the fluorescence maximum where presumably primary production predominantly takes place. Among them we

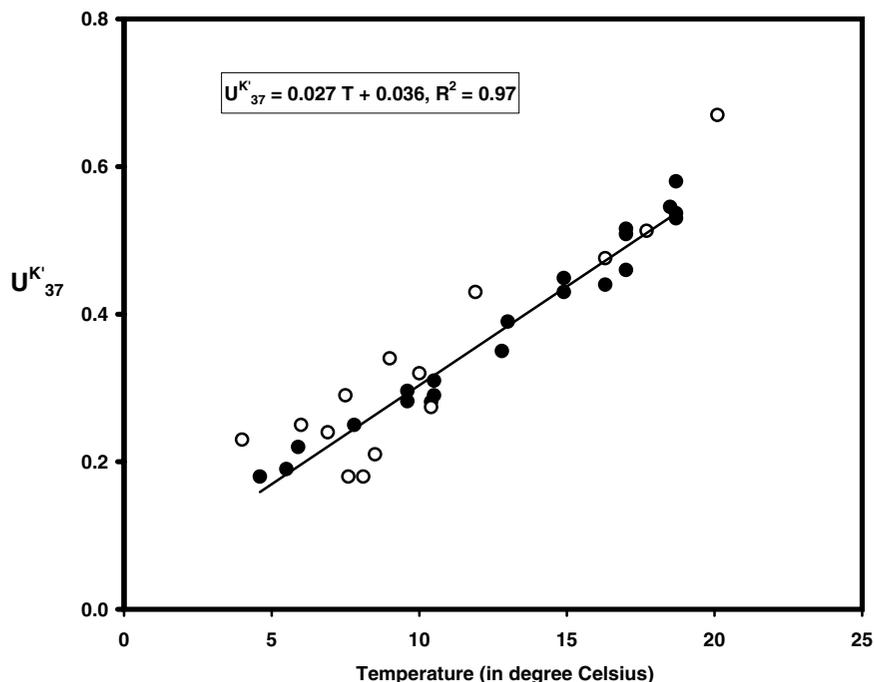


Figure 4. Plot of $U_{37}^{K'} = [C_{37:2}]/([C_{37:2}] + [C_{37:3}])$ against in situ temperatures. Solid circles are samples for which the fluorescence maximum lies within the mixed layer. Open circles represent samples exhibiting the fluorescence maximum in the thermocline or below. The calibration line is the linear fit calculated from the solid circle data ($U_{37}^{K'} = 0.027 T + 0.036$, $n = 21$; $r^2 = 0.97$).

distinguished two groups: one group (solid circles in Figure 4 and upper part of Table 1) representing water samples exhibiting maximum fluorescence within the mixed layer, as shown by Figure 5a. These samples represent ideal conditions for calibration because temperature is constant over the entire water thickness where fluorescence is most intense. Samples taken at any depth within the mixed layer should provide the same $U_{37}^{K'}$ values. The second group (empty circles and lower part of Table 1) is the samples for which the fluorescence maximum occurs within the thermocline (Figure 5b) or below it, thus making it more difficult to accurately assign temperature. When the thermal gradient is strong, i.e., $>0.5^{\circ}\text{C}/\text{m}$, and under rough weather conditions at sea, the sampling bottles may oscillate by 1 or 2 m around the selected sampling depth which can easily introduce 1°C of uncertainty between the actual sampled temperature and that provided by the CTD for the selected depth. Besides operational bias, a further concern is the precise knowledge of alkenone production temperature. Previous studies have suggested that under

depleted nutrient conditions alkenone producers might preferentially develop at greater depths where nutrients are available [Terzois *et al.*, 1997]. *E. huxleyi* can secrete a polysaccharide that causes coccoliths to stick together to form macro-aggregates allowing them to sink to deeper layers [Knappertsbush, 1993]. If this process takes place, alkenones when sampled within the thermocline may have been synthesized at shallower depths and warmer temperatures than measured at the time of sampling. In that case, sampled $U_{37}^{K'}$ will underestimate the growth temperature. If this process is occurring, it should have a limited effect though because alkenone producers rapidly adjust the unsaturation index to temperature [Prah *et al.*, 1988]. To evaluate potential bias from these factors, we fitted a linear regression for the solid circle data ($U_{37}^{K'} = 0.027T + 0.036$, $n = 21$; $r^2 = 0.97$; error on the slope is estimated to 0.002 at the 95% confidence interval) and a second one over the entire data set ($U_{37}^{K'} = 0.027T + 0.046$, $n = 35$; $r^2 = 0.91$; error on the slope is estimated to 0.003 at the 95% confidence interval). The two linear equations are not different,

