DOE/PC/30226--T2

MASTER

PROGRESS REPORT

Characterization of Western Coals
and Coal Macerals by Solid-State
Nuclear Magnetic Resonance Spectroscopy

Department of Energy Contract
No. DE-FG22-80PC30226

DOE/PC/30226--T2

DE82 011698

University of Utah
Salt Lake City, Utah 84112

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Ronald J. Pugmire
Department of Mining and Fuels Engineering

David M. Grant
Department of Chemistry

August 1, 1981 - January 31, 1982

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

I. INTRODUCTION

During the first year's effort on this contract, early delays were experienced in securing personnel and equipment. While the contract was initiated on September 1, 1980, it was not until November that Professor Qiu from Jilin University of the Peoples Republic of China joined our group. Dr. Karas joined our group in January 1981. The needed NMR equipment became operational in May 1981 but it was not until November 1981 that all of the petrographic analysis components and maceral separations equipment was finally assembled. Delays in the arrival of all of the latter equipment was due to delays of the vendors. For instance, a microscope reticle was back ordered for about four months and hence we were unable to begin doing point counts for our maceral analysis until late November 1981. In spite of these irritating delays, we have been able to initiate the full scope of our activities that were proposed for the first year of work.

Dr. Warner Woolfenden, a senior level spectroscopist, joined the group last summer and has made significant contributions to our NMR efforts. In addition, Dr. Mick Wilson from CSIRO in Australia made a major contribution to our NMR efforts. In December, Mrs. Vesna Bacic (B.S. in physics) joined our group as a graduate student to work with Dr. Karas on maceral separations. Mrs. Bacic will eventually use NMR techniques to study the separated coal macerals as part of her Ph.D. thesis.

During the first year's effort a significant amount of progress was made on the goals of this project. Two papers have appeared in print, one has been accepted for publication, and four additional manuscripts have been submitted for publication (see Appendix).

II. PROGRESS TO DATE

A. Maceral Separation

1. Coal Selection

The selection of coals for the density gradient centrifugal separation was based on the information from the Penn State Coal Sample Bank. The Bank contains over 1250 well-documented coal samples from coal seams within the entire United States (63 coals from Utah). The documentation includes geologic information, chemical, mineralogical and geographic data and some physical properties of coals. Coal samples are available in the form of -20 mesh particle size and sealed under nitrogen. The general criterion for selection is based initially on rank parameters and maceral composition with secondary consideration on depositional environment. The rank range of interest is lignite through anthracite. We will attempt to isolate pure macerals from these coals in order to have the maceral groups (e.g., liptinites, vitrinites, and inertinites) available from coals of the widest possible rank range. We have also attempted to select coals that have a relatively high proportion of a particular maceral which we will attempt to separate for detailed study. For instance, we are particularly interested in obtaining psuedovitrinite, bituminite, ulminite, alginite, fusinite, semi-fusinite, micrinite, and macrinite in order to assess the structural differences between these macerals as compared to the more abundant vitrinite and sporinite macerals. The coals thus selected are given in Table I. It is interesting to note that these coals contain essentially no sporinite, two contain large amounts of bituminite, one is almost pure ulminite, four contain appreciable amounts of psuedovitrinite, eight contain a high percentage of semi-fusinite in the inertinite group while only one is rich in fusinite. Hence, we feel that these coals will provide both a comprehensive and an interesting group for our future efforts. Variability within a given seam is also of interest

to us. We have previously reported data on PSOC-122, -123, and -124.

PSOC-122 is a channel-whole seam sample while -123 and -124 were lithotypes taken at 18 and 15 inches respectively from the seam floor. While these samples are from the West Virginia No. 5 Block of the Lower Kittanning Seam, they represent an interesting sample set for studying variability of coal structure within a seam. Petrographically, the samples are quite different and the preliminary CP/MAS spectra taken on these samples reflect diversity in maceral composition. The high micrinite content (24.3%) of PSOC-124 makes this an attractive sample for DGC separation.

We chose coal PSOC-2 for our first DGC separation. This coal is a durain of high volatile A bituminous rank. The petrographic analysis from Penn State has approximately equal amounts of each of the three main maceral groups, which should be separated by the DGC method. Some data on this coal is given in Table II. While this coal is not from a western coal province, the Penn State petrographic analysis (see Table II) suggested that it might be the ideal coal for our initial separation work. The particular petrographic analysis from Penn State indicates that the liptinite groups in this coal is mainly sporinite (90%), a very common liptinite maceral. However, our DGC separation did not provide a fractogram (Figure 1) that corresponded to equivalent amounts (vitritinite: 32.1%; inertinite: 31.7%; liptinite: 36.2%) of the three major maceral groups as specified in the Penn State Analysis. Our own petrographic analysis, given in Table IV, is consistent with the density distribution displayed in Figure 1. Hence, we feel that we have succeeded in separating the major maceral groups.

