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Modifications of the C37 Alkenone and Alkenoate Composition in the Water Column and Sediment: Possible Implications for Sea Surface Temperature Estimates in Paleoceanography

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Modifications of the C₃₇ alkenone and alkenoate composition in the water column and sediment: Possible implications for sea surface temperature estimates in paleoceanography

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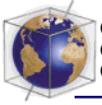
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[1] **Abstract:** The literature pertaining to C₃₇ alkenone and C₃₇ and C₃₈ alkenoate production and diagenesis has been reviewed and evaluated for issues that might jeopardize their usefulness in paleotemperature estimation. We also examined the use of the C₃₇ alkenones as paleoproductivity indicators, the stability of their $\delta^{13}\text{C}$ isotopic compositions, and their incorporation into the nonsolvent extractable organic matter fraction. Biological transformation of organic matter by bacteria and zooplankton does not appear to cause significant changes to the ratio of C_{37:2} and C_{37:3} alkenones, but there are major alterations in the relative composition of alkenoates. Studies of water column processes and postdepositional sedimentary changes indicate overall stability in the C_{37:2}/(C_{37:2} + C_{37:3}) ratio,



leading to effective preservation of the paleotemperature signal. This is not the case for alkenoates, and there also appear to be some doubts about the dependence between sea surface temperature and the sedimentary abundance of the C_{37:4} alkenone. C₃₇ alkenones may provide useful qualitative estimates of marine paleoproductivity. Although these compounds are apparently only derived from Haptophyceae, changes in their quantitative composition might reflect changes in nutrient availability that on sedimentary timescales should also be generally significant of other algal species. One caveat is that in highly productive upwelling systems, productivity may be expressed mostly in diatom growth and thus not measurable by the C₃₇ alkenones. No changes in $\delta^{13}\text{C}$ C₃₇ alkenone composition are observed upon zooplankton ingestion. Although this is expected from a theoretical perspective, further studies are encouraged in order to fully assess the stability of the isotopic signal during C₃₇ alkenone diagenesis. Finally, alkenones bound in the nonextractable fraction of sedimentary organics have not been adequately studied and further work is required to clarify any possible correspondence with a temperature signal.

Keywords: C₃₇ alkenones; sea surface temperatures; degradation; paleoproductivity; bound alkenones; alkenoates.

Index terms: Organic geochemistry; oceans; paleoclimatology; paleoceanography.

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Theme: Alkenones **Guest Editors:** John Hayes

1. Introduction

[2] The temperature estimates using the C₃₇ alkenones are based on the compilation of two indices that are linearly correlated with sea surface temperature (SST) [Brassell *et al.*, 1986a]:

$$U_{37}^K = (C_{37:2} - C_{37:4}) / (C_{37:2} + C_{37:3} + C_{37:4}), \quad (1)$$

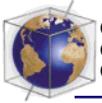
$$U_{37}^{K'} = C_{37:2} / (C_{37:2} + C_{37:3}), \quad (2)$$

where C_{37:X} denotes the concentration of the alkenone with x carbon-carbon double bonds.

[3] Examination of laboratory cultures of the precursor organisms [Prahl and Wakeham, 1987; Prahl *et al.*, 1988], water column parti-

culate organic matter [Prahl and Wakeham, 1987; Sikes and Volkman, 1993; Sikes *et al.*, 1997; Ternois *et al.*, 1997], and core tops [Sikes *et al.*, 1991; Pelejero and Grimalt, 1997; Rosell-Melé *et al.*, 1995; Sonzogni *et al.*, 1997; Müller *et al.*, 1998] have confirmed the linear dependence between $U_{37}^K/U_{37}^{K'}$ and SST, over a wide temperature range.

[4] According to the ratios defined above, SST estimation will be biased if selective transformation of C_{37:2}, C_{37:3}, or C_{37:4} alkenones occurs during transport through the water column or sediment storage. No bias will be produced if all C₃₇ alkenones are degraded in the same proportion, even in processes of extensive alteration.



[5] In principle, there is a general agreement that C₃₇–C₃₉ alkenones are among the most refractory lipids known. The causes of this resistance to degradation may be related to low-solubility, protective package within the algal cells and their unusual Z (trans) double bond configuration [Rechka and Maxwell, 1988] because many bacteria do not have enzymatic systems for the transformation of this type of double bonds [Brassell, 1983].

[6] The principal structural difference between the alkenones included in the U₃₇^K indices relates to the degrees of unsaturation, i.e., C_{37:2}, C_{37:3}, and C_{37:4}. In general, the more degrees of unsaturation, the more easily a lipid is degraded. However, in these alkenones the low number of double bonds in relation to the chain length and the wide separation of these bonds in the carbon chain [Rechka and Maxwell, 1988] a priori suggest similar refractory properties of all compounds. Obviously, this has to be tested by field measurements and microbial degradation experiments.

[7] Another aspect needing further evaluation is the usefulness of the C_{37:4} compounds for temperature measurement. In practice, most C₃₇ alkenone-based paleotemperature studies use the U₃₇^{K'} index. This is due to the low amount of the C_{37:4} alkenone in many sedimentary samples. However, attention should be paid to those cases in which the C_{37:4} alkenone is abundant.

[8] The C_{36:x} methyl and C_{38:2} ethyl alkenoates have also been proposed for evaluation of SST [Conte *et al.*, 1992]. Thus the influence of the degradation processes on these compounds requires evaluation.

[9] Given these considerations, the present report summarizes the available data on the transformation of C₃₇ alkenones and C_{36:x} and C_{38:2} alkenoates during passage through the

water column and after deposition in the sediments. The available information is interpreted in terms of the significance of these processes for paleotemperature estimation. Three main topics will be addressed: transformation by biota, changes in the water column, and post-depositional transformation. Other aspects such as the usefulness of the C_{37:4} alkenone, non-solvent extractable C₃₇ alkenones, their use as paleoproductivity indicators, and the stability of their δ¹³C composition are also considered.

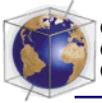
2. Possible Bias Due to the Analytical Methods

[10] Although the analytical problems associated with the use of C₃₇ alkenones for paleotemperature estimation are not the focus of the present report, some attention has to be devoted to this topic as analytical errors are sometimes attributed to selective alkenone degradation.

