Methods for evaluating the effects of diagenesis on the U^{K}_{37} index

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The $U^{K}_{37}{}'$ index is a climate proxy used for the reconstruction of palaeo-sea surface temperatures (SSTs). It is defined as a function of the relative concentrations of the di-, tri- and tetra-unsaturated methyl ketones (n-$C_{37:2}$, n-$C_{37:3}$ and n-$C_{37:4}$ respectively) found in the lipid fraction of sediments, water column particulates or algal cultures. The alkenones are biosynthesized from species of some marine algae of the class Prymnesiophyceae. The tetra-unsaturated component is not always detected in sedimentary samples so an alternative algorithm ($U^{K}_{37}{}'$) excludes the n-$C_{37:4}$ compound. The corresponding $U^{K}_{37}{}'$ and/or $U^{K}_{37}{}'$ value obtained for a particular sample can be correlated with the known growth SST of its source production to formulate a calibration equation. Values of $U^{K}_{37}{}'$ and/or $U^{K}_{37}{}'$ from down-core sediment samples can then be used to estimate palaeo-SSTs (see Brassell, 1993 for a review)

At present, a key assumption is made regarding the preservation potential of the alkenone biomarkers. Initial studies investigating the refractory nature of alkenones support the hypothesis that although the absolute abundance of alkenones may rapidly decrease during down water-column flux and early sedimentary diagenesis, the relative proportions of the individual di-, tri and tetra unsaturated molecules remain constant (e.g. Conte *et al.*, 1992 and Prahl *et al.*, 1989).

However, work by Flügge (1996) suggested that n-$C_{37:4}$ was more labile to sedimentary diagenesis than the other less unsaturated alkenones. More recent studies by Hoefs *et al.* (1998) demonstrate that under oxic sedimentary conditions there is evidence for preferential degradation of n-$C_{37:3}$ compared to n-$C_{37:2}$ to such an extent that the authors concluded that application of $U^{K}_{37}{}'$ derived absolute SSTs may not be justified at all. Such a categorical conclusion should not be accepted without further corroborative studies.

The work presented describes the methods adopted for preliminary investigations into the effects of diagenesis on the n-C_{37} alkenones by looking further into the 'free' and 'bound' lipid constituents of water-column and sedimentary material from well-constrained environments. These environments include contrasting anoxic and oxic basins of the Baltic Sea and the highly productive upwelling region of the Benguela Current in the South Atlantic off the west coast of Africa (ODP Hole 1084A). The free lipid fraction is obtained by either sonication for samples <2g or soxhlet apparatus for larger sample sizes (extraction solvent 3:1 CH_2Cl_2:CH_3OH v/v). The most common procedure entailed sonication of a 1–2 g freeze-dried sediment sample with extraction solvent (33 ml) in batches of test-tubes. The extract was washed with a weak aqueous solution of KCl by a modification of the 'Folch' method to remove non-lipid residues. The free hydroxyl groups were converted to their silyated derivatives using BSTFA to improve chromatographic performance. Analysis was performed by gas-liquid chromatography using flame ionisation detection with on-column injection. Compound identification and quantification was made by reference to an internal standard (n-C_{36} alkane) and external standard containing the n-C_{36} alkane and the n-$C_{37:2}$ and n-$C_{37:3}$ alkenones.

Bound lipids were released by basic hydrolysis of the free-lipid extract sediment residues. An 8% solution of KOH in 9:1 CH_3OH:H_2O Milli-Q grade (v/v) was added (25 ml) to the residues in sealed conical flasks under N_2. The mixture was agitated for 48hrs and the insoluble residues separated by centrifugation and washed with further CH_3OH and H_2O. The combined extract was acidified to pH 2. Any precipitated salts were dissolved with the addition of further H_2O. The lipids were then extracted into CH_2Cl_2 and prepared for analysis as above. The use of a phase transfer catalyst (Aliquat 336) to aid hydrolysis was also investigated.

The resulting data for the relative abundance of n-$C_{37:2}$ and n-$C_{37:3}$ alkenones in the free and bound fractions was interpreted for significant preferential degradation of an individual alkenone by developing degradation ratios similar to those used by Hoefs *et al.* (1998). These ratios express the differences in concentration of an individual alkenone between the degraded (e.g. in the equivalent oxic or sulphur rich environment) and less degraded (e.g. in the equivalent anoxic or sulphur poor environment) states. If these ratios are not equal for both the n-$C_{37:2}$ and n-$C_{37:3}$ alkenone then there is evidence for preferential degradation. This only becomes significant with corresponding shifts in $U^{K}_{37}{}'$ equivalent to a bias > ± 0.5°C of the interpolated SST. In addition, owing to its mathematical nature, the model is insensitive to small diagenetic changes for high and low $U^{K}_{37}{}'$ (i.e. for SSTs <5°C and >25°C). The degradation ratios in the free extract were compared with those calculated for the bound fraction to determine possible differences in the preservation potential between the two types of sedimentary matrix. Although the alkenones can not be directly linked to the ester-bound fraction of the sediments it is likely that the proto-kerogen/humin fraction consisting of ester cross-linkages incorporates a proportion of the alkenones within the macromolecular matrix and consequently gives protection from diagenetic alterations. This hypothesis has been supported to some extent by the results of Hoefs *et al.* (1998).

The results obtained from these experiments should allow conclusions to be made regarding the effects of early sedimentary diagenesis on $U^{K}_{37}{}'$ in oxic *vs* anoxic marine environments of 55°N in the Baltic Sea and in down-core profiles of the organic rich sediments underlying the Benguela upwelling region. These conclusions can then be used either to support the assumptions presently made in interpreting $U^{K}_{37}{}'$ data or reinforce the calls for a more cautious approach when using $U^{K}_{37}{}'$ in areas prone to significant sedimentary organic matter diagenesis. In either case, more work will still be needed to investigate the influence of diagenesis on $U^{K}_{37}{}'$ in further types of diagenetic regimes (e.g. highly bioturbated) and less easily constrained environments and to elucidate the possible mechanisms and products of the diagenetic process.

References

Conte, M.H., Eglinton. G., Madureira, L.A.S. (1992) *Org. Geochem.*, **19**, 287–98.

Flügge, A. (1996) PhD Thesis. Christian-Albechts-Universität zu Kiel, Germany.

Hoefs, M.J.L., Versteegh, G.J.M., Rijpstra, W.I.C., deLeeuw, J.W. and Damste, J.S.S. (1998) *Paleoceanography*, **13**, 42–9.

Prahl, F.G., de Lange G.J., Lyle., M. and Sparrow, M.A. (1989) *Nature*, **341**, 434–7.

Brassell, S.C. (1993) in *Organic Geochemistry, Principles and Applications*, 699–738, Plenum.