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Relationship of the tetra-unsaturated C_{37} alkenone to salinity and temperature: Implications for paleoproxy applications

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[1] This study assesses the relationship to salinity and temperature of the levels of the tetra-unsaturated 37-carbon methyl alkenone ($C_{37:4}$) in the surface ocean. $U_{37}^{K'}$, a measure of the relative abundances of the $C_{37:2}$ and the $C_{37:3}$ alkenones, has a well constrained linear relationship to temperature in the open ocean [*Prahl and Wakeham*, 1987] and is a well-established technique for estimating past sea surface temperatures in the sediments (e.g. [*Müller et al.*, 1998]). Unlike the di- and tri-unsaturated C_{37} alkenones, the temperature response of the tetra-unsaturated C_{37} alkenone is less certain [*Sikes et al.*, 1997], and recent work has suggested a relationship to salinity instead [*Rosell-Melé*, 1998; *Schulz et al.*, 2000]. Our study examined 106 surface water and sediment trap samples from the Atlantic, Pacific, and Southern Oceans to assess the relationship of the relative abundance of $C_{37:4}$ to temperature and salinity. We also examined the relative unsaturation of $C_{37:2}$ and $C_{37:3}$ (the parameter $U_{37}^{K'}$) to the same parameters to place the $C_{37:4}$ results in context. $U_{37}^{K'}$ has a strong correlation to salinity in the Atlantic, but the relationship does not hold worldwide, whereas $U_{37}^{K'}$ shows a strong linear relationship to temperatures in all ocean basins as shown in previous calibrations. The salinity response in the Atlantic does not confirm cause and effect and interpretation of the broader data set suggests any correlation is an artifact of the strong correlation of salinity to temperature in this basin implying salinity has no effect on the unsaturation of the $C_{37:2}$ or $C_{37:3}$ alkenones. The $C_{37:4}$ alkenone shows no discernable relationship to temperature or salinity across the several basins, even when correlations are restricted to cooler temperatures where the tetra-unsaturated alkenone would be expected to be present. These results indicate that $C_{37:4}$ alkenone levels in the open ocean do not reflect either salinity levels or temperature but respond most strongly to some other environmental variable, perhaps changes in growth rate, light, or nutrient supply as suggested by culture studies.

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1. Introduction

[2] Sea surface temperature (SST) is an extremely good indicator of climate. Just as records of SST lend information about heat and heat transport in the surface ocean, surface salinities contain information about evaporation, precipitation, and runoff inputs to the surface mixed layer. At the present time there are numerous quantitative SST proxies, but no well-established paleosalinity technique.

[3] It has been known for over a decade that the unsaturation levels of the 37-carbon chain length alkenones (C_{37}) vary with temperature [*Brassell et al.*, 1986; *Marlowe*, 1984]. The amount of unsaturation in a sample tends to increase with a decrease in temperature of the water in which the algae grew. It is generally expressed as the $U_{37}^{K'}$ ratio which is the ratio of the amount of di-unsaturated to the total of di- and tri-unsaturated C_{37} alkenones in the sample or:

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

This relationship was proposed by [*Prahl and Wakeham*, 1987] and includes only the di- and tri-unsaturated compounds. U_{37}^{K} was the original relationship suggested to describe the level of the unsaturation of alkenones in a sample and included the tetra-unsaturated compound as well [*Brassell et al.*, 1986]:

$$U_{37}^{K} = \frac{[C_{37:2}] - [C_{37:4}]}{[C_{37:2}] + [C_{37:3}] + [C_{37:4}]}.$$

This initial formulation was based on the supposition that all three of the C_{37} alkenones would demonstrate a roughly equivalent relationship to temperature. $U_{37}^{K'}$ has been more universally adopted because the $C_{37:4}$ alkenone is often absent. It has not been detected at temperatures above 15°C [*Brassell et al.*, 1986; *Prahl et al.*, 1988, 1995; *Prahl and Wakeham*, 1987; *Sicre et al.*, 2002], but it is also often absent from samples below this temperature as well (e.g. [*Conte and Eglinton*, 1993; *Sikes et al.*, 1997; *Ternois et al.*, 1998]).

[4] These C_{37} compounds are biosynthesized by a small number of haptophyte algae. Their production in the open ocean is limited almost exclusively to the coccolithophorid *Emiliania huxleyi* and to a lesser extent *Gephyrocapsa oceanica*. The relationship of $U_{37}^{K'}$ to temperature in field studies is linear across most of the range of SST in the open ocean [*Prahl and Wakeham*, 1987], is statistically very significant (with $r^2 > 0.9$), and has proven remarkably robust across the world ocean [*Brassell*, 1993; *Müller et al.*, 1998; *Rosell-Melé et al.*, 1995; *Sikes and Volkman*, 1993; *Sikes et al.*, 1997; *Ternois et al.*, 1997]; (see [*Herbert*, 2001] for a review). Despite this, there are indications that the slope of the temperature relationship flattens at high and low temperature extremes, with the evidence more discernable in water column than sediment studies [*Conte et al.*, 2001; *Pelejero and Grimalt*, 1997; *Sikes and Volkman*, 1993; *Sonzogni et al.*, 1997]. Additionally, culture studies have served to confound the details of that relationship. Although culture work consistently shows unsaturation levels decrease with increasing temperature, few studies show similar relationships to the field studies suggesting that the temperature response of $U_{37}^{K'}$ varies both intraspecifically and interspecifically among the alga that biosynthesize these compounds (see [*Herbert*, 2001] for a review). Indications are that other environmental factors such as nutrient stress, light levels, and changes in growth rate can influence the $U_{37}^{K'}$ value [*Epstein et al.*, 2001; *Herbert*, 2001; *Laws et al.*, 2001; *Prahl et al.*, 2000; *Versteegh et al.*, 2001].

