



The upper end of the $U_{37}^{K'}$ temperature calibration revisited

Carles Pelejero and Eva Calvo

Research School of Earth Sciences, The Australian National University, Canberra, ACT 0200, Australia

*Petroleum and Marine Division, Geosciences Australia, GPO Box 378, Canberra, ACT 2601, Australia.
(carles.pelejero@anu.edu.au; eva.calvo@anu.edu.au)*

[1] Being able to decipher paleo sea surface temperatures for warm oceanic waters is of the utmost importance to further evaluate the role of the tropics in global climate change. The $U_{37}^{K'}$ index is one of such paleothermometers, although the warm range of temperatures often poses serious analytical challenges. This paper discusses and reviews several important aspects of the $U_{37}^{K'}$ index calibration for waters warmer than 26° – 27° C. Amongst them, insights into the possible existence of a limit above which the $U_{37}^{K'}$ index is not able to accurately record temperature variations are presented. Some warnings are also given on the misleading practice and expected consequences of reporting $U_{37}^{K'}$ index values of unity in the cases when abundances of the minor triunsaturated alkenone below detection limit are encountered. Future directions toward an improved knowledge of the behaviour of the $U_{37}^{K'}$ calibration for warm waters are suggested.

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1. Introduction

[2] Since the initial definition by *Brassell et al.* [1986], the $U_{37}^{K'}$ index has become an invaluable tool for paleo-sea surface temperature (SST) reconstructions for ocean basins world wide. A large expansion in the practical application is evident when considering the exponential increase in the number of publications per year based on this index [*Eglinton et al.*, 2001]. The increasing number of paleoceanographic teams using this tool has even prompted the performance of an inter-laboratory calibration exercise involving 24 research groups [*Rosell-Melé et al.*, 2001].

[3] However, after one and a half decades of $U_{37}^{K'}$ reconstructions, there are still many oceanic areas for which data on this index has not been generated. The least studied areas tend to be the coldest and warmest waters of the oceans, with most of the $U_{37}^{K'}$ reconstructions focused in the mid range of water temperatures. For instance, the colder waters of the Southern Ocean have only been partially studied [e.g., *Ikehara et al.*, 1997], and many equatorial oceanic basins are still pending evaluation. This apparent lack of information can partially be explained by the low alkenone content of sediments beneath these areas. More importantly, the scepticism in the applicability of the $U_{37}^{K'}$ index

for extreme cold and warm temperatures has prevented researchers approaching these “difficult” oceanic realms. However, determinations of temperatures at both extremes are of the utmost importance in climate change research.

[4] Concerning the warmest temperatures, the role of the tropics as participants and drivers of long-term climate change has only very recently been recognised [e.g., *Cane*, 1998; *Kerr*, 2001; *Lea*, 2002]. This has been possible after the development of new temperature proxies and their application to the worlds warmest areas [e.g., *Beck et al.*, 1997; *Lea et al.*, 2000], which have resulted in larger sensitivities and earlier responses of the tropics to climate change than previously reported [*CLIMAP*, 1976].

[5] The present paper reviews and discusses the progress that has been made into the assessment of $U_{37}^{K'}$ - SSTs for warm waters. Evaluation of the strengths and weaknesses of this index, based on current calibrations, as well as theoretical and analytical considerations are presented. For simplicity and due to the general absence of the tetraunsaturated C_{37} alkenone ($C_{37:4}$) in warm waters, only the alkenones with three and two unsaturations ($C_{37:3}$ and $C_{37:2}$, respectively) will be considered in this work. We will refer to our index as $U_{37}^{K'}$, following the simplification by *Prahl et al.* [1988] ($U_{37}^{K'} = C_{37:2}/(C_{37:2} + C_{37:3})$) of the original U_{37}^K definition including $C_{37:4}$ by *Brassell et al.* [1986] ($U_{37}^K = (C_{37:2} - C_{37:4})/(C_{37:2} + C_{37:3} + C_{37:4})$).

2. Discussion

2.1. Theoretical Considerations When Approaching to $U_{37}^{K'}$ Values Closer to Unity

[6] A common characteristic of any reconstruction of temperatures at the warm-end of the $U_{37}^{K'}$ index is its inherent challenge in the determination of $C_{37:3}$ and $C_{37:2}$ alkenones. When analysed by Gas Chromatography (GC), optimum dilutions and capillary columns have to be selected in order to obtain a detectable signal of $C_{37:3}$ (usually present at very low concentrations) without overloading the chromatographic column with $C_{37:2}$ (usually present at very high concentrations). Apart from this chal-

lenge, $U_{37}^{K'}$ values closer to 1 are feasible, and have been reported for a variety of sites, including paleotemperature reconstructions [e.g., *Cayre and Bard*, 1999; *Rühlemann et al.*, 1999; *Kienast et al.*, 2001], core-top calibrations [e.g., *Pelejero and Grimalt*, 1997; *Sonzogni et al.*, 1997a, 1997b] and particulate matter [e.g., *Prahl and Wakeham*, 1987; *Goñi et al.*, 2001; *Harada et al.*, 2001].