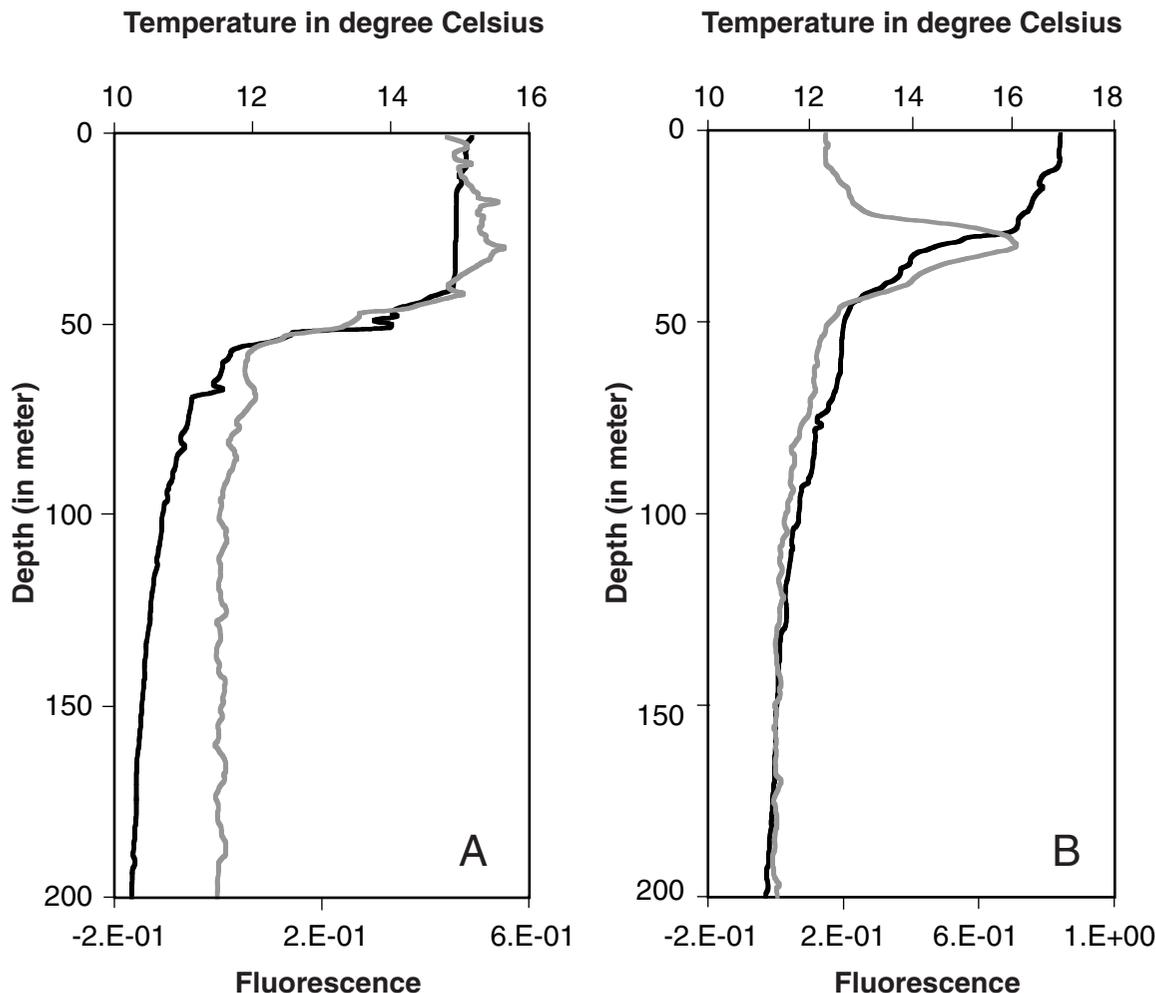


Figure 5. Vertical profiles of fluorescence (grey line) and temperature (black line) over the first 200 m in the water column (a) with the fluorescence maximum within the mixed layer and (b) with the fluorescence maximum lying within the thermocline.

