Pergamon

Geochimica et Cosmochimica Acta, Vol. 59, No. 15, pp. 3099–3107, 1995

0016-7037/95 $9.50 + .00

0016-7037(95)00199-9

Atlantic core-top calibration of the U^K_{37} index as a sea-surface palaeotemperature indicator

ANTONI ROSELL-MELÉ,[1,*] GEOFFREY EGLINTON,[1] UWE PFLAUMANN,[2] and MICHAEL SARNTHEIN[2]

[1]Organic Geochemistry Unit, School of Chemistry, University of Bristol, Bristol BS8 1TS, UK
[2]Geologisch-Paläontologisches Institut, University of Kiel, D24098 Kiel, Germany

(*Received October* 24, 1994; *accepted in revised form April* 13, 1995)

Abstract—A field calibration of the U^K_{37} index with sea surface temperature is discussed, through analysis of an extensive suite of surface sediments (n = 109) from the northeastern Atlantic (2°S–75°N). Values of U^K_{37} are compared with sea surface temperatures for overlying waters measured at different depths and seasons, to obtain a correlation suitable for palaeotemperature reconstructions. The best fit is obtained using surface (0 m) temperatures corresponding to caloric winter and autumn months. However, the annual average, spring and summer surface temperature equations also have high correlation coefficients, and are also appropriate for climatic studies. The results further validate the general applicability of the U^K_{37} as a climatic proxy, because the calibration equations are valid over a wide range of surface water temperatures (0–28°C) for different algal populations and are representative of the average contribution of alkenones to sediments, as found in sediment cores.

1. INTRODUCTION

The U^K_{37}[†] index (Brassell et al., 1986a,b) and its simplification, $U^K_{37}{}'$ (Brassell et al., 1986b; Prahl and Wakeham, 1987) are based on the relative abundances of long-chain alkenones with thirty-seven carbon atoms, which are ubiquitous biomarkers in the world's oceans, both in the water column and in sediments (Brassell, 1993). These indices relate to the temperature of the euphotic zone where the alkenones are biosynthesised by some Prymnesiophyceae algae (Volkman et al., 1980a,b; Marlowe, 1984) and are being used for reconstructing palaeo-sea-surface temperature (SST) records, in part in sediments devoid of any other SST proxy-indicator (e.g., microfossil transfer functions), through U^K_{37}-stratigraphic analysis of deep-sea cores (Poynter et al., 1989; Eglinton et al., 1992; Kennedy and Brassell, 1992; Lyle et al., 1992; Rostek et al., 1993). However, questions remain about their veracity, for instance, due to diagenesis of the alkenones, the species dependency of the temperature calibration, and their applicability in cold water regimes at high latitudes. Three approaches to calibration have been used (Table 1). The first attempts employed laboratory cultures of *Emiliania huxleyi* (Marlowe, 1984; Prahl and Wakeham, 1987; Prahl et al., 1988) and various other species (*Isochrysis galbana, Chrysotila lamellosa*) (Marlowe, 1984), and more recently, cultures of *Geophyrocapsa oceanica* (Volkman et al., 1995). The calibration equations are different for each of the species (Table 1). The second approach consisted of using water column particulate organic matter (Atlantic, Pacific, and Circum-Antarctic oceans and the Black Sea) (Prahl and Wakeham, 1987; Prahl et al., 1988, 1993; Conte et al., 1992; Freeman and Wakeham, 1992; Conte and Eglinton, 1993; Sikes and Volkman, 1993) to test, usually successfully, equations based on laboratory cultures of *E. huxleyi* and extend their application to cold water locations. In some cases, new calibration curves were suggested (Prahl and Wakeham, 1987; Conte et al., 1992; Conte and Eglinton, 1993; Sikes and Volkman, 1993). However, the results obtained from the water column show considerable temporal and spatial variability (Table 1). For example, Conte et al. (1992) found no significant $U^K_{37}{}'$-SST relationship for some samples from the Northeastern Atlantic (46–60°N), but they did observe a clear SST record (r^2 = 0.81) for the ratio of alkenones to alkyl alkenoates (the latter also biosynthesised by the same group of algae). However, based on an enlarged sample set, Conte and Eglinton (1993) demonstrated that $U^K_{37}{}'$ of suspended matter can provide a reliable measure of SST above 16°C for the northeast Atlantic. In contrast, in the Black Sea, the $U^K_{37}{}'$ based SST estimates appeared too low, perhaps due to the natural variability in water depth and the timing of alkenone biosynthesis (Freeman and Wakeham, 1992). Finally, a third approach to evaluate U^K_{37}-to-SST relationships is use of surface sediment extracts and compare values of U^K_{37} with those of temperatures from overlying surface waters. To date this has been attempted with limited numbers of samples in the Pacific (Prahl et al., 1988, 1993; McCaffrey et al., 1990; Kennedy and Brassell, 1992), the northeastern Atlantic (Conte et al., 1992), and in some parts of the global ocean (Sikes et al., 1991) (Table 1). In general, the U^K_{37} signal measured in sediment extracts agreed with the modern temperatures found in the overlying euphotic zone, when using the culture equation of Prahl and Wakeham (1987), revised by Prahl et al. (1988). Proper interpretation of the U^K_{37} values in terms of SST requires consideration of several factors and topics which are poorly understood. These include (1) the precise water depth and season(s) at which the alkenones are biosynthesised and their temperature signal is produced; (2) the temperature range to which any transfer equation applies, (3) which is linked to whether the relationship between U^K_{37} and SST is linear throughout; (4) the possible effect of varying composition of coccolith species on U^K_{37}-SST records; and finally, (5) the analytical quality of the U^K_{37} data (Brassell, 1993; Conte and Eglinton, 1993; Rosell-Melé, 1994; Rosell-Melé et al., 1994a).

* Author to whom correspondence should be addressed.
[†] Note: The index was originally defined as U^K_{37}, and the use of this designator should prevail rather than U^k_{37}.

