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**BIOMARKER DISTRIBUTIONS IN DIFFERENT TYPES OF SEDIMENTARY ORGANIC
MATTER ISOLATED FROM THE SAME SAMPLE:
IMPLICATIONS FOR BIOMARKER CORRELATIONS***

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**BIOMARKER DISTRIBUTIONS IN DIFFERENT TYPES OF SEDIMENTARY ORGANIC
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Abstract

The observation of qualitatively and quantitatively distinct biomarker distributions in the pyrolysates of Type II and Type III organic matter isolated from the same sample is reported. This demonstrates the clear need for a greater understanding of the relationship between biomarker distributions present in the different components of sedimentary organic matter, and those observed in liquid products generated by maturation. The data imply that it is possible that the biomarker distributions observed in petroleums derived from inhomogeneous source rocks may be disproportionately derived from the various organic components of the sediment. This may result in spurious conclusions concerning oil/source relationships and other geochemical parameters, which suggests that further investigation of these phenomena is well merited.

¹ Based in part on reference 1.

Introduction

Biological marker distributions are perhaps the most widely applied and important organic geochemical parameters, and are used in oil/source correlations, maturation and biodegradation studies, and numerous other aspects of organic geochemistry. Consequently, studies of factors which affect these distributions are of great importance. To date however, no report has appeared describing the distributions of biological markers in different types of organic matter isolated from the same sample.

The division of sedimentary organic matter on the basis of H/C and O/C ratios into three, and sometimes four classes, (vis, Type I-IV), by organic geochemists, is heavily entrenched in the geochemical literature. This system of classification developed out of the work of Van Krevelen², who used these ratios to describe the maturation pathways of coal maceral groups. Van Krevelen's system was latter extrapolated to sedimentary organic matter³; and in fact, the four organic matter types may loosely be described in petrographic terms as: Type I = alginite and related secondary macerals; Type II = other liptinites; Type III = vitrinite or huminite group macerals (often inaccurately ascribed by chemists as a single maceral); and Type IV = inertinite group macerals. Most geochemists now recognize that classification of organic matter as Type I, II, III, or IV on the basis of elemental composition alone, is unsatisfactory. Both chemical and petrographic analyses are necessary for a meaningful description of the nature of sedimentary organic matter.

Density techniques for the separation of the petrographic components many types of sedimentary organic matter are now well established^{4,5}, and have been widely applied in coal analyses⁶⁻⁸, and to a lesser extent to oil shales and similar materials⁹. To date however, these studies have not extended to analyses of biomarker distributions in dissimilar types of organic matter isolated from the same sample.

During the present study, density fractions in which (i) liptinite and (ii) huminite group macerals are concentrated, were prepared from each of the five lithotypes which occur in Victorian Brown Coal (VBC). These lithotypes, which are classified on the basis of their air-dried colour as pale, light, medium light (m.light), medium dark (m.dark), and

dark, are believed to primarily reflect differences in the depositional environments of accumulating peats^{1,10}, but all samples have very closely similar post-burial geologic histories. Density fractions of each lithotype were then characterized by Pyrolysis-Gas Chromatography-Mass Spectrometry (Py-GC-MS), Pyrolysis-High Resolution Mass Spectrometry (PY-HRMS), and Fourier Transform Infrared Spectroscopy. The results of Py-GC-MS analyses of biomarker distributions, and the potential implications of these results to biomarker correlations, are described herein. The results of other analyses are described elsewhere¹.

Experimental

Maceral group concentrates were prepared from each of the five lithotypes which occur in the Morwell No. 1 seam, Morwell open-cut mine, Morwell, Victoria, Australia. This seam forms part of an extensive series of brown coal seams and terrigenous source rocks found in the Gippsland basin.

Maceral group concentrates were prepared from these coals by sink/float separation of fluid energy mill ground coal in CaCl_2 /Brij-35 solutions of $\rho = 1.25$ g/ml. (A full description of these procedures is given elsewhere¹.) These preliminary concentrates were then purified (with respect to density) by semi-preparative density gradient centrifugation (DGC)¹¹. Semi-preparative DGC is simply a modification of analytical DGC in which 20-40 mg of sample are loaded onto the gradient instead of the normal 2 mg. Gradient fractions obtained by this procedure may then be filtered and recovered for further analysis. This procedure is useful when only small amounts of material are available for separation or further separation. The resulting products were determined to be >99% pure with respect to the density distribution of particles within each fraction, by analytical DGC^{4,5}. All samples were examined microscopically and were observed to be highly enriched in one maceral group. Low density fractions ($\rho < 1.25$ g/ml) were found to be enriched in liptinites and conversely, high density fractions ($\rho > 1.25$ g/ml) were found to be enriched in huminites. VBC's do not contain significant amounts of inertinite group macerals, except in unusual cases¹², and no significant amounts of inertinite were observed in the high density maceral group concentrates from these samples. Due to the ultra-fine particle sizes and

very limited available sample quantities (<10 mg in some cases) of the product density fractions, quantitative petrographic analyses were not possible. However, visual estimates of petrographic composition, based on fluorescence and reflectance, indicate a high degree of enrichment, estimated to be >90% for the liptinite maceral group concentrates and >98% for the huminite maceral group concentrates.

