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Mineral Matter in the Springfield-Harrisburg (No. 5) Coal Member in the Illinois Basin

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MINERAL MATTER IN THE SPRINGFIELD-HARRISBURG (NO. 5) COAL MEMBER IN THE ILLINOIS BASIN

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ABSTRACT

The lateral variation in the mineral matter of the Springfield-Harrisburg (No. 5) Coal Member has been studied in an area that covers southern and central Illinois and parts of Indiana and Kentucky. The study is based on X-ray diffraction analysis of low-temperature ash residues prepared from the coals and on quantitative assessment of nonclay minerals checked against independent chemical analysis. Following special dispersion techniques, oriented-aggregate diffraction analysis was carried out on the clay minerals, and a semiquantitative evaluation of the less than 2-micrometer fraction was performed.

The mineral assemblage in the coal is similar to that of other seams in the Pennsylvanian System in Illinois; quartz, calcite, pyrite, and a clay fraction consisting of illite, kaolinite, and randomly interstratified clay minerals are exhibited. The relative proportions of these constituents vary both vertically through the seam section and laterally across the basin and are particularly well expressed by the inverse relationship between kaolinite and the expandable clay minerals.

These variations have been interpreted in the light of the other geological features of the basin and are thought to reflect the balance between sediment supply and basin subsidence throughout the area. Kaolinite is less abundant and expandables more so in shelf and channel areas where the supply of sediment is greatest. Kaolinite becomes dominant at the expense of mixed-layer clays in the more basinward, sediment-starved regions. Pyrite and calcite also appear to reflect this trend in balance.

The kaolinite is thought to have formed by interaction of dissolved silica and alumina in the peat swamp; the interaction was aided by the catalytic action of organic acids. These organic acids also may have dissolved a certain amount of the expandable clay, and, together with some regrading of illite by potassium fixation in areas of marine influence, the acids have produced a slightly greater ratio of illite to mixed-layer clays than that observed in the associated noncoal strata. Pyrite was precipitated by bacterial action from the sulfate-rich, more reducing portions of the basin, and also is thought to reflect some marine influence. However, organic sulfur compounds are relatively more abundant in the channel and shelf regions. Part of the iron is present in the form of siderite.

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INTRODUCTION

The term "mineral matter" is currently used to describe all inorganic material present in coal. Mineral matter includes both discrete mineral phases and all inorganic elements other than hydrogen, nitrogen, oxygen, and sulfur that might be present in organic compounds (Rao and Gluskoter, 1973). The principal mineral species observed in coals by microscopic and chemical studies include carbonates (calcite), sulfides (pyrite), and silicates (the clay minerals and quartz). Except for quartz, all of these materials undergo significant chemical changes on heating; these reactions form an essential part of the combustion or carbonization process of coal.

Mackowsky (1968) has described a number of coal mining and utilization problems in which the nature of the mineral matter plays a part; the problems include aspects of colliery dust, coal washability, and ash fusion behavior. Other areas in which a knowledge of the mineral matter may be significant include boiler fouling and stack gas pollution, weathering or "slacking" of stockpiled coal, fluxing requirements for blast furnaces, and possible uses of coal washery refuse. However, because of the limitations of optical and chemical techniques, the exact mineral assemblage present in a coal seam has been very difficult to determine. Thus, the significance of a complete understanding of the mineral matter to these problems has not been fully assessed.

A relatively complete study of the mineral species in a coal can be carried out through the use of instrumental techniques such as X-ray diffraction, thermal analysis, or infrared spectroscopy. Although these techniques can be applied to the whole coal sample (for example, Warne, 1963), the instrumental methods give better results if the mineral matter is isolated in some way from the organic fraction of the coal. Because heating destroys many of the involved minerals, special processes have been developed to oxidize the coal so that the mineral residue is left unaltered.

Treatment of the coal with a liquid oxidizing agent, such as concentrated hydrogen peroxide, has been found to be a successful method of isolating the insoluble part of the mineral matter (Nawalk and Friedel, 1972; Ward, 1974). However, the most successful and widely used technique is the low-temperature ashing and radio-frequency oxidation method described by Gluskoter (1965). This technique allows the organic matter to oxidize at slightly more than 100° C in an atmosphere of electronically excited oxygen until a constant weight of mineral residue is attained. This residue consists of mineral matter that is essentially unaltered except for minor dehydration effects. The mineral matter residue can then be subjected directly to X-ray diffraction, thermal analysis, electron microscopy, or chemical studies. Radio-frequency low-temperature ashing was the method used to attain mineral matter for investigation in this study.

Mineralogical investigations of the low-temperature ash of Illinois coals have been carried out by Gluskoter (1967), Hughes (1971), and Rao and Gluskoter (1973). These studies have provided a good indication of the range of mineral assemblages in the coals. However, because of the economic importance, geological complexity, and area of accessibility of the Herrin (No. 6) Coal Member of the Carbondale Formation, studies have chiefly been concerned with the No. 6 Coal. The underlying coal seam, the Springfield-Harrisburg (No. 5) Coal Member, has only been given a brief examination.

The No. 5 Coal is second only to the No. 6 in the amount of available reserves [38 billion tons present over 7,299 square miles (Smith and Stahl, 1975)]. Also, No. 5 Coal is expected to contribute significantly to the total amount of coal mined in Illinois. Thus, a more detailed study of its mineral matter is warranted. This study is based on mineralogical analyses from 43 samples of the No. 5 Coal obtained from deposits throughout Illinois and adjoining areas of Indiana and Kentucky. The object of the study is to elucidate any lateral trends in the nature of mineral assemblage in the coal and to indicate the effect this might have on mining or utilization problems.

ACKNOWLEDGMENTS

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SAMPLING PROCEDURE

Samples of the Springfield-Harrisburg (No. 5) Coal from 32 localities were studied (fig. 1). Each sample was taken either from a drill core or a mine exposure that covered the whole of the coal seam at that locality; any sample having a mineral band of more than 3/8 inch in thickness was excluded from the study. All samples were collected by Illinois State Geological Survey personnel during the period between 1962 and 1975 and are cataloged in the Survey repository. Most of the mine samples are composites of several face-channel samples taken within a small area of the mine. Samples were collected and were made up following standard Survey procedure (Holmes, 1918).

In addition to these samples of the whole seam, a set of individual bench samples also was available from two localities. These samples represent the distinct benches or subsections that can be recognized in the seam exposure. The bench samples were used in the study of the vertical variability of the mineral matter within the seam.

To enable correlation of the present study with studies carried out previously on Illinois coals, an additional series of samples from the Herrin (No. 6) Coal was also studied. These samples and several of those from the No. 5 Coal described above were previously analyzed by Gluskoter (1967), Rao and Gluskoter (1973), and Ruch, Gluskoter, and Shimp (1974), although, in each case, different methods of calculating the mineralogy were adopted.

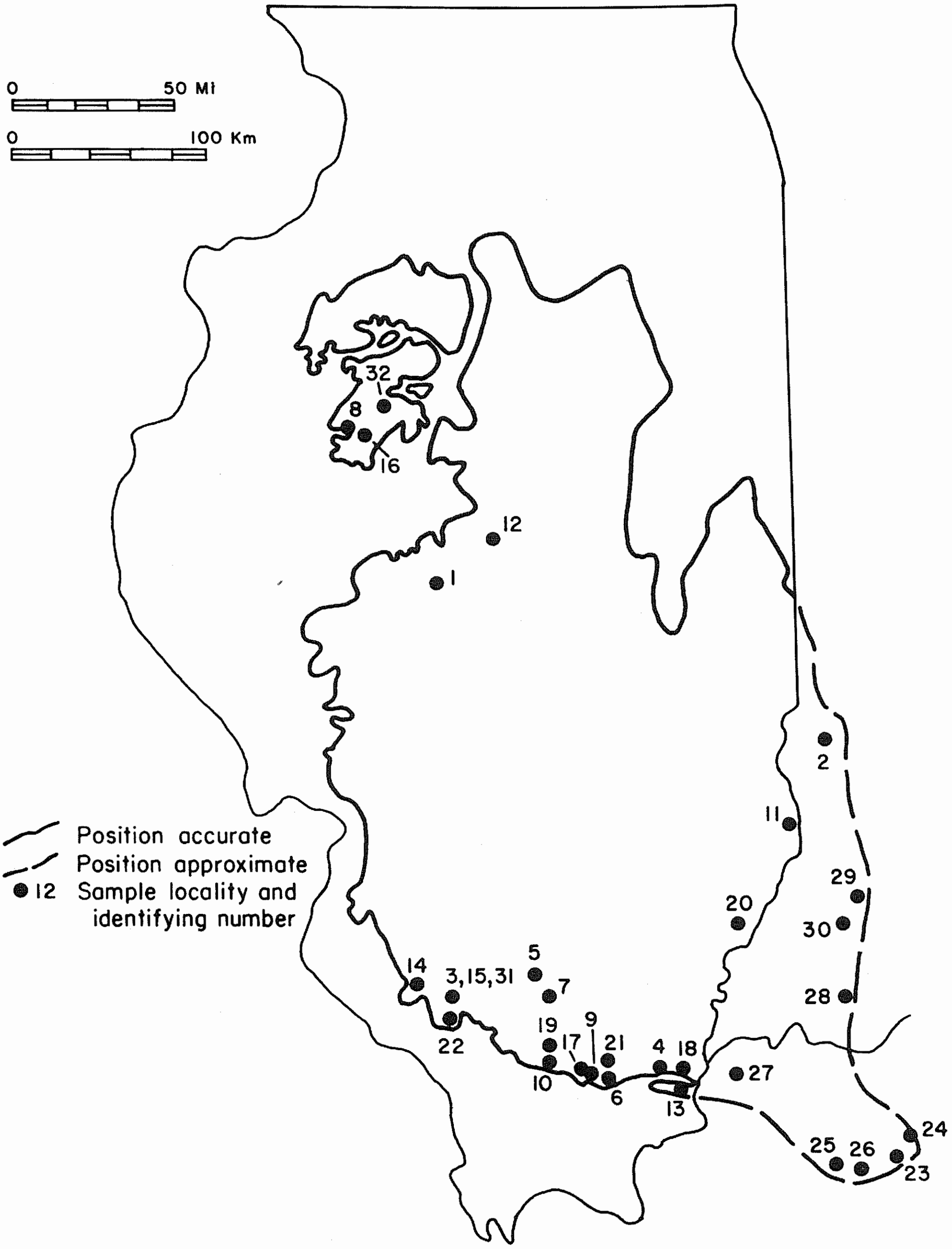

Fig. 1 - Index map showing 32 locations from which samples of the Springfield-Harrisburg (No. 5) Coal Member and equivalents were obtained. ("Position accurate" and "position approximate" refers to the outcrop of the No. 5 Coal and its equivalents.)

MINERALOGICAL ANALYSIS

Low-Temperature Ashing

The coal samples were ground to less than 20 mesh, were predried in a vacuum desiccator, and were allowed to oxidize at low temperature (less than 150° C) in an electronically excited oxygen plasma. Commercially available equipment first described by Gleit (1963) was used. At daily intervals during the oxidation process the samples were removed from the asher, were weighed, and were agitated to expose fresh material at the surface. When constant weight had been attained, the samples were removed, and the percentage of low-temperature ash (LTA) was calculated.

The effects of this ashing process on the mineral matter have been discussed by Gluskoter (1965) and by Rao and Gluskoter (1973). Expandable clay minerals may lose some of their interlayer water during ashing, the dehydration causing structural collapse. This is generally reversible for clay minerals in Illinois coals; that is, the layers can be rehydrated. If present in the coal, gypsum alters to the hemihydrate ($CaSO_4 \cdot 1/2\ H_2O$) or γ $CaSO_4$. Also, interaction between other minerals and the organic material produced during oxidation may form some new compounds (Rao and Gluskoter, 1973).

The percentage of mineral matter or low-temperature ash for the coals studied is generally between 1.25 and 1.40 times that of the standard (high-temperature) ash. The percentage of mineral matter is slightly higher than the amount of mineral matter as indicated by the Parr formula (M.M. = 1.08 × ash + 0.55 × total sulfur). This difference can be explained, in part, by the relatively large amounts of calcite and pyrite in most of the samples; these minerals suffer a weight loss of 44 and 33 percent respectively when the coal is burned. However, several samples show greater differences between the mineral matter yield from the oxidation process and that from the Parr formula, especially among the older coal samples (lower sample numbers). This is due to either incomplete oxidation of the organic material, or to pyrite decomposition in the coal during storage. As discussed below, the pyrite tends to react with oxygen and water in the air to form a range of hydrous sulfate minerals. These reactions take place in the time interval between performance of the preliminary analyses (proximate analysis, etc.) and the subsequent low-temperature ashing operation. With recently collected samples, the difference is less marked if the storage time has been relatively short; in some of the older samples, the percentage of LTA is more than twice that of high-temperature ash.

X-ray Diffraction of Whole Ash

A sample of the residue from the low-temperature asher was finely ground and was placed in a cavity mount. A diffractogram of this powdered material was run on a Phillips Norelco X-ray unit using CuK_α radiation with a LiF monochrometer attachment from 3° to 60° 2θ at a speed of 2° per minute. This diffractogram then was indexed and the minerals were identified from ASTM data. The minerals present in residues of the No. 5 Coal are listed in Table 1 and are discussed in detail below. A selection of typical diffractograms is given in Figure 2.