Table 1. Values of U^K_{37} or U^K_{37}', the equation coefficients (U^K_{37}=a+bT), temperature range and number of samples (n) of the linear calibrations published in the literature. Table based on Brassell (1993) compilation. The number of samples (n) do not include replicates of a sample at one water or growth culture temperature. The confidence intervals have been determined with a 95% significance. SPM: suspended particulate material; ST: vertically transported particulate material.

index	Sample type	a	b	n	r^2	T depth used for calibration	T	Estimated T U^K_{37} 0.2	0.5	0.9	location	references
	cultures										*strain*	
U^K_{37}	*E. huxleyi*	-0.282	0.036		0.764	culture growth		13	22	33		Brassell, 1993 (data from Marlowe, 1984 and Volkman *et al.* 1980a)
U^K_{37}	*E. huxleyi*	-0.110±0.190	0.040 ± 0.012	5	0.989	culture growth	8-25	8	15	25	NE Pacific	Prahl and Wakeham, 1987; Prahl *et al.*, 1988
U^K_{37}'	*E. huxleyi*	0.043	0.033	5	0.997	culture growth	8-25	5	14	26	NE Pacific	Prahl and Wakeham, 1987; Prahl *et al.*, 1988
U^K_{37}'	*E. huxleyi*	0.039±0.087	0.034±0.005	5	0.994	culture growth	8-25	5	14	25	NE Pacific	Prahl *et al.*, 1988
U^K_{37}	*I. galbana*	-1.120	0.052		0.791	culture growth		25	31	39		Brassell, 1993 (data from Marlowe, 1984)
U^K_{37}	*E. huxleyi*	-0.255	0.044		0.722			10	17	26		Brassell, 1993 (literature compilation)
	water column					*in situ measure*						
U^K_{37}'	ST and SPM	-0.070±0.082	0.037±0.004	25	0.983	mixed layer	10-28	7	15	26	mainly Pacific	Prahl and Wakeham, 1987
U^K_{37}'	SPM	-0.156	0.041	40	0.958	3-250	3.5-27	9	16	26	Southern Ocean and Pacific	Sikes and Volkman, 1993 (combined with Prahl and Wakeham, 1987)
U^K_{37}'	SPM	0.017	0.022	37	0.720	3-250	0-12	8	22	40	Southern Ocean	Brassell, 1993 (data from Sikes and Volkman, 1993)
U^K_{37}'	SPM	-0.090	0.033	23	0.808	3-250	4-12	9	18	30	Southern Ocean	Brassell, 1993 (data from Sikes and Volkman, 1993)
U^K_{37}'	SPM	-0.469	0.056	15	0.980	4-40	16-25	12	17	24	North Atlantic	Conte and Eglinton, 1993
U^K_{37}'	SPM	0.205	0.018	25	0.260	4-40	9-17	0	16	39	North Atlantic	Conte *et al.* 1992
U^K_{37}	SPM	-0.009±0.073	0.033±0.005		0.799	4-40		6	15	28	North Atlantic	Brassell, 1993 (data from Conte and Eglinton, 1993)
U^K_{37}'		-0.083	0.037		0.874		4-25	5	16	27		Brassell, 1993 (literature compilation)
	sediments											
U^K_{37}'	core tops	0.082±0.090	0.031±0.004	16	0.968	warm seasons	9-29	4	13	26	Atlantic, Pacific, Black Sea	Sikes *et al.* 1991
U^K_{37}	0-1cmbsf	0.093±0.024	0.030±0.001	109	0.979	summer, 0m	0-28	4	14	27	NE Atlantic	this paper

We report a systematic field calibration of the U^K_{37} index based on a suite of 109 surface sediment samples from the northeastern Atlantic which span the almost complete range of temperature regimes and the coccolithophorid biogeographic zones found therein (Fig. 1). Although *E. huxleyi* is the dominant species in the area (McIntyre and Bé, 1967; Okada and McIntyre, 1977) there are other major species present among the coccolithophorid/prymnesiophyte community, such as *G. ericsonii* and *G. muellerae* (Jordan, 1988), which may also biosynthesise the alkenones (Marlowe et al., 1990). The results for U^K_{37} are compared with modern average temperatures of the overlying waters (Levitus, 1982). Data from sediment surface samples represent an average signal of hundreds, or a few thousands of years of sedimentation depending on rates of bioturbation and sedimentation. Hence, the data discussed are representative of the long-term averaged input to the sediment of long-chain alkenones biosynthesised by natural populations of the algae. Therefore, interseasonal or interannual variability is not a factor, unlike water column samples. Prahl et al. (1989) demonstrated that the extensive oxidation loss of alkenones in bottom sediments had little effect on their unsaturation pattern. Similarly, for several cores in the northeastern Atlantic, the $U^K_{37}{}'$ values show very consistent values with depth in the top 10 cm, despite the substantial degradation of alkenones in the top 1 cm due to diagenesis (Conte et al., 1992; Madureira, 1994). Hence, since the latter Holocene temperatures are not believed to have changed greatly, it could be argued that the diagenetic effect has no great effect in U^K_{37} values. On the other hand, the samples may include laterally transported sediment, advected both in the water column and on the seafloor (Thomson et al., 1993). We have opted for use of the original U^K_{37} index instead of the more commonly used $U^K_{37}{}'$ index, where the tetraunsaturated alkenone is excluded, because, as noted previously (Rosell-Melé et al., 1994b), the tetraunsaturated alkenone becomes more significant with decreasing temperature, especially at the cold-end of the SST calibration, and both indices yield different values.

