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Exploring Biomarker Lipid Information Preserved in Complex Macromolecules

Gordon D. Love (g.d.love@ncl.ac.uk)

Newcastle Research Group (NRG) in Fossil Fuels and Environmental Geochemistry, Drummond Building, University of Newcastle upon Tyne, UK

Conventional biomarker approaches in earth and aquatic sciences make extensive use of the *free* hydrocarbons (alkanes and aromatic compounds) and low-molecular-weight functionalised lipids (alcohols, carboxylic acids etc.) that can be easily extracted from sedimentary organic matter (SOM) using common organic solvents such as chloroform, dichloromethane or methanol (or their mixtures). This type of treatment usually removes only a small proportion of the total OM (usually < 5% w/w), of which the free biomarker constituents represent only a small percentage. Typically over 90% w/w of the OM in sediments is insoluble in common organic solvents and non-oxidising acids (HCl/HF), and is operationally defined as kerogen. A quantitatively-significant proportion of the biomarker lipid input to sediments may become chemically-bound within kerogen from the earliest stages of diagenesis. Furthermore, an additional pool of biomarkers is found covalently-bound within macromolecular components of solvent-soluble OM (within resins and asphaltene fractions). Since diagenesis can be a highly selective process, it does not follow then that the distributions of free biomarkers in solvent extracts are necessarily representative of the total biomarker constituents. Thus, organic geochemists often utilise only a small (and potentially biased) part of the biomarker record on which to base their assessments.

In order to generate more accurate biogeochemical information from biomarkers then a higher proportion of the total biomarker record must be accessed. This means fragmenting macromolecular OM into smaller (readily-analysable) structural units to gain access to the *bound* pool of biomarkers. In general, conventional pyrolysis and chemolysis methods for liberating and analysing molecular components of kerogen are notoriously poor at providing quantitatively significant amounts of biomarkers and/or generating biomarker signals which accurately reflect the actual bound biomarker compositions. Ideally, reaction conditions are sought which can access a high proportion of the total bound biomarker pool whilst preserving the structural and stereo-chemical features of released products.

Pyrolysis assisted by high hydrogen gas pressures (>10 MPa, *hydro-pyrolysis*) eliminates the problem of low product yields often associated with the use of sterically-bulky chemical reagents and limits the extent of product structural alterations encountered with other analytical pyrolysis methods (e.g. flash-pyrolysis). Fixed-bed hydro-pyrolysis in the presence of a dispersed sulphided molybdenum catalyst gives rise to overall carbon conversions greater than 85% for petroleum source rock kerogens (Type I and Type II ancient SOM) and high volatile coals (Type III OM), with high selectivities to dichloromethane-soluble tar and low hydrocarbon yields. The very high yields of biomarker lipids which can be liberated from complex organic macromolecules (geo-polymers and biopolymers) along with the excellent preservation of molecular information (structural and stereo-chemical features) in products dictates that hydro-pyrolysis is a very powerful approach for biomarker geochemistry applications (Love *et al.*, 1995-1997).

Hydropyrolysis of algal and bacterial cultures has recently demonstrated that there are quantitatively-significant amounts of biomarker lipids present within microbial biomass (either covalently-bonded or physically-trapped) which are not accessible to conventional biochemical assay. Hydro-pyrolysis appears to be a rapid and convenient method for sample screening to identify characteristic lipid molecular markers for different microbial species to utilise as taxonomic markers in earth and aquatic sciences.

The fundamental message arising from this work is that there exists an abundant bound biomarker pool in both the biosphere and the geosphere which cannot be accessed using conventional chemical and pyrolysis methods and which contain important biogeochemical information. The hydro-pyrolysis approach has been fine-tuned to access these "hidden" information pools and, as such, the method has the capability to provide unique scientific insights. Some important new findings arising from hydro-pyrolysis of geo-macromolecules and microbial biomass will be presented which significantly aid our current understanding of the role that macromolecules play in preserving molecular fossil signals in the sedimentary record.

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