CHARACTERIZATION OF ORGANIC SULFUR IN MACERALS AND CHARS

Richard D. Harvey
Ilham Demir

CONTENTS

ABSTRACT

The objective of this project was to determine the spatial distribution of organic sulfur with respect to pyrite mineral impurities in coals and their heat-treated products (chars) and with respect to pores in the chars. A second objective was the study of the grain-size distribution of pyrite mineral impurities.

In 1989–90, we reported the results of charring and particle-size analyses of mineral matter of Illinois Basin Coal Sample Program (IBCSP) coals. The charring experiments indicated that some of the pyritic sulfur released during charring at 550° C is combined with the organic matrix rather than emitted to the atmosphere. The particle-size analyses indicated significant variations in size of minerals from one sample to another. The method that we used was a computer controlled particle-size analysis of low temperature ash. This method has much promise for use in coal testing.

In 1990–91, we separated and analyzed the density fractions of the nine samples in the IBCSP sample bank. The ash yield of the lightest fractions ranged from about 3 to 6 percent, considerably lower than that of the whole (feed) coal. As expected, the heaviest fractions contained abundant pyrite and ash relative to the lightest fractions. Surprisingly, the heaviest fractions also contained abundant organic sulfur (especially when expressed on the dry, mineral matter free basis). One sample, IBC-103, departed from this trend. Because the method we used did not permit us to distinguish elemental sulfur from organic forms of sulfur, it is possible that a minor part of the enrichment is due to the occurrence of elemental sulfur that could have formed in the samples by oxidation during processing, storage, and/or analysis.

Spot analyses of organic sulfur in macerals were performed by SEM-EDX methods in 29 samples from each of two columns of the Herrin coal: one set of the samples represented a seam thickness of 2.5 m under a marine shale roof and the other set represented a seam thickness of 2.3 m under a transitional shale roof. The organic sulfur content of a given maceral was notably variable in different layers of the seam, but on the average, it was higher for each maceral type in the column under the marine shale than that under the transitional shale. Relative concentration differences were the same between the different macerals in both column sets. The mean content of organic sulfur was highest in sporinite, intermediate in vitrinite and resinite, and lowest in fusinite.

EXECUTIVE SUMMARY

The main objective of this project was to determine the spatial distribution of organic sulfur with respect to pyrite mineral impurities in coals and their heat-treated products (chars) and with respect to pores in the chars. A second objective was to determine the size distribution of the mineral grains in the nine samples that were then part of the Illinois Basin Coal Sample Program (IBCSP).

In 1989–90, we reported on the results of charring tests and the grain-size analyses of mineral matter in IBCSP coals (Harvey and Demir 1990). The charring experiments indicated that some of the pyritic sulfur released during charring at 550° C is combined with the organic matrix rather than emitted to the atmosphere. The particle-size analyses indicated significant variations in size of minerals from one sample to another. The method of analysis that we used, a computer controlled particle-size analysis of low temperature ash, has much promise for use in coal testing.

The specific tasks for 1990–91 were:

(1) Prepare a quality assurance plan for the project.

(2) Determine and evaluate the heterogeneity of organic sulfur–mineral associations in all nine IBCSP coal samples.

(3) Determine the geological significance of organic sulfur patterns in macerals, distant from and adjacent to mineral inclusions, in separate layers of the Herrin Coal seam occurring under different types of roof strata in an Illinois mine.

The quality assurance plan was prepared and submitted with the first quarterly report. No notable changes were adopted during the course of the project.

The second task of 1990–91 involved studying the differences between the organic sulfur contents of the macerals in association with the main sulfide mineral impurity, pyrite, in the IBCSP samples. The mineral-rich and mineral-poor maceral matter were separated by first grinding the samples to about 80% -200 mesh or finer and then separating them into three density fractions: <1.3 g/cm^3 (low-mineral fraction), 1.3 to 1.5 g/cm^3 (intermediate-mineral fraction), and >1.5 g/cm^3 (high-mineral fraction). The differences between the organic sulfur in the three fractions, expressed on the dry, mineral matter free basis, provides a measure of the heterogeneity of organic sulfur with respect to mineral grains within the whole (feed) coal samples. These results also provided corroborative data for the SEM-energy dispersive x-ray (SEM-EDX) results obtained during the first year of this 2-year project (Harvey and Demir 1990).

The lightest density fractions yielded about 3 to 6 percent ash, considerably lower than that in the whole coal. The ash in the light fractions was mostly derived from disseminated mineral matter, microcrystalline pyrite, quartz, and clays enclosed within macerals. As expected, pyrite and other ash-forming minerals were concentrated in the heavy fractions. Of most interest, the analyses showed that the heaviest fractions contained higher organic sulfur (especially on dry, mineral matter free basis) than the lightest fractions for all of the tested coals except one.

For the third task of 1990–91, we determined the organic sulfur distribution using the SEM-EDX method in two sets of column samples. One column was of the Herrin Coal where the roof stratum is a marine type of shale (column M). The other column was collected some 600 feet

from the first along the same seam, a place where the roof is transitional to a fluvial shale (column T). Each sample in a column represents a thin increment, or layer, of the seam. The SEM-EDX results showed that the mean organic sulfur content was highest in sporinite, intermediate in vitrinite, and lowest in fusinite in all layers of both columns, with minor exceptions. This trend is consistent with our previous SEM-EDX results. The mean content of organic sulfur of a given maceral was moderately variable in different layers of the seam, with column M having slightly lower values near the top of the seam in both vitrinite and sporinite macerals. Most significantly, the data document that each maceral contained a higher percentage of organic sulfur in the coal that underlies the marine shale than that under the transitional shale. The results of this study lend support to the Williams/Keith–Gluskoter/Simon model for the relative level of sulfur in coal (Williams and Keith 1963, Gluskoter and Simon 1968).

INTRODUCTION

Objectives

The main objective of this project was to determine the spatial distribution of organic sulfur with respect to pyrite mineral impurities in coals and their heat-treated products (chars) and with respect to pores in the chars. A second objective was to determine the size distribution of the mineral grains in the nine samples that were then part of the Illinois Basin Coal Sample Program (IBCSP). The period of the project was 2 years, and this report briefly summarizes the first year's effort and gives a complete report of the second year.

In 1989–90, we reported the results of two tasks (Harvey and Demir 1990):

(1) Determine and compare the spatial distribution of organic sulfur in macerals adjacent to pyrite grains of measured size, and of pores in three Illinois Basin coals and their chars.

(2) Determine and compare the significance of the particle-size distribution of the mineral matter in all nine IBCSP samples.

The specific tasks for the 1990–91 year were:

(3) Prepare a quality assurance plan for the project.

(4) Determine and evaluate the heterogeneity of associations between organic sulfur and minerals in all nine IBCSP coal samples.

(5) Determine the geological significance of organic sulfur patterns in macerals and some macerals adjacent to minerals in layers of the Herrin seam occurring under different types of roof strata in an Illinois mine.

Certain fundamental questions regarding the physical characteristics and interactions between the main building blocks of coal remain largely unanswered. This is especially the case for the amount of sulfur in different macerals and in macerals adjacent to mineral impurities in untreated coals and their heat-treated products (chars).

Knowledge of the spatial distribution of organic sulfur in coals and chars with respect to other physical features, including the size and type of mineral impurities, is needed to understand the heterogeneous reactions that are involved in desulfurization and producing fuels and chemicals from coal. The results from this 2-year project will provide support data and help those who are designing new, more effective bench scale processes to desulfurize coal from the Illinois Basin. The data will also provide a geological assessment and possible correlations that may lead to useful guides to deposits of specific coal types.