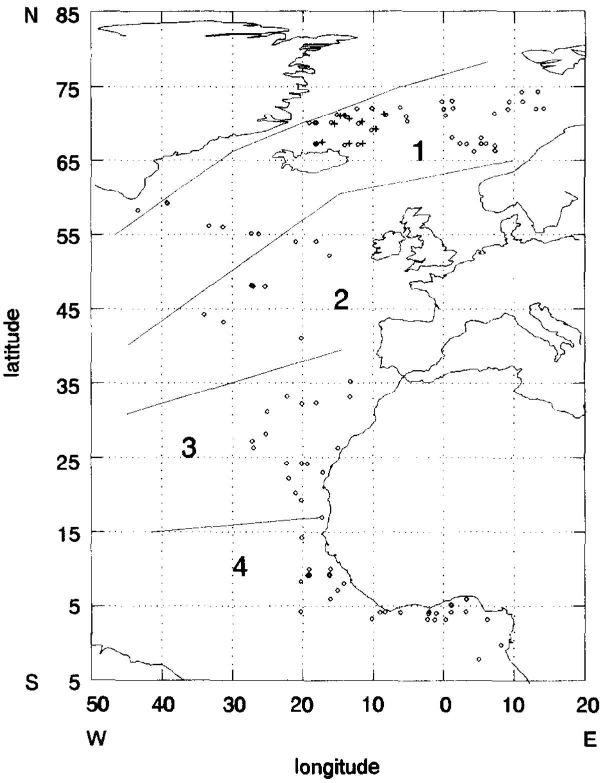

FIG. 1. The dots on the map indicate the locations of the surface sediment samples (top 1 cm) analysed in this study. The crosses indicate those locations believed to be affected by ice rafting of organic sediments. The coccolithophorid biogeographic zones are approximately drawn after McIntyre and Bé (1967): Tropical (4), Subtropical (3), Transitional or Temperate (2), and Subarctic (1).

EXPERIMENTAL

Full details of the analytical procedure are given elsewhere (Rosell-Melé, 1994; Rosell-Melé et al., 1994c). Briefly, the sediments were retrieved from the seafloor using box corers or multicorers, and a subsample from the top 1 cm was taken. Samples were freeze dried, solvent extracted in a sonication bath, and the total extract was cleaned with a commercial silica cartridge. The relative abundances of the C_{37} alkenones were measured using gas chromatography-mass spectrometry with ammonia chemical ionization. Three injection replicates were carried out for each sample extract.

RESULTS AND DISCUSSION

We have studied different SST datasets corresponding to different depths (0, 30, and 50 m) and caloric seasons (Fig. 2) to determine which temperature produced the best fit for deriving a general $U^K_{37} = f(T)$ equation (Table 2). In a previous comparable study using core-tops, Sikes et al. (1991) assumed that the sediment signal would reflect that of the warm seasons. We have preferred to carry out a pragmatic analysis of the data and explore other possibilities. The values of temperature used are the only variable that changes in the different equations obtained, with the same set of U^K_{37} values used throughout. Hence, the linear correlations produced can be compared on the basis of their correlation coefficients, because they only differ according to the temperature set used. Confidence intervals for the regression coefficients were determined with a significance level of 95% and must be used with caution when comparing coefficient probability ranges because the choice of significance level is arbitrary.

The best correlation between U^K_{37} and SST is obtained using water temperatures from 0 m depth for the autumn and winter seasons, which comprises the months from November to April, both inclusive. High correlation coefficients are also found with other temperature sets, particularly spring and summer at 0 m. The slopes of the regressions at 0 m are the same for all the seasons ($b = 0.029$), and only the y-intercepts vary. As the temperature values are those of deeper waters, for any season, the coefficient of correlation decreases (Table 2), mainly due to the appearance of clusters of samples in the plot (when $U^K_{37} > 0.7$ (or 0.85)), which do not plot linearly with samples with lower U^K_{37}. If the samples considered in the calibration are only those where $0.2 < U^K_{37} < 0.7$ (or 0.85), the water depth dependence of the correlation coefficients is much smaller (Table 2), and the regression coefficients are not significantly different. Samples with $U^K_{37} > 0.85$ come from low latitude locations with permanent thermocline and marked vertical temperature gradient, which decreases grad-

