

EVOLUTION OF TEMPERATURE CONTROL ON ALKENONE BIOSYNTHESIS. S. C. Brassell, Biogeochemical Laboratories, Department of Geological Sciences, Indiana University, Bloomington IN 47405-1403, USA (simon@indiana.edu).

Diagnostic Biomarkers: The ability to synthesize several molecular constituents of sedimentary organic matter is recognized to be confined to particular organisms [1]. Thus, the first appearances of such source-specific components can be expected to parallel the timing of the evolution of their presumed biological sources, their diversification, or their expansion to become significant contributors to preserved biomass [2,3]. For example, oleanane and 4,23,24-trimethylsteranes occur as a prominent constituent of Cretaceous and Permian sediments, respectively, consistent with the diversification of their putative source organisms, namely angiosperms [4] and dinoflagellates [5,6]. However, the connection between biomarker and biological source is not always established. The pronounced increase in 24-norcholestanes in the Cretaceous has been attributed to the evolution of diatoms [7], but this relationship has yet to be confirmed.

Origins and Utility of Alkenones: One of the most biologically restricted, but geologically significant, biomarkers are C_{37} to C_{39} di- and tri-unsaturated alkenones. These compounds are widespread in modern ocean sediments but occur in only a few living species of Haptophyta [8]. The proven value of alkenone unsaturation and carbon isotope composition as proxies for sea surface temperatures [9] and pCO_2 [10] prompts consideration of the timing of their first appearance and the development of their regulation of unsaturation as a response to temperature. The earliest occurrence of alkenones is in Albian sediments from the Blake-Bahama basin [11]. However, they differ from modern alkenone distributions in terms of their carbon number range (up to C_{41} and possibly C_{42}), carbonyl positions (odd-numbered alken-2-ones and even-numbered alken-3-ones) and presence as only diunsaturated components [12].

Alkenones in Paleogene Sediments: Alkenones were found in suites of Eocene and Oligocene sediments with $>0.2\%$ organic carbon contents from six Atlantic sites (Fig. 1). The low concentrations of alkenones in some samples raises concerns about partial degradation and the primary character of their distributions [13]. However, the abundance of alkenones in other samples attests to the indigeneity of their distributions. Some distributions differ from those of modern counterparts containing no alkadienones, but both C_{38} and C_{39} alken-2-ones, complemented by other, as yet unidentified, components structurally related to alkenones. Perhaps these distributions record variations in the biosynthetic pathways of alkenone-producing organisms during the Paleogene. By contrast, the alkenones in sediments from high latitudes closely resemble those characteristic of contemporary species and sediments (Fig. 2). Thus, the biosynthetic

characteristics of alkenones in modern coccolithophorids appear to be inherited from alkenone-producing species adapted to colder waters during the Paleogene.

References: [1] Brassell S. C. et al. (1983) *Biochem. Soc. Trans.*, 11, 575–586. [2] Summons R. E. and Walter M. R. (1990) *Amer. J. Sci.*, 290A, 212–244. [3] Brassell S. C. (1994) *ACS Symp. Ser.* 562, 2–30. [4] Moldowan J. M. et al. (1994). *Science*, 265, 768–771. [5] Summons et al. (1987) *GCA*, 51, 3075–3082. [6] Summons et al. (1992) *GCA*, 56, 2437–2444. [7] Holba A. G. et al. (1998) *Geology*, 26, 783–786. [8] Conte M. H. et al. (1994) in *The Haptophyte Algae* (J. G. Green and B. S. C. Leadbetter, eds.), pp. 351–377, Oxford. [9] Brassell S. C. (1993) in *Organic Geochemistry* (M. H. Engel and S. Macko, eds.), pp. 699–738, Plenum. [10] Jasper J. P. and Hayes J. M. (1990) *Nature*, 347, 462–464. [11] Farrimond P. et al. (1986) *Org. Geochem.* 10, 897–903. [12] Marlowe I. T. et al. (1990) *Chem. Geol.*, 88, 349–375. [13] Hoefs M. J. L. et al. (1998) *Paleoceanogr.*, 13, 42–49.

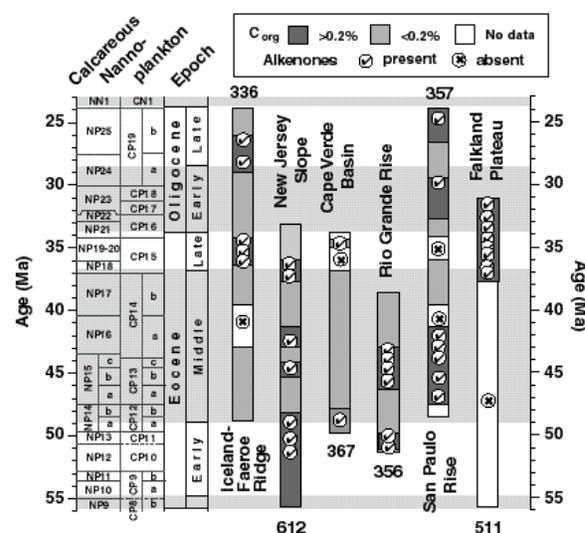


Fig. 1: Alkenones in Eocene and Oligocene sediments.

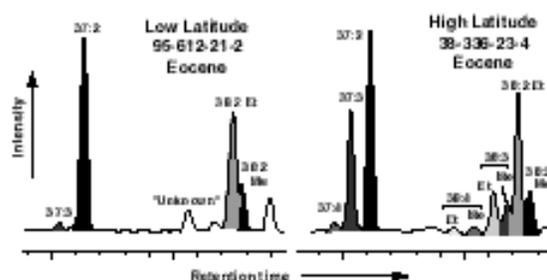


Fig. 2: GC traces of alkenones in Eocene sediments.