

Sea surface paleotemperature errors in $U^{K'}_{37}$ estimation due to alkenone measurements near the limit of detection

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Abstract. Major errors ($> 0.5^\circ\text{C}$) are produced in paleotemperature estimation with the C_{37} alkenone method when the amount of the diunsaturated or triunsaturated species, $C_{37:2}$ and $C_{37:3}$, respectively, approaches the limit of detection. These errors are more commonly encountered with $C_{37:3}$ because of its higher adsorption to gas chromatographic (GC) columns. They are particularly relevant at low sedimentary C_{37} alkenone concentrations and may easily increase to temperature differences of $2^\circ\text{--}4^\circ\text{C}$ depending on the $U^{K'}_{37}$ values and the ratio between the $C_{37:3}$ signal and limit of detection. Mathematical expressions for the description of the analytical constraints derived from this detection limit problem are given. A quality assurance guideline based on sample dilution (three times) and calculation of the sea surface temperature error is proposed for assessment of reliable measurements. Reevaluation of literature data in the light of the equations reported in the present study suggest that some previously reported alkenone geochemical effects, such as variation in $U^{K'}_{37}$ temperatures due to postdepositional oxidation, may reflect deviations in the GC measurements due to changes in C_{37} alkenone concentration.

1. Introduction

Sedimentary C_{37} diunsaturated and triunsaturated ketones (heptatriaconta-15E,22E-dien-2-one and heptatriaconta-8E,15E,22E-trien-2-one, $C_{37:2}$ and $C_{37:3}$, respectively) are now widely used for the estimation of sea surface temperatures (SST) during the Quaternary [Brassell *et al.*, 1986]. This approach is based on the preferential synthesis of one of the two unsaturated compounds by haptophytes in correspondence to the water temperature in which this algae grows.

A linear relationship between an unsaturation index $U^{K'}_{37}$, expressed as

$$U^{K'}_{37} = C_{37:2}/(C_{37:2} + C_{37:3}), \quad (1)$$

and growth temperature has been found from the study of the alkenone composition in cultures of *Emiliania huxleyi* [Prahel and Wakeham, 1987]. Linear relationships between SST and $U^{K'}_{37}$ have also been found when comparing the sedimentary C_{37} alkenone composition and averaged SST records throughout the world oceans [Rosell-Melé *et al.*, 1995b; Sikes *et al.*, 1991; Pelejero and Grimalt, 1997; Sonzogni *et al.*, 1997; Müller *et al.*, 1998].

The high specificity of these alkenones as haptophyte biomarkers [Marlowe *et al.*, 1990], their high concentrations in marine sediments [Rosell-Melé *et al.*, 1995b; Summerhayes *et al.*, 1995; Villanueva *et al.*, 1997a; Müller *et al.*, 1997], the resistance of the $U^{K'}_{37}$ ratio to biodegradation [Teece *et al.*, 1998] and oxidative diagenesis [Prahel *et al.*, 1989], and the widespread abundance of alkenone-synthesizing organisms, namely, *E. huxleyi* or *Gephyrocapsa* sp. [Conte and Eglinton, 1993; Okada and Honjo, 1973], in the marine system [Brassell, 1993] have promoted the increasing use of these alkenones for SST estimation.

Furthermore, the analysis of these C_{37} alkenones in sedimentary samples does not require sophisticated instrumentation in most cases. They are usually major components of the solvent extracts of sediments, and their low volatility facilitates gas chromatographic separation from most sedimentary lipids. Therefore they are currently analyzed by gas chromatography (GC) with flame ionization detection (FID) after some (sometimes none) clean up of the sample extracts.

The analytical work is further facilitated by the fact that the temperature estimate depends on the measurement of the relative proportion of two compounds of similar physical properties. As evidenced in the experimental procedures of most paleoceanographic studies using this method, determination of the linear response equations for absolute C_{37} alkenone concentrations is avoided because both compounds are determined using the same quantitation criteria. In most cases this approach may be correct, but it must also be consistent with the basic principles of the techniques used for analysis. Some analytical requirements concerning sample clean up [Villanueva *et al.*, 1997b] and instrumental measurement [Villanueva and Grimalt, 1997; Rosell-Melé *et al.*, 1995a] have been considered in previous studies.

To this end, adsorption of these alkenones in the chromatographic system and, among them, higher adsorption of $C_{37:3}$ than $C_{37:2}$ have been reported [Villanueva and Grimalt, 1997]. These effects may be relevant for measurements near detection limit which may severely distort the $U^{K'}_{37}$ ratio. However, even at concentrations higher than detection limit, the temperature estimates may be altered by the influence of this threshold. These types of problems are, in fact, common to all studies involving GC determination of trace compounds [Wells, 1993; Troost and Olavesen, 1996]. Surprisingly, despite the already abundant literature on $U^{K'}_{37}$ paleotemperature estimates, no evaluation of the restrictions derived from detection limits has been reported to date.