The finely ground residue was then mixed in a "Spex" mixer with a known amount of "Linde A" synthetic corundum (0.2 g corundum per g of ash) and again

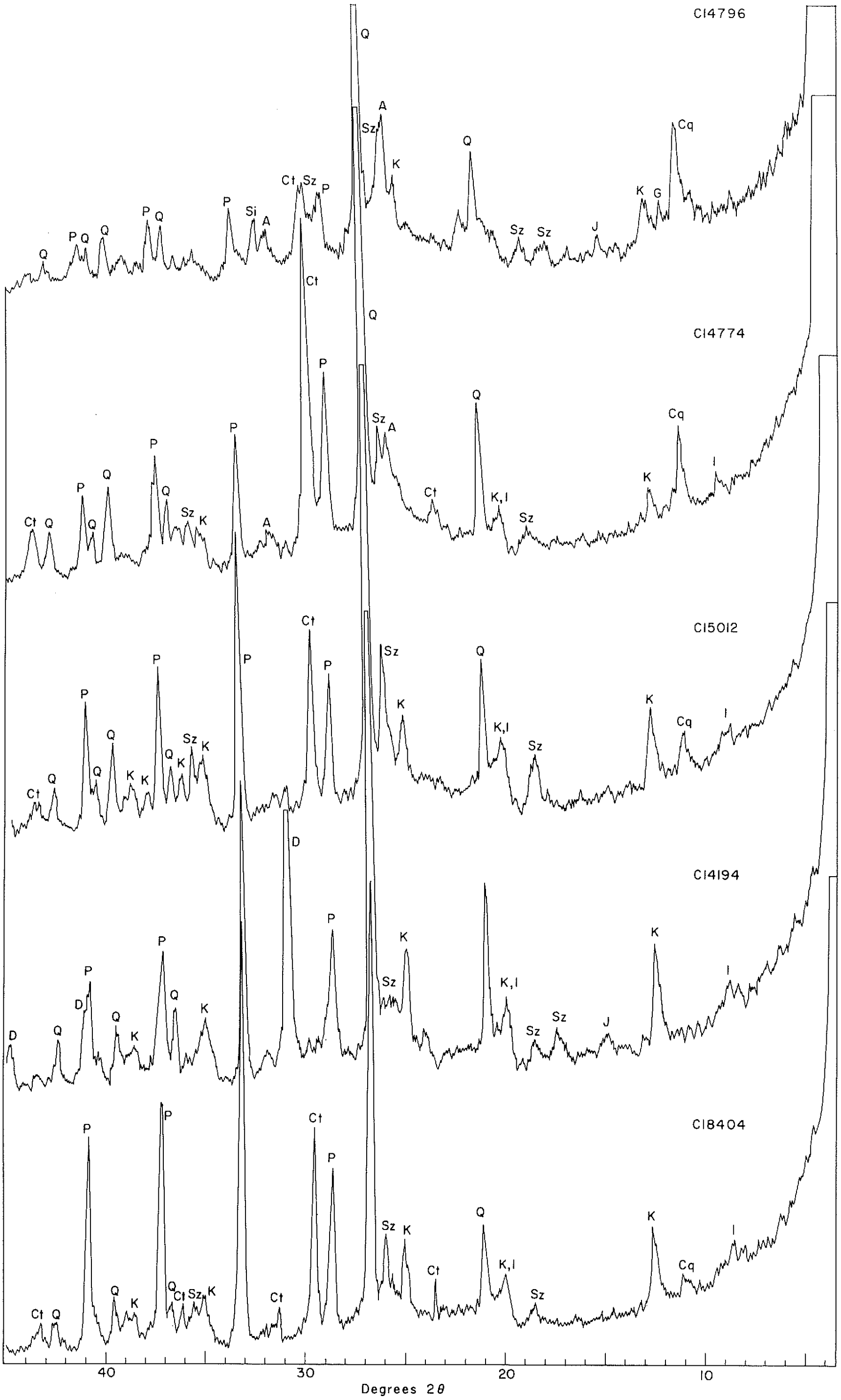

Fig. 2 - Typical X-ray diffractograms, using CuK$_\alpha$ radiation, of low-temperature ash residues of some samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents. A - anhydrite, Cq - coquimbite, Ct - calcite, D - dolomite, G - gypsum, I - illite, J - jarosite, K - kaolinite, P - pyrite, Q - quartz, Si - siderite, and Sz - szomolnokite.

TABLE 1 - MINERALS IDENTIFIED IN SPRINGFIELD-HARRISBURG (NO. 5) COAL MEMBER

Silicates	Carbonates	Sulfides	Sulfates
Quartz (SiO_2)	Calcite ($CaCO_3$)	Pyrite (FeS_2)	Gypsum ($CaSO_4 \cdot 2H_2O$)
Kaolinite ($Al_2Si_2O_5 \cdot H_2O$)	Dolomite [ferroan dolomite - (Ca, Mg, Fe) CO_3]		Anhydrite ($CaSO_4$)
Illite [K, Na, Ca (Al, Mg) (Si, Al) O, OH]	Siderite ($FeCO_3$)		Coquimbite [$Fe_2(SO_4)_3 \cdot 9H_2O$]
Chlorite (Mg - Fe - Si - Al - O - OH)			Szomolnokite ($FeSO_4 \cdot H_2O$)
Expandable clay minerals (mixed-layer, illite-montmorillonite)			Natrojarosite [(Na, K)$Fe_3(SO_4)_2(OH)_6$]

was X-rayed from 20°to 40° 2θ. The corundum was used as an internal standard. By reference to a series of calibration curves, this standard enabled a semi-quantitative assessment of the proportions of quartz, calcite, and pyrite that were present in the low-temperature ash (figs. 3, 4, 5). The curves had been prepared from diffractograms made under identical conditions from known mixtures of these materials and a matrix of clay minerals approximating the most common assemblage in the Pennsylvanian strata of Illinois. The quartz calibration curve contains an additional point which corresponds to the ratio of peak intensities for quartz and corundum in a 1:1 mixture (by weight) as established by the American Society for Testing and Materials (Berry, 1974).

Both the calibration curves and the subsequent mineralogical analyses are based on measurements of the area of the main diffractogram peaks for each mineral. The area is calculated from the height of the peak above background and the width of the peak at half its height. The ratio of the peak area for each major mineral to that of the main corundum peak was determined, and the percentage of that mineral was estimated from the curve. Because it is difficult to select a suitable standard of kaolinite or illite for preparation of a calibration curve, and because a wide range of sulfate minerals is present, no assessment of the proportions of any other materials in the ash was made with the internal standard technique.

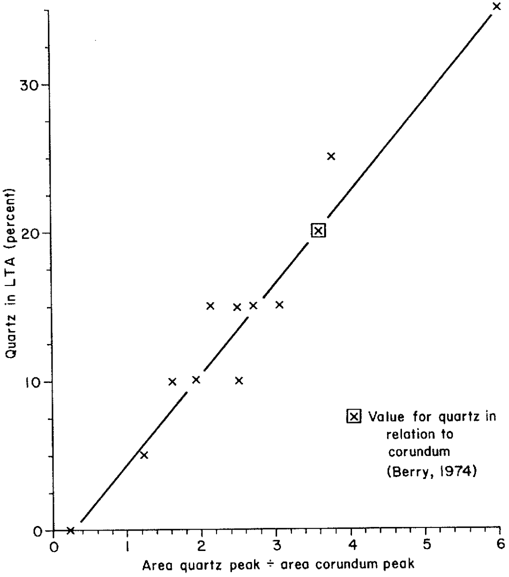

Fig. 3 - Calibration curve for quartz.

Peak area and other data used in preparation of the calibration curves are given in Table 2. The results obtained for the mineralogy of the No. 5 Coal residues are given in Table 3. Several of these coal samples previously had been analyzed with similar techniques by Rao and Gluskoter (1973); in Table 4 the results obtained from their study have been compared to those described above. To complete the comparison, a selection of coals from the Herrin (No. 6) Coal Member was also studied by the methods described in this report. The results have been included in Table 4.

Minerals Present Other Than Clays

The minerals present in Illinois coals have been described in detail by Rao and Gluskoter (1973). Low-temperature ash from the No. 5 Coal is composed chiefly of quartz, calcite, pyrite, and an assemblage of clay minerals; thus it is similar to that of other coals in the Illinois Basin. However, dolomite, probably a ferroan dolomite, has been identified in one sample (C14194) from southern Illinois, and a small amount of siderite is present in another sample from that area.

During storage, the pyrite oxidizes to form a range of iron sulfate minerals; strong peaks of coquimbite $[Fe_2(SO_4)_3 \cdot 9H_2O]$, szomolnokite $(FeSO_4 \cdot H_2O)$, and natrojarosite $[(\underline{Na}, K)Fe_3(SO_4)_2(OH)_6]$ have been observed in the present study, especially in the ashes of coals that had been stored for several years. In addition to these minerals, Gluskoter and Simon (1968) have noted the presence of melanterite $(FeSO_4 \cdot 7H_2O)$, rozenite $(FeSO_4 \cdot 4H_2O)$, and roemerite $[FeSO_4 \cdot Fe_2(SO_4)_3 \cdot 12H_2O]$ in Illinois coals, but they note that melanterite and rozenite dehydrate readily to form szomolnokite.

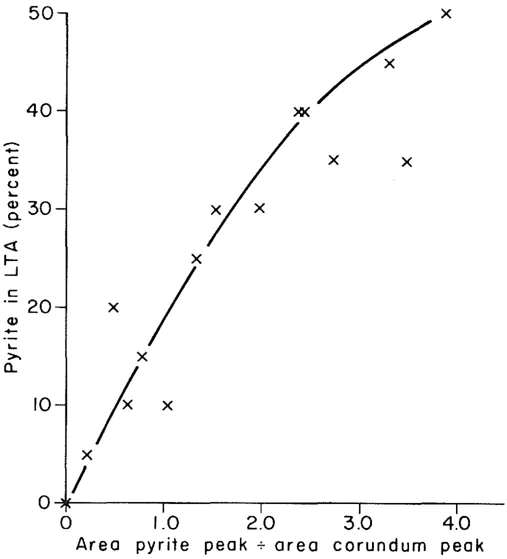

Fig. 5 - Calibration curve for pyrite.

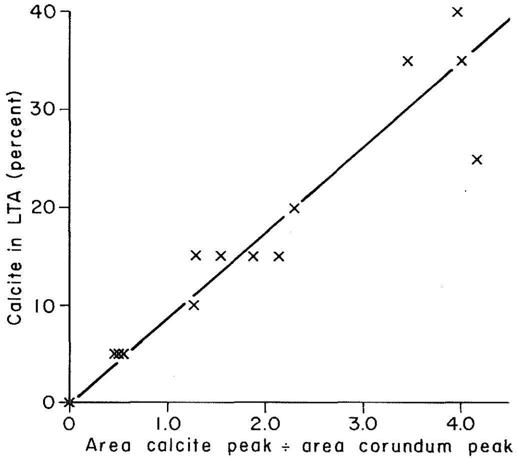

Fig. 4 - Calibration curve for calcite.

Peaks of the calcium sulfate minerals, gypsum $(CaSO_4 \cdot 2H_2O)$ and anhydrite $(CaSO_4)$, have also been observed in the low-temperature ash of the No. 5 Coal. The gypsum is thought to be formed by interaction between moisture and the oxidizing pyrite and calcite in the coal during storage. The anhydrite results either from dehydration of this material or it forms directly during the ashing process.

Comparison to Chemical Data

All the coals in this study have been analyzed for pyritic and sulfate sulfur, and a number of the coals, for a wide range of major and trace elements

TABLE 2 - MIXTURES USED FOR CALIBRATION CURVES

Mixture no.	Percent by weight*				Peak areas				Area ratios		
	Quartz	Calcite	Pyrite	Clay†	Quartz	Calcite	Pyrite	Corundum	$\frac{Q}{Co}$	$\frac{Ct}{Co}$	$\frac{Py}{Co}$
1	0	35	30	35	4	66	29	19	0.21	3.47	1.53
2	5	25	35	35	16	54	45	13	1.23	4.15	3.46
3	10	40	15	35	43	87	17	22	1.95	3.95	0.77
4	15	10	40	35	43	18	33	14	3.07	1.29	2.36
5	25	35	5	35	79	84	5	21	3.76	4.00	0.21
6	35	5	25	35	132	12	29	22	6.04	0.55	1.34
7	40	15	10	35	230	37	15	24	9.60	1.54	0.64
8	45	0	20	35	275	0	14	30	9.16	0	0.47
9	50	5	10	35	231	15	36	35	6.60	0.43	1.03
10	60	5	0	35	380	19	0	35	10.85	0.54	0
11	10	15	40	35	31	26	29	12	2.52	2.11	2.38
12	10	10	45	35	20	16	42	13	1.61	1.28	3.29
13	15	15	35	35	31	25	39	14	2.15	1.72	2.71
14	15	20	30	35	36	33	29	14	2.50	2.29	1.98
15	15	0	50	35	31	0	44	11	2.72	0	3.86

*0.2 g of corundum was added per gram of this mixture.
†Equal parts of kaolinite, illite, and montmorillonite

(Ruch et al., 1974). Therefore, an attempt was made to compare the amounts of quartz, calcite, and pyrite that were indicated by X-ray diffraction to that which could be calculated from the chemical data. The amount of pyrite in the low-temperature ash was calculated from the pyritic sulfur content of the air-dried coal when the coal first was sampled. The results are given with the X-ray determined values in Table 5. In most cases, the amount of pyrite indicated by X-ray diffraction is approximately equal to that indicated by the chemical data. But in a number of cases, especially with samples collected some years previously (lower sample numbers), oxidation appears to have reduced the amount of pyrite considerably. Only two samples have significantly more pyrite indicated by X-ray diffraction than is indicated by chemical analysis.

Table 5 also gives the proportions of quartz for the samples studied, as calculated from the analytical data of Ruch et al. (1974), in relation to that obtained by X-ray diffraction. With the assumption that all the Al is present in clay minerals such as kaolinite (20.9% Al) or illite (20.4% Al) and that the silicon not required for this clay is present as quartz, the amount of quartz in the low-temperature ash has been calculated from the Si and Al contents of the coal. The quartz content of the ash samples indicated by X-ray is generally a few percent lower than that indicated by calculation. This could be due to undetected small amounts of quartz in the other reference minerals used to prepare the calibration curves, to the presence of some opaline silica or other poorly crystallized phase, or to the fact that other clay minerals (for example, the expandable clays) contain more silica than the ideal kaolinite or illite mentioned above.

