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ELUCIDATING INDIVIDUAL BIOGEOCHEMICAL SIGNATURES OF OCEAN WATERS BY MEANS OF HIGH-RESOLUTION ORGANIC STRUCTURAL SPECTROSCOPY

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Natural organic matter (NOM), a very complex mixture of organic molecules, is synthesized within the general constraints of thermodynamics and kinetics from molecules of geochemical or ultimately biogenic origin. The diversity of NOM molecular signatures often approaches the very limits imposed by the laws of chemical binding. Degradative analysis of NOM destroys the sample in the beginning to recover a suite of known decomposition products, like amino acids, carbohydrates, lignin phenols and lipids. These targeted analyses typically account for about 2-30% of the organic carbon, depending on age, environment and diagenesis.

Successful non-target molecular-level analyses of NOM attempt to characterize the entire carbon present in NOM by means of information-rich detection methods such as NMR spectroscopy (nuclear magnetic resonance; provides unsurpassed insight into close-range molecular order) and FTICR mass spectrometry (Fourier transform ion cyclotron resonance; provides depiction of the compositional space with unsurpassed resolution). By these means, NOM of widely different origin and evolution has been characterized with extraordinary coverage of proton, carbon and heteroatom chemical environments, including marine organic matter, one of the largest, yet least characterized reservoirs of NOM on earth.

Marine organic matter isolated by solid phase extraction (SPE-DOM) represents a fair compromise between low expenditure and satisfactory recovery of carbon (commonly 40 %) and comprises molecular features which lead to slow transverse NMR relaxation, likely associated with its marginal metal content and near absence of very large molecules capable of strong interactions with solutes (like carbohydrate-rich marine gels). NMR and FTICR mass spectra of marine SPE-DOM exhibit superior resolution and coverage in comparison with those obtained from all other marine organic matter isolates obtained so far.

The two overwhelmingly present molecular motifs of marine SPE-DOM were extensive aliphatic branching near the statistical limits of molecular diversity and a distinctive average proximity of sp^3-hybridized (hydro)carbon units ($C_n\underline{\mathbf{C}}H_{4-n}$; n = 1-3) to carbonyl derivatives COX in carboxyl-rich alicyclic molecules (CRAM), suggesting a prevalent alicyclic geometry. In addition, an excess abundance of olefinic over aromatic unsaturation in marine SPE-DOM for both proton and carbon chemical environments was established and offers novel opportunities to trace the biogeochemical heritage of the oceans. The conformity of some key NMR and FTICR/MS signatures suggests the presence of a numerous set of identical molecules throughout the entire ocean column even if the investigated water masses belonged to different oceanic regimes and currents. FTICR mass spectra revealed a distinct CHOS chemistry for both surface (photochemistry) and abyssopelagic (sediment leaching) open ocean SPE/DOM.

Owing to excellent resolution and S/N ratio of high field NMR spectra (800 MHz; B_0 = 18.8 T), already one-dimensional ^{1}H NMR spectra of marine SPE-DOM obtained from different marine waters were remarkably dissimilar. Furthermore, COSY NMR spectra of marine SPE-DOM, which were not available from any previous marine organic matter, displayed several thousands of cross peaks, indicating >1500 compounds. COSY NMR spectra offer the best combination of sensitivity and resolution for comparative pattern recognition studies to differentiate oceanic water masses with respect to their organic biogeochemistry.

This contribution will demonstrate the capacity of modern organic structural spectroscopy to reveal the remarkable richness and diversity of marine organic matter. Individual biogeosignatures provide information about waters obtained at various depths, variable terrestrial influences at different locations, and seasonal variations.

High-quality molecular level characteristics of marine organic matter will carry a wealth of very specific information about the holistic biogeographical heritage of the oceans. Future in-depth functional biodiversity studies with a clear understanding of DOM structure and function might eventually lead to a novel, unified perception of biodiversity and biogeochemistry.

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