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Alkenones and alkenes in surface waters and sediments of the Southern Ocean: Implications for paleotemperature estimation in polar regions

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Abstract—The concentration of C_{37}-C_{39} long-chain alkenones and alkenes were determined in surface water and surface sediment samples from the subpolar waters of the Southern Ocean. Distributions of these compounds were similar in both sample sets indicating little differential degradation between or within compound classes. The relative amounts of the tri- to tetra-unsaturated C_{37} alkenones increased with increasing temperature for temperatures below 6°C similar to the di- and tri-unsaturated C_{37} alkenones. The C_{37} di-, tri-, and tetra-unsaturated methyl alkenones are used in paleotemperature calculations via the U^{K}_{37} and the $U^{K'}_{37}$ ratios. In these datasets, the relative abundances of the $C_{37:2}$ and the $C_{37:3}$ alkenones as a proportion of the total C_{37} alkenones were opposite and strongly related to temperature (the latter with more scatter), but the abundance of the $C_{37:4}$ alkenone showed no relationship with temperature. The original definition of U^{K}_{37} includes the abundance of 37:4 in both the numerator and denominator, and thus it is perhaps not surprising that there is considerable scatter in the values obtained for U^{K}_{37} at low temperatures. Of the two, we suggest that $U^{K'}_{37}$ is the better parameter for use in paleotemperature estimations, even in cold locations. $U^{K'}_{37}$ values in the sediments fall on virtually the same regression line obtained for the water column samples of Sikes and Volkman (1993), indicating that their calibration is suitable for use in Southern Ocean sediments. The comparison of water column data with sedimentary temperature estimates suggests that the alkenone distributions are dominated by contributions from the summer when the biomass of *Emiliania huxleyi* and presumably flux to the sediment, is expected to be high. *Copyright © 1997 Elsevier Science Ltd*

1. INTRODUCTION

The alkenone unsaturation ratio, $U^{K'}_{37}$, is becoming a widely used technique for estimating past sea surface temperatures (SST) of the world's oceans. The technique has attracted attention in the paleoceanographic community because it is the first quantitative method for SST estimation that is not based on microfossil tests. As such, it augments established techniques because it responds to a different set of environmental controls than those that influence foraminiferal assemblages or isotope values. The proportions of long-chain unsaturated ketones* on which $U^{K'}_{37}$ is based are varied by the organism in response to the water temperature in which it is growing (Prahl et al., 1988) and thus is distinct from other geochemical temperature proxies (such as $\delta^{18}O$) which are based on passive, equilibrium processes. $U^{K'}_{37}$ has been successfully applied to a wide variety of paleoceanographic topics, from decadal scale El Niño events to Milankovitch scale climate changes (see Brassell, 1993 for a literature review).

The alkenone unsaturation function $U^{K'}_{37}$ is defined as the ratio of the di- to tri-unsaturated long chain C_{37} methyl alkenones in the sample:

$$U^{K'}_{37} = [C_{37:2}]/([C_{37:2}] + [C_{37:3}])$$

The originally defined paleotemperature parameter was U^{K}_{37} which included the $C_{37:4}$ alkenone in the calculation as follows:

$$U^{K}_{37} = [C_{37:2}] - [C_{37:4}]/([C_{37:2}] + [C_{37:3}] + [C_{37:4}])$$

The $C_{37:4}$ alkenone was originally included in calculations because it was thought that it might also convey some temperature information (Marlowe, 1984). Prahl and Wakeham (1987) excluded the $C_{37:4}$ alkenone from the calculation because it is often not detectable in sediments (Brassell et al., 1986a,b) and because its exclusion improved the linearity of the relationship at lower temperatures (Prahl et al., 1988).

Numerous calibrations from batch cultures indicate large variations in temperature response between strains (e.g., Brassell, 1993) and species (Volkman et al., 1995), but work by Kenig et al. (1997) indicates that some of this variation may be attributable to differences in growth rates. Nonetheless, field calibrations of the technique have demonstrated that, despite variations in the several published relationships to growth temperature and real differences between local field calibrations (Conte and Eglinton, 1993; Brassell, 1993), the relationship between $U^{K'}_{37}$ and temperature is remarkably consistent and linear with SST in the world's oceans over a broad temperature range (5–25°C; Sikes and Volkman, 1993; Rosell-Melé et al., 1995; see Brassell, 1993

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* Namely: heptatriaconta-15E,22E-dien-2-one ($C_{37:2}$), heptatriaconta-8E,15E,22E-trien-2-one ($C_{37:3}$), heptatriaconta-8E,15E,22E,29E-tetraen-2-one ($C_{37:4}$).

for a review of the literature). The reduced slope at high and low temperatures (above 25 and below 5°C) first noted by Sikes and Volkman (1993) may be the effect of declining growth rates at extreme temperatures. The body of evidence indicates that local field calibrations are the best to use, however, the similarity of field calibrations suggests that the range in open ocean variations is sufficiently narrow that the use of a single worldwide calibration is within acceptable limits. The present best estimate is: $U^{K'}_{37} = 0.037T - 0.083$ (Brassell, 1993).

In addition to variation in the relationship between $U^{K'}_{37}$ and the temperature at the time of biosynthesis (i.e., the calibration used), seasonality and diagenetic effects have the potential to limit our ability to interpret paleotemperatures and paleoenvironmental information from the $U^{K'}_{37}$ signal in sediments. The season which the sedimentary $U^{K'}_{37}$-derived SST represents must be inferred. In many locations it appears that the temperatures recorded by the alkenones in the sediments represent the warm, or summer season (Sikes et al., 1991), but this is not strictly true. The $U^{K'}_{37}$-derived SST represents a weighted average of biomass production (or more strictly flux to the sediments) throughout the year (Prahl et al., 1993). Work by Prahl et al. (1993) from the northwest Pacific demonstrated that most of the flux to the sediments occurred in early summer but that the sedimentary $U^{K'}_{37}$-derived SST reflected summer thermocline temperatures (that is, from deep in the surface mixed layer), which were coincidentally the same as winter SST. The processes of degradation and diagenesis of the C_{37} alkenones are poorly understood. However, despite significant removal of alkenones in surface sediments, the unsaturation level (and hence the temperature signal) appears to be well preserved under a variety of conditions (Prahl et al., 1989; McCaffrey et al., 1990; Sikes et al., 1991; Madureira et al., 1995).

The unusual alkenones on which $U^{K'}_{37}$ is based are associated with several other C_{37}-C_{39} unsaturated methyl and ethyl ketones, as well as C_{37}-C_{39} alkenes and esters (Volkman et al., 1980a,b, 1995; Marlowe et al., 1984a,b, 1990; Conte et al., 1994). Work with microalgae in culture has established that the suite of long chain alkenones, alkenoates, and alkenes are produced by a very limited number of haptophytes (Volkman et al., 1980a,b, 1995; Marlowe et al., 1984a,b, 1990). In the open ocean the main source of the alkenones appears to be the two species *Emiliania huxleyi* and *Gephyrocapsa oceanica,* with the latter potentially an important contributor only in warmer tropical and subtropical regions (Rosell-Melé et al., 1994; Volkman et al., 1995). Notably, *G. oceanica* is a very minor constituent in Southern Ocean waters (less than 2% of the population for locations examined in this study; Nishida, 1986).

The relative abundances of alkenes, alkenones, and alkenoates varies between species (Volkman et al., 1995). However, the indication that alkenones and alkenoates degrade at appreciably different rates in the surface waters (Prahl et al., 1993) and in sediments (Prahl et al., 1989, 1993, 1995) suggests that temperature estimators which combine different compound classes (Conte et al., 1992; Conte and Eglinton, 1993) should be applied with some caution to the sediment record. However, the ratio of C_{37} to C_{38} alkenones is fairly consistent across all culture temperatures for each of the few species that have been studied (Prahl et al., 1988; Volkman et al., 1995). Thus, it appears that an examination of the relative amounts of all the alkenones and the ratio of C_{37} to C_{38} alkenones in particular may have the potential to provide paleoenvironmental information about the species contributing these compounds (Volkman et al., 1995).