The amount of calcite in the low-temperature ash can be estimated from the calcium content of the coal, as determined by Ruch et al. (1974). The amounts varied greatly in about one-half of the samples studied when compared to the calcite content, as determined by X-ray diffraction. This is probably true because of solution of calcite and formation of other compounds in conjunction with

TABLE 3 - ANALYTICAL DATA ON COALS IN STUDY

	Mine or drill core location	Proximate analysis (air-dried basis)				Mineral matter			Nonclay minerals by X-ray diffraction			Quartz and clay	Sulfur forms (air-dried basis)				Pyrite from pyritic sulfur	Total clay	<2 µm fraction			
Coal sample number	(fig. 1)	Moisture (%)	Volatile matter (%)	Fixed carbon (%)	Ash (%)	Parr formula (%)	LTA (%)	$\frac{\text{LTA}}{\text{Ash}}$	Quartz (%)	Calcite (%)	Pyrite (%)	[LTA - (C + P)] (% of coal)	Total sulfur (%)	Organic sulfur (%)	SO_4 (%)	Pyritic sulfur (%)	(%)	[100 - (Q + C + P)] (% of LTA)	Kaolinite (%)	Illite (%)	Expandable clays (%)	$\frac{100\ \text{I}}{\text{I + Ex}}$
C12495	1	5.2	40.3	44.4	10.1	13.2	23.5	2.32	8	1	10	18.3	4.12	1.53	0.06	2.53	21	70	-	-	-	-
C13046	2	4.2	41.3	44.1	10.4	13.7	11.3	1.09	15	6	17	5.2	4.49	1.59	0.01	2.89	48	69	31	56	13	81
C13983	3	2.7	39.4	47.6	10.3	13.4	16.4	1.59	13	5	13	11.2	4.15	1.73	0.02	2.40	27	55	23	45	32	58
C14194	4	1.1	31.5	54.0	13.4	16.4	17.3	1.29	14	17*	16	10.0	3.59	1.27	0.08	2.24	25	44	28	57	15	79
C14405	5	2.0	38.8	46.5	12.7	15.8	19.4	1.53	18	tr	31	14.9	3.84	1.40	0.02	2.42	23	59	28	49	23	68
C14609	6	2.4	35.4	52.0	10.2	12.6	14.3	1.40	8	8	12	9.3	2.85	1.04	0.04	1.77	27	57	38	53	9	85
C14735	7	1.8	38.7	47.6	11.9	15.0	18.9	1.59	15	11	28	11.7	3.94	1.62	0.02	2.30	27	47	24	47	29	62
C14774	8	3.2	40.8	43.6	12.4	15.4	16.5	1.33	15	17	13	11.4	3.56	2.17	0.02	1.37	14	54	29	38	33	54
C14796	9	2.1	33.6	54.2	10.1	11.6	13.2	1.31	10	6	10	11.0	1.31	0.57	0.02	0.72	11	73	17	46	37	55
C15012	10	5.2	37.2	51.3	11.5	14.1	14.5	1.26	12	7	19	10.0	3.17	1.11	0.02	2.04	24	57	32†	51	17	75
C15140	11	**	43.6	46.0	10.4	13.0	14.4	1.38	13	5	9	11.5	3.25	2.08	0.01	1.16	15	67	33	40	27	60
C15208	12	**	41.7	43.5	14.8	18.2	19.0	1.28	19	12	21	13.3	4.06	2.03	0.07	1.96	18	51	34	47	19	71
C15384	13	4.1	36.9	50.9	12.2	15.5	17.1	1.40	14	tr	12	13.0	4.12	1.53	0.06	2.53	24	62	29	51	20	72
C15448	14	**	40.2	47.1	12.7	16.4	17.6	1.39	11	tr	15	12.8	4.94	2.26	0.12	2.56	27	62	23	39	38	51
C15452	15	**	39.8	47.5	12.7	16.3	17.0	1.34	12	9	27	11.6	4.68	2.32	0.30	2.06	23	56	21	50	29	63
C16264	16	15.8	36.5	37.3	10.4	13.3	20.8	2.00	17	14	17	12.3	3.81	1.81	0.04	1.96	27	42	36	49	15	77
C16729	17	2.5	36.1	49.5	11.9	14.6	16.4	1.38	11	14	30	9.2	3.09	0.81	0.04	2.24	31	44	29	52	19	73
C17001	18	2.2	38.6	47.7	11.5	14.6	15.4	1.34	16	16	28	8.2	4.05	1.47	0.02	2.56	31	37	25	51	24	68
C17611	19	2.2	-	-	10.5	13.1	13.5	1.29	18	7	22	9.6	3.25	1.65	0.02	1.58	22	53	31	49	20	71
C17721	20	2.1	38.1	52.0	7.8	9.6	10.8	1.38	13	3	17	8.0	2.21	0.86	0.01	1.34	23	61	20	47	33	59
C17988	21	1.8	36.7	51.2	10.3	12.3	15.0	1.39	11	12	20	10.2	2.13	0.79	0.01	1.33	20	57	34†	44	22	67
C18040	22	2.0	40.1	45.7	12.1	15.2	15.4	1.27	19	25	30	7.7	3.78	2.06	0.01	1.71	25	31	26	44	30	59
C18392	23	5.6	39.7	45.7	8.9	11.5	12.4	1.39	15	3	27	8.8	3.24	1.49	0.04	1.71	26	56	30	51	19	73
C18395	24	2.9	39.8	47.6	9.7	12.8	12.5	1.29	9	tr	27	10.1	3.42	1.93	0.02	1.24	19	72	50	33	17	66
C18404	25	2.3	39.4	48.8	9.5	12.6	12.1	1.27	9	5	37	7.3	4.14	1.66	0.22	2.26	35	51	39	45	16	74
C18411	26	3.6	35.9	51.0	9.4	12.4	16.6	1.76	10	11	43	9.8	4.45	1.51	0.27	2.67	30	49	36	41	23	64
C18594	27	2.0	38.9	48.1	10.9	13.4	14.0	1.28	15	10	39	8.0	4.12	1.60	0.08	2.44	33	42	27	47	26	66
C18687	28	**	39.0	52.7	8.3	10.6	10.4	1.25	11	8	32	6.1	2.95	1.65	0.05	1.25	23	58	42	46	12	79
C18697	29	**	41.8	48.7	9.5	12.5	14.1	1.48	14	2	38	10.0	4.03	1.93	0.08	2.02	27	57	36	44	20	69
C18701	30	3.7	41.0	49.1	9.9	12.7	12.9	1.30	9	7	34	8.4	3.69	1.69	0.07	1.92	28	56	37	50	13	79
L1103	31	1.8	-	-	12.2	-	17.3	1.42	13	8	37	9.5	-	-	-	2.41	26	42	37	47	16	75
L1166	32	1.6	-	-	15.5	-	19.4	1.25	28	16	8	14.7	-	-	-	1.25	12	48	27	45	28	62

*Dolomite

†Trace of chlorite

**Dry basis given

TABLE 4 - COMPARISON OF SOME MINERALOGICAL ANALYSES TO THOSE OF PREVIOUS STUDIES

Coal sample no.	This study			Rao and Gluskoter (1973)			This study			Rao and Gluskoter (1973)		
	Quartz (%)	Calcite (%)	Pyrite (%)	Quartz (%)	Calcite (%)	Pyrite (%)	Kaol (%)	Illite (%)	Ex (%)	Kaol (%)	Illite (%)	Ex (%)
	Of mineral matter						Of <2μm fraction			Of total clays		
Springfield-Harrisburg (No. 5) Coal Member												
C12495	8	1	10	13	7	8				19	37	44
C14609	8	8	12	13	7	21	38	53	9	28	41	31
C14735	15	11	28	24	10	30	24	47	29	26	48	26
C14774	15	17	13	22	11	15	29	38	33	20	59	21
C14796	10	6	10	11	6	12	17	46	37	23	51	26
C15012	12	7	19	19	10	24	32	51	17	32	56	12
C15208	19	12	21	25	17	22	34	47	19	19	41	40
C15384	14	tr	12	18	9	22	29	51	20			
C15448	11	tr	15	13	10	19	23	39	38	25	44	31
C15452	12	9	27	11	10	18	21	50	29	16	37	47
C16264	17	14	17	13	14	21	36	49	15			
C16729	11	14	30	25	13	38	29	52	19			
Herrin (No. 6) Coal Member												
C13975	12	tr	8	24	9	20	32	37	31			
C14613	18	3	8	18	7	9	43	29	28	31	38	31
C14970	8	8	14	11	8	5	45	24	31	36	26	38
C16139	15	11	34	18	8	20	37	33	30	18	39	43

pyrite oxidation. Table 5 shows that, if the calcite content determined by X-ray diffraction is less than that from the chemical analysis, the samples are also deficient in pyrite. Independent determinations of the carbonate CO_2 content of the fresh coal, which could also be used to estimate the amount of calcite, are not available. The chemically determined carbonate content expressed as calcite for several LTA residues is given in Table 5 for additional comparison.

Although a high degree of precision is not possible by the use of X-ray diffraction in quantitative mineralogical analysis, the results of the present study seem to be reasonably consistent with those of previous studies. Except in cases involving pyrite oxidation, the calcite and pyrite determinations agree fairly well with those of Rao and Gluskoter (1973) and with the chemical data. The amount of quartz indicated by the present study is consistently a little less than that indicated by chemical analysis. Values from Rao and Gluskoter (1973) are generally more irregularly distributed. However, because of the effects of pyrite oxidation during storage, some care must be taken in relating the percentages determined by X-ray analysis of the ash to the mineralogy of the virgin coal.

Analysis of Clay Minerals

Because they occur as fine (<2 μm in size), flakey particles, the clay minerals are best studied by X-ray diffraction techniques that emphasize their basal {001} crystallographic spacing. For diffraction study, the clay fraction of the ash is mounted in such a way that these flakes lie parallel to each other on the surface of the specimen holder. There are many ways in which such mounts can be prepared (Gibbs, 1970), but limitations, which are imposed by the small amount of material available and the necessity for a considerable amount of treatment before mounting, make the pipette-on-glass-slide technique the most satisfactory for the present study.

The clay particles in the low-temperature ash occur in a highly flocculated state, partly because of their mode of formation and partly because of an abundance of Fe and other ions produced by oxidation of pyrite. To provide adequate orientation in the diffraction mount, the clay first must be fully dispersed by disaggregation and ion exchange techniques. For the present study, this dispersion has been accomplished by a method similar to that used by Jackson (1956) for the treatment of soil samples.

A small amount of the low-temperature ash (approximately 0.2 g) is placed in a 50 ml beaker with about 40 ml of distilled water and is agitated for approximately one minute by means of an ultrasonic probe. After a suitable time (1 to 2 hours) has elapsed to allow solution of any slowly soluble components, this suspension is transferred to a centrifuge and the supernatant liquid is removed. The clay is returned then to the beaker and is warmed in a dilute (5%) acetic acid solution for several hours to dissolve carbonates and other acid-soluble iron compounds. When cool, the suspension is again centrifuged to remove the excess acid, and then is washed and centrifuged with distilled water. The washed clay is transferred to a 100 ml beaker containing a solution consisting of 40 ml of 0.3M sodium citrate and 5 ml of 1M sodium bicarbonate. The suspension is then heated to between 75° and 80°C. Approximately 1 g of sodium dithionate ($Na_2S_2O_4$) is added, and the suspension is stirred thoroughly. Similar amounts of dithionate are added two more times at 15-minute intervals. The suspension then is cooled, and the liquid once again is removed in the centrifuge.

The dithionate-citrate treatment is used to reduce any ferric materials present to the more soluble ferrous state and to remove all soluble iron from the system. After this treatment and once the solution has been removed, the clay particles are invariably well dispersed. When suspended in water, the clay particles can only be settled by prolonged treatment in the centrifuge. Once the dithionate-citrate solution is removed, the clays are transferred to a 50 ml beaker containing distilled water and are left overnight to check that they do not flocculate.

TABLE 5 - COMPARISON OF MINERALOGICAL DATA DETERMINED BY X-RAY DIFFRACTION AND BY CHEMICAL ANALYSIS

Coal sample no.	Quartz (%)		Calcite (%)			Pyrite (%)	
	X-ray diffraction	Chemical analysis	X-ray diffraction	From calcium content	Chemical analysis	X-ray diffraction	From pyritic sulfur
C12495	8	13	1	10	n.d.	10	21
C13046	15	23	6	14	7	17	48
C14194	14	19	17*	32	17	16	25
C14609	8	13	8	16	n.d.	12	27
C14735	15	18	11	10	n.d.	28	27
C14774	15	21	17	20	7	13	14
C14796	10	10	6	9	5	10	11
C15012	12	19	7	7	3	19	24
C15208	19	17	12	21	3	21	18
C15384	14	18	tr	9	2	12	24
C15448	11	**	tr	7	2	15	27
C16264	17	10	14	7	n.d.	17	27
C16729	11	16	14	19	13	30	31
C17001	16	16	16	13	9	28	31
C17721	13	16	3	5	n.d.	17	23
C17988	11	16	12	20	n.d.	20	20
C18040	19	22	25	30	n.d.	30	25

*Dolomite
**Published results inconsistent

The suspension is then reagitated and is allowed to settle for approximately one hour to permit the particles of > 2 µm in diameter to settle. Using a pipette, 10 ml of suspension is taken from approximately 1 cm below the liquid surface. The suspension is diluted with 10 to 25 ml of water and is centrifuged until the supernatant liquid is clear and all of the clay has settled.

The liquid is carefully decanted and the clay is made into a slurry with approximately 3 ml of distilled water. This concentrated suspension is then transferred with a 3 ml pipette to a clean, labelled, 27 × 46 mm glass microscope slide and is allowed to dry in the laboratory atmosphere. The techniques used in preparation of the clay minerals are summarized in Figure 6.

Three diffractograms are prepared for each slide, covering the range between 3° and 35° 2θ. The slide is run first in the air-dried state (that is, as it dried in the laboratory atmosphere); then after saturation for at least 24 hours in an ethylene glycol atmosphere; and finally after heating at 300°C for approximately 1 hour, it is run again. Typical results of this investigation are given in Figure 7.