[11] No alteration of C₃₇ alkenone mixtures stored under current research storage conditions (5°–10°C ambient temperature, darkness and adequate wrapping for maintenance of the sediments with their original seawater content) was detected in the study conducted by Brassell *et al.* [1986b]. Similar results were reported by Sikes *et al.* [1991] in a work of sediments from the Equatorial East Atlantic. In this latter work, no significant changes between samples stored frozen and at room temperature (even after 2 years) were observed.

[12] Sikes *et al.* [1991] also reported no changes in C₃₇ alkenone composition after acidification for carbonate removal. They interpreted the results as indicating the persistence of the C₃₇ alkenone signal despite of carbonate dissolution in the marine environment.

[13] During repeated gas chromatographic measurements, major deviations of U₃₇^{K'} determinations have been observed as consequence of



capillary column adsorption effects [Villanueva and Grimalt, 1997]. These effects shift the $U_{37}^{K'}$ indices toward higher values (warmer temperatures) due to stronger adsorption of the C_{37:3} compound. The deviations are significant when the amount of C₃₇ alkenones injected onto the capillary column is low. This instrumental limitation defines a threshold of minimal sample concentration below which $U_{37}^{K'}$ determinations are not reliable [Villanueva and Grimalt, 1997].

[14] These adsorption effects may be significant in some studies reported in the literature. In the context of the present review, they are important for the interpretation of the results from one paper reporting postdepositional sedimentary alteration of $U_{37}^{K'}$ index in turbidites [Hoefs et al., 1998]. The implications will be discussed in the section on sediment changes.

3. Degradation Experiments With Biota

[15] Published information is restricted to bacteria and zooplankton. As far as we are aware, specific studies involving protists, benthic grazers, or burrowing metazoans have not been undertaken.

[16] Microbial degradation experiments of C_{37:3} and C_{37:2} alkenone mixtures with $U_{37}^{K'} = 0.78$ and 0.6 under oxic, sulphate-reducing, and methanogenic conditions showed that these compounds are degraded at a lower rate than most other lipids [Teece et al., 1995, 1998]. The maximal percentages of consumption in these experiments were 83, 43, and 80%, respectively. After this extent of degradation the differences in $U_{37}^{K'}$ index were +0.01, -0.013, and -0.003, respectively, involving less than 0.4°C bias in the worst case.

[17] For zooplankton, Volkman et al. [1980] reported feeding experiments of *Emiliania hux-*

leyi to *Calanus helgolandicus*, showing that only a very small percentage of alkenones was assimilated or transformed by the copepod. In contrast, ~70% of the fatty acids and sterols were consumed. Similar results were obtained in a subsequent study on the copepod *Temora longicornis* feeding on *Isochrysis galbana* in which it was found that C₃₇ alkenones were absent from the grazer bodies but abundant in the fecal pellets [Grice et al., 1998]. The maximal $U_{37}^{K'}$ difference between dietary algae and released pellets was 0.03, equivalent to 0.9°C. The same authors reported no significant changes in $\delta^{13}C$ alkenone composition of these two materials.

4. Postdepositional Sedimentary Changes

[18] The transformation of organic matter, including lipids, after sedimentation strongly depends on the activity of microbiota and benthic organisms, at least during the first stages of diagenesis. To this end, the above reported degradation experiments with different types of bacteria [Teece et al., 1998] are very relevant. However, studies addressing the transformation of the C₃₇ alkenones in real sedimentary environments are needed for a more complete understanding of the stability of the $U_{37}^{K'}$ ratio.

[19] One significant outcome from these studies of sediment cores documents a significant decrease in alkenone concentration during early diagenesis, e.g., in the upper sedimentary column [Sun and Wakeham, 1994; Gong and Hollander, 1999; McCaffrey et al., 1990; Madureira et al., 1995]. This decrease is common for all sedimentary lipids. In fact, the alkenones are one of the lipid groups more resistant to diagenesis [Sun and Wakeham, 1994; Gong and Hollander, 1997, 1999]. Fatty acids, sterols, and alkanols are degraded at faster rates than the alkenones that exhibit a resistance similar to long-chain alkanes, alken-



Table 1. Selected Data from *Hoefs et al.* [1998] Showing the Consistency of the Oxidized-Unoxidized Temperature Differences and Low C_{37:3} Concentrations Close to Limit of Detection

	C _{37:3} , μg/g dry wt	C _{37:2} , μg/g dry wt	C ₃₇ Alkenones, μg/g dry wt	U ₃₇ ^{K'}	Temperature, °C	Oxidized- Unoxidized Temperature Difference, °C
<i>Free Lipids</i>						
Late Pliocene						
Oxidized	0.06	0.23	0.29	0.79	22.2	0.7
Nonoxidized	3.06	10.3	13.4	0.77	21.5	
Early Pliocene						
Oxidized	0.02	0.26	0.28	0.93	26.2	1.9
Nonoxidized	2.43	15.45	17.88	0.86	24.3	
Late Miocene						
Oxidized	0.01	0.12	0.13	0.92	26.0	1.4
Nonoxidized	8.49	58.9	67.39	0.87	24.6	
<i>Bound Lipids</i>						
Late Pliocene						
Oxidized	0.20	0.86	1.06	0.81	22.7	0.4
Nonoxidized	0.59	2.32	2.91	0.80	22.3	
Early Pliocene						
Oxidized	n.d.	0.06	0.06	1	28.3	2.5
Nonoxidized	0.32	3.56	3.88	0.92	25.8	
Late Miocene						
Oxidized	n.d.	0.02	0.02	1	28.3	3.5
Nonoxidized	0.39	2.90	3.29	0.88	24.8	

Here n.d., *Hoefs et al.* [1998] report these concentrations as “not detected” and assume a value of 0 for the calculation of the U₃₇^{K'} index and temperature.

diols, and alkanonols [*Sun and Wakeham, 1994*].

[20] Obviously, the degradation rates depend on the sedimentary conditions. The concentrations of C₃₇ alkenones decrease faster in oxic [*Madureira et al., 1995; Gong and Hollander, 1997, 1999*] than in anoxic environments [*Sun and Wakeham, 1994; Gong and Hollander, 1997, 1999*]. Postdepositional oxidation episodes also involve strong decreases in C₃₇ alkenone concentrations [*Prahl et al., 1989a*].