[7] This inherent analytical problem can make it impossible to detect the minor $C_{37:3}$ constituent. In this case, it is tempting to assume an absence of this compound and thus derive a $U_{37}^{K'}$ value of 1, as has been published on several occasions [*Sikes et al.*, 1991; *Hoefs et al.*, 1998; *Sonzogni et al.*, 1998; *Harada et al.*, 2001; *Bentaleb et al.*, 2002]. Under these circumstances, any $C_{37:3}$ absence should be more appropriately reported as *undetected*, with no further $U_{37}^{K'}$ assignment. Obviously, any analytical determination is subject to detection limits below which no quantification is possible, and a *true zero* value cannot be ensured. On the other hand, arbitrary assignments of zero for C_{37} alkenone concentrations could lead to erroneous $U_{37}^{K'}$ index values. This is also true for the hypothetical case of an analysis with undetectable concentrations of neither $C_{37:3}$ nor $C_{37:2}$, resulting in $U_{37}^{K'} = \infty$. To avoid misinterpretations, we thus recommend not deriving $U_{37}^{K'}$ index values of unity in the cases where the $C_{37:3}$ homologue cannot be quantified.

[8] A water column study with a wide oceanographic coverage ranging from cold New Zealand coastal waters to the warm waters of the South China Sea comparing $U_{37}^{K'}$ values to in situ measured temperatures has recently been carried out [*Bentaleb et al.*, 2002]. This extensive work, which also compared alkenone data to coccolith distributions, failed to detect $C_{37:3}$ for a large number of samples corresponding to the warmest surface waters of the Western Pacific ocean. This absence led the authors to derive $U_{37}^{K'}$ index values of unity for 24 samples out of a total of 46. All such unity $U_{37}^{K'}$ values were included in their linear correlation computations leading the authors to conclude that $U_{37}^{K'}$ cannot be used as an accurate paleothermometer above 26.4°C. This specific value corresponds to the in situ measured temperature of a water sample where undetected amounts of $C_{37:3}$ were