[5] The relationship of the $C_{37:4}$ alkenone to temperature is uncertain. Its abundance has been linked to temperature similarly to the increase in $C_{37:3}$ with decreasing temperature [*Brassell et al.*, 1986; *Prahl et al.*, 1995]. Some culture studies show some relationship of the amount of the $C_{37:4}$ to temperature [e.g., *Marlowe*, 1984; *Prahl et al.*, 1988], and it has not been found in samples warmer than 15°C [*Prahl et al.*, 1988; *Sicre et al.*, 2002]. Water column work suggests there is not a consistent relationship between $C_{37:4}$ and temperature [*Sikes et al.*, 1997]. Significantly, a study on water column distributions and isotopes in the Black Sea suggested that the biosynthesis of the $C_{37:4}$ alkenone may be independent of the more saturated isomers [*Freeman and Wakeham*, 1992]. Core top studies show a weak relationship of $C_{37:4}$ to temperature, but the relationship only becomes statistically significant if

geographical and low temperature cutoffs are applied [*Rosell-Melé et al.*, 1994, 1995]. Important to the veracity of sediment calibrations is that the temperature is not measured but inferred from atlas values [*Sikes et al.*, 1991]. This requires a judgment as to the season represented by the sample to determine temperature, making temperature not a fully independent variable.

[6] Recently, it has been suggested that the relative percent of $C_{37:4}$ in a sample may show a relationship to salinity [*Rosell-Melé*, 1998; *Schulz et al.*, 2000]. Owing to the lack of a good paleosalinity marker, the potential for the $C_{37:4}$ alkenone to provide one has generated much interest. To date this relationship has only been examined in sediment samples from the North Atlantic and its marginal seas. In the open ocean, a relationship of percent $C_{37:4}$ to salinity was observed for the Nordic Seas but not the wider North Atlantic [*Rosell-Melé*, 1998]. In the Baltic Sea, alkenone distributions in samples with very low salinities showed different patterns from the open ocean, and it was suggested that alkenone producers in coastal areas might be different from the open marine environment, due to a shift in contributing organisms, but a quantitative relationship was not established [*Schulz et al.*, 2000].

[7] The interest and controversy over what other factors might influence the distributions of C_{37} alkenones besides temperature continues. Our study addresses the issue of the influence of salinity and temperature on the proportion of C_{37} compounds. Primarily, we focus on the $C_{37:4}$ compound that is biosynthesized by alkenone producers in the field and by inference what controls the amounts that will enter the sediment record to be used as a potential proxy. We do this by examining a suite of surface water column and sediment trap samples from several disparate locations in the open ocean for which salinity and temperature values were determined at the time of collection.

2. Methods

[8] Alkenone results from the Equatorial Atlantic and Equatorial Pacific are first reported here; all other alkenone data in this study has been previously published (Table 1). The method and details of sample collection, sample processing and analysis as well as absolute alkenone levels are fully described in those studies. Samples from the Equatorial Atlantic and Equatorial Pacific were processed following the methods of [*Ternois et al.*, 1997]. In all analyses, clean-up steps were performed prior to gas chromatographic analysis to eliminate the possibility of coelution with the closely related alkenoates [*Sikes and Volkman*, 1993].

[9] For water column studies, temperature and salinity data were collected in association with alkenone sample collection; salinity data is reported for the first time here. For sediment trap samples, salinity and temperature data were obtained from hydrocasts taken nearby the traps on dates overlapping or closely associated with the dates that individual traps were open. For the Southern Ocean (Kerfix) sediment traps, hydrocasts were taken within 1 min latitude and longitude of the trap locations and on dates either while the cups were open (five samples) or within 2–11 days of the cups' collection period (five samples). Data for which the hydrocasts did not overlap cup collection periods included only those hydrocasts for which the bracketing sample dates indicate that temperatures did not change by more than 0.5°C in that time and salinities did not change more than 0.1‰ during that period. Equatorial Atlantic sites are located in the upwelling system off Cape Blanc. Salinities and any temperature data from these sediment traps not previously published were obtained by going back to original cruise databases and matching it to sampling sites. For the Northwest Africa/Equatorial Atlantic (Eumeli) sediment traps, all alkenone data were calculated from the 250 m sediment trap and hydrocast data were collected within 10 days of the cup collection date. Hydrocasts were taken from within one nautical mile of the trap locations, except for two, which were taken within 0.5 min latitude and longitude of the trap locations. For the Equatorial Pacific, alkenones were measured in suspended particles from the surface waters of the Warm Pool during the WEPAMA cruise (IMAGES program) in May 2001. Temperature and salinity were obtained from the associated CTD casts. Sampling locations and numerical data are available from the World Data Center for Pale-

