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Occurrence and Distribution of Minerals in Illinois Coals

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ABSTRACT

Mineral matter from 65 coal samples from the Illinois Basin was obtained by radio-frequency low-temperature ashing. The mineral matter was investigated by X-ray diffraction analyses, chemical analyses, and microscopic analyses.

The minerals commonly occurring in Illinois coals are illite, kaolinite, mixed-layer clay minerals, quartz, calcite, and pyrite. Siderite, dolomite, feldspar, gypsum, marcasite, and sphalerite have been identified by X-ray diffraction but are generally present in only trace amounts. The relative abundances of the major minerals are similar in most of the mineral-matter samples; the mean values are: total clays, 52 percent; pyrite, 23 percent; quartz, 15 percent; and carbonates, 9 percent.

All but the extremely fresh coal samples also contain iron sulfate minerals that have formed from the oxidation of pyrite and marcasite. Szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) and coquimbite [$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$] are those most commonly observed.

Forty-one of the coal samples studied are from the Herrin (No. 6) Coal Member. The major minerals in this coal are similar in overall composition to the mineral matter in all Illinois coals studied and occur in the same relative order of abundance: total clays (55 percent), pyrite (21 percent), quartz (15 percent), and calcite (9 percent).

A model of the depositional environments of the Herrin (No. 6) Coal is proposed on the basis of (1) the mineralogical and chemical data presented here, (2) the results and interpretations of previous workers who have studied the stratigraphy of the coal and related strata, (3) the mineralogy of underclays and roof shales, and (4) the chemistry of the coal. A model of a delta system is proposed for the

southern portion of the Illinois Basin; it consists of three roughly parallel, contiguous paleoenvironmental zones: (1) a low positive area of shallow water on the northeast, (2) an area encompassing a sandstone (distributary) channel, and (3) a more open-marine area to the southwest. The distribution of the minerals in the coals can best be interpreted as a response to both the general northeast to southwest paleoslope and the presence of a distributary channel system contemporaneous with the coal swamp.

INTRODUCTION

The term "mineral matter" has been applied to all inorganic non-coal material occurring in coal and also to those elements usually considered to be inorganic, even if they are in organic combination. That is, all elements in coal except carbon, hydrogen, oxygen, nitrogen, and sulfur are considered to be part of the mineral matter, and four of these "organic" elements also occur in inorganic combination in coals. Carbon may be present in carbonates Ca(Fe,Mg)CO_3 ; hydrogen in free water and water of hydration; oxygen in water, oxides, carbonates, sulfates, and silicates; and sulfur in sulfides (primarily FeS_2) and sulfates.

Silicates, sulfides, sulfates, and carbonates are the most commonly occurring major minerals. The mineral matter in coal occurs predominantly as various mineral phases. The portion that exists in organic combination, although in some instances of great significance, is generally of less importance quantitatively.

As techniques for the utilization of coal have become increasingly more sophisticated, the detrimental effects of the mineral matter have become more significant, partly because larger amounts of coal are used in single installations.

Power plants have been confronted with problems of fireside boiler-tube fouling and corrosion as higher and higher superheater temperatures have been achieved. Problems of abrasion in the mills used to pulverize the coal prior to injecting it into a powder-fuel-fired boiler have also been encountered. Lower-temperature corrosion due to condensation of sulfurous acid also has had to be dealt with. Handling of vast quantities of coal ash and finding a profitable, or at least inexpensive, method for its disposal are another important consideration for the large consumer.

The minerals associated with the coal are of concern in the mining of the coal. Problems presented by large pyrite nodules ("sulfur balls") and by seams split by mineral bands are often encountered in mining.

Within the past few years, the widespread interest of the general public in both air and water pollution has presented both the coal consumer and the producer with a pressing need to know, in much greater detail than previously, the constitution of the mineral matter in coal and its products and by-products. Much of this interest has been directed to the forms of sulfur in coal and coal refuse, to the sulfur oxides formed during combustion of the coal, and to the sulfates that form when coal oxidizes. There has been a consequent demand for data concerned with the origin, distribution, and reactions of sulfur in coal.

There is also much demand for data about the concentrations and distribution of trace elements in coals and the effects of these elements on the environment.

Not all of the interest in the mineral matter in coal stems from its detrimental effects during the utilization of the coal. In some instances coal has been investigated as a source of desired elements, such as uranium, germanium, and sulfur; and in several of the processes for gasification and liquefaction of coal currently being investigated, sulfur is considered a potentially valuable by-product.

There has been a great demand for data about the origin, distribution, and geologic significance of mineral matter in coal; but the progress in this research is hindered, mainly because of the physical inaccessibility of the mineral matter in the coal.

All the techniques previously available for mineral separation were based on some type of gravity separation and were unsatisfactory because of the large amount of inseparable mineral matter in the coal. This difficulty has been partially overcome by the use of radio-frequency low-temperature ashing.

Much of the previous work on Illinois coals has been restricted to chemical analyses of coal (Cady, 1935, 1948; Gluskoter and Rees, 1964; Gluskoter and Simon, 1968), coal ash (the oxidized products of the mineral matter) (Rees, 1964; Zubovic, Stadnichenko, and Sheffey, 1964), minerals that could be separated from the coal (Ball, 1934, 1935), or the minerals in strata associated with coal seams (Parham, 1958, 1964; Odom and Parham, 1968). Although chemical analyses of coal have some practical advantages, serious errors are encountered in converting the raw analytical data to probable mineral entities. The high-temperature coal ash is composed of the residue resulting from the ashing of the coal. The reactions involved are: loss of the water of constitution of clay minerals, decomposition of carbonates and chlorides, and oxidation of pyrite to ferric oxide and sulfur dioxide. Calculations of mineral-matter content from ash analyses by means of various formulae are often ambiguous because of these drastic changes in mineral phases.

Another difficulty, more insidious and less amenable to solution, is encountered in the study of mineral matter in coal: the system being investigated is very complicated. The complications result from the variety of physical and chemical conditions that existed in the environment in which the coal-forming materials were deposited and in which the coal formed. The system with which we are concerned, "mineral matter in coal," was a relatively low-temperature, low-pressure system with a large number of component phases. The system is an open one, and many of the components are mobile. There is also the further complication that the system has been active and may have been in the process of altering at any time during its approximately 300 million years (for coals of the Pennsylvanian System) of existence.

The mineral matter or ash in coal has often been classified as inherent (stemming from the plant material in the coal swamp) and as adventitious (added after the deposition of the plant material in the swamp). This classification is misleading, especially in the use of the term "adventitious," a synonym of which is "accidental." The detrital and authigenic minerals associated with coal are definitely not there by accident. They are the necessary result of a definite set of biological, chemical, and physical conditions, all of which combined to provide an environment in which the minerals could be deposited or in which they could form.

In the present study, an attempt has been made to investigate the unaltered mineral constituents of 65 samples of Illinois coals. In addition to determining the absolute amount of these minerals and their stratigraphic and geographic variations, an attempt has been made to suggest the depositional environments in which the coals were deposited. The techniques used include radio-frequency low-temperature ashing, X-ray diffraction analyses, and chemical analyses.