[21] However, the relevant point for paleoceanographic studies is whether the U₃₇^{K'} ratio is altered as a consequence of these diagenetic processes. *McCaffrey et al.* [1990] in core tops from the Peru margin reported no significant changes in U₃₇^{K'} (corresponding to a variation

between 19.5° and 20°C only) despite a decrease of total alkenone concentration of 30%. Likewise, no modifications in U₃₇^{K'} were observed by *Madureira et al.* [1995] in the upper centimeters of oxic sediments (Biscay Abyssal Plain, North Atlantic) despite a significant decrease in C₃₇ alkenone concentrations (60%).

[22] In a study of Late Quaternary sediments from the Madeira Abyssal Plain, *Prahl et al.* [1989a] reported no changes in C₃₇ alkenone composition and therefore no changes in U₃₇^{K'}, despite of comprehensive postdepositional degradation of alkenones under contrasting (oxidized-unoxidized) redox conditions (Table 1 and 2).

[23] *Hoefs et al.* [1998] also analyzed the turbidites from the Madeira Abyssal Plain

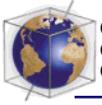


Table 2. Selected Data from *Prahl et al.* [1989] Showing the Lack of Temperature Differences Between Oxidized-Unoxidized Sediment Sections

	C _{37:3} , μg/g dry wt	C _{37:2} , μg/g dry wt	C ₃₇ Alkenones, μg/g dry wt	U ₃₇ ^{K'}	Temperature, °C	Oxidized- Unoxidized Temperature Difference, °C
Late Quaternary Core 86P5						
Oxidized	0.26	0.68	0.94	0.72	19.9	0.6
Nonoxidized	2.8	6.8	9.6	0.70	19.3	
Late Quaternary Core 86P25						
Oxidized	0.34	0.86	1.2	0.72	19.9	0.3
Nonoxidized	2.5	6.2	8.7	0.71	19.6	

(although in Pliocene and Miocene sections) and reported results different from those of *Prahl et al.* [1989a]. They noted that oxidation involved significant changes of the U₃₇^{K'} ratio in one of the sections. However, these latter measurements were made at extremely low alkenone concentrations (Table 1 and 2).

[24] A summary of the C₃₇ alkenone concentrations, U₃₇^{K'} and temperature measurements reported in the studies of *Prahl et al.* [1989a] and *Hoefs et al.* [1998] is shown in Table 1 and 2. There is a correlation between temperature differences of the oxidized-unoxidized sediment pairs and alkenone concentrations in the oxidized sections. Temperatures 2.5°–3.5°C warmer are calculated for the samples with lowest C_{37:3} alkenone concentrations (Table 1 and 2). Intermediate values (1.4°–1.9°C) are observed at C_{37:3} alkenone concentrations of 0.01–0.02 μg/g (Table 1 and 2), and finally, the smallest temperature deviations (0.4°–0.7°C) correspond to [C_{37:3}] = 0.06–0.2 μg/g (Table 1 and 2). In contrast, the lack of significant temperature differences between unoxidized and oxidized samples described in the study of *Prahl et al.* [1989a] (Table 1 and 2) is consistent with the considerably higher abundance of C_{37:3} alkenone concentrations in the samples analyzed in that study (0.25 μg/g or more in the oxidized samples).

[25] A representation of the temperature differences versus concentration of total C₃₇ alkenones in the oxidized sediments shows that the samples with highest temperature difference correspond to those of lowest C₃₇ alkenone concentrations (Figure 1). To this end, the oxidized sample studied by *Hoefs et al.* [1998] that has a similar C₃₇ alkenone concentration to those in the oxidized samples from *Prahl et al.* [1989a] exhibits a similar temperature difference as those in this latter study (Figure 1). In summary, the discrepant results of the two studies may reflect a case of measurement near the limit of detection in the samples considered by *Hoefs et al.* [1998].

[26] *Gong and Hollander* [1999] reported the selective degradation of the C_{37:3} alkenone when comparing sediment records in oxic and anoxic sediments from the Santa Monica Basin. In their study, they differentiated between bioturbation and degradation effects in reporting SST estimate offsets of the order of 2.5°C due to differential postdepositional transformation of the alkenone mixtures in the sediments. Stronger transformation was observed in the oxic than in the anoxic sediments, corresponding to basin margin and depocenter, respectively. Further investigation of the oceanic regime in this basin is needed for a better appraisal of the represen-

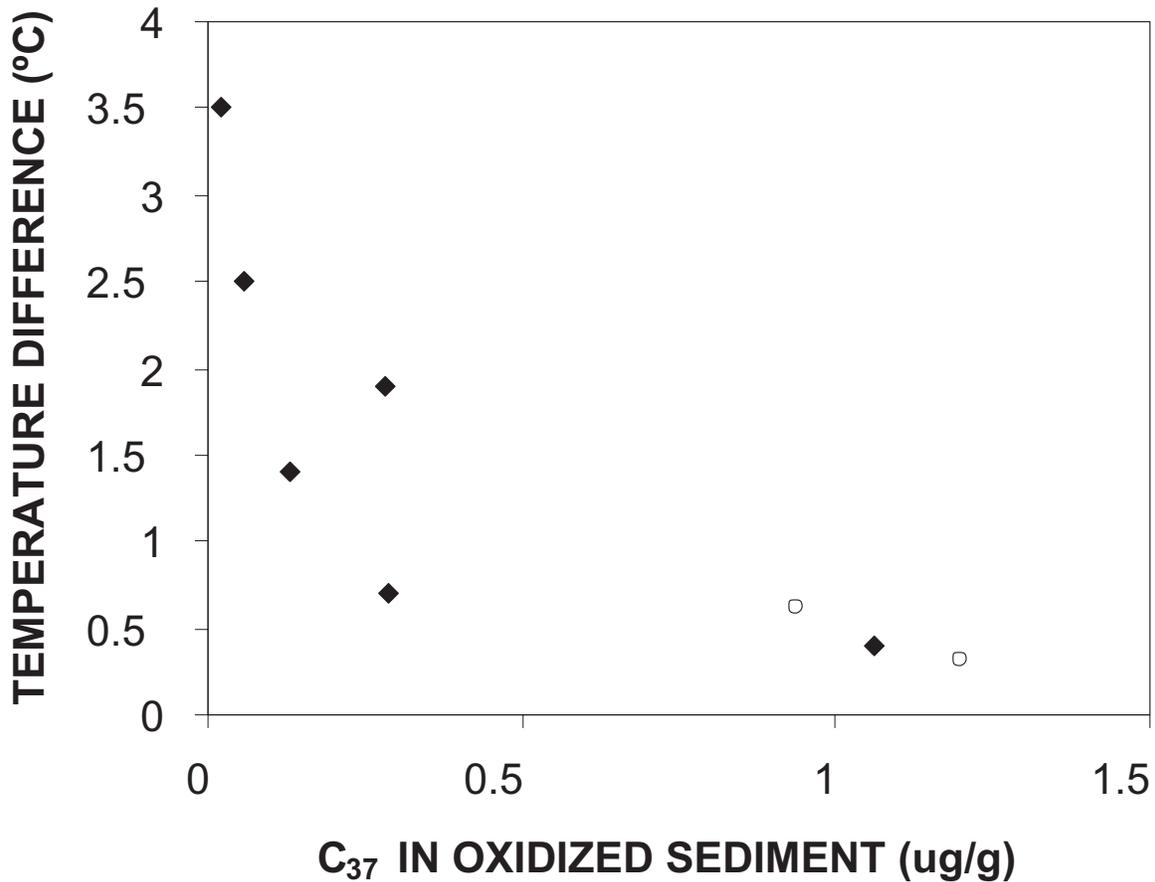
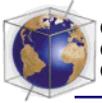


