

ALICYCLIC STRUCTURES IN ULTRAHIGH RESOLUTION MASS SPECTROMETRY OF HUMIC ACIDS IN COASTAL SEDIMENTS: A CLUE TO THE FATE OF LIGNIN AND ITS ROLE IN TYPE II KEROGEN FORMATION

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Introduction:

While the origin of coastal sedimentary organic matter that eventually forms Type II kerogen and associated Type II petroleum is considered to be mainly from marine autochthonous organic matter, photochemical and biochemical oxidation of lignin also generates organic matter that contributes. Oxidative degradation of lignin and terrestrial DOM leads to the production of substantial amounts of alicyclic structures that flocculate readily but can be redissolved in alkaline extracts called humic acids (Chen et al., 2014; Waggoner et al., 2015). This flocculating material is found in blackwater swamps but also exists in rivers and is likely to be transported to coastal and oceanic sediments to contribute to organic matter being deposited in sedimentary environments that are known to be petrogenic. Using a combination of NMR and ultrahigh resolution mass spectrometry, we provide evidence that some if not most of the humic organic matter observed in coastal marine sediments can derive from microbial and oxidative alteration of lignin. In addition, we propose a molecular scheme for how the typically aromatic lignin is converted to alicyclic structures upon oxidation that is either microbially or abiotically mediated. On a global scale, this process has important implications for understanding the origin of molecules in Type II petroleum.

Organic matter extracted by alkaline aqueous treatment of sediments followed by precipitation and redissolution in base (humic acids) was analysed by 12T Fourier transform ion cyclotron resonance mass spectrometry (FTICR-MS) using negative ion electrospray ionization (ESI). Peaks were assigned unique elemental formulas via an in house Matlab formula calculator. Elemental data from hundreds to thousands of these formulas were plotted on Van Krevelen diagrams to ascertain the nature of the formulas observed. These humic extracts were also examined by single and multidimensional NMR to ascertain the alicyclic nature of the aliphatic components.

Results:

Van Krevelen plots of the formulas obtained from FTICR-MS spectra of humic acids extracted from numerous riverine and coastal sediments show abundant series of aliphatic molecules having multiple degrees of unsaturation and the presence of both carboxyl and hydroxyl functionalities (Figure 1). In sediments of paralic basins (peat swamps) or river deltas (Mississippi Delta), condensed aromatic structures are also observed and these, we believe, derive also from oxidized lignin. The existence of these functional groups were deduced from Kendrick mass defect plots. Because these humic acids are thought to be involved in early diagenetic stages of kerogen formation, it is likely that the formula entities observed represent the primary structural elements of kerogen which undergoes thermal maturation with increased burial to produce petroleum. In separate studies, we have shown that lignin from terrestrial vegetation can be abiotically oxidized either photochemically (Chen et al., 2014) or by hydroxyl radical oxidation (Fenton chemistry, Waggoner et al., 2015) to produce molecular formulas that match those found in humic extracts of marine sediments and peats. Further work with microbial entities shows that lignin is also attacked oxidatively to yield alicyclic and

aromatic structures resembling those found in sediments. This suggests that there could be a major contribution of lignin to organic matter in marine and coastal sediments and that the alicyclic molecules that are derived from lignin could be major contributors to kerogen and eventually petroleum. The aromatic structures prevalent in peats and coastal sediments diminish in relative importance as one progresses away from the offshore and into more oceanic sediments. We suggest that the aromatic molecules succumb to further oxidative degradation similar to that of aromatic moieties in lignin.

It is well known that hydroxyl radical oxidation takes place in sediments through the action of microbial enzymes. We suggest that the alicyclic and aromatic molecules observed in sedimentary humic acids are derived in part from the action of hydroxyl radicals formed therein. The radicals promote oxidative hydroxylation of aromatic rings (both lignin and condensed aromatic structures) that facilitates ring-opening. Subsequently produced carboxylated and hydroxylated olefins then undergo electrocyclic ring closure and condensation to yield alicyclic structures. The continued production of hydroxyl radicals in oxygenated regimes can also lead to hydrogen abstraction reactions whereby alicyclic structures can potentially aromatize to form condensed aromatic structures or lead to organic radicals that can undergo condensation, decarboxylation, and a variety of other reactions. We believe that this is one of the main processes involved in humification of organic matter to form petroleum-producing kerogen in oceanic systems. Thus, many of the polar molecules observed in petroleum by ESI-FTICR-MS can be traced to alicyclic structures derived from lignin in modern sediments.

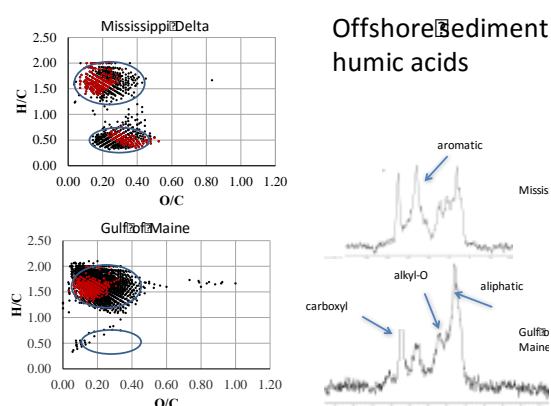


Figure 1. Van Krevelen plots (left) of elemental formulas (black dots) for humic acid extracts of sediments from the Mississippi Delta and offshore Gulf of Maine, examined by ESI-FTICR-MS with red dots showing exact matches to hydroxyl radical oxidation of lignin (Chen et al., 2014). Solid-state ^{13}C NMR spectra of the respective humic acids (right).

References:

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