Literature Review

Raymond and Gooley (1978) reviewed the literature on organic sulfur analysis in coal and applied a new method particularly suited for use with an electron microprobe. They found good agreement between their mean statistical results on vitrinite and the standard ASTM (1990, D 2492) results on the bulk coal. From 1982 to 1986, the Illinois Coal Development Board supported several projects headed by Wert on the direct measurement of organic sulfur in coal, based on transmission electron microscopy (Hsieh and Wert 1985, Tseng et al. 1986, Wert et al. 1987, Wert et al. 1988). Wert and his co-workers analyzed maceral fractions, which had been separated by a density gradient centrifugation method, and observed the mean organic

sulfur content to be highest in sporinite and associated liptinites, intermediate in vitrinite, and lowest in the inertinite macerals. Clark et al. (1984) measured organic sulfur in coal and semicoke samples from Kentucky and elsewhere using an SEM-EDX technique. Their results were also in good agreement with standard bulk analyses, and they observed a trend of increasing organic sulfur content with increasing log of the plasticity of the coals tested.

Harvey et al. (1989) modified procedures of the previous investigators to enable the determination of the organic sulfur content in identified maceral particles in coal. In that study, the mean SEM-EDX results for four different samples also proved to be in good agreement with the bulk analyses obtained by the standard method (ASTM 1990). The SEM-EDX method requires about 0.5 g of sample, as opposed to at least three times that much for the ASTM method. The SEM-EDX procedure has another advantage: it permits the analysis of sulfur at spots about a 0.5 μm or less in diameter within individual macerals.

Cleyle et al. (1984) found that thermal decomposition of pyrite in the range of 500° to 550° C enriched the organic sulfur in the surrounding maceral in a Nova Scotia coal. Their SEM-EDX measurements detected the enrichment of sulfur up to 15 μm into the maceral. They concluded from these and other data that the decomposition of pyrite within coal is affected by poorly known characteristics of the particular coal and that the behavior of sulfur adsorption during heating should be examined for each coal. Wert (1985) reported such data for tests on a sample of the Springfield Coal from Illinois. He found organic sulfur values in maceral matter near 1-μm and 5-μm diameter pyrite to first decrease between 350° and 425° C and then to increase at higher temperatures. The rate of increase was similar for both sizes of pyrite. We repeated these experiments for three Illinois Basin coals wherein the heating rate and time of heating were well documented and a wider grain-size range of pyrite was tested (Harvey and Demir 1990).

SUMMARY OF FIRST-YEAR RESULTS

Distribution of Organic Sulfur Near Pyrite in Coals and Chars (Task 1)

In the three untreated coal samples studied for this task, the organic sulfur content increased slightly as the distance to pyrite grains decreased in two samples (IBC-101 and IBC-102), but the reverse appeared to be the case for the third sample (IBC-107; fig. 1) (Harvey and Demir 1990). In addition, the mean spot values of organic sulfur for pyrite-bearing macerals were distinctly higher than those obtained by the bulk ASTM analysis for two samples. For the other sample (IBC-101, not shown in fig. 1), the organic sulfur content near pyrite was about the same as for the bulk coal (Harvey and Demir 1990).

For the untreated coals, we found that at a distance of 12 to 20 μm from pyrite grains, the mean organic sulfur content generally decreased with increasing size of pyrite grains. We interpreted these results to indicate that sulfur generally combines more efficiently with iron to make pyrite than with organic matter during coal formation.

The organic sulfur content was highest near pyrite grains for all three coals after they were pyrolyzed at 550° C (fig. 1), indicating that some of the sulfur from pyrite that was released during heating was subsequently moved into surrounding macerals as elemental sulfur or possibly it combined with the organic matter. These results are similar to those of Cleyle et al. (1984) and Hsieh and Wert (1985). The $\delta^{34}S$ values of the organic sulfur in an IBCSP coal (IBC-107) support the above conclusion concerning the capturing of pyritic sulfur by organic matrix during heat-treatment. The $\delta^{34}S$ results indicate that about 18 percent of the organic sulfur remaining in the 550° C chars was originally pyritic sulfur.
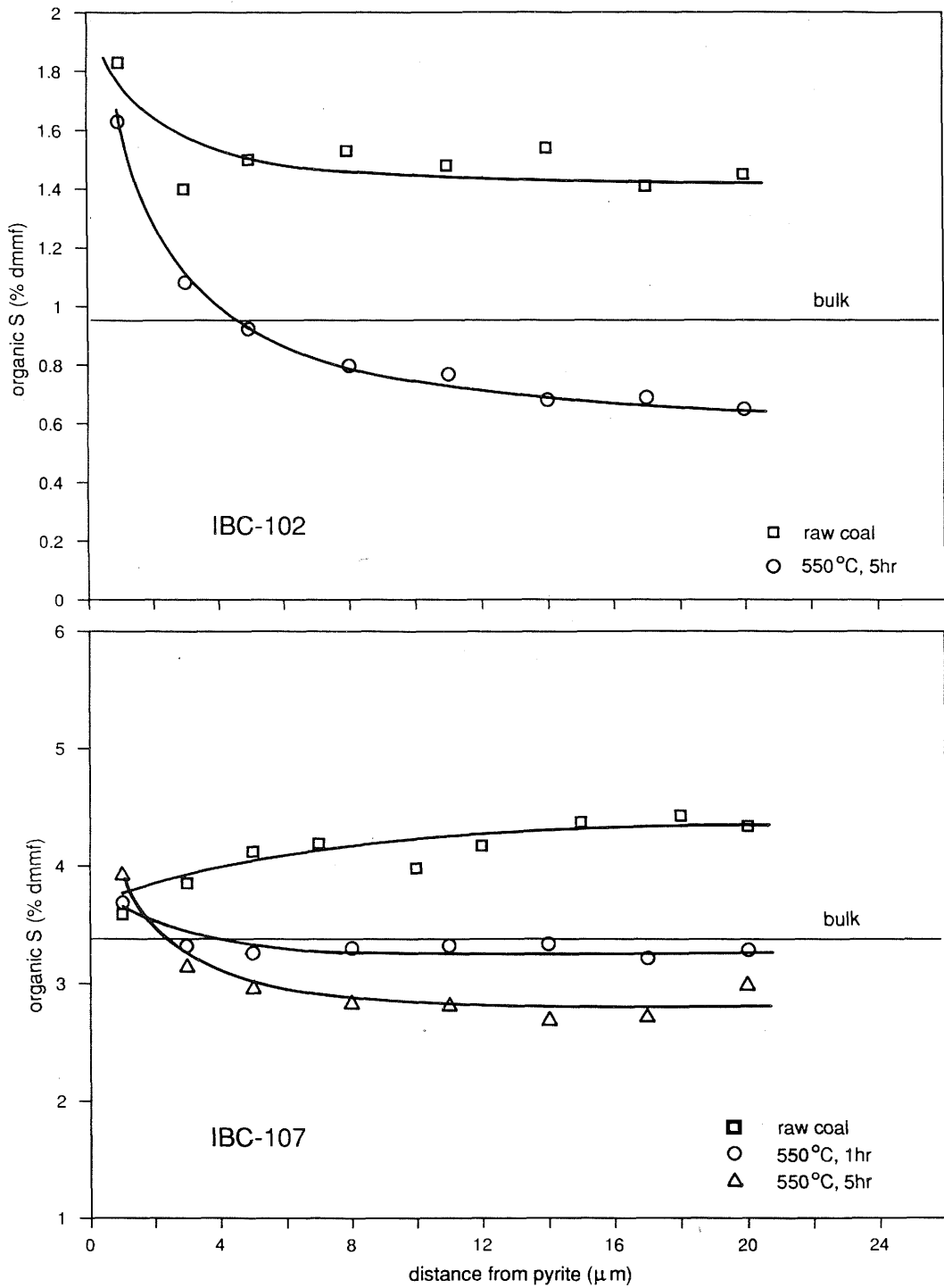
5

Figure 1 Distribution of organic sulfur near pyrite grains within vitrinite in IBC-102 (top) and IBC-107 (bottom). The value given at each point is the mean near at least 10 different grains. The result of the ASTM analysis of the bulk sample is noted for both.