Figure 1. Reported temperature differences between oxidized and nonoxidized sediments in the works of Hoefs *et al.* [1998] (black diamonds) and Prahl *et al.* [1989b] (open circles) versus C₃₇ alkenones in the oxidized sediment. Higher temperature differences are observed at lower C₃₇ concentrations.

tativeness of these results in open-marine systems.

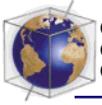
5. Degradation in the Water Column

[27] It is paramount that we fully understand the processes involved in the transfer of C₃₇ alkenones from the photic zone water column to the underlying sediment in order to correctly interpret the paleoceanographic significance of U₃₇^{K'} ratios. Issues such as seasonality and water depth of alkenone biosynthesis are very important. Transport mechanisms through the water

column and their influence in the preservation/transformation of the originally synthesized C₃₇ alkenone mixtures are also relevant. This section focuses on the possible degradation processes. Unfortunately, the data available in the literature do not always allow differentiating this single issue within the complexity of the water column-sediment interactions.

5.1. Difficulties for Comparison Between Water Column and Underlying Sediments

[28] The comparability of the C₃₇ alkenone composition in the water column and in under-



lying sediments is difficult owing to the huge timescale differences of the two compartments. Water column particles are collected either by active filtration systems or by passive collection devices, namely, sediment traps. In the first case, sample collection may involve hours or 1 or 2 days at the most. In the second, samples may be collected for 1 or 2 years at weekly or monthly intervals in the most favorable cases. These samples are compared with sediment sections that may represent time-integrated periods of hundreds of years. Furthermore, sediments are not always collected with devices ensuring collection of the true sediment-water interface section. It may happen that core top sediments available for comparison are 1000 or 2000 years old.

[29] These problems are common for all studies involving water column and sediment materials, both organic and inorganic. In the use of C₃₇ alkenones as paleothermometers they become particularly serious owing to the strong requirement for accurate measurements and the need for a correct interpretation of the paleoclimatic signal.

[30] The difficulties in water column-sediment comparison not only involve interannual water column differences but shorter-term changes as well. Seasonality, algal blooms, lateral currents, and many other factors may give rise to major differences in the composition of settling particles during the year. These problems are particularly relevant in suspended particle collection by filtration but also in sediment trap experiments because it has to be shown that the collected particles are representative of the settling flux incorporated into the sediment.

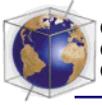
5.2. Stratified Water Column

[31] In this context, a direct test of the paleoceanographic significance of the U₃₇^{K'}

index is the comparison between geochemical analysis of filtered particles and in situ temperature measurements. This comparison was performed in the Gulf of Lions, under well-defined water column stratification conditions [Bentaleb *et al.*, 1999]. U₃₇^{K'} values measured at 5-, 30-, and 1100-m depth corresponded to the level of maximum Haptophyceae abundance (30 m). The U₃₇^{K'} index at 1100 m was the same as that found at 30 m. These results are in general agreement with sediment trap data from 42°N in the eastern Pacific Ocean where it was observed that alkenone production during periods of offshore stratification occurred at the subsurface chlorophyll maximum, and the U₃₇^{K'} index reflected the temperature measured at this depth [Prahl *et al.*, 1993]. Similar observations were made in depth range studies of alkenone production in the Pacific Ocean based on sediment transects and comparison to Levitus data [Ohkouchi *et al.*, 1999]. At high latitudes (40°–48°N) and in the equatorial region, sedimentary alkenone temperatures correlated well with those in the surface mixing layer, but those at midlatitudes, (19°–30°N) and south of the equator (5°–8°S) correlated with temperatures in thermocline waters below the surface mixing layer. In contrast, in the eastern South Atlantic Ocean U₃₇^{K'} core top data were always found to correlate with the surface waters' temperature [Müller *et al.*, 1998] probably reflecting low subsurface production due to lack of light penetration to the pycnocline.

5.3. Total Alkenone Loss

[32] Measurements of the vertical flux of long-chain alkenones and other types of planktonic lipids and comparison of these fluxes with accumulation rates in the underlying sediments showed that the alkenones were considerably more resistant to biodegradation in the settling



process than most other lipids of planktonic origin [Volkman *et al.*, 1983].

[33] However, in terms of quantitative transfer of these alkenones from the water column to the underlying sediment, contrasting results have been reported. In a comparison between sediment trap (390-m water depth) and underlying sediment composition (4400 m), *Prahl and Muehlhausen* [1989] observed that the ratio between concentrations of C₃₇ alkenones and total organic carbon (TOC) was 300 µg/g in the sediment traps and 115 µg/g in the underlying sediments (0.3% TOC). In a subsequent study, *Prahl et al.* [1993] reported that the degree of alkenone preservation changed with distance to coast and water column depth. The TOC-normalized alkenone concentrations in the underlying sediments were 81, 45, and 8% of those in the sediment traps (1000-m water depth) for locations situated nearshore (water depth 2712 m), further offshore (3111 m) and central gyre (3680 m), respectively. In agreement with this trend, no decrease in TOC-normalized alkenone concentrations was observed in the Gulf of California when comparing the compositions of sediment traps (500-m water depth) and underlying sediment (665-m water depth) (D. M. Hartz *et al.*, personal communication, 2000). *Conte et al.* [1992] also observed a decrease in sedimentary C₃₇ alkenone concentrations in the eastern North Atlantic, paralleling the decrease in TOC.