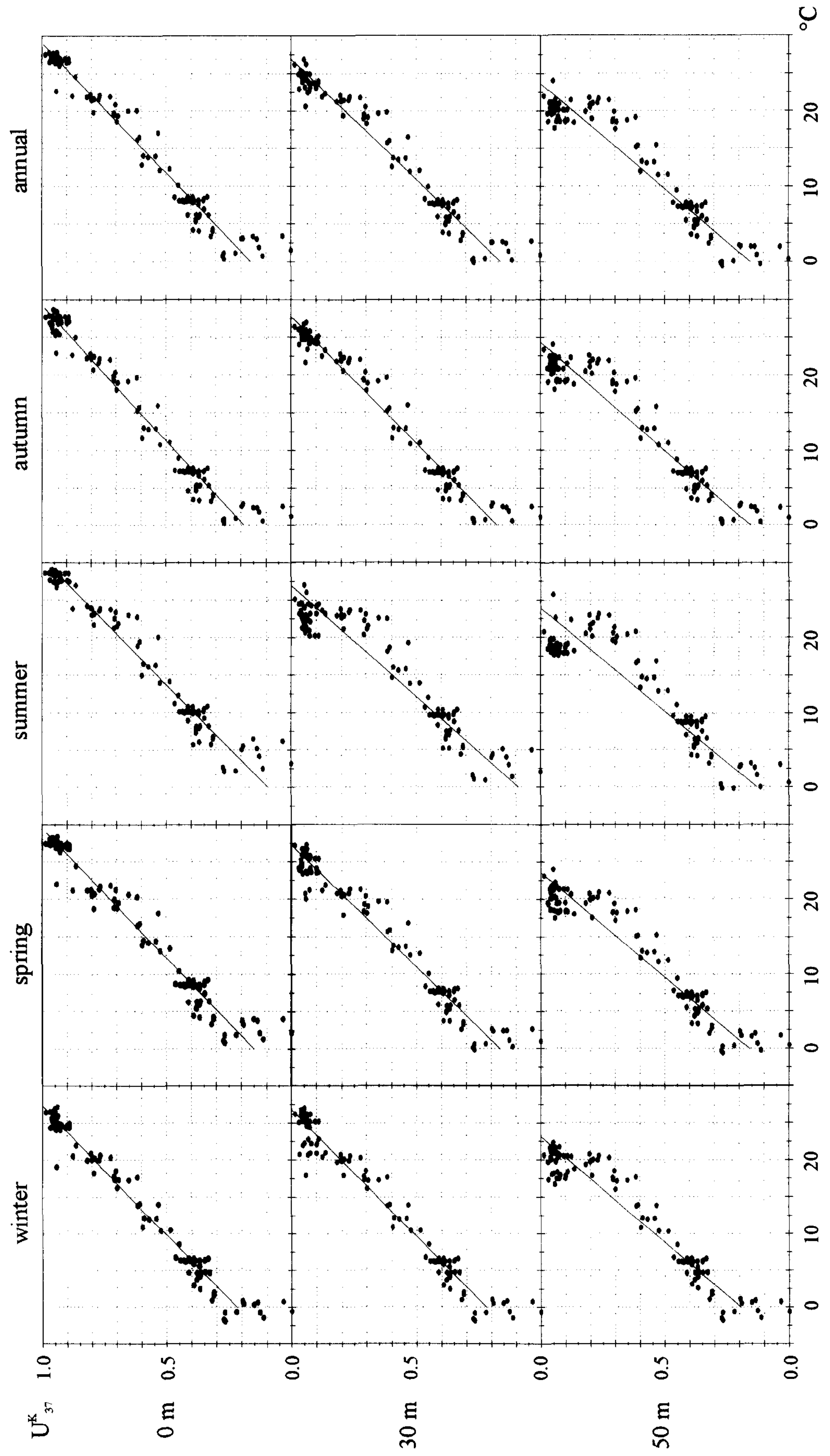

FIG. 2. Results of the regression analysis of U^{K}_{37} data and water temperature values for different caloric seasons and depths from Levitus (1982). The regression parameters are in Table 2.

Table 2. Coefficients of the regression analysis (U^K_{37}=a+bT) carried out between U^K_{37} data and water temperature values for different caloric seasons and depths. The coefficients stand for: a: y-intercept, b: slope, R: coefficient of correlation. The confidence interval has been determined with a significance level of 95%.

Depth (m)		*Winter*	*Spring*	*Summer*	*Autumn*	*Annual*
				0 < U^K_{37} < 1 (n=109)		
	a	0.217 ± 0.018	0.151 ± 0.022	0.093 ± 0.024	0.189 ± 0.020	0.162 ± 0.020
0	*b*	0.029 ± 0.001	0.029 ± 0.001	0.030 ± 0.001	0.028 ± 0.001	0.029 ± 0.001
	R	0.983	0.978	0.978	0.980	0.981
	a	0.219 ± 0.020	0.164 ± 0.023	0.090 ± 0.038	0.175 ± 0.021	0.159 ± 0.023
30	*b*	0.029 ± 0.001	0.031 ± 0.001	0.034 ± 0.002	0.030 ± 0.001	0.031 ± 0.001
	R	0.977	0.975	0.948	0.979	0.977
	a	0.195 ± 0.028	0.158 ± 0.031	0.126 ± 0.048	0.155 ± 0.032	0.154 ± 0.033
50	*b*	0.035 ± 0.002	0.036 ± 0.002	0.037 ± 0.003	0.035 ± 0.002	0.036 ± 0.002
	R	0.961	0.957	0.911	0.956	0.952
	a	0.207 ± 0.020	0.153 ± 0.023	0.090 ± 0.034	0.170 ± 0.022	0.154 ± 0.023
Mean	*b*	0.031 ± 0.001	0.032 ± 0.001	0.034 ± 0.002	0.031 ± 0.001	0.032 ± 0.001
	R	0.979	0.976	0.959	0.977	0.976
				0.2 < U^K_{37} < 0.85 (n=63)		
	a	0.260 ± 0.017		0.171 ± 0.025		0.218 ± 0.020
0	*b*	0.025 ± 0.001		0.024 ± 0.002		0.025 ± 0.002
	R	0.975		0.965		0.971
	a	0.261 ± 0.017		0.214 ± 0.023		0.236 ± 0.019
50	*b*	0.025 ± 0.001		0.024 ± 0.002		0.025 ± 0.002
	R	0.974		0.963		0.971
						0.227 ± 0.020
Mean						0.025 ± 0.002
						0.971
				0.2 < U^K_{37} < 0.7 (n=51)		
	a	0.273 ± 0.018		0.204 ± 0.025		0.238 ± 0.022
0	*b*	0.022 ± 0.002		0.021 ± 0.002		0.022 ± 0.002
	R	0.950		0.944		0.946
	a	0.273 ± 0.018		0.239 ± 0.022		0.253 ± 0.020
50	*b*	0.023 ± 0.002		0.021 ± 0.002		0.022 ± 0.002
	R	0.950		0.942		0.948
						0.246 ± 0.021
Mean						0.022 ± 0.002
						0.947

ually northwards. Thus, the increasing scatter at the top end of the calibration, with increasing water depth, indicates that the U^K_{37} signal in the sediment is representative of water temperatures at 0 m, despite the variable depths at which coccolithophorids are reported to dwell (Jordan, 1988). The temperatures at 0 m we have used for the calibration should not be taken strictly belonging only to that depth, but to the mixed layer, the depth of which varies latitudinally and seasonally, but is evident all the time in middle latitudes (ca. 0.4 < U^K_{37} < 0.7) between the surface and 30 m depth (Pickard and Emery, 1990). At high latitudes the depth temperature gradient is small and hence, the 0 m temperatures used to derive the U^K_{37} calibration may be extended to all the photic zone.