Clay Minerals in the No. 5 Coal

Kaolinite is present in all the oxidation residues studied. It exhibits very sharp diffractogram peaks at 7.15 Å and 3.59 Å, indicating a high degree of crystal ordering, although it does not show clear resolution of the {hkl} peaks (4.47 to 3.74 Å) in cavity mounts. Much of this kaolinite is probably of authigenic origin, because well formed crystals of the mineral are a common feature on the cleat surfaces of the coal (Ball, 1934; Hughes, 1971).

Illite is usually the most abundant mineral in the < 2 μm fraction of the low-temperature ash. It exhibits remarkably sharp peaks at 10.0, 5.0, and 3.33 Å, generally devoid of the asymmetry due to partial degradation that is usually associated with this mineral. The sharpness of these peaks also indicates a well crystallized structure.

Varying amounts of expandable clay minerals that consist either of partly degraded illite or irregularly interstratified clay minerals, principally illite-montmorillonite, are also present. These minerals are indicated by a broad zone of diffraction in air-dried slides at a spacing of greater than 10 Å, which expand to an irregular zone with slightly greater spacings when saturated with glycol. However, the expandable minerals collapse to a regular 10 Å spacing when heated and reinforce the illite peaks.

Also present in some samples is a trace of chlorite, indicated by a small peak at 14 Å that does not change position or intensity during the treatment process. In addition, in most of the slide studies, small amounts of quartz and pyrite are found; this indicates the very fine grain-size of some of these constituents.

The relative proportions of kaolinite (K), illite (I), and expandable (Ex) clay minerals were calculated for each < 2 μm sample, and the results are shown in Table 3 and Figure 8. These calculations are based on the technique described by Griffin (1970); the technique uses peak areas (height × width at $\frac{1}{2}$ height) rather than simple peak heights. The technique compares favorably to that used for many years by Dr. H. D. Glass in clay mineral studies at the Illinois State Geological Survey; it has the advantage that the differing diffraction characteristics of glycol-saturated and heated slides are taken into account. The formulas used in these calculations are:

(To be continued on page 16)

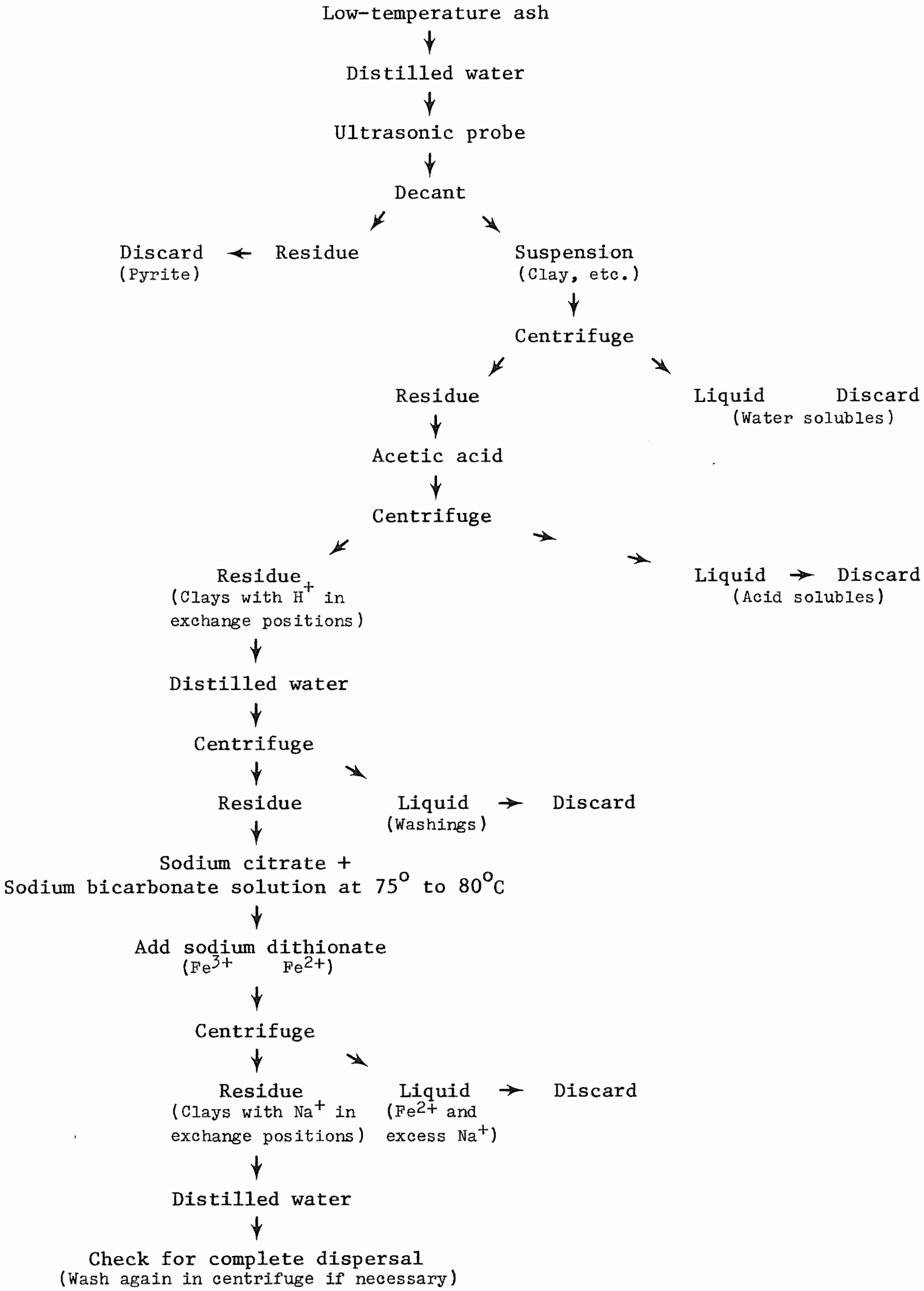

Fig. 6 - Flow sheet for clay dispersal.

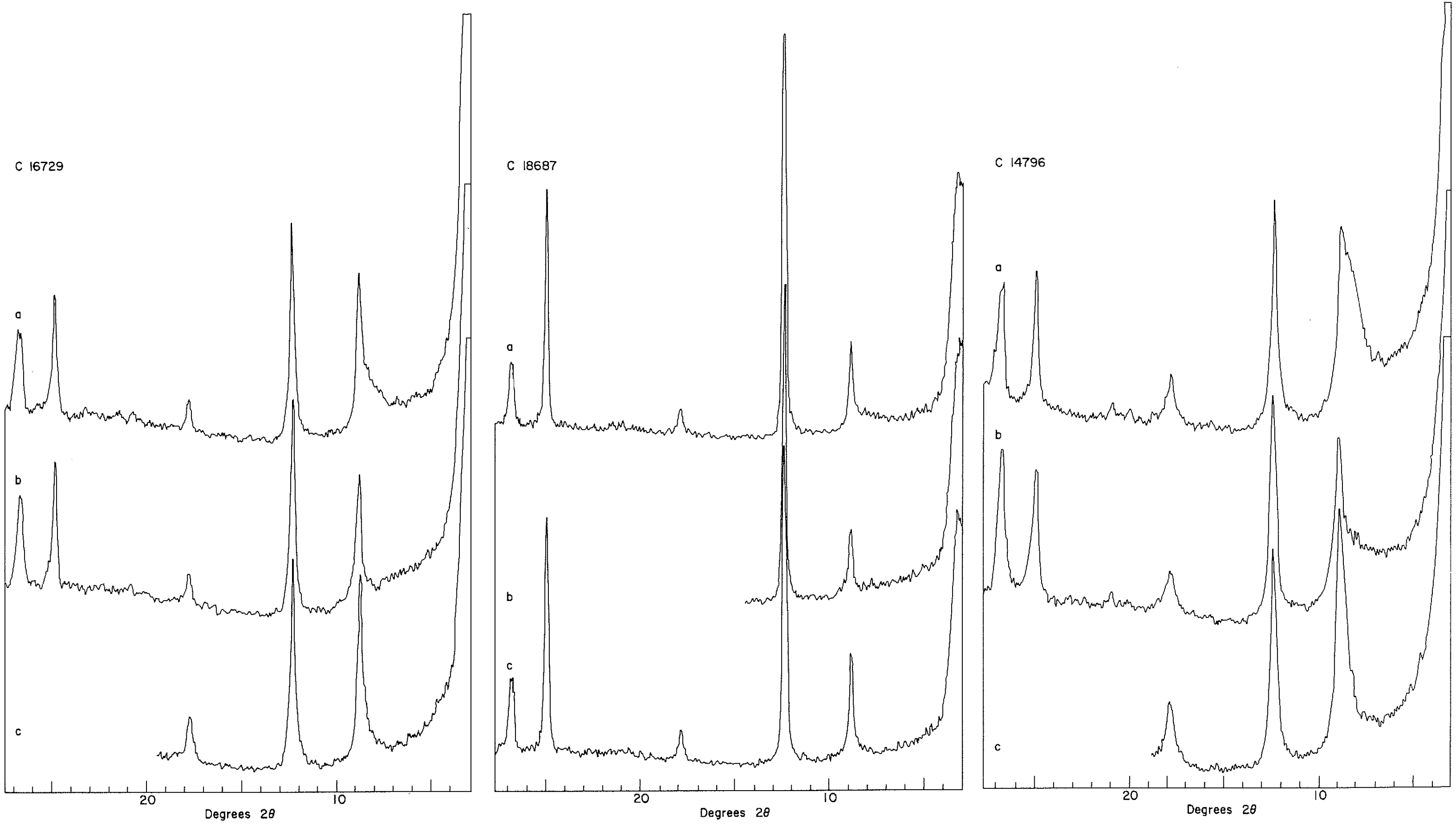

Fig. 7 - Oriented aggregate X-ray diffractograms, using CuK$_\alpha$ radiation, of typical < 2 µm samples of low-temperature ash from the Springfield-Harrisburg (No. 5) Coal Member and equivalent. a. - air-dried sample; b. - ethylene glycol saturated sample; c. - sample after being heated to 300°C for one hour.

$$\%K = \frac{A_{7H}}{2.5} \div \left(\frac{A_{7H}}{2.5} + A_{10H}\right) \times 100$$

$$\%(I + Ex) = 100 - \%K$$

$$\%I = \frac{A_{10G}}{A_{10H}} \times \frac{A_{7H}}{A_{7G}} \times \%(I + Ex)$$

$$\%Ex = \%(I + Ex) - \%I$$

where:

A_{7G} = area of 7.15 Å glycol-saturated peak

A_{7H} = area of 7.15 Å heated peak

A_{10G} = area of 10 Å glycol-saturated peak

A_{10H} = area of 10 Å heated peak

%K = percentage of kaolinite (+ chlorite) in <2 μm fraction

%I = percentage of illite in <2 μm fraction

%Ex = percentage of expandable clays in <2 μm fraction

%(I + Ex) = percentage of illite + expandables in <2 μm fraction

A correction can be made for chlorite, should it be present in sufficient quantities to enable its distinction from kaolinite, by the use of 3.59 and 3.54 Å peaks; this was not possible for the present study.

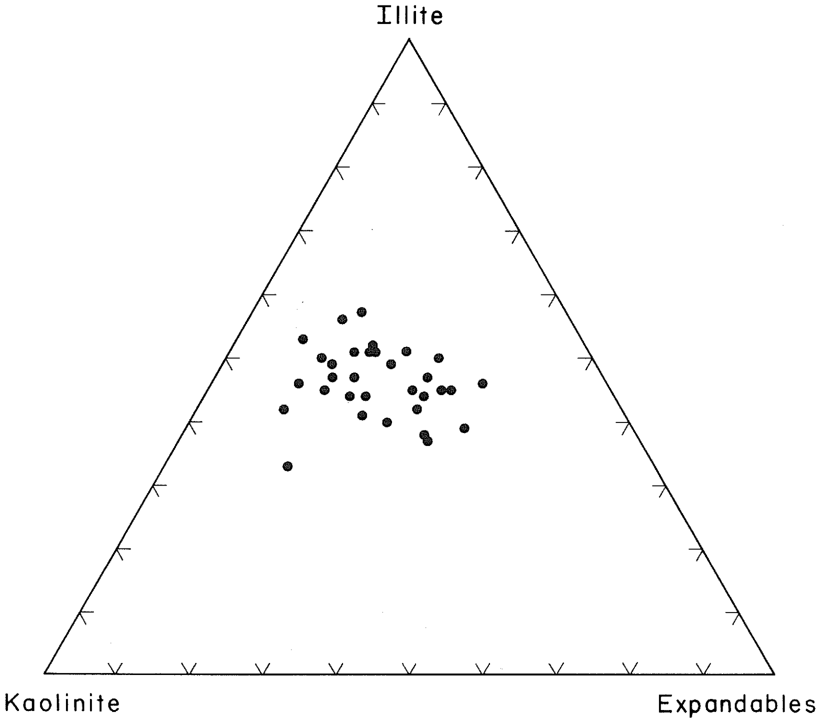

Fig. 8 - Mineralogy of less than 2 micrometer fraction of mineral matter.

MINERAL MATTER VARIATIONS IN THE NO. 5 COAL

Vertical Variations

Although only two sets of bench samples were available for the present study, the sets did provide an opportunity to examine variations that might occur within the individual seam section in the mineral matter in the coal. In Table 6 the mineralogy of the individual bench samples, generally the portions of the seam between recognized partings or clay bands, is given for the two sets in the study. Although these bench sets are 55 miles apart, both sets exhibit similar mineralogical trends, especially in the clay fraction.

The mineralogy of the coals differs substantially from the immediately adjacent underclay or roof shales. (Mineralogy of roof and floor are given in Table 7.) In comparison to the associated strata, the coal is considerably richer in kaolinite and also contains, at least in most of the benches, a greater ratio of illite to expandable clay minerals.

The topmost bench in each case has a lower ratio of illite to expandable clay. Apart from a greater amount of kaolinite, each topmost bench closely resembles the adjacent strata. Traces of chlorite are found in the lower benches at both localities but chlorite appears to be absent from the underclay immediately at the base of the seam at locality 31 (fig. 1, p. 4).