In our efforts to separate different coal macerals we chose for the second DGC PSOC-1111, a coal with a rather rare liptinite maceral - bituminite. Bituminite is described as a finely dispersed, streaky groundmass which exhibits a brown fluorescence in UV-light¹ Table IV provides some data on this coal.

The hardgrove grindability has a very high value, which was another important reason for our selection of this coal as one of the basic conditions for the coal maceral separation is the ability to grind the coal to a particle small size ($\sim 3 \mu\text{m}$).

2. Experimental

The entire experimental procedure used for the DGC maceral separation was the same as the technique developed in the Argonne National Laboratory.²⁻⁵

The coal samples obtained from Pennsylvania State University ($850 \mu\text{m}$) were ground in a ball mill to $200 \mu\text{m}$ particle size, followed by grinding in a fluid energy mill up to $\sim 10-3 \mu\text{m}$ using gaseous nitrogen as the grinding medium. The samples were then treated with HCl and HF to remove the mineral matter.

The density gradient centrifugation was performed in the J-21B Beckman preparative centrifuge with a JS-13 swinging bucket rotor for the analytical scale separation and JCF-Z titanium rotor with the standard core for the large scale zonal centrifugation.

Aqueous cesium chloride solution was used as the gradient medium. To prevent the agglomeration of coal particles, the surfactant Brig-35 (polyoxyethylene-23-lauryl ether) was added to the gradient (8 mg 1 ml of CsCl solution). The analytical scale DGC was performed in a 45 ml test tube. The coal amount was 2-3 mg with a rotor speed 10 K RPM for 30 minutes. For the large scale, preparative DGC we used $\sim 2\text{g}$ with a speed 12 K RPM for 60 minutes. The gradient was pre-formed at 2 K RPM in the centrifuge.

3. Results

PSOC-2

Figure 1 shows the results of the analytical scale DGC of PSOC-2. This analytical maceral separation run is used as a "qualitative"

analysis of the coal which is to be separated in a large scale zonal DGC. The isopycnically banded coal particles are monitored by a UV-detector as absorbance peaks. There are three absorbance peaks in Figure 1. The first at the density $\rho_{25} = 1.155$ g/cc which should correspond to the exinite, the second by $\rho_{25} = 1.270$ g/cc which indicates the vitrinite and the third as a shoulder on that peak with the density $\rho_{25} = 1.324$, which could be the inertinite. The gradient used for the separation was linear, with density 1.1 - 1.5 g/cc. It was a successful small scale separation and therefore we used the same gradient for the preparative DGC. After the separation at 12 K RPM was completed, the coal fractions were collected as previously described.²⁻⁵ Each fraction (35 ml) was filtered and the fraction weighed. The results of the preparative DGC are given in Figure 2. Both separation, the analytical and the preparative, show the same density distribution pattern of the coal particles. The results do not fully correlate with the petrographic analysis from Penn State University (see Table II.). However, our petrographic analysis on the coal sample used (see Table III) was consistent with the separation results.

PSOC-1111

We employed the same procedure for the analytical separation of PSOC-1111 as for the PSOC-2 and the results are presented in Figure 3. There were four absorbance peaks that were observed with the highest density peak found at $\rho = 1.51$ g/cc. However, there was still a large quantity of coal "sitting" on the bottom of the gradient. The gradient used ($\rho = 1.10 - 1.56$ g/cc) did not encompass the whole density range of this coal. Therefore, we repeated the separation using a gradient of $\rho = 1.10 - 1.80$ g/cc. The results are shown in Figure 4. The pattern of the particle density distribution has changed in the higher density range. The two low density peaks appear in the same density range. In the first run we increased the coal loading by a

fraction of two and observed what appeared to be either extensive coal agglomeration or the appearance of a higher density coal fraction than we had anticipated. We speculate that there was an overloading of gradient with coal. The analytical scale separation with a gradient of $\rho = 1.1 - 1.8 \text{ g/cc}$ was repeated at a higher speed (11.5 K RPM) and longer (60 min.) time for the centrifugation on a sample in which the coal loading was one half that employed in Figure 3. The results were the same as in the separation shown in Figure 4. The DGC analysis of PSOC-1111 gave some unusual and interesting results. We expected two peaks only: one peak for bituminite and the second one for vitrinite, as indicated by the data in Table IV. However, this particular coal is extensively oxidized (according to P. H. Given at Penn State) and the possibility exists that the two additional peaks may be due to the oxidized coal macerals. We are in the process now of carrying out a preparative scale run in order to begin an extensive analysis of these coal fractions.

