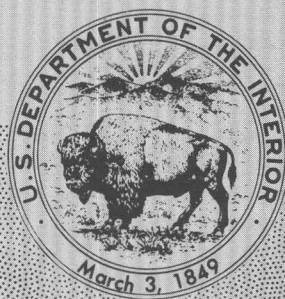


U. S. GEOLOGICAL SURVEY CIRCULAR 932



# Interlaboratory Comparison of Mineral Constituents in a Sample from the Herrin (No. 6) Coal Bed from Illinois



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Edited by Robert B. Finkelman, Faith L. Fiene,  
Robert N. Miller, and Frederick O. Simon

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U.S. GEOLOGICAL SURVEY CIRCULAR 932

**Department of the Interior**

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**U.S. Geological Survey**

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# **Interlaboratory Comparison of Mineral Constituents in a Sample from the Herrin (No. 6) Coal Bed from Illinois**

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## **ABSTRACT**

Approximately 20 kg of the Herrin (No. 6) coal was collected from a strip mine in St. Clair County, Ill. A 10-kg portion was ground to -60 mesh, homogenized, and riffled into 128 splits of 70-80 g each. Homogeneity of these splits was confirmed by moisture, ash, and sulfur analyses of six randomly selected splits. Results of these analyses were within the ASTM (American Society for Testing and Materials) guidelines for interlaboratory precision. Splits of the Herrin (No. 6) coal were then transmitted to more than 30 laboratories for analysis.

Low-temperature plasma oxidation was used to isolate inorganic matter for quantitative chemical and mineralogical analysis. Despite a wide variation in ashing conditions, only minor variations in ash yields were obtained; these variations were attributed to differences in operating temperature and moisture content. Mineralogical analyses of low-temperature ash (LTA) concentrates prepared by five different laboratories indicated variations within the limits of analytical error. The mean values, in weight percent, for the major minerals are as follows: calcite, 9; quartz, 20; pyrite, 23; kaolinite, 14; and illite+mixed-layer clays, 31. Normative mineralogical calculations and Fourier transform infrared analysis (FTIR) yielded results similar to those obtained from X-ray diffraction (XRD).

Choosing appropriate mineral standards was found to be critical for the proper use of analytical techniques such as XRD and FTIR.

Good interlaboratory agreement was obtained for most major, minor, and trace elements despite differences in analytical procedures and in the type of sample analyzed (coal, high-temperature ash, or LTA). Discrepancies between analyses for zinc, strontium, manganese, and iron may be attributed to sampling inhomogeneity problems. Mossbauer spectroscopy showed that approximately 44 percent of the pyritic sulfur was lost through weathering in the first year after preparation of the interlaboratory sample. Szomolnokite and possibly coquimbite and jarosite were also identified. Scanning electron microscopy studies indicated ubiquitous pyrite framboids and, less commonly, euhedral crystals, skeletal grains, irregularly shaped particles, and vein fillings. Minor accessory minerals such as rare-earth phosphates and possibly silicates, zircon, barium sulfate, titanium oxide, and sphalerite were also found. The textural evidence indicates that the minerals in the banded material are detrital whereas the minerals occurring as vein and pore fillings are authigenic. Magnetic measurements indicate that coal crushed in a steel pulverizer is contaminated by small quantities of abrasion fragments from the crusher, which seriously affect the measured magnetic properties of the coal.



## **Introduction**

**By R. B. Finkelman**

At a conference on mineral matter in coal (held in May 1978 at the University of Illinois Champaign-Urbana, Ill.), representatives from several laboratories described their procedures for obtaining X-ray diffraction (XRD) data from low-temperature ash (LTA). Each laboratory had selected or devised procedures for low-temperature ashing and XRD analysis to suit its particular needs. No two laboratories used the same procedure for preparing and analyzing the samples or for reducing the data. Difficulties were encountered in attempting to relate the data of any one laboratory to those of another. As a result, the conferees felt that a procedure should be developed that would permit interlaboratory comparison of data. One suggestion was to investigate the possibility of developing a single or "universal" procedure that could be used by all participating laboratories. Another suggestion was to have each participating group analyze subsamples of the same material; the resulting data could then be used in developing a basis for relating the data of one laboratory to those of another. The latter approach was agreed upon and a committee<sup>1</sup> selected to devise this X-ray "Rosetta Stone." The sample selected for this interlaboratory study was to be collected from the Herrin (No. 6) coal bed in St. Clair County, Ill.

The primary purpose of this interlaboratory study and this circular is to provide a means for interpreting XRD data on coal minerals reported by different laboratories. No attempt was made to standardize any of the analytical procedures, nor was the interlaboratory study designed to provide standard chemical, petrographic, or other types of analytical data. The data herein are intended to provide useful supplementary information and are not intended for use as standard values for this sample.

The maximum value of this study would be realized if every laboratory that is actively engaged in research on coal minerals were to participate in this comparison. In order to encourage such participation, a supply of the raw coal and the LTA used in the interlaboratory study has been reserved for future needs. This material may be obtained by writing to Frank G. Walthall, U.S. Geological Survey, 923 National Center, Reston, VA 22092, U.S.A.

### **ACKNOWLEDGMENTS**

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## Experimental Design and Preparation of a Homogeneous Sample

By F. L. Fiene

### COLLECTION AND PREPARATION OF THE COAL SAMPLE

The Herrin (No. 6) coal bed was chosen for the interlaboratory sample because it is known to contain a variety of mineral constituents and an ash content between 10 and 15 percent. Approximately 20 kg of coal was collected from an active strip mine in St. Clair County, Ill., in July 1978. The channel sampling procedure described by Schopf (1960) was followed. In this procedure, the face of the coal bed is sampled, excluding mineral bands, partings, and nodules greater than 1 cm in thickness. The coal bed had been exposed only a few hours prior to collection. There was no evidence of clay dikes, faulting, or other sources of contamination nearby. A vertical column of coal approximately 10 cm by 10 cm was chipped from the bed with a steel pick and immediately placed in plastic-lined (0.10-mm-thick) burlap bags, which were promptly sealed to retain moisture.

Within one week, the interlaboratory sample was prepared for analysis at the Applied Laboratory of the Illinois State Geological Survey, Champaign, Ill. The sample was first crushed by a roll mill to -10 mesh and air-dried at 85-90°C for 24 hours. Half of the dried coal (10 kg) was then ground to -60 mesh in a hammer mill and homogenized overnight in a V-type blender. Two Jones sample splitters with 3/8-in and 1/8-in chutes were used to sequentially riffle out 128 individual subsamples. Each subsample, containing 70-80 g coal, was put in a 4-oz glass screw-cap bottle and sealed in a CO<sub>2</sub> atmosphere. Six bottles were chosen at random for a check on homogeneity, and those remaining were randomly assigned numbers between 1 and 122. The numbered bottles and the remaining 10 kg of the original sample (-10 mesh, stored in plastic-lined cardboard cartons) were stored in a freezer.

### HOMOGENIZATION TESTS

The six subsamples selected for the homogeneity check were subjected to a series of tests considered to be the most reliable indicators of uniformity.

The six subsamples were first tested for moisture, ash, and forms of sulfur (total, pyritic, and sulfatic) contents. The results, summarized in table 1, are within the repeatability (intralaboratory precision) required for duplicate analyses of the same sample according to the American Society for Testing and Materials (ASTM) Annual Book of Standards, Part 26 (D2492, D3173, D3174, D3177). On this basis, it was concluded that the individual subsamples were representative of the original coal sample. Five participating laboratories prepared LTA from the chemically characterized subsamples to monitor the variability in both mineral content and composition under the ashing procedures used by the individual laboratories. The five laboratories were instructed to ash the samples by their routine procedure and to return about 1 g of the LTA to Laboratory 4 (participating laboratories are identified by number; the identification key is given in the Appendix) for mineralogical analysis. The LTA data generated by these laboratories are shown in table 2 (see section on methodology of low-temperature ashing for discussion). Although there are detectable differences in the LTA percentages, no major differences in mineralogy were detected within the experimental error of the analytical procedures (table 3).

The attempts to produce a homogeneous sample were not entirely successful. Laboratory 9 detected some inhomogeneity between two LTA samples with respect to calcite and sulfate (see the discussion of carbonate distribution, section F, and of trace-element data, section C). These inhomogeneities appear to be relatively minor and should not adversely affect the use of the interlaboratory sample as a standard for comparing X-ray diffraction analyses among laboratories.

### PREPARATION OF LOW-TEMPERATURE ASH

The five laboratories participating in the preliminary homogeneity test prepared the LTA used for general distribution. Because the LTA was to be homogenized by mixing the LTA from all five laboratories, no special precautions were

TABLE 1.—Comparison of chemical analyses for six randomly selected subsamples of the interlaboratory sample

[All analyses by Laboratory 1. Quantities are given as weight percent; moisture is on an as-received basis, all other analyses on a moisture-free basis. ISGS, Illinois State Geological Survey; SD, standard deviation; HTA, high-temperature ash]

Sample No.	ISGS-C20275	ISGS-C20276	ISGS-C20277	ISGS-C20278	ISGS-C20279	ISGS-C20280	Average	SD
Moisture <sup>1</sup>	6.7	6.9	7.0	7.1	7.0	7.1	7.0	0.14
Ash <sup>2</sup>	13.6	13.6	13.7	13.7	13.6	13.7	13.7	.05
Pyritic sulfur <sup>3</sup>	1.97	1.92	1.95	1.93	1.91	1.91	1.93	.03
Total sulfur <sup>4</sup>	4.07	3.97	3.88	3.80	3.83	3.78	3.89	.15

<sup>1</sup>ASTM repeatability: > 5% moisture = 0.3%

<sup>3</sup>ASTM repeatability: < 5% Pyritic sulfur = 0.05%

<sup>2</sup>ASTM repeatability: > 5% ash = 0.5%

<sup>4</sup>ASTM repeatability: > 2% sulfur = 0.1%

TABLE 2.—Amount of low-temperature ash, in percent, produced at five laboratories

[SD, standard deviation; LTA, low-temperature ash]

Laboratory Sample No.	24 ISGS-C20275	17 ISGS-C20276	4 ISGS-C20277	25 ISGS-C20278	1 ISGS-C20279	Average	SD
LTA	18.4	15.7	16.3	16.7	16.8	16.8	1.0

TABLE 3.—Mineralogy of low-temperature ash produced at five laboratories

[All analyses by Laboratory 4 and given as weight percent. Kaolinite determined by infrared analysis; pyrite, calcite, and quartz determined by X-ray diffraction analyses. SD, standard deviation]

Laboratory generating LTA	24	17	4	25	1	Average	SD
Pyrite	24	21	17	21	17	20	3
Calcite	4	6	6	6	5	5	1
Quartz	18	17	16	16	15	16	2
Kaolinite	15.6	16.3	15.4	14.7	14.6	15.3	0.7

taken to minimize the sources of bias resulting from the different low-temperature ashing procedures. However, to retard sample deterioration, the laboratories were instructed to store the LTA in airtight containers in either a vacuum desiccator or a freezer.

The LTA samples (approximately 100 g each) produced by the five laboratories were sent to a coordinating laboratory (USGS, Reston, Va.), where the combined samples were homogenized overnight in a V-type blender and then riffled into 2 equal parts. One part was returned to freezer

storage for reference and reserve purposes, and the other part was riffled into 32 1.5- to 2-g subsamples by using a Jones splitter with a 1/8-in chute. These subsamples were placed in glass pop-cap bottles, vacuum-sealed, numbered, and stored in a freezer until final distribution.

## DISTRIBUTION

More than 40 laboratories have participated in the interlaboratory study. Each laboratory received a sample of the prepared coal and (or) LTA according to its research interests and instrumental capabilities. No restrictions were placed on the types of analysis to be undertaken, but laboratories were encouraged to low-temperature ash the coal and to analyze the mineralogy of both the LTA they produced and the control LTA by X-ray diffraction (XRD) and any other analytical method at their disposal. The distributed samples were accompanied by a questionnaire requesting written documentation of methods and data.

## Basic Characteristics of the Interlaboratory Sample from the Herrin (No. 6) Coal Bed

By R. W. Stanton

Data from ultimate and proximate analyses and determinations of forms of sulfur for the interlaboratory coal sample are shown in table 4. Some differences are evident among the sets of data; the differences in the sulfate-sulfur values probably are the result of oxidation of pyrite before some of the analyses were performed.

The following list contains the ASTM standards for each test and the acceptable reproducibility or repeatability value for each specific determination. Although each laboratory was not required to follow ASTM procedures, these values are presented here to use as a basis for comparison of the data.

Some values in table 4 lie outside the acceptable differences among laboratories. However, the intent of these data is to provide information on the composition of the sample provided for round-robin laboratory analyses; the sample is not to be used as a standard.

Parr mineral matter values (Parr and Wheeler, 1909) were calculated from the data by using the equation

$$\text{Parr} = 1.08(A) + .55(S)$$

where A = high-temperature ash and S = total sulfur. This value includes both minerals and organically bound elements and can be compared to the LTA values, which average 16.8 percent (table 2).

Carbonization data for this sample appear in table 5.

### PETROGRAPHY

Five laboratories provided information on the

ASTM standard	Reproducibility	Repeatability (in ASTM, 1981)	Reference
D3177 Total sulfur	0.15	0.10	p.380-386
D2492 Sulfate sulfur	.04	.02	p.319-323
D2492 Pyritic sulfur	.30	.10	p.319-323
D3178 Carbon	---	.30	p.387-391
D3178 Hydrogen	---	.07	p.387-391
D3179 Nitrogen	---	.05	p.392-395
D2015 Calorific value	100.00	50.	p.389-397
D3175 Volatile matter	1.0	.50	p.372-375
D3174 Ash	.3	.20	p.370-371
D3302 Moisture	.50	.30	p.410-415

TABLE 4.—Chemical analyses of whole coal

[Moisture-free basis; oxygen determined by difference; all values are in weight percent except calorific value which is in Btu per pound]

Laboratory	1	9	26	27	Average
Total sulfur	3.78	4.16	4.19	4.08	4.05
Sulfate sulfur	.06	.23	.08	.19	.14
Pyritic sulfur	1.91	1.75	1.88	1.76	1.83
Organic sulfur	1.81	2.18	2.23	2.13	2.09
High-temperature ash	13.78	13.96	13.40	13.42	13.64
Moisture (as received)	7.1	7.4	7.21	6.98	7.17
Volatile matter	39.6	<sup>1</sup> 37.51	40.4	40.7	39.0
Carbon	67.64	67.10	68.15	----	67.63
Hydrogen	4.89	4.62	4.76	----	4.69
Nitrogen	1.24	1.39	1.01	----	1.20
Oxygen	8.75	<sup>2</sup> 7.49	8.51	----	8.00
Calorific value	12430	12107	12243	----	12337
Parr mineral matter	16.96	17.36	16.78	16.96	16.96

<sup>1</sup>Laboratory 9 reported that volatile matter was determined by Australian/British Standard 1038 (Australian Standard, 1979b), which specifies heating the sample to 900°C rather than 950°C as in ASTM D3175 (ASTM, 1981, p. 372-374). This lower temperature probably accounts for the poor agreement of the volatile-matter values.

<sup>2</sup>Analytical value.

TABLE 5.—Laboratory carbonization tests

[All tests performed by Laboratory 9]

Crucible Swelling Number (Australian Standards, 1979a)	
CSN = 3.5	
Automatic Gieseler Plastometer (Australian Standards, 1981)	
Initial softening temperature	381°C
Maximum fluidity temperature	409°C
Solidification temperature	434°C
Maximum fluidity (dial division per minute)	3
Log <sub>10</sub> maximum fluidity	0.4771
Plastic range	53°C
Audibert-Arnu Dilatometer (International Standards Organization, 1983)	
Percentage contraction	25
Percentage dilatation	Contraction only.
Temperature T <sub>i</sub>	325°C
Temperature T <sub>11</sub>	470°C
Temperature T <sub>111</sub>	Contraction only.

petrographic character of the interlaboratory sample. Representative splits of -10 mesh coal were obtained from the remaining 10 kg of the original sample described previously. Pellets were prepared in accordance with ASTM standard test D2797 (1981, p. 347-351).