Sikes and Volkman (1993) recently calibrated $U^{K'}_{37}$ in surface waters of the Southern Ocean for paleoclimatic temperature estimations. In this work we compare the alkenone and alkene distributions in surface water samples determined previously by Sikes and Volkman (1993) with the values in sediments deposited nearby in order to examine possible effects due to degradation and seasonality. We hope that this will allow a better understanding of the paleotemperature and paleoenvironmental record provided by $U^{K'}_{37}$ and its associated compounds in the Southern Ocean and, hence, allow more confident interpretations of the paleoclimate record.

2. MATERIALS AND METHODS

Samples of suspended particulate organic matter in surface waters were collected during two research cruises and analyzed as described in Sikes and Volkman (1993). Volumes as large as 180 L were collected on a single GFF glass fiber filter to provide sufficient material for lipid analysis. Filters were pre-cleaned by heating in a muffle furnace to 500°C for 24 h. Water samples were collected both from the ship's clean water intake line located at 3 m depth and from surface-tripped bottles of CTD casts. Temperature measurements were taken at the time of collection from the thermistor at the intake (for water line samples) or from the CTD thermistor (for bottle samples). Core top samples were supplied by the Southern Ocean paleoceanography research group in France (Laurent Labeyerie and Jean-Jacques Pichon) from their core library in Bordeaux. Additional core top samples were collected in collaboration with the Marine Geology group at the New Zealand Oceanographic Institution (NZOI).

Frozen filters were extracted ultrasonically in chloroform and methanol to provide a total lipid extract following procedures described in Volkman et al. (1988). Sediment samples were extracted following the same method but using 5–10 grams of wet sediment. In earlier studies of alkenones (Volkman et al., 1988), extracts were analyzed directly by capillary GC, but the $C_{37:2}$ peak in the chromatogram was very small, particularly for the cold water samples, and it occurred as a shoulder on a co-eluting C_{37} tri-unsaturated fatty acid methyl ester which made it impossible to measure it with an accuracy better than ±20%. Since a more accurate quantification of the C_{37} alkenones was needed, the extracts were saponified in 5% KOH in methanol and the neutral fraction containing the alkenones and alkenes obtained by partitioning into hexane-chloroform (Sikes and Volkman, 1993). For this study, extracts from a laboratory culture of a noncalcifying haptophyte (T. *Isochrysis* sp.) grown at 16°C, with approximately equal amounts of the $C_{37:2}$ and $C_{37:3}$ ($U^{K'}_{37} = 0.521$), was used routinely as a working standard in our laboratory. Variation in analyses of this standard over a year showed a standard deviation of 0.006 $U^{K'}_{37}$ units, which gives an analytical accuracy of approximately ±0.18°C (depending on the calibration used).

These fractions were analyzed by capillary GC using a HP-1 methyl silicone fused silica column (50 m × 0.32 mm id.). The samples were injected in chloroform using a cooled OCI-3 on-column injector. Hydrogen was the carrier gas. A temperature program of 50–150°C at 30°C min.^{-1} and 150–325°C at 3°C min.^{-1} was employed which gave good separation of all major constituents (Sikes and Volkman, 1993). Compounds were detected with a flame ionization detector and peak areas were measured using DAPA acquisition and processing software. For final compound identification, samples were analyzed by gas chromatography mass spectrometry (GC-MS) on a Hewlett Packard 5790 MSD connected by a direct capillary inlet to a HP 5890 gas chromatograph operated as described above. Typical MSD conditions were: electron energy 2200 volts, transfer line 310°C, electron energy 70 eV, 1.1 scans sec^{-1}, mass range 40–600 Da.

3. RESULTS AND DISCUSSION

3.1. Alkenone Distributions

For this study we analyzed forty-two filters from surface waters and twenty-eight surface sediment samples from the Southern Ocean. The water samples were taken during two transects south of Tasmania; one conducted in late winter to early spring (AA1/91) and one in late spring (FR9/86; Sikes and Volkman, 1993). The sediment samples are from three transects; one from south of Tasmania directly underlying one of the water transects, one from the western Indian Ocean, and one short transect from east of New Zealand (Fig. 1, Table 1). Of these, thirty-nine of forty-two particulate matter samples and twenty-five of twenty-eight sediment samples contained sufficient amounts of the C_{37}-C_{39} alkenones to permit their concentrations to be measured by capillary GC. Those water samples with alkenone levels too low to measure reliably were either from low volume samples, samples from beneath the ice, or from waters sampled deeper than 50 m. Those sediment samples with unmeasurably low levels of alkenones were from sites that have summer temperatures cooler than 4°C and are usually covered with winter sea ice.

It is well known that the relative abundances of the cellular concentrations of the C_{37}-C_{38} alkenones are related to temperature (Prahl and Wakeham, 1987; Prahl et al., 1988; Volkman et al., 1995). Additionally, growth rate may have a small effect on their unsaturation ratio and cellular concentrations (Kenig et al., 1997). In our water samples, the major long-chain constituent was the $C_{37:3}$ methyl alkenone; with decreasing water temperatures the relative abundances of the di-unsaturated compounds were very much reduced (Table 2). The alkenones were present in highest concentrations (>10 ng/L) in waters within the temperature range −0.2 to 3.2°C, where values for the $C_{37:3}$ were in excess of 40 ng/L. However, levels of $C_{37:3}$ in excess of 20 ng/L were found in waters warmer than 9°C, collected later in the season. Furthermore, concentrations of all alkenones tended to increase in waters of the same temperatures as the season progressed during the sampling cruise. We think that this is probably due to the onset and development of the spring bloom and the increase in growth rate associated with these conditions.

In sediment samples, overall alkenone abundances tend to increase with decreasing latitude (and hence increasing water temperature), although there is considerable variability with values ranging from 12 to 90 ng/g dry weight. This may reflect factors such as greater light and a longer growth season which would increase annual productivity in these otherwise similar Southern Ocean environments. There is a high latitude maximum in concentrations seen only in the KTB transect (Fig. 1) for sediment samples underlying summer SST's of 5–7.5°C, which is similar to that seen in the water samples.

To understand the differences between $U^{K'}_{37}$ and U^{K}_{37}, we have considered the relative abundances of the individual C_{37} compounds relative to the total C_{37} alkenones as a function of temperature (Fig. 2a, b, c). The relative abundance of the $C_{37:2}$ alkenone to the total of the C_{37} alkenones shows a particularly strong relationship to temperature both in water column and sediment samples ($r = 0.874$, see Fig. 2a). At temperatures above 16°C, the $C_{37:2}$ alkenone comprises more than 45% of the total C_{37} alkenones decreasing to less than 10% at temperatures below 10°C. Additionally, the scatter in this relationship is very low in comparison to that of the

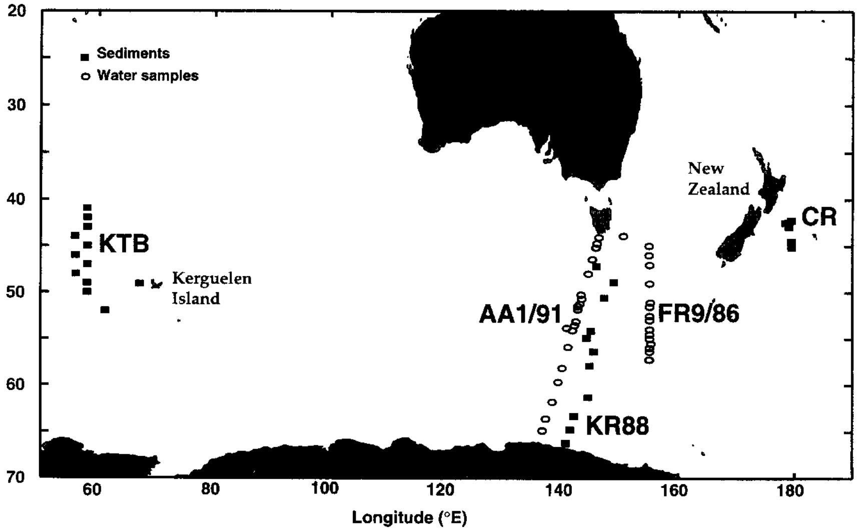

Fig. 1. Map of the sample locations. Surface water samples (open circles) were taken in two transects south and southeast of Tasmania. AA1-91 was a late winter cruise of the RV Aurora Australis in 1991, and FR9-86 was a spring summer cruise of the RV Franklin in 1986. Sediment samples (solid squares) were taken in three transects, south of Tasmania (samples designated KR88), in the western Indian Ocean (samples designated KTB) by the RV Marion Dufresne, and to the east of New Zealand (CR denotes samples from the Chatham Rise) by NZOI vessels.