B. NMR Analysis

1. CP/MAS Work

We have previously noted the value of examining maceral groups separated by DGC⁶⁻⁷ (this work was partially supported by other sources). We noted that a monotonic relationship exists between maceral density and f_a . The f_a values observed agree with those observed earlier for macerals of similar rank^{7,8} and range from 0.18 for the alginite from PSOC-297 to 0.83 in one of the high density inertinites in PSOC-106. It is interesting to note that the overall f_a for each parent coal gives little indication of the broad range in f_a for the component macerals. In PSOC-297 the overall value $f_a = 0.60$ for the coal is the sum of maceral groups which have f_a values in the range of 0.18 - 0.76 while for PSOC-106 the $f_a = 0.70$ is derived from maceral groups which have individual f_a values having a range of 0.43 to 0.83. Note that for these coals

it is the relative abundance of maceral groups which influences most the overall f_a value and not the rank of the coal. For example, the slightly higher rank PSOC-297 coal (carbon content 84.0%) has a lower f_a than PSOC-106 (carbon content 82.8%). This leads us to the conclusion that maceral composition can overshadow rank differences in NMR analysis. Miknis et al.^{11,12} reported data for a series of coals of wide range of rank (lignite through anthracite) which demonstrates that f_a does increase with rank. While this trend generally holds, CP/MAS results¹³ on a significant number of coals of known petrographic composition suggests that maceral composition must be taken into account when determining the f_a value.

We have examined the DGC fractions of PSOC-2 separated in our laboratory. The stacked CP/MAS spectra of the PSOC-2 whole coal and the sporinite, three vitrinite, and two inertinite fractions are given in Figure 5. These spectra display features similar to those reported earlier.^{8,9} Note the variation in the band shapes in the aliphatic regions of the vitrinite and inertinite maceral groups. These data clearly indicate the additional structural information that one can obtain from studies of coal maceral groups which have been separated from a given coal.

Additional information can be obtained on the structure of a given coal by means of the dipolar dephasing technique reported by Opella^{10,11} which can be used to separate protonated from non-protonated carbons in a CP/MAS spectrum. This separation is effected by utilizing the ^1H - ^{13}C distance dependence of the cross polarization time or the ^1H and ^{13}C dipolar relaxation rate differential of carbon magnetization under the influence of the full ^1H - ^{13}C dipolar interaction. Hagaman and Woody^{12,13} have reported the spectra of Illinois No. 6 coal by employing this technique. Through a study of model compounds, Alemany¹⁴ has observed that if a 40- μs delay in the

proton decoupling pulse is inserted between cross polarization and data acquisition sequences, all resonance due to CH and CH₂ carbons will be broadened out into the noise. The intensity of the non-protonated carbons experience only minor attenuation (Ca. 10-15%) during this interval. The time constant for the dephasing of a methyl group is more complex but approximately 50% of the methyl carbon signal is still observed. Hence, by appropriately fixing the decoupler pulse delay one can differentiate between methine, methylene, methyl and non-protonated carbons. Typical results are given in Figure 6 for the Aldwark, Silkstone exinite. The proportion of the total carbons that are aromatic and non-protonated, f_a^N , is obtained by comparing the relative intensities of the aromatic region of the spectra with decoupler pulse delays of 0 and 40 μ s before data acquisition. The fraction of total carbon that is protonated aromatic carbon is defined as f_a^H ; thus $f_a^H + f_a^N = f_a$. Using a solvent refined coal tar for which high resolution ¹H and ¹³C NMR data were taken, Wilson¹⁵ has obtained values of f_a , and f_a^H in the solid coal tar and these agree nicely with corresponding values obtained for the dissolved material. ($f_a = 0.62, 0.62$; $f_a^H = 0.24, 0.23$ for the solid coal tar and dissolved material, respectively).

Dipolar dephasing data^{12,13} have been acquired on 36 coal and maceral samples and some of the results are given in Table V. The data is indicative of the highly variable structure that is found in coal samples. For example, in the sample set of PSOC-2 and its separated maceral groups, the f_a values are in the order (as indeed they are for all maceral groups studied¹⁶ to date) exinite < vitrinite < inertinite. An interesting observation is that f_a^H , the fraction of the total carbon in the coal that is aromatic and protonated, increases in the order exinite < vitrinite < inertinite. These data imply that there is a significant diversity in the amount of ring substitution and/or cross linking among the aromatic carbons in the various

macerals as seen in the estimated values for the fraction of aromatic substituted and bridgehead carbons, f_a^S and f_a^B , respectively. This separation is based strictly on the chemical shift range of the non-protonated aromatic carbons; i.e., it is assumed that non-protonated carbon resonance shifts greater than 133 ppm are associated with substituted carbons while those with chemical shifts less than 133 ppm are bridgeheads.

