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Carbon Isotopic Variability between Carbohydrates and Lipids within a Single Organism: An Explanation of the Enriched $\delta^{13}C_{TOC}$ Values in the Kimmeridge Clay Formation

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The OM-rich Upper Jurassic Kimmeridge Clay Formation was deposited in a series of basins that extended from Greenland to Norway and the English Channel. The sediments display a cyclic sedimentation of shales, bituminous shales, oil shales and carbonates with total organic carbon (TOC) ranging from 0 to 60%. Significant stratigraphic variability $\delta^{13}C_{TOC}$ has been observed (Huc et al., 1992), generally displaying a positive correlation with%TOC. However, the $\delta^{13}C$ values of the individual biomarkers of algal and green sulphur bacterial origin and of kerogen pyrolysis products generally show only minor changes. Van Kaam-Peters et al. (1998) found a strong positive correlation between $\delta^{13}C_{TOC}$ and the relative abundances of $\delta^{13}C$ enriched linear C_1-C_3 alkylated thiophenes in the kerogen pyrolysate. These thiophenes are probably derived from sulphur-bound carbohydrates in the kerogen. Kok et al. (in press) found that sulphurisation of glucose resulted in the formation of a non-hydrolysable, solid material, which yielded high amounts of organic sulphur compounds upon pyrolysis, mainly short chain alkylthiophenes. It remains to be seen, however, whether the contribution of carbohydrates to the TOC can explain the large changes in $\delta^{13}C_{TOC}$? Carbohydrates are thought to be enriched relative to lipids within the same organism (Deines, 1980). However the magnitude of this enrichment is unclear and detailed isotopic molecular analysis of carbohydrates have been lacking.

For the present study samples were selected from three freshwater algae cultures (*Scenedesmus communis, Pediastrum boryanum* and *Tetraedron minimum*), two marine algae cultures (*Rhodomonas sp.* and *Isochrysus galbana*) and one algae during spring blooms in the western Dutch Wadden Sea and the southern North Sea (*Phaeocystis*). Additional samples were collected from two terrestrial plants (*Sphagnum cuspidatum* and *Erica tetralix*). The stable carbon isotopic compositions of their fatty acids, isoprenoids (phytol and sterols) and carbohydrates were determined as well as the bulk stable carbon isotopic composition of the total cell material. The carbohydrates are enriched in $\delta^{13}C$ relative to the fatty acids (1 to 1 per mill.), phytol (up to 16 per mill.) and sterols (up to 15 per mill.). In most cases the carbohydrates are the most $\delta^{13}C$-enriched compounds found. The carbohydrates $\delta^{13}C$ values are either the same or higher (up to 11 per mill.) than bulk cell material. The lipid compounds, such as fatty acids, phytol and sterols, are equal or depleted (up to 9 per mill.) in $\delta^{13}C$ compared to the bulk cell material.

From these results it can be concluded that, generally, the enrichment of carbohydrates in $\delta^{13}C$ relative to fatty acids in the same organism, is greater than previously measured. Deines (1980) reported carbohydrates to be 4 to 10 per mill. enriched in $\delta^{13}C$. We found carbohydrates to be enriched in $\delta^{13}C$ up to 19 per mill. This means that the contribution of carbohydrates to the TOC in sulphur-rich sediments as found by van Kaam-Peters et al.(1998) can indeed lead to a significant enrichment of the bulk organic carbon.

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