

**OPTIMIZATION OF THE PALEOBIOMARKER APPLICATIONS OF ALKENONES**

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The alkenones are long-chain unsaturated methyl and ethyl ketones that are synthesized by a limited number of haptophyte microalgae. The proportion of the C<sub>37</sub> di- and tri-unsaturated ketones varies in a systematic way with the growth temperature experienced by these organisms and an index, called  $U_{37}^k$  and defined as being the ratio  $[C_{37:2}] / ([C_{37:2}] + [C_{37:3}])$ , was proposed as palaeo-indicator of sea surface temperatures (SST). For alkenones to be reliable measures of SST in the geological record, it is essential that: (1) their sources are correctly attributed (since temperature calibrations can vary from one species to another) and (2) that any diagenetic effects that might alter the original temperature signal established during their initial biosynthesis can be estimated.

We have re-examined the double bond positions of the diunsaturated alkenones of several haptophytes (Prahl et al., 2006; Rontani et al., 2006a). We have demonstrated that the double bond positions in C<sub>37</sub>–C<sub>40</sub> homologues occur at a fixed carbon number from the carbonyl group, contrary to early speculations. These new data, complemented by analyses of Black Sea sediments, have allowed us to recognise 3 distinct “families” of alkenones for which we proposed different biosynthetic pathways (Rontani et al., 2006a). These data imply that alkenone sources in sediments include other species and genera in addition to the more familiar *Emiliania* and *Gephyrocapsa*.

We have studied the impact of bacterial degradation, autoxidation and thiyl radical-induced stereomutation processes on the alkenone unsaturation ratio ( $U_{37}^k$ ) in order to determine under what conditions these processes could lead to a significant bias during the determination of palaeotemperatures and to identify biomarker products from these processes. We isolated from microbial mats (Camargue, France) a bacterial community able to degrade these compounds very efficiently under aerobic conditions (Rontani et al., 2005). During these incubations, we observed variable selectivity during the attack of alkenones (variations of the  $U_{37}^k$  index ranged up to +0.10). Aerobic bacteria able to degrade alkenones selectively appeared to be also associated with some strains of *E. huxleyi* and are thus not limited to particular environments such as microbial mats.

The autoxidative reactivity of alkenones was determined using *in vitro* simulations (Rontani et al., 2006b). Alkenones appeared to be more sensitive towards oxidative free radical processes than analogues of other common marine lipids and their oxidation rates increase in proportion to their number of double bonds. As the result of this increasing reactivity with degree of unsaturation, the  $U_{37}^{K'}$  ratio increased significantly (up to 0.2) during the incubation. Autoxidative degradation of alkenones could also be demonstrated in cells of *E. huxleyi*. Free radical oxidation and aerobic bacterial degradation processes, which can act throughout the water column and in the oxic zone of the sediments, could explain the selective degradation of alkenones observed in some aerobic sediments and suspended particles. They are also consistent with the fact that  $U_{37}^{K'}$  values recorded in sediments are often higher than those in the particles settling through the overlying water column.

Several *in vitro* experiments allowed us to demonstrate that alkenone stereomutation may be induced by thiyl radicals (Rontani et al., 2006c). Based on these results, the *cis-trans* alkenone isomerisation previously observed during bacterial incubations of *E. huxleyi* cells under sulphate-reducing conditions was attributable to the formation of thiyl radicals either from methanethiol produced by bacterial degradation of DMSP or from oxidation of thiolate ions by transition metals. This process, which can occur in many anoxic environments, may cause a significant increase (ranging from +0.05 to +0.10) in the measured value for the palaeotemperature proxy  $U_{37}^{K'}$ .

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