An examination of the pure vitrinite series PSMC-67, -19, -34, -43, -47, and -53, which is a suite of samples from a common depositional environment but of varying rank, reveals a similar trend in samples of increasing rank. The CP/MAS data reported earlier⁹ exhibited a decrease in functionality with progressing rank (i.e., loss of alkyl and aromatic oxygen groups). The dipolar dephasing data indicate that this loss of functionality leads to a net increase in the fraction of protonated aromatic carbons. Ring condensation reactions alone cannot explain these results as ring condensation would produce an opposite effect. It appears that reactions associated with vitrinite maturation in these samples must also include some ring protonation reactions accompanying ring defunctionalization and the data suggests that these protonation reactions are preferred to ring condensation reactions.

We have also acquired data on British maceral concentrates supplied by Professor Peter Given at Penn State University. These data exhibit trends similar to those noted above. Comparing the f_a^H data on the inertinite fractions from PSOC-2, Wooley Wheatly Lime, Teversal Dunsil, and Aldwarke Silkstone reveals some significant differences between these samples from coals of high volatile bituminous rank (albeit, perhaps from quite different environments). The Wooley Wheatly lime sample is 93% fusinite while the Teversal Dunsil concentrate is 80% semi-fusinite with 13% fusinite. The Aldwarke Silkstone sample contains 43% fusinite and 43% semi-fusinite. The petrographic analysis of PSOC-2 reveals nearly equivalent amounts of

fusinite, semi-fusinite, micrinite, and macrinite (6.8, 8.1, 7.5, and 8.5% respectively in the whole coal). The differences in f_a^H values for these samples are greater than the experimental error and these differences suggest that NMR techniques may be useful in characterizing the chemical structural differences between inertinite macerals.

These data, then, demonstrate the importance of work in separation of macerals from coals and the potential for obtaining valuable information by means of NMR techniques.

2. Two-Dimensional Study of Coal Macerals

The use of 2-D ^{13}C NMR techniques in liquids has progressed from a novelty to a useful analytical tool. Under funding from a different source, we have recently obtained J-resolved spectra on a coal derived liquid that clearly exhibited significant amounts of additional structural detail. The use of 2-D pulse techniques on solids is not as far advanced but experiments on simple organic compounds have appeared in the literature.¹⁷

The principal value of 2-D spectroscopy in solid CP/MAS studies of coal and related macerals lies in the ability of such methods to separate spectral information which in the typical one-dimensional case appears as a single resonance response. For instance, carbon resonances arising from both non-protonated and protonated aromatic carbons may appear at the same frequency under proton decoupling. Yet these two resonances could possess very different relaxation behavior and in a solid would evolve very differently due to local proton dipolar fields which alternate with the carbon proton distances as $1/r_{\text{CH}}^3$. When the spin locking for proton and carbon-13 nuclei is turned off, carbons with directly bound protons such as methines and methylenes rapidly dephase in the local proton fields and their spectral response is rapidly diminished. The rapid internal motion of CH_3 groups greatly decreases the effectiveness of methyl protons. Non-

protonated carbons are only dephased by remote and therefore much weaker magnetic fields. This type of response is given in Figure 6 using the pulse sequences first proposed by Rybaczewski et al.¹⁷ and popularized by Opella^{10,11} for powders. These two spectral traces for different dephasing times, 0 μ sec. and 40 μ secs., respectively, demonstrate how carbon with protons are significantly attenuated after the latter dephasing time. Thus, the strong upper field portion of the aromatic peak due to protonated carbons and essentially all of the aliphatic region are attenuated leaving primarily the non-protonated aliphatic carbons and methyl carbons (two upper field peaks in the lower trace which have chemical shift values for aliphatic and aromatic CH_3 carbons) with a small vestigial remnant of the once very strong peak due to methylene peak (lowest field peak of the three distinct aliphatic peaks). Thus, this spectral response is limited to a subportion of the total spectrum contained in the upper trace. From the upper trace f_a can be obtained while f_a^N and $f_s^{\text{CH}_3} + f_s^N$ are directly obtainable from the lower trace.

Thus, otherwise overlapping spectral information has been obtained by employing in a subtle way the differing dipolar properties of the different types of carbons. If this spectral feature is made the basis of a two-dimensional, 2-D, FT spectrum, one may simultaneously obtain spectral information on both non-protonated and protonated carbons directly. Figures 7 and 8 contain such a 2-D spectrum for the Aldwarke Silkstone exinite. In Figure 7, a contour plot of the spectral intensities is given for the rate of dipolar dephasing along the Y-axis vs. chemical shift along the X-axis. Thus, the non-protonated and methyl carbons show steep fall off in the intensity contours while protonated carbons are represented by much broader (along y-axis) spectral responses. Vertical cuts through the 2-D surface are given in Figure 8. Hence, we observe in more typical format

