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# Investigation of the $U^{K}_{37}$' vs. SST relationship for Atlantic Ocean suspended particulate alkenones: An alternative regression model and discussion of possible sampling bias

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ABSTRACT

Alkenone unsaturation, expressed as the $U^{K}_{37}$' index, is closely related to growth temperature of prymnesiophytes, thus providing a reliable proxy to infer past sea surface temperatures (SSTs). Here we address two lingering uncertainties related to this SST proxy. First, calibration models developed for core-top sediments and those developed for surface suspended particulates organic material (SPOM) show systematic offsets, raising concerns regarding the transfer of the primary signal into the sedimentary record. Second, questions remain regarding changes in slope of the $U^{K}_{37}$' vs. growth temperature relationship at the temperature extremes. Based on (re)analysis of 31 new and 394 previously published SPOM $U^{K}_{37}$' data from the Atlantic Ocean, a new regression model to relate $U^{K}_{37}$' to SST is introduced; the Richards curve (Richards, 1959). This non-linear regression model provides a robust calibration of the $U^{K}_{37}$' vs. SST relationship for Atlantic SPOM samples and uniquely accounts for both the fact that the $U^{K}_{37}$' index is a proportion, and so must lie between 0 and 1, as well as for the observed reduction in slope at the warm and cold ends of the temperature range. As with prior fits of SPOM $U^{K}_{37}$' vs. SST, the Richards model is offset from traditional regression models of sedimentary $U^{K}_{37}$' vs. SST. We posit that (some of) this offset can be attributed to the seasonally and depth biased sampling of SPOM material.

## 1. Introduction

The $U^{K}_{37}$' index is a well-established paleoceanographic proxy, which has greatly contributed to the understanding of past-ocean systems (e.g., Marlowe et al., 1984; Prahl and Wakeham, 1987; Prahl et al., 1988; Sikes et al., 1991; Müller et al., 1998). Through the measurement of unsaturation ratios of sedimentary alkenones, past sea surface temperatures (SSTs) can be inferred. The $U^{K}_{37}$' index (Prahl and Wakeham, 1987) describes the relative proportion of biologically synthesized di-unsaturated (C37:2) and tri-unsaturated (C37:3) long-chained ketones, or alkenones, and is a simplified version of the $U^{K}_{37}$ index originally proposed by Brassell et al. (1986):

$$U^{K'}_{37} = C37{:}\ 2/(C37{:}2 + C37{:}\ 3) \quad (1)$$

Alkenones are robust biomarkers due to both their source specificity, as they are produced exclusively by prymnesiophytes, and their resistance to diagenesis (see review by Herbert, 2003). The dominant open ocean species *Emiliania huxleyi* and *Gephyrocapsa oceanica* produce alkenones in varying degrees of unsaturation in direct response to their growth temperature (Marlowe et al., 1984).

Reconstructions of SSTs derived from sedimentary alkenones rely on the underlying assumption that the $U^{K}_{37}$' recorded in alkenones is reflective of the water temperature at the time of algal growth. Systematic inconsistencies between $U^{K}_{37}$'-estimated SSTs and growth temperatures have been explained in some studies as evidence of species-specific, physiological or environmental controls on alkenone unsaturation (Yamamoto et al., 2000; Sikes and Sicre, 2002; Prahl et al., 2003, 2006; Rosell-Melé and McClymont, 2007; Ono et al., 2009). Sedimentary accumulation of alkenones integrates over long timescales (tens to thousands of years) and therefore sediment calibrations typically regress $U^{K}_{37}$' against mean annual climatological or satellite derived SSTs (maSSTs; e.g. Müller et al., 1998), rather than *in situ* SSTs, which are typically applied to suspended particulate calibrations (e.g. Sikes et al., 1997; Sicre et al., 2002; Bendle and