TABLE 6.—Maceral composition

[R<sub>o</sub> max., mean maximum vitrinite reflectance in percent vitrinite reflectance; all other data in volume percent on mineral-matter-free basis; T, trace, less than 5 counts/1000; --, not reported]

Laboratory number	1	9	25	24	26	Average
Vitrinite	82	--	87	90	88	87
Exinite (liptinite)	4	--	5	1	2	3
Sporinite	3	--	2	1	<1	<2
Cutinite	1	--	1	T	2	<1
Resinite	T	--	2	T	<1	<2
Inertinite	14	--	9	9	10	10
Inertodetrinite	--	--	1	3	--	2
Fusinite	2	--	2	1	3	2
Semifusinite	1	--	4	3	7	4
Micrinite	7	--	1	2	<1	2
Macrinite	3	--	T	T	T	2
Sclerotinite	T	--	--	--	<1	T
R <sub>o</sub> max.	0.57	0.54	--	--	--	0.55

Petrographic data reported are presented in table 6. The results show good agreement among the participating laboratories for most parameters. Because of the low metamorphic rank of this coal, there was some difficulty in differentiating among the varieties of vitrinite, which included abundant desmocollinite and corpocollinite as well as less abundant telocollinite and gelocollinite.



## The Methodology of Low-Temperature Ashing

By Robert N. Miller

The interlaboratory comparison of inorganic analytical methods was based on the combined subsamples produced in various laboratories by low-temperature plasma oxidation. This section of the report discusses the LTA methodology, its application in the interlaboratory study, the limitations of the present study with respect to LTA, and, finally, the problems associated with LTA procedures and possible solutions.

### BACKGROUND

The initial objective of the interlaboratory study was to compare variations among XRD methods used on LTA. It soon became apparent that various laboratories used widely different conditions for low-temperature ashing. This by itself introduced variations in the composition of the individual ashes. A preliminary screening of the interlaboratory sample by XRD showed no gross dissimilarities among ashes; however, the X-ray method was not capable of detecting minor components or noncrystalline species. Data summarizing the variations among the low-temperature ashing conditions used in the different laboratories appear in table 7.

Despite the consistency (coefficient of variation = 4 percent) of the LTA results, the ashing conditions used by the participating laboratories obviously lacked standardization. Both mineral and chemical analyses of an ash prepared by one LTA procedure in one laboratory may differ from the analyses obtained on an ash prepared in another laboratory using different ashing conditions. Recommendations for standardizing low-temperature ashing conditions are necessary before pursuing future interlaboratory comparisons.

In practice, a researcher will analyze the LTA prepared in his laboratory. What is done with the ash depends on the specific objectives of the research study. On one hand, if a researcher wants to analyze major species present in a prepared ash and report them as proportions of that ash, then the primary concern will be the reproducibility of

the analytical methods. This aspect was addressed as the primary purpose of the interlaboratory study—what methods can be used to quantitatively determine major mineral species in LTA? Suppose, however, that a researcher wants to report the mineralogical or chemical analysis of the LTA on a whole coal basis; that is, he wants to know what was in the coal. In this instance, the LTA yield must be known accurately. In addition, when species are analyzed on the LTA and then calculated back to the coal basis, it must be assumed that they were present in the same or a known form in the original coal sample. For some minerals and especially cations associated with organic acids in lower rank coals, this assumption may be questioned. Artifacts that are produced by ashing can be misinterpreted as being present in the original coal. In addition, if a researcher is concerned with the study of the oxidation-reduction states of various species, with the analysis of minor or trace mineral phases, or with the study of the noncrystalline inorganic components in a coal, then the question of alteration of the inorganic matter during low-temperature ashing of the coal becomes an important issue. The interlaboratory study dealt with only one sample of a bituminous coal and did not address the problems of mineralogical analysis of lignite or subbituminous coal. Low-rank coal behaves quite differently in an asher and poses its own set of unique problems. In the broad context of LTA methodology, the following discussion also pertains to inorganic reactions in low-rank coals.

### THE LTA PROCEDURE AND REACTIONS OF INORGANIC MATTER

Gluskoter (1965) introduced plasma oxidation as a technique for isolating inorganic materials from coal. Earlier methods were unsatisfactory for separating major portions of inorganic matter from the organic coal matrix. Ashing at high temperatures ( $> 500^{\circ}\text{C}$ ) or wet-chemical oxidative techniques significantly alter the mineral matter

TABLE 7.—*Interlaboratory comparison of low-temperature ashing conditions*

[Numbers in parentheses are calculated using 6.94% moisture; no corrections are made for moist LTA;— data not reported.]

Lab	Condition of coal prior to ashing	Condition final ash	Reported percent LTA		Layer density (mg/cm <sup>3</sup> )	g coal per dish	O <sub>2</sub> flow (cm <sup>3</sup> /min)	RF power (W/chamber)	Temperature (°C)	Ashing time (days)	No. of times stirred	Termination criterion
			Dry	As rec'd								
1	Dry	Vacuum dry (warm)	17.1	(15.9)	79	4.0	200	38	120-145	8	8	<1-mg loss/day
17	Dry	Vacuum dry	16.7	(15.5)	22	1.6	200	50	135-157	.5	6	<2-mg loss/2-hr period
3	Dry	Vacuum dry	18.3	(17.0)	42	1.5	60	15	<125	4.8	5	<5-mg loss/day
7	Dry	—	16.7	(15.5)	—	—	100	—	—	3-4	6-10	—
9	As rec'd.	Air dry	17.4	(16.2)	31	.6	100	58	170-180	3	9	Visual; residual C determined
4	As rec'd.	Air dry (warm)	(16.5)	15.4	64	4.0	100	50	135-160	4	12	<10-mg loss/7-hr period
22	As rec'd.	Air dry	(16.5)	15.4	26	2.0	—	50	—	4	8	<1-mg loss/4-hr period
2	As rec'd.	Vacuum dry	(16.0)	14.9	35	1.0	800	133	—	5	4	Constant weight
10	As rec'd.	Air dry	(16.4)	(15.3)	26	.4	100	50	—	6	5	<0.2-mg loss/3-hr period

<sup>1</sup>Corrected for unburned carbon and fixed sulfate. <sup>2</sup>Calculated on the basis of 6.8% moisture.

of most coals; physical separations based on gravity or particle size never succeed in separating submicrometer-sized inorganic components from the organic particles. Although the LTA technique was a significant breakthrough for coal mineral matter studies, it is not without problems. Plasma oxidation will generate artifacts by changing major minerals or forming new inorganic species from the breakdown of organic and inorganic complexes.

The plasma oxidation of coal is the combustion of organic matter at a relatively low temperature (<200°C). In contrast to the procedure for high-temperature combustion, the energy required to "gasify" the organic carbon is supplied by exposing the coal surface to oxygen molecules that have been "activated" in a radiofrequency (RF) field. Organic molecules react with the "RF-activated" oxygen releasing carbon, sulfur, and nitrogen oxides and water into the gas phase. Most of these combustion products are readily removed from the system by the vacuum pump, but some may react with the inorganic matter and remain in the ash. Thus, as the organic matter reacts, inorganic materials are concentrated as a residue. In addition to decomposing the organic matter, the ashing procedure may also decompose or alter some of the inorganic materials. Therefore, depending on the conditions of the experiment and on the nature of the starting coal, this residue (the LTA) may contain unaltered minerals, minerals whose elemental composition is unchanged but which have undergone crystallographic change, newly formed crystalline phases from gas or solid decomposition and oxidation reactions, amorphous inorganic species (see section J), and unburned residual organic matter. Table 8 summarizes some of the changes in the different types of inorganic matter. The inorganic alterations and the low-temperature ashing conditions that influence them are discussed below.

## THE OXIDATION EFFECT

The low-temperature asher is basically an oxidizing system, and therefore a species present in a reduced state is thermodynamically unstable. Hence, organic molecules are rapidly destroyed. Likewise, any mineral containing elements in a reduced state (such as pyrite) is unstable and can undergo reaction in the oxygen plasma. The crystalline surface chemistry of most individual

TABLE 8.—*Some inorganic products of low-temperature ashing*

Unaltered minerals	Quartz, kaolinite, illite.
Altered minerals	
- alteration of crystallinity	Montmorillonite, mixed-layer clays.
- alteration by oxidation	Ferrous to ferric sulfates. Sulfides ( $\text{FeS}_2$ ) to oxides or sulfates.
New phases	
- from dehydration	Bassanite [ $\text{CaSO}_4(\text{H}_2\text{O})_{1/2}$ ] from gypsum.
- from gas-solid reaction	Formation of gypsum and bassanite (from the reaction of $\text{SO}_3 + \text{CaCO}_3 + \text{H}_2\text{O}$ ); alkali nitrates and sulfates.
- from decomposition of organic salts	Alkali and metal oxides, carbonates, nitrates or sulfates.
- from decomposition of reduced minerals	$\text{Fe}_2\text{O}_3$ or $\text{Fe}_2(\text{SO}_4)_3$ from pyrite combustion.
Amorphous material	$\text{SiO}_2$ .
Unburned or charred carbonaceous material	

mineral grains is an effective kinetic barrier to oxidation, thus minimizing chemical reactions, but a poorly crystalline or defective mineral grain will be unstable in the plasma. Montano (1977) presented unequivocal evidence of the formation of a new mineral species [ $\text{Fe}_2(\text{SO}_4)_3$ ] from the oxidation of pyrite during the low-temperature ashing process. Miller and others (1979) observed that some pyrite grains actually ignite in the asher, emitting an obvious red glow, while other pyrite grains are unaffected. Hematite ( $\text{Fe}_2\text{O}_3$ ) was identified as the reaction product under their ashing conditions. During the oxidation of pyrite, "hot spots" are formed that may cause high-temperature alteration of neighboring mineral grains. In addition to the oxidation of discrete minerals, reduced metallic cations ion-exchanged onto clay minerals or coal or emplaced isomorphically in certain minerals can be oxidized. Montano (1977), using Mossbauer spectroscopy, observed a change from ferrous iron ( $\text{Fe}^{2+}$ ) to ferric iron ( $\text{Fe}^{3+}$ ) after low-temperature ashing.

### THE EFFECTS OF TEMPERATURE

The plasma operates at 100–200°C (see table 7). The heat in the chamber results from the energy dissipated during the RF discharge and also from the exothermicity of the organic matter combustion. Thus, the higher the RF field power, the

higher will be the background or normal operating temperature in the oxidation chamber. In the normal operating temperature range of the low-temperature asher, certain hydrated minerals and expandable clays that have attained a constant weight under normal drying conditions (110°C) will gradually lose additional moisture. This effect will be more severe the higher the chamber temperature. Gluskoter (1967) demonstrated that certain mixed-layer clays lose as much as 20 percent of their weight during ashing and attributed this to irreversible moisture loss from the interlayer; XRD scans indicated a substantial change in the c-axis spacing of the clay from 14.9 to 13.6 Å. It has also been demonstrated that chemical and crystal structural changes accompany dehydrations. Certain of the hydrated minerals that lose their water between 100 and 250°C will alter in the LTA. For example, gypsum [ $\text{CaSO}_4(\text{H}_2\text{O})_2$ ] is readily dehydrated to form bassanite [ $\text{CaSO}_4(\text{H}_2\text{O})_{1/2}$ ] at temperatures above 100°C but below 170°C; at temperatures above 170°C, the hemihydrate is irreversibly stripped of its remaining water to form anhydrite. In fact, these specific changes can act as a kind of thermometer for monitoring temperatures in the LTA.

There is yet another temperature-sensitive phenomenon that occurs during low-temperature ashing—this involves fixation reactions of combusted organic matter with reactive minerals. Sulfur, nitrogen, and carbon oxides, all products of

the organic-matter combustion, are acid gases. In the relatively stagnant conditions that prevail in the ashing chamber, these gases can react with inorganic bases to form sulfates, nitrates, and carbonates, respectively. The nature and extent of reaction depend on the particle size of the inorganic material, the partial pressure of the gas in the ashing chamber, and the operating temperature. As chamber temperatures vary, the absolute amount of sulfates or nitrates that are formed and deposited in the LTA will vary. Miller and others (1979) showed that the sulfate ion fixed in the ash decreased with increasing RF power. Apparently the reaction of a hydrated species of  $\text{SO}_3$  in the gas phase with solid carbonate in the ashing dish was sensitive to temperature in the normal operating range of LTA. Miller and others (1979) also observed that a peculiar ice-like condensate appeared on the surface of the ashing equipment when high-sulfur coal was ashed at low power but that this material evaporated at higher power. The substance was never positively identified but was found to be highly acidic upon exposure to air and did give a positive test for sulfate ion. Recently, F. Stohl (oral commun., 1980) at the Los Alamos National Laboratory in New Mexico identified a similar condensate found in the LTA at low power and obtained an X-ray pattern indicative of a hydrogen ammonium sulfate.

#### **DECOMPOSITION OF ORGANIC SALTS**

It is well known that alkali or alkaline-earth metallic ions will catalyze the gasification reactions of coal in oxygen. Alternatively, these same cations tend to deactivate the excited oxygen molecules during low-temperature ashing and therefore inhibit the rate of oxidation. One might then predict that coal containing alkali or alkaline-earth metals in a dispersed form will be the most difficult to ash. Lignite and subbituminous coal generally contain a large portion of their so-called "mineral matter" in a dispersed form, that is, bound as cations to oxygenated, acidic, organic functional groups. Therefore, it is not surprising that lignite ashes more slowly than do higher rank coals. The geochemical literature also suggests the presence of organometallic complexes in bituminous coal. The fate of these species during low-temperature ashing is unknown.

#### **QUANTITATIVE LOW-TEMPERATURE ASHING AND MINIMIZING REACTIONS OF THE INORGANIC MATTER**

Miller and others (1979) summarized the reactions that can significantly alter inorganic constituents in coals during low-temperature ashing. If reactive species are abundant in the coal, then the effect can be serious. Fortunately, many reactions can be minimized under carefully controlled experimental conditions, and, at least for bituminous coal, a good quantitative approximation of the mineral-matter content of a coal can be obtained. We propose several criteria for low-temperature ashing of bituminous coal that will minimize undesirable reactions due to temperature and oxidation. In addition, the inherent hygroscopic nature of coal and coal ash is important in establishing a standard experimental ashing procedure.

#### **THE RF POWER LEVEL**

Widely varying RF power levels (15–125 W/chamber) were used by the various laboratories in this study. Since the RF power level and the operating temperature in the ashing chamber are correlative, careful control of the RF power level should minimize temperature-sensitive reactions. In their discussion of quantitative ashing, Miller and others (1979) and Frazer and Belcher (1973) recommended the use of moderate power settings (30–60 W/chamber for their instruments from International Plasma Corp.). Miller and others (1979) chose 50 W/chamber as the level where fixation of organic sulfur and oxidation of pyrite were minimized. A moderate power setting is recommended because low wattage (<30 W/chamber) tends to greatly increase the fixation of products from gas-solid reactions, whereas high power levels (>70 W/chamber) cause increased dehydration of clay and oxidation of pyrite. Because the actual operating temperatures at all power levels might vary among instruments, the optimum operating conditions for a particular low-temperature asher will have to be determined by trial and error. A low-temperature asher can be calibrated by using the chemical thermometer method or by measuring levels of products from undesirable reactions, such as sulfate fixation. Stohl (1980) determined the LTA operating temperature by

using a chromel-alumel thermocouple with a stainless steel sheath inserted into the ashing chamber. The temperature can also be read by using a commercially available platinum resistance probe within a glass sheath.

### MOISTURE FLUCTUATIONS

The largest source of variation observed in the reported interlaboratory ashing conditions was the absence of standardization of the moisture content of the prepared ash and coal. Some laboratories ashed air-dried coal while others ashed "as received" coal. Further, the moisture content of the prepared ash was generally ignored. Since coal is extremely hygroscopic, standard procedures have been instituted to deal with its moisture determination (ASTM D3173 and D1412) under different conditions. Like coal, a freshly produced LTA is extremely hygroscopic and absorbs more than 90 percent of its moisture within several minutes of exposure to air. For the Herrin (No. 6) coal bed, this can represent as much as 3 percent by weight of the coal depending on the relative humidity in the laboratory. For example, if a dry LTA yield is 15 percent of dry coal, then a reported yield on an air-equilibrated ash might be 17 percent, a significant difference. This problem can be eliminated if one uses either of the following procedures:

- (1) The weight of coal used for the test and the final weight of LTA are obtained on dry samples. The coal can be dried using the standard ASTM procedure. A dry weight of LTA is best obtained by initially allowing the fresh LTA to equilibrate in lab air and then drying it under the *same conditions* as used for the coal. Note that weighing of ash directly out of the asher is not acceptable, since the drying conditions in the instrument may differ from the conditions used to dry the coal.
- (2) The weight of coal and the ash can be obtained on air equilibrated samples provided an independent determination of moisture is done on aliquots from both the coal and ash.

In either of the above methods, the final LTA percentage should be calculated to the dry basis to express results free from moisture variability.

Neavel and others (1980) have obtained data on nearly 50 bituminous coal samples which show a negligible mean difference (0.05) between dry-basis

LTA yields and formula-derived mineral-matter contents. LTA yields calculated from the weight of air-equilibrated ash show a significant bias in the mean difference (-1.13).