6

Pores in raw coals are much too small to analyze by the SEM-EDX method, but those in chars could be examined. Analyses near pores in 550° C chars suggest that there might be a slight reduction of organic sulfur content 1 μm from the pores, as compared with 10 μm. Reductions from 0.04 to 0.09 percentage points were observed. However, the application of the SEM-EDX method to evaluate these differences, so close to pores, is questionable (Harvey and Demir 1990).

Particle-Size Distribution of Mineral Matter in IBCSP Coals (Task 2)

The results of tests of the grain sizes of the mineral matter indicated that there is a significant variation in size of minerals from one sample to another: the smallest (IBC-108) was 4 μm and the largest (IBC-104) was 22 μm (mean diameter, area basis). This method provides data that may be applied to predict the degree of crushing needed to liberate a designated portion of the mineral matter (Keller 1986). The method of analysis developed has promise for use in coal testing, but the observed inconsistencies between the two expressions of the mean size, the diameter calculated from the volumetric or the area distribution, must be evaluated further before definite conclusions can be drawn. The reproducibility of the method, as applied to minerals in coal, also needs to be determined.

SECOND-YEAR RESULTS

Quality Assurance (Task 3)

A quality-assurance program was introduced throughout the Illinois State Geological Survey during August 1990. The program called for a specific quality-assurance plan to be prepared for projects such as this one. Thus, while this task was not a part of our original proposal, we introduced it at the start of this second year of the project.

A quality-assurance plan was written to cover this second year of the project. A copy was appended to our First Quarterly Technical Report, November 30, 1990. The plan covered the following topics: management, level of assurance required, tasks to be done, major instruments to be used and maintained, details of our sampling and laboratory procedures, analytical procedures, calibrations, data reduction, documentation, and audits. No notable changes were made to the plan during the course of the work. Intermediate audits were completed with satisfaction and the final audit occurred after this final report was completed.

Heterogeneity of Organic Sulfur–Mineral Associations (Task 4)
■ Experimental procedures

The heterogeneity of organic sulfur was evaluated by determining its concentration in three fractions of different density of finely ground samples: low, medium, and high. The bulk coal was wet-ground (750 g coal + 750 ml water) in a rod mill for 20 minutes, filtered under vacuum, and air-dried (fig. 2). Size analysis indicated that the grinding generally reduced the particle size of the coal to about 80% -200 mesh (74 μm), with a mean diameter (area basis) ranging from 5 to 19 μm (table 1).

Aqueous $ZnCl_2$ solutions were used as heavy media to carry out the density separation of the finely ground coal samples. For most samples, satisfactory yields for analysis of the separate fractions could be obtained with solution densities of 1.3 and 1.5 g/cm^3. Two samples were sufficiently unique that slightly different densities had to be used: for IBC-104, the best solution to separate the heaviest fraction was obtained at a density of 1.6 g/cm^3; and for sample IBC-108, solutions of 1.27 and 1.6 g/cm^3 were required to separate the heaviest and lightest fractions. The 1.6 sink, however, did not yield enough material for analysis of IBC-108.

Figure 2 Flow chart for the float-sink separations in zinc chloride ($ZnCl_2$)–water mixtures.

Table 1 Particle size of float-sink samples.

Sample	Mean diameter (μm)[*] volume	area	Standard deviation (μm)	Cum. distribution (<μm) 10%	50%	90%
IBC-101	42	14	34	5.7	33.7	87.2
IBC-102	48	16	38	6.1	38.2	106.8
IBC-103	47	19	36	7.9	39.0	100.2
IBC-104	27	9	23	3.1	20.0	59.9
IBC-105	33	11	26	4.4	26.4	70.3
IBC-106	47	17	36	7.1	38.1	100.4
IBC-107	48	15	38	5.7	37.2	106.4
IBC-108	10	5	6	2.1	7.0	20.8
IBC-109	50	18	39	7.8	45.5	109.8

* The volume measure is the mean diameter of the particle-size distribution based on a volumetric calculation, which is biased to the larger particles. The area measure is the mean diameter based on an area calculation, which is biased to the small ones.

8

Table 2 Standard analyses (ASTM) of IBC coals and float-sink fractions.

Sample	Whole coal & density fraction (g/cm³)	Wt yield (% dry)	Ash (% dry)	Pyritic S (% dry)	Sulfate S (% dry)	Organic S (% dry)	Organic S (% dmmf)*	Mineral matter (% dry)†
IBC-101	coal		10.50	1.27	0.05	3.00	3.43	12.5
	<1.3	9.0	4.55	0.20	0.04	3.41	3.59	5.2
	1.3-1.5	86.5	9.55	0.40	0.07	2.98	3.35	11.0
	>1.5	4.5	43.39	13.21	0.18	1.74	3.88	55.2
IBC-102	coal		6.90	2.29	0.06	0.94	1.03	8.9
	<1.3	49.4	4.40	0.39	0.20	1.13	1.19	5.2
	1.3-1.5	48.6	6.59	0.72	0.22	1.15	1.25	7.8
	>1.5	2.0	48.67	20.95	0.22	1.28	3.64	64.8
IBC-103	coal		8.70	1.11	0.02	1.16	1.29	10.4
	<1.3	49.9	5.13	0.24	0.16	1.04	1.11	5.9
	1.3-1.5	46.4	9.19	0.48	0.06	1.07	1.20	10.6
	>1.5	3.6	42.84	10.06	0.46	0.06	0.13	53.1
IBC-104	coal		38.30	2.57	0.03	1.57	2.82	44.5
	<1.3	nd	5.76	0.19	0.04	2.65	2.84	6.6
	1.3-1.6	nd	16.01	0.58	0.06	2.26	2.77	18.4
	>1.6	nd	45.21	2.42	0.12	1.38	2.89	52.2
IBC-105	coal		18.50	2.57	nil	1.94	2.49	22.1
	<1.3	3.7	5.46	0.23	nil	2.53	2.70	6.3
	1.3-1.5	81.2	14.09	0.72	0.01	2.24	2.68	16.3
	>1.5	15.1	36.23	9.91	0.01	3.13	5.75	45.6
IBC-106	coal		9.00	1.85	0.01	1.91	2.15	11.0
	<1.3	32.1	4.52	0.30	0.02	2.09	2.20	5.2
	1.3-1.5	63.2	8.97	0.71	0.11	1.99	2.22	10.5
	>1.5	4.7	43.55	16.45	0.12	2.37	5.50	56.9
IBC-107	coal		11.50	0.48	0.26	2.98	3.43	13.2
	<1.3	2.2	4.36	2.21	0.04	1.35	1.44	6.0
	1.3-1.5	93.7	10.27	0.14	0.40	2.94	3.33	11.7
	>1.5	4.1	36.45	4.53	0.02	3.95	6.97	43.3
IBC-108	coal		3.80	0.37	0.01	2.25	2.36	4.5
	<1.27	0.6	3.13	0.19	0.02	2.43	2.52	3.6
	1.27-1.6	99.3	4.58	0.25	0.03	2.36	2.49	5.3
	>1.6	0.1	nd	nd	nd	nd	nd	nd
IBC-109	coal		8.20	0.50	nil	0.63	0.70	9.5
	<1.3	31.6	4.55	0.14	0.01	0.65	0.69	5.2
	1.3-1.5	64.5	8.09	0.25	0.02	0.59	0.65	9.3
	>1.5	3.9	46.58	6.72	0.07	0.62	1.40	55.8

* Organic S_{dmmf} = $OrgS_{dry}$(100/(100 - mineral matter))

† 1.13(ash yield) + 0.47(pyritic S)

nd = not determined

The density fractions were analyzed for moisture, ash, and the forms of sulfur by the standard ASTM methods.

■ Results and discussion

Analyses of the density fractions indicated that the ash yields of the lightest fractions ranged from 3.13 to 5.76 percent, significantly lower than the original coal (table 2). The ash from the light fractions was derived from finely disseminated pyrite and clays enclosed in macerals and perhaps also from the discrete, colloidal size clays entrapped in the float. As expected, pyrite was concentrated in the heavy fractions.