the spectral response as a function of a dipolar dephasing frequency. For a solid powder, the C-H dipole-dipole vectors span all possible orientations and thus zero frequency responses are found for all resonances, albeit the spread in aliphatic response is distributed over such a much greater range of dephasing frequencies as to reduce this part nearly to the noise level. The successive slices in Figure 8 leaves the CH₂ peak persisting to higher dephasing frequencies as would be expected from the data in Figure 6. There is an inverse relationship between the time slices in Figure 6 and the frequency slices in Figure 8. Short times contain information corresponding to larger dephasing frequencies. The three-dimensional plot (Figure 9) of the aromatic portion of Figures 7 and 8 helps one to appreciate the above point. Note in the plot sharp peaks corresponding to non-protonated carbons having as their foundation a broader peak from protonated carbons. This feature is graphically shown in the 3-D portrayal. A single chemical shift slice through the aromatic region, also shown in Figure 9, emphasizes the dual nature of the spectral response with a sharp peak resting on a broad base peak. Curve fitting techniques can easily resolve the true components.

Thus, using very sophisticated spectral resolving techniques, important structural information on coal is now available from these techniques for the first time. We anticipate that considerable additional structural detail on coals and coal macerals will thus be obtained. Hence, multiple pulse/multidimensional spectroscopy offers an exciting new analytical tool for study of complex materials such as coal and coal macerals.

III. FUTURE WORK

Our previous work, some of which has been described in Section II, has demonstrated a high degree of variability in coals and coal macerals. We plan to continue to exploit this structural diversity by a combination of petrographic analysis, maceral separation of the selected coals, and NMR analysis based on conventional CP/MAS and multiple pulse multi-dimensional ^{13}C NMR spectroscopy of the separated macerals.

A. Sample Selection

We will continue to focus on the western coals (see Table I) of Cretaceous age along with some of the Alaskan coals of Cretaceous and early Tertiary age that we have. The general criterion for selection will be based on rank parameters and maceral composition with secondary consideration on depositional environment. The rank range of interest is lignite through anthracite. We will attempt to isolate pure macerals from these coals in order to have the maceral groups (e.g., liptinites, vitrinites, and inertinites) available from coals of the widest possible rank range. We are particularly interested in obtaining psuedovitrinite, bituminite, ulminite, alginite, fusinite, semi-fusinite, micrinite, and macrinite in order to assess the structural differences between these macerals as compared to the more abundant vitrinite and sporinite macerals. The coals in Table I contain essentially no sporinite, two contain large amounts of bituminite, one is almost pure ulminite, four contain appreciable amounts of psuedovitrinite, eight contain a high percentage of semi-fusinite in the inertinite group while only one is rich in fusinite.

B. NMR Analysis

The samples given in Table I will be examined by regular CP/MAS as well as the dipolar dephasing (DD) technique to obtain values for f_a , f_a^H , and f_a^N . The corresponding structural units in the aliphatic region of coals

and coal macerals will also be of interest since one observes practically no non-protonated carbons in the aliphatic region. The relative amount of non-protonated aliphatic carbon f_s^N , is small, e.g. $\leq 5-7\%$ of the total carbon. We have observed in our data a rather wide range of percentage of CH + CH₂ ($f_s^{CH} + f_s^{CH_2}$) groups in the maceral samples. In the Aldwarke Silkstone, Wooley Lime, and Markham Main, Barnsley exinite concentrates exhibit $f_s^{CH} + f_s^{CH_2}$ values of 0.40, 0.46, and 0.48 whereas in the North Celyen, Meadow Vein a much smaller value (0.13) is obtained. The distribution of protonated saturated aliphatics including also methyl groups $f_s^{CH_3}$ and non-protonated, f_s^N , will be explored for aliphatic carbons in these coals. We hope to be able to draw correlations between such structural parameters as f_a , f_s , f_a^H , f_a^N , f_s^{CH} , $f_s^{CH_2}$, f_s^N , $f_s^{CH_3}$ and liquefaction data that is available on these samples. Note that $f_a + f_s = 1$; $f_a = f_a^H + f_a^N$; and $f_s = f_s^{CH} + f_s^{CH_2} + f_s^{CH_3} + f_s^N$.

The single 2-D experiment, as described in the previous section, revealed a whole new dimension of structural information not previously available. The fact that one can resolve the CH, CH₂, aromatic methyl, and aliphatic methyl carbons provides reliable estimates of f_a^N , f_a^H and the various f_s values. Not only can one now compare the relative amounts of these structural units in a given coal or maceral but comparisons can be made between them as well. Using this information it may become feasible to reconstruct the average carbon skeleton of coals of different rank as well as different macerals. We have already observed structural variations and trends that are beyond experimental error. While data of this sort are still only at the exploratory level and will not permit us to draw final conclusions, the results are highly encouraging.