Table 1. Alkenone Studies Discussed in This Paper

Location	Type of Sample	Sample Number	Temperature Range	Salinity Range	Reference	Salinity and Temperatures
Studies in which 37:4 was detected						
North Atlantic	water column	35	4–20.1	34.2–36.1	*Sicre et al.* [2002]	obtained at cast
Southern Ocean (Indian Ocean sector)	sediment traps	5	1.6–3.9	33.8–33.9	*Ternois et al.* [1998]	obtained from nearby hydrocasts[a]
Southern Ocean (Australian sector)	water column	40	−1.9 to 12.2	33.8–35.1	*Sikes et al.* [1997]	obtained at cast
Total		80				
Studies in which 37:4 was not detected						
North Atlantic	water column	53	9.8–24.7	NA	*Conte and Eglinton* [1993]	obtained at cast
Mediterranean Sea	water column	20	13–19	~38	*Ternois et al.* [1997]	obtained at cast[a]
Chatham Rise	sediment traps	15	16	34–35	unpublished data	obtained from nearby hydrocasts[a]
Equatorial Atlantic/Northwest Africa	sediment traps	7	22.1–26.6	36.1–37.2	unpublished data	obtained from nearby hydrocasts[a]
Equatorial Pacific	water column	20	24–30	33–34.2	unpublished data	obtained at cast

[a] Salinity and temperature data from nearby hydrocasts were collected on closely associated dates (see text for detailed explanation).

oclimatology. For all studies, samples in which no alkenones were detected are not reported.

[10] Our purpose is to understand the relationship of the $C_{37:4}$ alkenone to salinity and temperature when present. Water column and sediment trap studies with temperatures below 15°C which did not detect $C_{37:4}$ alkenone in their alkenone analyses and for which salinity data were not available are reported in Table 1 but not included in the graphs or calculations in this study. For those studies with temperatures below 15°C, where $C_{37:4}$ alkenone was undetected, it is uncertain whether or not the systematic absence of the compound was biosynthetic in origin or due to the abundance of the compound being below detection limits (as in the case of a lean sample). The inclusion of these samples would confound the statistics in the present study by adding a large number of zero points to the temperature comparisons without comparable control for salinity relationships. Not reported here are water column or sediment trap studies for which the presence or absence of the $C_{37:4}$ was not reported nor described.

[11] Although $C_{37:4}$ alkenone was not detected in our West Pacific and Equatorial Atlantic sample sets, we have included these data sets here to illustrate the salinity to temperature relationship in the world ocean. The comparison of $U_{37}^{K'}$ to temperature and salinity here is intended solely to clarify the relationship of the $C_{37:4}$ alkenone to the same parameters. The bulk of the $U_{37}^{K'}$ data presented here has previously been published and interpreted relative to temperature elsewhere [*Sicre et al.*, 2002; *Sikes and Volkman*, 1993], only the analysis to salinity is new. We emphasize that discussion and analysis of the $U_{37}^{K'}$ relationship to temperature is intended to be illustrative of well-established principles and is not intended to promulgate a new calibration.

3. Results

[12] To examine the response of the $C_{37:4}$ alkenone to environmental parameters, it is most useful to express $C_{37:4}$ as the proportion of $C_{37:4}$ compounds over the total in the sample, (i.e., $[C_{37:4}]/[C_{37:2} + C_{37:3} + C_{37:4}]$ also called percent $C_{37:4}$ abbreviated $\% \, C_{37:4}$). The parameter $U_{37}^{K'}$ describes the change

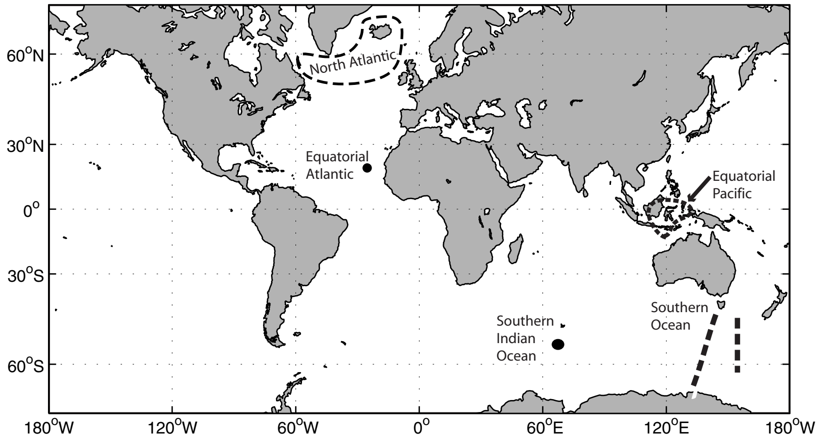

Figure 1. Map of study locations for samples included in this study. Samples labeled Equatorial Atlantic and Southern Indian Ocean are from sediment traps. Southern Ocean surface water samples were taken from two transects as indicated by the solid lines. North Atlantic and Equatorial Pacific water column samples were collected from sites within the dotted lines. Southern Ocean and North Atlantic alkenone samples used in this study have been previously published. See Table 1 for details.

in the relative proportions of the $C_{37:2}$ and $C_{37:3}$ alkenones alone, and although the parameter U_{37}^{K} includes the $C_{37:4}$ alkenone in its equation, in that formulation the $C_{37:4}$ is both subtracted from the $C_{37:2}$ in the numerator and added in the denominator. This masks the response of either of the compounds to the parameter of interest, such as temperature, because the individual compounds do not covary [e.g., *Sikes et al.*, 1997].