Selected samples were double-checked for accuracy and the results (table 2) are all within acceptable limits of reproducibility. Material balance calculations show reasonable comparisons between cumulative recovery and the feed coal for ash yield and organic sulfur content, but comparisons are poor for pyritic sulfur data, especially for IBC-102 and IBC-103 (table 3). This raises the possibility that some pyrite may have oxidized and removed as iron sulfate in solution, especially tiny grains in the heavy fractions, and some sulfur may also have been lost as H_2S during the analysis. Oxidation of pyrite does yield some elemental sulfur (Hackley et al. 1990). The net result of any oxidation would only add a small amount to the reported value for organic sulfur. If a significant amount of monosulfides, such as sphalerite (ZnS), actually occurred in the samples, they would also add to the net assay of organic sulfur. Trace element analyses indicate monosulfides would comprise less than about 0.2 percent elemental sulfur in the heavy fraction of IBC-101, and much less in the other samples.

For direct comparison of the heterogeneity of organic sulfur in the density fractions, the concentrations must be expressed on the dry, mineral matter free basis (dmmf, table 2). This is because of the preponderance of pyritic sulfur in the heavy fractions compared with the others. For seven of the nine samples, the >1.5 g/cm^3 fractions contained enriched amounts of organic

Table 3 Material balance for ash yield and sulfur forms in the density fractions.

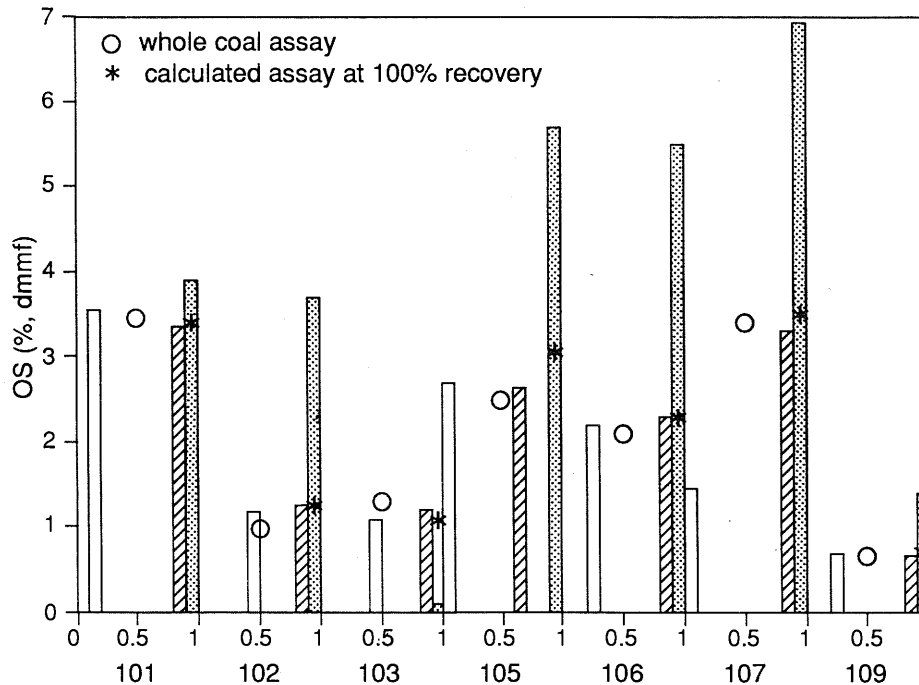| Sample | Ash yield (%, dry) | | Pyritic S (%, dry) | | Organic S (%, dmmf) | |
	In feed coal	Cumulative recovery from density fractions	In feed coal	Cumulative recovery from density fractions	In feed coal	Cumulative recovery from density fractions
IBC-101	10.50	10.62	1.27	0.96	3.43	3.40
IBC-102	6.90	6.35	2.29	0.96	1.03	1.27
IBC-103	8.70	8.37	1.11	0.71	1.29	1.12
IBC-105	18.50	17.11	2.57	2.09	2.49	3.14
IBC-106	9.00	9.17	1.85	1.32	2.15	2.37
IBC-107	11.50	11.22	0.48	0.37	3.43	3.44
IBC-109	8.20	8.47	0.51	0.46	0.70	0.69

Figure 3 Organic sulfur content versus recovery (in fractional units, 0–1) of the three density fractions of the indicated IBC samples. Open bars: <1.30 g/cm³; striped: 1.3–1.5 g/cm³; shaded: >1.5 g/cm³.

sulfur relative to the lightest fractions. The trend is opposite for the IBC-103 coal, and the other exception (IBC-108) can not be compared because the sample was too pure to yield sufficient material for a test of the heaviest fraction. The strong trend of enrichment of organic sulfur in association with pyrite-bearing particles is evident when we consider the recovery yield. In figure 3, the weight yields of the fractions are expressed on a cumulative recovery basis (0 to 1 for each sample). The recovery yields were notably higher for each sample except IBC-103. On the other hand, the corollary would be that the organic sulfur content of the lightest (clean) fraction would be lower than that of the whole (feed) coals. This was not demonstarted, however, by our results. Only IBC-103 and IBC-107 demonstrated this condition (fig. 3).

Sample IBC-103 had the highest rank among all the samples; thus, rank may be a related factor.

Our previous results of SEM-EDX analyses (Harvey and Demir 1990) lend support to a trend of increased organic sulfur content around pyrite grains. These data (fig. 1) showed the average organic sulfur content near pyrite grains is much greater than that in the whole coal (bulk) for IBC-102 and IBC-107 coals.

Enrichment of organic sulfur around grains of pyrite was also reported by Yurovskii (1974) to account for similar trends in density fractions of coal from five of six mines tested in the Soviet Union.

11

Geological Assessment of Organic Sulfur Distribution (Task 5)

■ Geologic setting

The rock strata that immediately overlie coals in most areas of the Illinois Basin are black, thin-bedded shales or gray limestones. Both of these rock types contain marine fossils. The coals under these rocks contain high amounts of sulfur, much too high to meet the current air-quality specifications for fuels at power plants. The widely accepted model (Williams and Keith 1963, Gluskoter and Simon 1968) that accounts for the high sulfur content in these coals contends that sea water flooded the ancient peat swamps along coastal areas and deposited marine shales and limestones on top of the peat surface. These deposits buried the vegetation, and the sulfate-bearing sea water saturated the peat. Sulfate ions were absorbed by the decaying plant debris, and these ions were soon reduced, mainly by bacteria in the presence of iron, to FeS_2 (pyrite or marcasite). Sulfur in excess of iron was fixed within the decaying carbonaceous matter as organically bound sulfur.

Conversely, a few coal deposits are known to underlie gray silty shales that are relatively thick (about 20 feet or more) and massive, like those we see in present day river or fresh-water lake sediments. These shales contain no marine fossils. To date, all coals under these types of rocks have been found to be relatively low in sulfur, generally less than 2.5 percent.

This model can be extended to conditions where the gray muds are not so thick and continuous, so that the "blanket" was not as impermeable, or that a mixture of fresh and brackish sea water was the depositing medium. Under such conditions, some diluted sea water could have entered the underlying peat, thus allowing intermediate levels of sulfur to be absorbed by the peat. Shales overlying such peats are referred to as transitional (DeMaris and Bauer 1978). The model can be applied to this geological condition as follows: silty and mud-laden river waters flooded the swamp at specific sites adjacent to the river, depositing large wedges of gray muds onto the peat. Where thick, these muds formed a blanket that prevented subsequent sea water from entering the underlying peat. The model suggests that these peats were never thoroughly saturated with sulfate-bearing sea water. Therefore, the coals that developed from such peats are relatively low in sulfur.