### STIRRING FREQUENCY AND ASHING DURATION

The longer a sample is exposed to the oxygen plasma, the greater the probability of unwanted reactions of the unstable materials. Miller and others (1979) pointed out that the extent of pyrite oxidation increased not only as a function of temperature but also as a function of ashing duration. Interlayer alteration of clays due to moisture loss may also be enhanced by long-term exposure in the plasma. Hence, the shorter the ashing time, the better. The rate of oxidation of the organic matter is relatively slow in the low-temperature asher because of the limited surface area of the sample. To increase the rate of ashing, a sample must be periodically removed from the asher and stirred. This is a tedious, time-consuming, but necessary operation, as all low-temperature asher users are aware. For a typical bituminous coal (that is, one with an ash content between 10 and 20 percent), the rate of oxidation of the organic matter drops after 1-2 hr exposure in the asher. Thus longer exposures and, especially, overnight ashing do not effectively oxidize much additional organic matter. Most of the interlaboratory data refer to durations of 2-5 days for complete ashing of the Herrin (No. 6) coal bed sample. If the sample layer density is less than about 30 mg/cm<sup>2</sup> (this corresponds to 1.5-2.0 g coal in a standard 6-cm petri dish) and if the sample is stirred every 1-2 hr, a quantitative ash for a typical bituminous coal can be obtained in 12-15 hr. This was verified by Neavel and others (1980) on 50 different North American bituminous coal samples, for which the total duration of ashing by this technique was never greater than 20 hours, and the average duration was 17 hours. An added advantage in ashing for shorter durations is decreased wear on the asher and pump and less subsequent down-time for maintenance and repairs.

The ashing duration also depends on the criteria used to determine if ashing is complete. We recommend these approaches:

- (1) The ashing of 1.5-2.0 g of coal can be considered complete when the measured weight

loss on dry ash is less than 2 mg per 2-hour ashing period.

- (2) When ashing a coal, a curve of weight loss against time can be plotted. When the weight loss levels off, ashing can be considered complete and the final weight recorded.
- (3) Generally the oxidation of organic matter is never 100 percent; hence, residual carbon can be measured on the ash to correct for incomplete combustion. Refer to the analytical tests below for procedures and precautions to employ.
- (4) Ashing of low-rank coals (that is, coal with dry mineral-matter-free oxygen contents greater than 16 percent) is extremely troublesome as the carboxylate cations inhibit the oxidation of the organic matter. Consequently, weeks of ashing may produce only an insignificant weight loss. To alleviate the problem, low-rank coals can be first treated with ammonium acetate or dilute hydrochloric acid, to remove the organically associated cations, and then ashed. Cation removal accelerates the ashing and ensures nearly complete combustion of the organic matter.

#### **ANALYTICAL CHECKS ON PROCEDURES**

Certain standard wet-chemical analyses are useful for monitoring the extent of certain inorganic reactions in the low-temperature asher. These tests also serve as independent quantitative measures of certain minerals or ions in the coal and ash. The following tests are recommended:

- (1) Carbon dioxide by acid evolution (ASTM D1756; ASTM, 1981, p. 252-254): This measures the carbonate contents of coal and ash; it will determine the extent of carbonate decomposition or formation in the LTA. Because this test serves as a quantitative measure of carbonate in the LTA, it can also be used to correct the total carbon value of the LTA to obtain the net residual carbon.
- (2) Pyritic sulfur and hydrochloric acid-soluble iron (ASTM D2492; ASTM, 1981, p. 319-322): This test will measure the extent of pyrite oxidation in coal and ash. The decrease in pyritic sulfur content is proportional to an increase in hydrochloric acid-soluble iron (Given and Miller, 1978). The test also serves

as a precise quantitative measure of the mineral pyrite in the LTA.

- (3) Sulfate sulfur (ASTM D2492; ASTM, 1981, p. 319-322): The amount of sulfate in the coal and in the LTA will indicate the extent of sulfate ion formation due to either organic sulfur fixation or pyrite conversion; this test is most useful when setting RF power levels. Also, if the organic sulfur fixation is extensive, the LTA can be corrected to a sulfur-free ash, which is a more precise measure of yield.
- (4) Moisture (ASTM D3173; ASTM, 1981, p. 367-369): This test measures the moisture content of coal and can also be used to measure the moisture content of the ash.
- (5) Carbon and hydrogen (ASTM D3178; ASTM, 1981, p. 387-391): A determination of total carbon and hydrogen in the LTA is useful for several reasons. Total carbon minus the carbon from carbonate decomposition (determined by the acid evolution test) will measure the residual or unburned carbonaceous matter in the LTA. The LTA analyses can subsequently be corrected for incomplete oxidation. The hydrogen determination can serve as an independent estimate of the water of hydration of the clay minerals in the LTA, providing a correction is first made for absorbed moisture.

#### **SUMMARY AND CONCLUSIONS**

The low-temperature plasma oxidation technique was selected by the Interlaboratory Committee for isolating the inorganic matter from the Herrin (No. 6) coal bed sample for subsequent quantitative chemical and mineralogical analysis. As part of the interlaboratory study, the experimental conditions of low-temperature ashing used by the participating laboratories were surveyed and were found to vary considerably. Despite this variation in experimental conditions, the reported ash yields were reasonably consistent. Nevertheless, some of the variation in results among laboratories can be attributed to variations in operating temperature and in sample moisture content.

The proposed recommendations for standardization of LTA methodology should allow a quantitative ash yield comparable to the mineral matter

content of a coal and should minimize many of the undesirable side reactions of the inorganic matter. The inorganic reactions that can occur during plasma oxidation are summarized; certain of these reactions are inherent to the technique and cannot

be avoided. Thus, future investigations using low-temperature ashing as the method of separation must assess the relevance of these factors before interpreting the data.





## Analytical Results from the Interlaboratory Sample from the Herrin (No. 6) Coal Bed

### A. X-RAY DIFFRACTION ANALYSIS

By J. J. Renton, R. B. Finkelman, and F. L. Fiene

The results of interlaboratory XRD determinations are presented in tables 9, 10, and 11. References describing the sample preparation techniques used by the participating laboratories are in table 13. As no independent analytical technique can determine the absolute composition of complex mineral mixtures, there can be no "correct" values. Therefore, no value judgements will be made, nor will any detailed statistical treatment of the data be offered. The results in table 9 are from laboratories that considered their data to be quantitative. It is evident that there is a substantial range of values for each mineral species. This wide range undoubtedly reflects differences in sample preparation procedures,<sup>2</sup> in equipment and standards, and in the treatment of the basic intensity data. In view of all these variables, as well as the inherent errors in the XRD technique, it is encouraging that so many of the laboratories generated similar values for most of the mineral species. It is also encouraging to note that there was relatively little difference in the results between the LTA sent to the laboratories and the LTA that they generated.

The major nonclay minerals (pyrite, calcite, and quartz) were detected or quantified by all reporting laboratories. Clay mineral data were reported in a number of different ways (table 9), which made direct comparisons difficult. Some basic statistics are presented in table 10. Three laboratories reported quantitative analyses for clay minerals on the basis of a separate analysis of the finer fraction of the LTA (table 12; and see section E). However, because of differences between laboratories in grain size of the fractions analyzed, pretreatment methods, and slide preparations, here too the results cannot be compared directly. The

data are probably a good indication of the bias introduced by using various preparation techniques. Marcasite, detected by most of the laboratories, was quantified by only three laboratories, probably due to difficulties caused by peak superposition with pyrite. Other minerals detected were bassanite (Laboratories 1 and 9), gypsum (Laboratories 6 and 23), chlorite (Laboratory 6), feldspar (Laboratory 9), and coquimbite and possibly siderite (Laboratory 23). Table 11 presents qualitative mineral analyses based on the intensity ranks and intensity percentages of major mineral peaks.

Several laboratories commented on their results. Laboratory 1 noted that the discrepancy between their first four pyrite values and the remaining two values is probably attributable to differences in the pyrite standards used. Laboratory 10 attributed their low values for illite to the fact that their illite standard had a higher degree of crystallinity than the illite in the LTA. They indicated that these low values would be omitted in favor of normative calculations. Laboratory 23 reported obtaining good results using Mo radiation on powdered whole coal. They stated that they can detect 1 percent or less of most major coal minerals and that they can quantify the pyrite content. They reported the following minerals in the interlaboratory LTA: illite, coquimbite, gypsum, kaolinite, quartz, calcite, pyrite, probably marcasite, and possibly siderite.

Opinions were solicited from those laboratories participating in the study as to the feasibility of standardizing the quantification procedure for XRD. All those replying believed that a standardized quantitative technique was desirable, although few offered suggestions as to how this could be accomplished. Skepticism was expressed as to the possibility of agreement on any single procedure. It is doubtful that one technique could be found that would simultaneously satisfy the

<sup>2</sup>As an example, Laboratories 1, 3, 8, and 9 used cavity powder mounts, Laboratories 7, 10 and 12 used pressed pellets, Laboratory 4 used a spinner mount, and Laboratory 11 used a slurry mount.

TABLE 9.—Quantitative XRD results from the interlaboratory sample, in weight percent

[tr, trace; Mx.L., mixed-layer-clays; —, not reported; Comm., LTA supplied to participating laboratory by the committee; Lab., LTA prepared by participating laboratory from Herrin (No. 6) interlaboratory sample supplied by the committee; Laboratories 10 and 11 used XRD plus optical examination.]

Laboratory	1		3		4		5		6		7		9		10		11		12
LTA produced by	Comm.	Lab.	Comm.	Lab.	Comm.	Lab.	Comm.	Lab.	Comm.	Lab.	Comm.	Lab.	Comm.	Lab.	Comm.	Lab.	Comm.	Lab.	Lab.
Mesh	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60	-60
Ill. + Mx.L. + Kaol.	135	136	154	138	154	138	154	138	154	138	154	138	154	138	154	138	154	138	154
Illite + Mx.L.	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Kaolinite	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Calcite	8	9	8	7	8	7	8	7	8	7	8	7	8	7	8	7	8	7	8
Quartz	21	22	14	21	13	21	18	20	19	17	10	10	10	10	10	10	10	10	10
Pyrite	36	39	20	34	21	17	20	17	30	19	3	3	19	18	20	17	15	15	20
Marcasite	—	—	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Gypsum	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Bassanite	—	—	2	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Chlorite	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—

<sup>1</sup>By difference. <sup>2</sup>Determined by infrared spectroscopy. <sup>3</sup>Includes 5.5 percent "other clays".

TABLE 10.—Statistics for major minerals in the interlaboratory sample LTA as determined by XRD

[Mean and range in weight percent]

Mineral	Number of laboratories	Mean	Range	
			Minimum	Maximum
Calcite	18	9	6	15
Quartz	18	20	13	25
Pyrite	18	23	10	39
Kaolinite	7	14	10	18
Illite + mixed-layer clays	8	31	18	40

TABLE 11.—Mineral analyses based on peak intensities determined by XRD of the interlaboratory sample

[Comm., LTA supplied to the participating laboratory by the Committee; Lab., LTA prepared by participating laboratory from Herrin (No. 6) coal bed interlaboratory sample supplied by the Committee. Data from laboratory 21 total more than 100 percent because of rounding]

Laboratory	14		16		21	
	Comm.	Comm.	Comm.	Comm.	Lab.	Lab.
Calcite	2	1	36	40	40	40
Pyrite	3	3	19	20	20	20
Kaolinite	4	4	22	20	20	20
Illite + mixed-layer clays	5	5	7	6	6	6
Marcasite	6	6	2	2	2	2

TABLE 12.—Clay analyses, in percent, of the finer fraction of the interlaboratory LTA sample by FTIR

[Laboratory 1 reported no chlorite and 64 percent random interlayering]

Laboratory	1	5	6
Expandable clays	65	50	39
Kaolinite	14	35	36
Illite	21	15	25
Size fraction	< 2 $\mu$ m		
Preparation method	Sedimented glass slide; pretreatment described in Russell and Rimmer (1979).	Ceramic tile.	< 10 $\mu$ m Sedimented glass slide; no pre-treatment.

need of one laboratory for very precise and accurate data on a few samples and the need of another laboratory for high-volume throughput. Finally, most laboratories resisted the idea of abandoning procedures that have proved to satisfy their own particular needs.

## B. INFRARED ANALYSIS

By Paul C. Painter and Norman Suhr

Two laboratories submitted data obtained from infrared spectroscopic methods. Both prepared LTA samples as KBr pellets and used Fourier

TABLE 13.—*Sample preparation techniques for X-ray diffraction analyses*

Laboratory	1. Russell, S. J. and Rimmer, S. M. 1979, Analyses of mineral matter in coal, coal gasification ash, and coal liquefaction residues by scanning electron microscopy and X-ray diffraction: <i>in</i> Analytical Methods for Coal and Coal Products, v. III, ed. Karr, C. Jr., p. 133-162.
Laboratory	3. Stohl, F. V., 1980, The analysis of minerals in coal: Sandia Laboratories Report No. SAND-79-2016, 43 p.
Laboratory	4. Given, P. H., Weldon, D. and Suhr, N., 1980, Investigation of the distribution of minerals of coals by normative analyses: The Pennsylvania State University Technical Report PSU-TR-22.
Laboratory	5. Hosterman, J. W., and Loferski, P. J., 1978, Sample preparation for clay-mineral analyses by X-ray diffraction: U.S. Department of Energy Morgantown Energy Technology Center, DOE/METC/2287-112, 9 p.
Laboratory	6. Schultz, L. G., 1964, Quantitative interpretation of mineralogical composition from X-ray and chemical data for the Pierre shale: U.S. Geological Survey Professional Paper 391-C, p. C1-C31.
Laboratory	7. Renton, J. J., 1979, Use of weighted X-ray diffraction data for semiquantitative estimation of minerals in low temperature ashes or bituminous coal and in shale: U.S. Department of Energy, METC/CR-75/5, 22 p.
Laboratory	9. Used slurry technique.
Laboratory	10. R. W. Schliephake, 1975, Röntgenographische Untersuchungen an Grubenstauben des deutschen Steinkohlenbergbaus: Reproduzierbarkeit der Quarzbestimmung und indirekte Ermittlung des Ashegehaltes Staub-Reinhalt, v. 35, no. 8, p. 295-297.
Laboratory	11. Used slurry technique (Duco cement and amyl acetate).
Laboratory	12. Williams, J. M., 1980, Qualitative and quantitative X-ray mineralogy: A layman's approach: Los Alamos Scientific Laboratory Information Report LA-8409-MS, 46 p.

transform infrared (FTIR) instrumentation. In addition, Laboratory 4 determined kaolinite by means of a conventional dispersive infrared (IR) spectrometer. Results are shown in table 14. Dispersive IR methods depend upon the measurement of the intensity of isolated absorption bands characteristic of a specific mineral. Errors and difficulties are introduced by the overlap and superposition of the bands of complex multicomponent systems. Computer methods for analyzing such multicomponent systems have become routine with the introduction of FTIR spectroscopy. Painter and others (1978) used the successive subtraction of the spectra of mineral standards from the spectrum of the LTA, starting with the most strongly absorbing species (usually kaolinite), for the analysis of minerals in the LTA. The spectrum of the mineral standard is multiplied by a scaling factor, which is altered on a trial-and-error basis until the bands are just removed. As an example, figure 1 shows the subtraction of the kaolinite component of the spectrum of the interlaboratory LTA sample. Provided that the weights of the LTA and the mineral standards used to prepare the KBr pellets are accurately known, then the weight fraction of each mineral in the LTA can be calculated from the scaling factor. Painter and others (1981) applied least-squares spectral fitting methods to the analysis of mineral mixtures. In

this method, a computer program is used to obtain the best fit between the spectra of a set of standards and the spectrum from an LTA. This method was used by Laboratory 4. Laboratory 15 synthesized spectra to match the spectrum of the coal.

There are a number of problems associated with FTIR methods, as recently discussed by Finkelman and others (1981). The most important problem is the choice of standards and is not unique to FTIR spectroscopy. A different kaolinite standard, used in the preliminary work, gave much lower values (7 percent, about half the final values) in the analysis of the interlaboratory LTA samples. To some extent the problem of selecting the appropriate standard has now been alleviated by the use of least-squares programs,

TABLE 14.—*Partial mineralogical analysis of the interlaboratory sample by FTIR*

[All results in weight percent]

Laboratory	4	15
Kaolinite	<sup>1</sup> 15	14
Montmorillonite	<sup>2</sup> 13	50
Montmorillonite	<sup>3</sup> 10	--
Illite	1.5	7
Quartz	25	8.5
Calcite	7	6

<sup>1</sup>Kaolinite determined by conventional IR spectroscopy, 12-15 percent.<sup>2</sup>Standard from Chambers, Ariz.<sup>3</sup>Standard from Amory, Miss.