5.4. Sediment and Sediment Trap U₃₇^{K'} Values

[34] U₃₇^{K'} indices in water column-suspended particles and underlying sediments were reported to be in good agreement between these two compartments, e.g., in the Southern Ocean [Sikes *et al.*, 1997]. More data are available on sediment traps that are currently used for studies of U₃₇^{K'} composition in deep particles. In contrast, data on C₃₇ and C₃₈ alkenoates are scarce.

[35] A very good U₃₇^{K'} correspondence was observed by *Sicre et al.* [1999] when comparing sediment traps deployed at 200- and 1000-m depth in the northwestern Mediterranean Sea, although the total alkenone flux decreased by 80% between the shallow and the deep trap. In a previous study in this area, *Ternois et al.* [1996] found a good correspondence for U₃₇^{K'} between particles collected with a sediment trap deployed at 200-m depth and the underlying sediment after flux-weighted averaging of the monthly index values. In the eastern North Atlantic, *Conte et al.* [1992] reported no change in the combined alkenone-alkenoate paleotemperature index between water column (down to 4 km) and underlying sediment (down to 4 cm).

[36] A summary of several reported data on U₃₇^{K'} values in sediment trap material and underlying sediments is given in Table 3. Good agreements were found in the Gulf of California (D. M. Hartz *et al.*, personal communication, 2000), the Norwegian Basin [Thomsen *et al.*, 1998] and the North Pacific off Japan [Sawada *et al.*, 1998]. The Gulf of California studies were performed in the Guaymas Basin. Complete elimination of the alkenones was observed in areas of high hydrothermal activity due to the high temperatures at the seafloor [Simoneit *et al.*, 1994]. In the Norwegian Sea the U₃₇^{K'} index of the sediment perfectly matched with the alkenone composition of material collected in a trap at 500-m water depth. However, the particles collected at 3000-m water depth exhibited an average index that was 0.6 units higher than in the underlying sediment [Thomsen *et al.*, 1998]. The sediment traps deployed in the North Pacific off Japan extend over the deepest water column ever investigated (9200 m). No significant change was observed between the average U₃₇^{K'} of sediment traps deployed at 1674-, 4180-, 5687-, and 8688-m depth (13 samples collected in successive time intervals)



and the underlying sediment [Sawada *et al.*, 1998].

[37] Some cases where there was no correspondence between particles settling through the water column and underlying sediments are also shown in Table 3. In the Barents Sea, sediment trap data at 1840- and 1950-m water depth and underlying sediment (2050 m) show considerable scatter. Resuspension and lateral advection have been proposed as explanation of these discrepancies [Thomsen *et al.*, 1998]. A major contrast between annual average sediment trap measurements at 3700 m and underlying sediment (4400 m) is reported in the Northeast Atlantic [Rosell-Melé *et al.*, 2000]. Alkenone inputs from elsewhere, e.g., the polar front, instead of overlying waters are proposed as explanation.

[38] A major difference between settling particles (400 m) and underlying sediment (2200 m) was observed in the Black Sea [Freeman and Wakeham, 1992]. The discrepancy could be due to the short sampling period over which the sediment trap was deployed (April–July 1988). However, water column alkenone distribution is complex. Water particles (filters) from several depths (10–2000 m) during July 1988 showed an increase with depth in both $U_{37}^{K'}$ and U_{37}^K . This increase was paralleled by a strong decrease in C₃₇ alkenone concentration (2 orders of magnitude). Lateral transport or phenomena specific to the euxinic environment may also explain this trend (S. G. Wakeham, personal communication, 1999).

[39] Contrasting results were obtained in the tropical North Pacific Ocean (1°N 138°W). Prahl and Muehlhausen [1989] found no significant alteration of the qualitative composition of the alkenone mixtures between sediment trap (water depth 3900 m, 434 days deployment) and underlying sediment (4400-m water depth) despite a decrease in the alkenone/TOC

ratio by a factor of 3. However, increasing differences in $U_{37}^{K'}$ index were found by Prahl *et al.* [1993] in the northeast Pacific Ocean in a transect of three sediment traps and underlying sediments extending from the coast to the open ocean (Table 3): 0.04 (nearshore), 0.05 (further offshore), and 0.12 (gyre).

[40] Overall, these results show a good correspondence between $U_{37}^{K'}$ indices in water column particles and underlying sediments, indicating that the processes involving quantitative changes in C₃₇ alkenones during particle settling do not result, in general, in significant changes of $U_{37}^{K'}$. To this end, the results of Sawada *et al.* [1998] concerning a water column of 9200 m are particularly significant.

[41] In contrast, there are examples of disagreement between settling water column particles and underlying sediments that cannot be dismissed (e.g., the examples from the Barents and the Black Sea and some case studies in the northeast Pacific Ocean). In the Northeast Pacific study, the authors suggest that the differences observed do not necessarily involve selective degradation of the more unsaturated alkenones. The discrepancies could arise from other mechanisms such as differential preservation of the settling particles arriving at the seafloor over the year because the $U_{37}^{K'}$ composition of the sediment trap particles collected monthly or weekly is not uniform. In the Barents Sea, Northeast Atlantic and the Black Sea studies the authors propose lateral transport as one of the possible factors explaining the differences. A similar process has been proposed to explain discrepancies between water column temperatures and sedimentary $U_{37}^{K'}$ measurements in regions of the western South Atlantic such as the Brazil-Falklands Confluence (35°–39°S) and the Falklands Current (41°–48°S) [Benthien and Müller, 2000]. In these regions, strong surface and bottom currents, benthic storms, and downslope processes

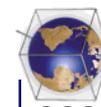
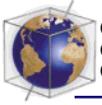


Table 3. Reported Average U₃₇^{K'} Data on Sediment Trap Particles and Underlying Sediments