The present study provides a quantitative description of this problem which may lead to large SST biases in paleoceanographic studies. As it will be shown in the discussion, the paleoclimatic significance of some previously reported results on $U^{K'}_{37}$ -SST should be reconsidered in the light of these analytical deviations.

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2. Experimental Procedure

2.1. Materials

Residue analysis iso-octane was from Merck (Darmstadt, FRG). The synthetic alkenone standards, heptatriaconta-15*E*,22*E*-dien-2-one and heptatriaconta-8*E*,15*E*,22*E*-trien-2-one, were kindly provided by James Maxwell (Environmental and Analytical Chemistry Section, University of Bristol) [Rechka and Maxwell, 1988].

2.2. Gas Chromatography

GC analyses were performed using a Varian STAR 3400 CX (Varian, California) equipped with a septum-programmable injector and a FID. Alkenones were separated using a 50 m x 0.32 mm inside diameter 0.12 µm film thickness CPSIL-5 CB column (Chrompack, Middleburg, Netherlands). Hydrogen was the carrier gas (50 cm s⁻¹). Oven temperature was programmed from 90°C (held 1 min) to 140°C at 20°C min⁻¹, then to 280°C at 6°C min⁻¹ (held 25 min), and finally to 320°C at 10°C min⁻¹ (held 6 min). The injector was used in splitless mode and programmed from 90°C (held 0.3 min) to 320°C at 200°C min⁻¹ (final holding time 55 min). Detector temperature was 320°C.

3. Results

3.1. Linear Response Factor Equations

One basic requirement of analytical instrumentation employed for quantitative work is the linearity between signal area *S* and analyte concentration *C*:

$$S = aC + b, \quad (2)$$

where *a*, slope, and *b*, intercept, are constants for a concentration range.

This relationship must be fulfilled for both compounds included in the U^K₃₇ index, C_{37:2} and C_{37:3}.

$$S_{37:2} = a_{37:2}C_{37:2} + b_{37:2}, \quad (3)$$

$$S_{37:3} = a_{37:3}C_{37:3} + b_{37:3}, \quad (4)$$

Several representative examples of these equations, which were obtained from GC analysis of several solutions prepared with the standards provided by the University of Bristol, are shown in Figure 1. The slopes, *a*_{37:2} and *a*_{37:3}, are similar, consistent with the universal sensitivity and general nonselectivity of FID as well as the close chemical composition of both alkenones. The intercepts reflect the differential adsorption of both alkenones in the gas chromatographic system. They have negative values and $|b_{37:3}| > |b_{37:2}|$ since C_{37:3} has higher adsorption than C_{37:2} [Villanueva and Grimalt, 1997]. This differential adsorption effect does not depend on the mode of injector, e.g., on column, splitless, and SPI, used for the analyses. The different slope and intercept constants shown in Figure 1 are simple examples of values encountered in capillary GC systems run under different conditions; other constants may be observed upon analysis with other instrumental set ups, e.g., column properties.

The detection limit threshold can be defined from these intercept values, e.g., 3 times the standard deviation of the blank signal [Miller, 1988]. The use of the intercept instead of detection limit provides a more meaningful value in terms of chromatographic performance. The intercepts can be related as follows:

$$r_b = b_{37:3}/b_{37:2}. \quad (5)$$

This ratio is constant and independent of the concentrations of the alkenones, C_{37:2} and C_{37:3}. The values shown in Figure 1 correspond to one possible common case in which *r_b* ≈ 10; in other cases it may approach 2.5 [Villanueva and Grimalt, 1997] or other values. These values may change according to the properties of the capillary column as it deteriorates with time. Among other factors, GC columns accumulate small nonvolatile residues present in the extracts that may modify the adsorption effects. However, these changes are normally slow, so that adsorption remains constant for long operational periods if the GC is run under stationary conditions, e.g., in the absence of significant changes in column resolution and selectivity or detector sensitivity.

The ratio will be higher than 1.0 owing to the higher adsorption of C_{37:3} ($|b_{37:3}| > |b_{37:2}|$). However, there is no mathematical restriction for the use of this ratio and the equations