Table 1: Location of samples and overlying water temperatures.

Sample	Latitude (°S)	Longitude (°E)	Water depth (m)	SST* (°C)	$U^{K'}_{37}$ SST † (°C)
FR9/86 Filters:					
FR9/86-9	57 13	154 56	surface	1.90	4.84
FR9/86-10	57 15	154 58	surface	1.90	5.10
FR9/86-12	56 22	155 03	surface	2.10	5.02
FR9/86-15	56 00	154 58	surface	1.50	8.69
FR9/86-18	55 33	155 15	surface	3.20	6.69
FR9/86-19	55 00	155 00	surface	4.20	6.02
FR9/86-22	54 31	155 02	surface	5.00	5.25
FR9/86-23	54 00	154 59	surface	7.00	8.56
FR9/86-27	52 59	154 59	surface	6.00	6.60
FR9/86-30	52 31	155 00	surface	6.50	14.55
FR9/86-34	51 30	154 59	surface	7.80	7.08
FR9/86-42	51 03	155 04	surface	9.00	7.28
FR9/86-47	49 00	154 59	surface	9.30	8.15
FR9/86-53	47 00	155 00	surface	9.80	8.64
FR9/86-56	47 00	154 59	surface	10.40	8.20
FR9/86-69	45 59	154 57	surface	11.70	10.87
FR9/86-75	44 58	154 55	surface	12.10	11.54
FR9/86-79	43 55	150 27	surface	12.20	11.48
AA1/91 Filters					
AA1/91-19	45 11	145 42	surface	9.50	9.23
AA1/91-20	45 11	145 44	surface	9.50	9.20
AA1/91-21	46 25	145 05	surface	9.50	11.83
AA1/91-22	46 27	145 05	surface	9.50	9.49
AA1/91-24	47 60	144 22	surface	8.80	10.82
AA1/91-27	50 13	143 11	surface	7.40	5.59
AA1/91-28	50 40	143 15	surface	5.60	5.14
AA1/91-29	51 27	142 35	surface	4.30	5.32
AA1/91-30	51 51	142 35	surface	3.90	4.98
AA1/91-32	53 08	142 15	surface	2.50	4.70
AA1/91-33	53 32	141 59	surface	1.40	5.04
AA1/91-34	53 51	140 40	surface	3.20	5.47
AA1/91-36	55 54	140 51	surface	1.20	4.53
AA1/91-38	58 08	139 50	surface	1.50	4.68
AA1/91-39	59 38	139 10	surface	-0.20	4.54
AA1/91-41	61 47	138 06	surface	-0.70	6.28
AA1/91-43	64 53	136 23	surface	-1.90	ND
AA1/91-44	64 53	136 24	surface	-1.90	ND
AA1/91-45	63 36	137 01	surface	-1.90	ND
AA1/91-49	54 07	141 40	surface	1.80	4.72
AA1/91-50	54 07	141 40	surface	1.80	6.92
AA1/91-51	51 15	142 54	surface	7.00	6.81
AA1/91-52	44 42	145 56	surface	9.80	8.87
AA1/91-54	44 06	146 15	surface	11.30	10.86
AA1/91-55	44 06	146 15	surface	11.30	11.58
KR88 Sediments:					
KR88-07	47 09	145 48	2890	12.00	13.55
KR88-08	49 15	148 48	3885	10.00	10.87
KR88-09	50 36	147 09	4350	9.00	12.42
KR88-10	54 11	144 48	2785	5.00	5.79
KR88-11	54 55	144 04	2880	5.00	5.35
KR88-12	56 24	145 17	3020	4.00	5.05
KR88-13	57 57	144 35	3740	4.00	4.56
KR88-14	61 17	144 26	4200	2.00	ND
KR88-15	63 18	141 55	3380	1.00	ND
KR88-16	64 46	141 13	3320	0.50	ND
KR88-17	66 12	140 30	180	-0.50	ND
KTB Sediments:					
KTB-01	49 06	67 01	1235	5.57	5.86
KTB-08	51 59	61 07	4710	3.68	ND
KTB-12	49 00	57 60	4390	4.84	7.09
KTB-14	50 00	57 60	4610	4.18	8.07
KTB-18	48 01	55 59	4245	5.50	7.07
KTB-20	47 00	58 00	4550	7.20	10.42
KTB-21	45 58	55 59	4195	8.28	7.97
KTB-22	45 60	55 60	4260	8.26	8.81
KTB-25	45 01	57 58	4680	10.50	10.77
KTB-26	43 58	55 58	4750	11.59	12.65
KTB-29	43 00	58 01	4765	13.49	13.62
KTB-31	40 59	57 59	4920	15.74	15.85
KTB-34	41 60	58 01	4795	14.70	14.60
CR Sediments					
W266	42 14	179 22	2540	17.00	16.35
W268	42 51	178 58	980	16.20	16.76
R657	42 32	178 30	1408	17.00	19.95
U938	45 05	179 30	2700	14.50	13.82
U939	44 32	179 30	1300	15.00	13.77

* SST was directly measured for water samples (FR9/86 and AA1/91). Levitus (1994) summer season surface temperatures for the overlying water were used for sediments (KR88, KTB and Chatham Rise).

† Estimates of SST were based on the $U^{K'}_{37}$ calibration of Sikes and Volkman, 1993.

$C_{37:3}$ and $C_{37:4}$ (Fig. 2b and c). The $C_{37:3}$ alkenone abundance is also related to temperature, but its relationship is the inverse of that of the $C_{37:2}$ alkenone and not as well correlated ($r = 0.660$, see Fig. 2b). The $C_{37:3}$ alkenone comprises 50–90% of the C_{37} alkenones throughout the temperature range up to 14°C, with a general trend to lower proportions with higher temperature (Fig. 2b: Note the considerable scatter in the values at lower temperatures).

The abundance of the $C_{37:4}$ methyl alkenone, on the other hand, shows no relationship to temperature ($r = 0.118$; Fig. 2c). In fact, for samples in the 3–5°C range, the relative abundance varies from almost zero to 45% of the total C_{37} alkenones. Some of this variation may reflect seasonal effects. For example, the $C_{37:4}$ methyl alkenone is virtually undetectable in the winter water samples and even in the coldest waters it is only a trace constituent (Table 1). However, it was present in water samples taken later in that cruise (AA1/91) and in most samples from the spring cruise as well as in the sediment samples warmer than 3.5°C. This distribution may be related to changes in growth rates, but requires more study to determine the controlling factors. In the sediment samples there appears to be an increase in relative abundance of the $C_{37:4}$ methyl alkenone with decreasing temperature (although still with significant scatter; Fig. 2c). This is consistent with the view that the alkenones in the sediment are mainly derived from a restricted time window when biomass is greatest, i.e., in the summer.