Location	Deployment Period	U ₃₇ ^{K'} Measurements		Reference
		Sediment Traps	Underlying Sediment	
Gulf of California (27°53'N,111°40'W)	Jan. 14, 1996, to Sept. 21, 1997	0.87 (500) ^a	0.90 (665) ^a	D. M. Hartz et al. (personal communication, 2000)
Northeast Pacific Ocean (41°55'N,125°40'W) (42°10'N,127°30'W) (41°35'N,131°45'W)	Sept. 22, 1987 to Sept. 16, 1988	0.38 (1000) 0.38 (1000) 0.33 (1000)	0.42 (2712) 0.43 (3111) 0.45 (3680)	<i>Prahl et al.</i> [1993]
Black Sea (43°N,34°E)	April–July 1988	0.15 (400)	0.41 (2200)	<i>Freeman and Wakeham</i> [1992]
Northeast Atlantic (47°54'N,21°30'E)	April 1989 to April 1990	0.40 (3700)	0.57 (4400)	<i>Rosell-Melé et al.</i> [2000]
Norwegian Basin (69°41.2'N, 0°27.8'E)	Aug. 1991 to July 1992	0.53 (500) 0.59 (3000)	0.53 (3290)	<i>Thomsen et al.</i> [1998]
Barents Sea (75°11.8'N,12°29.2'E)	March to July 1991	0.18 (1840) 0.76 (1950)	0.58 (2050)	<i>Thomsen et al.</i> [1998]
North Pacific off Japan (34°10'N, 142°E)	March 5, 1991 to March 2, 1992	0.76 (1674) 0.74 (4180) 0.74 (5687) 0.72 (8688)	0.74 (9200)	<i>Sawada et al.</i> [1998]

^aWater column depth is in meters.



were considered responsible for the colder temperature values recorded in the sediments. Irrespectively of the validity of lateral transport mechanisms in the Barents Sea and the Black Sea, further studies are needed to fully elucidate the factors leading to the water column-sediment discrepancies of SST measurements in these areas.

5.5. Water Column-Sediment Calibrations

[42] The discrepant results described above for sediment trap-sediment comparisons cannot be easily attributed to the selective degradation of the more highly unsaturated alkenones. Several examples of inadequate conclusions from the interpretation of discrepant results are available in the literature. In a sediment core top calibration of the U_{37}^K index versus water column temperatures [Levitus, 1992] in the Atlantic Ocean [Rosell-Melé et al., 1995], selective loss of the more unsaturated alkenones was invoked to explain the steeper slopes in the correlation diagram when compared to other calibrations based on algal cultures or water particles. However, the database on which this intercalibration was based exhibited a considerable amount of scatter at low temperatures. A subsequent study, also based on core tops and involving some of the same authors [Müller et al., 1998], showed a slope identical to the one based on algal cultures [Prah and Wakeham, 1987]. This was the case when data from the eastern South Atlantic was used or when globally compiling data from the Atlantic, Indian, and Pacific Oceans. In the latter case, since the database was restricted to latitudes between 60°N and 60°S, data points involving high scatter at the low-temperature end were not included. This second study argues for a general correspondence between the U_{37}^K index and water column temperatures. In this context, the above mentioned examples of discrepancies between sediment trap measurements and

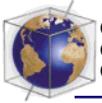
underlying sediments seem to be related to specific problems that do not jeopardize the general correspondence between water column temperatures and sedimentary U_{37}^K index.

6. C_{37:4} Alkenone

[43] Most of the aforementioned data concern the C_{37:2} and C_{37:3} alkenones. As indicated previously, the C_{37:4} alkenone generally occurs in low concentration in many samples and consequently is not considered in the majority of paleotemperature studies. Furthermore, evidence in favor of the simpler U_{37}^K index providing reliable SST results has led the tetraunsaturated alkenone being disregarded in many studies.

[44] However, the difficulties of including the C_{37:4} alkenone in paleotemperature estimation are not only of an analytical nature. Prah and Muehlhausen [1989] found better correlations between alkenone composition and *E. huxleyi* growth temperature in the tropical North-Pacific Ocean when the C_{37:4} alkenone was not included. They also reported discrepancies between the absence of C_{37:4} in the sediments and its presence in the *E. huxleyi* cultures used for temperature calibration. In agreement with these observations, Sikes et al. [1997] in a calibration between SST and C₃₇ alkenone composition in the Southern Ocean found no correlation between C_{37:4} content and SST. Similarly, Freeman and Wakeham [1992], in their analyses of Black Sea water particulates (filters) at several depths from 10 to 2000 m, observed that the concentrations of the C_{37:4} alkenone did not appear to be related to SST. Furthermore, the $\delta^{13}C$ composition of the C_{37:4} alkenones differed significantly from the isotopic composition of the co-occurring C_{37:2} and C_{37:3} alkenones (and showed more scatter).

[45] In any case, C_{37:4} alkenones are abundant in cold waters, and in these environments they



can be hardly ignored. *Rosell-Melé and Comes* [1999] pointed out the difficulties for both $U_{37}^{K'}$ and U_{37}^K in providing good estimates of SST during the last glacial maximum in the Nordic seas. Under these conditions a tentative approach based on the $C_{37:4}$ content relative to total C_{37} alkenones allowed the estimation of maximum temperatures of 6°C for this period.

[46] Good correlations between U_{37}^K and SST were found in cold marine environments when the relative abundance of the $C_{37:4}$ alkenone was lower than 5% [*Rosell-Melé*, 1998]. Conversely, no correlation with SST was found at relative abundances higher than 5%. Variations in salinity were proposed to explain the $C_{37:4}$ distributions in this marine environment at high $C_{37:4}$ content [*Rosell-Melé*, 1998]. The association between low salinities and relative proportion of $C_{37:4}$ may be related to changes in the alkenone precursor species. An early work of *Cranwell* [1985], for example, showed that some freshwater lakes contained unusual alkenone distributions characterized by high proportions of the $C_{37:4}$ component. These distributions could not be related to water temperature. Recently, a study on the Baltic Sea also showed the difficulties in relating the C_{37} alkenone distributions to SST in this basin [*Schulz et al.*, 2000]. Interestingly, the C_{37} alkenone distributions of the inner basins (with less saline waters) of the Baltic Sea exhibited a higher proportion of the $C_{37:4}$ alkenone. This enrichment may be due to a stronger influence of freshwater tributaries on these semienclosed areas.

7. C₃₇ and C₃₈ Alkenoates

[47] Alkenoates have been used for SST estimates in some marine paleoenvironments. They are usually found in higher abundance in the sediments from cold regions, namely, in the North Atlantic. Few data are available on the influence of postdepositional degradation on their composition.

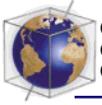
[48] In the studies of *Teece et al.* [1998], microbial degradation of alkenonates under anoxic conditions was observed, the triunsaturated compound being degraded at a faster rate than the di-unsaturated pseudohomologue. These authors concluded that their results invalidated in practice the alkenoates as sedimentary markers for SST changes.

