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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

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: In the recent months we have moved on from performing Raney nickel desulphurisation of the coals to a far more appropriate chemical degradation method. We have identified, initially from the literature, a more appropriate method which may be used to cleave organosulphur compounds from solid materials such as kerogens, coal matrix and asphaltenes. However the method described in the literature by Jenisch *et al.* (1990) used nickel(O)cene and lithium aluminium hydride had subsequently been improved upon by their research group at the Institute of Biogeochemistry and Marine Chemistry, University of Hamburg, Germany. They suggested that we use a newer technique utilising nickel chloride (NiCl_2) and sodium borohydride (NaBH_4) (Hefter *et al.*, 1995). While this technique has been used successfully on resin and asphaltene fractions of crude oils, it has not previously been used on coal matrix material.

Preliminary experiments were carried out and have proved highly successful. Resin, asphaltene and coal matrix samples from Illinois No. 6 coal have been used as a standard to test this method. Numerous organosulphur products have been observed following the chemical degradation procedure. These compounds are currently being identified by GC-MS. Other high sulphur containing coals are now being investigated by this protocol.

It has also been shown that this method can be adapted so that deuterium labelled reagents can be used during the chemical degradation procedure. During cleavage of the various organosulphur compounds, deuterium from the reagents labels the sites where sulphur bonds were in the precursor species. By monitoring the number of deuterium atoms present we can determine how many sulphur bonds were present and thus give information on the structure of the organosulphur compounds present. Again the Illinois No. 6 coal has been used to test this procedure, and we have again found it successful. This procedure will therefore be used on selected samples in the future.

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The final part of the analysis of coals by the method described by Hefter *et al.* (1995), is to perform ruthenium tetroxide oxidation on the polar material, following desulphurisation. In some cases, molecules may be bound by more than one link (e.g. bacteriohopanetetrol, the precursor to hopanes is bound by 4 links to macromolecular material), and by first cleaving any sulphur bonds in the presence of deuterium, followed by oxidation, we can determine whether some of these compounds were actually held in place by more than one bond type.

Future work: Once a suite of various high sulphur coals have been analysed by this method we hope to be able to pull as much available geological information relating to these coals together and assess whether the information we have obtained from the organosulphur compounds is of major geochemical significance (as is the case for organosulphur compounds in crude oils).

Again the use of gas chromatography-isotope ratio-mass spectrometry will be utilised in an effort to determine whether the origin of the free and sulphur-bound organic compounds are from similar or distinct sources on a molecular level.

The next stage of the work, following the analyses of a suite of coals by the nickel chloride/sodium borohydride chemical degradation method, will be to focus on a series of samples which have markedly differing depositional environments. The organosulphur compound distribution may aid in our understanding of the processes of deposition and diagenesis of bodies of coaly material as they are formed and buried.

Once we have accumulated a reasonable quantity of coal samples which we have characterised by the stepwise chemical degradation method, we will then analyse them by microscale pyrolysis methods and compare the results.