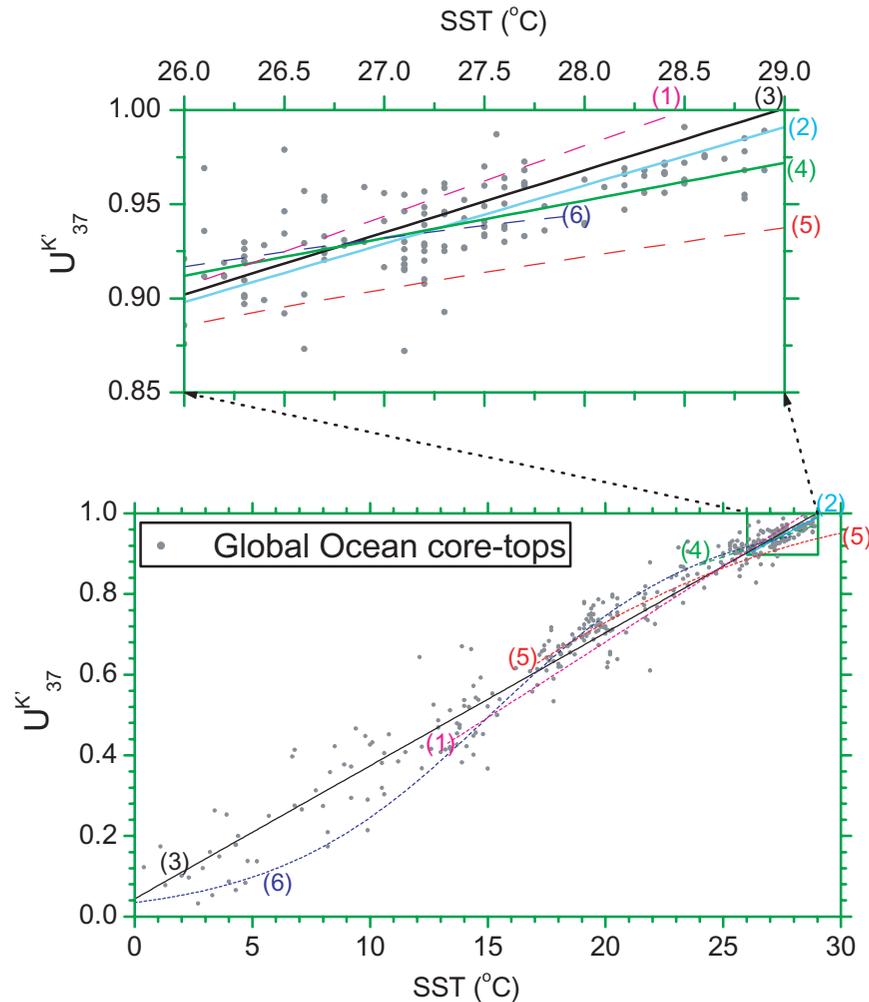


Figure 1. (bottom) $U_{37}^{K'}$ versus temperature fitted curves discussed in the text plotted in comparison to the global ocean core top calibration data set (grey circles) from Müller *et al.* [1998]. (1) Water samples linear curve fitting after Bentaleb *et al.* [2002] without considering $U_{37}^{K'}$ values of unity, $U_{37}^{K'} = 0.037T - 0.069$ ($R = 0.940$). (2) Core top calibration for the South China Sea, corresponding to annual averaged temperatures at 0–30 m depth, $U_{37}^{K'} = 0.031T - 0.092$, ($R = 0.926$ [Pelejero and Grimalt, 1997]). (3) Global ocean core top calibration linear fit for surface annual temperatures, $U_{37}^{K'} = 0.033T - 0.044$, ($R = 0.979$ [Müller *et al.*, 1998]). (4) Core top calibration for the Indian Ocean for temperatures above 24°C, $U_{37}^{K'} = 0.020T - 0.392$, ($R = 0.843$ [Sonzogni *et al.*, 1997b]). (5) Gulf of California sediment traps non linear fit after Goñi *et al.* [2001] ($U_{37}^{K'} = -0.295 + 0.0706T - 0.000969T^2$; $R = 0.970$). (6) Water samples non linear fit from Sikes and Volkman [1993] which includes data from Prahl and Wakeham [1987] ($U_{37}^{K'} = 1 / \{1 + e^{-0.22(SST-15.1)}\}$). (top) Zoomed upper end section of temperatures with the same suit of data values and fits. Dashed lines correspond to water samples or particulate matter while solid lines relate to core top calibrations.

encountered and a value of $U_{37}^{K'} = 1$ was erroneously ascribed. We have reevaluated all SST versus $U_{37}^{K'}$ data pairs presented in this work (omitting any $U_{37}^{K'} = 1$) and found a linear regression for $U_{37}^{K'} = 0.037 \text{ SST} - 0.069$ ($R = 0.940$). This equation, which includes $U_{37}^{K'}$ values for a range of temperatures between 13.3 and 29.1°C matches very closely the widely used core top calibration from Müller *et al.*

[1998], particularly for the warm-end of temperatures (Line 1 versus Line 3 in Figure 1, respectively). Thus, when excluding all $U_{37}^{K'} = 1$ values originally included in the regressions of Bentaleb *et al.* [2002], the robustness and suitability of the $U_{37}^{K'}$ index as a paleothermometer for waters warmer than 26.4°C to, at least, 29.1°C, is re-established. This latter temperature value corresponds to a

water sample included in this study for which $C_{37:3}$ concentrations indeed could be quantified.

2.2. Is There An Upper Limit for the $U_{37}^{K'}$ -SST Calibration?

[9] We are interested in testing if there is indeed an upper limit for the $U_{37}^{K'}$ -SST calibration where this method is not able to provide SSTs. Because most equations that translate $U_{37}^{K'}$ values into SSTs are linear regressions [e.g., *Prahl and Wakeham, 1987; Prahl et al., 1988; Müller et al., 1998*], a first approximation might be to extrapolate the existing equations to obtain an “SST maximum” (SST_{\max}) for a hypothetical $U_{37}^{K'} = 1$.

[10] However, this approach might be too simplistic for several reasons. First because every single equation will give a different value: For example, SST_{\max} could be taken as 29.0°C when considering *Müller et al. [1998]* global core-top calibration ($U_{37}^{K'} = 0.033 \text{ SST} + 0.044$) while SST_{\max} could reach 30.4°C after *Sonzogni et al. [1997b]* equation ($U_{37}^{K'} = 0.020 \text{ SST} + 0.392$ for $SST > 24^\circ\text{C}$). But more importantly because it still has not been demonstrated whether a linear regression applies to the whole range of SST (see discussion below). Extrapolating the existing equations to obtain an “SST maximum” (SST_{\max}) for a hypothetical $U_{37}^{K'} = 1$ is not a good solution.

[11] A more cautious approach for the assessment of the actual limitation of measuring SSTs might be to consider the warmest data point included in the published calibrations. In relation to core-top calibrations and after the extensive compilation by *Müller et al. [1998]*, SST_{\max} could be taken as 28.9°C corresponding to the $U_{37}^{K'}$ determination of two cores from the Indian Ocean (MD90950 and MD77195) [*Sonzogni et al., 1997b*]. However, taking particulate matter into consideration, it is remarkable that a recent study has been able to measure $U_{37}^{K'}$ for samples which correspond to temperatures up to 32.4°C [*Goñi et al., 2001*].