Py-GC-MS analyses were carried out using a C.D.S. "pyroprobe" pyrolyser, coupled to a Hewlett-Packard 5790B GC-MS system. Pyrolysis was carried out at 600°C for 20 sec in a H₂ atmosphere. Gas chromatographic separation was achieved using a 25 m, 0.22 mm (id) BP-5 capillary column, using the following temperature program: T_(initial) = 40°C, initial time = 2 min, ramp rate = 4°C/min, T_(final) = 310°C. H₂ carrier gas was used in all cases.

Results and Discussion

As a consequence of the limited sample capacity of semi-preparative DGC, which was used to purify the maceral group concentrates used in this study, and the low levels of liptinite in some lithotypes, the amount of isolatable, purified, maceral group concentrate, was very limited, in some cases <10 mg. Therefore, in order to maximize the geochemical information which could be measured from these samples, biomarker distributions as reflected by single and multiple ion chromatograms of characteristic ions, were determined by Py-GC-MS.

Py-GC-MS is in some respects, less than ideal for analysis of biological markers in sedimentary organic matter, due to problems associated with isomerization, dehydration, decarboxylation etc, which occur as the result of pyrolysis. It is also difficult to obtain accurate quantitative analysis by Py-GC-MS. It is noteworthy however, that Py-HRMS data¹, indicate that ions characteristic of a number of types of biomarkers, including triterpenoids and acyclic hydrocarbons (discussed below) are 5-9 times more abundant in the pyrolysates of liptinite maceral group concentrates, than in the corresponding huminite maceral group concentrates, indicating that these compounds are relatively concentrated in the liptinite concentrates.

In most cases, specific molecular structures of the compounds giving rise to characteristic ions could not be assigned with confidence, due to incomplete chromatographic separation of components and the close similarity of the mass spectra of many isomeric biomarkers. Correspondence of structure could, however, be established, by comparison of mass spectra and chromatographic behavior. This approach also enables characterization and comparison the distributions of biomarkers in different samples, based on the chromatographic distributions of characteristic ions.

Arguably, the biological marker distributions most widely used by organic geochemists are those based on acyclic hydrocarbons (specifically, n-alkanes, n-alkenes, and corresponding branched compounds), and those based on triterpenoids and steroids^{13,14}. Steroidal compounds are present in only very low abundances in VBC, and were therefore not characterized during this study. Both acyclic hydrocarbons and triterpenoids however, are abundant in the pyrolysates of VBC samples¹⁵, and hence analyses were concentrated on determining the distributions of these compounds.

In most cases, a number of characteristic ions may be used to determine the distribution of a series of related compounds. For the purposes of the present study, triterpenoid distributions were determined from single ion chromatograms of the characteristic ion $m/z=191$. This excludes many A-ring functionalized and unsaturated triterpenoids, but is a widely applied characteristic ion for biological markers which retain a saturated A and B ring structure, such as is observed in hopanes and numerous other triterpenoids. Acyclic hydrocarbon components of the pyrolysates of these samples were determined by monitoring of the distributions of both $m/z=99$ (alkane) and $m/z=97$ (alkene), since a considerable proportion, and in some cases a majority, of the acyclic hydrocarbon component of the pyrolysates of these samples were found to be unsaturated. Unsaturated acyclic hydrocarbon compounds are not typically observed in the solvent extracts of VBC's, and therefore, these compounds are thought to be derived from the pyrolysis products of fatty acids and fatty alcohols.

Multiple ion chromatograms (MIC) of $m/z=99 + m/z=97$ for each of the liptinite maceral group concentrates are illustrated in Figure 1. Corresponding MIC data for the huminite maceral group concentrates are illustrated in Figure 2. Comparison of the data illustrated in these figures indicates that in most cases, the distributions of acyclic hydrocarbons are broadly similar between maceral group concentrates. Details of the distributions, and the nature and abundance of specific acyclic hydrocarbon components, especially branched compounds however, often differ significantly between liptinite and huminite maceral group concentrates isolated from the same coal sample.

Extension of this type of comparison to the single ion chromatograms (SIC) of $m/z=191$ for these samples, illustrated in Figures 3-7, demonstrates that triterpenoid distributions are even more distinct between liptinite and huminite concentrates isolated from each of the five lithotypes. These data indicate that triterpenoid distributions differ significantly between liptinite and huminite concentrates isolated from the same sample, with respect to both the nature and relative abundance of the parent triterpenoids. This is true for each of the five lithotypes (and hence depositional environments) characterized. The observation that biological marker distributions in different types of sedimentary organic matter isolated from the same sample are distinct, has important implications for geochemists concerned with the use of biological marker distributions for source and other geochemical correlations.

