

## Postdepositional oxic degradation of alkenones: Implications for the measurement of palaeo sea surface temperatures

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**Abstract.** Free and "bound" long-chain alkenones ( $C_{37:2}$  and  $C_{37:3}$ ) in oxidized and unoxidized sections of four organic matter-rich Pliocene and Miocene Madeira Abyssal Plain turbidites (one from Ocean Drilling Program site 951B and three from site 952A) were analyzed to determine the effect of severe post depositional oxidation on the value of  $U_{37}^{k'}$ . The profiles of both alkenones across the redox boundary show a preferential degradation of the  $C_{37:3}$  compared to the  $C_{37:2}$  compound. Because of the high initial  $U_{37}^{k'}$  values and the way of calculating the  $U_{37}^{k'}$  this degradation hardly influences the  $U_{37}^{k'}$  profiles. However, for lower  $U_{37}^{k'}$  values, measured selective degradation would increase  $U_{37}^{k'}$  up to 0.17 units, equivalent to 5°C. For most of the  $U_{37}^{k'}$  band-width, much smaller degradation already increases  $U_{37}^{k'}$  beyond the analytical error (0.017 units). Consequently, for interpreting the  $U_{37}^{k'}$  record in terms of past sea surface temperatures, selective degradation needs serious consideration.

### 1. Introduction

The discovery of long-chain alkenones in sediments [Boon *et al.*, 1978; De Leeuw *et al.*, 1980] and their subsequent detection in the haptophyte alga *Emiliania huxleyi* [Volkman *et al.*, 1980a, b] served as a starting point for investigations of their palaeoenvironmental significance. It was demonstrated that a ratio between  $C_{37:2}$ ,  $C_{37:3}$ , and  $C_{37:4}$  methyl ketones (the  $U_{37}^k$ ) correlated with the sea surface temperature (SST) [e.g., Brassell *et al.*, 1986; Prahl and Wakeham, 1987]. This relation was defined by Brassell *et al.*, [1986] as:

$$U_{37}^k = \frac{[C_{37:2}] - [C_{37:4}]}{[C_{37:2}] + [C_{37:3}] + [C_{37:4}]} \quad (1)$$

where  $[C_{37:2}]$ ,  $[C_{37:3}]$  and  $[C_{37:4}]$  are the concentrations of the diunsaturated, triunsaturated and tetraunsaturated  $C_{37}$  alkenones, respectively. On the basis of additional cultures and ocean surface plankton tows a new relation was proposed, derived from (1) which excluded the  $C_{37:4}$  alkenone [Prahl and Wakeham, 1987; Prahl *et al.*, 1988]:

$$U_{37}^{k'} = \frac{[C_{37:2}]}{[C_{37:2}] + [C_{37:3}]} = 0.034T - 0.039 \quad (2)$$

where  $T$  is the temperature of alkenone synthesis. This discovery led to the widespread application of the  $U_{37}^{k'}$  for the reconstruction of paleo SST and its variations through time [e.g., Brassell, 1993;

Jasper *et al.*, 1994; Schneider *et al.*, 1995; Chapman *et al.*, 1996]. Generally, a good correlation is found between sea surface temperatures and the  $U_{37}^{k'}$  values obtained from surface sediments [e.g., Rosell-Melé *et al.*, 1995; Sikes *et al.*, 1997]. At increasing sediment depth the  $U_{37}^{k'}$  derived paleo SSTs generally correlate with temperature reconstructions based on other proxies [e.g., Brassell *et al.*, 1986; Sikes and Keigwin, 1994, 1996; Müller *et al.*, 1994; 1997], although there are also differences. Part of these differences may arise from differences in the degradation rates of both alkenones. The extra double bond of  $C_{37:3}$  alkenone should give this alkenone a higher reactivity than its  $C_{37:2}$  counterpart, and thus a higher degradation rate of the  $C_{37:3}$  alkenone might be expected.

Degradation of alkenones has been studied in the water column, in sediments, and in laboratory experiments under both oxic and anoxic conditions [Nichols and Johns, 1986; Prahl *et al.*, 1988, 1989, 1993; McCaffrey *et al.*, 1990; Sikes *et al.*, 1991; Freeman and Wakeham, 1992; Conte *et al.*, 1992, 1995; Kennedy and Brassell, 1993; Sun and Wakeham, 1994; Teece *et al.*, 1994, 1995; Madureira *et al.*, 1995; Flügge, 1996]. Except for Sun and Wakeham [1994], who found almost no degradation, all these studies suggest that both  $C_{37:2}$  and  $C_{37:3}$  alkenones significantly degrade under various environmental conditions. With respect to different degradation rates for the  $C_{37:2}$  and  $C_{37:3}$  alkenones, however, some authors report the  $U_{37}^{k'}$  to be independent of degradation [McCaffrey *et al.*, 1990; Prahl *et al.*, 1989; Sikes *et al.*, 1991; Conte *et al.*, 1992; Teece *et al.*, 1994, 1995; Madureira *et al.*, 1995] whereas others [Freeman and Wakeham, 1992; Kennedy and Brassell, 1993; Flügge, 1996] consider the opposite, although strong evidence often remains absent. Added to this controversy is the complication that virtually all studies on the effects of degradation on the  $U_{37}^{k'}$  consider exposure times of at most a few hundred years. In contrast, most studies on  $U_{37}^{k'}$