[49] These results are in agreement with those of a study of *Weaver et al.* [1999]. In a combined coccolithophorid, foraminiferal, and biomarker reconstruction of paleoceanographic conditions over the past 120 kyr in the northern North Atlantic, these authors observed that the alkenoates were degraded at a faster rate than the alkenones. Accordingly, the former were not suitable for downcore molecular stratigraphy.

8. Bound Alkenones

[50] Evidence of storage of alkenones after binding to other compounds is available. The identification of C_{37} and C_{38} linear sulfur compounds in ancient samples such as oil shales of Cretaceous origin (e.g., *Jurf ed Darawish* [*Sinninghe Damste et al.*, 1989]) or sulfur-rich Messinian sediments such as those in the Vena del Gesso Basin (northern Italy) [*Koopmans et al.*, 1997] indicates that the formation of sulfur bound compounds from Hapthophyceean lipids is possible. The occurrence of these sulfur-bound compounds is so far restricted to relatively old (e.g., Cretaceous, Miocene) sulfur-rich sedimentary samples, e.g., with an S_{org}/C ratio of 0.08 in the Vena del Gesso samples, which are significantly different from those currently considered in paleoceanographic studies in the Quaternary.

[51] Evidence of lipid sulfur binding in very short timescales is also available. It has been reported for sterols in soil residues [*Navarro et al.*, 1991] and lake sediments [*Kok et al.*, 1999] as well as for tricyclic terpenes in the Cariaco Basin [*Kok et al.*, 1999]. No reports are available



yet for the formation of sulfur-bound alkenones in recent sediments. However, the reports on the early sulfur bonding of other lipid molecules prompt researchers in paleoceanography to check for their possible occurrence in sulfur-rich marine sedimentary sequences. A priori sulfur bonding may not alter the U₃₇^K index [Koopmans *et al.*, 1997], but this aspect has to be confirmed if significant amounts of sulfur-bound alkenones being found.

[52] Significant amounts of O-bound alkenones are generated in heating experiments by hydrous pyrolysis (from 160° to 330°C for 72 hours) of the above mentioned Vena del Gesso sediments [Koopmans *et al.*, 1997]. However, these compounds were not initially present in the samples. These experiments mimic the first stages of sedimentary organic matter thermal transformation. However, the organic matter in Pleistocene sediments currently examined in paleoceanographic studies is considerably more immature.

[53] Evidence for the presence of alkenones in the nonsolvent extractable bound fraction released after sediment hydrolysis (1 N KOH) has been reported for Pliocene and Miocene sediments [Hoefs *et al.*, 1998]. Again, it remains to be elucidated whether this alkenone fraction may represent a significant proportion of the sedimentary alkenones encountered in Pleistocene sediments. Checking for their occurrence in current paleoceanographic studies, e.g., specific analysis in a representative subseries, may be recommended for inclusion in the good laboratory practices related to the use of alkenones as paleothermometers.

9. Use of C₃₇ Alkenones as Paleoproductivity Proxy

9.1. Productivity Records

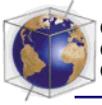
[54] Sedimentary C₃₇ alkenones have been proposed as indicators of paleoproductivity in

addition to TOC, which is also used for this purpose, e.g., in the Atlantic [Sikes and Keigwin, 1994, 1996; Rosell-Melé and Koç, 1997; Villanueva *et al.*, 1997, 1998; Weaver *et al.*, 1999; Sicre *et al.*, 2000; Ternois *et al.*, 2000; Werne *et al.*, 2000], Pacific [Farrington *et al.*, 1988; Kennedy and Brassell, 1992; Prahl *et al.*, 1989a; Herbert *et al.*, 1998; Ohkouchi *et al.*, 1999], and Indian Oceans [Sonzogni *et al.*, 1998] as well as in the Arabian Sea [Schubert *et al.*, 1998; Budziak *et al.*, 2000]. As with TOC and many other lipids and pigments, their usefulness as paleoproductivity markers is dependent on the uniformity of the preservation conditions in the period of study.

[55] C₃₇ alkenones reflect the productivity signal related to Haptophyceae because these compounds are specific markers of some species within this algal class. Thus positive correlations between C₃₇ alkenone concentrations and coccolith abundances have been reported [Weaver *et al.*, 1999].

[56] However, the environmental conditions giving rise to enhanced productivity by Haptophyceae, e.g., nutrient availability, are also adequate for the growth of many other algae. Thus the record of productivity signals integrated over long time periods show good parallels between abundances of C₃₇ alkenones and other proxies for global productivity such as total chlorin concentrations [Schubert *et al.*, 1998] or foraminifera accumulation rates [Sikes and Keigwin, 1994, 1996]. These apparently good correlations are also observed when comparing with specific biomarkers of algae other than Haptophyceae such as dinosterol and 4 α -methylstanols [Prahl *et al.*, 1989a; Schubert *et al.*, 1998] and brassicasterol [Schubert *et al.*, 1998].

[57] Therefore C₃₇ alkenones follow the global productivity record in many marine environments because increase of productivity



involves covariant changes in the abundance of many algal species. However, this is not always the case. Diatoms are the species of larger phytoplankton blooms in upwelling areas and are more representative of high-productivity conditions. In some of these systems, Haptophyceae may become relevant at lower productivity and not be correlated with the diatom markers. An example of the changes of C₃₇ alkenones and diatom sterols in a specific environment is that of the Cariaco Basin [Werne *et al.*, 2000]. In this case, low-productivity periods exhibited high C₃₇ alkenone concentrations and high-productivity episodes recorded high concentrations of brassicasterol, fucosterol, β -sitos-terol, Δ^{22} -cholesterol, and other diatom sterols. However, in more open upwelling systems, e.g., the northwestern African continental margin, paleoproductivity is recorded by C₃₇ alkenones as evidenced by the good parallelism between markers of wind intensity (*n*-alkanols) and these algal compounds [Ter-nois *et al.*, 2000].

[58] The use of C₃₇ alkenone concentrations/fluxes has successfully allowed the identifica-tion of a precessional forcing of algal produc-tivity in the North Atlantic Ocean [Villanueva *et al.*, 1998] and in the Arabian Sea [Budziak *et al.*, 2000]. Except for the above mentioned upwelling areas, the changes in C₃₇ alkenone fluxes in the sediment records could be inter-preted as diagnostic for marine productivity because these fluxes encompass long deposi-tion periods. The high resistance of alkenones to degradation compared to other lipids points to the alkenones as reasonable biomarkers for this purpose.