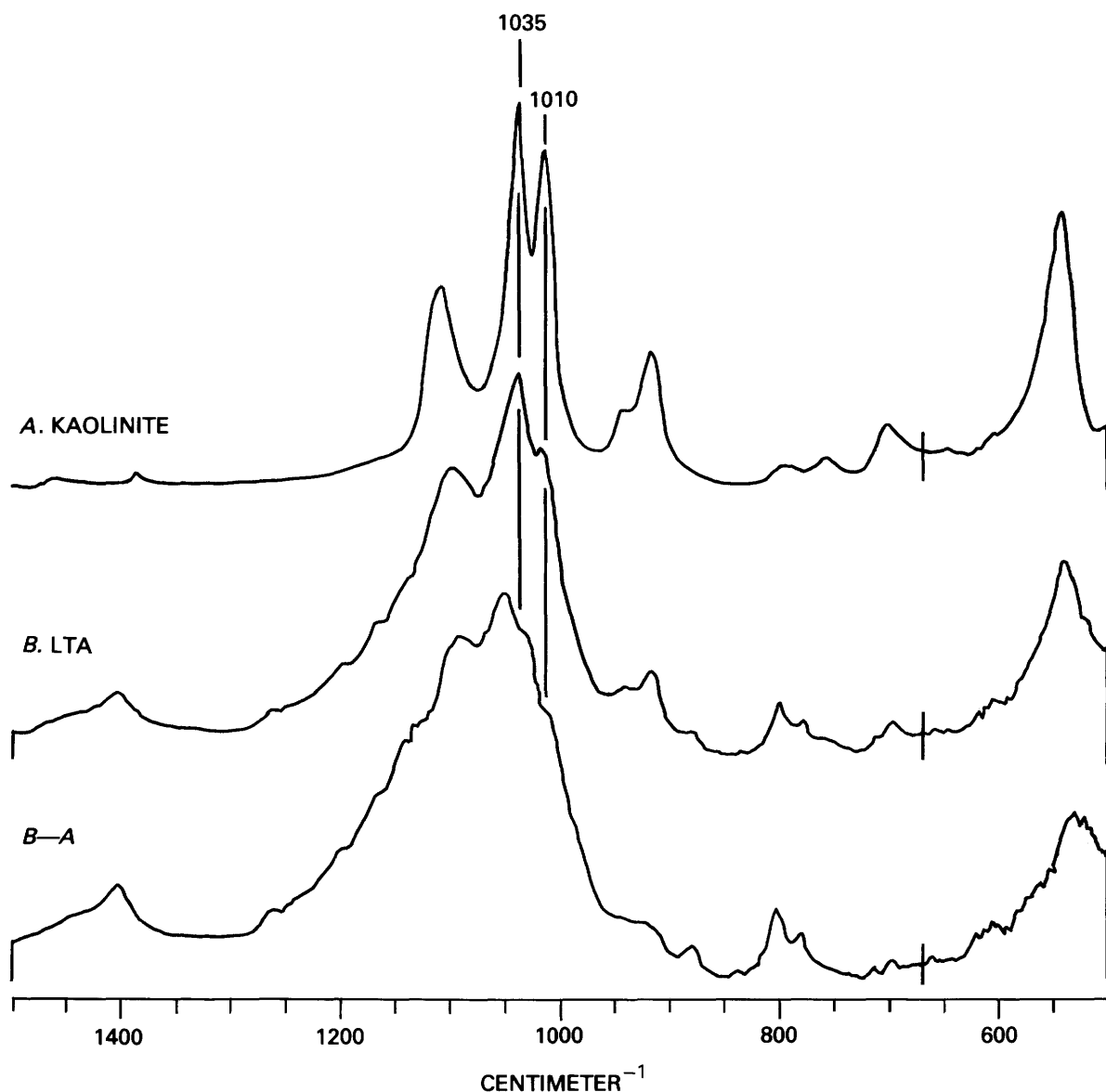


FIGURE 1.—Example of FTIR analysis. *A*, spectrum of kaolinite standard; *B*, spectrum of LTA; *B*–*A*, difference spectrum obtained by subtracting spectrum *A* from spectrum *B* so that the 1035 and 1010  $\text{cm}^{-1}$  bands are just removed.

which can determine the standard that gives the best fit to the spectrum of the LTA (Painter and others, 1981). In addition, the use of an entire spectrum rather than a single, usually weak, band in the analysis necessitates stringent sample preparation requirements. For example, the analysis of kaolinite by conventional dispersive methods is based on the relatively weak  $910\text{ cm}^{-1}$  band, so that about 1 mg of kaolinite could be used in preparing KBr pellets. However, when this

much sample is used, other bands absorb so strongly that the Beer-Lambert law is no longer obeyed. To avoid this problem, about 0.2 mg is required for optimum absorption of the strongest band. This necessitates accurate weighings and careful and consistent pellet preparation techniques. Finally, most FTIR instruments are set for the mid-IR range, where pyrite has no absorption bands. Conversion to the far IR is necessary to analyze this mineral.

In spite of these difficulties, FTIR methods appear to be a potentially powerful tool for mineralogical analysis, since all the major components (usually anything present to the extent of 3 percent or greater) can, in principle, be determined by this one method.

### C. CHEMICAL ANALYSIS

By R. B. Finkelman

Chemical analyses of the interlaboratory sample were provided by a number of laboratories using a variety of analytical techniques. The major- and trace-element data are presented in tables 15 and 16. Despite the differences in analytical procedures and the fact that some laboratories analyzed whole coal whereas others analyzed HTA or LTA, there is good agreement for most elements. Notable exceptions are iron, zinc, manganese, and strontium. The scatter in the analytical results for these elements may be attributable to sample inhomogeneity with respect to pyrite, sphalerite, and carbonate minerals. The scatter in the manganese analyses may be due to contamination by steel (see section H).

There was a rather serious discrepancy in the iron values. Those laboratories analyzing HTA or LTA had a range of 18.5 to 21.5 weight percent  $\text{Fe}_2\text{O}_3$ , whereas those laboratories determining Fe

on whole coal reported values ranging from 13.1 to 15.0 weight percent  $\text{Fe}_2\text{O}_3$ . Although the disagreement may have been exaggerated by recalculating to an ash basis, it is evident that a serious problem existed. Peter Zubovic (oral commun., 1979) suggested that the pyrite particles in the pulverized samples had begun to segregate during transportation and handling. Those laboratories analyzing whole coal may have just skimmed the top of the sample, thereby removing for analysis material depleted in pyrite. Those laboratories analyzing the ash required about 10 times more material for their analysis and would have dug deeper, thus removing a more representative sample. To test this suggestion, Laboratory 1 was asked to rehomogenize and reanalyze its sample. Their original value for  $\text{Fe}_2\text{O}_3$  on whole coal by X-ray fluorescence spectroscopy was 13.1 percent; rehomogenization of the sample and reanalysis in duplicate resulted in a value of 16.0 weight percent. A rehomogenized sample was resubmitted to Laboratory 22, resulting in a similar increase in  $\text{Fe}_2\text{O}_3$  values. Subsequent analysis of whole coal at the USGS (Reston) by quantitative dc-arc and energy-dispersive X-ray fluorescence spectroscopy gave values of around 20 weight percent for  $\text{Fe}_2\text{O}_3$ . In contrast, Laboratory 19 found little difference in the iron content of material taken at several intervals from the top to the bottom of their sample container. Evidently some segregation of pyrite had taken place in many of the interlaboratory

TABLE 15.—Major-element analyses of the interlaboratory sample

[--, not reported]

Laboratory	9	9	9	9	10	10	4	22
Sample type analyzed	LTA	LTA	LTA	LTA	HTA:800	HTA:800	HTA:750	HTA:550
Sample produced by (7)	Comm. [20]	Comm. [24]	Lab.	Lab.	Lab.	Lab.	Lab.	Lab.
Mesh	-60	-60	-60	-20	-60	-60	-20	-60
Analytical technique	XRF+AES	XRF+AES	XRF+AES	XRF+AES	XRF	XRF	XRF	XRF
$\text{SiO}_2$	47.2	47.2	47.1	47.2	47	47	47.1	44.51
$\text{Al}_2\text{O}_3$	17.2	17.0	17.4	17.5	17	17	17.4	16.96
$\text{TiO}_2$	.88	.90	.88	.93	.9	.9	.83	.81
$\text{Fe}_2\text{O}_3$	21.5	21.3	21.3	21.4	21.	20.	20.1	18.48
$\text{MgO}$	.96	.98	.95	.99	--	--	1.01	--
$\text{CaO}$	6.3	6.2	6.2	5.6	6.0	5.4	5.71	5.15
$\text{MnO}$	.04	.04	.05	.05	--	--	.036	.04
$\text{Na}_2\text{O}$	.61	.65	.60	.68	--	--	.71	--
$\text{K}_2\text{O}$	1.78	1.80	1.78	1.84	1.8	1.8	1.83	1.73
$\text{SO}_3$	(1)	(1)	(1)	(1)	3	3	6.5	2.25
$\text{P}_2\text{O}_5$	.03	.03	.03	.03	--	--	--	.05(6)
Total	96.5	96.1	96.3	96.2	96.7	95.1	101.2	90.0
$\text{H}_2\text{O}^+$	3.09	3.15	4.28	4.94	--	--	--	--
$\text{H}_2\text{O}^-$	6.45	5.75	4.53	4.18	--	--	--	--
$\text{CO}_2$	1.58	1.72	3.55	2.94	--	--	--	--
Residual C	.95	.86	.10	.08	--	--	--	--
Pyritic S	10.1	10.2	9.8	9.5	--	--	--	--

TABLE 15.—Major-element analyses of the interlaboratory sample—(Continued)

Laboratory	28	26	1	13	19	20		
Sample type analyzed	HTA:750	HTA:750	WC	WC	WC	WC		
Sample produced by (7)	Lab.	Lab.	Comm.	Comm.	Comm.	Comm.		
Mesh	-60	-60	-60	-60	-60	-60		
Analytical technique	AAS+AES	AAS	XRF	Wet Chem.	PIXE	XRF+AAS	Mean	S.D.
SiO <sub>2</sub>	43.6	46.88	49.9	43.4	48.2	47.4	48.28	2.01
Al <sub>2</sub> O <sub>3</sub>	18.3	18.1	19.8	20.9	18.3	22.7	18.94	1.58
TiO <sub>2</sub>	.76	1.10	1.0	.66	.8	.6	.89	.13
Fe <sub>2</sub> O <sub>3</sub>	20.8	20.3	13.1	18.3	13.3	19.8	20.08	2.91
MgO	.93	.93	—	1.46	—	.8	1.04	.19
CaO	5.62	6.07	5.2	8.2	5.9	5.5	6.11	.81
MnO	.05	—	—	—	—	—	.04	.01
Na <sub>2</sub> O	.60	.81	3(5)	1.39	—	1.65	.83	.40
K <sub>2</sub> O	1.68	1.81	1.5	1.58	1.5	—	1.80	.14
SO <sub>3</sub>	5.4	3.36	—	3.	8.4	—	—	—
P <sub>2</sub> O <sub>5</sub>	.11	—	.02	—	—	—	.04	.03
Total	97.8	99.4	90.8	98.9	96.4	98.4	—	—

Notes: (1) Recalculated based on 3% SO<sub>3</sub>.  
 (2) Recalculated based on 17.11% ash.  
 (3) Recalculated from submitted analysis.  
 (4) Recalculated based on 13.1% ash.  
 (5) Instrumental neutron activation analysis.  
 (6) Determined on whole coal.  
 (7) Comm.—Sample (LTA or WC) supplied to participating laboratory by the Committee; [ ] indicates split number.  
 Lab.—LTA prepared by participating laboratory from Herrin (No. 6) interlaboratory sample supplied by the Committee.

LTA—Low-temperature ash.  
 HTA—High-temperature ash at indicated temperature in degrees Celsius.  
 WC—Whole coal.  
 XRF—X-ray fluorescence spectroscopy.  
 AES—Atomic emission spectroscopy.  
 AAS—Atomic absorption spectroscopy.  
 PIXE—Proton-induced X-ray emission spectroscopy.  
 S.D.—Standard deviation.

samples. No differentiation of the trace elements was found that corresponded to the differentiation of the pyrite, indicating that the pyrite in the interlaboratory sample contains few trace elements. Nevertheless, it is evident that extreme care must be taken to be certain that the material analyzed is representative of the original sample.

The LTA chemical analysis supplied by Laboratory 9 included values for H<sub>2</sub>O+, CO<sub>2</sub>, carbon, and pyritic and sulfate sulfur. The availability of these data provided an opportunity to calculate the normative mineralogical composition of the LTA (see, for example, Pollack, 1979). The following steps outline the procedure:

- (1) Pyritic sulfur was combined with the appropriate amount of iron to form stoichiometric FeS<sub>2</sub> (reported as pyrite).
- (2) CO<sub>2</sub> was combined with CaO to form CaCO<sub>3</sub> (reported as calcite).
- (3) Sulfate sulfur was adjusted to account for organically bound sulfur. Sulfate sulfur was then combined with CaO and H<sub>2</sub>O to form CaSO<sub>4</sub>·H<sub>2</sub>O (gypsum).
- (4) TiO<sub>2</sub> was reported as rutile.
- (5) MgO was combined with appropriate SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, FeO, and H<sub>2</sub>O to form chlorite (30 percent SiO<sub>2</sub>; 20 percent Al<sub>2</sub>O<sub>3</sub>; 30 percent MgO; 8 percent FeO; 12 percent H<sub>2</sub>O).
- (6) K<sub>2</sub>O was used to form mixed-layer clays and il-

lite (50 percent SiO<sub>2</sub>; 25 percent Al<sub>2</sub>O<sub>3</sub>; 5 percent K<sub>2</sub>O; 7.5 percent FeO; 2 percent Na<sub>2</sub>O; 10.5 percent H<sub>2</sub>O).

- (7) Remaining Al<sub>2</sub>O<sub>3</sub> was used to form kaolinite (45 percent SiO<sub>2</sub>; 39 percent Al<sub>2</sub>O<sub>3</sub>; 14 percent H<sub>2</sub>O).
- (8) Remaining SiO<sub>2</sub> was reported as quartz.

About 1.6 weight percent FeO was unaccounted for in this procedure. Perhaps it occurred as iron sulfates, carbonates, or oxides or in organic association. The calculations require about 2 weight percent more H<sub>2</sub>O than allowed by analytical data. Perhaps the low H<sub>2</sub>O values are due to dehydration of the clays during low-temperature ashing.

In table 17, the results from the normative calculations are compared with mean values derived from the XRD data in table 10. The values are very similar. The analytical value for unassociated SiO<sub>2</sub> (quartz) in the LTA is 14.1 weight percent (Laboratory 13), suggesting that the XRD value may be high. However, Given and others (1980), in a critical evaluation of normative analysis, indicated that this procedure tends to underestimate quartz content. Laboratory 8, using normative calculations and qualitative XRD, obtained the following percentages: pyrite, 23; marcasite, 3; calcite, 10; kaolinite, 24; illite, 24; and quartz, 16.