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through geological time investigate open ocean sediments where sedimentation rates are low and oxygen penetration in the sediments is relatively deep, implying much longer exposure times of alkenones to oxidative degradative processes. Only *Prahl et al.* [1989] studied the long-term exposure of alkenones to degradative conditions in a Madeira Abyssal Plain (MAP) turbidite. They found that despite the prolonged exposure to oxygen, and consequent degradation of the alkenones, the U<sub>37</sub><sup>k'</sup> remained remarkably constant ( $0.68 < U_{37}^{k'} < 0.70$ ).

The MAP region is a unique site for the study of the effect of oxygen on the preservation of organic matter. The distal, meter thick organic-matter-rich turbidites, derived from the northwest African margin, are well mixed and laid down as homogeneous deposits [e.g., *De Lange et al.*, 1987; *Prahl et al.*, 1989; *Cowie et al.*, 1995; *Hoefs et al.*, 1997]. All of these turbidites contain a sharp oxidation front down to which bottom water oxygen has penetrated the sediment. This postdepositional oxidation process was terminated by the deposition of the next turbiditic sequence. The penetration of oxygen resulted in the destruction of up to 90% of the organic matter (OM) in a postdepositional oxidation event lasting several thousand years (e.g., ~8.4 kyr for the MAP f-turbidite [*Buckley and Cranston*, 1988]). Below this oxidation zone the organic matter has been exposed only to pore water sulphate for very long times (e.g., ~140 kyr for the MAP f-turbidite [*De Lange et al.*, 1987; *Weaver and Rothwell*, 1987; *Buckley and Cranston*, 1988]). Because of the homogeneous composition of the sediment at the beginning of the oxidation process, these so called "in situ oxidation experiments" form the natural equivalent of very long term laboratory experiments to assess the effect of severe oxidation by molecular oxygen on the alteration of U<sub>37</sub><sup>k'</sup>. Differences in U<sub>37</sub><sup>k'</sup> between the oxidized and nonoxidized layers can thus only be related to the effect of molecular oxygen on this ratio and not to a large number of other variables that normally affect the composition of the organic matter in marine sediments (e.g., varying productivity, sediment accumulation rate, organic matter source, reworking, bioturbation, and seasonality). The postdepositional oxidation process in the older turbidites recovered during ODP leg 157, resulted in exposure times of the sedimentary organic matter to oxygen estimated to be in the range of 1-50 kyr [*De Lange*, 1997]. There is thus no clear difference in the exposure times of the turbidites presented in this paper and, for example, the MAP f-turbidite.

The present study aims to provide new information on the relative stability of diunsaturated and triunsaturated alkenones in sediments over geological times by studying the effect of downward penetration of oxygen on these C<sub>37</sub> alkenones in several homogenous turbidites from the MAP.

## 2. Material and methods

During ODP leg 157 to the Madeira Abyssal Plain, several turbiditic sequences were recovered. Samples of three of them are derived from site 951B (32°1.895'N, 24°52.236'W, 5436.8 m water depth, and 351.6 m penetration); the remaining turbidite is derived from site 952A (30°47.449'N, 24°30.574'W, 5431.8 m water depth, and 425.9 m penetration). Turbidite identification is based on the color and lithology of the sediments; the redox fronts are defined by a sharp change of color whereas age assessment is based on the biostratigraphy of calcareous

nannofossils and planktonic foraminifera [*Shipboard Scientific Party*, 1995a, b] (Table 1).

Samples were ultrasonically extracted twice with a mixture of dichloromethane/methanol (7.5:1 vol/vol). This yielded the free lipid fraction. The residue after extraction was saponified to release ester-bound lipids by refluxing it with 1 N KOH in 96% MeOH for 1 hour. To facilitate analysis by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS), the carboxylic acid groups were derivatized to their corresponding methyl esters with diazomethane. The free hydroxyl groups were derivatized to their corresponding trimethylsilyl ethers by adding a mixture pyridine and Bis(trimethyl)-silyltrifluoroacetamide (BSTFA) with 1% Trimethylchlorosilane (TMCS) and heating for 30 min at 60°C in a sealed tube. To all lipid fractions a known amount of internal standard (2,3-dimethyl-5-(1,1-D<sub>2</sub>-hexadecyl)thiophene) was added directly after extraction.