[13] The data compiled for this study represents a selection from widely spaced areas of the world's oceans, comprising the Equatorial and North Atlantic, the western Equatorial Pacific, and the Indian Ocean and Pacific (Australian) sectors of the Southern Ocean (Figure 1). The $C_{37:4}$ alkenone is present across the colder range of water temperatures, 1.8°–13°C. It is absent from all samples above 13°C (i.e., 14°–30°C) and randomly absent from samples at other temperatures, or ~40% of the samples overall (41 out of 106; Figure 2a). The presence of $C_{37:4}$ in our samples with temperatures between 10°–13°C contrasts with the fact that $C_{37:4}$ was undetected in previous North Atlantic water column samples of 10°–14°C [*Conte and Eglinton*, 1993] (Table 1), providing a qualitative indication of variability in the production of the $C_{37:4}$ alkenone that is unrelated to growth temperature. Statistically, the relationship of the proportion of $C_{37:4}$ alkenone in the sample to temperature is poor in the accumulated data for this study. The correlation coefficient is well below the significant level indicating little or no relationship to temperature (r^2 = 0.078 n = 106) (Figure 2a). Owing to the absence of the $C_{37:4}$ alkenone at warmer temperatures, we considered the relationship of $C_{37:4}$ alkenones to temperature for only those samples colder than 13°C (Figure 3c). The relationship to temperature was not improved (r^2 = 0.000, n = 69). This is in contrast to the strong relationship of $U_{37}^{K'}$ to temperature for the same samples (see following paragraph) indicating that the inclusion of this compound in the parameter U_{37}^{K} adds increased variance or scatter but little temperature information across the temperature range where it is present, as was observed previously in the Southern Ocean [*Sikes et al.*, 1997].

[14] The $C_{37:4}$ is present across the fresher end of ocean salinities from 33.8–35.1‰ in samples colder than 13°C, but it is not present in the low salinity warm temperature samples from the west Equatorial Pacific (Figure 2b). The correlation of the proportion of $C_{37:4}$ alkenone to salinity is worse than its relationship to temperature, with r^2 = 0.015 (n = 106) indicating its variance has essentially no relationship to salinity. If the salinity relationship is considered only in samples from below 13°C, the relationship is

