SHORT RANGE RING STRUCTURING IN A META-ANTHRACITE COAL

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INTRODUCTION

X-ray characterizations of coals and coal products have occurred for many years.[1-9] Hirsch and Cartz[1], several years ago, measured the diffraction from several coals over the reciprocal space region from X = 0.02 $Å^{-1}$ to 1.2 $Å^{-1}$ (X = [2/λ]·sinθ). In these studies, a 9 cm powder camera was used to study the high angle region, and a transmission type focussing camera equipped with a LiF monochromator was used for the low angle measurements. They reported that the height of the [002] peak (at ca. 3.5 Å) measured for each coal is proportional to the % carbon in several coals. Hirsch[2] also suggests that the Pontyberem anthracite (94.1% carbon, 3.0% hydrogen, and 5.3% volatile matter with a specific gravity of 1.46) has a layer diameter of ca. 16 Å corresponding to an aromatic lamellae of ca. C_{87}. For coals with lower carbon content, Hirsch proposes much smaller lamellae; C_{19} for a coal with 80% carbon, and C_{24} for a coal with 89% carbon.

Because of the importance placed by coal scientists on correctly characterizing the nature of the cluster(s) in coals and because of improvements in both x-ray experimentation capabilities and computing power, we have measured the x-ray diffraction and scattering produced from irradiation of a meta-anthracite coal[10] with hard xrays.[11] The objective of our study is to determine the intra-planar, and where possible inter-planar, structural details of coals and to determine the extent to which layering in coals mimics that of crystalline graphite and/or synthetic polymers. To accomplish the former we have utilized the methods normally used for the molecular analysis of non-crystalline condensed phases such as liquids, solutions, and amorphous solids.[12-23]

The coal, a meta-anthracite which was derived from the Portsmouth, RI mine (southeastern Narragansett Basin), was supplied to us by Professor James W. Skehan, S. J. of the Department of Geology and Geophysics at Boston College.

Reported herein are the results obtained from the hard x-ray analysis of this coal.

EXPERIMENTAL

META-ANTHRACITE COAL. From a 10 gram sample of the coal, a 3 gram aliquot was ground into a fine powder using our SPEX ball mill. The resulting powdered coal was passed through a -100 mesh filter.

A 0.4869 g sample of the finely ground powder was mounted onto a PVC sampleholder and mounted into the x-ray diffractometer.

X-RAY EXPERIMENTS. Mo xrays were used as the exciting radiation. The diffractometer was equipped with a θ-compensating slit, a sample spinner, and a LiF crystal in the secondary x-ray beam.[11] A diffraction pattern of the powdered coal mounted onto the PVC substrate was obtained by collecting intensities for five second intervals at $d2\theta = 0.01^\circ$ over the range from $2\theta = 8.00^\circ$ to $2\theta = 120.00^\circ$. The diffraction pattern from the PVC sampleholder was obtained using exactly the same protocol.

A diffraction pattern of a 0.3878 g sample of reagent grade graphite (Alfa Products) was obtained using the same sampleholder and methodology.

RESULTS AND DISCUSSION

Shown in Figure 1 is the diffractogram of the meta-anthracite sample as well as the diffractogram of the graphite sample.

THE 3.4 Å DIFFRACTION PEAK. The location of this large peak in the meta-anthracite diffractogram corresponds to the [002] diffraction peak which dominates the diffraction pattern of graphite (d = 3.37 Å). Hirsch[1,2] and Franklin[3] report this peak at 3.5 Å in previous studies. Ebert, Scanlon, and Clausen[12] find a similar large first peak in the diffractogram of a combustion tube soot. Comparison of the diffractograms indicates that while the first peaks occur at ca. 3.4 Å, the details of these peaks are quite dissimilar, suggesting that the regularity of the inter-planar spacings, reported to be the cause of 3.4 Å peak, is considerably less in this meta-anthracite than in graphite.

AMORPHOUS SCATTERING DUE TO THE CARBONACEOUS CONTENT OF THE META-ANTHRACITE. Shown in Figure 2 is the separation of the diffraction peaks (2A) from the molecular scattering (2B) for the meta-anthracite. The molecular scattering curve, $I_A(2\theta)$, is similar in shape to the scattering curve obtained previously for an amorphous carbon black,[6] and also to the scattering curves measured for liquids, solutions, and other amorphous solids.[12-23]

The molecular scattering was fitted to the independent scattering curve[24-26] to obtain the reciprocal space interference curve i(s) where $s = (4\pi/\lambda)\sin\theta$. The latter is a description of the average 1-dimensional structural features of the meta-anthracite.

Using conventional methods the atom-pair radial-distribution function was calculated for the meta-anthracite from its

interference function via Fourier transform. The APRDF (Figure 4) provides a measure of the atom-pair distances and their relative importance in the non-crystalline material. The APRDF contains major peaks centered at 1.40 Å, 2.42 Å, 2.85 Å, 3.6 Å, 4.8 Å, 6.0 Å and to r → 15 Å.