Studies of Australian coals (Ward, 1976) have shown even more marked contrasts between the mineral matter in the coals and that of the roof and floor strata. Well crystallized kaolinite is abundant in the coals, but only average amounts of poorly crystallized material occur in the associated strata. In contrast to the No. 5 Coal of Illinois, illite is virtually absent from most Australian coals. Illite is a major constituent of the Australian shales above and below the seam, but a range of illite-montmorillonite interstratified clay minerals is developed instead.

TABLE 6 - MINERALOGY OF INDIVIDUAL BENCHES

			Low-temperature ash				<2 μm fraction			
Sample no.	Bench no.	LTA (%)	Quartz (%)	Calcite (%)	Pyrite (%)	Total clay (%)	Kaol. (%)	Illite (%)	Ex (%)	$\frac{100\ I}{I + Ex}$
			Locality 21							
C18003	1	24.3	6	3	28	63	13	47	40	54
C18004	2	12.5	9	3	17	71	44	44	12	79
C18005	3	5.5	8	11	20	61	54	29	17	63
C18006	4	9.7	7	5	30	58	43	39	18	68
C18007	5	12.4	12	7	15	66	29	49	22	69
C18008	6	13.4	21	19	9	51	43*	41	16	72
			Locality 31							
-	Roof	-	-	-	-	-	14	56	30	65
L00986	1	14.8	18	tr	30	52	34	38	28	58
L00987	2	12.7	11	11	43	35	53	36	11	77
L00988	3	6.7	6	36**	10	48	45*	43	12	78
L00989	4	16.7	16	10	41	33	36*	53	11	83
L00990	5	21.2	24	6	8	62	29*	58	13	82
-	Floor	-	-	-	-	-	6	60	34	64

*Trace of chlorite
**11% calcite + 25% dolomite

TABLE 7 - CLAY MINERALOGY OF ROOF AND FLOOR STRATA

Location on fig. 25	Core no.[a]	Depth of sample		Stratigraphic position[b]	<2 μm fraction			
		(ft)	(in.)		Kaol. (%)	Illite (%)	Ex (%)	$\frac{100\ I}{I + Ex}$
a	C141	223	0	roof	21*	49	30	62
a	C141	223	5	roof†	29*	40	31	57
a	C141	225	6	floor	47*	38	15	72
b	C1604	429	0	roof	1	22	77	22
b	C1604	430	0	floor	1	25	74	25
c	C4097	180	1½	roof	4*	41	55	43
c	C4097	187	7	floor	4	44	52	46
d	C4374	694	0	roof	13*	56	31	64
d	C4374	696	6	roof†	9*	66	25	73
d	C4374	700	5	floor†	3*	54	43	56
d	C4374	705	0	floor	19*	61	20	75
e	C4415	132	6	roof	9*	55	36	60
e	C4415	132	9	floor	6*	64	30	68
f	C6310	192	0	roof	7*	60	33	65
g	C6311	206	0	roof	10	57	33	63
h	C6347	218	0	roof	17*	63	20	75
h	C6347	221	0	floor	2	54	44	55
i	C6656	473	0	roof	10*	62	28	69
i	C6656	481	0	floor	12*	43	35	55
j	Loc. 31	-	-	roof	14	56	30	65
j	Loc. 31	-	-	floor	6	60	34	64

Note: a - Core held in Illinois State Geological Survey repository.
b - Location with reference to No. 5 Coal Member.

*Chlorite also present
†Immediate roof (or floor); immediately adjacent to coal seam.

Lateral Variations

Significant variations exist in the mineralogy of the residues of samples from different parts of the basin (table 3). The uneven distribution of samples makes a complete study of the variations somewhat difficult. Sufficient material is available from at least the southern part of the basin to delineate any significant trends and their relationship to other geological features. However, few samples are available from the Springfield-Peoria region to the north; therefore only generalized comments can be made concerning this area at this time.

Maps illustrating the trends in a number of mineralogical parameters are given in Figures 9 to 13, and 15 to 21. The total amount of mineral matter and the percentage of low-temperature ash in the coal (fig. 9) varies from 10 to 24 percent for the seam composites in the study. There is a general increase in the percent of LTA from the eastern and southeastern parts of the basin towards the northwestern sector, but this is difficult to delineate adequately by contouring. This trend is better defined if the pyrite and calcite are discounted and only the quartz and clay fraction of the ash is considered. By the use of the percentages of pyrite (from pyritic sulfur) and then the percentages both of this pyrite and of calcite (from X-ray diffraction), the proportion of the remaining components was calculated, and the results plotted in Figures 10 and 11. Because of the possibility that some of the calcite has been destroyed by reactions associated with pyrite oxidation, the percentages are circled for those samples where the amount of pyrite indicated by X-ray diffraction is significantly less than that calculated from the pyritic sulfur content of the coal. These samples have been treated with some degree of caution in the interpretation of the data, but it can still be seen that the lowest percentage of this essentially clastic ash is in the southeast, especially in Kentucky, and the percentage of pyrite increases to the northwest

The pyrite content of the mineral residue, as determined from the pyritic sulfur content of the coal, varies from approximately 10 percent (locality 9) to more than 30 percent (locality 17) in slightly more than a mile (fig. 12). A similar, but less marked variation also occurs at localities 8 and 16 (fig. 12), but apart from this the percentage of pyrite in the mineral matter remains between 20 percent and 30 percent throughout most of the basin. Values in excess of 30 percent of pyrite are found in the western part of Kentucky; a single value of 48 percent, in one sample from Indiana; and values of less than 20 percent are associated with contemporaneous channel sandstone deposits in parts of southeastern Illinois. The area containing lower pyrite content as depicted on Figure 12 is obviously influenced by the presence of the sandstone channel that trends from northeast to southwest.

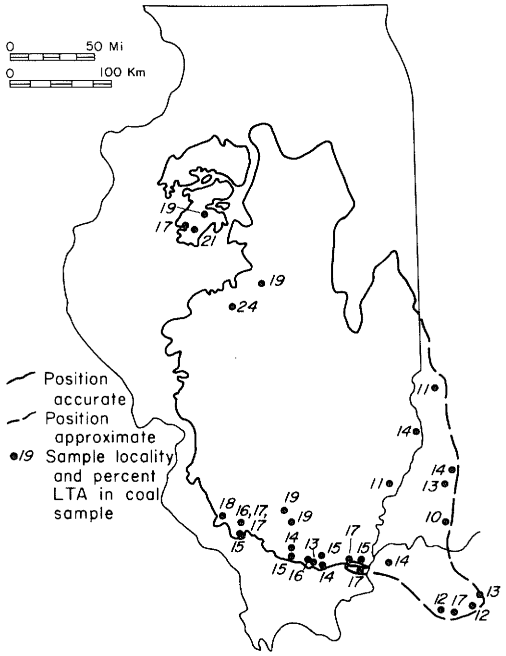

Fig. 9 - Percentage of low-temperature ash in samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents.

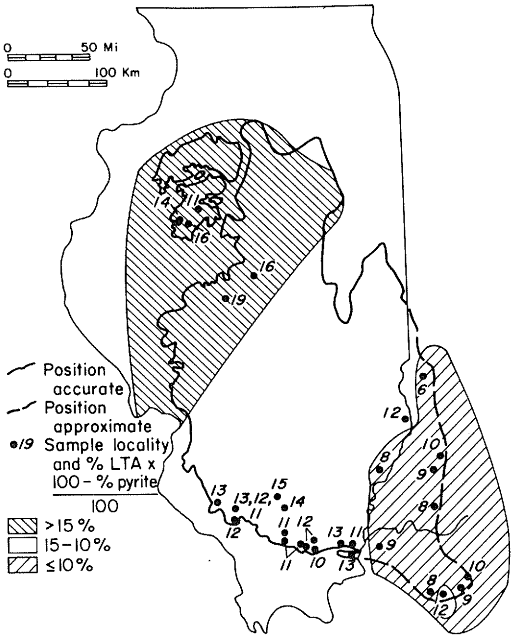

Fig. 10 - Percentage of mineral matter (corrected for pyrite) in samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents.

The ratio of pyritic sulfur to organic sulfur shows a fairly well defined trend (fig. 13). Low values, which indicate greater abundance of organic sulfur than pyrite, occur around the margins of the basin; high values, where pyrite is dominant, occur toward the center. A graphic plot of the pyritic and organic sulfur content of the coals in the study (fig. 14) shows no particular correlation of one form with the other.

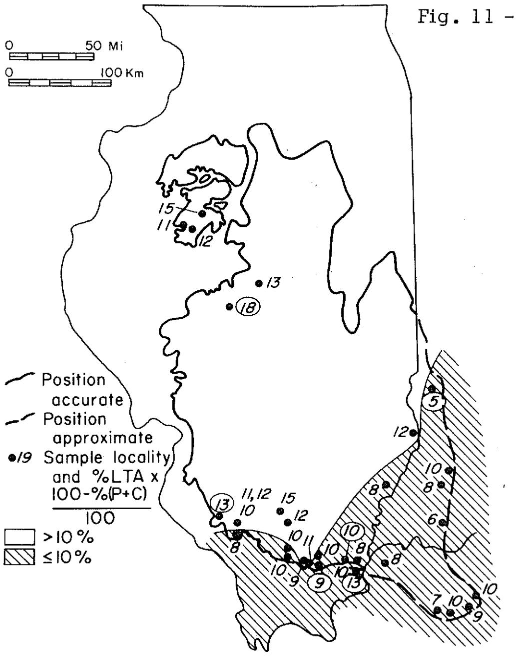

Fig. 11 - Percentage of mineral matter (corrected for pyrite and calcite) in samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents. (Circled percentages indicate that calcite value may be low because of pyrite oxidation.)

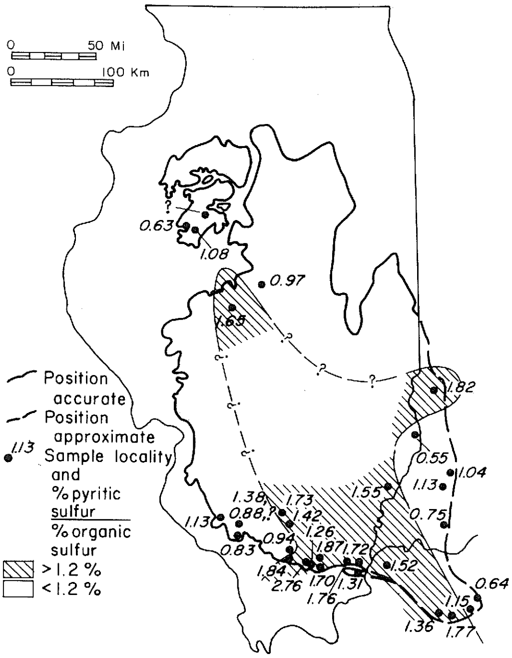

Fig. 13 - Ratio of pyritic sulfur to organic sulfur in samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents. (A question mark indicates that the pyritic-sulfur content has not been determined.)

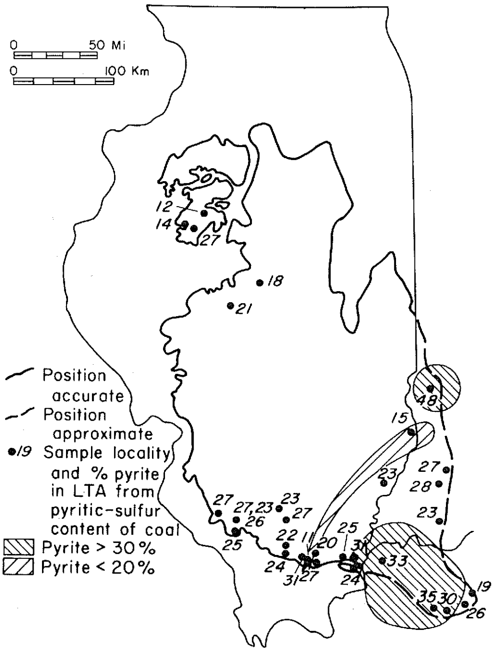

Fig. 12 - Pyrite content of mineral matter in samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents. (A question mark indicates that the pyritic-sulfur content has not been determined.)

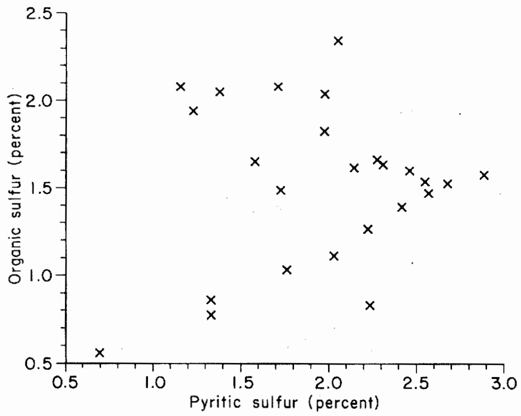

Fig. 14 - Graphic comparison of pyritic sulfur and organic sulfur content of samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents.

The percentage of quartz in the low-temperature ash, as indicated by X-ray diffraction, varies from 8 to 28 percent. However, the lateral distribution of these values, as shown in Figure 15, fails to show any particular trend; therefore, it is concluded that this mineral is essentially uniformly distributed throughout the basin.

Although the amount of calcite present may be reduced by reactions associated with pyrite oxidation, the calcite content of the ash varies from trace amounts to 25 percent in the study area (fig. 16). Most values are less than about 10 percent, but clusters of higher values occur in the Springfield-Peoria region and in southeastern Illinois.

Despite differences in analytical technique, the pattern that is exhibited by variations in the clay minerals in the No. 5 Coal is broadly similar to that pattern indicated for the Herrin (No. 6) Coal Member by Rao and Gluskoter (1973). However, as indicated below, because there are sufficient anomalies present, caution is required in the application of the above conclusions to the present studies.

Although the total amount of mineral matter in the coal varies significantly across the basin, the total clay content of the low-temperature ash itself [100 - (%Q + %C + %Py)] remains essentially constant except in the belt around the sandstone channel of southeastern Illinois. In this area, the total clay content approaches 70 percent of the mineral matter; elsewhere it is between 50 and 60 percent (fig. 17).