[12] The most significant issue in assigning an upper limit of SSTs relates to the actual shape of the calibration curve. Several studies have speculated about deviations from linearity and/or flattening of linear regression slopes toward the cold

and warm ends of the temperature range [e.g., *Sikes and Volkman, 1993; Volkman et al., 1995; Sawada et al., 1996; Sonzogni et al., 1997a, 1997b; Conte et al., 1998; Conte et al., 2001; Goñi et al., 2001*]. Amongst the non linear relationships attempted, some polynomial [e.g., *Conte et al., 1998, 2001; Goñi et al., 2001; Sicre et al., 2002*] and exponential [e.g., *Sikes and Volkman, 1993; Sawada et al., 1996*] fits have been tested (Figure 1). Such non-linear relationships further stress the difficulty in defining an actual limit for SST determination, particularly when considering the example equation suggested by *Sikes and Volkman [1993]* ($U_{37}^{K'} = 1/\{1 + e^{-0.22(\text{SST}-15.1)}\}$). This function approaches $U_{37}^{K'} = 1$ asymptotically at the warm-end of the temperature range (Figure 2). In case this equation would describe the global behaviour of $U_{37}^{K'}$ at the warmest waters, no theoretical limit of temperatures could be derived. Indeed, the recent study by *Goñi et al. [2001]*, which includes particulate matter from waters up to 32.4°C, adopts a similar fit and matches very closely the exponential curve of *Sikes and Volkman [1993]* (Figure 2). However, we stress that these two examples should be taken only to illustrate the difficulties in defining any upper limit of the $U_{37}^{K'}$ calibration at the present stage. The upper temperature of the $U_{37}^{K'}$ calibration remains undefined and may extend beyond values outlined above.

2.3. Core Top Calibrations for Warm Temperatures

[13] Several attempts to calibrate $U_{37}^{K'}$ versus SST at the upper-end have been performed based on core tops. The most extensive are a series of studies covering waters from the Indian Ocean [*Sonzogni et al., 1997a, 1997b*] and the South China Sea [*Pelejero and Grimalt, 1997*]. The Indian Ocean calibrations indicate a flattening of the linear relationship with slope values of 0.020 ($R = 0.843$ [*Sonzogni et al., 1997b*]) (curve 4 in Figure 1) and 0.023 ($R = 0.856$ [*Sonzogni et al., 1997a*]) for the compilation of data pairs in the 24 to 29°C range. The calibration for the South China Sea, however, did not detect any flattening in the 26.7 to 28.2°C temperature range studied, obtaining a slope of 0.031 ($R = 0.926$ [*Pelejero and Grimalt, 1997*]) (curve 2 in Figure 1; Figure 3). This absence of a

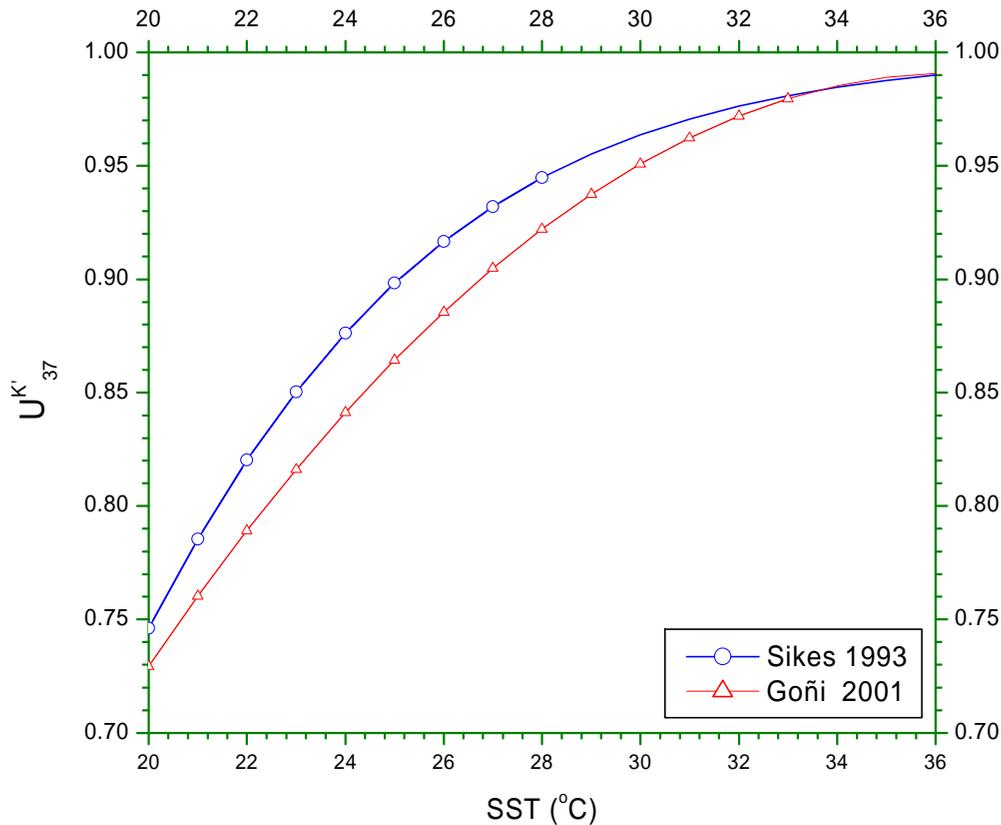


Figure 2. Comparison of the behavior of two selected nonlinear fittings in the warm-end of temperatures: $U_{37}^{K'} = -0.295 + 0.0706T - 0.000969T^2$ for Gulf of California sediment traps [Goñi *et al.*, 2001] and $U_{37}^{K'} = 1/[1 + e^{-0.22(SST-15.1)}]$ from Sikes and Volkman [1993] which includes data from Prahl and Wakeham [1987]. Lines with markers indicate the temperature ranges which included measured values, the rest (solid line without markers) is the extrapolation of the equations.