It is possible to carry out a number of other multiple pulse multi-dimensional experiments. One can obtain 2-D spectra using interactions associated with $^1H_{T_{1\rho}}$, $^{13}C_{T_{1\rho}}$, $^1H_{T_1}$, T_{CH} , and T_2 experiments as well. We have

performed these experiments in the one dimensional mode on coals and a great deal of important information on spin dynamics involving stable free radicals and bound water has been obtained.²² The development of the 2-D experiments on coals is supported by other sources but we propose to use these additional multiple pulse experiments on the coals in Table I and the macerals we separate from them. As our 2-D spectroscopic methods are developed for a variety of interactions, such as relaxation, J-, and D-couplings, etc., we will immediately apply them to the coals to be studied in this project. New structural features found in these solids will undoubtedly suggest further basic developments.

C. Summary

Our goals are to: 1) separate macerals (liptinite, vitrinite and inertinite) of various rank. Furthermore, we hope to be able to 2) separate fusinite, semi-fusinite, pseudovitrinite, micrinite, macrinite, in order to compare structural similarities and differences (e.g., fusinite and semi-fusinite). We will 3) employ multiple pulse multi-dimensional techniques to obtain structural detail on these materials. We will then 4) compare the various structural features (f_a , f_a^N , f_a^H , f_s^H , f_s^N , and f_s^M) for the different maceral groups and maceral groups vis-a-vis rank.

REFERENCES

1. E. Stach et al., Coal Petrology, 2nd revised ed., Geb. Borntraeger, Berlin 1975.
2. G. R. Dyrkacz, C. A. A. Bloomquist, L. H. Fuchs, and E. P. Horwitz, Separation of Coal Macerals, Division of Fuel Chemistry, American Chemical Society, Vol. 25, No. 3, page 216.
3. G. R. Dyrkacz and E. P. Horwitz, Fuel 1982, 61 (in press).
4. G. R. Dyrkacz, C. A. A. Bloomquist, and E. P. Horwitz, Sep. Sci, and Tech., 1982, in press.
5. G. R. Dyrkacz, C. A. A. Bloomquist, R. E. Winans, and E. P. Horwitz, Proceedings of the International Conference on Coal Science, Dusseldorf, Sept. 7-9, 1981, page 34-38.
6. R. J. Pugmire, K. W. Zilm, W. R. Woolfenden, D. M. Grant, G. R. Dyrkacz, C. A. A. Bloomquist, and E. P. Horwitz, Proceedings of the International Conference on Coal Science, Dusseldorf, Germany, September 7-9, 1981, p. 798-806.
7. R. J. Pugmire, K. W. Zilm, W. R. Woolfenden, D. M. Grant, G. R. Dyrkacz, C. A. A. Bloomquist, and E. P. Horwitz, Carbon-13 NMR Spectra of Macerals Separated from Individual Coals, submitted for publication.
8. K. W. Zilm, R. J. Pugmire, S. R. Larter, J. Allen, and D. M. Grant, Fuel, 1981, 60, 717.
9. R. J. Pugmire, D. M. Grant, S. R. Larter, J. Allen, A. Davis, W. Spackman, and J. Sentfle, New Approaches in Coal Chemistry, ACS Symposium Series No. 169, 1981, p 23.
10. S. J. Opella and M. H. Fry, J. Amer. Chem. Soc., 1979, 101, 5854.
11. S. J. Opella, M. H. Fry, and T. A. Cross, J. Amer. Chem. Soc., 1979, 101, 5856.
12. E. W. Hagaman and M. C. Woody, Proceedings of the International Conference on Coal Science, Dusseldorf, Sept. 7-9, 1981 page 34-38.
13. Ibid, Fuel, 1982, in press.
14. L. B. Alemany, R. J. Pugmire, D. M. Grant, T. D. Alger, and K. W. Zilm, Cross Polarization and Magic Angle Spinning NMR Spectra of Model Organic Compounds III. The Effect of the Dipolar Interaction on Cross Polarization and Carbon-Proton Dephasing, manuscript in preparation.
15. M. A. Wilson, R. J. Pugmire, N. J. Russell, and D. M. Grant, Structure of Australian Oil Shales and Solvent Refined Coal as Revealed by ^{13}C CP/MAS Studies, manuscript in preparation.

16. H. N. M. Dormans, F. J. Hutjens, and D. W. Van Krevelen, *Fuel*, 1957, 36, 321.
17. E. F. Rybaczewski, B. L. Neff, J. S. Waugh, and J. S. Sherfinski, *J. Chem. Phys.*, 1977, 67, 1231.