GC was performed on a Carlo Erba Fractovap 4160 instrument equipped with an on-column injector and a flame ionization detector (FID). A fused silica capillary column (25 m x 0.32 mm, CP-Sil 5 coating, and film thickness 0.12 µm) was used with He as the carrier gas. The samples were dissolved in ethyl acetate prior to injection. The temperature program used was 70-130°C at 20°C min<sup>-1</sup>, 130-320°C at 4°C min<sup>-1</sup>, and 320°C for 20 min. GC-MS was performed on a Hewlett-Packard 5890 series II gas chromatograph interfaced to a VG Autospec Q Ultima mass spectrometer operated at 70 eV with a mass range of m/z 40-800 and a cycle time of 1.7 s (resolution 1000). The GC column had a film thickness of 0.2 µm. The other GC conditions were as described above.

Absolute amounts (µg g<sup>-1</sup> dry weight sediment) of the long-chain alkenones in the free and bound lipid fractions were determined by integration of their individual peak areas and that of the internal standard from FID gas chromatograms. No correction was made for different response factors between thiophene and alkenones. This has no implications for the observed trends. Some samples with low alkenone concentrations were concentrated and measured again. U<sub>37</sub><sup>k'</sup> values thus measured were identical to those previously obtained, indicating that nonlinearity of the GC response at low alkenone concentrations played no role [*Villanueva et al.*, 1997].

To quantify the effect of oxidation on the alkenones and organic matter a degradation factor (DF) has been defined:

$$DF = \frac{[A]_{\text{red}}}{[A]_{\text{ox}}} \quad (3)$$

where DF is the degradation factor; [A] is the concentration of compound a; red is the unoxidized sample; and ox is the oxidized sample. Differences in degradation rates between the C<sub>37:3</sub> and C<sub>37:2</sub> alkenones are quantified by a degradation ratio (DR):

$$DR = \frac{DF_{C_{37:3}}}{DF_{C_{37:2}}} \quad (4)$$

where, DR= degradation ratio and DF<sub>C<sub>37:3</sub></sub> and DF<sub>C<sub>37:2</sub></sub> are the degradation factors of the C<sub>37:3</sub> and C<sub>37:2</sub> alkenones, respectively. The DR needed to obtain a deviation x for a given U<sub>37</sub><sup>k'</sup> value is calculated according to

$$DR = \frac{C_{37:3}(C_{37:2} + C_{37:2}\Delta U_{37}^{k'} + C_{37:3}\Delta U_{37}^{k'})}{C_{37:2}(C_{37:3} - C_{37:2}\Delta U_{37}^{k'} - C_{37:3}\Delta U_{37}^{k'})} \quad (5)$$



**Table 1.** Location, Depth, Age, Concentrations of Total Organic Carbon (TOC), and Free and Bound Alkenones for the Four Turbidites Investigated

Age <sup>a</sup>	Sample <sup>a</sup>	Depth <sup>a,b</sup>	TOC <sup>c</sup>	Free <sup>d</sup>		Bound <sup>d</sup>	
				C <sub>37:3</sub>	C <sub>37:2</sub>	C <sub>37:3</sub>	C <sub>37:2</sub>
Late Pliocene	157-952A-9H-5, 50-57 cm	82.80	0.14	0.06	0.23	0.20	0.86
	157-952A-9H-5, 94-104 cm	83.24	0.73	3.04	10.2	0.58	2.24
	157-952A-9H-6, 10-20 cm	83.55	0.78	3.08	10.4	0.61	2.40
Early Pliocene	157-952A-18X-3, 101-111 cm	159.61	0.45	0.02	0.26	n.d.	0.06
	157-952A-18X-3, 121-131 cm	159.81	1.64	3.02	19.0	0.34	3.57
	157-952A-18X-4, 55-64 cm	160.65	1.53	1.85	11.9	0.31	3.56
Late Miocene	157-952A-23X-5, 46-52 cm	210.26	0.21	0.01	0.12	n.d.	0.02
	157-952A-23X-5, 74-84 cm	210.54	1.16	10.9	74.8	0.45	3.42
	157-952A-23X-6, 31-41 cm	211.61	1.06	6.09	43.0	0.33	2.38
Middle-Late Miocene	157-951B-3X-4, 79-84 cm	279.59	0.18	n.d.	0.10	n.d.	n.d.
	157-951B-3X-4, 93-101 cm	279.73	1.14	1.40	18.6	n.d.	n.d.
	157-951B-3X-4, 107-117 cm	279.87	1.33	1.73	19.6	0.28	5.38

The abbreviations are defined as follows: TOC, total organic carbon; and n.d., not detected.

<sup>a</sup> Shipboard Scientific Party [1995a, b].

<sup>b</sup> Depth in meters below seafloor.

<sup>c</sup> In percentage of dry sediment, data from *De Lange* [1997].