Acknowledgments

Randall E. Hughes developed the analytical techniques for the determination of the clay minerals by X-ray diffraction that were used in this study. Bruce Bohor was of invaluable assistance in the studies of mineral matter made by use of the scanning electron microscope.

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Chemical analyses reported in this paper have all been done in the Analytical Chemistry Section of the Illinois State Geological Survey. Analysts who have been involved in these investigations include R. R. Ruch, Joyce Kennedy Frost, J. A. Schleicher, J. K. Kuhn, C. W. Beeler, L. R. Camp, L. R. Henderson, L. B. Kohlenberger, J. D. Hauri, P. E. Gardner, and D. B. Heck.

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METHODS OF ANALYSES

Sampling of Coals

All of the coal samples that were subsequently subjected to radio-frequency low-temperature ashing and investigated quantitatively for mineral content were either face-channel samples or diamond-drill core samples. With both kinds, all mineral bands, partings, and nodules over three-eighths inch thick were excluded from the sample. This procedure follows a long-standing practice at the Illinois State Geological Survey and is based on a technique described by Holmes (1918).

Low-Temperature Ashing

The mineral-matter content of the 65 coals studied ranged from 9.29 percent to 22.34 percent. A technique of radio-frequency electronic low-temperature ashing was used in order to liberate the minerals from the coal in a relatively unaltered form (Gluskoter, 1965).

Several companies are currently manufacturing radio-frequency low-temperature ashing devices. In all of them, oxygen is passed through a high-energy electromagnetic field produced by a radio-frequency oscillator. The oscillator tube operates on a frequency of 13.56 Mhz in compliance with Federal

Communications Commission requirements for scientific and medical equipment. The units used in this study are Model LTA-600 manufactured by Trapelo (formerly Tracerlab), a division of LFE Corporation. Other radio-frequency ashing devices are also currently in use in the Illinois State Geological Survey laboratories, but they were not acquired until after the ashing of the specific set of samples described herein was completed.

Within a low-temperature asher oxygen is passed through the radio-frequency field and a discharge takes place. The activated gas plasma "is ... a mixture of atomic and ionic species as well as electronically and vibrationally excited states" (Gleit, 1963). The activated oxygen passes over the coal sample, and oxidation of the organic matter takes place at relatively low temperatures (less than 150°C in this study). The electronics involved are discussed in articles by the developers of the instrument (Gleit, 1963; Gleit and Holland, 1962).

Coal to be ashed in this system is ground to pass 20 mesh, placed in Pyrex boats, and predried in a vacuum desiccator prior to being put into the ashing chamber. The ashing takes place in a controlled vacuum at a pressure of 1 to 3 torr with an oxygen flow rate of 50 to 100 ml per minute. The plasma temperature may be varied by changing the radio-frequency power level. At a radio-frequency power of 100 watts the plasma temperature is approximately 70°C . Higher temperatures are reached in the ashing chambers as a result of the exothermic oxidative reaction between the activated gases and the coal. Ashing temperatures were not allowed to exceed 150°C in this study. The temperature is monitored using a Raynger model LTX-28 infrared remote thermometer.

The ashing rate is variable, depending on the strength of the radio-frequency field and on the surface area of sample exposed to activated oxygen. Therefore, the rate of ashing is influenced by the size of particles, the configuration of the sample boat, the amount of sample, the position of the sample boat in the chamber, and the frequency with which the sample is stirred. It is necessary to stir most samples in order to expose unoxidized surfaces to the oxidizing gas stream. In this investigation, 3 grams of coal were placed in each of five sample boats and the entire 15 grams of coal was ashed in approximately 72 to 90 hours. Generally, less than 2 percent of the low-temperature ash of bituminous coal in this study was composed of organic carbon.

The effects of low-temperature ashing and of the oxidizing gas stream upon pure minerals and upon minerals in coal have been discussed in earlier papers (Gluskoter, 1965, 1967). No oxidation of mineral phases present has been reported, and the only phase changes observed were those to be expected at a temperature of 150°C and a pressure of 1 torr. Therefore, of the major mineral constituents of coals, pyrite, kaolinite, illite, quartz, and calcite are unaffected by the radio-frequency ashing. Mixed-layer illite-montmorillonite clays lose interlayer water, but this loss is reversible and does not involve a phase change. Gypsum alters to hemihydrate ($\text{CaSO}_4 \cdot 1/2 \text{H}_2\text{O}$) and to $\gamma\text{-CaSO}_4$.

Although the minerals present in the coal are not affected to any appreciable degree by the low-temperature ashing of the coal, it is possible that new compounds are produced during the ashing process. In bituminous coal this effect is apparently limited to fixing sulfur, originating as organic sulfur in the coal, as a sulfate in the low-temperature ash. The number of lignites and sub-

bituminous coals that we have ashed is small, but some are much more difficult to oxidize than are bituminous coals and significant amounts of oxalate and nitrate minerals have been identified in their ash, primarily $\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (whewellite) and NaNO_3 (soda niter). The presence of these minerals in the low-rank coals is problematic and they may have formed during ashing.

X-Ray Diffraction

Sample Preparation

In order to obtain reproducible results of X-ray analyses, different sample preparation techniques were tested (alcohol smears, water smears, and cavity mounts). In preparing smears, the mineral-matter residue obtained from the low-temperature asher is finely ground, using mortar and pestle. Both alcohol-smear (95 percent) and water-smear sample preparation techniques produced chemical reactions and orientation effects in the sample. The results derived from them were only poorly reproducible. The small amount of water in 95 percent ethanol is enough to react with iron sulfate and iron sulfide minerals in the sample to form sulfuric acid, which immediately reacts with calcite and results in the formation of gypsum (fig. 1). The conversion of calcite to gypsum was confirmed on X-ray analyses of all water-smeared samples. The calcite peak on the X-ray diffractogram of the water-smeared sample is either completely lost or decreased in intensity.

To overcome the drawbacks mentioned, a cavity-mount technique was used in all the X-ray analyses. In this technique finely powdered mineral-matter residue is transferred to a thin aluminum holder which has been covered with a clean glass slide and bound firmly with transparent tape. The powder is gently tamped into the cavity of the holder with the edge of a small spatula. The excess powder is scraped level to the surface of the mount. The surface of the holder is wiped clean and a clean glass slide is taped over the filled cavity. The cavity-mount assembly is then turned over and the glass slide covering the upper surface is removed, with care being taken not to slide it across the surface before X-ray analysis.

Qualitative and Semiquantitative Analyses

The mineral-matter analyses of low-temperature ash (lta) are made by using a Phillips Norelco X-ray Diffraction System. Each powder-packed cavity mount is first X-rayed ($\text{CuK}\alpha$ radiation and X-ray focusing monochrometer) from 4° to 60° 2θ with a scanning speed of 2° per minute and a chart speed of 24 inches per hour for qualitative mineral analyses. The samples are again X-rayed from 4° to 33° 2θ with a scanning speed of $1/2$ degree per minute and a chart speed of 12 inches per hour to obtain more accurate peak-height measurements of minerals. The basic peak-height measurements made are the intensities of the (001) kaolinite, (001) illite, (101) coquimbite, (100) quartz, (111) szomolnokite, (104) calcite, and (311) pyrite. These peak-height measurements are used as an approximate estimate of the concentration of these minerals in the low-temperature ash.