It appears from our data that the dominant influence on U^{K}_{37} is the changing proportion of the $C_{37:2}$ alkenone and only secondarily the change in relative amount of the $C_{37:3}$. The $C_{37:4}$ abundance, if used at all, is best only included in the denominator (Fig. 2a and b). At low temperatures there is little to be gained by the inclusion of the $C_{37:4}$ alkenone in the calculation due to the considerable variability in its relative abundance. Of the two established parameters we suggest that $U^{K'}_{37}$ is the better for use in paleotemperature estimations, even in cold locations.

Previous studies have shown that the $C_{37:4}$ methyl alkenone is usually undetectable in sediments underlying warmer waters, leading to identical values of U^{K}_{37} and $U^{K'}_{37}$. Additionally, in colder samples, the exclusion of the $C_{37:4}$ alkenone was found to increase the linearity of the temperature relationship (Prahl et al., 1988) as well as causing the parameters to diverge (Rosell-Melé et al., 1994). Rosell-Melé et al. (1994) investigated the relative abundance of the C_{37} alkenones to the total of the C_{37}-C_{39} alkenones and alkenoates in sediment samples from the North Atlantic. The $C_{37:4}$ alkenone abundance showed no change with temperature between 10 and 3°C and then a stepwise jump in the relationship, with an accompanying increase in the scatter. These authors also compared $U^{K'}_{37}$ to U^{K}_{37} in the same samples and found that the parameters diverge below approximately 8°C (i.e., $U^{K'}_{37}$ below 0.4) and that there was an increase in scatter of the data as the relative amounts of the $C_{37:4}$ and the $C_{37:2}$ alkenones became similar. They did not have a clear explanation of the scatter but suggested that it may have been due to lateral advection of organic material. Our water column data from the Southern Ocean suggests that the scatter is due to the $C_{37:4}$ alkenone abundance responding most strongly to factors other than temperature. Additional scatter may be introduced by the possibility that alkenones having different degrees of unsaturation may degrade at different rates (Freeman and Wakeham, 1992), but evidence for this is lacking. The scatter introduced by the inclusion of the $C_{37:4}$ alkenone into temperature estimations in North Atlantic sediments leads to values of U^{K}_{37} from 0.035 to 0.321 (one third of the total possible range) for sea surface temperatures of 3.0–3.3°C (n = 6; Rosell-Melé et al., 1994). Therefore, despite the apparently lower sensitivity (Rosell-Melé et al., 1994), we suggest that better SST estimates can be obtained by using $U^{K'}_{37}$ in cold waters, particularly those above 4°C.

Both $U^{K'}_{37}$ and U^{K}_{37} lose their sensitivity to temperature in waters below 5°C in the North Atlantic (Rosell-Melé et al., 1994). In the Southern Ocean, the slope of the relationship of $U^{K'}_{37}$ to sea surface temperature decreases below 4°C (Sikes and Volkman, 1993). This effect may be related to very low growth rates at such low temperatures. However, in both oceans, the increase in scatter at low temperatures may reflect a limit to the use of changes in the degree of alkenone unsaturation by the organism as a means of coping with temperature change. This is demonstrated by the poor relationship to temperature of $U^{K'}_{37}$ below 6°C ($r^2 = 0.005$ $r = 0.07$ slope = 0.064). Clearly there is no statistical relation of $U^{K'}_{37}$ to temperature in very cold waters.

Prahl et al. (1988) and Volkman et al. (1995) observed that the ratio of C_{37} methyl alkenones to the total of C_{38} methyl and ethyl alkenones in cultures of *E. huxleyi* and *G. oceanica* changed little with temperature. Volkman et al. (1995) showed that values of this ratios were ~0.70 (with a range of 0.59–0.81) for *G. oceanica* and 1.46 (with a range of 1.18–1.70) for *E. huxleyi.* Conte et al. (1994) found a range of 0.86–2.16 (average 1.16) for cultures of *E. huxleyi.* In our water samples the ratio ranges from 0.7 to 1.8 (average 1.3). This is consistent with the range of results for *E. huxleyi* in culture, but not *G. oceanica* and supports earlier work (Sikes and Volkman, 1993) which suggested that *E. huxleyi* is the dominant alkenone-producing species in the Southern Ocean.

In the sediments the ratio of C_{37}/C_{38} alkenones ranges from 0.4 to 1.4 (average 1.0). In both water and sediment samples this relationship shows no relationship to temperature (Fig. 3). Several of the sediments have quite low values, within the range normally found in *G. oceanica,* even those from the sediment transect (KR88) which directly underlies one of the water sample transects (AA1-91, Fig. 1). This suggests that the use of this parameter in sediments to assess the paleo-algal sources of these compounds may be limited. Determining the algal source of the alkenones is important to accurately determine paleo-temperatures because the two species show a different relationship of $U^{K'}_{37}$ to temperature (Volkman et al., 1995). This becomes especially important in cases where the sediments were laid down prior to the first appearance of *E. huxleyi,* where the paleo-distributions of *E. huxleyi* are not well known or where the species assemblages are known to be different from today.

3.2. Alkene Distributions

The C_{37} and C_{38} n-alkenes have previously been detected in some of the haptophytes that produce the long chain alkenones (Volkman et al., 1980a,b; Conte et al., 1994), although this may not be true of all strains of *E. huxleyi.* From alkenone and alkene distributions in Southern Ocean water, Sikes and Volkman (1993) suggested that the hydrocarbons might accumulate in the cells exposed to extremely cold temperatures. Indeed, C_{37} and C_{38} *n*-alkenes were detected in all water samples and become significant constituents relative to the alkenones in Southern Ocean waters cooler than 6°C (Table 2).

The sum of the C_{37} *n*-alkene abundances is approximately equal to the sum of the C_{37} methyl alkenones at temperatures around 0°C with relative amounts declining to near-zero with increasing temperatures to 14°C (Fig. 4a). Although there is scatter in the data it is apparent that there is a significant trend to higher alkene abundances with decreasing temperatures as proposed by Sikes and Volkman (1993). The relationship can be written Σ C_{37}-ene/Σ C_{37}-one = −0.049T + 0.826 ($r = 0.611$, $r^2 = 0.373$). The slope of this relationship is comparable in magnitude to that of $U^{K'}_{37}$, however, it seems that this relationship may be of limited value in paleoclimate studies due to the scatter in the data, the apparent variability in alkenone abundance between species of haptophytes, and the possibility of differential degradation between compound classes in sediments (J. K. Volkman, unpubl. data, 1992; Brassell, 1993). Sinninghe Damsté et al. (1989) reported a number of long chain organic sulfur compounds in anoxic sediments which appeared to have resulted from incorporation of sulfur into alkenes, but not alkenones (Brassell, 1993). This differential degradation of alkenes and alkenones would make parameters based on alkene to alkenone ratios of little use as paleotemperature indicators in anoxic sediments. Note that alkenes and alkenones were below detection levels in sediments deposited below waters having summer temperatures of less than 4°C, probably because of low algal biomass.

The possibility that the degree of unsaturation of the alkenes might respond to changes in temperature in a similar way as the alkenones was investigated by plotting the abundance of the $C_{37:3}$ alkene against the sum of the C_{37} alkenes (in this case just $C_{37:3}$ plus $C_{37:4}$). The two sets of water column samples showed the same behavior (Fig. 4b), but the datasets were not superimposable. From 0 to 6°C, there was a systematic decrease in the relative abundance of the $C_{37:4}$ alkene to about 6°C, above which there was no change in the ratio since the $C_{37:3}$ alkene dominated the distribution and represented over 90% of the alkenes. At higher temperatures, the alga is probably unable to modify the distribution of alkenes further, so the biochemical response to changes in temperature is seen increasingly in the alkenone distributions. As noted above, the relative abundance of alkenes decreased with increasing temperature to the point where they were very minor constituents above 10°C. At first sight, it might appear that this change in $C_{37:3}$ alkene abundance from 0 to 6°C could provide a useful paleoclimate proxy. Unfortunately, this seems unlikely when one considers the considerable scatter in the sediment data plotted on the same figure (Fig. 4b).