<sup>d</sup> In  $\mu\text{g g}^{-1}$  dry sediment.

with:

$$\Delta U_{37}^k < \frac{C_{37:3}}{C_{37:2} + C_{37:3}} \quad (6)$$

### 3. Results

Of each of the four turbidites, two samples from the nonoxidized part and one sample from the oxidized part were analyzed. Strictly, only one sample from each lithology would suffice to estimate the effect of oxidation, but to obtain an indication of the homogeneity of the initial turbidite, each time, two samples have been taken from below the redox front. In all turbidites a decrease in total organic carbon (TOC) and alkenone concentrations across the redox boundary is noted (Table 1 and Figures 1a and 1b) [*De Lange*, 1997]. Compared to changes over the redox front, such a consistent trend is absent between the nonoxidized samples and variation is only minor (though larger for alkenones than for TOC). Over the redox front, alkenone degradation is much more severe than for TOC as is indicated by the DFs (Table 2). The extent of degradation varies considerably for the alkenones (DFs of 44-626 for free alkenones and 3-117 for "bound" alkenones). In some cases, DFs of the C<sub>37:3</sub> alkenone could not be defined because of the concentrations below the level of detection in the oxidized samples or coelution with other compounds. Significant amounts of long-chain alkenones were present in the bound lipid fractions. More extensive extraction of a set of samples from another turbidite failed to extract these bound alkenones. In general, they have significantly lower DFs than the free alkenones.

In all four turbidites, DFs are larger for the C<sub>37:3</sub> isomer than for the C<sub>37:2</sub> isomer (Table 2). The U<sub>37</sub><sup>k</sup> values (all >0.75) show only small changes through the turbidites, but consistently higher

values above the redox front are noted (Table 2 and Figure 1c). Preferential degradation is more clearly indicated by the C<sub>37:3</sub>/C<sub>37:2</sub> ratio (Figure 1d) and the degradation ratios (DRs) which vary between 1.1 (almost no apparent degradation) and 2.1 (Table 2).