The coal samples used in this study are not known to be petroleum source rocks, but terrigenous organic matter almost certainly related to these coals, which is present in other Gippsland basin strata, is thought to be the predominant source of significant off-shore crude oil accumulations. The data reported here, therefore, are relevant to petroleum generation from terrigenous organic matter.

Anhydrous pyrolysis in an inert atmosphere does not accurately simulate the generation of liquid products by natural maturation processes. Therefore, the biomarker distributions observed in these experiments do not necessarily reflect the biomarker distributions which would occur in petroleum generated from these coals by natural

processes. As a consequence, these data establish only that the biomarker distributions in these petrographically different materials, isolated from each of the five coals characterized, are distinct. They do not necessarily reflect the biomarker distributions of liquid products derived from each of the maceral group concentrates by natural processes. It is also not possible to determine from these data, or any other currently available data of which the author is aware, the relative contribution of biological markers from each maceral group to petroleum produced from these coals by natural maturational processes. It has not been established that such distributions are the simple weighted sum of the biomarker compositions of the different petrographic components of the source rock.

VBC's are typically comprised of approximately 5-20% Type II organic matter (liptinite) and 80-95% Type III organic matter (huminites), depending on lithotype¹². Type II materials are generally considered to be moderately oil prone and Type III materials are normally considered gas prone, with little potential for petroleum generation³. Hence, if with further maturation these samples were able to act as source rock for petroleum generation purposes, the bulk of the liquid materials produced would therefore be expected to be generated predominantly from the Type II (liptinitic) component. As a result, the biomarker composition of the resulting liquid product would also be dominated by the biomarker composition of the Type II component especially since these compounds are apparently concentrated in this component¹. Since it is unclear what proportion of biomarkers derived from each class of organic matter ultimately contribute to the derived petroleum, analysis of whole rock (coal) samples by simple extraction or pyrolysis to establish source/oil correlations may be misleading, due to disproportionate representation of the biological marker distributions of the different source components in the derived liquid products.

Whilst the above case is hypothetical, the implications of the data illustrated in Figures 1-7 for oil/source correlations in source rocks which contain several different types of organic matter are none-the-less apparent. It is clearly very important in such cases to be able to take into account differences in the biomarker composition and petroleum generation potential of the different petrographic components of the suspected source rock.

This conclusion does not affect oil/source correlation where the petrographic composition of the potential source rock is homogeneous, but it is equally as true of mixed Type I/Type II, Type I/Type III, and Type I/Type II/Type III sedimentary organic matter samples as it is in the present Type II/Type III case.

The results of this study, do not establish that geochemical conclusions based on analysis of biological marker distributions in sedimentary samples containing more than one organic matter type are necessarily erroneous. It is possible that factors which were not able to be taken into account here, such as "extraction" of the Type III component by liquid products formed by cracking of the Type II component, may affect the biomarker distributions observed in petroleum and source rock analyses. It is also possible that biomarkers in both Type II and III materials exist in similar microenvironments at a submaceral level, and are therefore proportionately released in liquid products as a consequence of maturation. The results of the present study however, do indicate the need for a much greater understanding of the association of biological markers with different types of sedimentary organic matter, especially in mixed samples, than is currently apparent from the geochemical literature.

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Figure 1.

MIC data of $m/z=99 + m/z=97$ for liptinite maceral group concentrates isolated from VBC lithotypes. Carbon numbers of n-alkanes are indicated for pale lithotype sample. Branched compounds elute between n-alkyl compounds (ie: do not fit regularly eluting n-alkane series).

Figure 2.

MIC data of $m/z=99 + m/z=97$ for huminite maceral group concentrates isolated from VBC lithotypes. Carbon numbers of n-alkenes are indicated for pale lithotype sample. Branched compounds elute between n-alkyl compounds (ie: do not fit regularly eluting n-alkane series).

Figures 3-7.

SIC data of $m/z=191$ for liptinite and huminite maceral group concentrates isolated from VBC lithotypes, showing differences between the distributions of triterpenoid biological markers in different types of sedimentary organic matter isolated from the same sample. LIP = liptinite maceral group concentrate, HUM = huminite maceral group concentrate.

PALE-LIP.d

Ion 191.00 amu. from PALE-LIP.d

Ion 191.00 amu. from PALE-HUM.d

Ion 191.00 amu. from LIGHT-LIP.d

Ion 191.00 amu. from LIGHT-HUM.d

Ion 191.00 amu. from M.LIGHT-LIP.d

Ion 191.00 amu. from M.LIGHT-HUM.d

Ion 191.00 amu. from M.DARK-LIP.d

Ion 191.00 amu. from M.DARK-HUM.d

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Ion 191.00 amu. from DARK-HUM.d

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