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

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P.I.:

Prof. R. P. Philp,
School of Geology and Geophysics,
University of Oklahoma,
100 E. Boyd St., Rm. 810,
Norman, OK-73019.

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U.S. Department of Energy,
Pittsburg Energy Technology Center,
Attn: Document Control Center,
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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: As well as studying coal samples from Oklahoma and Missouri States (samples supplied by Brian Cardott and the Penn State Coal Sample Bank respectively), we have now completed the preliminary part of a study of a well know high organosulphur containing coal, Illinois No. 6 (also supplied by the Penn State Coal Sample Bank). The results of the former samples were recently reported in a poster presented at the 17th International Meeting of Organic Geochemists in San Sebastian, Spain. A copy of this poster was sent to Paula Flenory in September of this year.

As a number of other research groups have used Illinois No. 6 for study, we thought it wise to also analyse this coal for comparison of our method with existing data reported in the literature. To date, analyses of the aliphatic fractions of the free maltene components (Figure 1a) and the aliphatic hydrocarbons isolated following desulphurisation of the free maltene polar fraction (Figure 1b and 1c), asphaltenes (Figure 2a and 2b) and pre-extracted coal matrix (Figure 2c and 2d) have been performed in duplicate. So far, most of these samples have been analysed by GC and subsequently quantified using $n\text{-C}_{24}\text{D}_{50}$. As Figures 1 and 2 show, the duplicates for the desulphurised products (e.g. Figure 2a and 2b of desulphurised asphaltenes) while showing broad similarities, do not appear to be identical. This is emphasised by differences in the yields of n -alkanes generated, quantified in Table 1. Abundance of corresponding n -alkanes are often quite variable for duplicate analyses, which have been normalised to the quantity of original starting material. While inhomogeneity of sampling can easily explain the variation in

abundance of products generated for the asphaltenes and coal matrix, the same cannot be said for the free polar compounds, which dissolve easily in the methanol/tetrahydrofuran solvent system used in the desulphurisation process. It would therefore appear that desulphurisation experiments should be performed at the very least, in duplicate to gain a clear impression of the distribution and abundance of aliphatic products cleaved from organosulphur compounds.

The GC analysis also appears to show that there are different organosulphur compound precursors trapped in the different fractions of the coals. It seems that we have been able to cleave alkyl chains of significantly different length from each of these fractions, which leads us to believe that the precursors are potentially quite different also. This observation may be confirmed by the use of the D-labelled reagents in experiments currently being performed for the Illinois No. 6 coal. The coal matrix products of the Illinois No. 6 sample appear to be dominated by lower molecular weight isoprenoid-type components (Figure 2c and 2d), while the free polar compounds (Figure 1b and 1c) tend to contain a broader distribution of organosulphur products, from components in the *n*-C₁₆ range, to heavier species in the range of *n*-C₃₅.

The yields of products vary between the different organic fractions to quite significant extents (Tables 1 and 2). In the case of the results from Illinois No. 6 coal studied, this may be due to the fact that organosulphur compounds may be concentrated in, for example, the asphaltenes, and only present in minor abundance in the maltenes and coal matrix (Table 1). If this is the case, a study of individual coal macerals is indeed the appropriate step to take next in this study, as the organosulphur species may be further concentrated in specific maceral types.

The abundance of aliphatic products vary significantly from other samples studied, for example samples from Oklahoma and Missouri (Table 2). Here the distribution of products suggests that more organosulphur compounds were present in the free polar

material than in the asphaltentes in both cases. In the Oklahoma coal, desulphurisation products of the free polar compounds are remarkably high.

Currently the aliphatic hydrocarbon fractions described above and shown in Figures 1 and 2 are being analysed by GC-MS for more accurate determinations of the identity of the products generated. Residues have been sent for C/S analysis as a further means of estimating the success of the desulphurisation procedure. Remaining residual material is also being put through the RuO_4 oxidation process for additional information on the structure of the Illinois No. 6 coal sample.

