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**Organosulphur compounds in coals as determined by reaction
with Raney nickel and microscale pyrolysis techniques.**

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Quarterly Report

Project Title: Organosulphur compounds in coals as determined by reaction with Raney nickel and microscale pyrolysis techniques.

Investigators: Linda Stalker and R. Paul Philp.

Work in Progress: Since the last report, we have reached the point in the project that we are satisfied with the nickel boride chemical degradation method, and are now working our way through the large amounts of data collected by GC-MS analysis.

While we have tentatively identified a variety of compounds produced by the chemical degradation method with spectra from the literature, we have yet to confirm many of these identifications with pure standards or specialised oil samples. As a result, we will present in this report chromatograms of one of the coals (Illinois No. 6) and compare the free aliphatic hydrocarbons with those compounds cleaved from the polar extract, asphaltenes and pre-extracted coal matrix.

Method Development

We have already discussed some of the general differences in the overall distribution of hydrocarbons in each of the fractions analysed, first of all by GC (see previous report, and Figure and 2). However, owing to limitations of that analytical technique, we were unable to identify very many compounds. We have subsequently discovered a minor problem with some of the data, as the unusual distribution of compounds shown in the duplicate asphaltene chemical degradation experiments has been identified by GC-MS as a complex series of plasticiser compounds. Under normal circumstances, only one plasticiser would be present as a contaminant. However, we have

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found a suite of plasticisers, identified by their diagnostic fragment ions during GC-MS analysis of $m/z = 149, 265, 293$ (shown in Figure 3).

Fortunately, the presence of these contaminants does not affect our analysis and identification of other compounds present in the aliphatic hydrocarbon products of the asphaltene desulphurisation experiments.

We are currently investigating the procedures involved in the desulphurisation experiments to determine the source of this contamination.

Distributions of *n*-alkanes

Unlike oils and marine source rocks, the aliphatic hydrocarbons isolated from the total extract of the coal, and all the desulphurised fractions are not dominated by the presence of *n*-alkanes. The *n*-alkane distribution, highlighted by the m/z 71 chromatograms (Figure 4), shows that there are large variations in distribution and abundance between the free *n*-alkanes and those cleaved from the polar, asphaltene and coal matrix fractions.

The free *n*-alkanes are somewhat dominated by the presence of a high abundance of pristane, typical in coals. Despite this, there still appears to be evidence of a bimodal distribution of *n*-alkanes, maximising around *n*-C₁₉ and again at *n*-C₂₉. This bimodal trend is also seen in the products cleaved from the polar fraction, maximising at *n*-C₁₇ to *n*-C₁₈ and again at *n*-C₂₅. *n*-Alkane distributions from both the asphaltene and matrix desulphurisation experiments are dominated by lighter *n*-alkanes in the range *n*-C₁₆ to *n*-C₂₃.

Generally in coals, the bulk of *n*-alkanes are derived from terrestrial organic matter, notably higher plant waxes (Eglinton and Hamilton, 1963). Marked odd over even predominance in *n*-alkanes in the *n*-C₂₇ to *n*-C₂₉ region is also typical of terrestrial organic matter, as seen in the free aliphatic hydrocarbons in Figure 4.

Common Biomarker Hydrocarbons

The distribution of the more common biomarkers is also quite varied between the free and sulphur bound products cleaved from the polar, asphaltene and coal matrix fractions of the Illinois No. 6 coal.