decrease in slope in the South China Sea can be easily seen when the values from this study are plotted together with the world wide core-top compilation by Müller *et al.* [1998] (Figure 3). This comparison also exhibits a decrease in the total dispersion of the South China Sea data points when compared to the whole global data set (zoomed panel in Figure 3). This observation suggests that, under certain circumstances, local core-top calibrations might reconstruct past temperatures more accurately. However, in this particular case both local and global equations result in fairly similar $U_{37}^{K'}$ -SST values with differences of only 0.5°C amongst them. Moreover, both equa-

tions are almost identical for the whole range of temperatures (Figure 3). This might be only a coincidence given that the South China Sea calibration focused only in the warm-end of temperatures (26.7 to 28.2°C). In summary, the existence or not of a flattening in the $U_{37}^{K'}$ versus SST relationship and the possible initial temperature of this change needs to be further evaluated and might not be the same for all ocean basins.

[14] Interbasinal differences for the warm-end of the temperature calibration could have some relation with the physiological and ecological aspects of the alkenone producing haptophytes. Indeed,

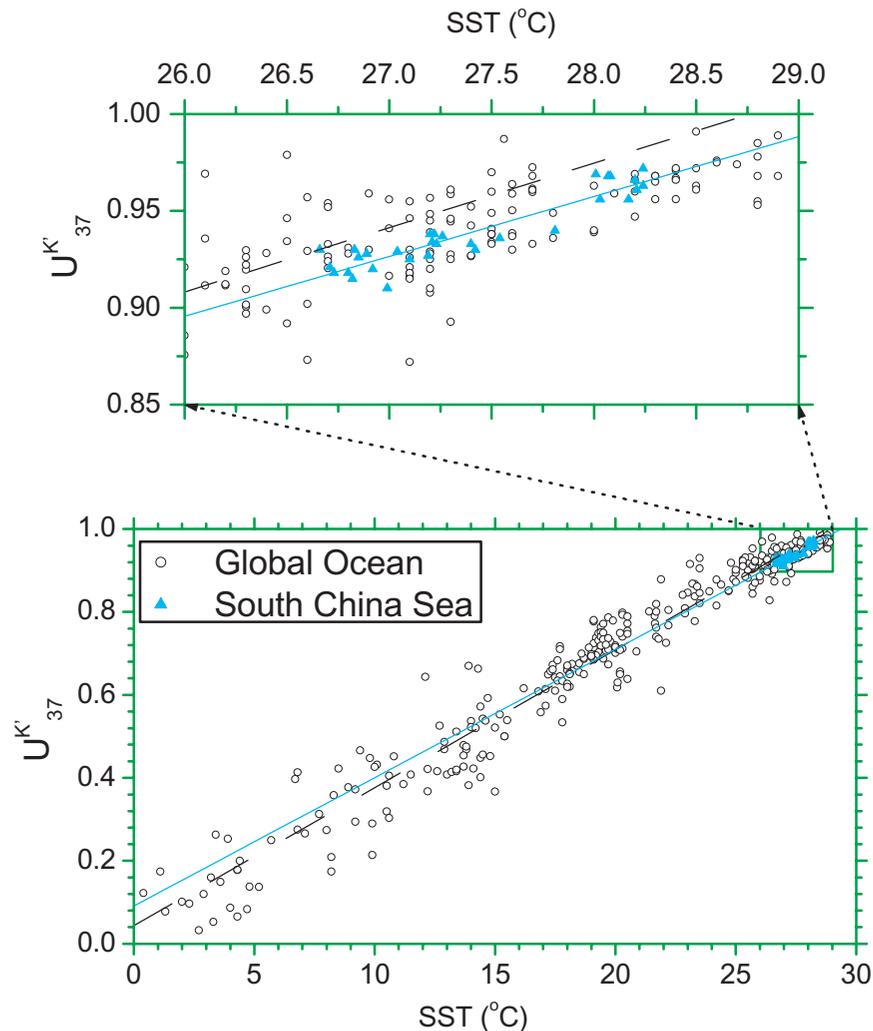


Figure 3. (bottom) Comparison of the warm-temperatures calibration from the South China Sea, filled triangles and solid regression line $U_{37}^K = 0.031T - 0.092$, ($R = 0.926$ [Pelejero and Grimalt, 1997]) versus the global ocean core top calibration data set, circles and dashed regression line $U_{37}^K = 0.033T - 0.044$, ($R = 0.979$ [Müller et al., 1998]). (top) Zoomed upper end section of temperatures with the same suit of data values and fits.