except for a slight increase in scatter. The slope of the regression line is significantly lower than that calculated from the suspended matter data of *Prahl and Wakeham* [1987] in the Pacific Ocean ($U_{37}^{K'} = 0.037T - 0.07$; 11° – 28°C ; error on the slope is estimated to 0.003 at the 95% confidence interval), or by *Sikes and Volkman* [1993] for the Pacific and Southern oceans ($U_{37}^{K'} = 0.0414T - 0.156$, 4° – 25°C ; error on the slope is estimated to 0.003 at the 95% confidence interval) and *Ternois et al.* [1997] for the Mediterranean Sea ($U_{37}^{K'} = 0.041T - 0.21$; 13° – 19°C ; error on the slope is estimated to 0.003 at the 95% confidence interval). Differences between the above calibrations may reflect distinct regional oceanographic features as it has often been sug-

gested. However, if we assume that the calibration curve is nonlinear and have a mathematical form similar to cultures [*Conte et al.*, 1998], different slopes calculated over different temperature ranges for each oceanic basin may reflect incremental change of the $U_{37}^{K'}$ index relative to temperature. Combining our data with those of suspended matter from the Pacific Ocean, Mediterranean Sea, and Southern Ocean and calculating the best fit of the data produces the following relationship: $U_{37}^{K'} = 0.001T^2 + 0.008T + 0.008$; $r^2 = 0.93$; (Figure 6). This is roughly equivalent to $T = -12.203 (U_{37}^{K'})^2 + 37.831 U_{37}^{K'} + 0.577$; $r^2 = 0.87$. For the Southern Ocean we only considered the high production seasons, spring and summer. Attention has been

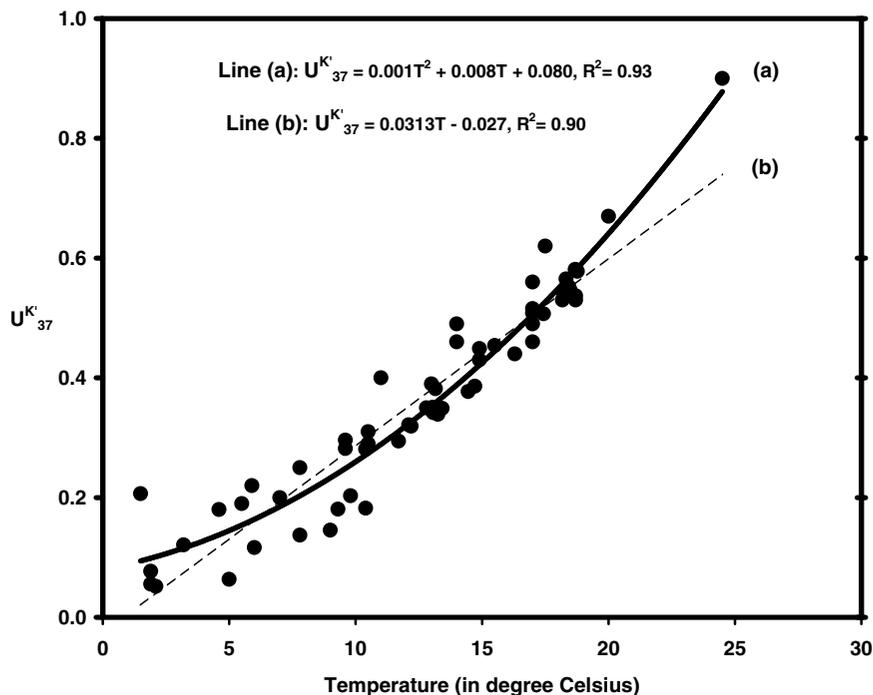


Figure 6. Plot of the water column suspended particles from the Pacific Ocean [Prah1 and Wakeham, 1987], Mediterranean Sea [Ternois et al., 1997], Southern Ocean [Sikes and Volkman, 1993] and this study. Line a represents second order polynomial fit of the data; line b is linear fit on the same data set.

