Alkenones as proxies of sea surface temperatures: Seasonal production of alkenones in Guaymas, Carmen and Santa Barbara Basins

S. C. Brassell — Biogeochemical Laboratories, Department of Geological Sciences, Indiana University, Bloomington, IN 47405, USA

J. A. Kennedy — Earth Systems Program, Stanford University, Stanford, CA 94305, USA

Use of molecular proxies in palaeoceanography began with the realization (Brassell *et al.*, 1986) that the biosynthesis of unsaturation in alkenones (codified as U^K_{37}) by haptophyte algae is temperature-dependent and can survive in sediments to provide a record of sea-surface temperatures (SSTs). A combination of culture experiments, field collections and sediment analyses (e.g. Prahl *et al.*, 1988; Rosell-Melé *et al.*, 1995) has established the veracity of U^K_{37} as a measure of SSTs and subsequent investigations have further confirmed, developed and calibrated the application of alkenones as palaeoclimatic indicators. They also prompt continuing efforts to examine and critically evaluate environmental controls on the timing and intensity of seasonal production of alkenones in the modern ocean and concurrent assessment of the transport of these alkenone SST records through the water column to the underlying sediments.

Here, sediment trap studies help provide a critical link between the production of alkenones in surface waters and their sedimentary records that form the basis for molecular palaeoclimatic studies. Specifically, exploration of U^K_{37}-temperature relationships in sediment trap particulates recovered during long-term, high-frequency, time series affords the opportunity to monitor seasonal changes in alkenone production and to determine the temporal character of the temperature signal recorded by the annual flux of alkenone sedimentation. The locations chosen in this study provide characteristics well-suited to addressing these goals. The Gulf of California (GoC) experiences a sharp seasonal contrast in SSTs as seasonal shifts in winds cause changes in surface water masses which produce an annual temperature range of >15°C. The recent historical record of alkenones in the Santa Barbara basin (SBB) is well documented (e.g. Kennedy and Brassell, 1992) enabling direct comparison of current sedimentation with past events. Furthermore alkenone-producing species of haptophytes are prevalent among the phytoplankton in both settings.

Sampling procedures. Samples of sinking particulate matter were collected at two-week intervals in automated Honjo sediment traps deployed at 500 m water depth in the GoC (Guaymas and Carmen basins) from February 1991 until August 1992 and in the SBB from August 1993 through October 1994. Alkenones were extracted from splits of trap materials, fractionated and analysed by gas chromtography (GC) according to established procedures (cf. Kennedy and Brassell, 1992). The $U^{K'}_{37}$ values calculated from GC were converted into SST estimates using the well-established calibration $U^{K'}_{37} = 0.034T + 0.039$ derived from culturing experiment with *Emiliania huxleyi* (Prahl *et al.*, 1988). SSTs were estimated from weekly composite data from satellite Advanced Very High Resolution Radiometry (AVHRR) at the GoC sites and were recorded as average temperatures over each sampling interval in the SBB.

Temporal changes in alkenone-derived SSTs

The temperatures inferred from alkenone $U^{K'}_{37}$ values show seasonal changes that parallel the measured SST records (Fig. 1). These trends demonstrate that alkenone production tracks seasonal temperature changes. This marked covariance, without time lag, also suggests that the transport of alkenones through the water column is rapid thereby preserving real-time signals of their production in the biweekly samples. The temporal similarily, however, is not matched by the actual temperatures. U^K_{37} values for both sites in the GoC correspond to a narrower range of temperature, based on use of the standard calibration equation (Prahl *et al.*, 1988), than that estimated from the satellite data. In part this reflects the fact that SSTs during the summer months exceed the maximum response for $U^{K'}_{37}$, but the discrepancies

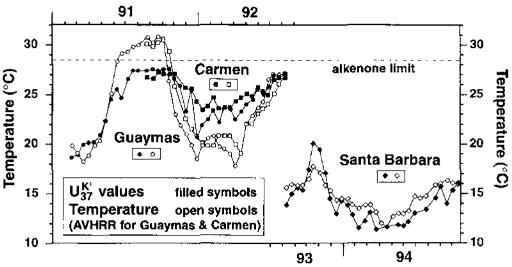

FIG. 1. Temporal trends in $U^{K'}_{37}$-derived and measured temperatures for the three study sites.