most of western Pacific and Indian Ocean marginal seas (including the ocean basins for which existing specific core-top calibrations have been discussed) are dominated by *Gephyrocapsa oceanica* relative to *Emiliania huxleyi* [e.g., Okada and Honjo, 1973; Houghton and Gupta, 1991; Bentaleb et al., 2002], the latter being the most abundant alkenone producer in open oceans [e.g., Brassell, 1993]. Cultures of different *G. oceanica* strains at various temperatures have provided contrasting results, some of them deviating substantially from cultures of *E. huxleyi* [Volkman et al., 1995], while others better approximate both species behaviours [Sawada et al., 1996; Conte et al., 1998]. For the

sedimentary record, however, a thorough comparative study of alkenone production and coccolith distribution from a South-eastern Atlantic sediment core suggests no effect of drastic changes in Haptophyta species population on the U_{37}^K -SST estimations [Müller et al., 1997].

[15] The same conclusion may be reached when considering the robust linear relationship exhibited by the global core-top data set, which includes 370 sites from oceans all over the world, and encompasses materials from a wide range of Haptophyta algae distributions [Müller et al., 1998]. Moreover, the addition of further core-top values to this global

calibration from western tropical Atlantic, the Brazil Current region, the South Atlantic Tropical Gyre north of 32°S [Benthien and Müller, 2000] and the California Margin [Herbert *et al.*, 1998] yields an updated equation based on 456 core locations virtually identical ($U_{37}^{K'} = 0.033 \text{ SST} + 0.047$, $R = 0.980$ [Benthien and Müller, 2000]) compared to $U_{37}^{K'} = 0.033 \text{ SST} + 0.044$, ($R = 0.979$ [Müller *et al.*, 1998]). This lack of sedimentary variability, as compared to algae culture and water column studies, might be due to the temporal averaging effect of the $U_{37}^{K'}$ signature in deep sea sediments [e.g., Herbert, 2001]. Altogether, it is clear that despite the inherent challenge in measuring $U_{37}^{K'}$ ratios at warm temperatures, core-top calibrations in these areas have been possible despite variations in algae populations.

2.4. Examples of Warm Temperature Reconstructions

[16] The feasibility of reconstructing warm temperatures (up to 29°C) by means of the $U_{37}^{K'}$ can also be exemplified by several successful reconstructions in that range. Many studies have been able to measure $U_{37}^{K'}$ indexes corresponding to waters warmer than 26.4°C [Lyle *et al.*, 1992; Ohkouchi *et al.*, 1994; Emeis *et al.*, 1995; Schneider *et al.*, 1995; Bard *et al.*, 1997; Rostek *et al.*, 1997; Sonzogni *et al.*, 1998; Cayre and Bard, 1999; Pelejero *et al.*, 1999; Rühlemann *et al.*, 1999; Dooze-Rolinski *et al.*, 2001; Herbert *et al.*, 2001; Huang *et al.*, 2001; Kienast *et al.*, 2001], a value recently reported as the upper limit for feasible $U_{37}^{K'}$ determinations [Bentaleb *et al.*, 2002]. Some of them are depicted in Figure 4. As can be seen in this Figure, four sediment cores from the South China Sea covering the last deglaciation (Figures 4a–4d) succeeded in detecting, for example, the Bølling warming and subsequent Younger Dryas cooling [Pelejero *et al.*, 1999; Kienast *et al.*, 2001]. This feature, which was found irrespective of waters warmer or colder than 26.4°C, led to the assertion of synchronies in the deglacial warming in the South China Sea and Greenland [Kienast *et al.*, 2001].

[17] Another warm-water study from the western tropical Atlantic Ocean (Figure 4e) showed pronounced warmings corresponding to Heinrich

Event 1 and the Younger Dryas [Rühlemann *et al.*, 1999]. These warmings (the first occurring below the 26.4°C level but the second above it) led the authors to extract important information on the behaviour of thermohaline circulation during the last deglaciation [Rühlemann *et al.*, 1999]. Moreover, Figures 4f and 4h also depict interesting similarities between two cores from the South China Sea, one of them with temperatures mostly higher than 26.4°C while the other comprising slightly colder values [Pelejero *et al.*, 1999]. As can be seen, the glacial to interglacial behaviour is parallel between both “warm” and “cold” records. Furthermore, even shorter oscillations such as a temperature maximum between 90 and 80 ky BP are recorded irrespective of the warmth of waters (see asterisk in Figures 4f and 4h).