*Abbreviations:* AMT20, Atlantic Meridional Transect 20; IPT, integrated production temperature; maSST, mean annual sea surface temperature; RMSE, root-mean-square error; SPOM, suspended particulate organic material; WOA, World Ocean Atlas

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Rosell-Melé, 2004; Conte et al., 2006). A generally well accepted global calibration describing the relationship between $U^{K}_{37}$' measured in sediments and mean annual sea surface temperatures (maSST) has been developed by Müller et al. (1998) and is statistically identical to the linear algal culture calibration initially developed by Prahl et al. (1988):

$$U^{K'}_{37} = 0.034T + 0.039 \quad (2)$$

While the $U^{K}_{37}$' index is a widely accepted SST proxy, uncertainties remain regarding the physiological mechanisms ultimately regulating the alkenone unsaturation in prymnesiophytes (Epstein et al., 1998, 2001; Prahl et al., 2003; Yamamoto et al., 2000), and there is a lack of consensus on a single and universal calibration model (e.g. see the regional calibration model developed by Sonzogni et al., 1997). The proposal that a non-linear calibration model, with a reduction in slope at both the warm and cold ends, best describes the relationship between $U^{K}_{37}$' and growth temperature for suspended particulate alkenones challenges the reliability of a single calibration model for alkenone $U^{K}_{37}$' signatures across sample types (i.e. core-top sediment, culture and suspended particulates). Notably, Conte et al. (2006) describe a third-order polynomial regression for the $U^{K}_{37}$'vs. SST relationship in a global suspended particulate alkenone dataset. Apparent inconsistencies between calibration models developed for core-top sediments (e.g. Müller et al., 1998) and those developed for surface suspended particulates organic material (SPOM) (e.g. Sikes et al., 1997; Sicre et al., 2002; Bendle and Rosell-Melé, 2004; Conte et al., 2006) also stand unresolved, highlighting uncertainties associated with the transport and preservation of the alkenone unsaturation signal from the surface oceans to the sediments. This offset between core-top sediment and surface particulate calibrations has been attributed to a possible seasonality in alkenone flux to the seafloor in combination with diagenetic alteration of the $U^{K}_{37}$' in the sediments (e.g. Conte et al., 2006, Rosell-Melé et al., 1995).

The present study explores the relationship between $U^{K}_{37}$' and SST for Atlantic Ocean surface suspended alkenones, based on a total of 394 previously published $U^{K}_{37}$' values, complemented by 31 new data points collected along the Atlantic Meridional Transect (AMT20 RRS James Cook JC053, http://www.amt-uk.org/Cruises/AMT20). This new transect, which spans 100° in latitude, in many regions of the Atlantic basin provides some of the only truly open ocean SPOM alkenone samples (see Fig. 1). With this synthesized dataset we propose an alternative non-linear model, the Richards curve (Richards, 1959), that better captures the apparent non-linear relationship between in situ SST and suspended particulate $U^{K}_{37}$' in the Atlantic basin. We also entertain the possibility that the offset between this new calibration model (and other published SPOM calibrations) and the well accepted global sedimentary calibration (Müller et al., 1998) is influenced less by diagenetic alteration in the sediments, as suggested in Conte et al. (2006) analysis, but rather by artifacts inherent to SPOM sampling itself.

## 2. Methods & dataset description

### 2.1. Atlantic Ocean suspended particulate $U^{K}_{37}$' dataset

A set of 31 filtered sea surface (0–5 m) suspended particulate samples taken between October and November of 2010 along a transect spanning approximately 100° of latitude in the Atlantic Ocean, from Southampton, UK to Punta Arenas, CL were analyzed in this study (Fig. 1, Table 1). In situ surface mixed layer temperatures (°C) and salinities were obtained from the ship's hull-mounted SBE45 MicroTSG thermosalinograph recorded at one minute intervals while underway. An average of 515 ± 170 l of sea surface water were filtered through 142 mm glass fibre filters (0.45 μm pore size) per sample. The samples were filtered over a period of 10 h on average, travelling a distance of approximately 60 nautical miles during sampling. In situ SSTs during single filtrations varied, on average, by 0.54 ± 0.62 (°C), ranging from a maximum variation of 2.69 (°C) to a minimum of 0.01 (°C). Filters were subsequently wrapped in pre-combusted aluminum foil, contained within plastic zip-locked bags onboard the research vessel and stored in a freezer (−20 °C) in preparation for analysis.