In addition to the trace-element values in table

TABLE 16.—Trace-element analyses of the Herrin (No. 6) interlaboratory sample

[All values in ppm on a whole-coal basis. ---, not reported]

Laboratory	9	9	1	22	22	22	22	14	28	19	20	29
Sample type analyzed	WC	WC	WC	WC	HTA:550	HTA:550	WC	LTA	HTA:750	WC	WC	WC
Sample produced by (4) Mesh	Comm. -60	Comm. -20	Comm. -60	Comm. -60	Lab. -60	Lab. -60	Comm. -60	Lab. -60	Lab. -60	Comm. -60	Comm. -60	Comm. -60
Analytical technique	XRF	XRF	NAA	NAA	AAS	AES	AES	AES	AES	PIXE	NAA	NAA
Ag	---	---	<0.3	---	---	0.02	---	---	---	---	<0.3	---
As	3	3	1.7	1.5	---	---	---	---	2.3	1.8	1.4	1.8
Au	---	---	<.05	---	---	---	---	---	---	---	<.01	---
B	---	---	---	---	---	>130	460	160	---	---	---	---
Ba	54	55	---	---	---	46.8	52	48	---	47.7	<84	84
Be	---	---	---	---	---	1.3	---	---	1.35	---	---	---
Bi	1	2	---	---	---	---	---	---	---	---	---	---
Br	3	3	2.9	2.15	---	---	---	---	---	2.8	1.4	2.2
Cd	<4	<4	---	---	.18	---	---	---	.08	---	<4.8	---
Ce	19	21	10	9	---	24.7	---	---	---	---	9.8	---
Cl	---	---	---	160	---	---	---	---	---	---	---	110
Co	2	2	5	3.9	---	4.4	5	---	5.2	---	4.7	4.32
Cr	---	---	15	13.8	---	16.9	20	---	17.7	20	14.7	13
Cs	<.5	<.5	.9	.9	---	---	---	---	---	---	1.0	.9
Cu	3	5	---	---	8.7	6.4	13	---	10.8	7.9	2(5)	---
Eu	---	---	.23	.18	---	---	---	---	---	---	.24	.21
F	---	---	---	---	32(1,2)	---	---	---	---	---	---	---
Ga	5	4	3.7	---	---	4.0	<4	---	---	3.4	---	---
Ge	7	8	---	---	---	6.2	---	16	---	6.6	---	---
Hf	---	---	.5	.4	---	---	---	---	---	---	.5	---
Hg	<2	<2	---	---	.042(1)	---	---	---	---	---	.36	---
La	<3	<3	6	5	---	6.5	---	---	---	---	5.1	5.2
Li	---	---	---	---	8.8	---	---	---	---	---	---	---
Lu	<2	<2	.08	.10	---	---	---	---	---	---	.08	.2
Mn	45	47	40	---	36.4	66.3	55	80	42.8	24	24(5)	37
Mo	<1	<1	4	---	---	4.6	6	---	---	3.6	---	---
Nb	---	---	---	---	---	2.0	---	---	---	2.0	---	---
Nd	---	---	---	<30	---	---	---	---	---	---	<23	---
Ni	17	19	20	---	---	16.9	24	16	16.0	17.3	26.0	---
Pb	---	---	---	---	3.8	7.9	---	---	6.2	6.4	---	---
Rb	13	13	13	---	---	---	---	---	---	13.2	17.7	12
Sb	<1	<1	.3	.2	---	---	---	---	.31	---	.16	.2
Sc	4	4	2.0	2.37	---	3.1	---	---	---	---	3.0	2.68
Se	2	2	2.0	1.9	---	---	---	---	2.04	1.8	1.9	2.2
Sm	---	---	1.1	.8	---	---	---	---	---	---	1.0	---
Sn	---	---	---	---	---	5.5	---	---	---	6.5	---	---
Sr	30	30	11	---	---	44.2	---	20.8	---	28.2	---	---
Ta	---	---	.15	.08	---	---	---	---	---	---	.17	.13
Tb	---	---	.13	.15	---	---	---	---	---	---	.24	.07
Th	1	1	1.9	1.9	---	---	---	---	---	1.8	2.5	.2
U	1	<1	1.1	.85(3)	---	---	---	---	---	1.5	.8	.9
V	24	25	---	---	---	19.5	25	16	23.78	13.0	---	21.3
W	<2	<2	.3	.3	---	---	---	---	---	---	---	---
Y	6	6	---	---	---	6.0	---	---	---	6.0	---	---
Yb	---	---	.7	.6	---	.7	---	---	---	---	.58	---
Zn	38	53	22	27	33.8	31.2	---	22.4	33.3	45	65.9(6)	---
Zr	23	25	---	---	---	15.6	<23	32	---	21.2	---	---

Notes: (1) Determined on whole coal.

(2) Ion-specific electrode.

(3) Delayed neutron activation analysis.

(4) Comm.—Sample (LTA or WC) supplied to participating laboratory by the Committee.

Lab.—LTA prepared by participating laboratory from Herrin (No. 6) interlaboratory sample supplied by the Committee.

(5) Determined by AAS.

(6) AAS value: 30 ppm Zn.

LTA—Low-temperature ash.

HTA—High-temperature ash at indicated temperature in degrees Celsius.

WC—Whole coal.

XRF—X-ray fluorescence spectroscopy.

AES—Atomic emission spectroscopy.

AAS—Atomic absorption spectroscopy.

PIXE—Proton-induced X-ray emission spectroscopy.

NAA—Neutron activation analysis.

TABLE 17.—Comparison of normative calculations with XRD results from table 10

[--, no data]

	Normative Calculation	Mean value from XRD
Pyrite	20.7	23
Calcite	8.3	9
Gypsum	1.4	--
Rutile	0.8	--
Chlorite	2.8	--
Mixed-layer clays + illite	31.0	31
Kaolinite	17.0	14
Quartz	16.7	20

16, Finkelman and Aruscavage (1981) obtained the following values (whole-coal basis): Pt < 2 ppb; Pd < 1 ppb; Rh < 0.5 ppb.

#### D. QUANTITATIVE ANALYSIS OF PYRITIC SULFUR BY MEANS OF MOSSBAUER SPECTROSCOPY

By Pedro A. Montano

Mossbauer spectra and background radiation (fig. 2) were recorded for six pellets of different thicknesses prepared from the interlaboratory sample. Total spectral area is plotted against thickness in milligrams per square centimeter in figure 3. The amount of pyritic sulfur in each of the six pellets was determined from the total spectral area. These values appear to be very consistent (table 18). Other than  $\text{Fe}^{2+}$  in  $\text{FeS}_2$ , only a very small amount of  $\text{Fe}^{2+}$  (probably in illite) was detected. The values are close to those observed for  $\text{Fe}^{2+}$  in clays.

Figure 4 is a spectrum of the interlaboratory coal sample taken 1 year after it was received. It can be seen that the overall shape of the spectrum has changed. Only about 1.1 percent pyritic sulfur remains, and there is now very clear evidence of weathering; szomolnokite and possibly coquimbite are present, as is ferric sulfate. The amount of szomolnokite is so large that it almost completely covers the contribution of the  $\text{Fe}^{2+}$  impurities in the clays. The coal was stored in a desiccator, which was evacuated to avoid moisture absorption by the sample. However, the period of time that the sample was exposed to air when being used for other studies (from 1 hour to 12 hours) was enough to alter the iron constituents. The ferric sulfate is probably jarosite. The ferrous sulfate was unequivocally identified as szomolnokite. Care must

be taken in analyzing the interlaboratory sample due to the effects of weathering. LTA of the samples was also analyzed, and no other iron-bearing mineral was found.

The pyritic sulfur values determined in Laboratory 27 by Mossbauer spectroscopy (Huffman and Huggins, 1978) are very close to the value of 1.76 percent obtained by the ASTM test method for forms of sulfur performed in the same laboratory (ASTM, 1981). The results of triplicate Mossbauer analyses by this laboratory are shown in table 19. The Mossbauer spectra consist of three absorption doublets arising from pyrite, jarosite, and an unidentified ferrous phase. This last absorption doublet is very broad, and its parameters are not compatible with any expected mineral (closest is melanterite,  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ); it most likely arises from two or more very minor ferrous minerals. Scanning electron microscopy-automated image analysis (SEM-AIA, see section G) indicates the presence of small amounts of iron sulfate, iron-rich clay (chlorite), and possibly siderite, in addition to the clay mineral illite, which may contain minor  $\text{Fe}^{2+}$ . The combination of melanterite [isomer shift (IS) = 1.29, quadrupole splitting (QS) = 3.18 mm/s], szomolnokite (IS = 1.26, QS = 2.71 mm/s), and ferrous clay (IS = 1.13, QS = 2.65 mm/s) could well result in such a doublet.

The QS ( $0.587 \pm 0.008$  mm/s) measured for  $\text{FeS}_2$  in this coal is significantly less than that for pure pyrite (0.61 mm/s) and approaches the QS of marcasite (0.51 mm/s), the polymorph of pyrite. This reduction suggests that as much as 25 percent of the  $\text{FeS}_2$  absorption may be due to marcasite.

#### E. QUALITATIVE CLAY MINERAL ANALYSIS

By R. S. Dean

A mineralogical analysis of the interlaboratory sample was carried out by XRD techniques. The basal reflections from the clay minerals were studied in oriented mounts prepared from the  $-5\text{-}\mu\text{m}$  size fraction of the LTA. Clay mineral  $hk$  reflections and reflections from nonclay minerals were examined in the unfractionated and  $-5\text{-}\mu\text{m}$  LTA by a Guinier-deWolff powder camera. A detailed description of the procedures followed and results obtained has been reported (Dean, 1979).



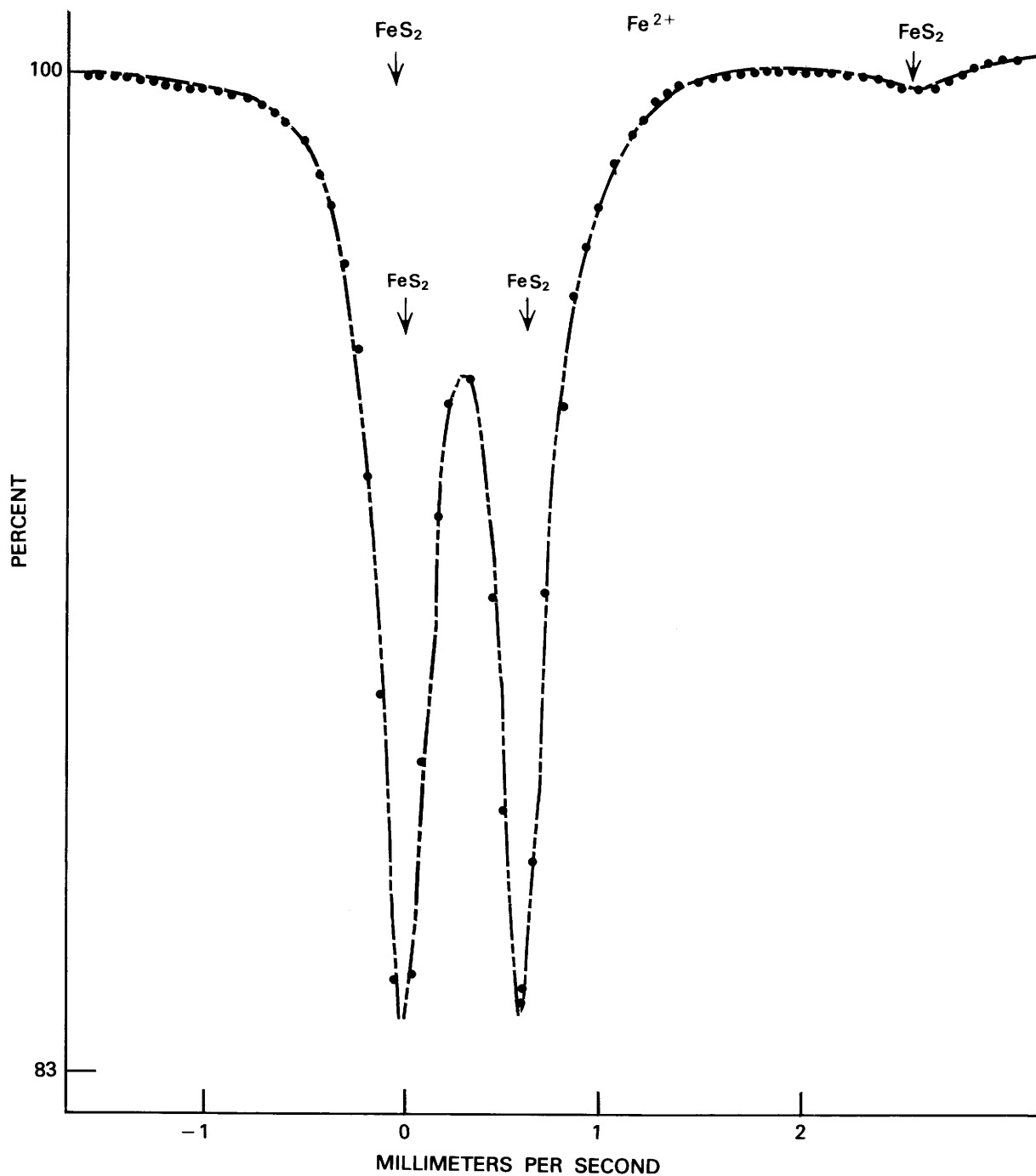


FIGURE 2.—Mossbauer spectrum at room temperature of the fresh Herrin (No. 6) interlaboratory sample. Pyrite ( $\text{FeS}_2$ ) is the dominant phase.  $\text{Fe}^{2+}$  in clays is also indicated. A small amount of  $\text{Fe}^{3+}$  may be present, but it is negligible compared to the other two species.

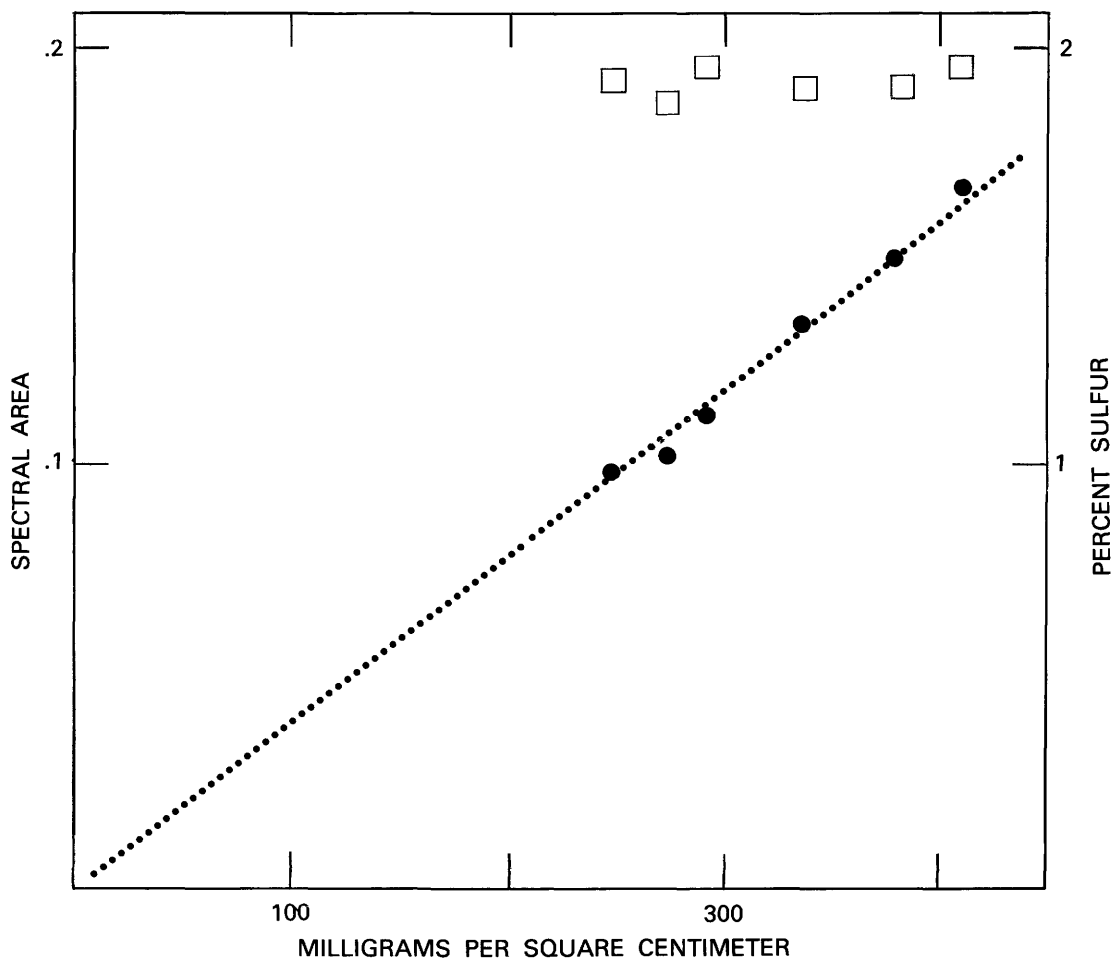


FIGURE 3.—Pyritic sulfur determination in coal using Mossbauer spectroscopy. The left ordinate indicates the spectral area (closed circle) and the right ordinate indicates the weight percent pyritic sulfur (open square) determined from the spectral area.

The mineralogical composition of the unfractionated LTA was found to be as follows:

Abundant: Quartz, mixed-layer 2:1 layer silicates (including chlorite), pyrite

Moderately abundant: Kaolinite (fairly well crystallized), calcite

Rare: Illite, marcasite

Trace: Anatase

The clay minerals are concentrated within the  $-5\text{-}\mu\text{m}$  size fraction of the LTA and consist of fairly well crystallized kaolinite, the mixed-layer assemblage, and minor illite. Transmission (Guinier) powder photographs of the  $-5\text{-}\mu\text{m}$  LTA following NaOH dissolution of dehydroxylated kaolinite by the method of Hashimoto and

TABLE 18.—Mossbauer determination of pyritic sulfur in the interlaboratory coal sample

Sample number	Weight percent pyritic sulfur
1	1.97
2	1.88
3	1.91
4	2.08
5	1.91
6	1.95
Mean	1.95
Standard deviation	0.07

Jackson (1960) showed no mica polymorph reflections, indicating that the illite is stacking disordered (1Md).