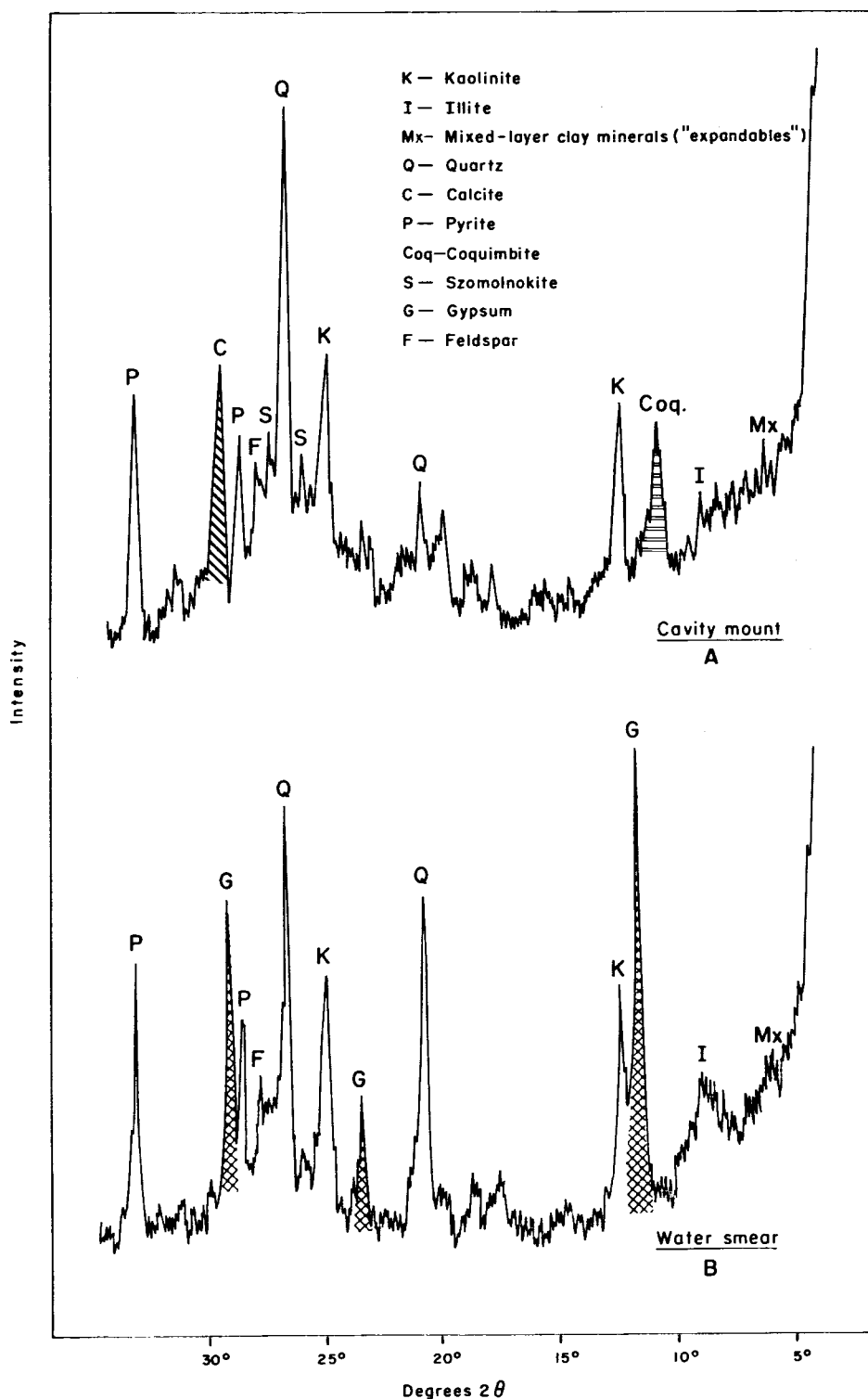


Fig. 1 - Cavity-mount (A) and water-smear (B) X-ray diffractograms of minerals from low-temperature ash. Note the formation of gypsum and the loss of calcite, szomolnokite, and coquimbite in the sample prepared with water.

Quantitative Analyses

1. Tennant and Berger Method

Tennant and Berger (1957) developed an X-ray method for the determination of the percentage of dolomite in a carbonate rock. The procedure consists of measuring the largest intensities of calcite and dolomite in a series of standard mixtures of known proportions and plotting the X-ray intensity ratio of calcite to dolomite against the percent by weight of dolomite. In the present study this method is extended to calcite and pyrite by preparing the calibration curve for a series of standard mixtures of known proportions (table 1) and plotting the X-ray peak-height ratios of calcite to pyrite against the weight percent of calcite (fig. 2). By referring to figure 2, the percent by weight of calcite in the total of calcite plus pyrite is obtained.

2. Internal Standard Method

A. Calibration curves

The internal standard method as applied to the investigation of the composition of low-temperature ashes of Illinois coals is modified from the procedures of Alexander and Klug (1954) and Diebold, Lemish, and Hiltrop (1963). Alexander and Klug (1954) used calcium fluoride as an internal standard for the determination of quartz. This method was expanded to include the determination of quartz, calcite, and dolomite, using calcium fluoride as an internal standard (Diebold, Lemish, and Hiltrop, 1963). These methods involved the measuring of intensities of X-ray diffraction peaks of mineral(s) and of the internal standard in a series of standard mixes of known proportions and empirically constructing the calibration curves.

In the present X-ray analyses, two modifications of these methods are made: (1) A clay mixture, comprising equal amounts of illite, kaolinite, and iron-bearing montmorillonite, approximating the average composition of clay minerals in Illinois, was prepared. This clay mixture was added to the series of standard mixes in an amount equivalent to the total weight of calcite, pyrite, and quartz (table 2) so that the composition of standard mixes would be close to that of low-temperature ashes. (2) An internal standard of 0.2 grams of calcium fluoride was added to the standard mixes and to 1 gram of low-temperature ash, the sample was X-rayed, and absolute amounts of calcite, quartz, and pyrite were read directly from calibration curves.

The modified method involves the measuring of peak-height intensities (fig. 3) of the (001), (104), and (311) reflections of quartz, calcite, and pyrite, respectively, and the (111) reflection of calcium fluoride (fluorite) in a series of standard mixes of known proportions (table 2). Proper grinding and mixing and a uniform grain-size are obtained by using small sample holders with a tungsten ball in each of them and placing them in a Spex Mixer for 30 minutes. The mixtures are X-rayed, using cavity-mount sample preparation technique, from 19° to $33^{\circ} 2\theta$ with a chart speed of 12 inches per hour and a scanning speed of $1/2^{\circ}$ per minute. Peak-height measurements are made in recorder chart units (200 counts full scale). The calibration curves of quartz, calcite, and pyrite are constructed by plotting the respective X-ray intensity (peak height) ratios of these minerals with calcium fluoride as the ordinate and grams of the respective minerals per 0.2 grams of fluorite as the abscissa (figs. 4, 5, and 6).