Large blooms of algae have been reported in spring (Barnes and Hughes, 1988) and hence, their productivity is thought to be higher then than during the rest of the year, although winter blooms in the trade wind belt and autumn blooms have also been reported (Halldal, 1953; Barnes and Hughes, 1988). In some studies the U^K_{37}-temperature signal has been related to euphotic zone water temperature during the springtime period rather than the annual average (Conte et al., 1992;). Thus, it is not very surprising that the summer temperature equation at 0 m is the most similar to those from previous calibrations (Table 1). Prahl et al. (1993) suggested that alkenone fluxes in northeastern Pacific sites derived from cold, subsurface waters within the euphotic zone. Although they found an alkenone flux throughout the year, it showed a consistent seasonal maximum in late spring. However, the annual average U^K_{37} value corresponded to regional winter-spring water SST. These authors argued that a biological (U^K_{37} species dependence) rather than geochemical mechanism could explain it. In our data, the average U^K_{37} signal in

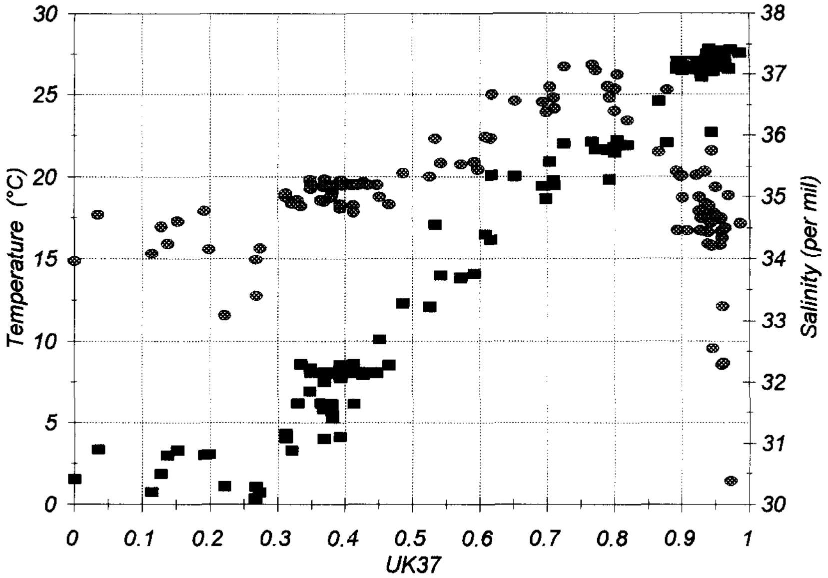

FIG. 3. U^K_{37} values, for the samples considered in this study, plotted against annual average at O m depth water temperature (squares) and salinity (circles). The data is derived from Levitus (1982).

the sediment is more representative of the autumn-winter months, apparently similar to Prahl et al. (1993) findings. However, the poorer fit we obtain for the seasons comprising the spring/summer months from May to October may be due to the formation of the middle latitudes "seasonal" thermocline in the upper photic zone, which would make more critical the depth of the temperature chosen, as the Prymnesiophyceae are not likely to live exactly at 0 m. Thus, it could be that a better fit may be found using temperatures from around five to ten meters depth, instead of zero meter, but these temperatures are not available. Besides which it is the time when most of the alkenones reach the seafloor, we have four $U^K_{37} = f(T)$ calibrations (at 0 m depth), one for each season, which in principle are equally applicable to palaeo-SST reconstructions. Then, for $U^K_{37} = 0.5$ the temperature estimates are 9.9°C (winter), 11.2°C (autumn), 12.1°C (spring), and 13.1°C (summer), which are significantly different because the standard error of our analytical procedure for U^K_{37} is 0.01 (Rosell-Melé, 1994; Rosell-Melé et al., 1994c), which would translate in a confidence interval of ±0.7°C (95% significance) not considering the error of the regression. Similarly, the annual average temperature at 0 m produces a good fit with U^K_{37} (Table 2 and Fig. 2), and we regard this correlation as also appropriate to use for deriving mean sea surface palaeotemperature records from marine sediment cores ($U^K_{37} = 0.5$, SST = 11.8°C). In principle these equations can be applied over a range of temperatures between 0–28°C. However, caution is needed at the cold end of the regression because of the larger scatter below 3–4°C, which needs to be further investigated, and is similar to Sikes and Volkman (1993) reported deviation from linearity below 3.5°C for the $U^K_{37'}$ and water temperature relationship in the Southern Ocean. Due to the close geographical location of these samples, West of the Norwegian/Greenland/Iceland Sea (Rosell-Melé et al., 1994b), we think that the shift of U^K_{37} estimates toward lower values may be due to local oceanographic conditions. Perhaps due to sea-ice advected material, from colder locations east of Greenland to the north of Iceland, an area frequently affected by the southwardly and sea-ice covered North Iceland Current (sample locations marked on Fig. 1). However, this would imply below 0°C biosynthesis of the alkenones, and it seems unlikely that Prymnesiophyte alkenone producers dwell at such low temperatures. Another hypothesis is that changes in salinity or water density (the area is one of the main sources of Atlantic deep bottom-water) may affect the biosynthetic capabilities of the alkenone producers and the U^K_{37} is not longer strictly temperature dependent. However, in samples from low latitudes with high salinity differences (30–37‰) (Fig. 3) the U^K_{37}/temperature linear relationship is preserved, whereas the low temperature anomalities take place over a similar range of salinities, which would suggest that salinity alone does not influence U^K_{37} (ten Haven et al., 1987; Sikes et al., 1991). In certain coastal areas, where *E. huxleyi* is also the main alkenone producer, very low values (negative) of U^K_{37} have been found and the index often does not correlate with water temperature (M. H. Conte et al., unpubl. data), with no clear explanation. At this stage, we suggest to assign to U^K_{37} below 0.16 (when T = 0°C; equation: annual average at 0 m depth) a value of 0°C, until the question is resolved.