### 2.2. Laboratory analysis

A subsection of each 142 mm filter, approximately 1/8th the size of the full filter, was cut with sterile scissors and placed in a 40 ml combusted glass vial. An internal standard (75 μl of hexatriacontane from Sigma, cat#52919) was added to each vial prior to lipid extraction, as a reference for determining alkenone concentrations. A 93:7 (ratio by volume) dichloromethane-methanol solution was used to extract organic matter from the filter, facilitated by three consecutive, ten-minute sonication periods. Lipid material was separated from the dichloromethane-methanol solution using a mixture of nano-pure water and hexanes. The resulting hexane solution containing lipids was subsequently removed from each vial using a sterile glass pipette, and concentrated into 100 μl vials. Individual samples of 1 μl were then injected by autosampler into a gas chromatographer (GC, Agilent Technologies 6890N Network GC system coupled with a 7683B Series Injector). A standard GC coupled Flame Ionization Detector (FID) was used for alkenone detection and quantification, based on retention time in comparison to an *Emiliania huxleyi* culture extract. The analytical precision of the GC was determined from 10 repeat injections of a selected alkenone extract resulting in a standard deviation of ± 0.003 $U^{K}_{37}$' units, well within the published analytical error of ± 0.01 $U^{K}_{37}$' units (Müller et al., 1998).

$U^{K}_{37}$' values for the 31 Atlantic samples range between 0.312 and 0.987. In situ SSTs range between 12.17 °C and 27.81 °C (Table 1). A strong positive relationship exists between $U^{K}_{37}$' and in situ SST for this new dataset, where a linear regression yields $U^{K}_{37}$'=0.048 (SST)–0.288 ($R^2$=0.93, RMSE=0.063).

### 2.3. Combined suspended particulate $U^{K}_{37}$' dataset

These new data complement the dataset published by Conte et al. (2006) (n=389, Fig. 1), which include $U^{K}_{37}$' values between 0.054 and 0.992 and in situ SSTs between 3.8 °C and 29.5 °C, together providing a comprehensive collection of data covering almost the entire range of possible SSTs. Following Conte et al. (2006), this dataset does not include those deemed as statistical outliers in their regression analysis (Conte et al., 2006). In addition, and again following Conte et al. (2006), a subset of 16 coincident surface particulate samples off the southern coast of South Africa (−48.05°N, 20.92°E, Benthein, A., unpublished data) were combined together, and an average $U^{K}_{37}$'value was derived from these for use in the data analysis. We also include Rodrigo-Gamiz et al. (2015) surface particulate data (n=5, Fig. 1) from offshore Iceland, which range in $U^{K}_{37}$' values between 0.260 and 0.530 and in situ SSTs between 9.5 °C and 12 °C.

## 3. Statistical analysis

Regression analysis was used to quantify the $U^{K}_{37}$' vs. in situ SST relationship, including the linear and polynomial regressions traditionally used to model the $U^{K}_{37}$' vs. SST relationship. In order to constrain the model such that $U^{K}_{37}$' values are inherently restricted between 0 and 1, and account for the observed sigmoidal shape of the relationship, we propose the use of a Richards Curve as an alternate regression model for this dataset. The Richards Curve takes the form

$$y = (1 + be^{gx})^{c} \quad (3)$$

with $x$ representing SST and $y$ representing $U^{K}_{37}$'. The parameters $b$, $g$, and $c$ control the flexible sigmoidal shape of the function. Non-linear