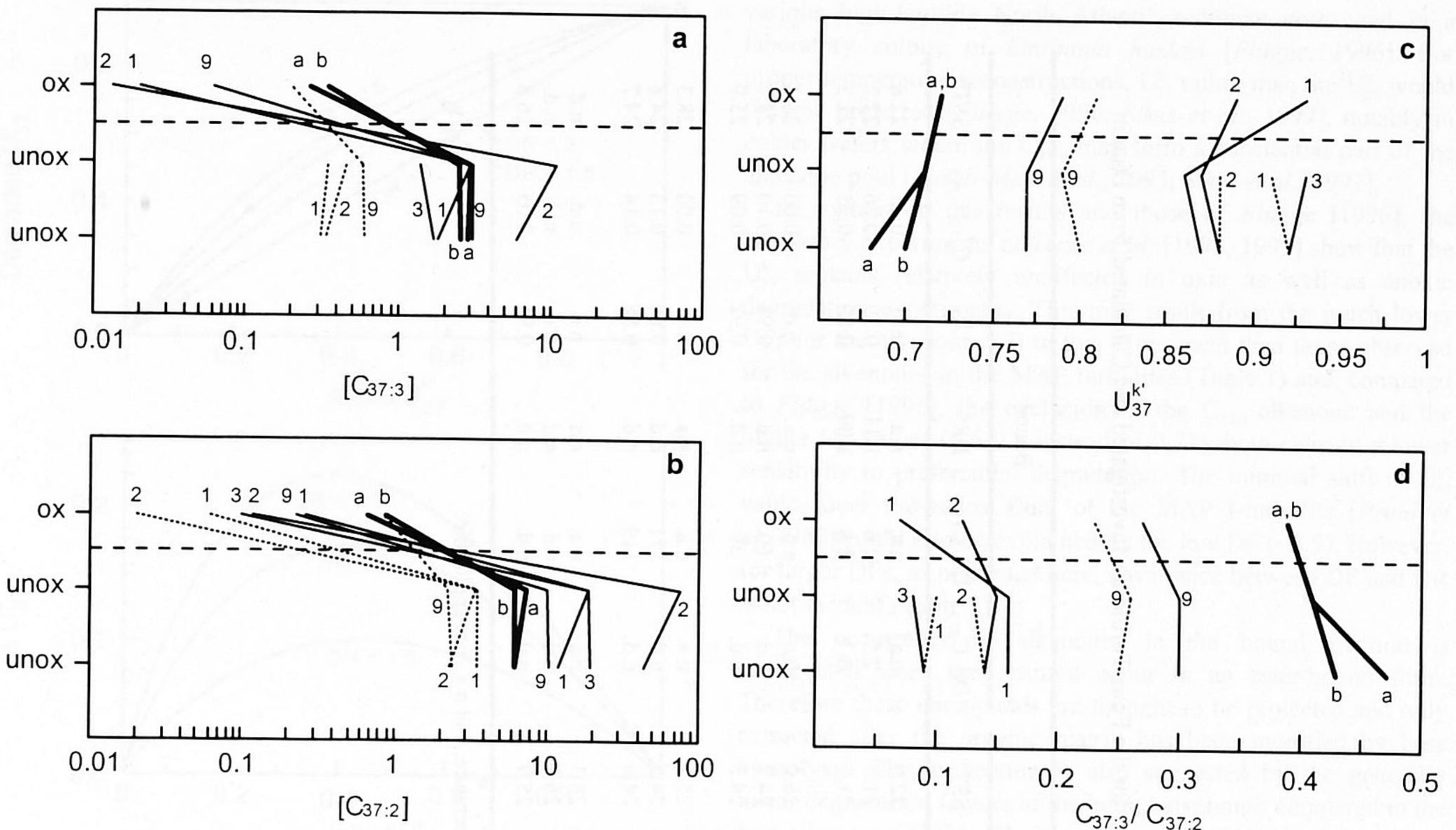
### 4. Discussion

Before redeposition the sediments forming the MAP turbidites had already experienced some OM degradation during deposition and burial on the continental shelf and slope. Changes over the redox front in the turbidite thus show the fate of OM after removal of its most easily degradable part. The higher DFs for alkenones compared to TOC indicate, even after initial degradation and on a geological time scale, that the alkenones belong to the more easily degradable fraction of the carbon pool. This was also observed for the MAP f-turbidite [*Prahl et al.*, 1989]

Changes over the oxidation front are more severe than differences observed between the unoxidized samples. Furthermore, they always show the same trend. Both observations demonstrate the prime influence of oxidation on OM composition and simultaneously support the hypothesis of relative homogeneity of the initial turbidites [*McCave and Jones*, 1988; *Prahl et al.*, 1989; *Hoefs et al.*, 1997; *Cowie et al.*, 1995]. The robustness of these trends is apparent by their consistent occurrence in all four turbidites, irrespective of their age, initial TOC and degree of oxidation (Table 1 and Figure 1).

In addition to the absolute decrease in alkenone concentrations over the redox front, the observation that all DRs are >1 indicates that degradation is selective, with the C<sub>37:3</sub> alkenone lost consistently faster than the C<sub>37:2</sub> (Table 2). For the turbidites presented here this results in higher U<sub>37</sub><sup>k</sup> values for the oxidized samples. This has also been reported for the MAP f-turbidite





**Figure 1.** Depth profiles for concentrations of (a) C<sub>37:3</sub> and (b) C<sub>37:2</sub> alkenones both in µg g<sup>-1</sup> dry sediment, and (c) U<sub>37</sub><sup>k'</sup> and (d) C<sub>37:3</sub>/C<sub>37:2</sub> ratio for oxidized (ox) and unoxidized (unox) samples from Madeira Abyssal Plain turbidites. Note the logarithmic concentration scales. Samples with the same relative position in the turbidites have been assigned to the same depth. The horizontal dotted line symbolizes the position of the redox front. The hooked lines connect samples from the same turbidite profile, full for free lipids, dotted for bound lipids and bold for f-turbidite profiles investigated by *Prahl et al.* [1989]. Numbers "1," "2," "3," "9," refer to turbidites investigated in sections 157-952A-18X-3/4, 157-952A-23X-5/6, 957-951B-3X-4, and 157-952A-9H-5/6, respectively (corresponding numbers in bold) Codes "a" and "b" refer to cores 86P5 and core 86P25 from the f-turbidite.

[*Prahl et al.*, 1989]. *Prahl et al.* [1989] concluded, on the basis of the minor trends in both their U<sub>37</sub><sup>k'</sup> records, that U<sub>37</sub><sup>k'</sup> was not influenced by postdepositional oxidation. The small magnitude of the changes in U<sub>37</sub><sup>k'</sup> partly originates from the way the U<sub>37</sub><sup>k'</sup> is calculated, which makes it insensitive to changes in the alkenone composition at high or low U<sub>37</sub><sup>k'</sup> values (Figure 2). For the high U<sub>37</sub><sup>k'</sup> values observed in the four turbidites studied here (>0.75) the U<sub>37</sub><sup>k'</sup> is thus not suitable for detecting relative changes in the alkenone composition. When selective degradation observed in the turbidites is applied to moderate U<sub>37</sub><sup>k'</sup> values, however, its potential impact on the U<sub>37</sub><sup>k'</sup> record becomes clear (Figure 2a). For a DR of 2 the maximum shift induced is 0.17 U<sub>37</sub><sup>k'</sup> units (Figure 2c), which averaged over all U<sub>37</sub><sup>k'</sup> temperature calibrations [e.g., *Rosell-Melé et al.*, 1995] equals a 5°C change (the range is 1.5-9.4°C; s<sup>2</sup>=2.6°C; and n=32). The maximum shift migrates to lower initial U<sub>37</sub><sup>k'</sup> values as degradation proceeds (Table 3). The analytical error of U<sub>37</sub><sup>k'</sup> measurements is often estimated to be ~0.017 units or 0.5°C. For a DR <2.0 a deviation >0.017 is obtained for 0.02 < U<sub>37</sub><sup>k'</sup> < 0.96, almost the entire U<sub>37</sub><sup>k'</sup> range. Even for a DR <1.10, this deviation is exceeded for 0.22 < U<sub>37</sub><sup>k'</sup> < 0.75 (Figure 2c). It would be highly interesting to investigate if the predicted degradation-induced changes in U<sub>37</sub><sup>k'</sup> do indeed occur in a "cooler" water equivalent of the MAP turbidites (which would have lower initial U<sub>37</sub><sup>k'</sup> values).