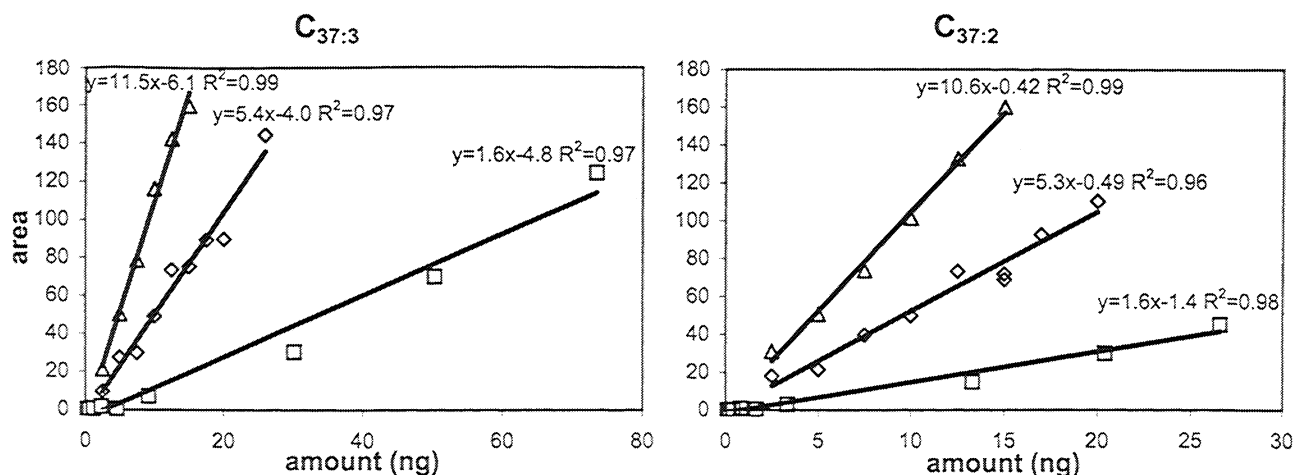


Figure 1. Representative examples of the response factor linear equations obtained in the gas chromatographic analysis of the C_{37:3} and C_{37:2} alkenones. Note that for each pair of equations (triangles, diamonds and squares) the slopes are similar and the intercept of C_{37:3} is higher than of C_{37:2} (in absolute values). The constant values merely illustrate currently found cases; other figures are possible.