drawn by Conte et al. [1992] to the presence of residual amounts of alkenones in particulate detritus that may have been responsible for some of the scatter in their data in the North Atlantic. It has also been shown that alkenones produced at the end of fall in the Mediterranean Sea can be retained in the surface waters until winter storm events advect them to deeper layers [Ternois et al., 1996; Sicre et al., 1999]. These processes would increase the dispersion of the data by increasing the uncertainty on growth temperature when water is collected in winter or out of the major periods of alkenone production. To avoid these sources of discrepancy we did not consider the winter samples of the Southern Ocean in the compilation. Our calculations indicate that the polynomial function improve only slightly the correlation with respect to the linear fit ($U_{37}^{K'} = 0.031T - 0.027$, $r^2 = 0.90$, Figure 6). However, residual analyses indicate a major change between relationships below 5°C and above 20°C. At $U_{37}^{K'}$ of 0.9, the linear calibration produces a temperature estimate that is warmer by 5°C than predicted by the polynomial fit. Estimates from the linear fit is more reliable at the low temperature end and differs only

by 1°C for a $U_{37}^{K'}$ value of 0.1. Figure 6 also shows that warm samples at $T > 20^\circ\text{C}$ are lacking to further test the mathematical function, since it is at warmer temperatures that both functions diverge. Nevertheless, core-top data from the Indian Ocean suggest a reduced slope of the regression line at the warm temperature end [Sonzogni et al., 1997], thus reinforcing the idea of a nonlinear fit of $U_{37}^{K'}$ and temperature, most likely exponential.

3.3. SST Reconstruction in the Nordic Seas

[13] In a former study, Rosell-Melé [1998] noted the lack of correlation between core-top $U_{37}^{K'}$ values and SSTs, for the low temperatures of the Nordic seas. Our data shows that, in the cold surface waters, these two parameters are linearly correlated. The difficulty in assigning hydrological parameters such as SSTs to sediment data is a possible source of uncertainty in sediment studies in particular for samples taken across temperature and salinity gradients as in the East Greenland Current. Other reasons may be invoked to explain this apparent disagreement. It is unlikely that diagenesis is

responsible for the absence of correlation between sedimentary U_{37}^K and SSTs for the North Atlantic. Herbivory feeding experiments have shown that only a small fraction of alkenones is assimilated through food web processes [Volkman *et al.*, 1980]. Other feeding experiments have shown no significant changes in U_{37}^K values upon injection by copepods [Grice *et al.*, 1998]. Indirect approaches based on field data have reached similar conclusions either by comparing sediment trap material with surface sediments [Ternois *et al.*, 1996; Prah *et al.*, 1993] or core top with water column calibrations in the same oceanic setting [Sikes *et al.*, 1997]. Most recently, a thorough review on this topic by Grimalt *et al.* [2000] concluded that there was no consistent evidence of selective degradation of $C_{37:2}$ and $C_{37:3}$. Lateral advection is proposed as an alternative explanation as some evidences from near-bottom sediment traps deployed in the Norwegian Sea have shown that cross-slope lateral particle transport and resuspension occur in pelagic sediments today and that these processes become important on continental margins [Thomsen *et al.*, 1998]. Alkenones accumulated in the Nordic sea sediments could thus be partly composed of advected material. Downcore studies in the northern North Atlantic already pointed to bias from sedimentary processes but during the last glacial period, where significant amounts of reworked nannofossils were found [Weaver *et al.*, 1999]. In the Nordic seas, Rosell-Melé and Comes [1999] have also shown surprisingly warmer SSTs during the Last Glacial Maximum (LGM) relative to the present, from which they concluded that U_{37}^K and U_{37}^K could not be interpreted in terms of SSTs, at least at the cold temperature end. These authors suggested that the alkenone record may have been perturbed by admixtures of allochthonous alkenones containing a warm temperature signal. Because $C_{37:2}$ prevails in warm waters, this assumption, that significant allochthonous material may be influencing SST reconstructions in the northern North Atlantic, implies that a major fraction of the $C_{37:2}$ accumulated in glacial sediments is of allochthonous origin. $C_{37:4}$ would subsequently represent the autochthonous signal, as it is generally absent in warm waters and rather produced in cold waters. In this situation, SST reconstruction

would thus rely on the existence of a relationship between T and $\%C_{37:4}$. Rosell-Melé [1998] showed that core-top values of $\%C_{37:4}$ linearly correlate to summer SSTs for $\%C_{37:4}$ ranging from 0 to 5% ($\%C_{37:4} = -0.45T + 6.46$, $r^2 = 0.41$ and $n = 25$) but do not for values higher than 5% (i.e., for $T < 6^\circ\text{C}$). Our water column data indicate that $\%C_{37:4}$ and temperature are linearly correlated at $T < 12^\circ\text{C}$ ($\%C_{37:4} = -3.7T + 43.7$, $r^2 = 0.50$; $n = 16$, $4^\circ - 12^\circ\text{C}$). Note that $\%C_{37:4}$ and salinity are more strongly correlated ($\%C_{37:4} = -48.1S_{\text{‰}} + 1691$, $r^2 = 0.78$). The correlation coefficient calculated between salinity and temperature is 0.77 over the entire data set but only 0.32 over the subset of data. These results suggest a salinity dependence of the production of $C_{37:4}$. However, more data from other oceanic basins would be needed to test further this hypothesis.

