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Characterizing intramolecular carbon and hydrogen isotope structures of higher n-alkanes by GC-Orbitrap

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Higher n-alkanes (C_{9+}) are abundant in sedimentary environments and are considered to be molecular fossils of aliphatic lipids. The carbon and hydrogen isotope compositions of lipids are regulated by physiologic and metabolic processes, and additional ecological, environmental, and diagenetic and catagenetic effects control the isotopic contents of n-alkanes preserved in sedimentary records.

Intramolecular isotopic variations in lipids have been hypothesized [1] and observed in fatty acids [2,3], and are interpreted to reflect biosynthetic pathways and enzymatic isotope effects. Site-specific carbon isotope compositions of some terminal carbon positions have been characterized for commercially available higher n-alkanes by NMR [4] and on-line pyrolysis GC-irMS [5,6]. But demands on sample size, potential matrix effects and inaccessibility of hydrogen isotope contents present analytical challenges and limitations for applications to natural samples.

Here we develop a method to simultaneously probe the intramolecular carbon and hydrogen isotope structures of n-alkanes with nanomole sensitivity. We measure the relative abundances of isotopologues of C_4H_9, C_5H_{11} and C_6H_{13} fragment ions of n-alkanes by GC-electron-impact ionization (EI)-Orbitrap with precisions of <1‰ and 3‰ for ^{13}C and D substituted fragments, respectively. We investigate the provenance of carbon and hydrogen atoms in the fragments using isotopic labeled standards and build a model for EI chemistry [7]. We study the catagenetic effect on the isotopic structures of n-nonadecane ($n$$C_{19}$) by time-series anhydrous pyrolysis of $n$$C_{19}$. We will discuss the results and implications for cracking chemistry. We will also report progress on probing intramolecular isotopic structures of biological and abiotic higher n-alkanes.

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