2.5. Future Directions

[18] Several aspects still need to be evaluated in relation to the warm-end of the $U_{37}^{K'}$ temperature calibration, but any progress will depend on our ability to detect and accurately quantify the $C_{37:3}$ alkenone. Furthermore, preferential adsorptions of the $C_{37:3}$ alkenone in the capillary GC column may also lead to deviations in the SST estimations, particularly when the concentration of these compounds is relatively low [Rosell-Melé *et al.*, 1995; Villanueva and Grimalt, 1996]. In this sense, a threshold value of 10 ng of total C_{37} alkenone introduced in the GC system has been reported as the minimum amount of alkenones required to obtain reliable SST estimations [Villanueva and Grimalt, 1996; Sonzogni *et al.*, 1997b]. However, this threshold also depends on the sensitivity of the equipment and technique used, and amounts as low as 3–5 ng have also been reported [Rosell-Melé *et al.*, 1995]. The use of new automated extraction systems, such as pressurised liquid extraction, might be very useful to handle larger amounts of material in order to avoid working with such extreme low concentrations [Richter *et al.*, 1996; Schantz *et al.*, 1997]. However, limited sample capacities typical of conventional capillary GC might pose a problem with determination of the $C_{37:2}$ homologue due to overloading. Choosing thicker film chromatographic columns may help solve some overloading

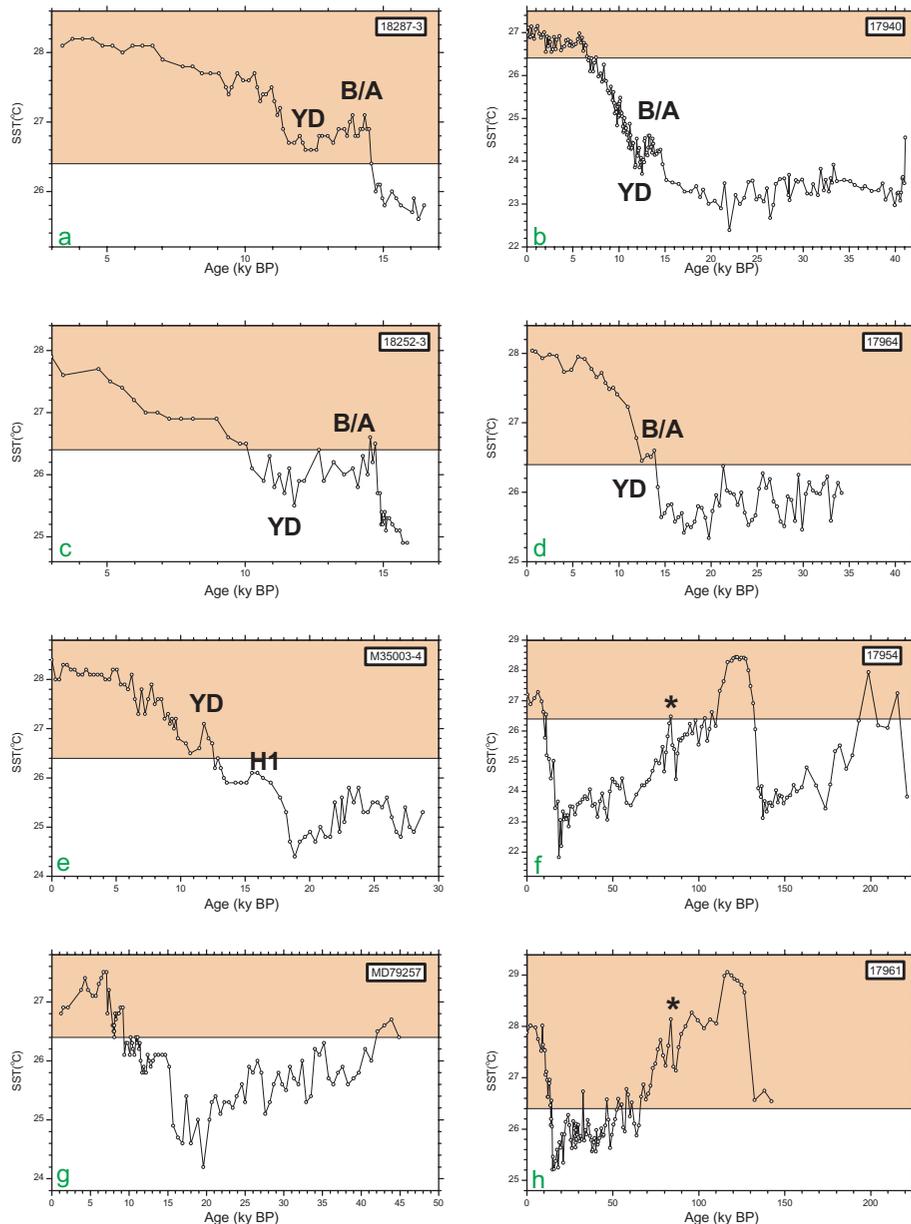


Figure 4. Summary of several $U_{37}^{K'}$ -SST reconstructions at the upper end of temperatures. (a) and (c) South China Sea cores 18287-3 and 18252-3, respectively [Kienast *et al.*, 2001]; (b), (d), (f), and (h) South China Sea cores 17940, 17964, 17954 and 17961, respectively [Pelejero *et al.*, 1999]; (e) Western tropical Atlantic Ocean core M35003-4 [Rühlemann *et al.*, 1999]; (g) Indian Ocean core MD79257 [Sonzogni *et al.*, 1998]. Orange-shaded areas highlight the reconstructed temperature ranges above 26.4°C, recently suggested by Bentaleb *et al.* [2002] to be the limit of feasible $U_{37}^{K'}$ -SST reconstructions. YD, Younger Dryas; B/A, Bølling Allerod; H1, Heinrich Event 1. The asterisk relates to the short warming event recorded simultaneously at 17961 and 17954 South China Sea cores.

problems, but can also hamper the resolution needed to separate both alkenones.