TABLE 1 - STANDARD SAMPLE DATA FOR CALCITE-PYRITE CALIBRATION CURVE
BASED ON METHOD OF TENNANT AND BERGER (1957)

Mixture number	Pyrite (grams)	Calcite (grams)	Pyrite (percent)	Calcite (percent)	$\frac{\text{Calcite peak height}}{\text{Pyrite peak height}}$
1	0.90	0.10	90	10	1.44
2	0.80	0.20	80	20	2.43
3	0.70	0.30	70	30	4.02
4	0.60	0.40	60	40	6.04
5	0.50	0.50	50	50	10.68
6	0.40	0.60	40	60	18.44
7	0.30	0.70	30	70	26.92
8	0.20	0.80	20	80	48.67
9	0.10	0.90	10	90	72.39

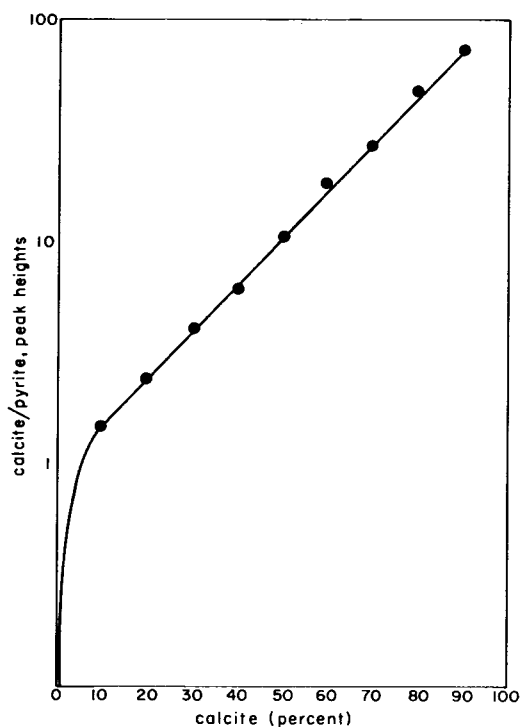
Fig. 2 - Calcite-pyrite calibration curve.
(After method of Tennant and Berger, 1957.)

TABLE 2 - STANDARD SAMPLE DATA FOR CALIBRATION CURVES

Mixture number	Calcite (grams)	Quartz (grams)	Fluorite (grams)	Pyrite (grams)	Clay mineral mixture	Peak-height ratio		
						H_C/H_F	H_Q/H_F	H_P/H_F
1	0	0.40	0.20	0.40	0.80	0	0.46	0.80
2	0.04	0.36	0.20	0.36	0.76	0.10	0.42	0.68
3	0.08	0.32	0.20	0.32	0.72	0.29	0.38	0.59
4	0.12	0.28	0.20	0.28	0.68	0.45	0.34	0.49
5	0.16	0.24	0.20	0.24	0.64	0.60	0.29	0.39
6	0.20	0.20	0.20	0.20	0.60	0.76	0.25	0.28
7	0.24	0.16	0.20	0.16	0.56	0.95	0.21	0.21
8	0.28	0.12	0.20	0.12	0.52	1.10	0.17	0.16
9	0.32	0.08	0.20	0.08	0.48	1.25	0.13	0.11
10	0.36	0.04	0.20	0.04	0.44	1.46	0.09	0.07
11	0.40	0	0.20	0	0.40	1.64	0	0

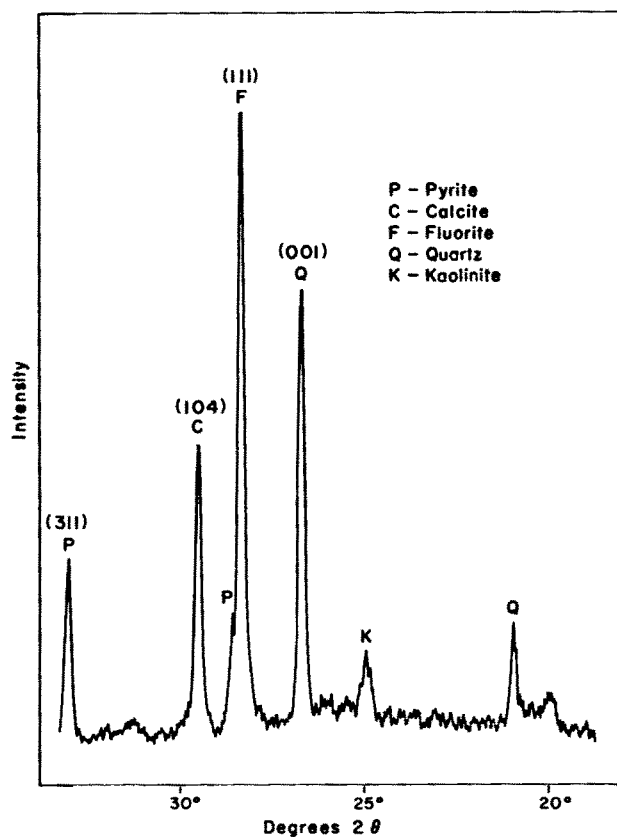


Fig. 3 - X-ray diffractogram of low-temperature ash with fluorite as an internal standard. (One gram lta and 0.2 gram fluorite; chart speed of 12 inches per hour and a goniometer scanning speed of 1/2 degree per minute.)

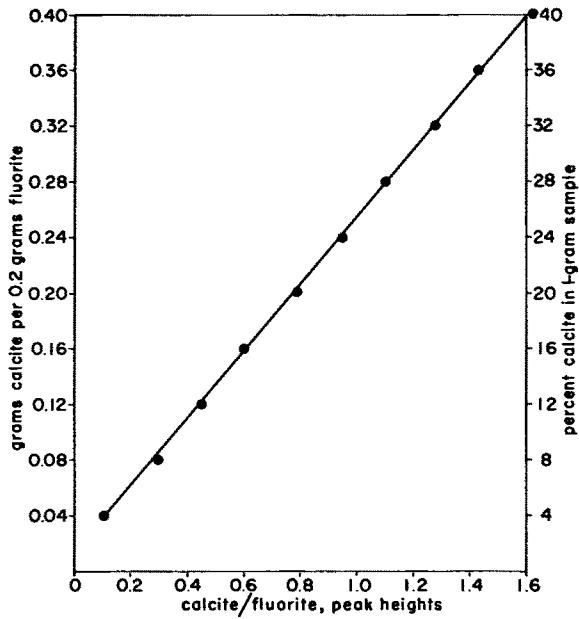


Fig. 4 - Calcite-fluorite calibration curve.

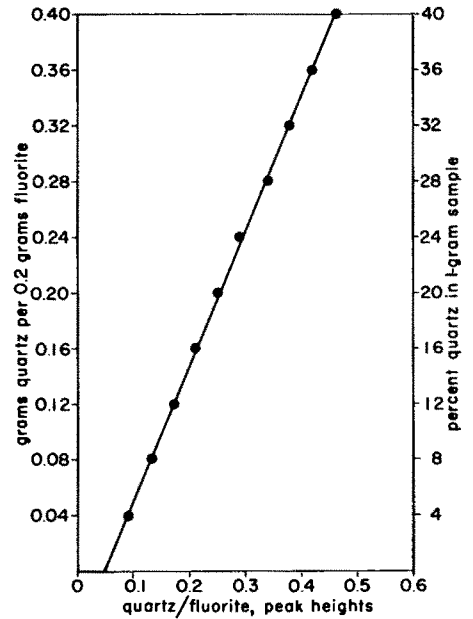


Fig. 5 - Quartz-fluorite calibration curve.