3.3. Calibration of $U^{K'}_{37}$ for Paleo-Sea Surface Temperature Estimation

The relationship of U^{K}_{37} and $U^{K'}_{37}$ to water (growth) temperature has been studied in cultures (Prahl and Wakeham,

Table 2: Concentrations of long chain alkenones and alkenes in seawater and sediment samples.

Sample	Long chain alkenes* (ng/L or ng/g)				Long chain alkenones † (ng/L or ng/g)								
	37:4HC	37:3HC	38:4HC	38:3HC	37:4MK	37:3 MK	37:2 MK	38:3EK	38:3MK	38:2EK	38:2MK	39:3EK	39:2EK
AA1/91 filters													
AA1/91-19	0.0	0.8	0.0	0.3	1.2	2.7	0.8	1.4	1.0	0.3	0.1	0.5	0.0
AA1/91-20	0.0	0.6	0.0	0.3	0.0	8.2	2.4	3.0	2.7	1.5	0.4	0.6	0.0
AA1/91-21	0.0	3.2	0.0	0.0	0.0	3.8	1.9	2.0	1.8	1.6	1.0	0.6	0.0
AA1/91-22	0.1	0.6	0.0	0.0	0.2	6.4	2.0	3.4	3.1	2.3	0.5	0.0	0.0
AA1/91-24	0.0	2.8	0.0	0.4	0.2	5.8	2.4	1.9	1.4	1.5	0.5	3.0	0.0
AA1/91-27	0.3	0.8	0.0	0.2	0.0	1.3	0.1	0.6	0.5	0.0	0.0	0.2	0.0
AA1/91-28	0.3	5.6	0.0	0.8	0.2	11.3	0.7	4.2	3.4	1.1	0.3	0.7	0.1
AA1/91-29	0.6	9.2	0.2	1.5	0.1	16.9	1.2	6.7	5.2	1.7	0.3	1.1	0.2
AA1/91-30	1.1	10.2	0.2	1.6	0.3	19.9	1.1	8.4	5.6	2.0	0.5	1.6	0.1
AA1/91-32	3.5	16.9	0.5	2.5	0.5	24.8	1.0	11.4	7.2	1.4	0.2	1.9	0.3
AA1/91-33	5.6	23.2	0.8	3.2	2.8	45.2	2.5	20.1	12.6	1.3	0.0	3.3	0.5
AA1/91-34	1.5	8.1	0.0	1.1	0.2	12.9	1.0	5.1	3.3	1.1	0.0	1.1	0.4
AA1/91-36	5.9	18.8	0.7	2.7	0.9	33.9	1.1	16.9	9.7	5.2	1.5	2.7	0.8
AA1/91-38	5.1	17.1	0.6	2.8	0.7	28.3	1.1	13.8	8.6	1.4	0.2	2.3	0.6
AA1/91-39	6.4	13.8	0.5	1.8	1.0	22.0	0.7	13.9	6.1	0.8	0.0	2.2	0.6
AA1/91-41	1.7	2.9	0.2	0.4	0.5	3.6	0.4	2.9	1.1	0.0	0.0	0.0	0.0
AA1/91-43	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AA1/91-44	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AA1/91-45	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
AA1/91-49	5.0	17.8	0.0	2.8	1.1	25.6	1.0	13.4	7.1	1.3	0.0	1.0	0.0
AA1/91-50	2.5	9.4	0.5	25.7	3.0	14.5	2.2	7.9	4.9	3.5	1.8	0.0	0.0
AA1/91-51	0.0	2.0	0.0	0.4	0.3	3.2	0.5	1.3	1.1	0.5	0.3	0.2	0.0
AA1/91-52	0.2	5.1	0.0	1.4	0.0	33.7	9.0	11.4	12.7	5.0	2.3	2.1	0.0
AA1/91-54	0.0	2.2	0.0	0.0	0.0	15.2	6.3	4.1	4.4	3.2	1.1	0.4	0.0
AA1/91-55	0.7	19.8	0.0	0.0	0.0	9.3	4.4	4.2	3.7	1.9	1.1	0.0	0.0
FR9/86 filters													
FR9/86-9	0.5	0.9	0.2	0.4	0.1	1.2	0.1	0.7	0.4	0.1	0.0	0.1	0.1
FR9/86-10	11.5	39.6	1.6	5.5	ND	34.1	2.0	16.6	6.2	14.6	4.1	3.5	3.1
FR9/86-12	7.1	25.3	1.2	6.1	2.4	40.3	2.2	20.0	12.2	3.3	0.5	2.9	0.7
FR9/86-15	2.9	5.2	0.6	1.0	2.1	12.3	3.2	5.6	3.2	1.4	0.0	0.0	0.0
FR9/86-18	7.5	29.4	3.5	6.2	ND	32.0	4.4	26.5	12.0	5.0	2.0	1.4	0.0
FR9/86-19	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
FR9/86-22	1.6	9.6	0.0	1.7	0.4	16.2	1.1	6.8	5.2	1.6	0.3	1.0	0.1
FR9/86-23	1.5	6.8	0.0	1.1	1.9	8.8	2.2	7.4	4.2	2.8	2.4	3.3	2.7
FR9/86-27	1.1	8.2	0.0	1.1	0.4	15.9	2.1	6.1	5.0	2.3	0.6	1.3	0.4
FR9/86-30	0.7	3.9	0.0	0.6	0.5	11.8	9.5	3.8	3.0	8.8	0.7	0.5	0.5
FR9/86-34	0.3	2.4	0.2	0.4	0.0	4.4	0.7	1.6	1.2	0.5	0.1	0.2	0.0
FR9/86-42	0.0	5.9	0.0	3.0	ND	18.2	3.1	5.3	4.7	2.2	0.7	0.0	0.0
FR9/86-47	1.2	9.8	0.0	1.1	0.6	24.5	5.4	8.3	8.1	3.8	1.8	2.1	1.3
FR9/86-53	0.4	3.3	0.0	0.4	3.1	15.3	3.9	5.3	5.5	2.3	0.8	0.5	0.8
FR9/86-56	0.4	3.8	0.0	0.4	0.4	13.0	2.9	4.5	3.9	1.9	0.6	0.4	0.8
FR9/86-69	0.0	2.0	0.0	0.0	0.6	12.7	5.3	4.5	4.2	3.6	1.4	0.5	0.6
FR9/86-75	0.2	0.4	0.0	0.0	1.2	1.9	0.9	0.8	0.7	0.7	0.2	0.0	0.1
FR9/86-79	2.0	4.8	0.0	0.8	0.0	51.4	24.1	19.2	11.9	12.9	2.6	1.6	2.5
KR88 sediments													
KR88-07	4.7	7.3	0.0	3.6	9.1	55.9	38.0	25.7	18.8	29.3	25.5	4.7	0.7
KR88-08	3.2	9.5	0.0	2.8	6.7	39.2	16.3	14.1	10.9	17.8	22.4	4.2	0.6
KR88-09	3.2	5.7	2.4	2.5	6.4	25.1	14.0	31.8	40.6	12.3	4.0	3.3	0.4
KR88-10	4.7	14.5	3.1	9.9	17.8	37.0	3.4	21.2	10.1	0.0	0.0	4.1	0.0
KR88-11	5.3	13.8	0.0	0.0	6.8	27.8	1.9	20.4	9.8	2.0	1.6	3.1	0.0
KR88-12	3.8	14.3	0.0	2.4	1.8	12.4	0.7	9.3	3.3	1.2	0.0	1.9	0.0
KR88-13	5.3	9.1	0.0	0.8	3.3	13.4	0.5	19.6	19.6	2.8	0.0	2.2	0.0

1987; Prahl et al., 1988; Volkman et al., 1995) and in water column samples from many locations worldwide (Prahl and Wakeham, 1987; Prahl et al., 1988; Conte et al., 1992; Conte and Eglinton, 1993; Sikes and Volkman, 1993). Although the general relationship between $U_{37}^{K'}$ and water temperature is similar in most regions (Brassell, 1993), it is clear that due to the differences in this relationship between sites (perhaps as a function of growth rates or different strains), the most accurate paleotemperature estimation can be obtained by using a local calibration. Sikes and Volkman (1993) established a calibration for the Southern Ocean based on the same water column samples used in this study.