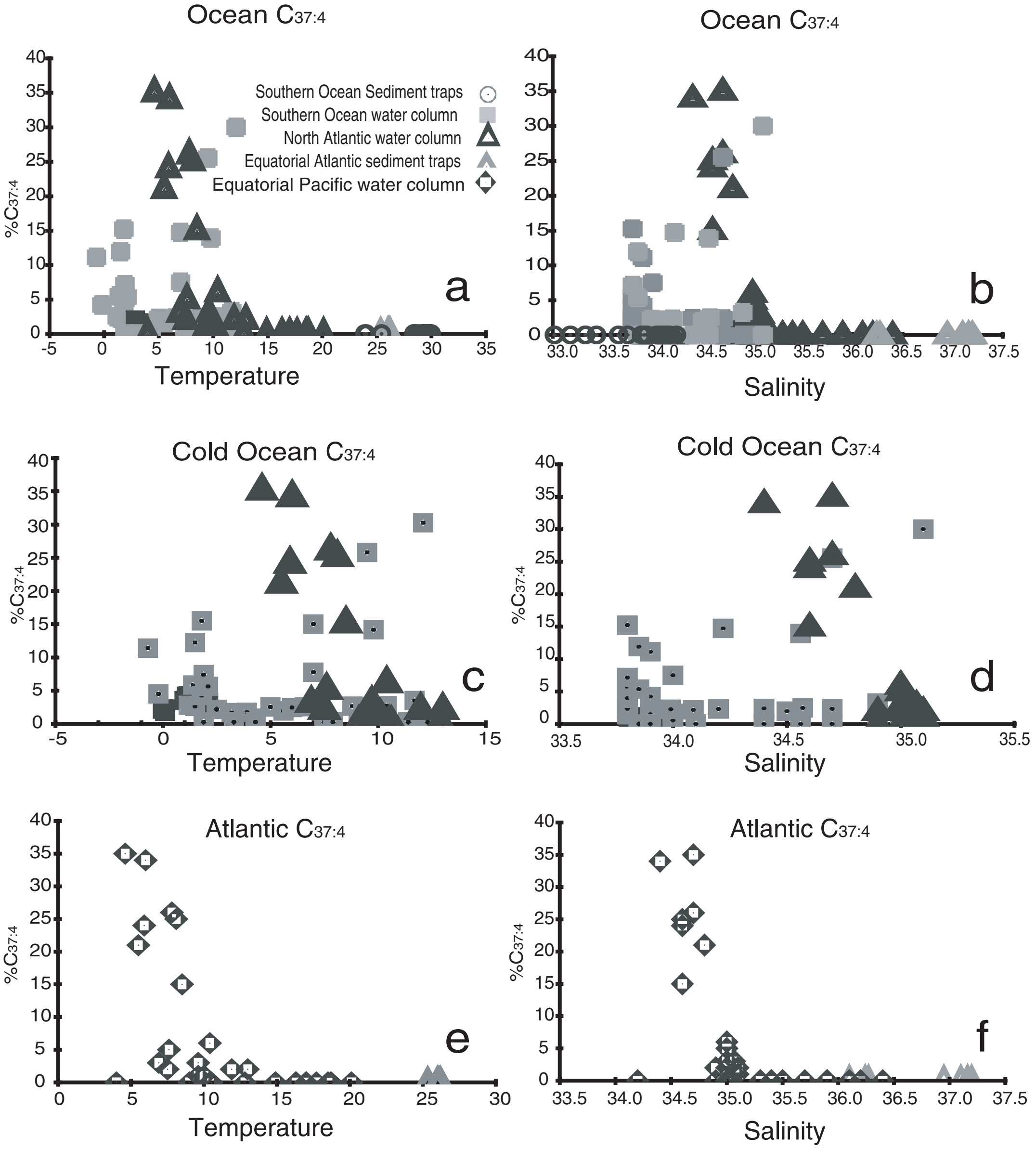

Figure 2. Relationship of the proportion of $C_{37:4}$ alkenones in a given sample to temperature and salinity. Black squares are Southern Ocean sediment traps, grey squares are Southern Ocean water column samples, solid triangles are North Atlantic samples, grey triangle are Equatorial Atlantic, black squares are western Equatorial Pacific samples. (a) Relationship of $C_{37:4}$ abundance versus temperature for all samples. (b) Relationship of $C_{37:4}$ abundance versus salinity for all samples. (c) Relationship of $C_{37:4}$ abundance versus temperature for samples with temperatures below 13°C. (d) Relationship of $C_{37:4}$ abundance versus salinity for samples with temperatures below 13°C. (e) Relationship of $C_{37:4}$ abundance versus temperature for Atlantic samples. (f) Relationship of $C_{37:4}$ abundance versus salinity for Atlantic samples. For all comparisons the relationship of $C_{37:4}$ abundance to salinity or temperature is not statistically significant. For all samples the r^2 values are below 0.1, for Atlantic samples only r^2 values are less than 0.5.

similar (r^2 = 0.014, n = 69) and is still well below significant (Figure 2d).

[15] The $U^{K'}_{37}$ values in this study show the familiar linear relationship across the full range of growth temperatures found in the world ocean ($U^{K'}_{37}$ = 0.035T − 0.044, r^2 = 0.956, n = 106; Figure 3a). This contrasts markedly with the relationship of percent $C_{37:4}$ to temperature for the same samples. The linear fit of the $U^{K'}_{37}$ data

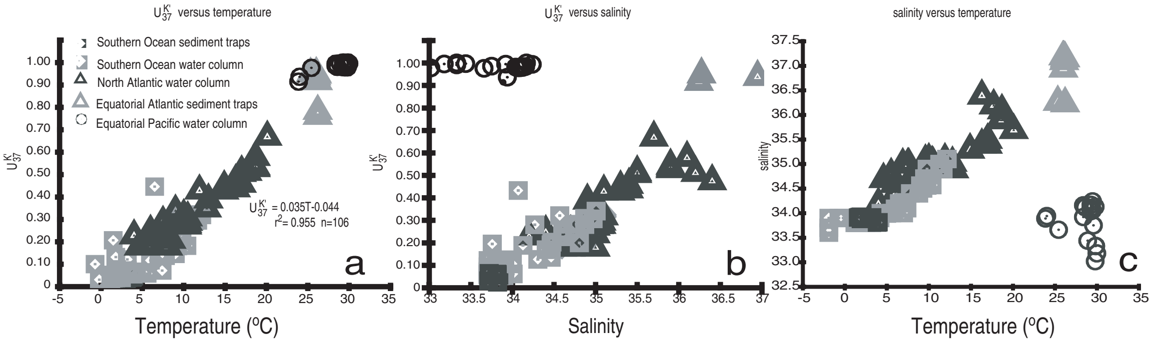

Figure 3. Relationship of $U^{K'}_{37}$ to temperature and salinity. Black squares are Southern Ocean sediment traps, grey squares are Southern Ocean water column samples, solid triangles are North Atlantic water column samples, grey triangle are Equatorial Atlantic sediment trap samples from off Northwest Africa, black squares are western Equatorial Pacific water column samples. (a) Relationship of $U^{K'}_{37}$ to temperature for samples used in this study. The relationship is strongly linear ($U^{K'}_{37}$=0.035T − 0.044, r^2 = 0.955, n = 106) but shows flattening of the relationship at temperature extremes. (b) Relationship of $U^{K'}_{37}$ to salinity. There is a strong correlation to salinity across the Atlantic and Southern Oceans but this does not hold for the entire suite of samples, in particular, the Equatorial Pacific. (c) Relationship of salinity to temperature. Salinity and temperature covary strongly in the Atlantic and Southern Oceans. The relationship of $U^{K'}_{37}$ to salinity is restricted to those areas where temperature and salinity covary, suggesting that any relationship to salinity is an artifact of the covariance of salinity with temperature in those locations.

here is virtually identical to the standard in the field ($U^{K'}_{37} = 0.034T + 0.039$ [*Prahl et al.*, 1988]) and falls within the range of other field studies [*Prahl et al.*, 2000], supporting the use of the [*Prahl et al.*, 1988] for paleotemperature estimation [*Herbert*, 2001]. The two samples from the Equatorial Atlantic that fall below the line are from hydrocasts slightly farther from the traps which may have introduced some scatter into those results due to mesoscale differences. The relationship flattens somewhat at both low and high growth temperatures supporting the suggestion of some previous studies that the relationship becomes nonlinear at ocean temperature extremes [*Conte et al.*, 2001; *Sikes and Volkman*, 1993]. This phenomenon may be environmentally significant or it may simply reflect the fact that the alkenone thermometer looses sensitivity at temperature extremes. However, determining the cause of this phenomenon is not within the scope of this study.