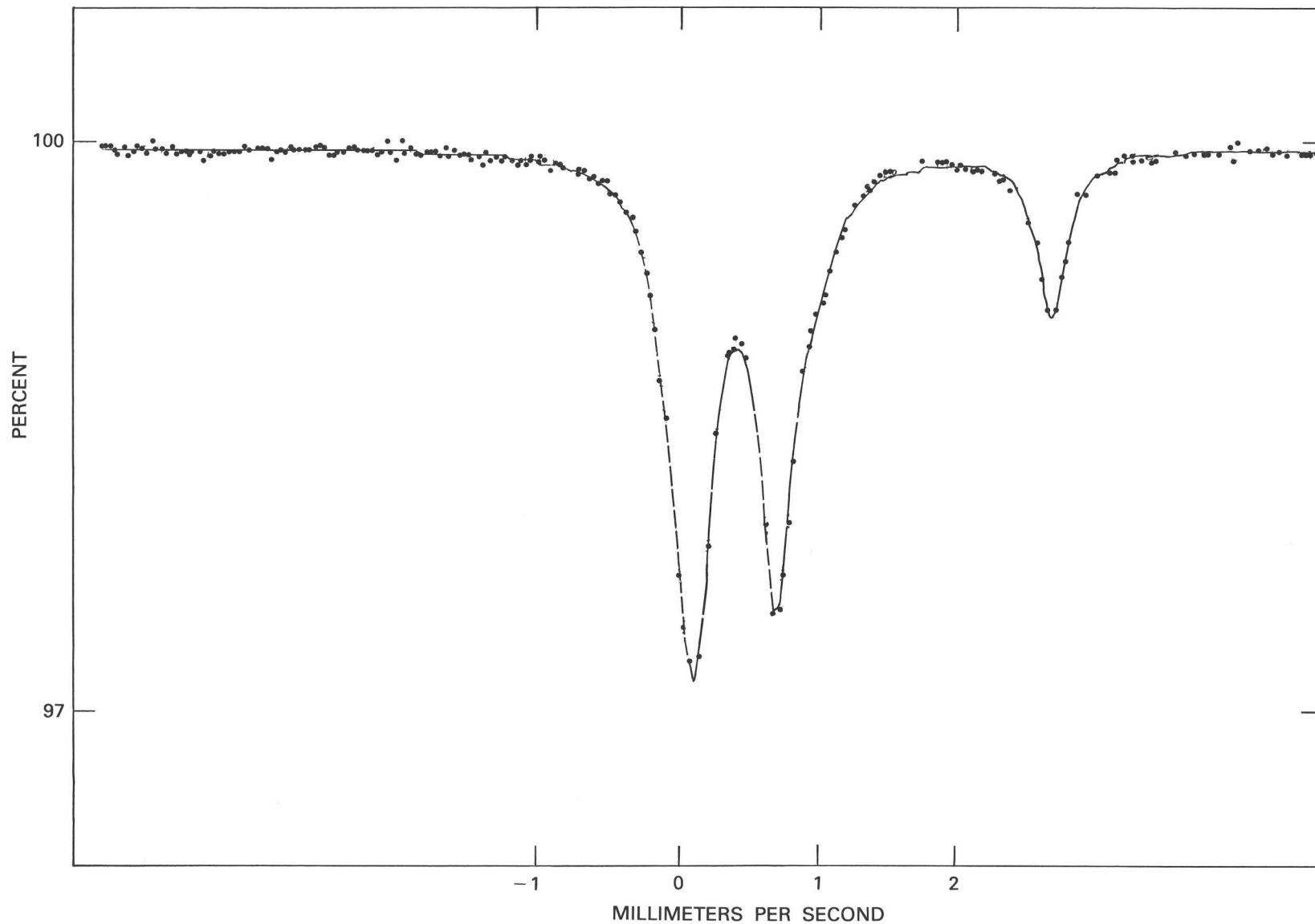


FIGURE 4.—Mossbauer spectrum at room temperature of the Herrin (No. 6) interlaboratory sample after 1 year in a vacuum desiccator. There is strong evidence that pyrite is transformed to szomolnokite and coquimbite.

TABLE 19.—*Mossbauer data for the Herrin (No. 6) interlaboratory sample*

[Isomer shift (IS) in mm/s relative to Fe foil, quadrupole splitting (QS) in mm/s, and percentage of total iron contained in the different minerals (Pct). Values in parentheses for samples 1 through 3 represent statistical uncertainties in terms of least significant digit shown; i.e., IS for pyrite of 0.312(1) indicates a value of  $0.312 \pm 0.001$ . For the average, the uncertainties quoted also include variation between the three samples and represent approximately one standard deviation in terms of the least significant figure shown.  $\text{Fe}^{2+}$ , unidentified ferrous phases (see text).]

Sample		Mossbauer parameters			Pct pyritic sulfur <sup>1</sup>
		IS	QS	Pct	
1.	Pyrite	0.312(1)	0.587(1)	92(1)	1.75(2)
	$\text{Fe}^{2+}$	1.22(3)	3.06(5)	3(1)	
	Jarosite	.40(2)	1.13(4)	5(1)	
2.	Pyrite	.307(1)	.596(1)	94(1)	1.84(2)
	$\text{Fe}^{2+}$	1.21(2)	3.00(4)	3(1)	
	Jarosite	.40(1)	1.12(2)	4(1)	
3.	Pyrite	.306(1)	.579(1)	94(1)	1.77(2)
	$\text{Fe}^{2+}$	1.22(2)	3.05(4)	2(1)	
	Jarosite	.37(1)	1.13(2)	4(1)	
Average of 3	Pyrite	.308(4)	.587(8)	93(1)	1.79(5)
	$\text{Fe}^{2+}$	1.22(2)	3.04(4)	3(1)	
	Jarosite	.39(2)	1.13(3)	4(1)	

<sup>1</sup>Weight percent pyritic sulfur (as-received coal basis) determined from Mossbauer data as described in Huffman and Huggins (1978).

The mixed-layer assemblage consists of two mixed-layer systems, each of which is sufficiently extensive to diffract X-rays independently. The first of these is an interstratified mixture of illite and expandable 2:1 layer silicates; the second appears to be a three-component mixed-layer system containing illite, expandable 2:1 layer silicates, and ferromagnesian chlorite layers. Identification of the last phase was facilitated by heat treatment at 550°C, the temperature at which chlorite inter-layer dehydroxylation occurred. The distribution of illite layers within the mixed-layer assemblage was studied by using the  $\text{LiNO}_3$  fusion technique of Murthy and others (1973). Within the mixed-layer systems, illite and chlorite layers are most likely discontinuous and have a "frayed edge" relationship with the expandable layers; that is, there are continuous compositional gradations between illitic or chloritic "core" areas and crystallite areas rich in expandable layers.

It is suggested that both mixed-layer systems are diagenetic alteration products of a pre-existing major smectite-like phase. The minor illite occurring as a separate phase is likely the end product of the development of the illite-expandable layer-mixed layer system. The absence of stacking order within the unmixed illite is consistent with its probably diagenetic origin.

## F. SCANNING ELECTRON MICROSCOPY STUDY

By Robert B. Finkelman

Two coal blocks (cut perpendicular to the bedding, approximately 2 cm on edge) were polished, carbon coated, and examined with a scanning electron microscope (SEM) equipped with an energy dispersive detector. (For details of sample preparation and analysis see Finkelman, 1978; Finkelman and Stanton, 1978; Stanton and Finkelman, 1979.)

In the SEM, the two coal blocks exhibited distinct banding, some bands containing mineral grains covering more than 75 percent of the surface area. Inertinite macerals, primarily fusinite and semifusinite but also including sclerotinite, are common (figs. 5, 6). Globular organic particles are common; the low contrast and low relief suggest that they may be corpocollinite. The banded

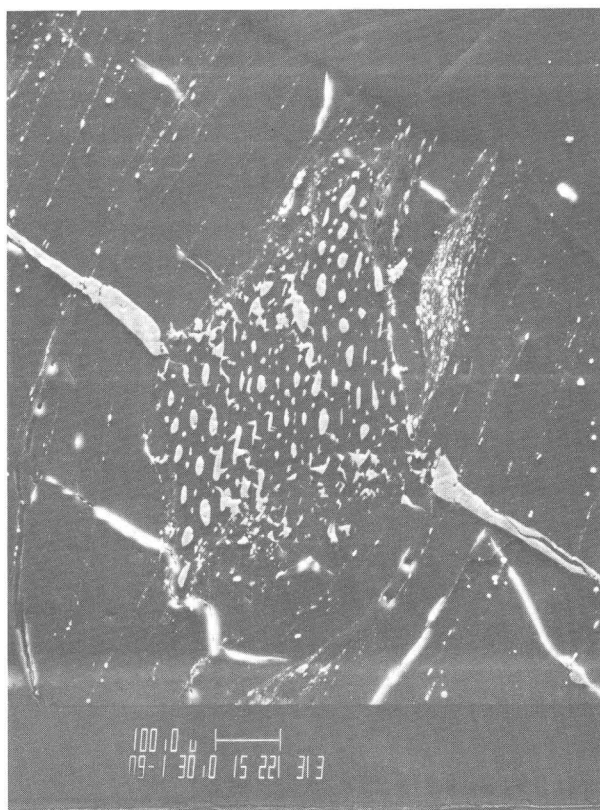


FIGURE 5.—SEM photomicrograph of a polished block of the Herrin (No. 6) coal depicting kaolinite filling veins and inertinite pores. Scale bar is 100  $\mu\text{m}$ .

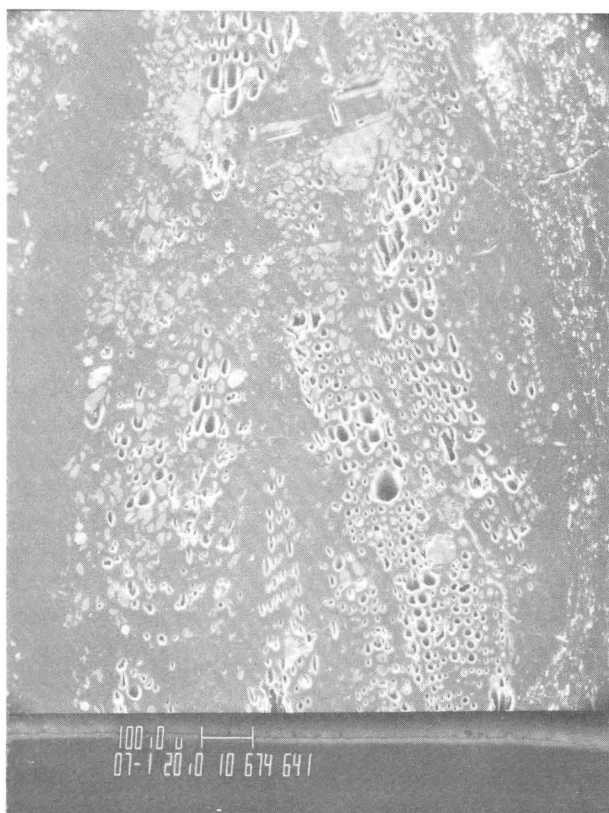


FIGURE 6.—SEM photomicrograph of a polished block of the Herrin (No. 6) coal depicting a large inertinite fragment. Many inertinite pores are filled with kaolinite; others are empty, perhaps due to plucking during polishing. Scale bar is 100  $\mu\text{m}$ .

material consists predominantly of illite, mixed-layer clays, and subrounded to angular quartz particles (most  $<10\ \mu\text{m}$ ). Pyrite framboids are ubiquitous. Other pyrite morphologies, such as euhedral crystals, skeletal grains, irregularly shaped particles, and vein fillings, are less common. Inertinite pore fillings are exclusively kaolinite (fig. 5). Many noncrushed inertinite pores are devoid of minerals, probably an indication of substantial plucking during polishing (fig. 6). Kaolinite also occurs as vein fillings (fig. 5). Kaolinite-quartz intergrowths were noted. Contamination of the polished surface by flecks of cerium-oxide polishing compound made it difficult to detect the micrometer-sized accessory phases. Those that were detected include rare-earth phosphates and possibly rare-earth silicates occurring in the banded material and in the vitrinite, a zircon included within a quartz grain, a barium sulfate (association unclear), a titanium oxide particle in

the banded material, a lens of an iron magnesium aluminum silicate (chlorite?), and a sphalerite pore filling. The textural evidence indicates that the minerals in the bands (quartz, illite, mixed-layer clay, zircon, rare-earth minerals, rutile?) are detrital, whereas those minerals occurring as vein and pore fillings (kaolinite, pyrite, sphalerite) are authigenic (Finkelman, 1982). No carbonates were observed in the polished blocks. The absence of carbonates may indicate that carbonate minerals are epigenetic, occurring in veins and cleats, and are not intimately associated with the coal. A density separation was made of the interlaboratory LTA. Abundant pyrite was found by SEM in the LTA fraction that sank in liquid having a specific gravity of 3.3. No other heavy minerals were observed.

#### G. SCANNING ELECTRON MICROSCOPY— AUTOMATED IMAGE ANALYSIS

By F. E. Huggins, G. P. Huffman, and R. J. Lee

Scanning electron microscopy-automated image analysis (SEM-AIA) was performed as described by Huggins and others (1980) on two separate samples (A and B in table 20), one of which was analyzed twice in different areas (A1 and A2). More than 3,000 mineral particles were examined in the course of these analyses, and 16 individual minerals were recognized on the basis of the energy-dispersive X-ray spectra. The results of the three runs, adjusted for pyrite overestimation (Huggins and others, 1980), are shown in table 20. Excellent agreement among the three determinations is found. The principal minerals found are pyrite, quartz, illite, kaolinite, and calcite. The mixed-silicate category also makes a sizable contribution; it consists mainly of intimately associated combinations of quartz and illite. Mixed-layer clays (for example, illite-montmorillonite) are also in this category. The only other significant category is the silicate-sulfur category, which represents the association of silicate minerals and sulfur. The strong sulfur background from the high organic sulfur content was sufficient to cause some of the silicate minerals to fall in this category.

A summary of the results is presented in table 21. The left-hand column is an average of the three SEM-AIA determinations shown in table 20. The

TABLE 20.—Results of SEM-AIA analysis of the Herrin (No. 6) interlaboratory sample, in weight percent

[tr, trace, &lt;5 particles]

Mineral category	A1	A2	B
Quartz	15	16	13
Kaolinite	4	5	6
Illite	5	4	5
Montmorillonite	2	tr	tr
Mixed silicates	26	23	26
Pyrite	25	28	28
Calcite	7	5	5
Siderite-Fe oxide	tr	1	tr
Fe sulfate	tr	1	1
Sulfur	tr	tr	1
Others <sup>1</sup>	3	5	4
Silicate-sulfur	7	7	7
Silicate-pyrite	3	2	1
Unknown	2	2	2

<sup>1</sup>Includes chlorite, jarosite, gypsum, K-feldspar, TiO<sub>2</sub>, apatite, ZnS, BaSO<sub>4</sub>.

TABLE 21.—Minerals in Herrin (No. 6) interlaboratory sample, in weight percent

[Average is for 3 SEM-AIA analyses from table 20; for adjusted average, illite, quartz, and kaolinite values are recalculated to include mixed silicates, silicate-sulfur, and silicate-pyrite]

Mineral category	Average	Average adjusted
Quartz	15	24
Kaolinite	5	8
Illite	5	23
Mixed silicates	25	--
Pyrite	27	28
Calcite	6	6
Silicate-sulfur	7	--
Silicate-pyrite	2	--
Others <sup>2</sup>	6	8
Unknown	2	2

<sup>1</sup>Mossbauer data indicate that as much as one-fourth of the pyrite (7 wt. pct of mineral matter) may be marcasite.<sup>2</sup>Includes the following: 1-2 wt. pct—montmorillonite, iron sulfate, sulfur; 0.2-1 wt. pct—chlorite, jarosite, gypsum, K-feldspar, siderite-Fe oxide; <0.2 wt. pct—apatite, TiO<sub>2</sub>, ZnS, BaSO<sub>4</sub>.

right-hand column is derived from the left-hand column and should permit a more direct comparison with XRD and FTIR spectroscopy determinations. These data were obtained by apportioning the mixed-silicate, silicate-sulfur, and silicate-pyrite categories among the principal minerals. On the basis of the average compositions of these categories, the silicate fractions were apportioned in the ratio illite:quartz:kaolinite = 6:3:1. The Mossbauer data (see section D) indicate that as much as one-fourth of the pyrite could actually be marcasite. Also shown in table 21 are the approximate abundances of the numerous minor phases that contribute to the "others" category.