The Walshville channel (fig. 4) marks the course of an ancient river that flowed through the extensive Herrin peat swamp (Smith and Stall 1975). Bauer and DeMaris (1977) and Johnson (1979) located places in a mine (Old Ben No. 24) where the roof lithologies varied systematically. The mine worked the Herrin Coal seam along a drift that passed from under transitional type shales (the Energy Shale Member) to a marine shale (the Anna Shale Member). The Energy Shale is not present in all parts of the mine, but the black Anna (of marine origin) is present everywhere and overlaps the Energy where the Energy occurs (fig. 5).

Johnson (1979) took samples of each layer of the seam (a column) at several sites along the drift and we selected two of his columns for detailed analysis for this project. The seam was 2.5 m thick at the one site and 2.3 m thick at the other site. The distance between the two columns is about 183 m (about 600 ft). We labeled the two columns as column T (under the transitional roof) and column M (from under the marine roof). They are shown positioned in figure 5 in their approximate location with respect to the geological setting.

■ Sample preparation

Samples of each layer of the seam had previously been crushed, mounted in epoxy, and polished for the original study by Johnson (1979). To save time, we excluded 15 of his 45 original specimens from column M and 16 of his original 44 from column T. The 29 specimens we selected from each column for our detailed study can be considered representative of the
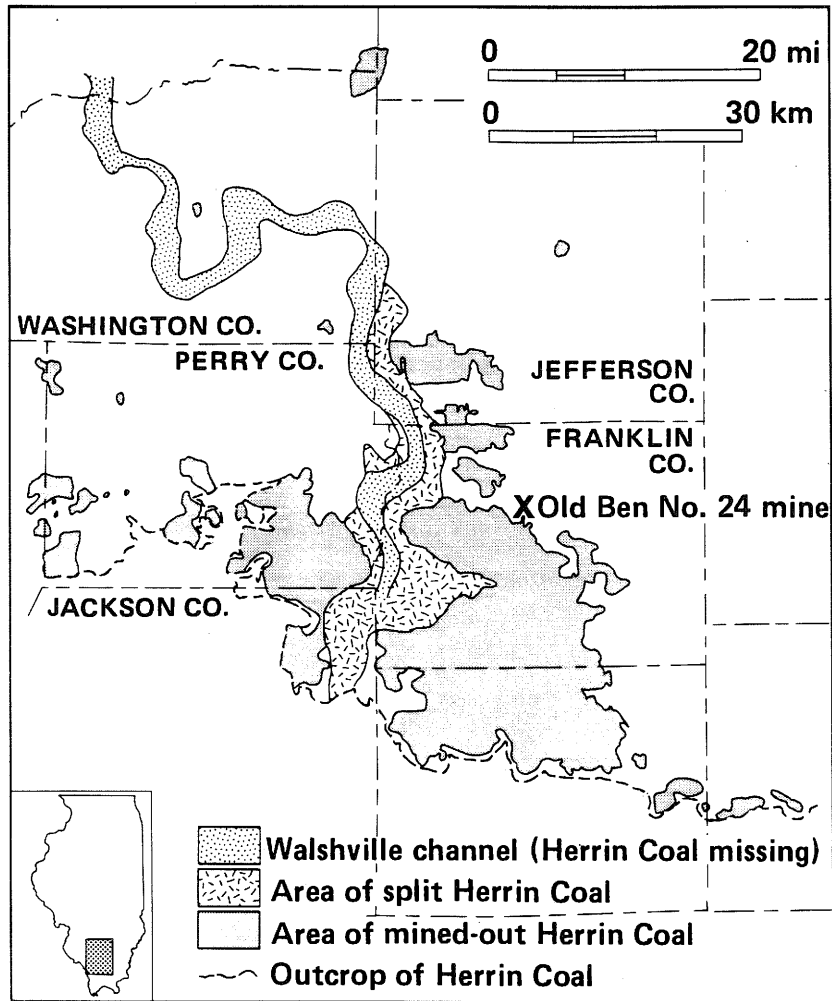
12

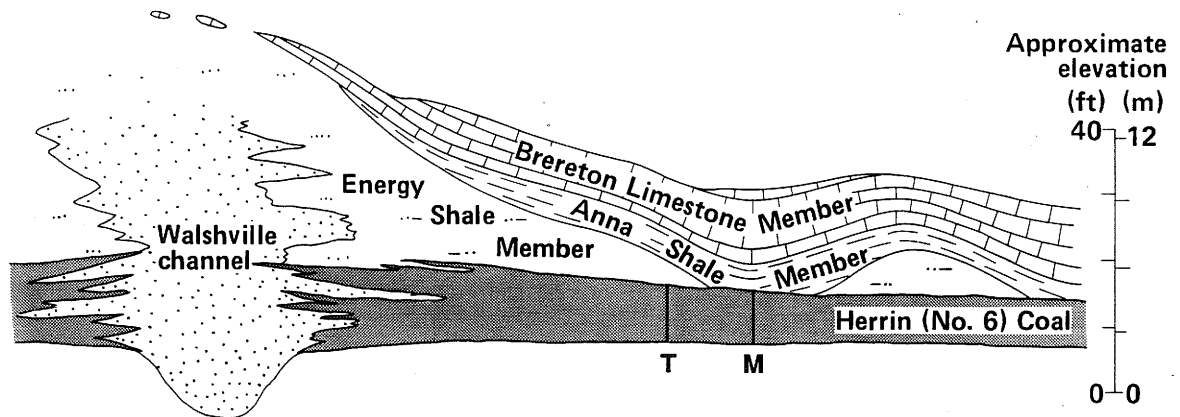**Figure 4** Location of Old Ben No. 24 mine.

Figure 5 Generalized relationship of the Walshville channel with the Herrin Coal and overlying rock units (after W. J. Nelson, Illinois State Geological Survey, personal communication). The relative positions of columns M and T are shown.

13

seam at the two sites. We ground down the surface of the original specimens about 2 mm to reveal fresh surfaces of coal and repolished the specimens for analysis. Next, we studied the specimens with a petrographic microscope to identify the macerals we wanted to analyze and map their locations. Figure 6 shows examples of macerals selected. The specimens were then briefly etched in a low-temperature asher and subsequently sputter coated with carbon before the start of the SEM-EDX analysis.

■ SEM-EDX procedures

The specimens were analyzed for organic sulfur using the procedure of Harvey et al. (1989). The identified macerals were relocated in the SEM and analyzed as detailed in table 4. Spectra were collected at selected spots that were less than 1 μm in diameter. We deemed the sulfur signal, in the absence of signals from Fe, Ca, and other possible inorganic elements that combine with sulfur, to be that of organic sulfur. Thus, the method does not permit us to distinguish the small amounts of elemental sulfur that may be present in oxidized samples.

Table 4 SEM-EDX procedures for the determination of organic sulfur.

(1) Move the specimen to the optically selected spot within a maceral.

(2) Set the SEM as follows:
   Beam current to 1.3 to 1.6 nA (picoammeter monitored),
   Count rate to 2,000 to 3,000 counts per second,
   Dead time to 15% to 30%,
   Magnification to 3,000X,
   Operate in the spot mode.

(3) Acquire a sulfur spectrum for 30 seconds and record the observed sulfur peak area. Disregard the spectrum if any iron or calcium is observed at the spot. Move to the next spot.

(4) Record the beam current after each set of five spots and calculate the average for each set.

(5) Divide the observed sulfur peak area at each spot by the calculated average beam current for the set.

(6) Plot the ratio for each spot on the calibration curve, or use the regression equation (fig. 7), to obtain the organic sulfur content at each spot.

A calibration curve (fig. 7) was established using three vitrain standards with organic sulfur contents of 0.69, 1.45, and 2.61 percent. The peak areas of the sulfur signal from the standards and samples were normalized to beam current for the calibration curve, as well as for all of the project samples. Each point on the curve is the mean of 50 measurements.