P_1 (centered at 1.40 Å) is due to the bonded C-C distance, i.e. C_r-C_1 in Figure 3. The 2.42 Å peak (P_2) is due to the nearest non-bonded C··C atom-pairs. From P_1 and P_2, the average C-C-C bond angle was calculated to be 120° (±4°). P_3 (centered at 2.84 Å) is also attributed to non-bonded C··C atom-pairs. The relative P_1, P_2, and P_3 distance and magnitudes as well as the C-C-C bond angle indicate that the average PAH ring is quite similar to those found in anthracene, napthalene, and pyrene.[27-32] The remaining several peaks in the RDF are due to inter-ring C··C atom-pairs and are being used to estimate the planarity and size of the average PAH cluster in the meta-anthracite. Our results will be compared to those presented by other investigators.[33-39]

REFERENCES

1. Cartz, L. and Hirsch, P. B., 1960 (252) 68.
2. Hirsch, P. B., 1954 (226) 143.
3. Franklin, R. E., Acta Crystallogr., 1950 (3) 10.
4. Kwan, J. T. and Chen, T. F., Proc. Div. Fuel Sci., 1976 (21) 67.
5. Diamond, R., Act Crystallogr., 1958 (11) 129.
6. Wertz, D. L., Powder Diff., 1988 (3) 153.
7. Wertz, D. L., Smithhart, C. B., and Wertz, S. L., Adv. X-Ray Anal., 1990 (33) 475.
8. Davis, B. L., Powder Diffr.,.1986 (1) 244.
9. McCarthy, G. J., Powder Diffr., 1986 (1) 50.
10. Skehan, J. W., Rast, N., and Mosher, S., "Paleonenvironmental and Tectonic Controls of Sedimentation in Coal-Forming Basins of Southeastern New England", Geological Society of America, Special Paper 210, 1986; Skehan, J. W. and Rast, N., Pre-Mesozoic Evolution of Avalon Terranes of Southern New England. Geological Society of America, Special Paper 245, 1990.
11. Wertz, D. L., Powder Diffr., 1990 (5) 44.
12. Mitchell, G. R. and Windle, A. H., J. Appl. Crystallogr., 1980 (13) 135.
13. Wertz, D. L. and Kruh, R. F., J. Chem. Phys., 1967 (47) 388.
14. Levy, H. A., Danford, M. D., and Narten, A. H., ORNL Report No. 3960, 1966.
15. Harris, R. W. and Clayton, G. T., J. Chem. Phys., 1966 (45) 2681.
16. Ohtaki, H. and Wada, H., J. Solution Chem., 1985 (14) 3.
17. Lovell, R., Mitchell, G. R., and Windle, A. H., Acta Crystallogr., 1979 (A35) 598.
18. Johansson, G. and Wakita, H., Inorg. Chem., 1985 (24) 3047.
19. Yamaguchi, T. S., Hayashi, T., and Ohtaki, H. Inorg. Chem., 1989 (28) 2434.
20. Bell, J. R., Tyvoll, J. L., and Wertz, J. Am. Chem. Soc., 1973 (95) 1456.
21. Wertz, D. L. and Hicks, G. T., J. Phys. Chem., 1980 (84) 521.
22. Wertz, D. L. and Holder, A. J., J. Phys. Chem., 1987 (91) 3479.
23. Wertz, D. L. and Cook, G. A., J. Solution Chem., 1985 (14) 41.
24. Hajdu, F., Acta Crystallogr., 1971 (A27) 73; 1972 (A28) 250; Palinkos, G., private communications, 1980.
25. Kruh, R. F., Chem. Rev., 1962 (62) 319.
26. Konnert, J. H. and Karle, J., Acta Crystallogr., 1973 (A29).
27. Cruickshank, D. W. J., Acta Crystallogr., 1959 (12) 208.
28. Abrahams, S. C., Robertson, J. M., and White, J. G., Acta Crystallogr., 1949 (2) 233.
29. Cruickshank, D. W. J., Acta Crystallogr., 1957 (10) 504.
30. Ahmed, F. R. and Cruickshank, D. W. J., Acta Crystallogr., 1952 (5) 852.
31. Cruickshank, D. W. J., 1956 (9) 915.
32. Robertson, J. M. and White, J. G., J. Chem. Soc., 1947 358.
33. Solum, M. S., Pugmire, R. J., and Grant, D. M., Energy Fuels, 1989 (3) 187.
34. Sethi, N. K., Pugmire, R. J., Facelli, J. C., and Grant, D. M., Anal. Chem., 1988 (60) 1574.
35. Murphey, P. D., Cassady, J. J., and Gerstein, B. C., Fuel, 1981 (61) 1233.
36. Miller, D. J., Hawthorne, S. B., and Timpe, R. C., Div. Fuel Chem. Am. Chem. Soc., 1988 (33) 455.
37. Wornat, M. J., Sarofim, A. F., and Longwell, J. P., Energy Fuels, 1987 (1) 431.
38. Aigbehinmua, H. B., Darwent, J. R., Gaines, A. F., Energy Fuels, 1987 (1) 386.
39. Wertz, D. L., Bissell, M., and Vorres, K. S., unpublished results, 1991.