[19] Analytical approaches to overcome such difficulties include preparative capillary gas chroma-

tography, a technique proven successful in the isolation of the large amounts of individual biomarkers needed to perform single compound radiocarbon measurements [Eglinton *et al.*, 1996, 1997]. It is worth mentioning that this technique has

recently been applied successfully to date C_{37} alkenones [Uchida *et al.*, 2001; Ohkouchi *et al.*, 2002]. On the other hand, the high sensitivity and specificity of GC coupled to mass spectrometry (MS) with ammonia chemical ionization [Rosell-Melé *et al.*, 1995] might be also appropriate to detect the low abundances of $C_{37:3}$ alkenone without interferences from $C_{37:2}$. Moreover, $NaBH_4$ reduction of alkenones to the corresponding alkenols and GC-MS analyses may help to determine $U_{37}^{K'}$ ratios closer to 1, when taking advantage of the very useful and specific electron impact mass spectra of the derivatised compounds [Rontani *et al.*, 2001].

[20] As previously mentioned, and apart from the analytical challenge of measuring low concentrations of alkenones, a better knowledge of the shape of the calibration curve in the warm-end section of the temperature range is also needed. This issue would be more easily addressed if the biochemical function and biosynthetic pathways of the alkenones were known. It has been suggested that alkenones could be located in the cellular membrane as fluid stabilizers [Prahl *et al.*, 1988]. However, cell fractionation experiments [Conte and Eglinton, 1993] and photodegradation studies [Rontani *et al.*, 1997] indicated that alkenones were located elsewhere in the cell and, as suggested by Epstein *et al.* [2001], used as metabolic storage molecules. Further studies of the metabolic role of alkenones in Haptophyta algae and the physical properties of these alkenones at different temperatures, in particular higher than $25^\circ C$, will help to better understand the temperature dependence of these compounds in the upper end of the temperature range.

[21] Now that single compound radiocarbon measurements for C_{37} alkenones are feasible [Uchida *et al.*, 2001; Ohkouchi *et al.*, 2002], the possibility of lateral transport of suspended alkenones, either old or with a different temperature signal, can be assessed [Ohkouchi *et al.*, 2002]. It would be valuable to apply this new approach to verify whether the sedimentary alkenones used in core-top calibrations are modern and have not been transported from other areas. The occurrence of laterally transported alkenones originated in colder

waters was easily detected for samples from the western South Atlantic after encountering large temperature biases in the order of $6^\circ C$ [Benthien and Müller, 2000]. This prevented their inclusion into the world ocean global compilation of core-tops. Compound radiocarbon measurements for C_{37} alkenones could be of use to detect temperature biases of less magnitude which might be more difficult to recognize. This technique could be then used to discern to which extent transported alkenones could pose a problem to $U_{37}^{K'}$ calibrations, and for which areas.

[22] It would also be useful to collect more data on $U_{37}^{K'}$ indexes for modern surface sediments in the open Equatorial Pacific and particularly the Western Pacific Warm Pool, where data is still very scarce. This would upgrade the global compilation of core-tops at the upper end of temperatures and could shed some light on the calibration shape at this range.

3. Concluding Remarks

[23] Analytical determination of alkenones from materials corresponding to warmer waters poses serious analytical problems. Detection of the $C_{37:3}$ compound in the presence of major $C_{37:2}$ homologue abundances is not simple, and analyses with undetected amounts of $C_{37:3}$ can occur. Under these circumstances, results should always be reported as undetected, with no further $U_{37}^{K'}$ index assessment. Otherwise, misleading interpretations can be derived, especially when such artificial unity values are introduced into computation of potential correlations.

[24] At the present status of the research on the $U_{37}^{K'}$ index, it is still not possible to define an upper limit of temperature for the $U_{37}^{K'}$ calibration. A crucial aspect also is the actual shape of the $U_{37}^{K'}$ versus temperature relationship, which has been suggested to be non linear in several occasions. However, the temperature of transition from a linear to curved $U_{37}^{K'}$ versus SST relationship needs to be further evaluated and might not be the same for all basins.

[25] A substantial number of $U_{37}^{K'}$ - SST reconstructions including temperatures above $26.4^\circ C$ has



been reported to date. Close comparisons and examination in detail of such records argues against a recent claim of 26.4°C as the upper temperature limit of the U₃₇^{K'} application. On the contrary, these published reconstructions demonstrate that elucidating temperatures with this method are feasible, at least, up to 29°C. Higher temperatures are potentially achievable if proper analytical techniques are developed.

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