■ Results and discussion

Tabulated results of exact organic sulfur analyses in the column samples are not included here because of limited space, but these data are available from the authors upon request. Instead, the results are graphically illustrated in figures 8 and 9. The organic sulfur content of a given maceral is moderately variable throughout the seam thickness. Column M had slightly lower values near the top of the seam in both vitrinite and sporinite macerals. Otherwise, no hint of a pattern of distribution or organic sulfur is evident in the different layers of the seam. A
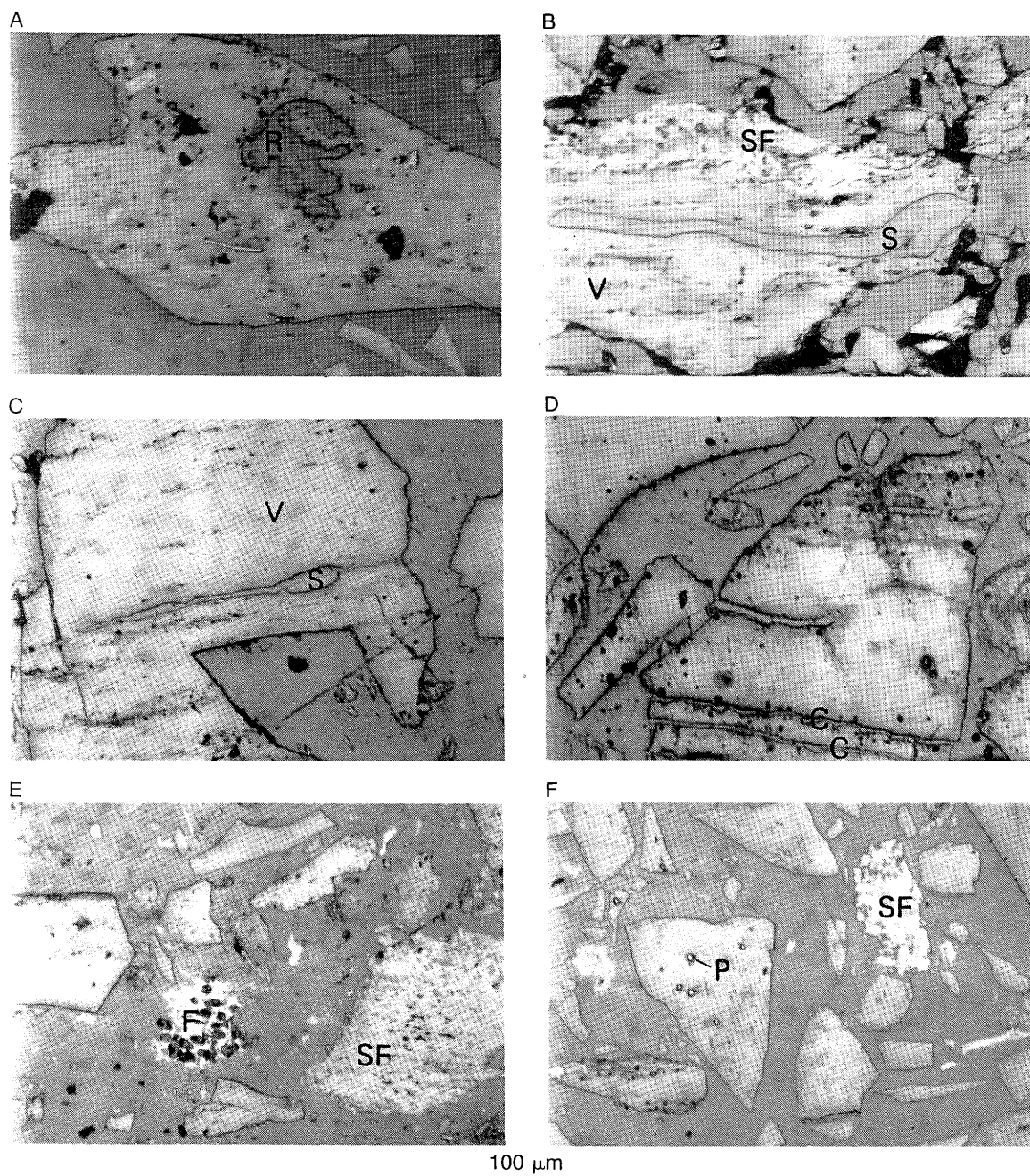
Figure 6 Photomicrographs of the macerals analyzed for their organic sulfur content. Maceral particles are embedded in epoxy (mid-gray) and black areas and spots are pores of minute mineral grains. A: Faintly visible resinite (R, above the center); B: a large sporinite (S) in vitrinite (V), and associated with semifusinite (SF); C: vitrinite (V) and a thin sporinite (S); D: two thin cutinites (C, along the bottom); E: a small fusinite particle (F) with pores and mineral matter, also a semifusinite particle (SF); F: tiny pyrite grain (P) enclosed in vitrinite.
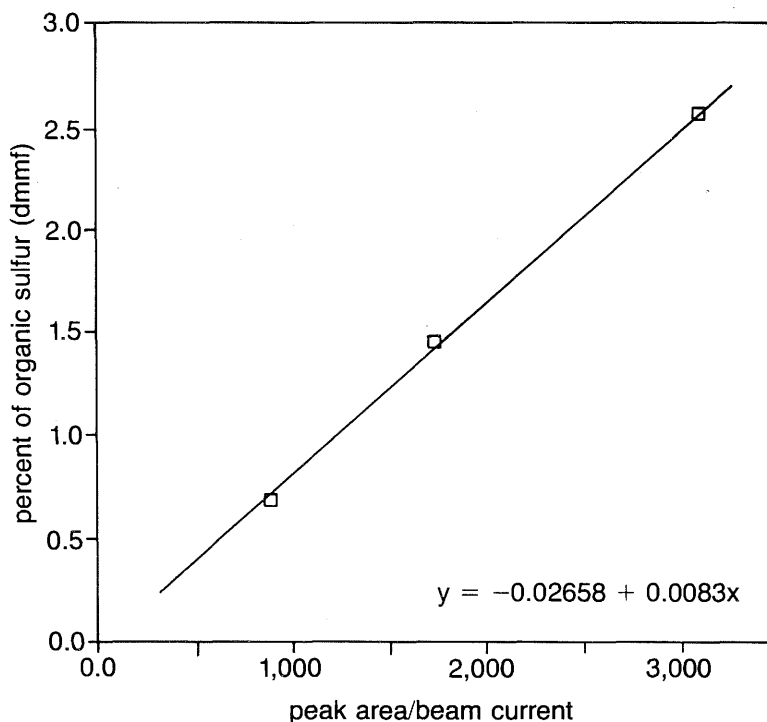
15

Figure 7 Calibration curve for the concentration of organic sulfur versus its x-ray peak intensity (normalized to beam current) in the three standard samples. The equation is that of the best fit line.

comprehensive statistical analysis of the column data might reveal a pattern that we did not observe.

These results showed the organic sulfur content of semifusinite to be intermediate between that of fusinite and vitrinite (with few exceptions), and the contents of cutinites and resinites are in some layers lower and in others higher than that of vitrinite in the same layer. Sporinite is consistently the highest and fusinite the lowest in organic sulfur content. In all but a few layers, the relative levels of organic sulfur in the various macerals are consistent with our previous findings for IBCSP coals that the organic sulfur is most abundant in sporinite and least in fusinite (Demir and Harvey 1990).

Organic sulfur content of vitrinite did not show any noticeable change for spots as distant as 5 µm from a pyrite grain (figs. 8 and 9). In that respect, these two column sets are similar to IBC-101 coal (table 2), which had similar organic sulfur content in its lightest (pyrite-poor) and heaviest (pyrite-rich) fractions.

Most significantly, the results show that for each maceral type, the organic sulfur content is highest in the coal that underlies the marine shale (table 5). The ratio of the organic sulfur content of the macerals in columns M to those in T is nearly 1.4 for each of the macerals except sporinite, which is 1.15, and fusinite, which is 1.2. These differences are not deemed to be particularly important unless these data were compared with other such column studies in the future.