In our samples, there were sufficient alkenones found in all core-tops underlying waters with summer temperatures greater than 4°C to permit quantitative determination of C_{37} and C_{38} alkenone abundances (Table 1). In these sediments $U_{37}^{K'}$ shows excellent correlation with summer sea surface temperature averages overlying the core-top locations (Levitus, 1994; Fig. 5a). The linear regression of these data can be expressed as $U_{37}^{K'} = 0.038T - 0.082$ ($r = 0.960$, r^2

Table 2. (Continued)

KR88-14	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
KR88-15	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
KR88-16	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
KR88-17	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
KTB sediments													
KTB-01	61.8	289.9	0.0	47.8	93.2	276.6	26.2	288.2	67.8	99.1	0.0	57.1	30.9
KTB-08	34.8	86.9	0.0	39.6	137.4	208.5	0.0	133.2	49.3	42.3	0.0	24.3	0.0
KTB-12	74.7	123.6	0.0	19.1	137.7	309.0	49.3	141.9	82.0	55.5	0.0	43.4	21.3
KTB-14	21.0	46.0	7.5	10.2	61.1	149.4	32.3	107.4	54.8	26.5	6.2	17.2	4.9
KTB-18	160.0	143.1	0.0	0.0	185.3	297.1	47.1	196.5	76.7	89.9	13.9	38.9	ND
KTB-20	35.9	72.6	12.6	14.8	52.8	159.8	60.7	90.8	56.6	43.5	15.9	16.7	6.0
KTB-21	26.3	176.4	10.2	32.6	45.5	280.8	59.0	139.5	94.0	51.9	11.5	21.0	6.8
KTB-22	35.2	68.8	0.0	12.3	8.3	74.2	17.4	59.3	33.8	59.2	0.0	10.2	ND
KTB-25	33.4	35.0	0.0	0.4	54.1	62.7	25.6	48.9	19.3	42.6	3.9	12.4	0.0
KTB-26	0.0	48.2	8.7	18.6	63.1	144.7	84.2	81.8	55.7	60.3	20.4	9.9	7.8
KTB-29	ND	ND	6.0	17.5	41.6	163.0	112.3	76.5	53.4	73.9	24.3	10.5	8.9
KTB-31	11.6	34.2	0.0	16.8	66.8	193.3	193.4	71.3	53.0	121.7	30.3	11.3	40.0
KTB-34	ND	68.8	8.8	16.8	48.5	192.1	156.1	97.8	63.8	101.2	42.0	12.4	15.1
CR sediments													
R657	0.0	0.0	0.0	0.0	89.4	475.5	967.5	205.5	199.9	493.4	185.4	88.8	52.7
U938	0.0	0.0	0.0	0.0	4.4	16.0	11.4	6.4	5.9	7.6	2.0	ND	ND
U939	0.0	0.0	0.0	0.0	23.8	126.1	89.0	43.1	45.2	56.9	18.2	ND	ND
W266	0.0	0.0	0.0	0.0	236.2	833.1	907.2	232.2	281.5	607.1	237.9	47.5	77.5
W268	0.0	0.0	0.0	0.0	216.7	587.1	685.0	212.8	221.0	455.7	158.4	37.1	59.7

* HC = alkenes

† MK = methyl ketones; EK = ethyl ketones

= 0.921). The slope of this line (0.038) is not significantly different from that of the Southern Ocean water column data above 4°C (0.041; Sikes and Volkman, 1993) by a two-way t-test at the 95% confidence interval ($p < 0.05$). This suggests that the calibration of Sikes and Volkman (1993) is suitable for use in paleo-temperature estimation in Southern Ocean sediments.

In our study and in previous work (Sikes et al., 1991; Prahl et al., 1993; Rosell-Melé et al., 1995), the slope of the sediment linear regression is slightly lower than that of the local water column data although it is not demonstrated from statistical analyses in this or previous studies (Sikes et al., 1991) whether this effect is real or not. This sediment relationship would result in paleotemperature estimations slightly cooler than what would be predicted from the water column calibration. This offset has been suggested to be due to faster degradation of the more unsaturated alkenones (Prahl et al., 1988, 1993; Sikes et al., 1991; Freeman and Wakeham, 1992; Rosell-Melé et al., 1995) although there is no hard evidence for this. Interestingly, the relationship based on these Southern Ocean sediments is very similar to the global compilation of Brassell (1993).

An additional concern in calibrating the sedimentary alkenone record for paleotemperature estimations is determining which season's SST is reflected in the sediments. Previous sediment studies (Sikes et al., 1991; Rosell-Melé et al., 1995) have demonstrated that sediments show a similar relationship to atlas-derived temperatures as do water column samples and that they accurately reflect overlying water temperatures with few exceptions (Conte et al., 1992; Freeman and Wakeham, 1992). The sediment trap study by Prahl et al. (1993) showed that the $U^{K'}_{37}$ temperature recorded in the sediments reflects the time of maximum productivity and flux of these compounds to the sediment (even if the temperature recorded was that of the lower mixed layer). In the Southern Ocean, as in most locations, maximum biomass production occurs during the phytoplankton blooms of the spring-summer.

Rosell-Melé et al. (1995) correlated sedimentary U^{K}_{37} to all four seasons of Levitus (1982) and for temperatures at water depths of 0, 30, and 50 m in the North Atlantic. In this study they determined that the season with the best linear fit of sediment U^{K}_{37} to temperature was that of winter SST. Their results also showed that highest correlations for all seasons were consistently associated with surface temperatures (0 m), although all regressions in all seasons were highly correlated ($r > 0.900$). As they pointed out, because the surface mixed layer generally has a very small temperature gradient the consistently good correlation for all depths is not surprising, even if most of the biomass is not forming at 0 m. We used atlas surface temperature values for our comparisons.

Because water column calibrations are based on the direct measurement of the temperature at which the alkenones were produced, they represent a truly empirical dataset. We suggest a better way to assess the validity of any sedimentary $U^{K'}_{37}$ calibration (based on temperatures taken from atlas values for overlying waters in a chosen season) is to compare it to the relationship obtained from water column samples. We obtained winter atlas SST estimates, 0 m depth (Levitus, 1994, COADS World Ocean Atlas, 1996) for the waters overlying our sediment samples and compared them to our water column samples (Fig. 5b). The winter sediment correlation is clearly offset from that of the water column. In contrast, the relationship of our summer SST estimates for the sediment samples is not significantly different from the water column data by a two way t-test as discussed above (Fig. 5a). The same exercise can be done for the spring and