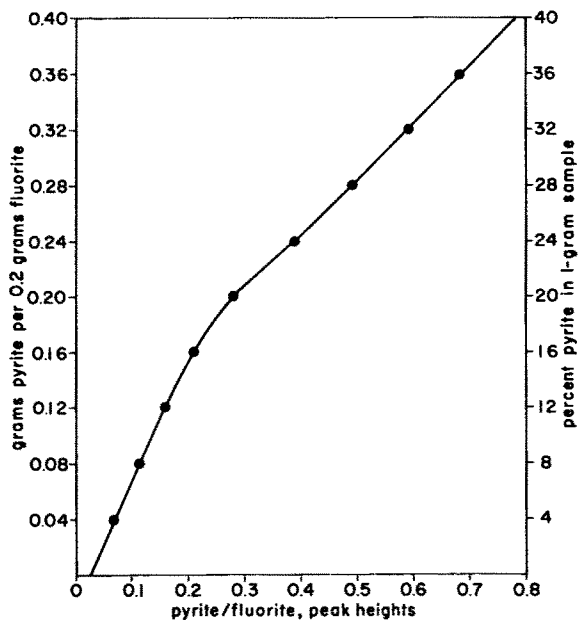


Fig. 6 - Pyrite-fluorite calibration curve.

B. Determination of absolute percentages of calcite, quartz, pyrite, and total clay

In order to determine the absolute percent of minerals in Illinois coals, 0.2 grams of fluorite is added to 1 gram of low-temperature ash (lta). As in the preparation of calibration curves, proper grinding and mixing and a uniform grain size are achieved by using small sample holders in a Spex Mixer for 30 minutes. Cavity-mounted samples are X-rayed from 19° to $33^{\circ} 2\theta$ with a chart speed of 12 inches per hour and a scanning speed of $1/2^{\circ}$ per minute. X-ray peak-height intensities are made in recorder chart units and in fixed time per count X-ray technique. Fixed time was set for 20 seconds and fixed count for 10,000 counts. The X-ray peak-height intensity ratios of calcite, quartz, and pyrite for both types of measurements are calculated with respect to fluorite. If there is a disparity between the ratios of actual number of counts and the peak-height ratios in a sample, the analysis is repeated. Absolute percentages of the minerals are obtained by referring directly to their respective calibration curves, on which are plotted the standard peak-height ratios (figs. 4, 5, and 6).

The percent of pyrite in the lta is also calculated from the percent of pyritic sulfur reported in the chemical analysis of the coal. The pyrite values (X-ray and chemical analyses) are compared, and the higher number is considered as the absolute pyrite percent in the lta. If the amount of pyrite from the chemical analysis is greater than that from the X-ray analysis, the difference is considered here as equivalent to iron sulfate minerals, such as coquimbite, szomolnokite, roemerite, and jarosite. The amounts of sulfate minerals calculated to be present in the lta to make up the differences between the two analyses correlate fairly well with the peak heights of those minerals on the X-ray diffractogram (fig. 7), even though the heights of X-ray diffraction peaks of the iron sulfate minerals are not qualified by calibration.

The calcite percentages of the lta samples also correlate well (± 3 percent) with the carbonate equivalents calculated on the basis of CO_2 and CaO from the chemical analyses of 12 lta samples (table 4).

The total clay-mineral content is obtained by subtracting the amounts of calcite, quartz, pyrite, and iron sulfate from the total weight of the lta (1 gram).

C. Determination of clay minerals

The percentages of clay minerals are determined following the procedure of Hughes (1971) for low-temperature ash samples of Illinois coals. This method involves adding a known amount of talc (5 percent) to lta samples and X-raying the smeared slides. The ratios of peak areas (peak height times width at half-peak height) beneath different clay-mineral basal peaks to the peak area of talc are calculated. These ratios are multiplied by empirically determined R-factors for different clay minerals and by the amount of talc added as a standard.

The R-factors are derived from the ratios of peak areas of known weights of clay minerals to the peak area of a known weight of talc added as a standard. These R-factors depend on both the form and the structural character of different clay minerals compared to those of talc and on the resolution limits of the X-ray unit being used. The R-factors were experimentally determined for illite (6.0), smectite (0.8), attapulgite (1.2), and kaolinite (1.1, authigenic; 2.0, detrital). Chlorite has the same R-factor as detrital kaolinite at 7\AA ($12.4^{\circ} 2\theta$).

Each slide (smear) was X-rayed three times to complete the clay-mineral analyses. First, the untreated lta smears, to which 5 percent talc was added,

were X-rayed. The samples were then placed in a desiccator jar containing glycol for at least 3 days and X-rayed again. The amount of kaolinite and illite was calculated from peaks 12.4° and $8.8^{\circ} 2\theta$, respectively, as described previously. After being heated for 1 hour at 330°C , these samples were again X-rayed to calculate the "expandable" clay minerals. The ratio between the heated "expandable" peak area (illite + smectite + mixed layer) and the talc peak area was multiplied by the R-factor (6.0, similar to illite) and the percent of talc. The amount of expandables (smectite + mixed layer) is equivalent to the difference between this amount (illite + smectite + mixed layer) and the illite percent determined on the glycolated slide.

The proportion of a clay mineral relative to talc is used to calculate its absolute percentage in the lta from the total clay, determined using fluorite as an internal standard.

Accuracy of X-ray Quantification

In order to test the accuracy of the data obtained by X-ray diffraction analyses of lta mineral matter, these data are compared with the results of the chemical analyses of the same lta samples. This test provides an independent check of the methods used. Chemical analyses of the low-temperature ash of 12 different coals are given in table 3, and the X-ray diffraction data are compared to the data from chemical analyses in table 4.

The amount of calcite present in the low-temperature ash may be calculated from either the CaO or the CO_2 content. The calculated calcite values from CaO ($\text{CaO} \times 1.27$) are higher than those from CO_2 ($\text{CO}_2 \times 2.27$). However, these values are in all cases within 3 percent of the calcite analyzed by X-ray diffraction. The average values of calcite as calculated from CO_2 (5.9 percent), from CaO (8.5 percent), and from X-ray (9.0 percent) are in close agreement.