16

Figure 8 The relative thickness and lithotype of coal, and variation of mean organic sulfur content in macerals by layers in column M (under marine shale). Lithotype abbreviations: Cc, bright and coarse banded clarain; Cf, fine banded clarain; V, vitrain; D, durain; F, fusain; P, pyrite; and Sh, shale.
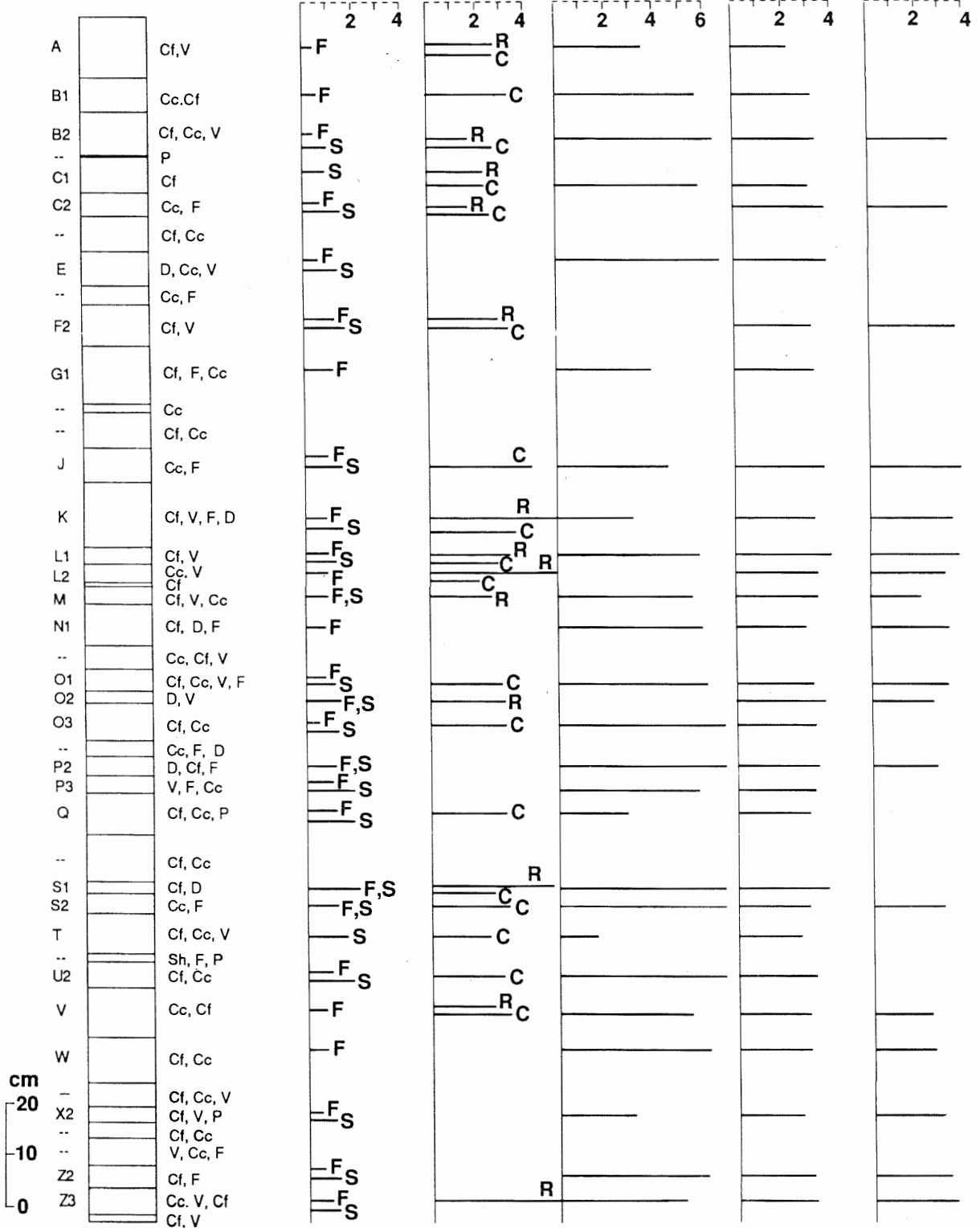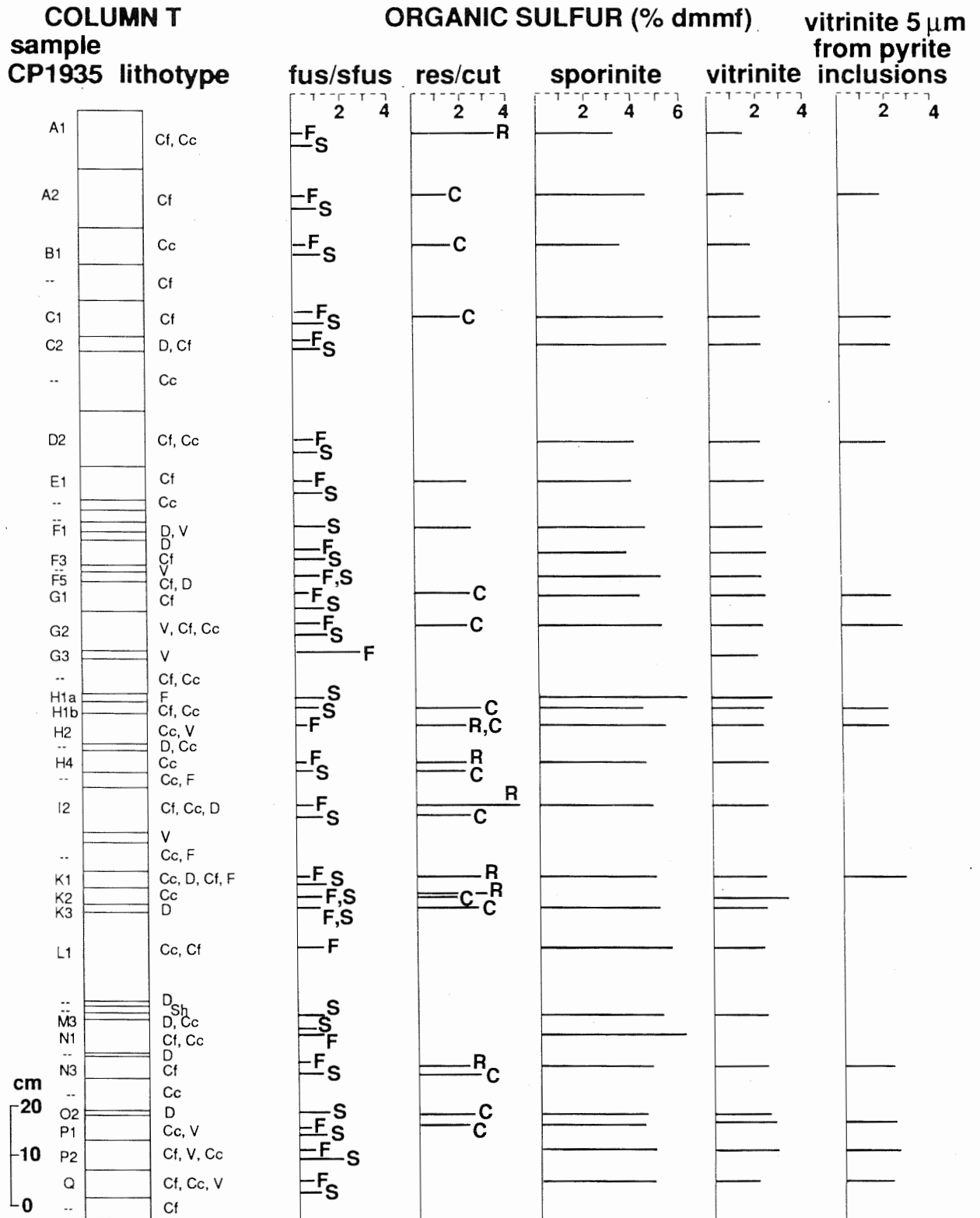
17

Figure 9 The relative thickness and lithotype of coal, and variation of mean organic sulfur content in macerals by layers in column T (under shale transitional to nonmarine). See fig. 8 for the lithotype abbreviations.