In conclusion, the mineralogy of this coal is dominated by about equal amounts of quartz, illite, and pyrite and lesser amounts of kaolinite, calcite, and possibly marcasite. Minor amounts of 12 other minerals were observed, none of which contributes more than 2 weight percent of the mineral matter.

#### H. MAGNETIC CONTAMINATION OF THE PULVERIZED INTERLABORATORY SAMPLE

By F. E. Senftle, A. N. Thorpe,  
C. C. Alexander, and R. B. Finkelman

Except for some specific studies, most coal research is carried out on coal samples that have been pulverized in a steel crusher and grinder. It is generally recognized that steel pulverizers

undergo significant abrasive wear even when soft materials such as coal are crushed (Suh, 1978; Douglas and Ditchburn, 1980). Therefore, some contamination of crushed coal by abraded metal is to be expected. In most cases, such as major-element analysis, the contamination of coal from abrasion is negligible. However, for trace analysis of specific elements, abrasion can be a serious source of contamination. Schultz and others (1975) found a twofold increase in the manganese concentration in a coal sample after pulverizing in a manganese steel jaw crusher. Although there is about 6 to 10 times more iron than manganese in manganese steel, the concentration of iron in most bituminous coals is generally so high that abrasion does not pose a serious contamination problem for chemical analysis. Except where trace quantities of those elements found in the steel are a problem, coal samples can be pulverized in a steel pulverizer without significant contamination.

However, for magnetic studies of coal, abrasion particles from the crusher and grinder can conceivably be a problem. Ergun and Bean (1968), for instance, noted that magnetic susceptibility studies of pulverized coal were meaningless because of ferromagnetic contamination. In a more recent study of pulverized coal, Jacobs and others (1978) found the magnetization was enhanced by the pulverization process. They attributed the increase in part to the conversion of pyrite to pyrrhotite but were unable to account for a significant fraction of the increased magnetization. In the course of a study on the magnetic properties of coal (Alexander and others, 1979), we observed, in

some instances, significant variations in magnetic susceptibility among several small samples of powdered coal from the same bulk powdered sample. To determine the significance of possible contamination due to pulverizing coal in a steel crusher and grinder, samples of the interlaboratory coal sample were studied in detail.

## EXPERIMENTAL

Because of the large amount of coal (approximately 20 kg) that was processed for the interlaboratory study, the coal was initially crushed in a manganese steel jaw crusher and grinder. The magnetic susceptibilities of six powdered samples from bottle 2 and one sample from bottle 27 were initially measured at room temperature and also at liquid nitrogen temperature as a function of the magnetic field up to 6 kilo-oersteds (kOe). The same samples were then measured as a function of temperature at a fixed field strength (1.85 kOe). The details of the method of magnetic measurement are given in Alexander and others (1979). Because the low field measurements showed the presence of abnormally high paramagnetism, additional studies were made on a few selected samples at slightly higher magnetic fields (approximately 10 kOe) using a commercial magnetometer and using a Faraday balance at several fixed temperatures at various field strengths to a maximum of 4.5 kOe. For comparison, unpulverized single fragments were also measured. A relatively large single piece of coal from the interlaboratory coal sample was fragmented in a porcelain mortar, and five small fragments, each a little less than 100 mg, were measured under the same conditions as the powders. Separates removed from the pulverized interlaboratory sample with a hand magnet were examined by the SEM and analyzed with the energy-dispersive X-ray analyzer (EDAX).

## RESULTS AND DISCUSSION

The analytical results on the pulverized coals and coal fragments are presented in table 22. The room-temperature magnetic susceptibility of all the powder is positive in spite of the preponderance of diamagnetic material in the coal. Most bituminous coal samples usually have a negative (diamagnetic) magnetic susceptibility, as shown

by the fragments. The positive value of the susceptibility indicates that some part of the powdered specimens is making a substantial paramagnetic and (or) ferromagnetic contribution to the total magnetic susceptibility.

The specific magnetization of all the samples was determined from an Owen-Honda plot (Owen, 1912; Honda, 1910), that is,  $\chi = \chi_o + s/H$  (where  $\chi$  = the magnetic susceptibility,  $s$  = the magnetization, and  $H$  = the magnetic field strength), at fields as high as 6 kOe. If all the ferromagnetic minerals or fragments in the samples are completely saturated, this type of plot yields a straight line whose slope is the specific magnetization,  $s$ . The coal fragments yielded normal monotonically increasing straight-line curves indicating complete saturation, whereas straight-line relations were obtained for the pulverized samples only at fields in excess of 2 kOe. Apparently, a significant fraction of the abrasion fragments was not saturated at fields less than 2 kOe. Alexander and others (1979) gave a more detailed discussion of the type of plot relative to coal. In a few cases the plots of the  $\chi$  versus  $1/H$  data in the vicinity of 2 kOe showed a slight inflection, and the value of  $s$  was obtained from the best straight-line fit to the data. In these cases, the value of  $s$  may be slightly lower than the true value. The pulverized Herrin (No. 6) coal had specific magnetizations that were approximately two orders of magnitude larger than the specific magnetization measurements of the fragments. Again, this indicates the presence of a significant amount of a ferromagnetic phase in the pulverized samples. The presence of this phase was confirmed by washing several pulverized samples in warm HCl. After washing, this ferromagnetic phase was absent, the specific magnetization was reduced essentially to zero, and the magnetic susceptibility returned to  $-0.3 \times 10^{-6}$  emu  $g^{-1}$  (electromagnetic units per gram), a value close to that found for the single fragments of coal. The only problem with this explanation is that the intercept,  $\chi_o$ , on the same plot is positive for the powdered specimens rather than negative as found for most coal fragments. This suggests that a substantial paramagnetic phase also may have been introduced into the ground coal.

The presence of a paramagnetic phase can best be studied by measuring the Curie constant. To determine this constant, the magnetic susceptibility was plotted as a function of the reciprocal temperature ( $1/T$ ) from 77 to 300 K, at a fixed field,

1.85 kOe. The slope of the resulting straight line is the Curie constant,  $C$ , and the intercept on the axis is the temperature-independent susceptibility,  $\chi_i$ .  $\chi_i$  includes the diamagnetism, the paramagnetism, and the sum of the temperature-independent ferromagnetic components ranging from fully saturated to unsaturated phases. Complete saturation could be obtained at higher fields, but at high fields the magnetic susceptibility of the saturated ferromagnetic components ( $\chi_i = s/H$ ) included in  $\chi_i$  will necessarily become smaller. To accentuate the value of  $\chi_i$  and to obtain a better estimate of the saturable and nonsaturable ferromagnetic components, the magnitude of the field should be below that required for complete saturation. The ferromagnetic component,  $\chi_r$ , has been subtracted from  $\chi_i$  to obtain the temperature-independent susceptibility,  $\chi'_i$ , of the diamagnetic and paramagnetic components only. Thus  $\chi'_i = \chi_i - \chi_r$ .

The average value of  $C$  for the pulverized coal samples was found to be 2 to 3 times larger than that for the coal fragments. Ferromagnetic particles from the grinder should not substantially change the Curie constant, and therefore this result was unexpected. The abnormally high values of  $s$  and  $C$  indicate that a substantial amount of both ferromagnetic and paramagnetic contamination was introduced during the pulverizing process. Similarly, the pulverized samples had

values of  $\chi'_i$  significantly higher than those of the fragments.  $\chi'_i$  for most coals is generally less than  $-0.6 \times 10^{-6}$  emu  $g^{-1}$  because of the preponderance of diamagnetic hydrocarbon material.

To determine whether, owing to pulverization, some iron mineral had been oxidized to  $Fe_3O_4$ , as suggested previously (Ergun and Bean, 1968; Jacobs and others, 1978), or to free radicals, three of the measured fragments were pulverized in an agate mortar and the same magnetic properties were remeasured. The results are not very different from the whole-fragment data (table 22). These same samples were remeasured approximately a month later to check for oxidation, and the results were virtually the same. The large values of the magnetic properties observed for coal ground in a steel pulverizer thus could not have been due to oxidation or to magnetic centers introduced by the grinding process, and the suspected contamination must, therefore, have come from the grinder itself.

To confirm that the steel pulverizer was a source of contamination, a hand magnet was used to separate a ferromagnetic fraction from the pulverized samples and also from a coal fragment freshly powdered in a porcelain mortar. The pulverized samples contained microscopic ferromagnetic fragments (1–20  $\mu m$ ) which, under the influence of a small hand magnet, formed

TABLE 22.—Magnetic properties of the Herrin (No. 6) interlaboratory sample

[The magnetization,  $s$ , the magnetic susceptibility at infinite field,  $\chi_o$ , at room temperature (298 K) and at 77 K, and the corrected temperature-independent susceptibility,  $\chi'_i$ , are in electromagnetic units (emu)  $g^{-1}$ ; the Curie constant,  $C$ , is in emu K  $g^{-1}$ ]

Sample No.	Mass (mg)	298 K		77 K		C ( $\times 10^{-4}$ )	$\chi_1'$ ( $\times 10^{-6}$ )
		s	$\chi_o$	s	$\chi_o$		
		( $\times 10^{-4}$ )	( $\times 10^{-6}$ )	( $\times 10^{-4}$ )	( $\times 10^{-6}$ )		
Pulverized samples							
H984A	70.65	95.0	.85	86.0	2.80	1.57	— .21
H984B	71.66	95.0	.85	86.0	2.80	1.57	— .21
H984H	73.11	95.0	.85	65.5	5.15	2.66	—3.62
H984J	68.98	99.0	1.0	77.0	5.60	3.12	—3.81
H984K	66.48	71.0	.90	64.3	5.40	2.27	—2.55
H984L	64.98	79.5	1.1	81.0	5.15	3.87	—3.02
H1007	60.50	67.3	.55	81.0	2.10	1.73	— .39
Single fragments							
H984C	83.33	.35	— .36	3.65	.29	.73	— .68
H984D	74.50	.58	— .32	1.55	.52	.82	— .705
H984E	89.57	.35	— .36	1.55	.51	.89	— .77
H984F	85.71	0	— .44	.90	.14	.765	— .625
H984G	93.92	0	— .30	1.50	.89	.92	— .625
Samples fragmented in agate mortar							
H984C	56.84	0	— .44	0	.44	.91	— .75
H984E	57.11	0	— .30	0	.58	.90	— .59
H984G	61.30	0	— .30	— .45	.60	.84	— .57



magnetic chains of irregularly shaped particles. Only a few ferromagnetic particles were recovered from the mortar-ground coal. Under the optical microscope, no elongated or lustrous metallic fragments, such as might be expected from a steel pulverizer, could be observed in either sample. With the SEM, set at higher magnification, a few peeled and knurled fragments were observed in the magnetic fraction separate from the pulverized sample (fig. 7). EDAX analysis of these fragments showed the presence of iron and a small amount of manganese. Approximately the same analysis was obtained on particles picked up with sticky tape from the grinder plate used to process the Herrin (No. 6) coal sample. An XRD pattern of the ferromagnetic material from the pulverized coal sample showed that it was  $\alpha$ -iron. In a similar ferromagnetic fraction separated from the single piece of coal crushed in the mortar, only iron was

observed by means of EDAX, and a diffraction pattern of magnetite,  $\text{Fe}_3\text{O}_4$ , was obtained.

Although the steel particles were smaller than expected, the abraded iron as seen by means of the SEM had particles that appeared to be larger than a single magnetic domain. If we assume that virtually all the steel particles were multidomain, the magnetization,  $s$ , should be the only seriously affected magnetic property in the powdered coal. However, as shown in table 22, the susceptibility,  $\chi_o$ , the Curie constant,  $C$ , and the temperature-independent susceptibility,  $\chi_i$ , which are all primarily paramagnetic properties, were abnormally high in the pulverized specimens compared with the fragments or mortar-ground samples. A possible explanation of the high paramagnetic properties observed in the pulverized coal samples is the presence of superparamagnetic contamination in addition to the ferromagnetic steel particles. We have examined the superparamagnetic properties of the contaminating particles in more detail in a separate paper (Senftle and others, 1982). It was found that the abraded steel particles were about 1.5 nm in diameter and that these small particles tended to agglomerate into multidomain particles in a magnetic field. The clusters significantly changed the magnetization of the whole coal. The total concentration of contaminating steel from the grinder is approximately  $2.1 \times 10^{-4}$  g/g of coal.

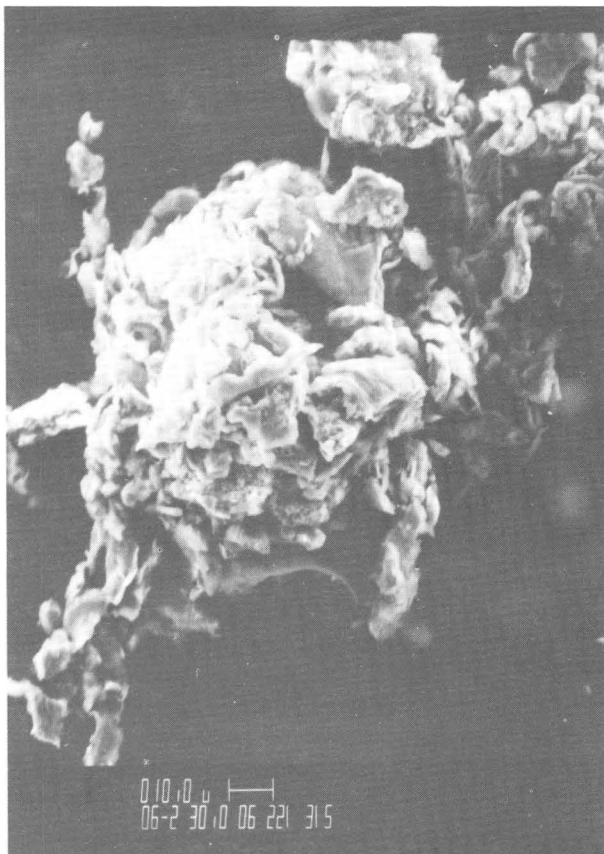


FIGURE 7.—SEM photograph of ferromagnetic particles extracted from the Herrin (No. 6) interlaboratory sample. Lumps of magnetic particles of knurled and curled shavings composed of Fe (major) and Mn (minor) are believed to have originated when the sample was powdered in a steel crusher.

## SUMMARY

The SEM-EDAX results confirm the inferences from magnetic measurements; namely, that coals crushed in a steel pulverizer are most certainly contaminated by abrasion fragments from the crusher and that the contamination seriously affects the measured magnetic properties of the coal. For a relatively soft material, such as coal, the abraded particles are very small compared to similar particles formed during the grinding of rocks, and therefore they initially were not detected by means of an optical microscope.

## I. MINERALOGY OF "DEMINERALIZED" COAL

By Robert B. Finkelman and Frederick O. Simon

Increasing use is being made of "demineralized" coals both in laboratory experiments (Kuhn and

others, 1978) and in technological processes (Jones and Rottendorf, 1980). Treating ground coal in various mineral acids presumably removes most, if not all, of the minerals in the coal, resulting in a clean ("demineralized") coal sample.

A subsample of the interlaboratory coal sample was "demineralized" according to the procedure outlined by Kuhn and others (1978). The -60 mesh coal was separated in a liquid having a specific gravity of 1.40. The float fraction was refluxed with 10 percent  $\text{HNO}_3$  for 2 hours. The  $\text{HNO}_3$  was separated by centrifugation, and the coal was washed with distilled water and dried on a steambath (at approximately  $70^\circ\text{C}$ ). The coal was then treated with 48 percent  $\text{HF}$  for 2 hours at  $70^\circ\text{C}$ . After centrifugation and rinsing with distilled water, the coal was treated with 1:3  $\text{HCl}$  for 1 hour at  $70^\circ\text{C}$ . The subsample was washed with distilled  $\text{H}_2\text{O}$  and dried at  $70^\circ\text{C}$ . This procedure brought the LTA content of the float fraction down from 8 weight percent to 1.5 weight percent for the coal washed in  $\text{HNO}_3$  and  $\text{HF}$  and to 0.5 weight percent after the  $\text{HCl}$  wash.

Polished pellets prepared from these two "demineralized" subsamples (1.5 percent and 0.5 percent LTA) were examined in the SEM. It was evident that the demineralization procedure was very efficient but very specific. The coal particles, most of which appeared to be fractured, were virtually devoid of mineral grains. Essentially all the clays and quartz grains had been removed by the  $\text{HF}$  treatment. Only one unfractured coal particle contained clay particles. Many of the coal particles appeared pitted. These pits were generally aligned, similar to the banded minerals in the untreated coal. These pits probably represented the clays and quartz grains that had been leached from the coal. Iron sulfides were common. The sulfides (presumably pyrite) occurred in fusinite pores, as clusters in vitrinite, and even as isolated massive particles. The only carbonate grain detected was a large calcite particle completely embedded in an unfractured coal particle. Numerous acid-resistant minerals were observed in both mounts. These include (in order of decreasing abundance) titanium oxides, zircon, laths of an iron aluminum silicate, niobium oxide, yttrium phosphate, and a crystal of aluminum oxide. There did not appear to be any significant difference in the mineralogy of the two samples.

