

## Compound-Specific Stable Carbon Isotopes: The Effect of Biosynthetic Pathways

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Since the development of the isotope ratio monitoring-gas chromatography mass spectrometers (irm-GCMS) at the end of the 80's and its commercial availability at the beginning of the 90's compound specific stable carbon isotope analysis has established itself firmly in the field of (organic) geochemistry. A number of applications have already been demonstrated and are now extensively used. For instance, stable carbon isotopic analysis of sedimentary alkenones are thought to reflect, under constant growth conditions of the alkenone-producing algae, the  $\text{pCO}_2$  of ancient oceans (e.g. Pagani et al., 1999). Shifts in  $^{13}\text{C}$ -contents of terrestrial n-alkanes can reveal the predominance of C3 or C4-plants and indicate shifts in  $\text{pCO}_2$  and humidity (Kuypers et al., 1999). Extremely  $^{13}\text{C}$ -depleted compounds can reveal the presence of methane-consuming organisms (e.g. Freeman et al., 1989). The interpretations of stable carbon isotopic compositions of sedimentary lipids have for the most part relied on culture studies of organisms. Two steps are important in this respect: Firstly, the fractionation of  $^{13}\text{C}$  from inorganic carbon to the fixation site within the cell and secondly, subsequent fractionation from the fixed carbon to the compounds of interest. The first step, fractionation during carbon assimilation, has been and still is extensively studied. Most studies are concerned with discerning the different effects of environmental and species-specific parameters. For instance, the stable carbon isotope fractionation during fixation of inorganic carbon by the haptophyte *Emiliana huxleyi* has been extensively studied (e.g. Bidigare et al., 1997) and different models for its fractionation pattern have been proposed (Popp et al., 1998; Keller and Morel, 1999). Far less attention has been focused on the second step, the fractionation in  $^{13}\text{C}$  from the fixed carbon to the compounds of interest. A few pioneering studies on the fractionation patterns of lipid biosynthesis have been done (e.g. Monson and Hayes, 1982) and a number of empirical observations on stable carbon isotopic compositions

of different compounds classes have been reported, some of them predating the advent of irm-GCMS. Clearly more research is needed here to better understand the particular biosynthetic steps involved in determining the eventual isotopic composition of specific compounds. Here we present for a number of organisms (algae, bacteria and plants) the results of different types of analysis aimed at a better understanding of the effects of biosynthetic pathways on the stable carbon isotopic composition of lipids. These analyses involved the determination of stable carbon isotopic compositions of storage products such as sugars and polyhydroxy alkanolic acids and the intramolecular distributions of  $^{13}\text{C}$  in isoprenoids. The results show that biosynthetic pathways can have dramatic effects on the  $^{13}\text{C}$ -contents of individual compounds, causing significant dispersity and thus complicating the interpretation of stable carbon isotopic compositions of sedimentary compounds.

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