In many open ocean sediments, sedimentation rates and bottom water oxygen levels are comparable to those of the MAP. In contrast to the MAP turbidites, where the oxygen supply is cut off through deposition of the next turbidite, exposure to oxygen is even longer. The effects of oxidation on the alkenone record in such open ocean sediments will likely be at least as severe as those observed for the MAP turbidites. Down core interpretation of the U<sub>37</sub><sup>k'</sup> record becomes further complicated if one considers that factors modifying oxygen exposure of alkenones, like sedimentation rate or bottom water oxygen content, may covary with climate change. An independent assessment of the preservation history of the investigated sediments would be needed to estimate the diagenetic overprint of the original U<sub>37</sub><sup>k'</sup> signal. Differences in alkenone preservation are not readily reflected in calibrations of core top U<sub>37</sub><sup>k'</sup> values with sea surface temperatures [e.g., *Rosell-Melé et al.*, 1995; *Sikes et al.*, 1997]. This may be due to a high proportion of "fresh" alkenones at the sediment surface which have not yet been subject to selective degradation. Some evidence of selective degradation of alkenones in surface sediments might be indicated by those studies where the U<sub>37</sub><sup>k'</sup> temperature relation derived from sediments has a somewhat lower slope than the relation obtained from local water column data [*Sikes et al.*, 1997]. There is, however, statistically no strong evidence that this offset is indeed caused by selective



**Table 2.** Degradation Factors, Degradation Ratios, U<sub>37<sup>k</sup></sub>, and Reconstructed Sea Surface Temperatures for the Four Turbidites Investigated and Calculated from Data in Table 1

Sample <sup>a</sup>	Free						Bound						
	DF <sup>b</sup> , TOC	DF, C <sub>37:3</sub>	DF, C <sub>37:2</sub>	DR <sup>c</sup>	U <sub>37<sup>k</sup></sub>	C <sub>37:2</sub> /C <sub>37:3</sub>	SST <sup>d</sup>	DF, C <sub>37:3</sub>	DF, C <sub>37:2</sub>	DR <sup>c</sup>	U <sub>37<sup>k</sup></sub>	C <sub>37:2</sub> /C <sub>37:3</sub>	SST <sup>d</sup>
157-952A-9H-5, 50-57 cm	n.a.	n.a.	n.a.	n.a.	0.79	0.26	22.0	n.a.	n.a.	n.a.	0.81	0.23	22.8
157-952A-9H-5, 94-104 cm	5.2	51	44	1.14	0.77	0.30	21.5	2.9	2.6	1.11	0.79	0.26	22.2
157-952A-9H-6, 10-20 cm	5.6	51	45	1.14	0.77	0.30	21.5	3.1	2.8	1.09	0.80	0.25	22.3
157-952A-18X-3, 101-111 cm	n.a.	n.a.	n.a.	n.a.	0.93	0.08	26.2	n.a.	n.a.	n.a.	n.d.	0.00	28.3
157-952A-18X-3, 121-131 cm	3.6	151	73	2.07	0.86	0.16	24.2	n.d.	60	n.d.	0.91	0.10	25.7
157-952A-18X-4, 55-64 cm	3.4	93	46	2.02	0.87	0.16	24.3	n.d.	59	n.d.	0.92	0.09	25.9
157-952A-23X-5, 46-52 cm	n.a.	n.a.	n.a.	n.a.	0.89	0.11	25.1	n.a.	n.a.	n.a.	n.d.	0.00	28.3
157-952A-23X-5, 74-84 cm	5.5	838	629	1.33	0.87	0.15	24.5	n.d.	171	n.d.	0.88	0.13	24.8
157-952A-23X-6, 31-41 cm	5.0	468	361	1.30	0.88	0.14	24.6	n.d.	119	n.d.	0.88	0.14	24.7
157-951B-3X-4, 79-84 cm	n.a.	n.a.	n.a.	n.a.	1.00	0.00	28.3	n.a.	n.a.	n.a.	n.d.	n.d.	n.d.
157-951B-3X-4, 93-101 cm	6.3	n.d.	186	n.d.	0.93	0.08	26.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
157-951B-3X-4, 107-117 cm	7.4	n.d.	196	n.d.	0.92	0.09	25.9	n.d.	n.d.	n.d.	0.95	0.05	26.8

The abbreviations are defined as follows: DF, degradation factor; DR, degradation ratio; SST, sea surface temperature; and n.a., not applicable.