[14] The comparison of the water column with the sediment equations above suggests that the relationship linking $\%C_{37:4}$ to temperature in surface waters could have been modified in surface sediments. As discussed above, U_{37}^K and temperature are also correlated in cold water temperatures, while they show no correlation in surface sediments [Rosell-Melé, 1998]. This is in contrast with the Southern Ocean data where it has been shown that the equation for sedimentary U_{37}^K and summer SSTs and that for surface waters agree [Sikes *et al.*, 1997]. However, agreement is partly achieved when comparing our North Atlantic equation to the one produced by Weaver *et al.* [1999] from 2° to 29°C ($U_{37}^K = 0.026T + 0.186$, $r^2 = 0.95$) using U_{37}^K data of Rosell-Melé *et al.* [1995] and summer temperature at 0 m from 75°N to 5°S . The latter calibration covers a wide range of SSTs and encompasses several provinces of the North Atlantic where surface sediments may not have been perturbed. Examination of these data indicate more scatter at low temperatures, which again suggests that in the Nordic seas the local temperature signal recorded in surface sediments may have been altered by postdepositional processes such as fine particle entrainment from the shelves via advective processes, for example, nepheloid layer and bottom water current transports. Overall, these findings show that there is undoubtedly much to be

learned about sedimentation in this region to clarify the causes of discrepant results in cold waters.

4. Conclusions

[15] Cold waters from high latitudes of the North Atlantic reveal high abundances of $C_{37:4}$ for temperatures ranging from 4° to 10°C. Abundances of $C_{37:4}$ were found to be correlated to temperature and even more strongly to salinity. However, the relationship linking % $C_{37:4}$ to temperature is different from that earlier found from surface sediments. Similarly, the comparison of the regression equation calculated from ($U_{37}^{K'}$, T) pairs in surface waters of the North Atlantic and sedimentary data suggests that postdepositional processes may have altered sedimentary $U_{37}^{K'}$ values in its northern portion, the Nordic seas. Although this finding requires further data to be confirmed, it also suggests that sedimentary reconstruction or calibration of SSTs from alkenones must be treated with caution.

[16] The compilation of our data with those previously obtained in the water surface waters of other oceanic regions indicates that the relationship linking $U_{37}^{K'}$ and temperature may not be linear. In the absence of reference data from warm waters, the polynomial equation may provide a better description of the water column data. More importantly this result suggests that the observed differences between water column equations earlier published may not reflect regional differences. Yet, water column data are needed to better constrain the relationship at temperatures above 20°C and evaluate the mathematical function best fitting $U_{37}^{K'}$ and temperature over the entire range of oceanic temperatures, which is likely to be exponential as earlier suggested by Sikes and Volkman [1993].

Acknowledgments

This research would not have been possible without the logistic and financial supports of IFRTP and the crew of the R/V *Marion Dufresne* during the cruise (June–September 1999). Specifically we thank Y. Balut, P. Sangiardi and C. Bourmot for their efforts on board. We also thank E. Jansen and E. Cortijo for organizing the IMAGES V cruise and J.-J. Motte

for drawings. Analyses have been funded by INSU, Groupe Adhoc Ocean and PNEDC. We also thank E. Sikes for improving this manuscript. This is LSCE contribution 0687.