The differences between the three approaches to calibrate U^K_{37} (culture, water column, and sediment samples) are illustrated in Figs. 4, 5, and 6. The graphical comparison is done using summer temperatures because most authors have used temperatures corresponding to warm seasons. In general, the water column particulate material and culture experiments yield lower U^K_{37} (or $U^K_{37}{}'$) compared to those from sediment samples for temperatures below ca. 20°C (water column) or 15°C (cultures), converging above these temperatures (Figs. 4 and 5). Whereas, Sikes et al. (1991) sediment data and our data plot similarly (Fig. 6). The use of $U^K_{37}{}'$ instead of U^K_{37} would make the index in the sediments appear even higher at colder temperatures (Rosell-Melé et al., 1994b). Hence, the U^K_{37} sediment data is skewed, and U^K_{37} may shift to higher

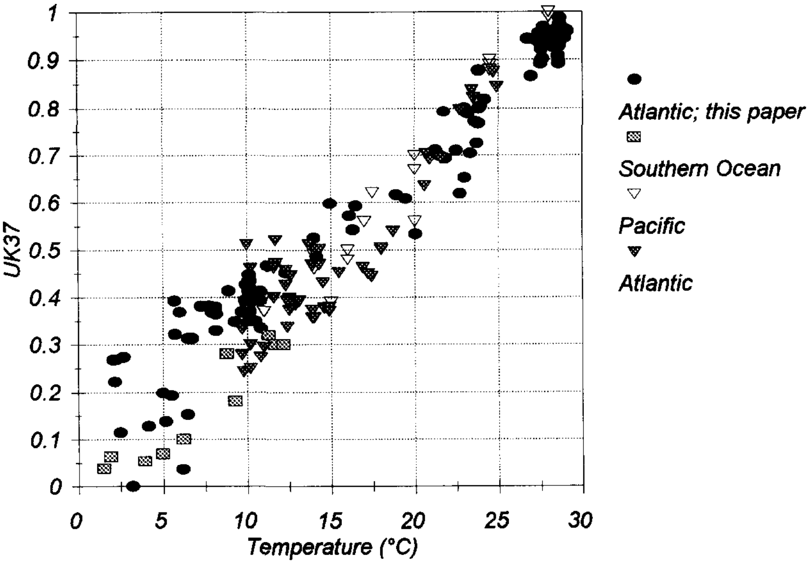

FIG. 4. Relationship between U^K_{37} and temperature for particulate organic matter and bottom sediments data from this work (summer temperatures at 0 m; circles). Data sources are as follows: Southern Ocean: Sikes and Volkman (1993); Pacific: Prahl and Wakeham, 1987; Atlantic: Conte and Eglinton, 1993.

values on sedimentation, thus appearing "warmer" in the sedimentary record. This is in agreement with reported "warmer" sediment U^K_{37} measurements (1–3.3°C) compared to sediment trap-based estimates in three sites in the northeastern Pacific (Prahl et al., 1993). However, Conte et al. (1992) found no difference between the sediment signal and that from the water column, whereas Freeman and Wakeham (1992) reported too cold U^K_{37} estimates in water column samples in the Black Sea. Furthermore, laboratory experiments showed the apparent consistency of U^K_{37} after extensive removal of alkenones under oxic, sulphate reducing and methanogenic conditions (Teece et al., 1994). Nevertheless, the differences we observe between culture and water column versus sediment data are significative (at 10°C, $\Delta U^K_{37} > 0.1$) and likely consequence of higher degradation rates for the more unsaturated of the alkenones (37:4 > 37:3 > 37:2) (Prahl et al., 1998, 1993). The magnitude of the U^K_{37} shift may depend on the resident time of the alkenones in the water column, their diagenetic pathway, and sedimentary conditions during deposition, and not strictly dependent on oxic/anoxic conditions as laboratory work suggests (Teece et al., 1994). The larger the difference in relative abundance between the tri- and tetra-unsaturated vs. the di-unsaturated alkenone (e.g., cold samples) the larger the shift in U^K_{37}. The differences be-

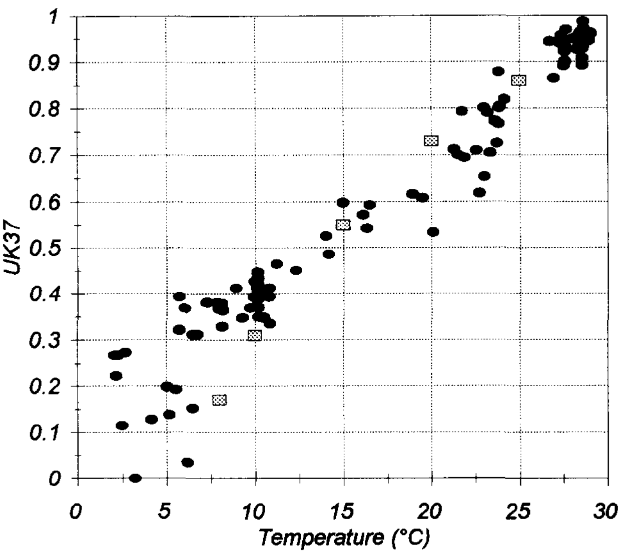

FIG. 5. Relationship between U^K_{37} and temperature for *E. huxleyi* cultures (Prahl and Wakeham, 1987; Prahl et al., 1988) and bottom sediments data from this work (summer temperatures at 0 m; circles).