The kaolinite content of the < 2 μm fraction of the ash is highest in the eastern and southeastern parts of the study area, and reaches 50 percent in one of the samples from Kentucky (fig. 18). High values, in excess of 30 percent, also are found in the eastern part of the Springfield-Peoria region, but too few samples are available to adequately define the trend in this area. The belt of thick coal that was delineated by Hopkins (1968) in southwestern Illinois

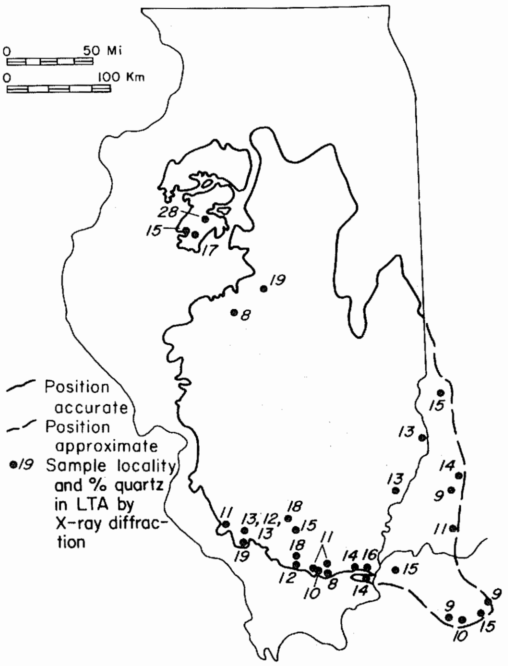

Fig. 15 - Percentage of quartz in mineral matter of samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents.

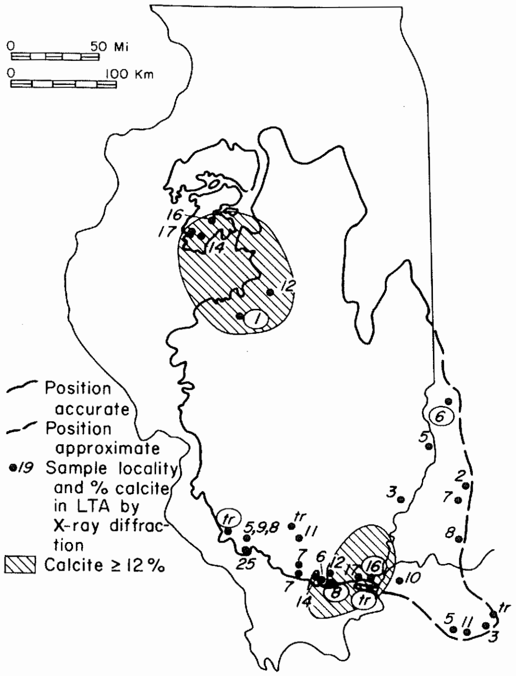

Fig. 16 - Percentage of calcite in mineral matter of samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents. (Circled percentages indicate that calcite value may be low because of pyrite oxidation.)

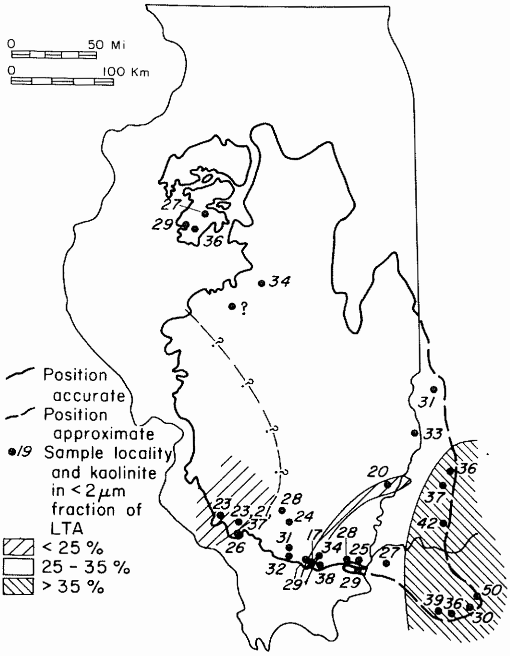

Fig. 18 - Percentage of kaolinite in <2 μm fraction of mineral matter in samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents.

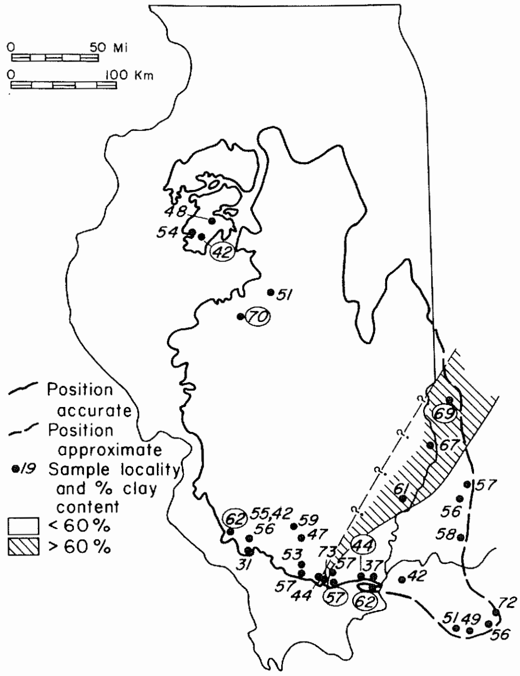

Fig. 17 - Total clay content of mineral matter in samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents. Value determined by equation [100 - (% Quartz + % Calcite + % Pyrite)]. (Circled percentages indicate that clay content may be high because calcite might be lost because of pyrite oxidation.) (A question mark indicates that the pyritic-sulfur content has not been determined.)

also corresponds to a zone where the kaolinite content of the ash is low, in fact, even lower than that farther west. Kaolinite also is much less abundant in the roof and floor strata of the seam. The mineral matter of the coal in this zone approaches the composition of these rocks more than that from other parts of the basin. However, the coal seam is still free of visible clay bands and contains no more quartz and clay than is found in the surrounding areas.

The illite content of the clay fraction is mostly between 40 and 50 percent, although values to 57 percent have been determined for a few samples. In this study there does not appear to be any significant variation in the proportion of illite in the < 2 μm fraction of the ashes; therefore, a uniform distribution is interpreted (fig. 19).

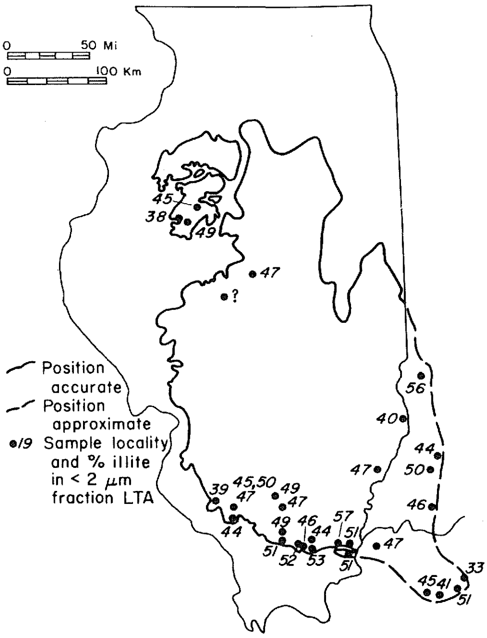

Fig. 19 - Percentage of illite in < 2 μm fraction of mineral matter in samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents.

The expandable clay minerals exhibit no particular regularity of structure; they can only be adequately evaluated when heated, oriented aggregate mounts are used. The proportion of expandable minerals, as shown in Figure 20, varies from less than 10 percent (locality 6) to almost 40 percent (locality 14). The proportion is particularly low in the southeast; with one or two exceptions, all values in Indiana and Kentucky are less than 25 percent. The percentage of expandable clays is also low in the samples from the eastern part of the Springfield-Peoria region, but the percentage increases in the southwestern corner of the study area. The belt of thick coal in southeastern Illinois also is associated with an increase in the proportion of expandable clay minerals. In fact, the study indicates that the proportion of expandable clays is highest in those areas where the kaolinite content of the ash is lowest.

The relative abundance of expandable clays in relation to the illite content of the < 2 μm fraction of the low-temperature ash is best illustrated by the variation in their ratio, expressed by the formula:

$$100 \times \frac{I}{I + Ex} \quad \text{or} \quad \frac{100\ (\text{Illite }\%)}{(\text{Illite }\% + \text{Expandable }\%)}$$

It is necessary to consider these two clay mineral phases alone, without the influence of the kaolinite present in the sample, because of the large amount of diagenetic kaolinite present in these coals. The ratio used here is almost identical to the "diffraction effect ratio" used by Gluskoter (1967) to illustrate trends in the Herrin (No. 6) Coal Member, but the results cannot be directly compared because of differences in the methods of calculating the clay mineral proportions. The lateral variation in this ratio (fig. 21) shows that areas that have relatively low values of illite will have correspondingly higher values of expandable clay minerals. This is true in the sandstone channel area, and, again, in the western part of the basin, although the remaining areas exhibit no particular trend. A graphic plot of this ratio to the kaolinite content of the < 2 μm fraction (fig. 22) shows a positive correlation similar to that described in the No. 6 Coal by Gluskoter (1967).

DISCUSSION

Geologic Setting of the No. 5 Coal

The stratigraphy of the Pennsylvanian of Illinois is summarized by Willman et al. (1975). According to this summary, the sediments were deposited in a gently subsiding trough that was open towards the south until it was closed by uplift of the Pascola Arch during post-Pennsylvanian times. Isopach studies show that the greatest subsidence took place in the southeastern part of the state, and that in the southwestern and northern regions a more stable shelf was developed.

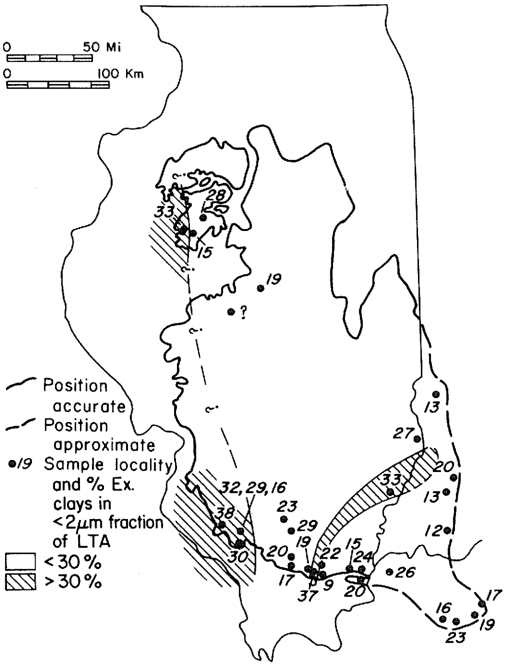

Fig. 20 - Percentage of expandable clays in < 2 μm fraction of mineral matter in samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents.

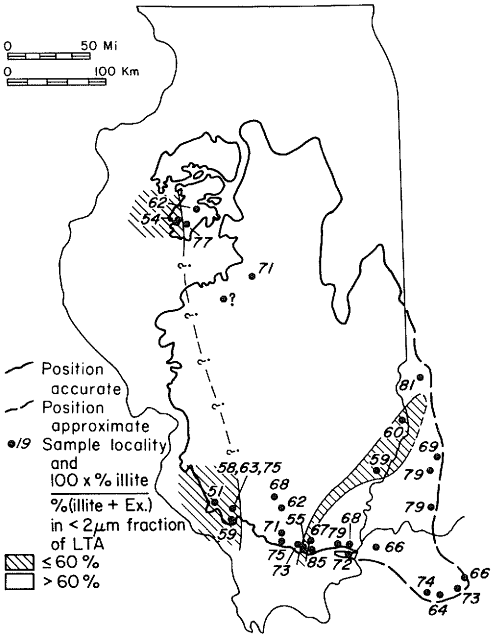

Fig. 21 - Ratio of illite to expandable clays in < 2 μm fraction of mineral matter in samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents.

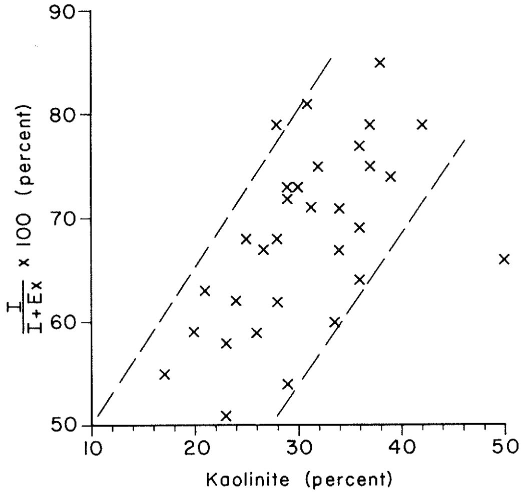

Fig. 22 - Graphic plot showing relationship of illite and expandable clays content to kaolinite content in < 2 μm fraction of mineral matter in samples from Springfield-Harrisburg (No. 5) Coal Member and equivalents.

According to Wanless et al. (1969) the sediments were introduced from source areas in the north, northeast, and east, with some additional material from the northwest. In periods of marine regression, rivers flowed southwestward across Illinois to build extensive delta complexes out into shallow seas. The cyclothems, long recognized in this area, may be interpreted as records of individual delta progradations in which the coal formed on broad delta plains a short distance above sea level at the top of each sequence during the final phase of sedimentation. Because of decreasing or shifting sediment supply, the coals were gradually overwhelmed by marine conditions that caused laminated black shales to be deposited on top of them. However, in places such as the thickened belt in the No. 5 Coal of southeastern Illinois, river action was stronger; gray, terrestrial shales were deposited on top of the coals prior to, or during, the early stages of the marine transgression (Hopkins, 1968).

Isopach studies of both the No. 5 Coal and the interval between it and the Herrin (No. 6) Coal Member show substantial thinning in a belt running southwestward from Vermilion County to the shelf area in the west of the basin (figs. 23 and 24). This belt, which probably is related to structural features in the area, separates the basin into two regions where substantial coal accumulation occurred. The two regions are separated by what appears to have been a more positive area where deposition was limited by slower subsidence. Thick coal was deposited in the Springfield area, where isopachs of the Carbondale Formation show an overall thinning of the sequence (Clegg, in Willman et al., 1975, p. 180) and subsequent development of a separate delta lobe. However, the major zone of deposition was to the south of this barrier; the Carbondale Formation, the No. 5 Coal, and associated strata thicken rapidly in southeastern Illinois and the adjoining parts of Indiana and Kentucky.