Hopanes

The normal hopane hydrocarbons are well illustrated by the m/z 191 ion chromatogram (Figure 5). While the hopane distributions in the free hydrocarbons, and the products cleaved from the asphaltenes and matrix of the coal are grossly similar, the hopanes cleaved from the polar fraction are far different. In the polar products, the hopane distribution is totally dominated by an abundance of C_{35} hopanes, and to a lesser extent, the C_{30} hopanes, with a very low abundance of hopanes in the range C_{31} to C_{34} . However, the C_{35} hopanes totally dominate over all the other components in the aliphatic hydrocarbon fraction produced by the desulphurisation of the free polar material extracted from the coal. This suggests that in the polar fraction, the precursor bacteriohopanetetrol has most likely been bound into macromolecular material by C-S bonds (Figure 6). As C-S bonds are broken at much lower energy levels than C-C or C-O bonds, the whole sidechain of the C_{35} hopanoid skeleton has a tendency to remain intact, rather than broken randomly along the sidechain, as C-C and C-O bonds have similar strengths. Clearly there must be some mechanism for controlling the concentration of totally sulphur bound bacteriohopane precursors in the polar fraction, however, we are unable to suggest what this mechanism might be as yet.

Higher abundances of C_{30} hopane in the polar and other fractions studied may be due to cleavage of C-C and C-O bonds along the sidechain of the C_{35} precursor, or alternatively it may be that a different precursor species, namely diplopterol (C_{30} precursor; Figure 7) has been preferentially concentrated in the other fractions of the coal. This cleavage of C-S bonds, which replaced the single -OH binding function of

diplopterol, would easily account for the high levels of C_{30} present in both the polar fraction products and in the other fractions too.

Hopanoid hydrocarbons are of interest as they act as source indicators for bacteria, as well as terrestrially derived material such as ferns (Philp, 1985). As well as being a source indicator of terrestrially derived organic matter, the relationship between the different stereoisomers may be used as an indication of the relative maturity of an oil or source rock. As yet, we have not quantified the hopanes in the different fractions, as absolute verification of the different compounds has not been carried out as yet.

Steranes

A range of regular steranes have been tentatively identified in the range of C_{27} to C_{29} , illustrated by the $m/z=217$ ion chromatogram (Figure 8). The presence of regular steranes is quite limited in the desulphurisation products of the polar, asphaltene and matrix fractions (Figure 8). In particular, the presence of any regular steranes is so low that they were barely detected in the desulphurisation products of the coal matrix. This is not unusual in coal samples in themselves, as we have seen a complete lack of steranes in other coal desulphurisation experiments with Iowa and Oklahoma coals.

The steranes from the polar and asphaltene degradation experiments have produced abundant C_{28} and C_{29} steranes, however there is a virtual absence of C_{27} steranes relative to the free aliphatic hydrocarbons.

Steranes are derived from biological precursors called sterols. Sterols may have a marine or non-marine source. In general terms, it is believed that C_{27} steranes come from marine derived sources and that C_{29} steranes are from a higher plant source (Huang and Meinschin, 1978). This distribution is observed in the steranes cleaved by desulphurisation of the polar, asphaltene and matrix fractions of the coal, but not in the free aliphatic hydrocarbons extracted from the same coal (Figure 8).

In addition, the distribution of sterane stereoisomers can also be used to determine the relative maturity of a source rock or oil sample. Again no analysis of this sort has been performed yet, as absolute compound identification has not been completed.

Mono-aromatic Steroids

The diagnostic fragment ions for mono-aromatic steranes is m/z 211 (A-ring aromatic steranes) and m/z 253 (C-ring aromatic steranes). Mono-aromatic steroids were found in both the free aliphatic and the desulphurisation products of each fraction (Figure 9). Some of the mono-aromatic steroids appear to contain one double bond in the sidechain of the molecule, (i.e., $M^+ = 364$, instead of $M^+ = 366$). The distribution of the tentatively identified C_{27} mono-aromatic steroids appear similar in each case, apart from the desulphurisation products of the polar fraction, where the relative abundance of the mono-aromatic steroids marked A, B, C and D is far lower than for any of the other extracts.

The mono-aromatic steroids have the same types of biological precursors as the regular steranes, however they have been diagenetically altered in slightly different ways. Again the distribution of different mono-aromatic steroids can be used as source and maturity indicators.

C_{20} diterpenoids

Quite an extensive range of C_{20} diterpenoids were observed in the free products of all the desulphurisation experiments (Figures 10, 11, 12).