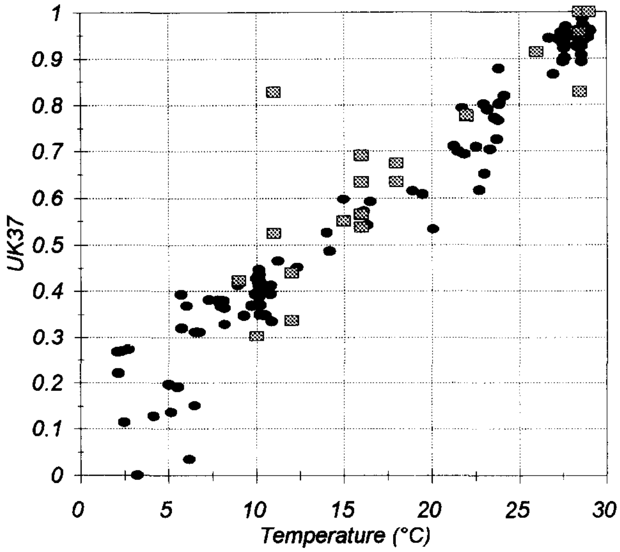

FIG. 6. Relationship between U^K_{37} and temperature for bottom sediments. Data corresponds to the study of Sikes et al. (1991) using $U^{K\prime}_{37}$ vs. CLIMAP sea surface temperatures for warm seasons (squares) and this paper, with U^K_{37} vs summer temperatures at 0 m (circles).

tween the three calibration approaches is not probably related to change in the alkenone producers population. U^{K}_{37} data derived from *E. huxleyi* cultures co-plot linearly with sediment data above 15°C, which is in agreement with suggestions (Volkman et al., 1980a; Brassell et al., 1986b) that this algae is a major source of alkenones to the present-day oceanic environment, despite the co-occurrence of other coccolithophorids. In waters below 15°C, in the temperature and subarctic biogeographic zones (Fig. 1), where *E. huxleyi* is the most abundant coccolithophorid (C. Samtleben et al., unpubl. data) the discrepancies between sediment and water column/culture data are more pronounced. In view of these results, the scatter at the cold-end of our calibration could be caused by smaller degradation of the alkenones (perhaps fast sinking of organic matter) in the location where they are produced. The shift in U^{K}_{37} to "warmer" values on sedimentation could also explain the best correlations with temperatures from 0 m depth. Production of the alkenones occurs in deeper cooler waters, but is skewed to warmer values when the sediments are considered. The importance of a sediment-based calibration, where the water column diagenetic alteration of U^{K}_{37} is considered, is now even more relevant. The interpretation of U^{K}_{37} stratigraphic data in temperate and cold locations may now be more complicated, if changes in the extent of degradation of the alkenones have taken place through time, and U^{K}_{37} is also diagenetically dependent.

CONCLUSIONS

Core tops from the eastern North Atlantic have yielded seasonal linear correlations between U^{K}_{37} and SST across the range of temperatures of coccolithophorid habitats. This correspondence extends over different coccolithophorid biogeographic zones and depositional settings. The fact is significant providing proof that U^{K}_{37} effectively registers climatic information, like a biophysical thermometer, and that is preserved in the deep-sea sedimentary record despite reworking of organic matter prior to its burial, and irrespective of the different populations of coccolithophorids contributing alkenones to the environment. Hence, the equations obtained are applicable to North Atlantic open-sea sediments for palaeotemperature reconstructions, akin to calibrations based on cultures or water column experiments, but which may not reflect the likely U^{K}_{37} water column diagenetic transformation included in the sedimentary calibration. Finally, the number of samples and their widespread distribution further endorse the veracity of the calibration.

Acknowledgments—We thank Jim Carter for assistance in running the samples in the mass spectrometer, the Natural Environmental Research Council for providing mass spectrometry facilities (GR3-6619 and F60-G6-36-10), and the European community EPOCH and Environment programs for financial support. U.P. and M.S. thank Kiel SFB313 for its support. We thank the reviewers, and especially Simon Brassell for his contribution to the interpretation of the data.

Editorial handling: J. D. Macdougall

REFERENCES

Barnes R. S. K. and Hughes R. N. (1988) *An Introduction to Marine Ecology*. Blackwell.

Brassell S. C. (1993) Applications of biomarkers for delineating marine palaeoclimatic fluctuations during the Pleistocene. In *Organic Geochemistry: Principles and Applications* (ed. M. H. Engel and S. A. Macko), pp. 699–738. Plenum Press.

Brassell S. C., Brereton R. G., Eglinton G., Grimalt J., Liebezeit G., Marlowe I. T., Pflaumann U., and Sarnthein M. (1986a) Palaeoclimatic signals recognized by chemometric treatment of molecular stratigraphic data *Org. Geochem.* **10,** 649–660.

Brassell S. C., Eglinton G., Marlowe I. T., Pflaumann U., and Sarnthein M. (1986b) Molecular stratigraphy: a new tool for climatic assessment. *Nature* **320,** 129–133.

Conte M. H. and Eglinton G. (1993) Alkenone and alkenoate distributions within the euphotic zone of the eastern north Atlantic: correlation with production temperature *Deep-Sea Res.* **40,** 1935–1961.

Conte M. H., Eglinton G., and Madureira L. A. (1992) 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.

Eglinton G., Bradshaw S. A., Rosell A., Sarnthein M., Pflaumann U., and Tiedemann R. (1992) Molecular record of secular sea surface temperature changes on 100-year timescales for glacial terminations I, II and IV. *Nature* **356,** 423–426.

Freeman K. H. and Wakeham S. G. (1992) Variations in the distributions and isotopic compositions of alkenones in Black Sea particles and sediments. *Org. Geochem.* **19,** 277–285.

Halldal P. (1953) Phytoplankton investigations from weather ship M in the Norwegian Sea. *Hvalrad. Skr. Norske Vidensk. Akad.* **38,** 5–91.

Jordan R. W. (1988) Coccolithophorid communities in the North East Atlantic. Ph.D. thesis, Univ. Surrey.

Kennedy J. A. and Brassell S. C. (1992) Molecular records of twentieth-century El Nino events in laminated sediments from the Santa Barbara basin. *Nature* **357,** 62–64.

Levitus S. (1982) *Climatological Atlas of the World Ocean* U.S. Govt. Printing Office.

Lyle M. W., Prahl F. G., and Sparrow M. A. (1992) Upwelling and productivity changes inferred from a temperature record in the central equatorial Pacific. *Nature* **355,** 812–815.

Madureira L. A. (1994) Lipids in recent marine sediments of the eastern North Atlantic. Ph.D. dissertation, Univ. Bristol, UK.