<sup>a</sup>Shipboard Scientific Party, [1995a, b].

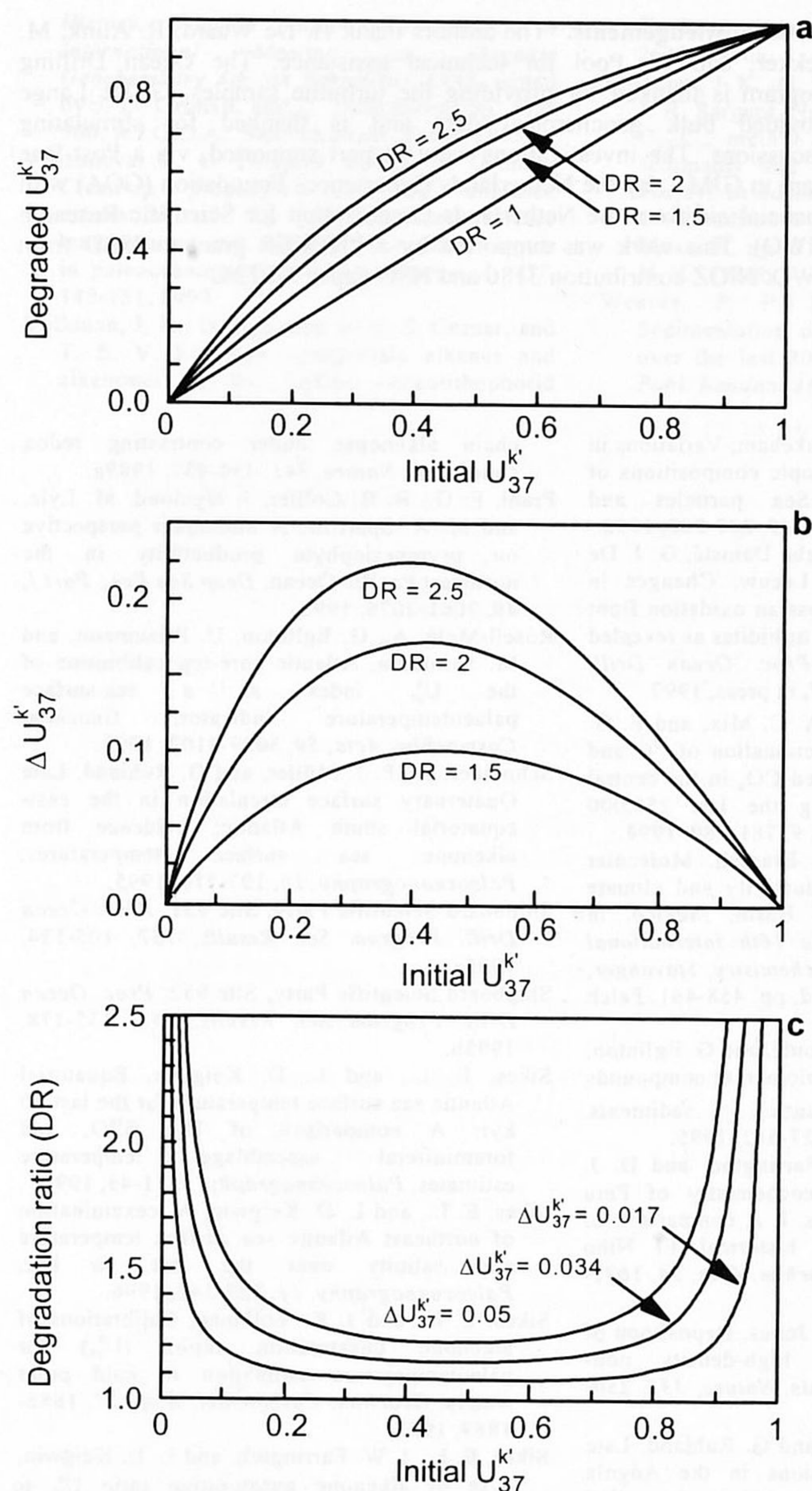
<sup>b</sup>DF calculated according to (3).

<sup>c</sup>DR calculated according to equation (4).

<sup>d</sup>reconstructed SST calculated according to (2), from *Prahl et al.* [1988].

n.d. = not determined; n.a. = not applicable.