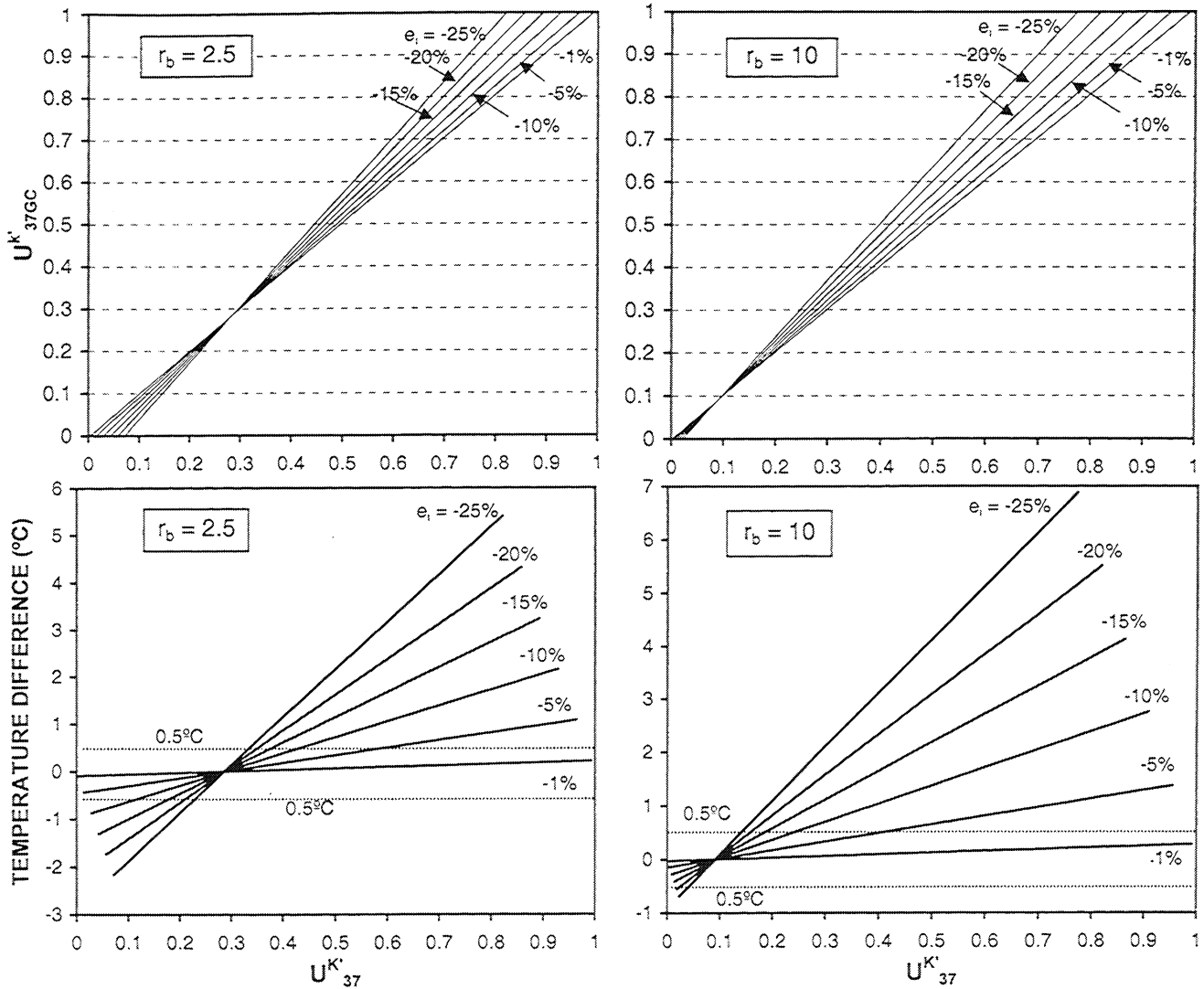


Figure 2. Changes in (top panel) U'_{37} index and (bottom panel) temperature differences between true values and GC measurements at various intercept errors, e_i (equation (8)). Here r_b is the ratio between the intercepts of the two alkenones (equation (5)).

described below in a hypothetical case of higher adsorption of C_{37:2} ($r_b < 1$).

3.2 Temperature Errors at Varying U'_{37}

U'_{37} is theoretically defined as in (1). However, the instrumental determination of this index is performed from direct measurement of signal areas, U'_{37GC} . From (3) and (4),

$$U'_{37GC} = S_{37:2}/(S_{37:2} + S_{37:3}) = (a_{37:2}C_{37:2} + b_{37:2})/(a_{37:2}C_{37:2} + b_{37:2} + a_{37:3}C_{37:3} + b_{37:3}), \quad (6)$$

Since $a_{37:2} \cong a_{37:3}$, a simplified equation for the distortion effects associated to $b_{37:3}$ and $b_{37:2}$ can be developed:

$$U'_{37GC} = (a_{37:3}C_{37:2} + b_{37:2})/(a_{37:3}C_{37:2} + b_{37:2} + a_{37:3}C_{37:3} + b_{37:3}), \quad (7)$$

and $b_{37:3}$ and $b_{37:2}$ can be scaled to the signal of C_{37:3} and C_{37:2} using an error index:

$$e_i = 100(b_{37:3} + b_{37:2})/(a_{37:3}C_{37:3} + a_{37:3}C_{37:2}), \quad (8)$$

where e_i has negative values since $b_{37:3}$ and $b_{37:2}$ are negative.

Combination of (1), (5), (7) and (8) affords an expression relating U'_{37} and U'_{37GC} .

$$U'_{37GC} = (U'_{37}100(r_b + 1) + e_i)/[(r_b + 1)(100 + e_i)], \quad (9)$$

This equation involves some restrictions in terms of the U'_{37} range that can be measured as a consequence of the analytical conditions of the instrument.

$$\text{Upper value } (U'_{37GC} = 1): U'_{37} = 1 + (e_i/100)\{r_b/(r_b + 1)\}, \quad (10)$$

$$\text{Lower value } (U'_{37GC} = 0): U'_{37} = -e_i/[100(r_b + 1)], \quad (11)$$

The difference between U'_{37GC} and U'_{37} describes the error due to the intercepts of the response factor linear equations. This difference can be transformed into temperature units using the slope values of the calibration curves described in the literature, e.g., 0.033 [Prah and Wakeham, 1987].