The fully saturated C_{20} diterpanes are best illustrated by the chromatogram of the molecular ion for these diterpanes which is $M^+ = 276$ (Figure 10). The saturated C_{20} diterpanes are most abundant in the free aliphatic hydrocarbon fraction, and in the products of the desulphurisation experiment with polar compounds. The abundance of

saturated C₂₀ diterpanes is virtually negligible in the asphaltene and matrix fractions of the coal.

C₂₀ mono-unsaturated diterpenes (Figure 11) are more common in both the free aliphatic hydrocarbons and in each of the desulphurisation products, except for the coal matrix products, where there is an absence of these components.

In contrast, the C₂₀ diterpenes containing 2 double bonds (Figure 12) are found in abundance in the products from the coal matrix and are also present in the free aliphatic hydrocarbons and the polar and asphaltene fractions.

Some tentative identifications have been made as to the structure of some of these diterpenoid compounds based on comparisons of the mass spectra of these components with spectra taken from Philp (1985). Further work will have to be performed before we can confirm these structures.

The diterpenoids are generally absent in most oils, but abundant in terrestrially derived organic material. They are widely distributed in higher plants (Philp, 1985). Unfortunately, it is difficult to determine the absolute structure of many of these compounds as few authentic standards exist.

Evaluation of Method

Based on the duplication of the results from this series of nickel boride desulphurisation experiments, it is quite clear that we are able to extract large amounts of information from one coal sample by the chemical degradation method alone. We have now reached the stage where the method appears to have been perfected, and our established expertise in compound identification by GC-MS analytical methods has proven invaluable.

Future Work

We expect now to be able to examine several moderate to high organosulphur containing coal samples over the next few months and gain a greater insight into the distribution and abundance of organosulphur compounds for coals of different origins and diagenetic histories. In addition, it is expected that several publications will result from this work in the near future, based on the success of the current experiments.

Figure 1: Illinois No. 6 Coal: aliphatic hydrocarbon fractions from (a) the maltenes, and (b) and (c) the polar compounds from the maltene fraction. (b) and (c) are duplicated analyses.

Figure 2: Illinois No.6 Coal: aliphatic hydrocarbon fractions from (a) and (b) the asphaltenes isolated from the extract of the coal, and (c) and (d) the degradation of the pre-extracted coal matrix..

Figure 3:
Evidence of contamination by plasticisers in the products of the
asphaltene degradation experiments, shown by the chromatograms above.

Figure 4:
Distribution of n-alkanes in the free aliphatic hydrocarbons and
aliphatic hydrocarbons cleaved from the polar, asphaltene and matrix

Figure 5:

Distribution of hopanes in the free aliphatic hydrocarbons and aliphatic hydrocarbons cleaved from the polar, asphaltene and matrix fractions.

Figure 6:

Possible means of incorporating the C35 bacteriohopane(tetrol) biological precursor to the hopanoids via oxygen or sulphur links.

Figure 7:

Possible means of incorporating the C30 diplopterol biological precursor to the hopanoids via oxygen or sulphur links.

Figure 8:
Distribution of regular steranes in the free aliphatic hydrocarbons and
aliphatic hydrocarbons cleaved from the polar, asphaltene and matrix fractions.

Figure 9:
Distribution of mono-aromatic steroids in the free aliphatic hydrocarbons and aliphatic hydrocarbons cleaved from the polar, asphaltene and matrix fractions.

Figure 10:
Distribution of C20 diterpanes in the free aliphatic hydrocarbon fraction and aliphatic hydrocarbons cleaved from the polar, asphaltene and matrix fractions.

Figure 11:
Distribution of C20 mono-unsaturated diterpenes in the free aliphatic hydrocarbons and aliphatic hydrocarbons cleaved from the polar, asphaltene and matrix fractions.

Figure 12:
Distribution of C20 diterpenes (2 double bonds) in the free aliphatic hydrocarbons and aliphatic hydrocarbons cleaved from the polar, asphaltene and matrix fractions.