When all this information is collated, we will then begin the deuterium labelling experiments with Illinois No. 6 coal so that the type of organosulphur compounds may be identified. This will be combined with the current data to produce a paper discussing the success of the nickel boride procedure on the study of organosulphur compounds in coals which we hope to complete early in the new year.

Future Work: Similar procedures to those described above will be performed on the remaining coal sample. In addition, some of the residual material will be analysed by Py-GC to again determine what types, if any, organosulphur compounds remain following the desulphurisation process.

Figure 1: Illinois No. 6 Coal: aliphatic hydrocarbon fractions from (a) the maltenes, and (b) and (c) the free 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..

Table 1: Quantification of aliphatic hydrocarbons cleaved from various fractions of Illinois No. 6 coal by the nickel boride desulphurisation method. These experiments were performed in duplicate and normalised to the quantity of original starting material used.

	Illinois No. 6 (1)				Illinois No. 6 (2)		
	Maltenes	Matrix	Asphaltenes	Free	Matrix	Asphaltenes	Free
				Polars			Polars
	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
	coal	matrix	asphaltenes	polars	matrix	asphaltenes	polars
<i>n</i> -C ₁₆		0.651	16.77	5.05	0.276	8.51	4.14
<i>n</i> -C ₁₇	0.012	0.398	18.23		0.333	8.45	12.74
Pristane	0.200	0.615	7.61		0.258	4.70	3.60
<i>n</i> -C ₁₈	0.010		15.28		0.716	8.80	10.71
Phytane	0.034		15.06		3.127	8.80	19.40
<i>n</i> -C ₁₉	0.011		7.53	5.72	0.609	3.97	5.20
<i>n</i> -C ₂₀	0.006		5.43	6.18	0.725	1.87	2.69
<i>n</i> -C ₂₁	0.014	0.178	6.69	5.88	0.674	1.87	3.53
<i>n</i> -C ₂₂	0.008	0.202		8.70	0.767	12.94	4.76
<i>n</i> -C ₂₃	0.008	0.135		7.66	0.523	1.15	4.37
<i>n</i> -C ₂₄	0.008	0.153	8.66	10.56	0.523	1.62	6.63
<i>n</i> -C ₂₅	0.010	0.337		23.87	1.976	19.42	5.94

Table 2: Quantification of aliphatic hydrocarbons cleaved from various fractions of Oklahoma and Missouri coal by the nickel boride desulphurisation method. These experiments were normalised to the quantity of original starting material used.

Compound	Oklahoma				Missouri			
	Maltenes	Matrix	Asphaltenes	Free Polars	Maltenes	Matrix	Asphaltenes	Free Polars
	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g	ug/g
	coal	matrix	asphaltene	polars	coal	matrix	asphaltene	polars
<i>n</i> -C ₁₆	0.19	0.50			0.16	0.11	3.76	2.51
Pristane	1.78	0.21			2.89		7.59	1.36
<i>n</i> -C ₁₇	0.26	0.66		6.25	0.22	0.10	3.64	4.85
Phytane	0.49	0.26		6.50	0.36	0.27	1.31	4.61
<i>n</i> -C ₁₈	0.19	0.72	0.82	28.05	0.15	0.16	2.12	6.04
<i>n</i> -C ₁₉	0.22	0.35	1.52	58.64	0.14		0.90	2.59
<i>n</i> -C ₂₀	0.31	0.39	2.80	81.41	0.27	0.07	0.43	2.98
<i>n</i> -C ₂₁	0.27	0.25	2.69	71.85	0.14	0.16	0.77	2.98
<i>n</i> -C ₂₂	0.24	0.31	3.84	61.45	0.11	0.87	2.05	3.24
<i>n</i> -C ₂₃	0.23	0.19	3.12	57.06	0.13	0.18	0.52	2.86
<i>n</i> -C ₂₄	0.21	0.23	3.02	47.78	0.12	0.84	1.28	2.13
<i>n</i> -C ₂₅	0.22	0.30	3.34	43.99	0.16	0.24	0.48	1.72