FIGURE ONE. DIFFRACTOGRAMS

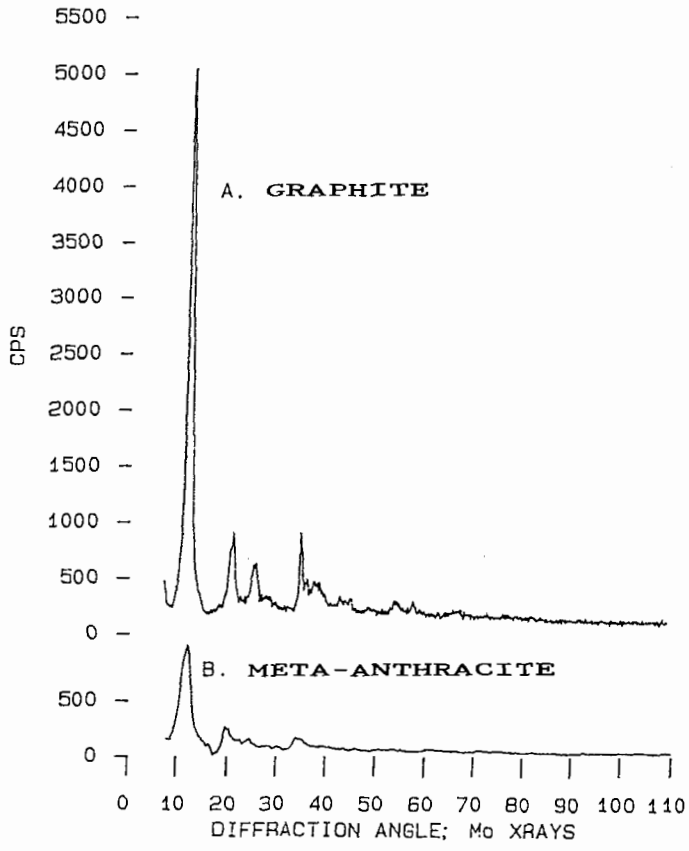


FIGURE TWO. SEPARATION OF DIFFRACTOGRAM INTO COMPONENTS

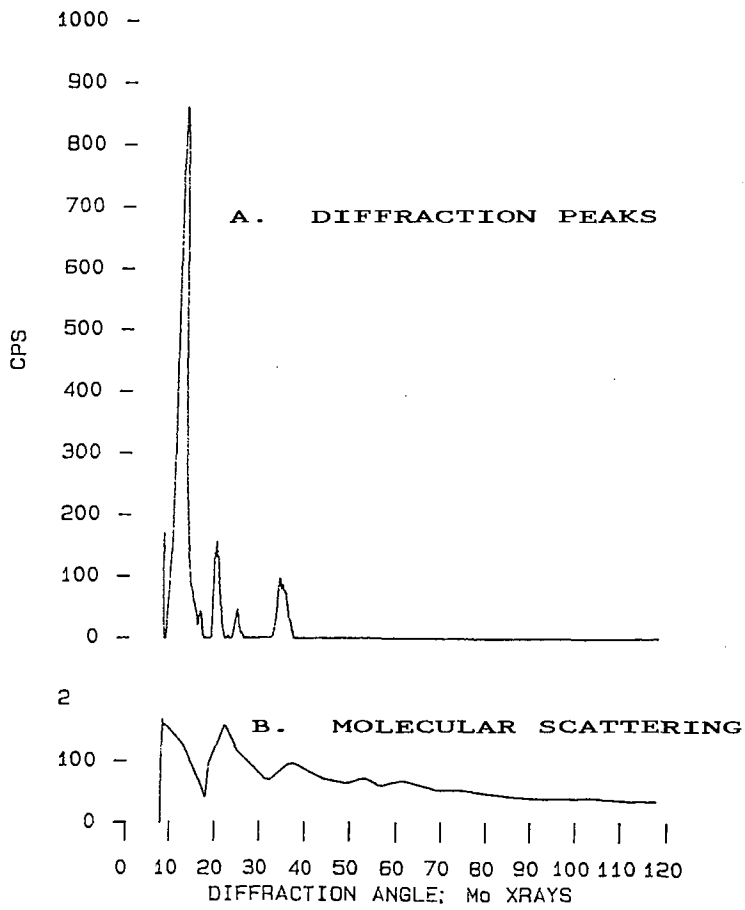
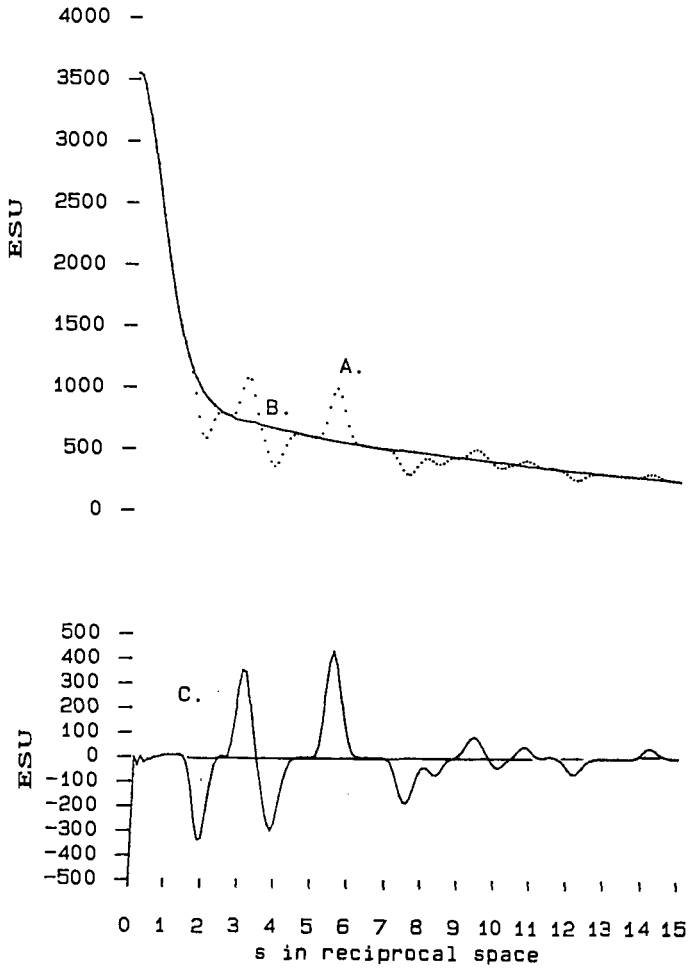