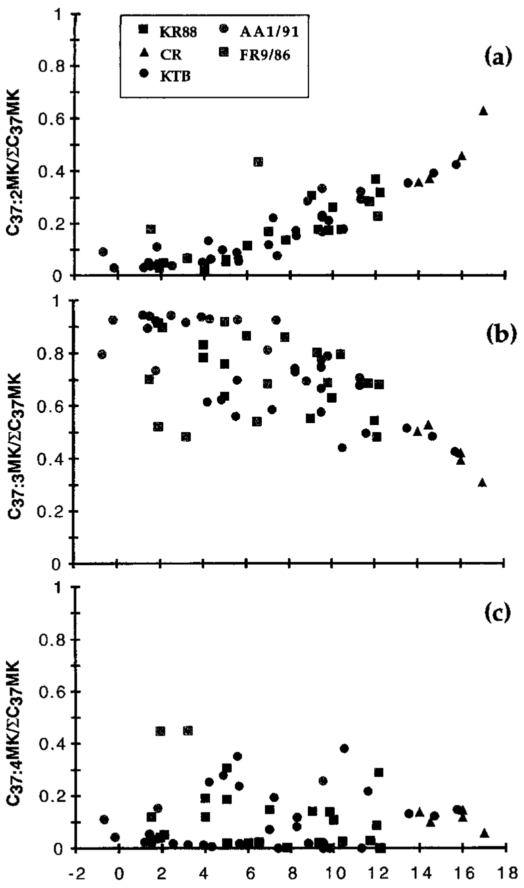

Fig. 2. Relative abundances of each of the C_{37} alkenones as a proportion of total C_{37} alkenones plotted against temperature. This shows a comparison of their relative amounts across a wide range of absolute concentrations and productivities to elucidate their individual relationship to temperature. (a) Relation of $C_{37:2}/(C_{37:2} + C_{37:3} + C_{37:4})$ to temperature $r = 0.874$, slope = 0.028, y intercept = −0.021; (b) Relation of $C_{37:3}/(C_{37:2} + C_{37:3} + C_{37:4})$ to temperature $r = 0.660$, slope = −0.025, y intercept = 0.884; (c) Relation of $C_{37:4}/(C_{37:2} + C_{37:3} + C_{37:4})$ to temperature $r = 0.118$, slope = −0.0003, y intercept = 0.138. Note that the slope in (a) and (b) are approximately the inverse of one another and the regression coefficients indicate a good relationship to temperature, whereas in (c), the $C_{37:4}$ concentration data show no trend with temperature.

autumn seasons, but the values consistently fall between winter and summer, so we do not discuss them here for brevity and clarity (see Rosell-Melé et al., 1995). The closest association between water column and sedimentary values is for summer temperature estimates.

The difference in agreement between summer and winter sediment estimates with that of the water column is even more evident if the available global dataset is used (Fig. 6). For this, we have estimated winter SST for the sediment data of Sikes et al. (1991) and presented it with the winter estimates from this study and those of Rosell-Melé et al. (1995) and compared it to all published water column measurements (Prahl and Wakeham, 1987; Conte and Eglinton, 1993; and this study: Sikes and Volkman, 1993). If winter SST estimates are used the sediment relationship to temperature is offset from that of the water column (Fig. 6b). If summer SST estimates are used for the sediments, the two data sets and their relationship to temperature coalesce (Fig. 6a).

The better agreement of the summer dataset to the water column samples indicates that it is the summer not winter season that is reflected in the sediment record (as also implied by the alkenone flux measurements of Prahl et al., 1993). This suggests that despite the apparently cooler-than-summer surface temperatures reflected in the sedimentary record by Prahl et al. (1993, 1995) and the better fit seen in the Rosell-Melé et al. (1995) data it is the summer season that is generally recorded in the sediments and it is that relationship that should be used when making paleotemperature estimates. The good correlation with winter temperatures in the North Atlantic may occur simply because the annual average difference between the two seasons is consistent in the same way that a given season's average temperatures are consistent year to year. Although using a local winter calibration will give excellent winter temperatures for modern sediments (Rosell-Melé et al., 1995) despite the fact that the alkenones are produced in the summer (Prahl et al., 1993), any change in the inter-seasonal temperature range will make paleo-SST estimations inaccurate because the winter relationship is derived from the present winter-summer temperature spread. An illustration of this seasonality effect can be seen by comparing summer and winter sediment data from the northern North Atlantic and the Southern Oceans (temperatures below about 15°C in Fig. 6). Summer core top estimations from both oceans generally fall together on the graph. In contrast, winter estimates from the two oceans are reasonably separate fields. This is because the seasonal range of temperature in the Southern Ocean is much less than that of the North Atlantic. Thus, even under modern conditions, the North Atlantic winter temperatures are more offset from the water column calibration than those in the Southern Ocean.

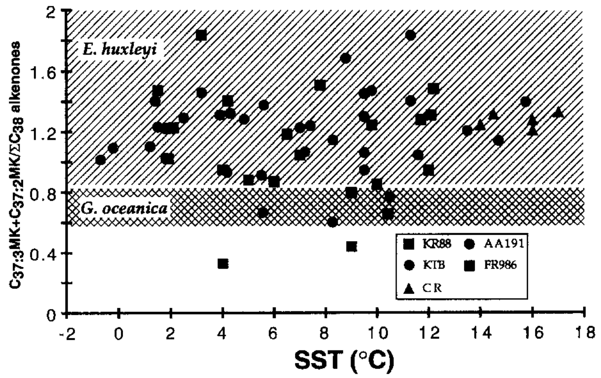

Fig. 3. Relationship of the ratio of C_{37} methyl ketones to C_{38} methyl and ethyl ketones ($C_{37:2}$ + $C_{37:3}$ methyl ketones/($C_{38:2}$ + $C_{38:3}$ methyl + $C_{38:2}$ + $C_{38:3}$ ethyl ketones) to temperature. The data show no systematic change with temperature. The upper (hatched) area indicates the range of this ratio observed for cultures of *Emiliania huxleyi*. The lower (double hatched) area is the range of values of this ratio observed for cultures of *Gephyrocapsa oceanica* (Volkman et al., 1995). The results for the water column are consistent with the view that the main algal source of these compounds in the Southern Ocean is *E. huxleyi*. (see the text for a more detailed discussion).

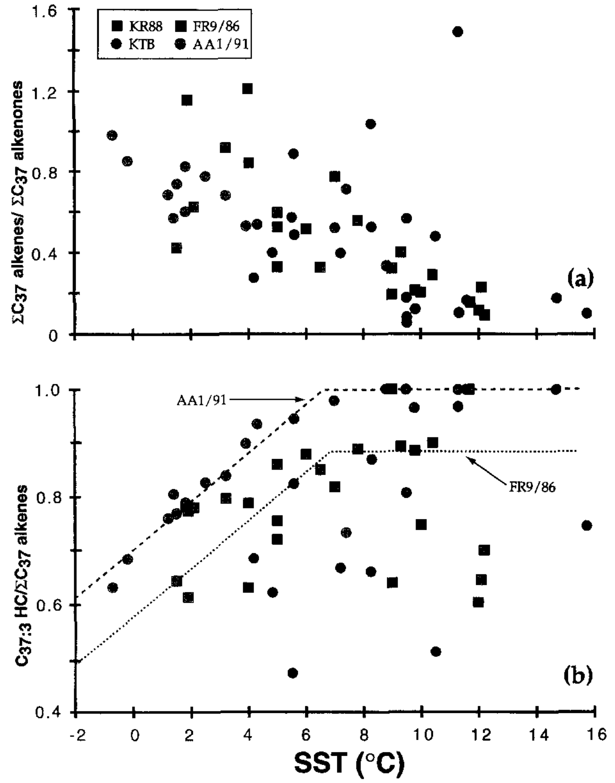

Fig. 4. Relationship of alkene abundances to temperature in the Southern Ocean. Solid symbols are sediment samples and shaded symbols are water column samples. (a) Plot of the relative abundance of total C_{37} alkenes over total C_{37} methyl alkenone ($C_{37:3}$ + $C_{37:4}$ HC/$C_{37:2}$ + $C_{37:3}$ + $C_{37:4}$ MK) vs. temperature. The amount of the alkene in the sample increases relative to the amount of alkenone with decreasing temperature. This parameter shows a linear relationship to temperature which is the opposite to that of $U_{37}^{K'}$. Σ C_{37}-ene/ Σ C_{37}-one $= -0.049T + 0.826$ ($r = 0.611$, $r^2 = 0.373$). Below 8°C the alkene amounts are generally one half to two times the amount of the alkenones. (b) Plot of the unsaturation ratio of the C_{37} hydrocarbons ($C_{37:3}$ HC/$C_{37:3}$ + $C_{37:4}$) of water samples vs. temperature. Lines are hand-drawn approximations of the relationship to temperature. The water column data show an increase up to 6°C where the samples are >90% $C_{37:3}$. Above that there is no change with temperature and increased scatter. The sediments show no discernible relationship with temperature.