The amount of pyrite and/or marcasite in the sample may also be calculated from two values in the chemical analyses of the lta, the Fe_2O_3 content and the total S content. In both cases, it is assumed that all of the Fe and S are totally present in the original coal sample as FeS_2 . This assumption is not quite accurate, for iron may also be contained in the carbonate minerals and in the clay minerals, and organic sulfur in the coal may be fixed in the low-temperature ash during ashing. The calculated mean pyrite percentages from the sulfur content (24.52) and the iron content (26.11) are slightly larger than the pyrite content determined by X-ray analyses (23.83). It is also possible to estimate the amount of pyrite in the samples from the pyritic sulfur analyses of the whole coal, and this value (table 4) also agrees well with the other experimental values (mean 23.0 percent). The total pyrite as determined by X-ray analysis is

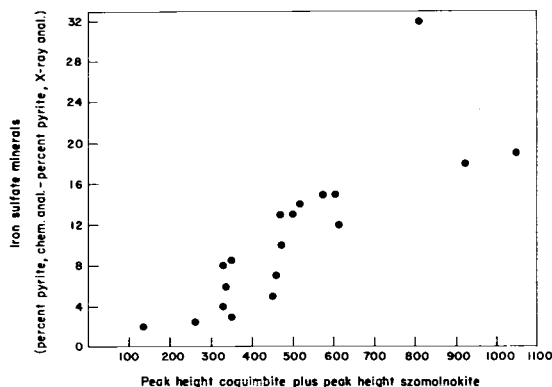


Fig. 7 - Iron sulfate minerals calculated from chemical analyses compared to X-ray diffraction peak heights of coquimbite and szomolnokite.

TABLE 3 - CHEMICAL ANALYSES OF LOW-TEMPERATURE ASH OF ILLINOIS COALS*

Sample number	1	2	3	4	5	6	7	8	9	10	11	12
Laboratory number	C-16582	C-16583	C-16584	C-16585	C-16586	C-16588	C-16589	C-16590	C-16592	C-16593	C-16594	C-16595
SiO ₂	38.4	34.1	34.8	38.0	32.4	24.2	41.8	18.4	33.7	35.1	29.9	33.5
TiO ₂	0.61	0.62	0.74	0.89	0.68	0.53	0.90	0.30	0.53	0.45	0.65	0.63
Al ₂ O ₃	12.4	12.1	15.8	22.3	15.4	12.1	20.5	16.2	10.9	9.48	14.0	14.4
Fe ₂ O ₃	18.3	16.1	17.1	9.60	17.4	22.1	9.25	26.5	19.9	14.2	17.8	12.9
MnO	0.24	0.21	0.22	0.14	0.26	0.30	0.12	0.35	0.27	0.20	0.25	0.19
MgO	0.18	0.04	0.04	0.50	0.53	0.47	0.79	0.28	0.39	0.47	0.49	0.51
CaO	4.64	4.14	5.18	7.17	7.23	5.14	3.81	4.52	4.73	11.8	7.16	9.30
K ₂ O	1.10	1.10	1.18	2.17	1.18	1.23	1.61	0.57	1.05	0.98	0.95	1.17
P ₂ O ₅	0.02	0.10	-	0.55	-	0.03	0.34	-	0.10	-	0.29	0.05
CO ₂	1.76	1.76	1.94	2.81	1.94	2.12	2.30	2.48	2.30	3.88	4.06	3.88
S	14.53	14.39	13.79	7.15	13.56	15.54	7.08	14.35	16.76	11.12	12.65	10.33
Total carbon	2.23	2.39	1.75	1.99	2.04	2.00	1.29	3.49	3.60	2.22	3.03	2.11
Inorganic carbon	0.48	0.48	0.53	0.77	0.53	0.58	0.63	0.68	0.63	1.06	1.11	1.06
Organic carbon	1.75	1.91	1.22	1.22	1.51	1.42	0.66	2.81	2.97	1.16	1.92	1.05

*All values are percent of the low-temperature ash.

Identification of samples:

Sample number	Coal member	Location	Low-temperature ash (percent of coal)
1 C-16582	Herrin (No. 6)	Montgomery County	15.58
2 C-16583	Herrin (No. 6)	Christian County	17.85
3 C-16584	Herrin (No. 6)	Franklin County	13.31
4 C-16585	Harrisburg (No. 5)	Saline County	12.17
5 C-16586	Herrin (No. 6)	Perry County	14.37
6 C-16588	Colchester (No. 2)	Peoria County	12.80
7 C-16589	Herrin (No. 6)	Franklin County	10.70
8 C-16590	Colchester (No. 2)	Fulton County	15.89
9 C-16592	Harrisburg (No. 5)	Franklin County	17.15
10 C-16593	Springfield (No. 5)	Fulton County	16.68
11 C-16594	Harrisburg (No. 5)	Saline County	13.85
12 C-16595	Danville (No. 7)	Vermilion County	12.91

obtained from the sum of the pyrite diffraction peaks and the iron sulfate diffraction peaks. The iron sulfate is assumed to have formed upon the oxidation of the pyrite, mainly after the sample was collected.

In order to compare the quartz values from chemical and X-ray analyses, the SiO₂ is first distributed to clay minerals on the basis of the Al₂O₃ content as determined by chemical analyses of the lta and the relative amounts of the various clay minerals and the total clay-mineral content of the lta as determined by X-ray diffraction. Because the composition of kaolinite is 2Al₂Si₂O₅(OH)₄, or 2SiO₂ · Al₂O₃ · 2H₂O per unit cell with no isomorphous substitution, the amount of SiO₂ in kaolinite is twice the amount of Al₂O₃, whereas in illite and expandables, SiO₂ is approximately equal in amount to Al₂O₃. The SiO₂ remaining after distribution to clay minerals is considered in this study as equivalent to quartz. The mean value of quartz as calculated (14.84 percent) is in close agreement with the X-ray determined percentage of quartz (14.45).

The agreements between the amounts of pyrite, calcite, and quartz as calculated from the chemical analyses and as determined by X-ray diffraction analyses suggest that the methods of quantification of mineral matter in low-temperature ash as described previously are accurate within reasonable limits of experimental error.

OCCURRENCE OF MINERAL MATTER IN ILLINOIS COALS

Relation of Mineral Matter to Ash Content of Coals

The X-ray diffraction data making up the major portion of this report were all determined on samples of mineral-matter residue obtained by the electronic

TABLE 4 - COMPARISON OF DATA FROM X-RAY DIFFRACTION AND CHEMICAL ANALYSES OF LOW-TEMPERATURE ASH*

Sample number	CALCITE			PYRITE							QUARTZ	
	Calculated from chemical analysis		Determined by X-ray diffraction	Calculated from chemical analysis			Determined by X-ray diffraction		Calculated from chemical analysis of whole coal	SiO ₂ contained in clay minerals	Calculated from SiO ₂ remaining	Determined by X-ray diffraction
	From CO ₂	From CaO		From S	From Fe ₂ O ₃	Pyrite	Iron sulfate	Pyrite & iron sulfate				
1 C-16582	3.99	5.89	8	27.19	27.40	31	0	31	24.08	14.4	24.0	16
2 C-16583	3.19	5.25	7	26.92	24.10	16	4	20	19.63	14.4	19.7	11
3 C-16584	4.40	6.57	7	25.80	25.60	19	2	21	20.82	18.9	15.9	18
4 C-16585	6.37	9.10	6	13.38	14.37	12	0	12	10.65	28.5	9.5	11
5 C-16586	4.40	9.18	12	25.37	26.05	19	3	22	22.30	20.0	12.4	16
6 C-16588	4.81	6.52	9	29.08	33.08	24	7	31	31.23	14.5	9.7	10
7 C-16589	5.22	4.83	9	13.25	13.85	11	0	11	9.59	26.8	15.0	19
8 C-16590	5.62	5.74	8	26.85	39.67	26	19	45	45.17	19.2	-0.8	2
9 C-16592	5.22	6.00	10	31.36	29.79	30	5	35	34.74	13.4	20.3	24
10 C-16593	8.80	14.98	11	20.81	21.26	15	1	16	15.45	11.3	23.8	22
11 C-16594	9.21	9.09	7	23.67	26.65	21	3	24	24.44	17.9	12.0	11
12 C-16595	8.80	11.81	14	19.33	19.31	12	6	18	17.89	17.5	16.0	18
Arithmetic mean	5.89	8.54	9	24.52	26.11	19.7	4.2	23.8	23.00	18.1	14.84	14.5