$$E = (U'_{37GC} - U'_{37})/0.033, \quad (12)$$

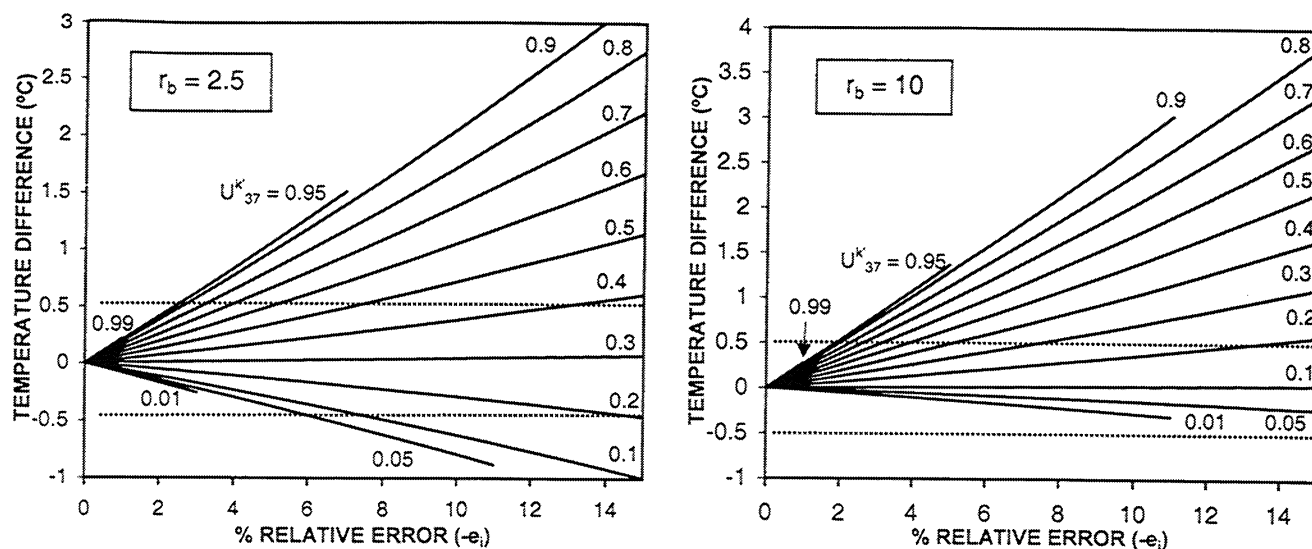


Figure 3. Temperature differences between true and GC measured U^K_{37} index in the analysis of mixtures of uniform $C_{37:2}/C_{37:3}$ ratios. r_b is the ratio between the intercepts of the two alkenones (equation (5)). Note that e_i is defined from negative values but the absolute value is indicated in abscissas.

The SST errors derived from this equation are summarized in Figure 2 for an e_i range between -1 and -25%. As expected, the error increases at higher $|e_i|$ values. There is also a dependence from U^K_{37} . Higher errors are encountered at higher U^K_{37} . As expected, the U^K_{37} -derived error also depends on r_b . High r_b values (higher differential adsorption of the triunsaturated

alkenone) result into higher errors. Note that SST errors are also encountered at the lower end of the U^K_{37} range as consequence of the adsorption of the diunsaturated alkenone. Again, the influence of the adsorption of this compound depends on r_b .

Thus, at $e_i = -5\%$, errors higher than 0.5°C can be encountered for most of the U^K_{37} range ($U^K_{37} > 0.4$ for $r_b = 10$ or $U^K_{37} > 0.6$