during winter and spring, when U^{K}_{37} values are up to 5°C warmer, suggest that other factors are also responsible. Perhaps alkenone production occurs primarily not at the surface, but at a subsurface chlorophyll maximum where the haptophyte population is greatest. However, it is difficult to envisage how $U^{K'}_{37}$-derived temperatures for subsurface waters could be several degrees warmer than the surface AVHRR values. It therefore appears more likely that the standard temperature calibration is not applicable for the GoC.

In the SBB the two sets of temperature more closely parallel one another in terms of both their temporal trends and their temperatures, which remain within about ± 2°C of each other.

Temperature calibration of $U^{K'}_{37}$

Linear regressions of $U^{K'}_{37}$-temperature for the three data sets differ significantly from each other and from the standard calibration in terms of their slopes and intersects (Table 1). For the GoC sites, the correlations may by distorted by those samples with temperatures >30°C, especially if alkenone production is predominantly occurring in subsurface waters. The marked differences in the correlations support the idea that alkenone production by haptophytes may be tuned to the specific conditions of their environment, as suggested by the wide variety of temperature calibrations observed in culturing experiments with *E. huxleyi* (Conte *et al.*, 1998).

However, when combined as a single data set the $U^{K'}_{37}$ values for the three environments correspond well as a polynomial fit to temperature, $U^{K'}_{37} = -0.002T^2 + 0.130T - 0.891$ ($r^2 = 0.926$), behaviour comparable to that seen in various culture studies (Conte *et al.*, 1998). Thus, the disparate data from the sediment trap studies can be interpreted in terms of a uniform, physiological response of a single strain of haptophyte to temperature change thereby obviating the need to invoke separate, independent strains of haptophytes in each setting to account for the results observed.

Seasonal productivity of alkenones

Alkenone abundance trends interpreted from these time series of samples reflect the productivity cycle of alkenone-producing haptophytes, enabling recognition of the timing of peak alkenone biosynthesis at each of the sampling sites (Table 1). The concentrations of alkenones in Guaymas and Santa Barbara basins are broadly comparable and markedly higher than their abundance in Carmen basin samples.

Annually averaged alkenone temperatures

Combination of temporal changes in alkenone abundances and $U^{K'}_{37}$ values from the long-term trap experiments permits determination of the annual average temperature represented by the flux of alkenones to the sediment. In all three settings the annual average $U^{K'}_{37}$-derived temperature using the standard calibration (Prahl *et al.*, 1988) corresponds to temperatures during the time period of peak alkenone production (Table 1). These values differ slightly from the annual average temperature calculated from the actual temperature records. For example, these values for the Santa Barbara basin are 13.3°C and 14.5°C, respectively. The latter value closely matches the historical average for non-El Niño years (Kennedy and Brassell, 1992).

These results confirm that the annual flux of alkenones is strongly tied to their peak production and supports the idea that variations in alkenone temperature records can denote palaeoclimate conditions that induce changes in the seasonal timing of alkenone production (cf. Chapman *et al.*, 1996).

References

Brassell, S.C., Eglinton, G., Marlowe, I.T., Pflaumann, U. and Sarnthein, M. (1986) *Nature*, **320**, 129–33.

Chapman, M.R., Shackleton, N.J., Zhao, M. and Eglinton, G. (1996) *Paleoceanography*, **11**, 343–57.

Conte, M.H., Thompson, A., Lesley, D. and Harris R.P. (1998) *Geochim. cosmochim. Acta*, **62**, 51–68.

Kennedy, J.A. and Brassell, S.C. (1992) *Org. Geochem.*, **19**, 235–44.

Prahl, F.G., Muehlhausen, L.A. and Zahnle, D.L. (1988) *Geochim. cosmochim. Acta*, **52**, 2303–10.

Rosell-Melé, A., Eglinton, G., Pflaumann, U. and Sarnthein, M. (1995) *Geochim. cosmochim. Acta*, **59**, 3099–107.