*All values are percent of low-temperature ash.

low-temperature ashing technique. The amount of low-temperature ash (lta) recovered ranged from 9.29 percent to 22.34 percent, with a mean value for all samples of 15.37 percent. The high-temperature ash content of these samples ranged from 7.34 percent to 15.8 percent. The high-temperature ash content is determined by heating the sample slowly to 750° C and continuing heating at that temperature until constant weight is attained (Rees, 1966). The amount of high-temperature ash was less than the amount of low-temperature ash in each of the 65 coal samples studied (appendix).

The differences between the high- and low-temperature ashes are the result of reactions that take place in the mineral matter at the high temperature. The major mineral phases present in the coals are: (1) clay minerals — kaolinite, illite, and mixed-layer clays; (2) iron sulfide minerals — pyrite and marcasite; (3) calcite; and (4) quartz. Gypsum has also been observed in several coals. Of these five minerals or groups of minerals, all but one lose weight upon high-temperature ashing, either by oxidation or dehydration.

1. Clay minerals. The clay minerals in coal all contain water bound within their lattices. Kaolinite contains 13.96 percent, illite 4.5 percent, and montmorillonite 5 percent of this bound water. In addition, the montmorillonite in the mixed-layer clays also contains interlayer or adsorbed water. All of the water is lost during the high-temperature ashing, but only the interlayer or adsorbed water is lost during low-temperature ashing.

2. Iron sulfide minerals. During high-temperature ashing, the FeS_2 minerals are oxidized to Fe_2O_3 and SO_2 . Some of the SO_2 may remain in the ash in combination with calcium, but much is lost. If all the SO_2 were emitted during ashing, there would be a 33 percent loss in weight with respect to the weight of pyrite or of marcasite in the original sample.

3. Calcite. The CaCO_3 is calcined to lime (CaO) during high-temperature ashing with a loss of CO_2 . This loss results in a 44 percent reduction in weight from that of the original calcite.

4. Gypsum. The dehydration of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) takes place in two steps, the first resulting in the formation of the hemihydrate ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$) and the second in the formation of anhydrite (CaSO_4). The complete dehydration and a subsequent loss of weight of 20.9 percent would be expected during high-temperature ashing. The predominant phase remaining in the low-temperature ash is the hemihydrate, representing a loss in weight of 15.2 percent from the original gypsum.

5. Quartz. The stable mineral quartz (SiO_2) is the only major mineral found in coal which is inert during high-temperature ashing.

The changes in the mineral-matter content in coal during ashing have long been recognized. A number of workers have suggested schemes by which one could calculate the true mineral-matter content from the determinations made during the chemical analyses of coal. One of the earliest of such schemes and still the most widely used is that of Parr (1928), in which only the total sulfur and ash contents were considered in developing the conversion formulae. A more sophisticated method was suggested by King, Maries, and Crossley (1936), and this "KMC" method considers the loss of CO_2 from carbonates and considers the decomposition of the chlorides in addition to the factors considered by the Parr formula. Further modifications of these techniques have been suggested by Brown, Caldwell, and Fereday, 1952; Pringle and Bradburn, 1958; and Millot, 1958. Recently the problem of converting raw chemical analytical data to a pure coal basis by subtracting the calculated mineral-matter content has been discussed in detail by Given (1969).

In order to compare the values for mineral matter obtained by low-temperature ashing (low-temperature ash - lta) with the calculated Parr mineral matter, data representing over 700 separate low-temperature ashings of coals from 37 mines are summarized in figure 8. The Parr mineral matter was calculated using the original Parr formula:

$$\text{Parr mineral matter} = 1.08 \times \text{Ash} + .55 \times \text{Sulfur}.$$

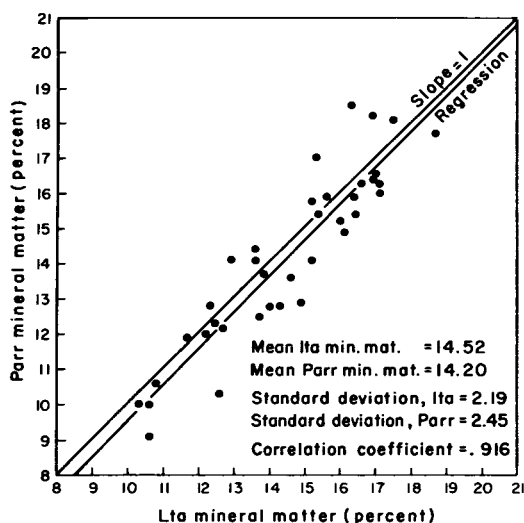


Fig. 8 - Lta mineral matter versus Parr mineral matter.

The correlation between the two values is good (correlation coefficient = .92). Although the points are scattered around a line with a slope of 1 (Parr mineral matter equals lta mineral matter), the lta mineral matter is, on the average, slightly greater than the Parr value.

Low-temperature ash and high-temperature ash of four coal samples were chemically analyzed for the major and minor elements (table 5). The results of the Si, Fe, Al, and Ca determinations are shown on figure 9. The high-temperature ash values were recalculated to a low-temperature ash equivalent prior to being plotted on figure 9. If there were absolutely no experimental errors introduced by the ashing procedure or by the chemical analyses and if there were no loss of any of these elements during either

type of ashing, all points would fall on the line with a slope of 1. All of the points in figure 9 do lie fairly close to this line. The same generally good agreement is also found with the minor element constituents, Na, K, and Ti. This agreement is not found with P and S, however, since these elements are lost during the high-temperature ashing of coal.

TABLE 5 - CHEMICAL ANALYSES OF HIGH-TEMPERATURE AND LOW-TEMPERATURE ASHES OF COALS

	Herrin (No. 6) Coal Member, Marion County		Herrin (No. 6) Coal Member, Fulton County		Herrin (No. 6) Coal Member, Perry County		Springfield (No. 5) Coal Member, Sangamon County	
	hta* (%)	lta (%)	hta* (%)	lta (%)	hta* (%)	lta (%)	hta* (%)	lta (%)
Si	13.8	13.3	12.02	12.32	14.63	14.29	11.47	12.61
Al	6.10	5.40	6.14	6.19	6.29	5.98	3.60	3.49
Fe	12.86	13.28	9.06	10.28	9.35	9.37	10.61	11.11
Ca	3.39	3.97	3.86	3.51	5.48	4.95	3.52	3.09
Na	1.18	1.50	0.46	0.47	0.17	0.24	0.53	0.57
K	0.79	0.87	1.17	0.73	1.10	0.92	0.70	0.61
Ti	0.36	0.32	0.31	0.41	0.33	0.39	0.22	0.32
S	1.61	12.67	1.26	13.21	1.05	10.58	1.72	12.24
P	0.04	0.08	0.002	0.06	N.D.†	0.12	N.D.†	0.17
High-temperature ash (%)		13.0		10.34		11.85		10.66
Low-temperature ash (%)		17.57		16.85		16.83		18.18
Parr mineral matter (%)		16.26		13.03		14.73		13.90
Ratio: $\frac{\text{lta mineral matter}}{\text{Parr mineral matter}}$		1.08		1.29		1.14		1.31

*High-temperature ash. All high-temperature ash values recalculated to a low-temperature ash equivalent.