FIGURE THREE. RECIPROCAL SPACE FUNCTIONS

3A. Molecular Scattering Curve (dots)
3B. Calculated Independent Atom Scattering Curve
3C. Interference Curve



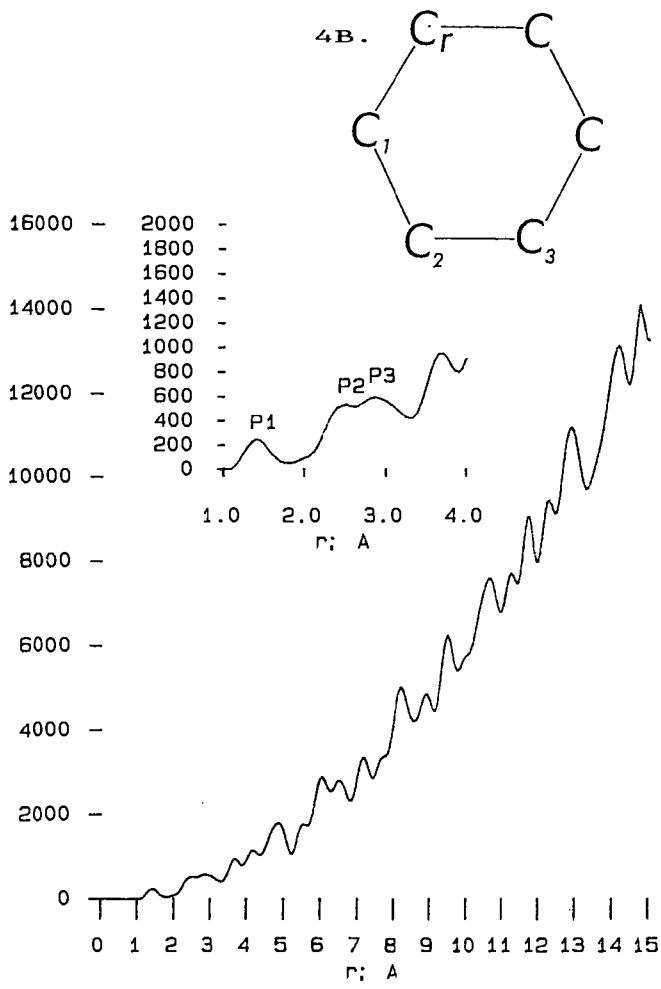


FIGURE FOUR. THE APRDF AND AN AROMATIC RING (4B)