TABLE I

Coal Samples Selected for Study

Sample	Rank	Maceral Composition ^a		(DMME Volume %)
		Liptinites	Vitrinites	Inertinites
PSOC-1108	Lig. A	13.8	69.2	16.7 (10 SF)
-1109	HVCb	69.1 (52.3 Bit)	26.7	3.9
-1110	Sub C	65.3 (53.5 Bit)	29.1	5.5
-1111	MVb	16.1 (11.0 Bit)	80.0	3.9
-1113	MVBb	2.1	82.3	15.6 (11.3 SF)
-1114	HVBb	2.7	83.1	14.2 (11.1 SF)
-1115	HVAb	2.0	87.0	11.0
-1117	HVAb	1.4	89.8	8.8
-1118	HVBb	1.4	83.7	14.9 (9.4 SF)
-155	HVCb			
-157	MVb	0.1	92.0 (13.3 PV)	7.9
-161 ^b	SA	0.0	88.5	15.6 (11.3 F)
-232	HVCb	2.2	88.6	9.2
-236	MVb	0.0	92.2 (18.5 PV)	7.8
-238	HVAb	2.9	85.2 (10.0 PV)	11.9
-249	HVBb	3.0	70.2 (12.5 PV)	26.7 (12.2F, 6.6 SF 6.8 Mi)
-850	HVCb		91.5	7.9
-858	HVBb	2.5	53.9	43.6 (39.7 SF)
-859	HVAb	1.4	55.3	43.3 (37.1 SF)
-860	HVAb	N/A	51.7	43.1 (40.0 SF)
-861	HVAb	1.2	60.5	38.3 (30.9 SF)
-474	Sub B	0.5	97.2 (Ulm)	2.3

a. As determined by Penn State University

b. Sample badly weathered ulm = ulminite, Bit = bituminite, PV = psuedovitrinite,
SF = semi-fusinite, F = fusinite, Mi = micrinite.

TABLE II

PSOC # 2 data from the Penn State Coal Data Base

Sample Location:	Kentucky, Letcher
Coal Region:	Appalachian
Seam Name:	Upper Elkhorn # 3
Apparent Rank:	High Volatile A Bituminous
% Volatile Matter:	37.62 (DAF)
% Carbon:	85.61 (DMMF) ultimate analysis
% Mineral Matter:	4.49 (0.04% Fe S ₂)
Maceral Composition:	DMMF - volume %
Vitrinite	32.1
Inertinite	31.7
Liptinite	36.2
Hardgrove Grindability:	42.1

TABLE III

Petrographic Analysis on PSOC-2

	DMMF % by volume
Vitrinite:	53.0
Exinite:	33.4
Inertinite:	13.4
	(1000 points counted)

TABLE IV

PSOC #1111 Data from the Penn State Coal Data Base

Sample Location:	Utah, Kane
Coal Region:	Southwestern Utah
Apparent Rank:	Medium Volatile Bituminous
% Volatile Matter:	33.39 (DAF)
% Carbon:	62.43 (DMMF) ultimate analysis
% Mineral Matter:	39.50 (0.3% Fe S ₂)
Maceral Composition:	DMMF - Volume %
Vitrinite	80.0
Inertinite	3.9
Liptinite	16.1 (includes 11.1% bituminite)
Hardgrove Grindability:	171.7

TABLE V
Structural Parameters of Coals and Coal Macerals

	H/C	%C (DMMF)	f_a	f_a^H	f_a^N	f_a^B	f_a^S	f_s^H	f_s^{N*}
PSOC-2	0.79	86.61	0.60	0.39	0.21	0.11	0.10	0.36	0.05
E	-	-	0.34	0.24	0.10	0.02	0.07	0.59	0.06
V-1	-	-	0.61	0.41	0.20	0.07	0.13	0.33	0.06
V-2	-	-	0.70	0.45	0.25	0.10	0.15	0.26	0.04
V-3	-	-	0.67	0.47	0.20	0.11	0.09	0.26	0.07
I-1	-	-	0.75	0.59	0.17	0.06	0.11	0.21	0.04
I-2	-	-	0.76	0.63	0.13	0.05	0.08	0.19	0.07
PSMC-67	0.80	82.2	0.74	0.30	0.44				
-19	0.86	84.4	0.71	0.27	0.44				
-34	0.75	83.9	0.79	0.32	0.47				
-43	0.78	87.0	0.72	0.35	0.37				
-47	0.73	88.0	0.80	0.38	0.42				
-53	0.63	89.1	0.85	0.41	0.44				
Aldwarke Silkstone									
Exinite	1.02	87.2	0.53	0.26	0.27	0.14	0.13	0.40	0.07
Vitrinite	0.75	86.9	0.80	0.38	0.42	0.21	0.21	0.15	0.05
Inertinite	0.48	92.1	0.89	0.59	0.30	0.17	0.13	0.10	0.01
Toversil Dunsil									
Vitrinite	0.75	81.5	0.78	0.30	0.48	0.23	0.25	0.18	0.04
Inertinite	0.53	87.7	0.86	0.37	0.49	0.21	0.28	0.12	0.02
Wooley, Wheatley, Lime									
Exinite	0.95	87.9	0.47	0.29	0.18	0.09	0.09	0.46	0.07
Vitrinite	0.78	86.6	0.77	0.48	0.29	0.12	0.17	0.20	0.03
Inertinite	0.37	93.7	0.89	0.53	0.36	0.21	0.15	0.09	0.02
Markham Main									
Exinite	1.08	82.6	0.45	0.25	0.20	0.09	0.12	0.48	0.07
Vitrinite	0.80	82.2	0.73	0.32	0.41	0.23	0.18	0.21	0.06
Inertinite	0.47	91.6	0.82	0.51	0.31	0.18	0.13	0.15	0.03
North Celyen									
Exinite	0.65	90.6	0.83	0.44	0.39	0.21	0.18	0.13	0.04
Vitrinite	0.67	89.9	0.84	0.44	0.40	0.24	0.17	0.11	0.05
Inertinite	0.61	91.3	0.84	0.47	0.37	0.24	0.13	0.12	0.04
PSOC-1108	0.65	68.0	0.43	0.29	0.14	0.06	0.08	0.46	0.11
PSOC-1110	0.93	72.5	0.16	0.03	0.13	0.06	0.07	0.65	0.19
Beluga Lignite	0.94	65.7	0.64	0.17	0.47	0.07	0.40	0.25	0.11