[16] The relationship of $U^{K'}_{37}$ to salinity is also strongly linear for the Atlantic and Southern Oceans (r^2 = 0.871, n = 87), which are the basins where the relationship of salinity to temperature is also very strong (r^2 = 0.892, n = 87) (Figures 3b and 3c). Samples from the western Equatorial Pacific form a separate field reflecting the low salinities but high temperatures of the area. This location provides data for which salinity and temperature do not covary with the same relationship as in the North Atlantic. When the west Pacific samples are included in the analysis, the relationship of $U^{K'}_{37}$ to salinity becomes insignificant (r^2 = 0.033, n = 106), as does the relationship of salinity to temperature (r^2 = 0.050, n = 106). The relationship of $U^{K'}_{37}$ to salinity for the world ocean contrasts sharply with the strong relationship of $U^{K'}_{37}$ to temperature.

4. Discussion

[17] Although $U^{K'}_{37}$ consistently shows a strong relationship to growth temperature for all locations, the relationship to salinity only holds in those basins where temperature and salinity covary (Figure 3). The main axis of this correlation is linear from cold-fresh to warm-salty conditions (Figure 3c). The fact that salinity varies linearly with temperature across the Atlantic and Southern Oceans (Figure 3c) suggests that the cause of a good correlation between $U^{K'}_{37}$ and salinity for those locations is an artifact of the strong relationship of salinity and temperature.

The dependence of $C_{37:4}$ (or $U_{37}^{K'}$) on salinity separate from temperature can be assessed by comparing low salinty and low temperature samples of high northern and southern latitudes (Nordic Seas and Southern Ocean) with low salinity and warm temperature samples (equatorial Pacific). Whereas in both cases salinities are low, only the cold water samples contain $C_{37:4}$. Indeed, salinity values in the equatorial Pacific (33–34.2 psu) are lower than the northern North Atlantic and some samples in the Southern Ocean and yet do not contain any $C_{37:4}$ nor do they have lowered $U_{37}^{K'}$ values. Qualitatively, this strongly suggests that temperature is a control on overall unsaturation as well as $C_{37:4}$ content while salinity is not. Importantly, although the results here suggest a correlation of $U_{37}^{K'}$ to salinity in the North Atlantic (r^2 = 0.712, n = 34) similar to that of percent $C_{37:4}$ [*Sicre et al.*, 2002], a statistical relationship between two parameters does not prove a causal relationship. Significantly, the lack of influence of salinity on $U_{37}^{K'}$ has previously been noted [*Sikes et al.*, 1991; *Sonzogni et al.*, 1997]. Whereas no study has suggested that $U_{37}^{K'}$ is influenced by salinity, the proportion of $C_{37:4}$ in the sample has been proposed as a salinity marker in the North Atlantic [*Rosell-Melé*, 1998; *Rosell-Melé et al.*, 1995] despite the fact that the relationship of $U_{37}^{K'}$ to salinity is stronger than it is for percent $C_{37:4}$ there (Figures 2f versus 3b).

[18] To eliminate any temperature bias from our assessment caused by the absence of the tetra-unsaturated alkenone above ~15°C [*Prahl and Wakeham*, 1987], we considered separately those samples with temperatures <14°C (Figures 2c and 2d). The relationship of $C_{37:4}$ to both temperature and salinity is insignificant (r^2 < 0.015 for both). The salinity effect on $U_{37}^{K'}$ or $C_{37:4}$ distinct from temperature can be assessed qualitatively by focusing on areas in the ocean where the two do not covary so strongly as in the North Atlantic. This occurs in the Southern Ocean cooler than 5°C (Figure 3c), where the $C_{37:4}$ proportion of the alkenones is least well correlated with salinity (Figure 2d) [*Sikes et al.*, 1997]. In the Southern Ocean, water masses and hydrological features such as frontal zones separate areas with distinct temperature-salinity relationships preventing the good correlation of temperature to salinity. These water masses also have different nutrient contents which have been suggested to affect the alkenones response to temperature [*Laws et al.*, 2001; *Versteegh et al.*, 2001]. In contrast, North Atlantic changes in temperature are well correlated with significant changes in salinity, there are no major nutrient boundaries, and it is here that the strongest relationship of $C_{37:4}$ to temperature or salinity is observed. Thus we suggest that any improved correlation of $C_{37:4}$ to salinity determined for the open North Atlantic, distinct from other areas of the world ocean, is likely to be an artifact of the strong and consistent relationship of salinity to temperature there.

[19] Previous sediment-based studies which suggested a relationship of $C_{37:4}$ percent to salinity suggested that alkenone producers in the North Atlantic are genetically different from elsewhere in the ocean [*Rosell-Melé*, 1998; *Schulz et al.*, 2000], with one water column study showing a relationship to salinity there [*Sicre et al.*, 2002]. This impels us to consider Atlantic samples separately. For Atlantic water column samples, the relationship of $C_{37:4}$ proportion to both temperature and salinity are better than for the whole ocean (r^2 = 0.46 and r^2 = 0.41, respectively n = 39) but are still not significant (Figures 2e and 2f). The slope for the Atlantic relationship of percent $C_{37:4}$ to salinity is an order of magnitude larger than for other areas in the ocean (−15.3), but the relationship to salinity is still too weak for its use to be statistically sound. Significantly, the slope of the Atlantic relationship is opposite that for the greater ocean (0.035). Thus, over broader environments, even if the relationship were statistically sound, the salinity influence on $C_{37:4}$ abundance is too slight to be of use as a paleoproxy. The relationship observed in the North Atlantic appears to be isolated to that environment and is likely to be an artifact of the relationship to temperature [e.g., *Sicre et al.*, 2002].