References

- Brassell, S. C., G. Eglinton, I. T. Marlowe, U. Pflaumann, and M. Sarnthein, Molecular stratigraphy: a new tool for climatic assessment, *Nature*, 320, 129–133, 1986.
- Conte, M. H., and G. Eglinton, Alkenone and alkenoate distributions within the euphotic zone of the eastern North Atlantic: Correlation with production temperature, *Deep Sea Res.*, 40, 1935–1961, 1993.
- Conte, M. H., G. Eglinton, and L. A. S. Madureira, Long-chain alkenones and alkyl alkenoates as palaeotemperature indicators: Their production, flux and early sedimentary diagenesis in the Eastern North Atlantic, *Org. Geochem.*, 19, 287–298, 1992.
- Conte, M. H., A. Thompson, D. Lesly, and R. P. Harris, Genetic and physiological influences on the alkenone/alkenoate versus growth temperature relationship in *Emiliania huxleyi* and *Gephyrocapsa oceanica*, *Geochim. Cosmochim. Acta*, 62, 51–68, 1998.
- Cranwell, P. A., Long-chain unsaturated ketones in recent lacustrine sediments, *Org. Geochem.*, 49, 1545–1551, 1985.
- Freeman, K. H., and S. G. Wakeham, Variations in the distributions and isotopic compositions of alkenones in Black Sea particles and sediments, *Org. Geochem.*, 19, 277–285, 1992.
- Grice, K. W. C., M. K. Breteler, S. Schouten, and V. Grossi, Effects of zooplankton herbivory on biomarker records, *Paleoceanography*, 13, 686–693, 1998.
- Grimalt, J. O., J. Rullkötter, M.-A. Sicre, R. Summons, J. Farrington, H. R. Harvey, M. Goñi, and K. Sawada, Modifications of the C_{37} alkenone and alkenoate composition in the water column and sediment: Possible implications for sea surface temperature estimates in paleoceanography, *Geochem. Geophys. Geosyst.*, 1 (Article), Paper number 2000GC000053 [9792 words], 2000. (Available at <http://g-cubed.org>)
- Knappertsbush, M., Geographic distribution of living and Holocene coccolithophores in the Mediterranean Sea, *Micropaleontology*, 21, 219–247, 1993.
- Li, J., R. P. Philp, F. Pu, and J. Allen, Long-chain alkenones in Qinghai Lake sediments, *Geochim. Cosmochim. Acta*, 60, 235–241, 1996.
- Marlowe, I. T., S. C. Brassell, G. Eglinton, and J. C. Green, Long-chain alkenones and alkenoates and the fossil coccolith record of marine sediments, *Chem. Geol.*, 88, 349–375, 1990.
- Müller, P. J., G. Kirst, G. Rhuland, I. von Storch, and A. Rosell-Melé, Calibration of the alkenone paleotemperature index $U_{37}^{K'}$ based on core-tops from the eastern South Atlantic and the global ocean (60°N–60°S), *Geochim. Cosmochim. Acta*, 62, 1757–1772, 1998.
- Prahl, F. G., and S. G. Wakeham, Calibration of unsaturation patterns in long-chain ketone compositions for paleotemperature assessment, *Nature*, 330, 367–369, 1987.
- Prahl, F. G., L. A. Muehlhausen, and D. L. Zahnle, Further evaluation of long-chain alkenones as indicators of paleocea-