The two "demineralized" coal samples were ashed in a low-temperature ashing unit and the

resultant ash studied in a transmission electron microscope (TEM). The residue appeared to be structurally amorphous. There was some scattered crystalline material, such as cubic clusters, spheres, laths, needles, and hexagonal plates. Energy-dispersive X-ray analysis of the material on the TEM grid indicated that the crystals were dominantly zirconium silicates, titanium oxides, and iron sulfides. The structurally amorphous material, which constituted the bulk of the material on the grid, contained aluminum as the only major cation.

Crystals extracted from the LTA of these samples included calcium-aluminum and calcium-iron silicates and calcium sulfates (probably formed during the ashing process). An XRD pattern of the LTA from the sample washed in  $\text{HNO}_3$  and  $\text{HF}$  yielded a pattern of anatase. The sample washed in all three acids yielded a pattern containing lines of goeite [BaAl<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>(OH)·5H<sub>2</sub>O] and a few spot lines of zircon. Preliminary chemical analysis indicates that the concentration of chemical elements is consistent with the mineralogical observations.

## **J. ANALYSIS OF THE LOW-TEMPERATURE ASH FROM THE INTERLABORATORY SAMPLE BY ANALYTICAL ELECTRON MICROSCOPY**

**By Necip Guven and Robert B. Finkelman**

LTA of the interlaboratory sample has been examined with a JEM-100 CX<sup>3</sup> analytical electron microscope (AEM). In the AEM, transmitted electrons are used to form TEM images when the primary electrons are held stationary, and scanning transmission electron (STEM) images are formed when the primary electrons are scanned. Characteristic X-rays are generated from the individual particles in both the stationary ("spot") mode and the scanning ("area") mode. These characteristic X-rays are detected by an energy-dispersive X-ray analyzer. For semiquantitative determination of chemical compositions, the X-ray spectra are collected in a given mode for 100 seconds (live time),

<sup>3</sup>Use of trade names is for identification purposes only and does not imply endorsement by the U.S. Geological Survey.

and the intensities are normalized, usually with reference to  $\text{SiK}\alpha$  line. Elemental intensity ratios obtained in this manner are used in this report for characterization of the mineral matter in the LTA.

Transmitted electrons are also used to obtain electron-diffraction patterns of the individual particles in the following modes:

Selected-area diffraction of an area of about  $0.5\ \mu\text{m}$  in diameter.

Micro-diffraction of an area of about  $0.2$  to  $0.1\ \mu\text{m}$  in diameter.

Micro-micro diffraction of an area of about  $0.1\ \mu\text{m}$  to  $200$  angstroms in diameter.

### SAMPLE PREPARATION

Samples for AEM were prepared from dilute suspensions of the LTA. The suspensions were made with the addition of  $0.07$  percent tertiary butyl amine in order to minimize water surface tension and allow a satisfactory dispersion of the particles. Both copper and beryllium  $200$ -mesh grids were used. The grids were coated with a thin polycarbonate film upon which a drop of sample suspension was dried in air. The grids with the sample particles were then coated with carbon and gold in a vacuum evaporator. The grids were examined at a  $100\text{-keV}$  potential.

### ANALYTICAL ELECTRON MICROSCOPY OF THE LTA

#### CLAY MINERALS

Illite occurs in the form of irregular platelets, as shown in figure 8. The irregular morphology of these platelets indicates a detrital origin. The characteristic X-ray spectrum obtained from these platelets (see caption to fig. 8) is in good agreement with spectra obtained from the standard illites. The selected-area electron-diffraction pattern of the illite fragment is given in figure 9. The six inner spots (that is, the spots with indices  $\bar{1}1$ ,  $\bar{1}\bar{1}$ ,  $1\bar{1}$ ,  $11$ ,  $02$ , and  $0\bar{2}$ ) of this pattern display an intensity distribution in which the  $02$  and  $0\bar{2}$  spots are much weaker than the other four spots. This pattern is typical for dioctahedral  $2\text{M}$ -type micas like muscovite. The  $2\text{M}$  polymorph of illite is generally considered to be detrital in origin.

Kaolinite occurs in aggregates of irregular platelets, as shown in figure 10. These morphological features also suggest a detrital origin for

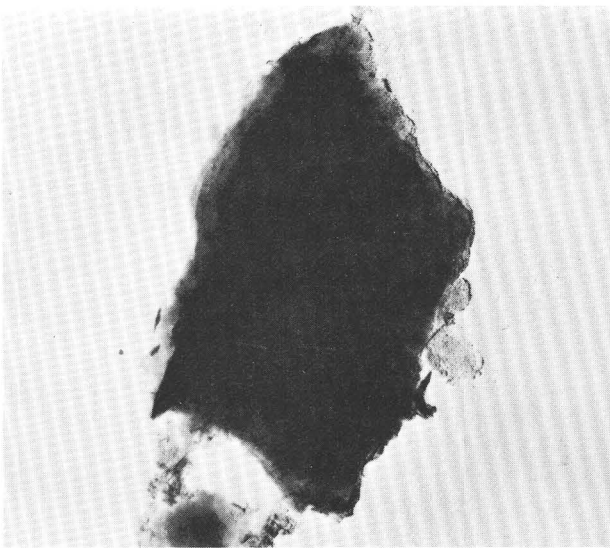


FIGURE 8.—Illite platelet; irregular morphology suggests a detrital origin. Magnification:  $\times 6,000$ . The characteristic X-ray spectrum from the particle is given below:

Element	Intensity (counts/100 s)	Intensity ratio/Si
Al	3616	0.45
Si	8040	1.00
Fe	570	.07
K	1758	.22



FIGURE 9.—Selected-area electron-diffraction pattern obtained from illite platelet in the previous figure. The intensity relationships of the inner six spots are typical of  $2\text{M}$  dioctahedral micas like muscovite. This polymorph indicates a detrital origin for the illite.

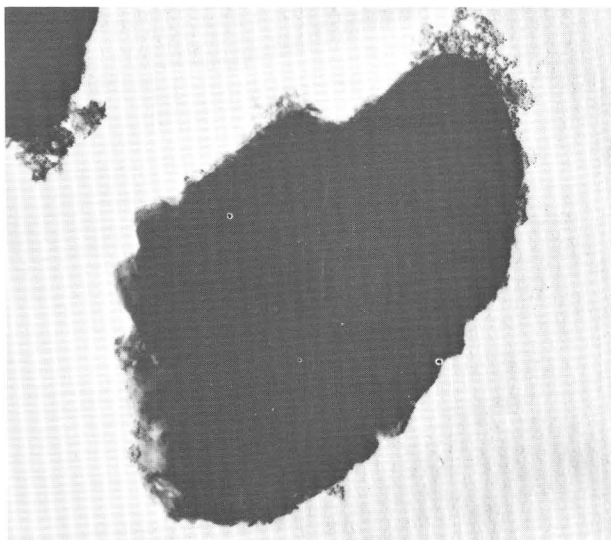


FIGURE 10.—A typical kaolinite particle in the ash, which consists of an aggregate of small and irregular platelets. Magnification:  $\times 16,000$ . The characteristic X-ray spectrum is given below:

Element	Intensity (counts/100 s)	Intensity ratio/Si
Al	10849	0.65
Si	16779	1.00
Fe	866	.05

the kaolinite. The characteristic X-ray spectrum obtained from the kaolinite particle of figure 10 shows traces of iron contamination (possibly iron hydroxides), as indicated in the caption for figure 10. The selected-area electron-diffraction pattern of kaolinite displayed in figure 11 is similar to patterns obtained from standard kaolinites.

#### OTHER MINERAL MATTER

Pyrite and quartz grains were also found along with the detrital clay particles. A rather interesting feature of the sample is the amorphous material, which is shown in figure 12. At low magnification ( $32,000\times$ ), the amorphous material seems to consist of fine grains, which give a speckled appearance to the aggregate. At higher magnifications (to  $332,000\times$ ), the individual particles are clearly discernible as platy, disklike

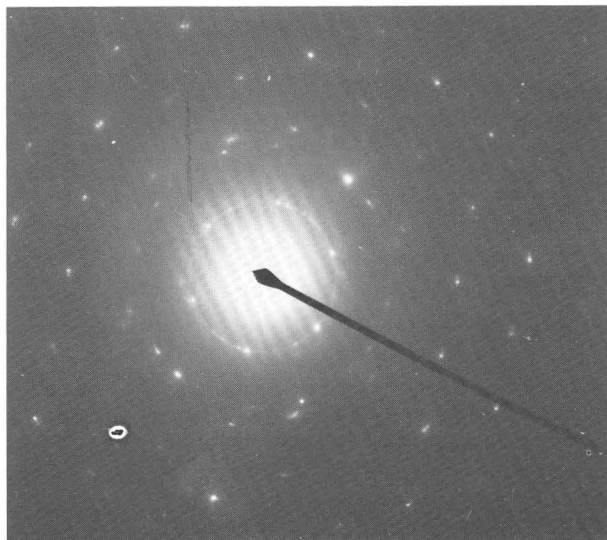


FIGURE 11.—Selected-area electron-diffraction pattern of the kaolinite particle in figure 10.

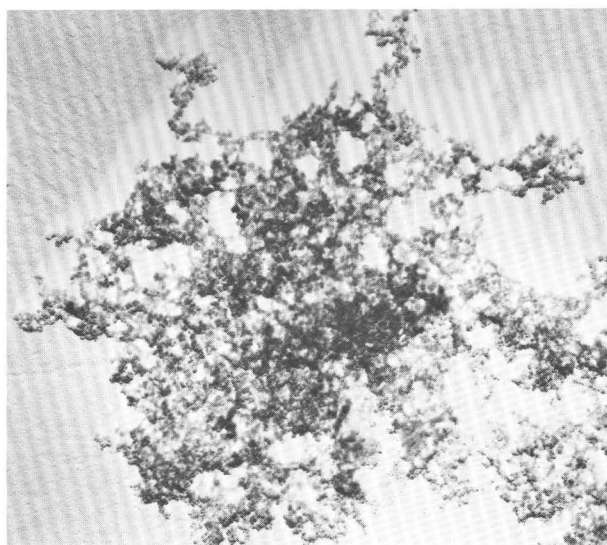


FIGURE 12.—Amorphous material consisting of fine-grained particles. See the following figure for closer view. Magnification:  $\times 32,000$ . The characteristic X-ray spectrum of these particles is given below:

Element	Intensity (counts/100 s)	Intensity ratio/Si
Al	314	7.48
Fe	638	15.19
Ti	214	5.09
Ca	165	3.93
Si	42	1.00

forms (fig. 13). Some of the platelets have ill-defined outlines, but others are disks or doughnuts about 200 Å in diameter. Neither aggregates nor individual particles gave electron diffraction patterns in micro-diffraction and micro-micro diffraction modes with STEM. We therefore assume that this material is amorphous. X-ray fluorescence spectra have been obtained from these amorphous aggregates in "area" and in "spot" modes. The X-ray spectra indicate that the amorphous material contains significant amounts of iron, titanium, and aluminum. In "spot" mode, the spectra were obtained from an individual particle in the aggregate, whereas in "area" mode the spectra were obtained from the left-central section of the aggregate. This amorphous material seems to be an iron-rich gel with significant concentrations of titanium and aluminum. This gel often engulfs particles of other minerals, such as kaolinite and pyrite. Some amorphous aggregates show rather high silicon content suggesting the presence of amorphous silica. The iron and titanium contents of the silica-rich aggregates are also rather high. A second type of amorphous material consists of crumpled thin films from which acicular units grow. This second form of amorphous material is less common than the first type, granular-platy aggregates. The X-ray spectra obtained from the second type of aggregate (the crumpled films) are similar to those from the granular-platy grains, except the titanium and calcium contents are higher in the granular-platy particles.

A preliminary AEM examination of a pulverized split of the interlaboratory coal sample was also made to find out whether or not the amorphous material forms during low-temperature ashing. The common mineral particles detected in the unashed sample include detrital mica, kaolinite, and pyrite. The amorphous material in the coal sample is similar to the second type of aggregate

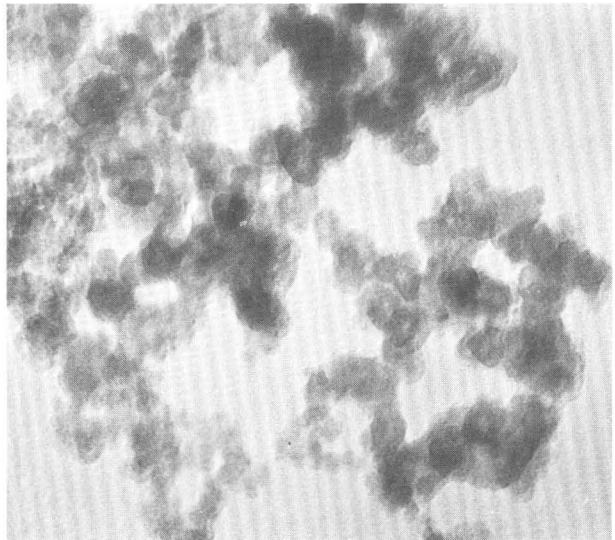


FIGURE 13.—A very high magnification ( $\times 332,000$ ) image of the particles in figure 12 reveals that most particles are platy disks and some are doughnut shaped.

found in the LTA (crumpled thin films with acicular units growing from them). The X-ray spectra indicate that the titanium content of the amorphous material is lower in the coal sample than in the LTA.

It is probable that the granular amorphous material, which makes up more than 10 percent of the LTA, is produced during the ashing process. The iron, titanium, and aluminum found in this material may have originally been associated with the organic constituents. The crumpled filmy amorphous material found both in the LTA and in the unashed coal must have formed prior to the low-temperature ashing. It may have been created by reaction of the LTA and the coal with distilled water. However, additional research is needed to confirm this hypothesis.





# Interlaboratory Study of the Herrin (No. 6) Coal Bed Sample: Conclusions and Recommendations

By R. N. Miller and R. B. Finkelman

The preparation techniques used in this study have adequately produced homogenized coal sub-samples as determined by a combination of total sulfur, pyritic sulfur, ash, and moisture analyses. Proximate, ultimate, mineralogical, and chemical analyses have produced a precise and thorough characterization of the coal sample. Splits of this coal sample are now available to the scientific community to provide a basis for the comparison of analytical data.

## LOW-TEMPERATURE ASHING

Different laboratories used widely different conditions to produce LTA. The result of nonstandardization of the LTA technique has been some variation in the reported LTA yields. The principal sources of variation between laboratories were operating temperature (RF power) and sample and ash preparation and handling techniques.

We recommend the adoption of a standard LTA procedure that specifies moisture conditions for sample preparation and product handling.

## MINERAL ANALYSIS

There was a substantial range of values for each mineral species from XRD data obtained from all the participating laboratories. This undoubtedly reflected differences in sample preparation procedures, in equipment, in standards, and in the treatment of the basic intensity data. In spite of these differences, many of the laboratories generated similar values for most of the mineral species. XRD remains the foremost procedure for determining the mineralogical composition of a complex mixture. However, consideration should be given to techniques such as IR spectroscopy, Mossbauer spectroscopy, and differential thermal analyses for their superior detection capabilities for individual minerals and as corroborative procedures to supplement XRD data.

Clearly more work is necessary to develop reliable quantitative XRD procedures for the analysis of coal LTA. The use of a uniform set of

mineral standards and some standardization of analytical techniques would go a long way toward improving confidence in interlaboratory comparison of XRD data. Perhaps we should try to develop two standardized XRD procedures: a high-throughput, semiquantitative procedure and a low-throughput, more quantitative procedure. Finally, consideration should be given to the amount of X-ray amorphous material generated in the low-temperature ashing procedure.

## CHEMICAL ANALYSES

There is good agreement for most determinations of major, minor and trace elements despite differences in analytical procedures and in the type of sample analyzed (raw coal, HTA, or LTA). The determinations of zinc, strontium, manganese, and iron showed serious discrepancies, which can be attributed to sampling inhomogeneity problems. Mineral-matter determinations by normative analysis are very close to the mean values reported from the XRD data. With the appropriate analytical data on the LTA (including  $H_2O$ ,  $CO_2$ , and pyritic S), normative analysis can be a very valuable corroborative tool.

## MISCELLANEOUS COMMENTS

The appropriate choice of mineral standards is critical for the proper use of many analytical techniques (for example, XRD, FTIR, and differential thermal analysis); this aspect should not be minimized.

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