[20] $C_{37:4}$ alkenone proportions in our water column samples are similar in both the North Atlantic and the Southern Ocean (Figure 2). *Rosell-Melé*

[1998] compared sediment samples between these oceans and found $C_{37:4}$ levels were higher in Southern Ocean sediments relative to the North Atlantic and suggested genetic differences to be the cause. Comparison of water column samples between the two oceans shows North Atlantic water samples have similar or higher proportions of $C_{37:4}$ than the Southern Ocean, indicating that the differences found in the [*Rosell-Melé*, 1998] comparison may have been the result of differential breakdown of $C_{37:4}$ alkenones in the sediments, a factor previously noted in the Black Sea [*Freeman and Hayes*, 1992], rather than interhemispheric genetic differences. Although we cannot assess here the genetic controls on alkenone unsaturation levels, our results suggest that in open ocean sediments, temporally changing environmental conditions and or sedimentary diagenesis are a stronger control on the levels of $C_{37:4}$ than is temperature, salinity, or genetics.

[21] Our results indicate there is no salinity influence on $C_{37:4}$ in the open ocean even in cold waters (Figures 2a and 2b). In contrast, there is evidence that species restricted to coastal, brackish, or fresh water produce alkenones in very different proportions from open ocean species [*Conte et al.*, 1998; *Cranwell*, 1985; *Li et al.*, 1996; *Schulz et al.*, 2000; *Volkman et al.*, 1988]. Nonetheless, the fact that they thrive in different salinities from the open ocean does not imply cause and effect of salinity levels on unsaturation levels and does not confirm that their different unsaturation levels contain salinity information. It is probable that these differences do have genetic or other environmental causes. Our results suggest that the input of alkenones to the sediment record produced by these species either to coastal waters, or by lateral transport offshore, is more properly interpreted as a coastal, ecologically based signal. Any fundamental relationship to salinity itself has yet to be established even for waters in restricted seas [*Schulz et al.*, 2000].

[22] The lack of a $C_{37:4}$ response to salinity or temperature suggests that its relative abundances vary in response to some other environmental parameters. In the Southern Ocean, it has been noted that percent $C_{37:4}$ may be related to growth rates with a higher proportion of $C_{37:4}$ measured at the start of the productive season and lower levels detected at times of low productivity [*Sikes and Volkman*, 1993; *Sikes et al.*, 1997]. The absence of $C_{37:4}$ in all North Atlantic and Equatorial Atlantic water column samples from temperatures above 13°C confirms culture work on *E. huxleyi* which did not detect the tetra-unsaturated compound above that temperature [*Conte et al.*, 1998; *Prahl et al.*, 1988; *Prahl and Wakeham*, 1987; *Volkman et al.*, 1995]. Thus, although numerous results confirm that temperature has at least a qualitative influence on $C_{37:4}$ amounts by precluding its synthesis above 13°–15°C, below that cut off temperature appears to have little influence on its presence. There is both some field evidence [*Sikes et al.*, 1997] and extensive culture work to suggest that the relative amounts of alkenones biosynthesized responds to factors such as nutrient levels, light levels, and growth rate [*Conte et al.*, 1998; *Epstein et al.*, 2001; *Laws et al.*, 2001; *Versteegh et al.*, 2001]. There is no data on what may be controlling the $C_{37:4}$ amounts in the field. An attempt to assess overall nitrate influence by correlating atlas values of annual average nitrate concentrations with $C_{37:4}$ percent in sediments showed no relationship [*Rosell-Melé*, 1998]. However, this approach is almost certainly not sensitive enough to assess the effects of variable nitrate levels on alkenone synthesis. Atlas nutrient data are annual averages and represent an average over many years, making these values too broad to assess nutrient effects on alkenone synthesis and/or phytoplankton growth rates for which microscale values are necessary. Culture studies suggest that light, phosphate, and growth rate may affect unsaturation levels more strongly than nitrate, and that response to these factors is rapid [*Epstein et al.*, 1998; *Versteegh et al.*, 2001]. The data in this study represent all seasons of the year with potentially a wide range of growth rates, nutrients, and light levels, but assessing the relative influence of these factors would require coordinating data on these parameters and is beyond the scope of this paper. Nonetheless, the physical evidence presented here suggests that unlike the $C_{37:2}$ and $C_{37:3}$ alkenones, $C_{37:4}$ levels may respond more strongly to these other factors than to temperature. Determining what controls $C_{37:4}$ levels may serve as

a key to understanding the other influences on $U_{37}^{K'}$ besides temperature.

5. Conclusions

[23] A compilation of alkenone levels in water column samples for several areas in the Atlantic, Pacific, and Southern Oceans shows that the relative abundance of $C_{37:4}$ does not show a discernable response to temperature or salinity. Specific conclusions are as follows:

1. The lack of a relationship of $C_{37:4}$ to temperature or salinity suggests that the $C_{37:4}$ alkenone responds most strongly to some other variable such as changes in growth rates, light levels, or nutrient supply.
2. The relative abundances for the $C_{37:2}$ and the $C_{37:3}$ alkenones, as summarized in the parameter $U_{37}^{K'}$, show a strong linear response to temperature. A correlation to salinity is also evident in the Atlantic, but global evidence suggests this is most likely an artifact of the strong correlation of salinity to temperature in that ocean.
3. This study examines samples from the North and Equatorial Atlantic, the western Equatorial Pacific, and the Australian and Indian sectors of the Southern Ocean. Further work examining samples from the subtropical to temperate Pacific would verify these relationships for the world ocean.