$$f_a = f_a^H + f_a^N = f_a^H + f_a^S + f_a^B \quad f_s = f_s^H + f_s^N$$

$$f_a + f_s = 1$$

* f_s^N = Non-protonated aliphatic carbon plus methyl carbons.

Figure 1. Absorbance record of PSOC #2 coal, analytical scale DGC.
Density ρ_{25} estimated by Refractive Index measurements.

Figure 2. Preparative DGC of PSOC #2 density ρ_{25} estimated by refractive index measurements. Gradient linear, $\rho = 1.1 - 1.50$ g/cc.

Figure 3. Absorbance record of PSOC #1111 coal analytical scale DGC. Gradient linear: $\rho = 1.1. - 1.56 \text{ g/cc}$. Density of each peak is calculated as ρ_{25} .

Figure 4. Absorbance record of PSOC #1111 analytical DGC.
Gradient linear: $\rho = 1.1 - 1.8$ g/cc

Figure 5. CP/MAS spectra of PSOC-2 whole coal and the maceral groups separated from the coal by density gradient centrifugation. The density ranges represent the range of densities for samples employed. f_a values are given for each sample.

Figure 6. CP/MAS (top) and dipolar dephasing data with lower trace acquired following 40 μ sec. pulse delay. Note three separate peaks in the aliphatic region due to methyls and CH₂'s.

PUG₈₂ 18

Aldwarke, Silkstone Exinite

Figure 7. Contour plot for 2-D dipolar dephasing experiment.

F₂

PUG₈₂ 20

PUG_{SL} 21

PUG_{SL} 19

APPENDIX

Papers Accepted for Publication

1. M. A. Wilson, R. J. Pugmire, K. W. Zilm, K. M. Goh, S. Heng, and D. M. Grant, Cross-Polarization ^{13}C NMR Spectroscopy with Magic Angle Spinning Characterized Organic Matter in Whole Soils, *Nature*, 1981, 294, 648-650.
2. R. J. Pugmire, K. W. Zilm, D. M. Grant, S. R. Larter, J. Allen, J. T. Sentfle, A. Davis, and W. Spackman, Carbon-13 CP/MAS Study of Coal Macerals of Varying Rank, *New Approaches in Coal Chemistry*, Ed. B. D. Blaustein, B. C. Bockrath, and S. Friedman, ACS Symposium Series No. 169, Washington, D. C., 1981, pp 23-42.

Papers Submitted for Publication

1. Z. W. Qiu, D. M. Grant, and R. J. Pugmire, Paramagnetic Carbon-13 Shifts Introduced by the Free Radical TEMPO. I. Simple Aromatic and Paraffinic Carbons, *J. Am. Chem. Soc.*, 1982, in press.
2. M. A. Wilson, S. Heng, K. M. Goh, R. J. Pugmire, and D. M. Grant, Studies on Soil Organic Matter Fractions Using ^{13}C -Cross Polarization Nuclear Magnetic Resonance Spectroscopy with Magic Angle Spinning.
3. M. A. Wilson, R. J. Pugmire, N. J. Russell, and D. M. Grant, Structure of Australian Coals, Oil Shales, and Solvent Refined Coal as Revealed by ^{13}C CP/MAS Studies.
4. N. J. Russell, M. A. Wilson, R. J. Pugmire, and D. M. Grant, Preliminary Studies on the Aromaticity of Australian Coals Using Solid State Nuclear Magnetic Resonance Techniques.