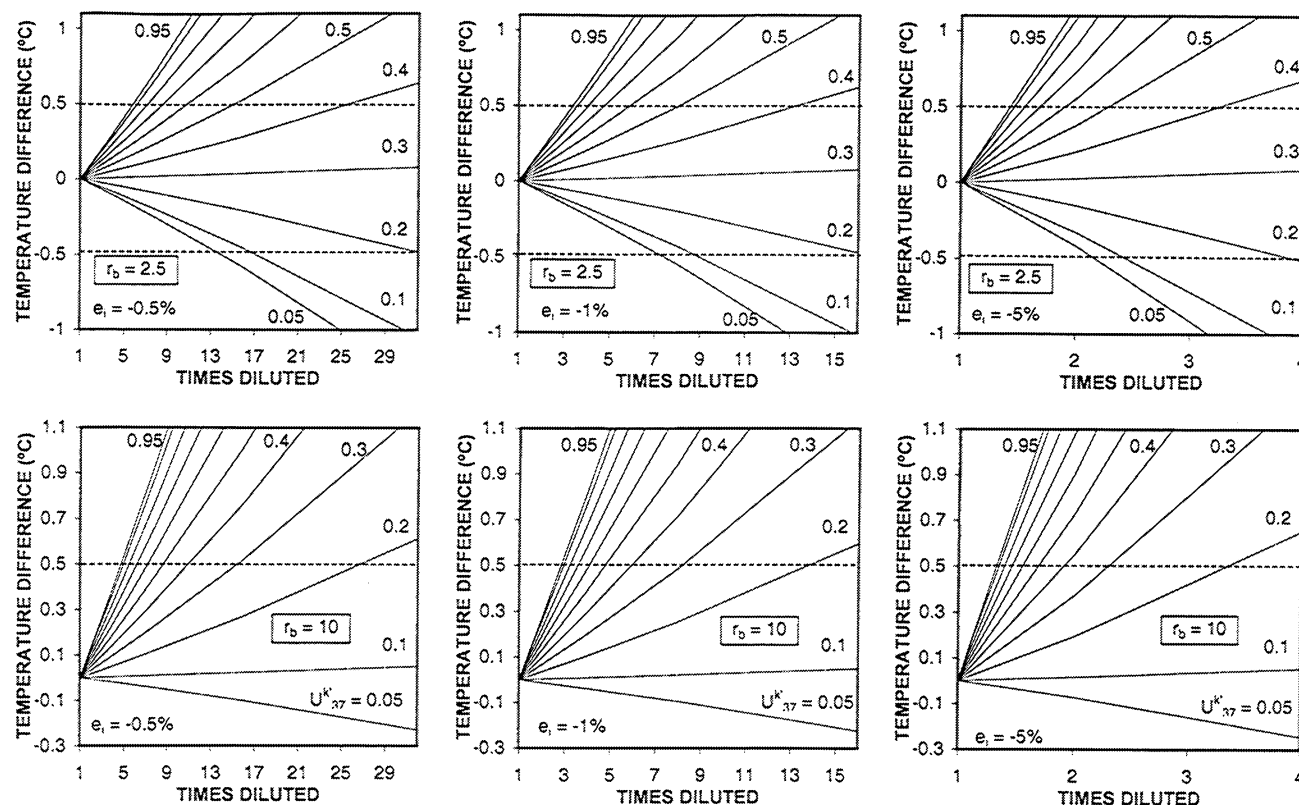


Figure 4. Temperature differences for increasing extract dilution. Here r_b is the ratio between the intercepts of the two alkenones (equation (5)). Dilution factors involving SST differences $> 0.5^\circ\text{C}$ are not acceptable.

for $r_b = 2.5$; Figure 2). Above these $|e_i|$ values the range of accurate measurement of $U^{K'}_{37}$ is even smaller, e.g., at $e_i = -10\%$, only $U^{K'}_{37}$ values between 0.15 and 0.4 for $r_b = 2.5$ or between 0.02 and 0.23 for $r_b = 10$ give errors lower than 0.5°C .

3.3 Temperature Errors at Constant $U^{K'}_{37}$

The influence of the intercepts at constant $U^{K'}_{37}$ values can also be evaluated from combination of (9) and (12). At $|e_i| > |5\%|$, large errors in SST determinations ($>0.5^\circ\text{C}$) are observed for $U^{K'}_{37} > 0.6$ or > 0.4 at $r_b = 2.5$ or 10, respectively (Figure 3). As shown in figure 3, accurate measurements of $U^{K'}_{37}$ at values higher than 0.95 can only be achieved if $|e_i| \leq |2\%|$. In contrast, low $U^{K'}_{37}$ indices, e.g., lower than 0.05, can be determined at $|e_i|$ higher than this limit since $C_{37:3}$, the alkenone with higher adsorption, has only a minor contribution at these index values. $U^{K'}_{37}$ measurements at values of 0.99 can only be determined for $|e_i| \leq |1\%|$.

4. Discussion

4.1 Temperature Errors

The errors described by the above equations involve major restrictions in terms of analytical performance for the measurement of reliable $U^{K'}_{37}$. These restrictions are severe at values near the cold and warm limits, particularly at warm temperatures where this index approaches 1.0.

These results derive from the straightforward application of the linear equations resulting from quantitative GC analysis and the observed higher adsorption of C_{37:3} than C_{37:2} [Villanueva and Grimalt, 1997]. The same equations are applicable in a hypothetical case of higher adsorption of C_{37:2} than C_{37:3}. In that case, the equations proposed in the present study would give rise to figures exhibiting symmetrical plots as those in Figures 2 and 3 and higher SST deviations at low $U^{K'}_{37}$ values.

By no means can the errors described above be related to an improper use of the technique. They must be considered as analytical restrictions due to the influence of the intercept. In the case of $U^{K'}_{37}$ this condition might not appear to apply because the relationship is based on a ratio and not on absolute alkenone concentrations. However, the $U^{K'}_{37}$ ratio is only valid as far as it is based on true concentration measurements.

Unfortunately, analytical-grade standards for the C_{37:3} and C_{37:2} are not easy to obtain. Thus current $U^{K'}_{37}$ analysts will have difficulties for the determination of e_i and r_b in their GC system. However, this aspect does not prevent checking for possible performance problems related to these adsorption effects. The most simple and immediate way is dilution of the extracts, reinjection in the GC, system and comparison of both $U^{K'}_{37}$ indices.

Equations. (8) and (9) can be used for the calculation of the SST error as a consequence of progressive sample dilution. Since $b_{37:3}$ and $b_{37:2}$ are independent of C_{37:3} and C_{37:2}, the dilution factor x can be represented from the ratio between e_i and C₃₇ concentrations. Subtraction of the signal ($U^{K'}_{37\text{GC}}$) from the undiluted sample extract and the extract diluted x times provides the following temperature error:

$$E = 100e_i (1 - x) [U^{K'}_{37} (r_b + 1) - 1] / \{0.033(r_b + 1) / 10000 + 100(1+x) e_i + x e_i^2\} \quad (13)$$

where $x = 1$; no dilution, $x = 2$ is dilution to double volume, and so forth.

Obviously, no change in $U^{K'}_{37}$ should be observed if the analytical measurements are free from intercept influence. In

practical terms, this condition is better expressed by reference to the 0.5°C threshold (Figure 4). As indicated above, the range of correct SST- $U^{K'}_{37}$ determination may vary significantly depending on $U^{K'}_{37}$ values. At relative errors of $e_i = -0.5\%$ and intercept ratios of $r_b = 2.5$, mixtures of alkenones in the 0.05-0.5 $U^{K'}_{37}$ range can be diluted up to 14 times. The alkenone mixtures of higher $U^{K'}_{37}$ can be diluted less, e.g., up to 11 and 5 times for $U^{K'}_{37} = 0.6$ and 0.95, respectively.

