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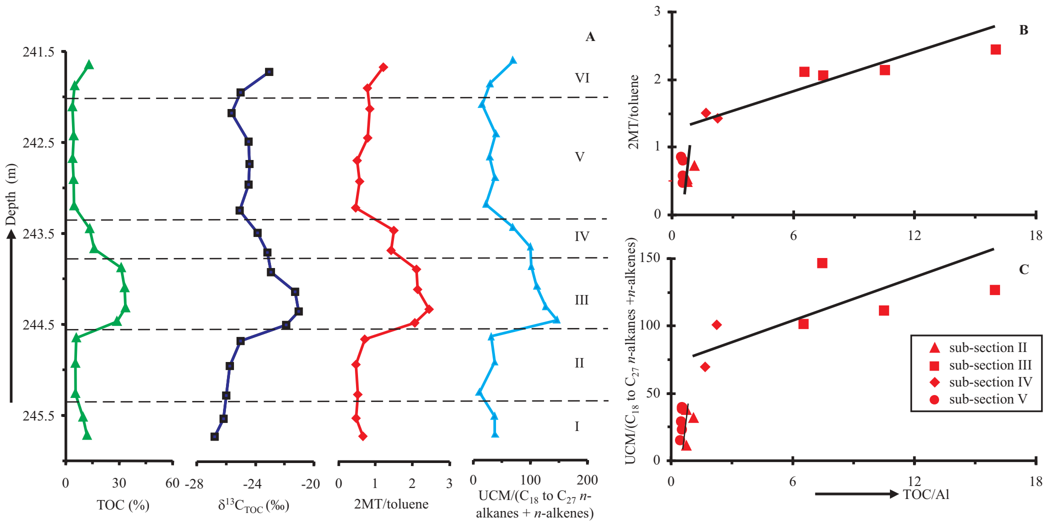
Carbohydrates make up the largest part of the organic matter in the biosphere and serve living organisms as carbon and energy source as well as metabolic intermediates. Carbohydrates are generally thought to be remineralized during early diagenesis in the water column and sediment and are thus not preserved in substantial amounts. However, some studies have suggested that preservation of carbohydrates through sulfurization could be an important pathway for the preservation of sedimentary organic matter. However, it is still unclear to what extent carbohydrates can be preserved through this pathway in sedimentary organic material and what the consequence of a substantial preservation of carbohydrates is for the chemical and isotopic composition of the total organic carbon (TOC). The primary goal of this study, supported by NEBROC, is to test the hypothesis that preservation of carbohydrates through sulfurization may be an important pathway for the preservation of organic matter and, if so, to determine what the consequences for TOC and ^{13}C contents of TOC ($\delta^{13}C_{TOC}$) records are.

First the sulfurization of carbohydrates was mimicked in laboratory experiments which showed that at relatively low temperatures (50°C) monosaccharides are completely converted into organic sulfur compounds (OSC). Monosaccharides with the carbonyl function replaced by sulfur formed a substantial part of the low molecular weight OSC. However, most of the sulfurization products were of high molecular weight and linked through monosulfide linkages. These results provide experimental evidence that sulfurization of monosaccharides at relatively low temperature can result in the formation of OSC, most likely starting with sulfurization of the carbonyl functionality.

Organic geochemical analyses of a TOC cycle in the Jurrassic Kimmerdige Clay Formation (KCF) comprising the extreme TOC-rich (34%; Fig. 1) Blackstone Band sediment showed that the enhanced TOC values are most likely caused by an increase in the accumulation rates of organic matter and not by a decrease in the accumulation rate of inorganic matter. A linear correlation is observed between the $\delta^{13}C_{TOC}$, and the amounts of short-chain alkylated thiophenes and the S-rich unresolved complex mixture (UCM) found in the kerogen pyrolysates and the TOC/Al ratios for TOC/Al ratios >2 (Fig 1B and C). Detailed analyses of an S-rich UCM revealed that it probably consists of a large number of S-bound and O-bound, short chain, carbon skeletons. These most likely originate from carbohydrates incorporated into macromolecular organic matter through sulfurization during early diagenesis. Together with the alkylated thiophenes, also likely originating from sulfurized carbohydrate carbon, this indicates that the primary cause of the TOC maximum is the enhanced contribution of carbohydrate carbon to the organic matter. Estimations of primary production rates and preservation factors based on the barium and aluminium contents show that the primary production increased only by a fac-



(A) Depth profiles of TOC, δ^{13}CTOC, the ratio of 2-methylthiophene over toluene and UCM/(C_{18} to C_{27} *n*-alkanes + n-alkenes). (B) Cross-plot of the TOC/Al ratio and 2-methylthiophene over toluene and (C) UCM/(C_{18} to C_{27} *n*-alkanes + *n*-alkenes) in kerogen pyrolsates. The different sub-sections are indicated with roman capital letters. MT= methylthiophene.

tor 2 in the Blackstone Band, while the preservation factor of the carbohydrates increased by a factor 18. These results strongly suggest that preservation of carbohydrates through sulfurization may thus be an important pathway of preservation of organic matter, especially in shallow euxinic shelf seas.

Stable carbon isotope composition analyses of individual monosaccharides and lipids, as well as the bulk stable carbon isotope composition of total cell material from different aquatic and terrestrial plants showed that, in general, monosaccharides are 0 to 9‰ enriched in ^{13}C compared to total cell material and substantially enriched, 1 to 16‰, in ^{13}C compared to lipids within single organisms. The magnitude of the differences between the ^{13}C values of carbohydrates and total cell material or lipids is far greater than previously reported. This suggests that an enhanced contribution of carbohydrates to sedimentary organic carbon can significantly affect $\delta^{13}C_{TOC}$ values, explaining the linear correlation of $\delta^{13}C_{TOC}$ with TOC in the KCF.
In general this study strongly suggest that preservation of carbohydrates through sulfurization may thus be an important pathway of preservation of organic matter. This enhanced contribution of normally labile organic carbon to sedimentary organic carbon can have substantial impacts on TOC records and $\delta^{13}C_{TOC}$ records.