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References

Brassell, S. C., Applications of biomarkers for delineating marine paleoclimate fluctuations during the Pleistocene, in *Organic Chemistry*, edited by M. H. Engel and S. A. Macko, pp. 699–738, Plenum, New York, 1993.

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. Part I*, *40*, 1935–1961, 1993.

Conte, M. H., A. Thompson, D. Lesley, 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.

Conte, M. H., J. C. Wefer, L. L. King, and S. G. Wakeham, The alkenone temperature signal in western North Atlantic surface waters, *Geochim. Cosmochim. Acta*, *65*, 4275–4297, 2001.

Cranwell, P. A., Long-chain unsaturated ketones in recent lacustrine sediments, *Org. Geochem.*, *49*, 1545–1551, 1985.

Epstein, B. L., S. D'Hondt, J. G. Quinn, J. Zhang, and P. E. Hargraves, An effect of dissolved nutrient concentrations on alkenone-based temperature estimates, *Paleoceanography*, *13*, 122–126, 1998.

Epstein, B. L., S. D'Hondt, and P. E. Hargraves, The possible metabolic role of C_{37} alkenones in *Emiliania huxleyi, Org. Geochem.*, *32*, 867–875, 2001.

Freeman, K. H., and J. M. Hayes, Fractionation of carbon isotopes by phytoplankton and estimates of ancient CO_2 levels, *Global Biogeochem. Cycles*, *6*, 185–198, 1992.

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.

Herbert, T. D., Review of alkenone calibrations (culture, water column, and sediments), *Geochem. Geophys. Geosyst.*, *2*, Paper number 2000GC000055, 2001.

Laws, E. A., B. N. Popp, R. R. Bidigare, U. Riesbell, S. Burkhardt, and S. G. Wakeham, Controls on the molecular distribution and carbon isotopic composition of alkenones in certain haptophyte algae, *Geochem. Geophys. Geosyst.*, *2*, Paper number 2000GC000057, 2001.

Li, J., R. P. Philp, F. Pu, and J. Allen, Long-chaine alkenones in Qinghai Kake sediments, *Geochim. Cosmochim. Acta*, *60*, 235–241, 1996.

Marlowe, I. T., Lipids as palaeoclimatic indicators, Ph.D. Thesis, 273 pp. Univ. of Bristol, Bristol, 1984.

Müller, P. J., G. Kirst, G. Ruhland, I. V. Storch, and A. Rosell-Melé, Calibration of the alkenone paleotemperature index $U^{K'}{}_{37}$ based on coretops from the eastern South Atlantic and the global ocean (60°N–60°S), *Geochim. Cosmochim. Acta*, *62*, 1757–1772, 1998.

Pelejero, C., and J. O. Grimalt, The correlation between the Uk37 indes and sea surface temperatures in the warm boundary: The South China Sea, *Geochim. Cosmochim. Acta*, *61*, 4789–4797, 1997.

Prahl, F. G., and S. G. Wakeham, Calibration of unsaturation patterns in long-chain ketone compositions for palaeotemperature 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 paleoceanographic conditions, *Geochim. Cosmochim. Acta*, *52*, 2303–2310, 1988.

Prahl, F. G., N. Pisias, M. A. Sparrow, and A. Sabin, Assessment of sea-surface temperature at 42°N in the California Current over the last 30,000 years, *Paleoceanography*, *10*, 763–773, 1995.

Prahl, F., T. Herbert, S. C. Brassell, N. Ohkouchi, M. Pagani, D. Repeta, A. Rosell-Melé, and E. Sikes, Status of alkenone paleothermometer calibration: Report from Working Group 3, *Geochem. Geophys. Geosyst.*, *1*, Paper number 2000GC000058, 2000.

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

Rosell-Melé, A., 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.

Schulz, H.-M., A. Schöner, and K.-C. Emis, Long-chain alkenone patterns in the Baltic Sea–An ocean-freshwater transition, *Geochim. Cosmochim. Acta*, *64*, 469–477, 2000.

Sicre, M.-A., E. Bard, U. Ezat, and F. Rostek, Alkenone distributions in the North Atlantic and Nordic sea surface waters, *Geochem. Geophys. Geosys.*, *3*(2), 1013, doi:10.1029/2001GC000159, 2002.

Sikes, E. L., and J. K. Volkman, Calibration of alkenone unsaturation ratios ($U_{37}^{k'}$) for paleotemperature estimation, *Geochim. Cosmochim. Acta*, *57*, 1883–1889, 1993.

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

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: Implications 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 alkenone ratios measured in surface sediments from the Indian Ocean, *Quat. Res.*, *47*, 344–355, 1997.

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. Part I*, *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 sector of the Southern Ocean, *Org. Geochem.*, *28*, 489–501, 1998.

Versteegh, G. J. M., R. Riegman, J. W. D. 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., H. R. Burton, D. A. Everitt, and D. I. Allen, Pigment and lipid compositions of algal and bacterial communities in Ace Lake, Vestfolds Hills, Antarctica, *Hydrobiologica*, *165*, 41–57, 1988.

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