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Tracing Biogenic Links of Natural Organic Substances at the Molecular Level with Stable Carbon Isotopes : *n*-Alkanes and *n*-Alkanoic Acids from Sediments

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Abstract: The $^{13}C/^{12}C$ compositions of *n*-alkanes and *n*-alkanoic acids from Eocene sediments are correlated in the 20-29 carbon number range.

n-Alkanes are an important class of natural compounds occurring almost ubiquitously in organic-rich sediments such as soils, petroleums and coals[1]. Although extensively studied, the origin of sedimentary *n*-alkanes is still unclear, mainly because of the lack of structural information of these substances. They might derive from biological aliphatic precursors such as *n*-alkanes, *n*-alkohols, *n*-alkanoic acids or biopolymers[1-3]. Recent studies suggest that $^{13}C/^{12}C$ compositions of molecular fossils could provide more information about their possible precursors in living organisms[4]. Indeed, the isotopic composition of molecular fossils depends on the carbon source and the metabolic reactions of the biological precursor, and further transformations in sediments. Among various possible pathways of formation, sedimentary alkanes are presumably derived from alkanoic acids *via* decarboxylation[2]:

$$\mathbf{R\text{-}CO_2H} \longrightarrow \quad \longrightarrow \mathbf{R\text{-}H}$$

Scheme. Postulated formation of alkanes from alkanoic acids in sediments.

We would like now to report the correlation of *n*-alkanes and *n*-alkanoic acids from Eocene sediments by isotopic means. The geological samples studied belong to the lacustrine Eocene formation (60×10^6 years) of Green River (Colorado, USA) and are located at depths varying between 300 m and 800 m. Alkane and acid fractions were separated from sediment extracts by silica gel chromatography[5] and analysed by gas chromatography-combustion-mass spectrometry (GC-C-MS) monitoring the $m/z = 44$, 45 and 46 ion currents which correspond mainly to $^{12}C^{16}O_2$, $^{13}C^{16}O_2$, $^{12}C^{16}O^{17}O$ and $^{12}C^{16}O^{18}O$. Isotopic compositions are expressed in $\delta^{13}C$‰ units versus Pee Dee Belemnite standard: $((^{13}R_{sample}/^{13}R_{standard}) - 1) \times 1000$ where $^{13}R = {}^{13}C/^{12}C$.

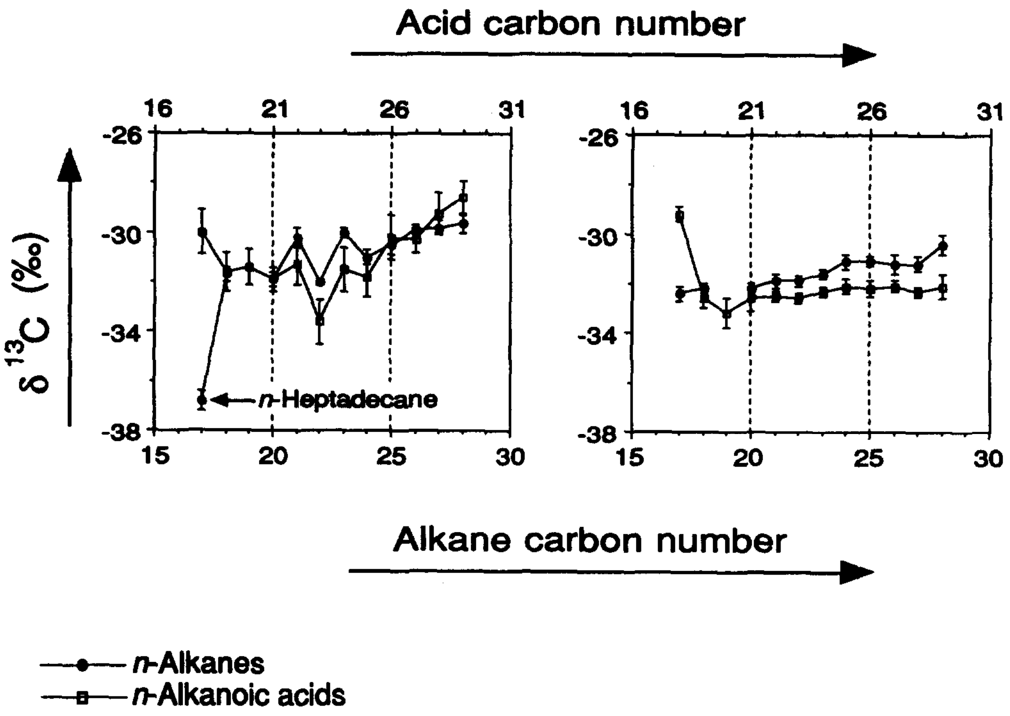

Fig. Isotopic compositions of *n*-alkanes and *n*-alkanoic acids at 312 m (left) and 718 m depth (right).

In the 20-29 carbon number range, the isotopic compositions of x carbon-numbered *n*-alkanes and x+1 carbon-numbered *n*-alkanoic acids are close and display similar variations with increasing carbon number (Figure). Since various carbon sources with various isotopic compositions are available along the food chain, this correlation between two classes of organic substances suggests their biogenic link. Moreover, *n*-alkanes, which are rare in living organisms, could derive from *n*-alkanoic acids occurring ubiquitously in eukaryots and eubacteria as triglyceride esters. This correlation also suggests the formation of alkanes *via* decarboxylation[2], accounting probably for the large amounts of carbon dioxide produced in sediments[1]. On the other hand, the large isotopic composition difference observed between *n*-heptadecane and *n*-octadecanoic acid could arise from a different pathway of formation.

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