4. CONCLUSIONS

In the cold waters of the Southern Ocean, it appears that variations in the unsaturation ratio of long chain alkenes and alkenones in response to temperature are at the limit of their effectiveness for the organisms that produce them. At near zero temperatures, the phytoplankton produce alkenes and the degree of unsaturation decreases with increasing temperature ($C_{37:4}$ declines relative to $C_{37:3}$). At 6°C more than 90% the alkenes consist of the less unsaturated compound. At this point the alkenones begin to show a significant response to temperature, and we conclude that the organism switches from altering the degree of unsaturation of hydrocarbons to altering the unsaturation of the alkenones in response to temperature change. From 6°C, with increasing temperature, they produce greater proportions of the less unsaturated alkenones ($C_{37:3}$ declines relative to $C_{37:2}$) which is reflected in the $U_{37}^{K'}$ relationship to temperature.

The relative abundances of the alkenes and alkenones suggest three important findings: (1) Distributions of the alkenes and alkenones in these high latitude samples show little differential degradation between compound classes in water column and surface sediment samples. The ratio of the C_{37} alkenes to the C_{37} alkenones is related to temperature and may be useful in determining relative temperature change in samples where the $C_{37:2}$ alkenone abundance is very low. Values of $U_{37}^{K'}$ in the sediments show a relationship to summer sea surface temperature that is not statistically different from water samples further supporting the evidence in the literature that $U_{37}^{K'}$ measurements in the sediments are a robust proxy for paleotemperature. (2) The ratio of the sum of C_{37} methyl alkenones to the sum of the methyl and ethyl C_{38} alkenones is generally similar in sediments and overlying waters, with some significant exceptions. Our results suggest that some caution is needed when this parameter is used to determine the likely paleo-algal source of these compounds. (3) The variation in the relative abundances of the $C_{37:2}$, $C_{37:3}$, and the $C_{37:4}$ alkenones with temperature indicate that

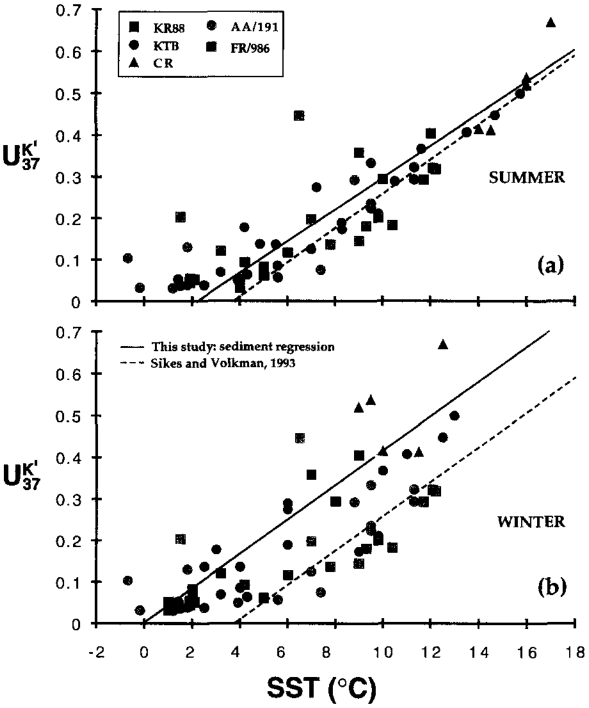

Fig. 5. The values of $U_{37}^{K'}$ determined in the sediment (solid symbols) and water column (shaded symbols) in the Southern Ocean. (a) Plot of the water column $U_{37}^{K'}$ values vs. the temperature measured in those samples and of the sediment data vs. summer SST for the overlying water (Levitus, 1994). Dotted line is the linear correlation of Sikes and Volkman (1993) for the water column. Solid line is the regression of the sediment data $U_{37}^{K'} = 0.038T - 0.082$ ($r = 0.960$, $r^2 = 0.921$). The two are not significantly different at the 95% confidence interval (see the text for discussion). (b) Sediment data plotted vs. winter SST (Levitus, 1994); solid line is the linear regression for this data ($r^2 = 0.834$, $r = 0.913$, slope $= 0.039$, y-intercept $= 0.021$). Water column data and regression are the same as in Fig. 5a. The water column and sediment regression are significantly different if the winter season is assumed to represent the sediment $U_{37}^{K'}$ values. Note that if summer temperatures are used for the sediments the two data sets overlap.

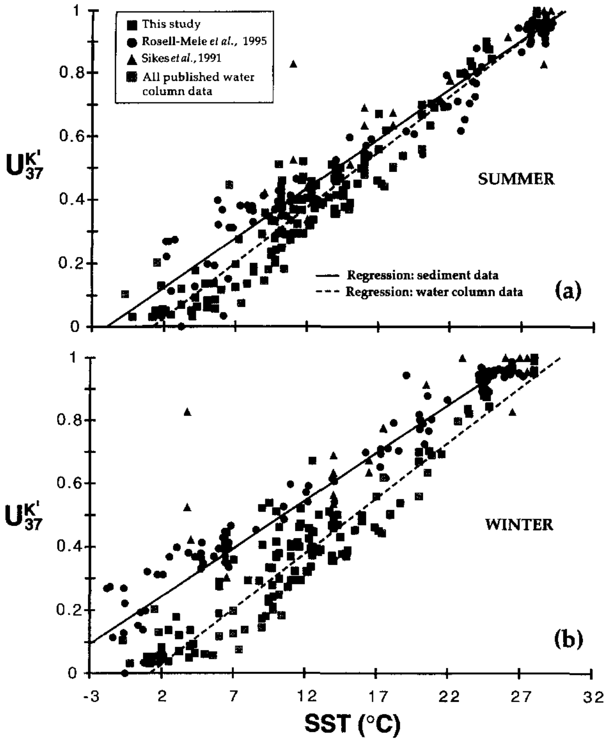

Fig. 6. All published sediment data for $U^{K'}_{37}$ (solid symbols), including this study, (Sikes et al., 1991) and U^{K}_{37} (Rosell-Melé et al., 1995) and all published water column data for $U^{K'}_{37}$ (Prahl and Wakeham, 1987; Sikes and Volkman, 1993) and U^{K}_{37} (Conte and Eglinton, 1993) (open symbols). If the published data consisted of only $U^{K'}_{37}$, this would pull U^{K}_{37} points up on the graph for values less than 0.4 (Rosell-Melé et al., 1994), but this does not affect the discussion here because it affects both seasons equally. (a) Water column data plotted vs. measured temperature and sediment data vs. summer SST for the overlying water. Solid line is the linear regression of the sediment data ($r^2 = 0.936$, $r = 0.968$, slope = 0.031, y-intercept = 0.057). (b) Sediment data plotted vs. winter SST for the overlying water (We have estimated overlying winter SST for the Sikes et al. (1991) data). Solid line is the linear regression of the sediment data ($r^2 = 0.915$, $r = 0.955$, slope = 0.030, y-intercept = 0.184), dotted line is the linear regression of the water column data set. Water column data and regression line are the same as Fig. 6a. Note that for summer temperature estimates (Fig. 6a) the water and sediment data sets overlap and their linear regression lines are very close, whereas if winter SST estimates are used for the sediments (Fig. 6b) the two datasets separate. Although the statistics on the two different sediment calibrations are similarly good, the fact that the summer sediment estimates agree better with the water column samples for which the temperature was directly measured suggests that it is the summer season that is preserved in the sediment record.

all the quantitative temperature information is found in the relative amounts of the di- and tri-unsaturated compounds. This suggests that the $C_{37:4}$ should not be included in temperature calculations. We suggest that $U^{K'}_{37}$ should be used rather than U^{K}_{37} even in cold locations.

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