9.2. Marine Versus Terrigenous TOC

[59] A direct proportion between marine TOC and C₃₇ alkenones was observed in a 105-kyr Deep Sea Drilling Project core from the Pigmy Basin (Gulf of Mexico), which is under the

influence of the Mississippi River discharges [Jasper and Gagosian, 1993]. Comparison of C₃₇ alkenone/TOC and $\delta^{13}\text{C}_{\text{org}}$ values mea-sured on total organic carbon showed a linear correlation between the two parameters ($r = 0.85$). The obvious interpretation of this corre-lation is a constant C₃₇ alkenone/C_{marine org} ratio and a correspondence between $\delta^{13}\text{C}_{\text{org}}$ and relative content of terrigenous/marine organic matter supply.

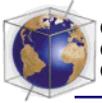
[60] Positive correlations between C₃₇ alkenone concentrations and TOC were also observed in the Arabian Sea [Schubert *et al.*, 1998], the Indian Ocean [Rostek *et al.*, 1994], the African continental margin [Ter-nois *et al.*, 2000] and the equatorial Atlantic [Sikes and Keigwin, 1994]. A constant C₃₇ alkenone/TOC ratio was also assumed in the mass balances of terrigenous and marine organic matter in the North Atlantic that allowed a successful description of sedimentary TOC origin during the last interglacial period [Villanueva *et al.*, 1997].

10. Stability of the $\delta^{13}\text{C}$ Composition of Alkenones

[61] Although the biochemical fate of alke-nones may vary among different compartments of the algal cell, no changes in $\delta^{13}\text{C}$ composi-tion should be expected in residual C₃₇ alke-none after degradation. Accordingly, no significant changes were observed by Grice *et al.* [1998] in experiments involving the inges-tion of *Isochrysis galbana* by the copepod *Temora longicornis*. However, the paucity of literature evidence on the stability of the $\delta^{13}\text{C}$ isotopic signal in the alkenones should stimu-late caution and further investigation.

11. Conclusions

[62] There is no consistent evidence of selective biogenic degradation of the C_{37:2} and C_{37:3}



alkenones by biota. Studies in the literature reporting no or minor changes of $U_{37}^{K'}$ as a consequence of C₃₇ alkenone degradation in sediments or in the water column outweigh those in which significant changes were observed. However, the amount of data on this topic is clearly insufficient. Many more experiments encompassing the whole range of $U_{37}^{K'}$ values, different water column environments, and sedimentary conditions are needed.

[63] Reports indicating lacking, weak, or no dependence of the C_{37:4} alkenone on growth temperature suggest that in most cases the $U_{37}^{K'}$ ratio will be a better proxy for paleotemperature estimate than U_{37}^K . This conclusion is consistent with most of the work in the literature involving the use of C₃₇ alkenones for paleo-SST estimation. However, in high latitudes, e.g., the Nordic Seas, the C_{37:4} alkenone is needed for a global understanding of the dependence between C₃₇ alkenone distributions and SST.

[64] The C₃₇ and C₃₈ alkenoates exhibit major changes in relative proportion upon degradation under anoxic conditions. These compounds may only be useful for paleotemperature estimation in very specific environments.

[65] C₃₇ alkenones can be used, as many other proxies (including organic carbon), to get qualitative estimates of paleoproductivity changes over “long” sedimentation periods (circa kiloyears). This application depends on the uniformity of the degradation conditions, as is the case for TOC and other lipids and pigments.

12. Recommendations

[66] 1. Studies of SST using the $U_{37}^{K'}$ index should always include concentration data of all alkenones, both those used in SST calculation and others that may be observed but not used. The C_{37:4} alkenone should be included

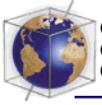
where observed. In the case of small data sets, numerical values should be tabulated in the article. For larger data sets, electronic access by the scientific community should be arranged by either inclusion in currently established databases or via linkages to related sites. Consideration should be given to a global database of alkenone distributions in water columns and sediments.

[67] 2. Information on the intermediate products and likely reaction pathways of degradation during alkenone diagenesis is needed. This will help to evaluate whether the first site of attack is at the keto group (no effect on $U_{37}^{K'}$ expected) or at the double bonds, which may affect the alkenone index over long timescales in sediments.

[68] 3. Information on the effects of bioturbation on selective preservation of alkenones in surface sediments is lacking. Although experimental studies in water columns indicate that microbial and mesozooplankton grazers do not alter the index, this should be validated for benthic consumers.

[69] 4. Further assessment is needed on the possible transformation of the $U_{37}^{K'}$ ratio upon sedimentation under oxic-anoxic sedimentary conditions. Despite the overwhelming evidence for the postdepositional stability of this index, the data from the Santa Monica Basin [Gong and Hollander, 1999] suggest that assessment on the postdepositional changes of the relative composition of C_{37:2} and C_{37:3} alkenones should be continued. A larger number of cores in this basin should be studied for a better understanding of the changes observed. Other basins encompassing oxic-anoxic sedimentary conditions should also be considered.

[70] 5. Other sedimentary lipids, namely, those more labile than the alkenones, can be used as indicators of possible alkenone degradation in



the sedimentary system under study. Quantitative analysis of these lipids and evaluation of their downcore degradation trends may provide a useful comparison for the stability of the U₃₇^{K'} index.

[71] 6. The processes of alkenone binding, including sulfurization or direct coupling, to macromolecular organic matter are not known. Studies that consider the mechanisms of lipid binding over long timescales would be useful. In practice, C₃₇ alkenone users should evaluate whether these processes are relevant for their samples under study. Analysis of subseries of sediments for this purpose may be included as a good laboratory practice in the use of alkenones as paleothermometers.

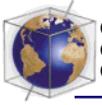
[72] 7. Knowledge is needed on the distribution of alkenones among different size fractions of particles in the water column and surface sediments. This would allow the reconstruction of alkenone transport pathways in water columns and provide insight into their potential redistribution at the sediment-water interface.

[73] 8. Organic carbon and pigment content should be included among the parameters measured wherever possible. This is of particular interest given the links between alkenone contents in sediments and issues of paleoproductivity and preservation.

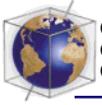
[74] 9. The integrity of the isotopic signal during diagenesis should be validated.

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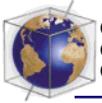
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