SST errors increase substantially with dilution if the GC system has high intercept errors. Thus, at $e_i = -1\%$ and intercept ratios of $r_b = 2.5$ the mixtures in the 0.05-0.5 $U^{K'}_{37}$ range can be diluted up to 7 times to remain within the 0.5°C SST threshold. The alkenone mixtures of $U^{K'}_{37} = 0.6$ and 0.95 can be diluted up to 6 and 3 times, respectively. At $e_i = -5\%$ the dilution ratio may be up to 2 for the mixtures with $U^{K'}_{37} = 0.05-0.5$ and < 2 for $U^{K'}_{37} > 0.5$. Similar results are obtained at higher r_b (e.g., $r_b = 10$;

Table 1. Selected Data From Hoefs *et al.* [1998] and Prahl *et al.* [1989] Showing the Consistency Between Estimated SST Differences in Oxidized (ox) and Unoxidized (unox) Sediments and Low C_{37:3} Concentrations Close to the Limit of Detection.

	C _{37:3} , μg g ⁻¹ dry wt	C _{37:2} , μg g ⁻¹ dry wt	U ^{K'} ₃₇	SST °C	ox-unox SST difference, °C
<i>Hoefs et al.</i> [1998]					
Free lipids					
Late Pliocene					
Oxidized	0.06	0.23	0.79	22.2	0.7
Unoxidized	3.06	10.3	0.77	21.5	
Early Pliocene					
Oxidized	0.02	0.26	0.93	26.2	1.9
Unoxidized	2.43	15.45	0.86	24.3	
Late Miocene					
Oxidized	0.01	0.12	0.92	26.0	1.4
Unoxidized	8.49	58.9	0.87	24.6	
Bound lipids					
Late Pliocene					
Oxidized	0.20	0.86	0.81	22.7	0.4
Unoxidized	0.59	2.32	0.80	22.3	
Early Pliocene					
Oxidized	n.d. ^a	0.06	1	28.3	2.5
Unoxidized	0.32	3.56	0.92	25.8	
Late Miocene					
Oxidized	n.d. ^a	0.02	1	28.3	3.5
Unoxidized	0.39	2.90	0.88	24.8	
<i>Prahl et al.</i> [1989]					
Late Quaternary					
Core 86P5					
Oxidized	0.26	0.68	0.72	19.9	0.6
Unoxidized	2.8	6.8	0.70	19.3	
Core 86P25					
Oxidized	0.34	0.86	0.72	19.9	0.3
Unoxidized	2.5	6.2	0.71	19.6	

^a For n.d., Hoefs *et al.* [1998] report these concentrations as not detected, and these authors assume a value of zero for the calculation of the $U^{K'}_{37}$ index and temperature.

Figure 4). The main difference concerns higher errors at higher $U_{37}^{K'}$ ratios, which is reflected in lower dilution potentials to avoid SST deviations $> 0.5^\circ\text{C}$.

These results are useful for defining a criterion for good analytical performance based on a dilution test. Alkenone extracts providing unchanged $U_{37}^{K'}$ ratios (SST error $< 0.5^\circ\text{C}$) upon 3 times dilution could be reasonably accepted as indicative of reliable measurements. In the case that this condition cannot be fulfilled, changes leading to the introduction of higher alkenone amounts into the GC system should be considered. Among others, these could involve extraction of larger sediment amounts, concentration of the alkenone solutions, or injection of larger volumes.

4.2 Critical Evaluation of Previously Reported $U_{37}^{K'}$ Data

Equations (9) and (12) may also be used for the evaluation of the possible dilution errors in paleoceanographic studies. For example, large variations in C_{37} alkenone concentration have been reported in a study of Pliocene and Miocene Madeira Abyssal Plain turbidites [Hoefs et al., 1998]. The significant changes in $U_{37}^{K'}$ between oxidized (low concentration) and unoxidized (high concentration) sediment sections were attributed to postdepositional alkenone degradation. These results contrasted with those of a previous study in similar turbidites [Prah et al., 1989] in which no changes in $U_{37}^{K'}$ were observed despite differences in the C_{37} alkenone concentration between oxidized and unoxidized layers.

Although the timescales involved are vastly different, the results of Hoefs et al. [1998] were also in disagreement with laboratory experiments of C_{37} alkenone microbial degradation under oxic and anoxic (sulphate reduction and methanogenesis) conditions, which again failed to show significant changes in $U_{37}^{K'}$ [Teece et al., 1995; 1998].