In the central part of this area the coal is cut out by a channel-fill sandstone, but immediately adjacent to the channel, abnormally thick coal is developed. Hopkins (1968) has interpreted this zone as the infilling of a major delta distributary, which persisted as an open, active channel throughout the period of peat accumulation. This channel lies along the belt of maximum thickness for the Carbondale Formation; it probably formed in the zone of maximum subsidence for the basin at that time. Remnants of other smaller channels have also been noted in various parts of the basin.

Mineralogical Trends in the Basin

Noncoal strata

Factors that control the petrology and clay mineralogy of the Pennsylvanian strata of Illinois are discussed by Glass (1958). More detailed studies of a number of underclays of major coal seams have been made by Parham (1962) and Odom and Parham (1968). According to Glass (1958), the strata of the Carbondale Formation belong to a subgraywacke (lithic sandstone) suite that includes sandstones composed of quartz, feldspar, mica, rock fragments, and chlorite. The less than 2 micrometer fraction of the shales contains kaolinite (approximately 15%), illite (45%), mixed lattice clays (15%), and chlorite (25%).

Glass pointed out that the shales from parts of the cyclothem underlying the coal seams were richer in kaolinite and mixed-lattice minerals and were poorer in illite and chlorite than those shales of the beds above the coal. These differences were interpreted as reflections of environmental conditions associated with the coal swamp and the immediately underlying sediments, rather than reflections of the effects of changes in source materials.

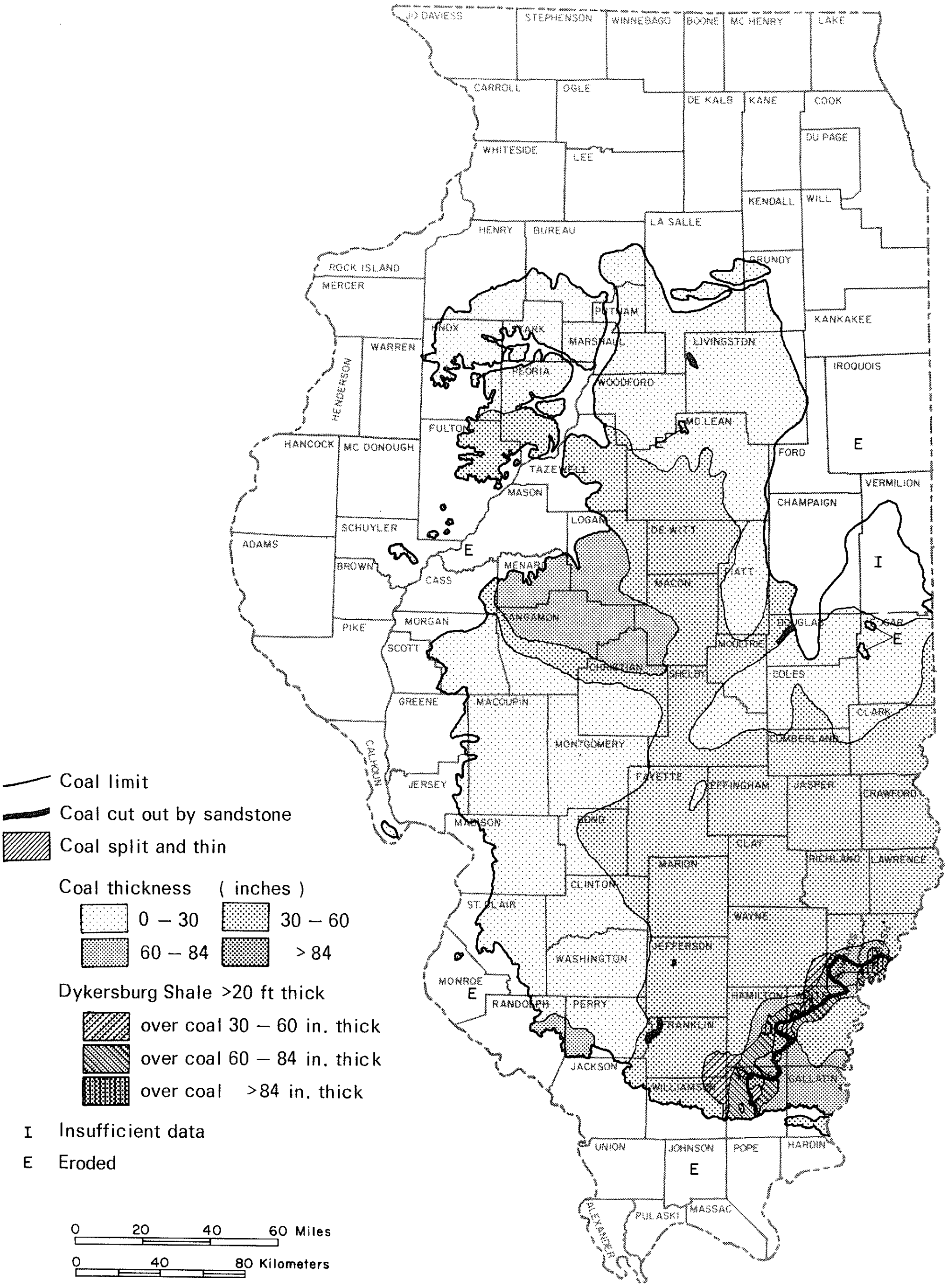

Fig. 23 - Generalized thickness of Springfield-Harrisburg (No. 5) Coal Member and equivalents (from Smith and Stall, 1975, p. 26).

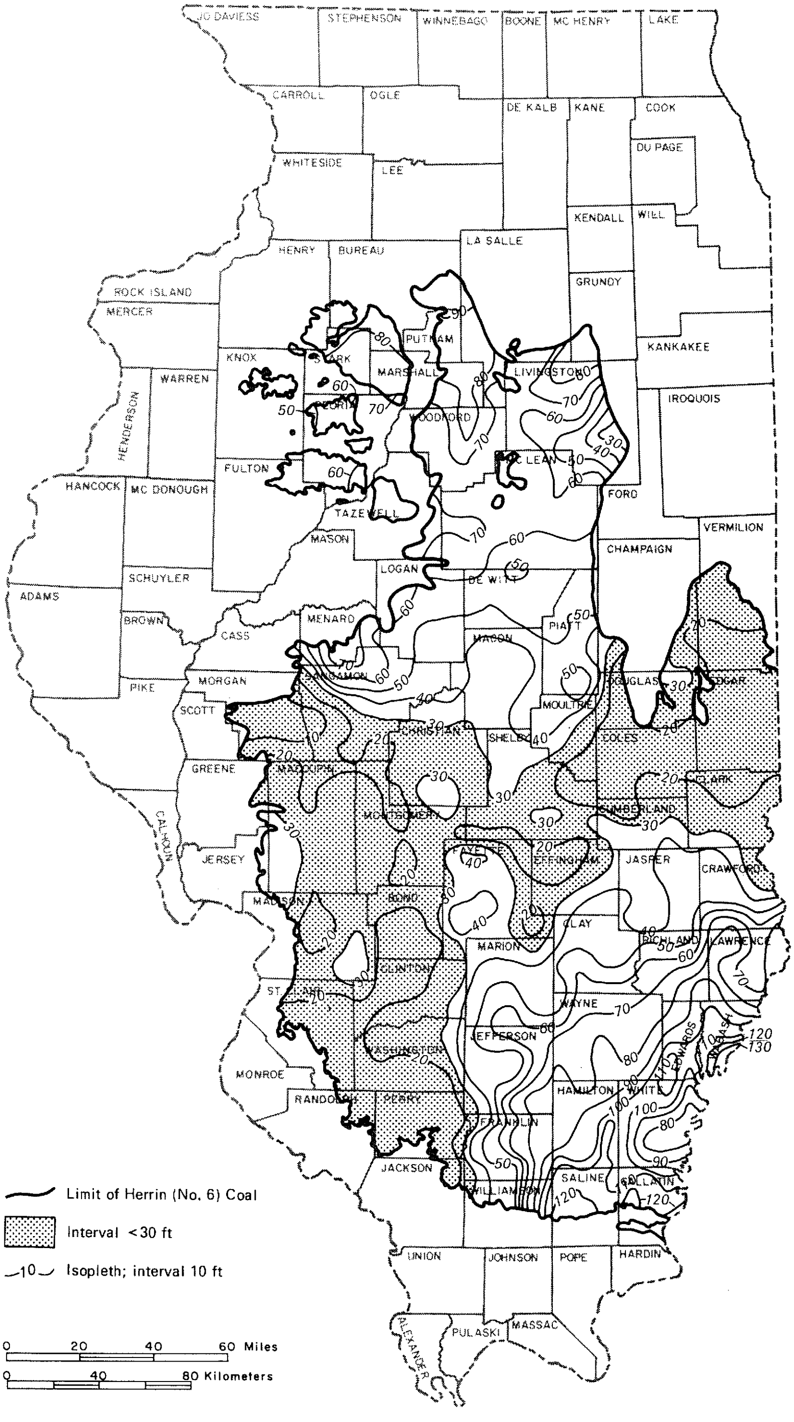

Fig. 24 - Generalized thickness of the interval between the Herrin (No. 6) and Springfield-Harrisburg (No. 5) Coal Members and equivalents (from Smith and Stall, 1975, p. 30).

Odom and Parham (1968, p. 13) found the underclay of the No. 5 Coal to be generally of uniform mineralogy throughout most of the basin; the clay fraction consisted mainly of illite, a small amount of kaolinite, and varying proportions of expandable clays and chlorite. Expandable clays are more abundant in the Springfield-Peoria area, where lesser amounts of illite are present and chlorite is generally absent.

The clay mineralogy of 21 argillaceous rocks from strata comprising roof and floor of the No. 5 Coal Member was investigated in order to supplement the information from the coal itself. These samples were taken from one outcrop in a strip mine (locality 31, fig. 1) and from 9 boreholes, the cores of which were available in the repository of the Illinois State Geological Survey. The locations of these samples are shown in Figure 25, and their mineralogy is given in Table 7. The results obtained generally confirm the observations of Glass (1958), but have illustrated a much greater degree of variability for the mineralogy of these rocks as compared to that of the low-temperature ash of the coal.

Except for some of the samples taken from immediately adjacent to the coal seam, the roof and floor rocks contain much less kaolinite than do the mineral matter residues from the coals. In some cases, only a trace of kaolinite can be detected. Chlorite is present in most of the samples in the study; chlorite may also constitute the bulk of the material that is described as kaolinite in those samples where the 7 Å peak is of low intensity. However, as was indicated earlier in this text, reliable resolution of the chlorite and kaolinite peaks is not possible for the samples in this study.

The proportion of expandable clays in relation to illite, expressed by

$$\frac{100 \times I}{(I + Ex)},$$

is generally slightly lower for the claystones than that proportion observed for the coals in the same area. Expandable clays are particularly abundant near the western edge of the basin (localities b and c, fig. 25), but are much less abundant in samples taken only a short distance away. This variability probably is due, in part, to differences in grain size of the sediment and to differences in relative stratigraphic position. More samples are needed to adequately define the trends.

The mineralogy of the samples taken from immediately adjacent to the seam, in some cases, resembles very closely that of typical coal samples; these materials probably represent an extension of the coal swamp conditions. Similar trends of kaolinite enrichment close to the coal contact were also noted by Odom (1963), but, as can be

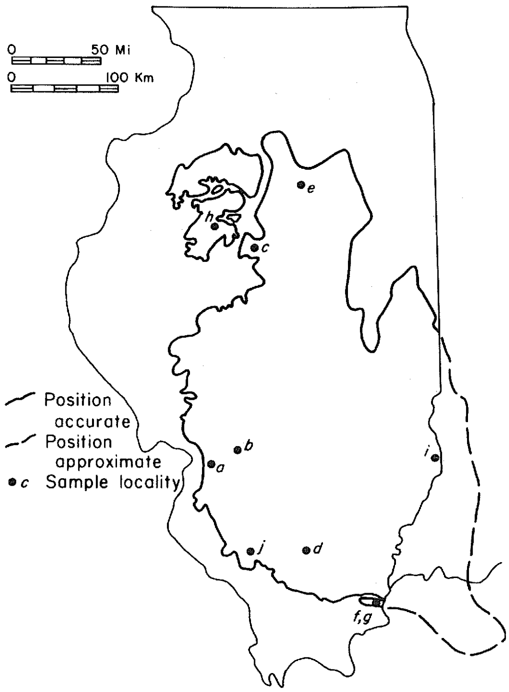

Fig. 25 - Location of samples from rocks comprising roof and floor of Springfield-Harrisburg (No. 5) Coal Member and equivalents. See table 7 for sample identification and other details.

seen from Table 7, this feature is only sporadically developed. In fact, the kaolinite-rich lutites may represent patches where the peat has been decomposed by oxidation shortly after formation, and the mineral matter is left to accumulate as a carbonaceous shaley deposit until burial by other clastic debris.

Other coal seams

In their study of the mineral matter in the Herrin (No. 6) Coal Member, Rao and Gluskoter (1973) found that the percentage of calcite in the ash increased from east to west across the basin, although the total clay content decreased. Illite decreased from east to west, and expandable clay minerals increased in the same direction. Kaolinite and quartz were found to be most abundant in the zone surrounding the contemporaneous channel-fill structure within that seam, although the percentage of pyrite was lowest in this area. The ratio of pyritic sulfur to organic sulfur decreased in the western part of the basin.

These changes were considered to reflect a westward transition into progressively more saline swamp waters; differential sedimentation, aided by preferential flocculation, caused kaolinite and illite to be deposited in the landward regions and the mixed layer clays to be carried farther seaward. Such a mechanism was first suggested by Parham (1962) in his study of the underclay of the No. 6 Coal, and was applied to the mineral matter in the coal by Gluskoter (1967). An investigation of the boron content of the illite in this coal (Bohor and Gluskoter, 1973) confirmed the increasing marine influence away from the channel zone, and suggested that the western side of the channel exhibited evidence of higher paleosalinity than did the eastern side.