Marlowe I. T. (1984) Lipids as palaeoclimatic indicators. Ph.D. thesis, Univ. Bristol.

Marlowe I. T., Brassell S. C., Eglinton G., and Green J. C. (1990) Long-chain alkenones and alkyl alkenoates and the fossil coccolith record of marine sediments. *Chem. Geol.* **88,** 349–375.

McCaffrey M. A., Farrington J. W., and Repeta D. T. (1990) The organic geochemistry of Peru margin surface sediments: I. A comparison of the C37 alkenone and historical El Niño records. *Geochim. Cosmochim. Acta* **54,** 1671–1682.

McIntyre A. and Bé A. W. H. (1967) Modern coccoliths of the Atlantic Ocean, I. Placoliths and cyrtoliths. *Deep-Sea Res.* **14,** 561–597.

Okada H. and McIntyre A. (1977) Modern coccolithophores of the Pacific and North Atlantic oceans. *Micropaleontol.* **23,** 1–55.

Pickard G. L. and Emery W. J. (1990) *Descriptive Physical Oceanography: An Introduction,* 5th ed. Pergamon Press.

Poynter J. G., Farrimond P., Brassell S. C., and Eglinton G. (1989) Molecular stratigraphic study of sediments from holes 658A and 660A, Leg 108. *Proc. Ocean Drill. Prg.* **108,** 387–394.

Prahl F. G. and Wakeham S. G. (1987) Calibration of unsaturation patterns in long-chain ketone compositions for palaeotemperature assessment. *Nature* **320,** 367–369.

Prahl F. G., Muehlhausen L. A., and Zahnle D. L. (1988) Further evaluation of long-chain alkenones as indicators of paleoceanographic conditions. *Geochim. Cosmochim. Acta* **52,** 2303–2310.

Prahl F. G., de Lange G. J., Lyle M., and Sparrow M. A. (1989) Post-depositional stability of long-chain alkenones under contrasting redox conditions. *Nature* **341,** 434–437.

Prahl F. G., Collier R. B., Dymond J., Lyle M., and Sparrow M. A. (1993) A biomarker perspective of prymnesiophyte productivity in the northeast Pacific Ocean. *Deep-Sea Res.* **40,** 2061–2076.

Rosell-Melé A. (1994) Long-chain alkenones, alkyl alkenoates and total pigment abundances as climatic proxy-indicators in the Northeastern Atlantic. Ph.D. thesis, Univ. Bristol.

Rosell-Melé A., Eglinton G., and Grimalt J. (1994a) Organic compounds as proxy-indicators of sea surface palaeotemperature. The U^{K}_{37} index. In *Long-Term Climatic Variations-Data and Modelling; NATO ASI Series* (ed. J.-C. Duplessy and M.-T. Spyridakis), pp. 239–249. Springer-Verlag.

Rosell-Melé A., Carter J., and Eglinton G. (1994b) Distributions of long-chain alkenones and alkyl alkenoates in marine surface sediments from the North East Atlantic *Org. Geochem.* **22**, 501–509.

Rosell-Melé A., Carter J., Parry A., and Eglinton G. (1994c) Novel procedure for the determination of the U^{K}_{37} in sediment samples. *Anal. Chem.* (in press).

Rostek F., Ruhland G., Bassinot F., Muller P. J., Labeyrie L., Lancelot Y., and Bard E. (1993) Reconstructing sea-surface temperature and salinity using $\delta^{18}O$ and alkenone records. *Nature* **364**, 319–321.

Sikes E. L. and Volkman J. K. (1993) Calibration of alkenone unsaturation ratios (U^{K}_{37}) for paleotemperature estimation in cold polar waters. *Geochim. Cosmochim. Acta* **57**, 1883–1889.

Sikes E. L., Farrington J. W., and Keigwin L. D. (1991) Use of the alkenone unsaturation ratio U^{K}_{37} to determine past sea surface temperatures: core-top SST calibrations and methodology considerations. *Earth Planet. Sci. Lett.* **104**, 36–47.

Teece M. A., Maxwell J. R., Getliff J. M., Parkes R. J., Briggs D. E. G., and Leftley J. W. (1994) Laboratory degradation of lipids of the marine prymnesiophyte *Emiliania huxleyi* and significance for sediment studies. In *Biomolecular palaeontology; Lyell Meeting Volume* (ed. G. Eglinton and R. L. F. Kay), pp. 5–8. NERC Special Publication 94/1.

ten Haven H. L., Baas M., Kroot M., de Leeuw J. W., Schenck P. A., and Ebbing J. (1987) Late Quaternary Mediterranean sapropels: III. Assessment of source of input and palaeotemperature as derived from biological markers. *Geochim. Cosmochim. Acta* **51**, 803–810.

Thomson J., Colley S., Anderson R., Cook G. T., Mackenzie A. B., and Harkness D. D. (1993) Holocene sediment fluxes in the NE Atlantic from ^{230}Th(excess) and radiocarbon measurements. *Paleoceanography* **8**, 631–650.

Volkman J. K., Eglinton G., Corner E. D. S., and Forsberg T. E. V. (1980a) Long-chain alkenes and alkenones in the marine coccolithophorid *Emiliania huxleyi. Phytochemistry* **19**, 2619–2622.

Volkman J. K., Eglinton G., Corner E. D. S., and Sargent J. R. (1980b) Novel unsaturated straight-chain C37-C39 methyl and ethyl ketones in marine sediments and coccolithophore *Emiliana huxleyi.* In *Advances in Organic Geochemistry 1979* (ed. A. G. Douglas and J. R. Maxwell), pp. 219–227. Pergamon.

Volkman J. K., Barrett S. M., Blackburn S. I., and Sikes E. L. (1995) Alkenones in *Gephyrocapsa oceanica:* Implications for studies of paleoclimate. *Geochim. Cosmochim. Acta* **59**, 513–520.