A summary of C_{37} alkenone concentrations, $U_{37}^{K'}$, and temperature measurements reported in the study of Hoefs et al. [1998] is shown in Table 1. These data show a correlation between alkenone-based temperatures and alkenone concentrations in the oxidized versus unoxidized sections. In some cases, the $C_{37.3}$ concentrations in the oxidized samples are at the limit of detection (reported as not detected by Hoefs et al. [1998]), and the temperature differences are higher as $C_{37.3}$ concentration approaches this limit (Figure 5).

In agreement with the calculations discussed above, the observed temperature offsets are in the same direction as and of similar magnitude to the temperature differences predicted by (8) and (9). Differences of $2.5^\circ\text{--}3.5^\circ\text{C}$ warmer are similar to the predicted values at $|e_1| = 12\%$ or higher. These are the samples with lowest $C_{37.3}$ concentrations in Table 1. The intermediate values, $1.4^\circ\text{--}1.9^\circ\text{C}$, are in correspondence with $|e_1|$ between 7 and 8% ($C_{37.3} = 0.01\text{--}0.02 \mu\text{g g}^{-1}$ in Table 1), and finally, the lower temperature deviations, $0.4^\circ\text{--}0.7^\circ\text{C}$, agree with $|e_1|$ of the order of 3–4% ($C_{37.3} = 0.06\text{--}0.2 \mu\text{g g}^{-1}$ in Table 1).

In contrast, the lack of significant temperature differences between unoxidized and oxidized samples described in the study of Prah et al. [1989] (Table 1 and Figure 5) is consistent with the considerably higher abundance of $C_{37.3}$ alkenone concentrations in the samples analyzed in this study ($0.25 \mu\text{g g}^{-1}$ or more in the oxidized samples). In summary, irrespective of the possible differential loss of the $C_{37.3}$ alkenone when sediments are highly oxidized, the divergent results of the two studies likely reflect a case of measurement near the limit of detection in the samples considered by Hoefs et al. [1998].

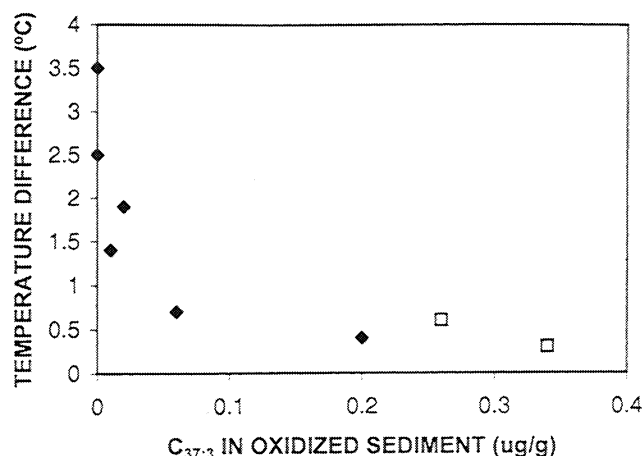


Figure 5. Reported temperature differences between oxidized and nonoxidized sediments of Hoefs et al. [1998] (diamonds) and Prah et al. [1989] (squares) versus $C_{37.3}$ in the oxidized sediment. Higher temperature differences are observed at low $C_{37.3}$. Note, however, that the concentration threshold below which high temperature differences are observed only concerns this specific example. Other thresholds will be observed upon analysis of different sediment amounts.

5. Conclusions

Major errors are produced in the determination of $U_{37}^{K'}$ paleotemperatures at GC conditions approaching the detection limit of the alkenones, particularly for $C_{37.3}$. These errors are particularly relevant at low C_{37} alkenone concentrations and may be described using the intercept of the linear response factor equation for the diunsaturated and triunsaturated compounds that are used to derive the $U_{37}^{K'}$ index. SST deviations are already significant (errors $> 0.5^\circ\text{C}$) at e_1 ratios of $|10\%|$ for $U_{37}^{K'}$ values higher than 0.6.

The SST errors are more relevant at the cold and warm ends of the $U_{37}^{K'}$ values, particularly at the warmer end since $C_{37.3}$ usually shows higher intercepts than $C_{37.2}$. Thus accurate measurements of $U_{37}^{K'}$ values of 0.95 or 0.99 require detection limit errors equal or lower than $|2\%|$ or $|1\%|$, respectively.

The potential SST errors reported here are generated under optimal GC conditions. In light of these results, users should check for the possible influence of these analytical problems by dilution of their $U_{37}^{K'}$ extracts, GC analysis, and calculation of the SST deviations. Reliable measurements are obtained if the SST difference is $< 0.5^\circ\text{C}$ for a dilution factor of 3.

The results of the present study prompt a reinterpretation of previously reported data on changes of $U_{37}^{K'}$ values between oxidized and unoxidized sediments [Hoefs et al., 1998]. The C_{37} alkenone concentrations in the two types of samples and the obvious proximity to the $C_{37.3}$ detection limit of the reported data suggest that the observed $U_{37}^{K'}$ temperature discrepancies simply reflect deviations due to the GC measurements instead of effects of selective preservation.

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