**Figure 2.** Modeled influence of selective degradation of alkenones on the  $U_{37}^k$ . DR is the degradation ratio; the initial  $U_{37}^k$  is the  $U_{37}^k$  before degradation;  $\Delta U_{37}^k$  is the difference between the  $U_{37}^k$  before and after selective degradation. (a)  $U_{37}^k$  obtained from the initial  $U_{37}^k$  for different DR (DR=1 means no degradation). (b) Deviation from the initial  $U_{37}^k$  for different DR. (c) The DR needed to achieve a given  $\Delta U_{37}^k$  for different initial  $U_{37}^k$ . A  $\Delta U_{37}^k$  of 0.017 corresponds to  $\sim 0.5^\circ\text{C}$ . Note the nonlinear relation between initial and resulting  $U_{37}^k$ .

degradation [Sikes *et al.*, 1997]. The phenomenon, however, remains suggestive. The insensitivity of the  $U_{37}^k$  to small changes in the alkenone composition at low and high  $U_{37}^k$  values may (partly) explain the nonlinearity of the  $U_{37}^k$  temperature, as observed, for example, by Sikes and Volkman [1993].

On the basis of theoretical considerations the faster degradation of the C<sub>37:3</sub> alkenone compared to the C<sub>37:2</sub> alkenone is due to its higher degree of unsaturation. Therefore an even higher degradation rate would be expected for the C<sub>37:4</sub> alkenone. This higher degradation has been suspected by others [e.g., Prahl *et al.*, 1988; Freeman and Wakeham, 1992] and has recently been observed in degradation profiles of the organic matter from

various high-latitude North Atlantic sediment cores and in a laboratory culture of *Emiliana huxleyi* [Flügge, 1996]. For proper temperature reconstructions,  $U_{37}^k$  rather than the  $U_{37}$  would thus be preferred [Flügge, 1996; Sikes *et al.*, 1997], notably in colder waters where the C<sub>37:4</sub> may form a substantial part of the alkenone pool [Rosell-Melé *et al.*, 1995; Sikes *et al.*, 1997].

In contrast to our results and those of Flügge [1996], the laboratory experiments of Teece *et al.* [1994, 1995] show that the  $U_{37}^k$  remains relatively unaffected in oxic as well as anoxic degradation experiments. This may result from the much lower DFs for the alkenones (7) in this experiment than those observed for the alkenones in the MAP turbidites (Table 1) and, compared to Flügge [1996], the exclusion of the C<sub>37:4</sub> alkenone and the higher  $U_{37}^k$  values (0.6-0.8 instead of 0.23), both causing a lower sensitivity to preferential degradation. The minimal shift in  $U_{37}^k$  values over the redox front of the MAP f-turbidite [Prahl *et al.*, 1989] could also be explained by the low DF ( $\sim 8.5$ ). However, for larger DFs, as presented here, covariance between DF and DR is not evident (Table 2).

The occurrence of alkenones in the bound fraction is unexpected since they cannot occur in an ester-bound form. Therefore these compounds are thought to be protected and only extracted after the organic matrix has been modified by base hydrolysis. This protection is also suggested by the generally lower degradation factors of the bound alkenones compared to the free alkenones (Table 2). These lower degradation factors may suggest that for palaeotemperature reconstruction a  $U_{37}^k$  based on these alkenones may be preferred over a  $U_{37}^k$  based on the free alkenones. However, before this idea can be put into practice a rigid extraction procedure would be needed whereas the relation of the  $U_{37}^k$  to these bound alkenones to sea surface temperature as well as factors that may disturb this relation, like preferential degradation of the C<sub>37:3</sub> alkenone, should be investigated further.

## 5. Conclusions

Compared to TOC, the alkenones belong to the readily degradable part of the organic matter on geological timescales. The  $U_{37}^k$  values for those samples that have undergone postdepositional oxidation agree with preferential degradation of the C<sub>37:3</sub> isomer compared to the C<sub>37:2</sub> isomer.

Comparison of the effects of selective degradation on initial  $U_{37}^k$  values further shows that (1) because of the way the  $U_{37}^k$  is calculated, low or high  $U_{37}^k$  values are hardly influenced by degradation. (2) The  $U_{37}^k$  at which degradation induces the largest shift changes with increasing degradation from 0.5 (no degradation) to ultimately 0 (infinite degradation). (3) Even for a

**Table 3.** The  $U_{37}^k$  With the Largest Deviation in  $U_{37}^k$  and  $U_{37}^k$ -Based Sea Surface Temperatures for Different Degradation Ratios

DR	Initial $U_{37}^k$	Degraded $U_{37}^k$	$\Delta U_{37}^k$	$\Delta T^a$
1.0	0.50	0.50	0	0
1.5	0.45	0.55	0.10	2.9
2.0	0.41	0.58	0.17	5.0
2.5	0.39	0.61	0.22	6.5
$\infty$	0	1	1	29.4

<sup>a</sup>Calculated  $U_{37}^k$  according to (2)



low degree of selective degradation, a shift in U<sub>37</sub><sup>k</sup> beyond the analytical error is estimated for most of the U<sub>37</sub><sup>k</sup> range. Our results thus indicate that if there is no independent assessment on the amount of predepositional and postdepositional "removal" of the long-chain alkenones, the U<sub>37</sub><sup>k</sup> derived palaeo SST should be applied with caution whereas the use of absolute SST may not be justified at all.

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