- nographic conditions, *Geochim. Cosmochim. Acta*, *52*, 2303–2310, 1988.
- Prahl, F. G., R. B. Collier, J. Dymond, M. Lyle, and M. A. Sparrow, A biomarker perspective on prymnesiophyte productivity in the northeastern Pacific Ocean, *Deep Sea Res. Part I*, *40*, 2061–2076, 1993.
- Prahl, F. G., T. Herbert, S. C. Brassell, N. Ohkouchi, M. Pagan, D. Repeta, A. Rosell-Melé, and E. Sikes, Status of alkenone paleothermometer calibration: Report from Working group 3, *Geochem. Geophys. Geosyst.*, *1* (Article), Paper number 2000GC000058 [4880 words], 2000. (Available at <http://g-cubed.org>)
- Rosell-Melé, A., Interhemispheric appraisal of the value of alkenone indices as temperature and salinity proxies in high-latitude locations, *Paleoceanography*, *13*, 694–703, 1998.
- Rosell-Melé, A., and P. Comes, Evidence for a warm Last Glacial Maximum in the Nordic seas or an example of shortcomings in $U_{37}^{K'}$ and U_{37}^K to estimate low sea surface temperature?, *Paleoceanography*, *14*, 770–776, 1999.
- Rosell-Melé, A., G. Eglinton, U. Pflaumann, and M. Sarnthein, Atlantic core-top calibration of the U_{37}^K index as a sea-surface paleotemperature indicator, *Geochim. Cosmochim. Acta*, *59*, 3099–3107, 1995.
- Rosell-Melé, A., M. Weinelt, M. Sarnthein, N. Koç, and E. Jansen, Variability of the Arctic front during the last climatic cycle: Application of a novel molecular proxy, *Terra Nova*, *10*, 86–89, 1998.
- Schulz, H.-M., A. Schönner, and K.-C. Emeis, Long-chain alkenone patterns in the Baltic Sea- an ocean-freshwater transition, *Geochim. Cosmochim. Acta*, *64*, 469–477, 2000.
- Sicre, M.-A., Y. Ternois, J.-C. Miquel, and J.-C. Marty, Alkenones in the Northwestern Mediterranean Sea: interannual variability and vertical transfer, *Geophys. Res. Lett.*, *26*, 1735–1738, 1999.
- Sikes, E. L., and J. K. Volkman, Calibration of alkenone unsaturation ratios ($U_{37}^{K'}$) for paleotemperature estimation in cold polar waters, *Geochim. Cosmochim. Acta*, *57*, 1883–1889, 1993.
- Sikes, E. L., J. K. Volkman, L. G. Robertson, and J.-J. Pichon, Alkenones and alkenes in surface waters and sediments of the Southern Ocean: Implication for paleotemperature estimation in polar regions, *Geochim. Cosmochim. Acta*, *61*, 1495–1505, 1997.
- Sonzogni, C., E. Bard, F. Rostek, D. Dollfus, A. Rosell-Melé, and G. Eglinton, Temperature and salinity effects on alkenones ratios measured in sediments from the Indian Ocean, *Quat. Res.*, *47*, 344–355, 1997.
- Ternois, Y., M.-A. Sicre, A. Boireau, J.-C. Marty, and J.-C. Miquel, Production pattern of alkenones in the Mediterranean Sea, *Geophys. Res. Lett.*, *23*, 3171–3174, 1996.
- Ternois, Y., M.-A. Sicre, A. Boireau, M. H. Conte, and G. Eglinton, Evaluation of long-chain alkenones as paleotemperature indicators in the Mediterranean Sea, *Deep Sea Res.*, *44*, 271–286, 1997.
- Ternois, Y., M.-A. Sicre, A. Boireau, L. Beaufort, J.-C. Miquel, and C. Jeandel, Hydrocarbons, sterols and alkenones in sinking particles in the Indian Ocean sector of the Southern Ocean, *Org. Geochem.*, *28*, 489–501, 1998.
- Thiel, V., A. Jenisch, G. Landmann, A. Reimer, and W. Michaelis, Unusual distributions of long-chain alkenones and tetrahymanol from the highly alkaline Lake Van, Turkey, *Geochim. Cosmochim. Acta*, *61*, 2053–2064, 1997.
- Thomsen, C., D. E. Schulz-Bull, G. Petrick, and J. C. Duinker, Seasonal variability of the long-chain alkenone flux and the effect on the $U_{37}^{K'}$ -index in the Norwegian Sea, *Org. Geochem.*, *28*, 311–323, 1998.
- Versteegh, G. J. M., R. Riegman, J. W. de Leeuw, and J. H. F. Jansen, $U_{37}^{K'}$ values for *Isochrysis galbana* as a function of culture temperature, light intensity and nutrient concentrations, *Org. Geochem.*, *32*, 785–794, 2001.
- Volkman, J. K., G. Eglinton, E. D. S. Corner, and J. R. Sargent, Novel unsaturated straight-chain C_{37} – C_{39} methyl and ethyl ketones in marine sediments and a coccolithophorid *Emiliania huxleyi*, in *Advances in Organic Geochemistry*, edited by A.G. Douglas and J.R. Maxwell, pp. 219–227, Pergamon, New York, 1980.
- Volkman, J. K., S. M. Barrett, S. I. Blackburn, and E. L. Sikes, Alkenones in *Gephyrocapsa oceanica*: Implications for studies in paleoclimate, *Geochim. Cosmochim. Acta*, *59*, 513–520, 1995.
- Weaver, P. P. E., M. R. Chapman, G. Eglinton, M. Zhao, D. Rutledge, and G. Read, Combined coccolith, foraminifera, and biomarker reconstruction of paleoceanographic conditions over the last 120 kyr in the northern North Atlantic (59°N–23°W), *Paleoceanography*, *14*, 336–349, 1999.