18

Table 5 Organic sulfur in macerals of the two columns.

| Maceral | Organic sulfur (%, dmmf) | | | |
| | Column M | | Column T | |
	Mean	Range	Mean	Range
Vitrinite	3.03	1.93–5.60	2.06	1.14–2.93
Sporinite	5.10	1.28–7.55	4.44	3.05–5.91
Resinite	3.43	1.38–6.86	2.62	1.72–4.31
Cutinite	2.77	1.57–4.98	1.99	1.29–2.68
Fusinite	0.84	nil–1.88	0.70	nil–2.52
Semifusinite	1.32	0.75–2.17	0.96	0.45–1.64

The results of this study lend support to the Williams/Keith–Gluskoter/Simon model for the relative level of sulfur in coal (Williams and Keith 1963, Gluskoter and Simon 1968). These data are in agreement with the interpretation that the source of the sulfur was dissolved sulfate in the ancient sea water that transgressed over the Herrin peat. One possible mechanism to account for the organic sulfur enrichment in spores is that the structure of spores of ancient plants were notably more porous than other plant parts, so that adsorption of pore water was facilitated by spores. Another possibility is that sulfur-reducing bacteria might have preferentially located themselves on and perhaps had bored inside of the ancient spores, where more abundant proteins and animo acids were available for their use. A third possibility is that the chemical composition of sporinite might be more suitable to react with sulfur compared with other macerals.

CONCLUSIONS AND RECOMMENDATIONS

Organic sulfur analysis of samples of the Herrin seam show moderate variability among the different layers. The macerals from under a marine shale show consistently higher assays of organic sulfur than those under a transitional roof shale. In other words, each maceral group in almost every layer of the seam contains more sulfur at the site under the marine shale than at the site under the transitional roof. These data are in agreement with the interpretation that the source of the sulfur was the ancient sea that transgressed over the Herrin peat.

The standard ASTM bulk analyses of various density fractions of the IBCSP coals reveal the heterogeneities of organic sulfur within macerals in association with mineral matter. We succeeded in concentrating macerals, and thereby obtaining ash yields for the lightest density fractions in the range of 3.1 to 5.8 percent. The heaviest fractions are enriched not only in ash-generating minerals, including pyrite, but also they are enriched in organic sulfur relative to the lightest fractions for most of the coals tested.

Comparison of the relative organic sulfur contents in the density fractions are best made on the dry, mineral matter free basis. On this basis, the relative enrichment of organic sulfur is readily compared. Because the fine-grained pyrite in the heavy fractions is prone to oxidize and yield elemental sulfur during processes of float-sink and analysis, some of the observed enrichment may prove to be an artifact of the testing process. Another possible artifact is that there may be traces of monosulfide (e.g., sphalerite, ZnS) in the tested samples. Sulfur in sphalerite would test as organic sulfur in the ASTM method of analysis. We conclude, however, that these artifacts are negligible and that the enrichment is significant.

The observed strong trend of organic sulfur enrichment in macerals associated with pyrite in the coals tested, appears to be an important finding. We recommend these tests be repeated in experiments where the mass balance of the organic sulfur contents are more fully accounted for than was achieved in this project. If the enrichment found here is confirmed and found to apply to other Illinois Basin coals, further research and development of improved grinding and deep cleaning processes of ultra-fine coals would be justified. New designs for some coals would yield products that would have significantly lower sulfur levels than are possible for existing plants that process only coarsely crushed coals.

REFERENCES

ASTM, 1990, Annual Book of ASTM Standards, Sect. 5, vol. 05.05 Gaseous Fuels; Coal and Coke, ASTM, Philadelphia, 469 p.

Bauer R. A., and P. J. DeMaris, 1977, Geologic conditions of a longwall mining demonstration at the Old Ben No. 24 Mine: AIME-SME, St. Louis, MO, October 19–21, Preprint 77-I-349, 12 p.

Chou, C.-L., 1984, Relationship between geochemistry of coal and the nature of strata overlying the Herrin coal in the Illinois Basin: Memoir of the Geological Society of China, no. 6, p. 269–280.

Clark, C. P., G. B. Freeman, and J. C. Hower, 1984, Non-matrix corrected organic sulfur determination by energy dispersive x-ray spectroscopy for western Kentucky coals and residues, *in* G. M. Roomans, editor, Scanning Electron Microscopy/II: SEM Inc., Chicago, p. 537–545.

Cleyle, P. J., W. F. Caley, I. Stewart, and S. G. Whiteway, 1984, Decomposition of pyrite and trapping of sulphur in a coal matrix during pyrolysis of coal: Fuel, v. 63, no. 11, p. 1579–1582.

DeMaris, P. J., and Bauer, R. A., 1978, Geology of longwall mining demonstration at Old Ben No. 24: Roof-lithologies and coal-balls: Illinois Mining Institute, v. 85, p. 80–91.

Gluskoter, H. J., and Simon, J. A., 1968, Sulfur in Illinois coals: Illinois State Geological Survey, Circular 432, 28 p.

Hackley, K. C., D. H. Buchanan, K. Coombs, C. Chaven, and C. W. Kruse, 1990, Solvent extraction of elemental sulfur from coal and a determination of its source using stable sulfur isotopes: Fuel Processing Technology, v. 24, p. 431–436.

Harvey, R. D., and P. J. DeMaris, 1987, Size and maceral association of pyrite in Illinois coals and their float-sink fractions: Organic Geochemistry, v. 11, no. 5, p. 342–349.

Harvey, R. D., and I. Demir, 1990, Characterization of Organic Sulfur in Macerals and Chars: Final Technical Report to CRSC: Illinois State Geological Survey, 24 p.

Harvey, R. D., I. Demir, C. A. Wert, and D. J. Lowry, 1989, Spatial Distribution of Organic Sulfur in Selected Illinois Basin Coals: Final Technical Report to CRSC: Illinois State Geological Survey, 25 p.

Hsieh, K. C., and C. A. Wert, 1985, Direct determination of organic sulphur in coal: Fuel, v. 64, no. 2, p. 255–261.

Johnson, P. J., 1979, Petrology and environments of deposition of the Herrin (No. 6) Coal Member, Carbondale Formation: M.S. thesis, University of Illinois, Urbana, 169 p.

Keller, D. V. Jr., 1986, Separation of mineral matter from Pittsburgh coal by wet milling, *in* K. S. Vorres, editor, Mineral Matter and Ash in Coal: American Chemical Society Symposium Series 301, p. 473–484.

Raymond, R. Jr., and R. Gooley, 1978, A review of organic sulfur analysis in coal and a new procedure, *in* Scanning Electron Microscopy/Vol.I: SEM Inc., Chicago, p. 93–107.

Smith, W. H., and J. B. Stall, 1975, Coal and water resources for coal conversion in Illinois: Illinois State Geological Survey and Illinois State Water Survey, Cooperative Resources Report 4, 79 p.

Tseng, B.-H., M. Buckentin, K. C. Hsieh, C. A. Wert, and G. R. Dyrkacz, 1986, Organic sulphur in coal macerals: Fuel, v. 65, no. 3, p. 385–389.

Wert, C. A., K.-C. Hsieh, B.-H. Tseng, and Y.-P. Ge, 1987, Applications of transmission electron microscopy to coal chemistry: Fuel, v. 66, p. 914–920.

Wert, C. A., Y. Ge, B. H. Tseng, and K. C. Hsieh, 1988, Analysis of organic sulfur in coal by use of transmission electron microscopy: Journal of Coal Quality, v. 7, no. 4, p. 118–121.

Williams, E. G., and M. R. Keith, 1963, Relationship between sulfur and occurrence of marine roof beds. Economic Geology, v. 58, p. 720–729.

Yurovskii, A. Z., 1974, Sulfur in coals (transl. from Russian): Indian National Scientific Documentation Centre, New Delhi, 455 p. Availalable from U.S. Dept. Commerce, NTIS, TT-70-57216.