A selection of the samples of the Herrin (No. 6) Coal Member that were studied by Rao and Gluskoter (1973) was re-examined using the techniques of the present study. Although only four samples were used for this aspect of the program, the samples were taken from widely separated parts of the basin. Because the results were found to be in reasonable agreement with those of Rao and Gluskoter (1973), this number is considered to be a sufficient basis for at least a preliminary comparison.

The proportions of nonclay minerals in the Herrin and Springfield-Harrisburg Members were found to be very similar, although the pyrite content of the mineral matter residue does not exceed 30 percent for the No. 6 Coal. However, the mineralogy of the clay fraction does show significant contrasts; the Herrin Coal Member is richer in expandable clays and poorer in illite and kaolinite when compared to the No. 5 seam. Chlorite is also present in trace amounts in a few samples of the No. 6 Coal. Similarly, this mineral is not sufficiently abundant in the Springfield-Harrisburg Member to appear in more than a few of the samples.

ORIGIN OF THE MINERAL MATTER AND ITS VARIATIONS

Interpretations regarding the origin of the mineral matter in the No. 5 Coal must take into consideration the contrasts between the assemblage in the coals and that of the other Pennsylvanian strata and the lateral variations in this mineral assemblage throughout the basin. The abundance of kaolinite in the coals compared to its presence in the roof and floor rocks is one of the most significant features; similar trends are reflected elsewhere in the world (Ward, 1976). It is also significant that, for most samples, the coals are deficient in expandable clay minerals and enriched in well ordered illite when compared to samples from the associated noncoal strata. In fact, the illite to expandables ratio

$$\left[\frac{100 \times I}{I + Ex}\right],$$

in a number of cases, is greater even than that for marine shales in the roof of the seam.

For the present study, the Illinois Basin is divided into three types of depositional areas, areas representing an extension of those illustrated by Glass (1958). The first of these areas referred to in Figure 26 as the "shelf facies" corresponds to the belt where both the No. 5 Coal and the overlying strata are relatively thin—in some cases, where no coal is present. In western Illinois, the eastern boundary of this zone is marked by the Du Quoin Monocline; in the eastern part of the state, although its position is uncertain, it is probably influenced by the La Salle Anticlinal Belt. This zone is believed to be an area where the rate of subsidence was lower than that for the remainder of the basin. The zone is restricted to the basin margins except for the area in central Illinois where it separates the sequence in the Springfield region from that to the southeast.

The two areas that are away from the shelf facies contain a much thicker sedimentary succession, and the No. 5 Coal is usually about 4 feet thick. The rate of subsidence appears to have been greater in this region, particularly in the southeastern section, which is also the site where the Carbondale Formation as a whole attains its maximum thickness. In this study, these two areas are called the "basin facies"; they represent the areas in which marine incursion into the basin is more likely to have occurred and where the peat is least likely to have been exposed for any length of time.

Within the basin facies in southeastern Illinois is the belt of thick coal that is previously mentioned in this text. This coal belt is associated with a sandstone-infilled distributary channel and areas of split coal. This zone is referred to as the "channel facies." It represents a major delta distributary, which was established along, or close to, the area of maximum subsidence at the time of coal accumulation. Other channels of similar type are indicated by additional "washout" structures in Franklin and Douglas Counties (Smith and Stall, 1975, p. 26), but these are relatively minor features that are close to the shelf facies of the coal basin.

In the channel facies, the mineral assemblage in the coals most closely resembles that of the associated noncoal strata. The amount of kaolinite is low, and the proportion of expandable

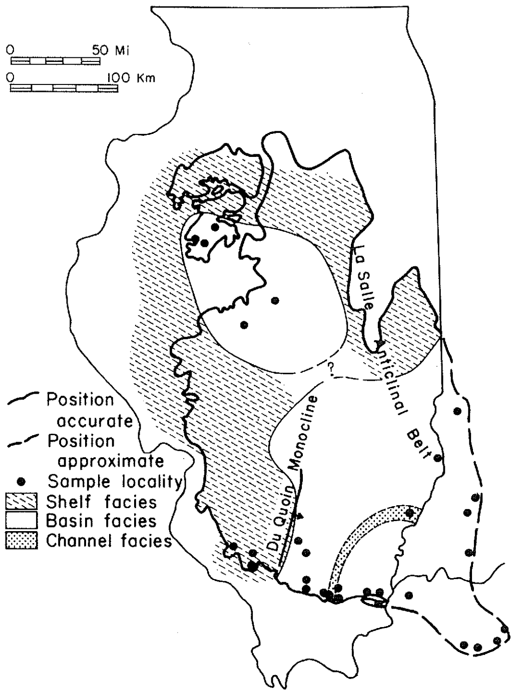

Fig. 26 - Distribution of shelf, basin, and channel facies (based on thickness and mineralogical data) of Springfield-Harrisburg (No. 5) Coal Member and equivalents.

clays is relatively high. In diffractograms derived from air-dried slides, the diffraction zone of the expandable clays merges with the 10 Å illite peak. This pattern suggests that a higher proportion of expandable clays is related to the illite structure than in other samples in the study. Pyrite and calcite are present only in small amounts; total sulfur content generally is low; and a trace of siderite also is present in one sample from the channel facies area.

The coals of the basin facies, however, are dominated by kaolinite and pyrite, with calcite or dolomite being locally abundant. The percentage of expandable clays is low, and the 10 Å illite peak is quite sharp in diffractograms of air-dried samples.

In part, this contrast can be explained by the rate of clastic influx in each part of the basin. Near the distributary channel, overbank deposits of suspended clay could contaminate the peat more readily than in more distant areas because obstruction by the growing vegetation would prevent much of this material from penetrating to the peat (Frazier and Osanik, 1969). In the area of the channel, the swamp waters would also be flushed frequently by fresh water. In the more basinward regions, the circulation would be limited, and, as suggested above, the waters may be partly marine.

One of the effects of these conditions in the basin facies was probably solution of part of the expandable clay fraction by organic acids. Huang and Keller (1972) produced a marked sharpening of the 10 Å illite peak in experiments using an illite sample from Fithian, Illinois, that was treated for over 500 days with salicylic acid. They suggested that this pattern reflected selective solution of material with larger "d" spacings. Such a process is a more likely explanation for the ratio of high illite to expandables in the coals of the basin facies rather than regrading of the illite by K+ ions in the swamp. The process accounts for the fact that more well ordered illite is present in the coals than in the marine shales where the regrading process would be at a maximum. However, the two processes probably acted together in this particular situation. The effects of these acids would be less noticeable in the channel region, where the combination of more sediment influx and better water circulation would tend to preserve at least some of the mixed-layer material, and in the shelf area, where a slower rate of peat formation was involved and the rate of clastic accumulation was relatively higher.

At least part of the kaolinite in the coals of Illinois is authigenic (Ball, 1934; Gluskoter, 1967), authigenic meaning that it was formed at the site of deposition (Gary et al., 1972). No attempts have yet been made to explain the actual processes surrounding its crystallization. The occurrence of kaolinite as a coating on cleat surfaces suggests that much of this material may have formed relatively late in the coalification process, possibly by deposition from circulating groundwaters. However, the presence of kaolinite-rich carbonaceous shales that are immediately adjacent to the seam means that the material was more likely a syngenetic deposit formed at the same time as peat accumulation. The kaolinite-rich shales do not exhibit the coatings on their joint surfaces; probably these shales represent mud that accumulated from the peat swamp without the coal-forming organic matter.

Well ordered kaolinite is also abundant in a number of other American coals (O'Gorman and Walker, 1971) and in coals from Australia (Ward, 1974). Kaolinite is not infrequently the only significant clay mineral detected in oxidation residues; it can occasionally be seen in petrographic studies as a crystalline infilling of cell cavities in the coal macerals (Kemezys and Taylor, 1964). Well crystallized kaolinite also forms the major constituent of kaolinite claystones (flint clays or tonsteins), which are common in coal-bearing sequences throughout the world (Keller, 1968; Loughnan, 1971a). These claystones, too, show textural evidence that at least part of the kaolinite was precipitated in situ (Carozzi, 1960).

The fact that most kaolinite claystones occur as the roof, floor, or intraseam bands of coal seams (for example, Loughnan, 1971b; 1975) suggests that the origin of the stones is related to that of the kaolinite in the coals themselves. Keller (1968) considered that leaching of more mobile cations from normal clastic sediment by upward dialysis of the swamp waters was responsible for the formation of this kaolinite and, in extreme cases, even produced bauxite minerals. Leaching, or a similar mechanism, was applied by Hughes and White (1969) to the formation of an impure flint clay in the Carbondale Formation in Sangamon County, Illinois; such a process may also be applied to the present study of the No. 5 Coal Member. Kaolinite is most abundant in the basin facies, where reduced influx of clastic debris and of fresh water means that the activity of the swamp will extract more of the mobile ions from the sediment than elsewhere in the area.

However, a number of other features of the kaolinite claystones throughout the world and the fact that not all of them occur in coal-bearing sequences suggest that the kaolinite is derived from lateritic weathering in the sediment source area (Loughnan, 1970). The occurrence of bauxite minerals in these rocks is considered particularly to favor such an origin (Curtis and Spears, 1968), as is the discovery of lateritic paleosols associated with some of these beds in at least one coal-bearing sequence (Loughnan, 1975).

If the kaolinite in the No. 5 Coal was derived by simple detrital action from such a source area, kaolinite would be expected to be most abundant in the channel facies, and would be prevented from reaching the more basinward regions by flocculation and settling. However, if the silica and alumina, liberated by perhaps only moderate weathering, were introduced to the basin in the form of solutions or gels, interaction that forms kaolinite could have taken place in any depositional environment free of other clastic activity. Experiments by La Iglesia Fernandez and Martin Vivaldi (1972) have shown that kaolinite can be produced from solutions with relatively low concentrations of SiO_2 and Al^{3+}, if fulvic acid, which is extracted from modern-day peat, is present as a catalyst. The coal swamp is thus an ideal place for such precipitation to occur, particularly those areas where other clastic debris does not penetrate readily.

Curtis and Spears (1968) have suggested that illite will be produced in addition to kaolinite, if the SiO_2 and Al_2O_3 were to come together in a marine environment, because of the incorporation of K^+ in the structure. Also, a range of mixed-layer clays might be produced, if other cations were present. By such an explanation, a single process would account for the clay minerals in the No. 5 Coal; illite would form along with kaolinite in the basin facies under the influence of marine waters; and expandable, mixed-layer clays would form in the less saline channel and shelf facies. However, more research on these aspects is required before it is known if such a process is possible under sedimentary conditions.

The distribution of the other minerals in the coals also conforms with the interpretations given above. Pyrite is most abundant in the more actively subsiding parts of the basin facies, where it was probably produced by bacterial reduction of sulfate ions (Gluskoter and Hopkins, 1970). The sulfate ions, in turn, were most likely to be introduced by marine incursions. As discussed above, the area of basin facies would be the principal area where at least brackish waters would be found.

By contrast, pyrite is considerably less abundant in the channel facies, where the swamp waters would have been relatively fresh because of proximity to the major distributary system. This pattern could have been aided by the development of a slightly higher Eh in that area because of the greater degree of water circulation, and because of dilution of the chemical sediments with additional detrital mud. A combination of these reasons, but to a lesser degree, was also responsible for a slight reduction in the pyrite content of the coals in the area of the shelf facies.

Also, the presence of a small amount of siderite in one sample taken from the channel region suggests that lesser amounts of sulfate ions were present, and that at least some of the iron was available to react with dissolved CO_2 in the swamp waters. According to Kemezys and Taylor (1964), siderite in Australian coals is found only in seams that are associated with fresh water strata, rather than in marine beds. This statement gives further support to the interpretation of the channel as a delta distributary.

The other carbonate minerals in the coal are more abundant in parts of the basin facies, but, because the determination of the amount present is open to some problems, less definite conclusions can be drawn. Calcite and dolomite appear to be formed in some coals at a later stage than most of the other minerals (Kemezys and Taylor, 1964); in some cases, calcite and dolomite may owe their origin to relatively late deposition from ground water.

The total amount of "essentially detrital" mineral matter in the coal (that is, the percentage of low-temperature ash corrected for pyrite and calcite) decreases markedly in the area that is south of the channel facies. As indicated above, this trend appears to follow the subsidence pattern of the Carbondale Formation as a whole. It is believed that this pattern reflects a regional increase in detrital activity and/or a decrease in subsidence rate for the northwestern part of the basin, relative to the actively subsiding zone in the southeast. The amount of detritus, which accumulated per unit volume of coal, increased accordingly in the northern area.

This trend is not strongly reflected by the actual mineral assemblage that is present in the coal. The "total clay" content of the mineral matter does show a marked increase in the channel facies as compared to that of the remainder of the basin; this is thought to reflect the greater clastic influx and reduced chemical activity of that zone in the coal swamp as described above.

The vertical trends in the mineralogy of the No. 5 Coal have yet to be fully evaluated by a systematic sampling program. In both bench sets studied, the increased proportion of expandable clays near the top of the seam is thought to reflect increased clastic activity, or a declining rate of peat formation as the swamp was "drowned" by the subsequent marine transgression. The presence of chlorite in the lower benches is noteworthy in view of its alleged instability in swamp conditions. However, except for the possibility of the appropriate cations reacting with silica and alumina to form chlorite, rather than mixed-layer clays, no explanation can be put forward at this stage other than simple detrital accumulation.

Comparison with the Herrin (No. 6) Coal Member shows that expandable clays and chlorite generally are more abundant throughout the basin than they are in the No. 5 Coal. This is probably due to the fact that the channel facies of the No. 6 Coal occupies a much larger part of the basin than it does for the No. 5 Coal Member, so that many more samples of that type of coal are available. However, large areas of the basin exist where neither coal member has been sampled at a sufficiently close interval. More work is needed to adequately evaluate these trends.

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