†N.D. - not detected.

From the comparison of these analyses the following conclusions can be drawn:

1. The differences between Ita mineral matter and Parr mineral matter shown on figure 8 are real and are not the result of the low-temperature ashing techniques used. The ratio of Ita mineral matter to Parr mineral matter ranged from 1.08 to 1.31 for the four samples chemically analyzed. If the variation in this relationship were the result of incomplete ashing or other artifact, the values for the elements in the two types of ash would not agree.

2. The elements Si, Fe, Al, Ca, Na, K, and Ti are refractory in both high- and low-temperature ashing and remain entirely in the ash. The only other interpretation possible is that each of these elements is lost in the same proportion from each of the coals during the two different ashing procedures, and that possibility is certainly not likely.

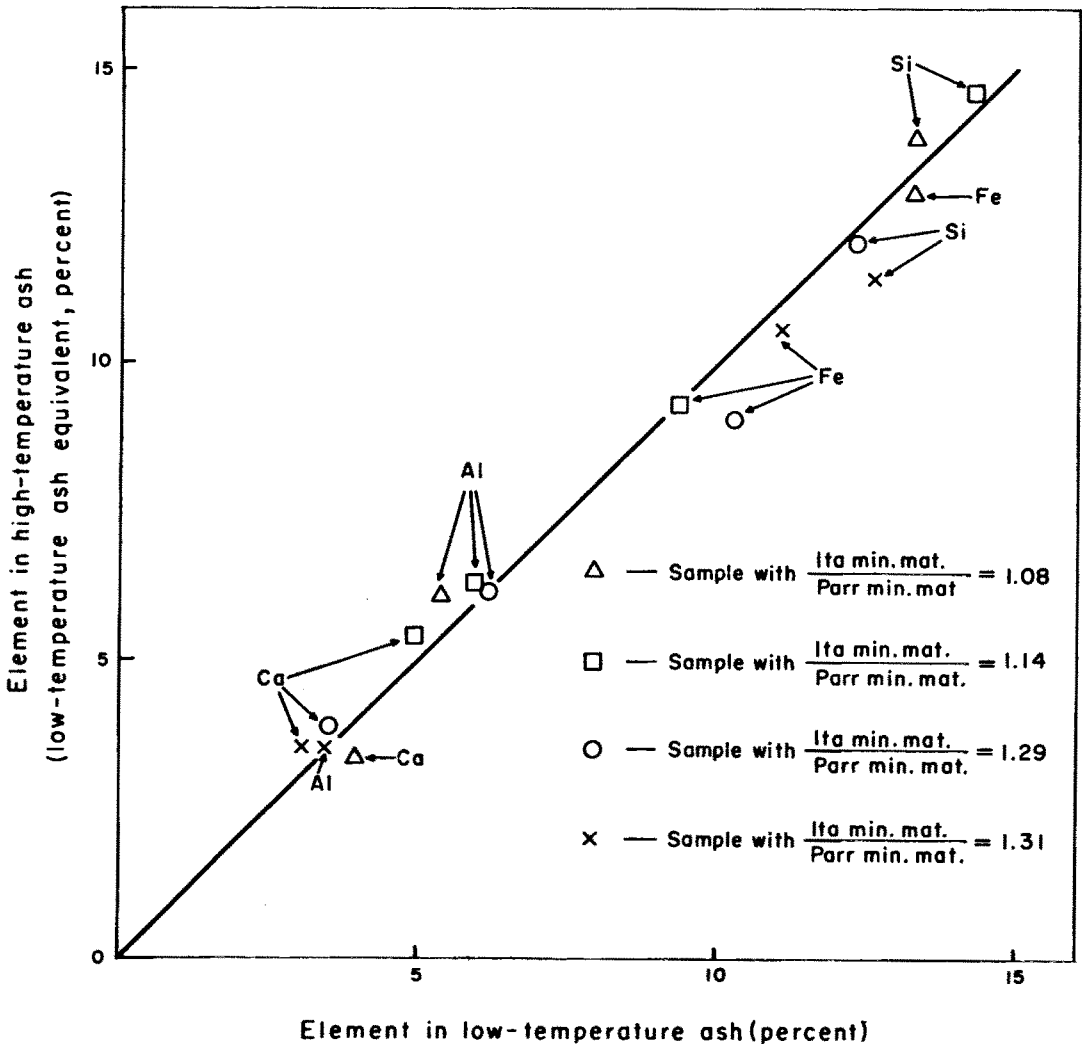


Fig. 9 - Concentration of major elements in high- and low-temperature ash.

Major Minerals in Illinois Coals

On the basis of qualitative X-ray analyses of lta samples, the most common minerals in Illinois coals are: illite, kaolinite, mixed-layer clay minerals, quartz, calcite, and pyrite. Scanning electron photomicrographs of several of these minerals are shown on plate 1. Iron sulfates such as coquimbite and szomolnokite form from the oxidation of pyrite, even when sealed in a container in the laboratory, and are therefore identified in the low-temperature ash (appendix). Calcite is the dominant carbonate mineral; siderite and dolomite occur only in trace amounts. Marcasite and sphalerite are present in small amounts in a few samples, and feldspar and gypsum are other minor constituents.

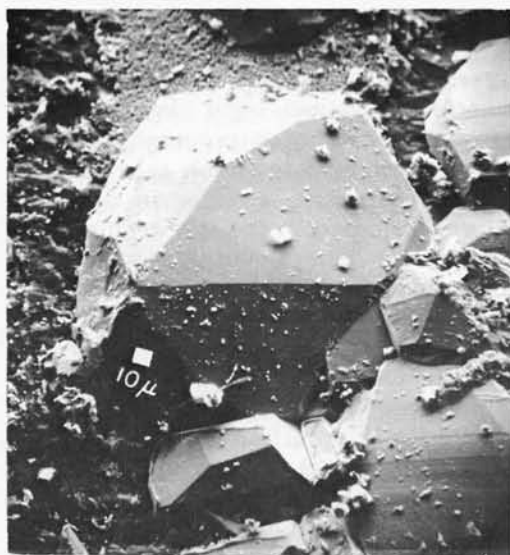
The major mineral assemblages in the 65 samples analyzed are very similar, for the most part; the total clays dominate (mean clay content is 53 percent) followed by the total amount of pyrite and its iron sulfate alteration products (23 percent), quartz (15 percent), and carbonates (9 percent). However, the absolute amounts of calcite, quartz, pyrite, iron sulfates, total clays, illite, kaolinite, and expandables (appendix) may vary in response to changing depositional and/or diagenetic environments.

Carbonate Minerals

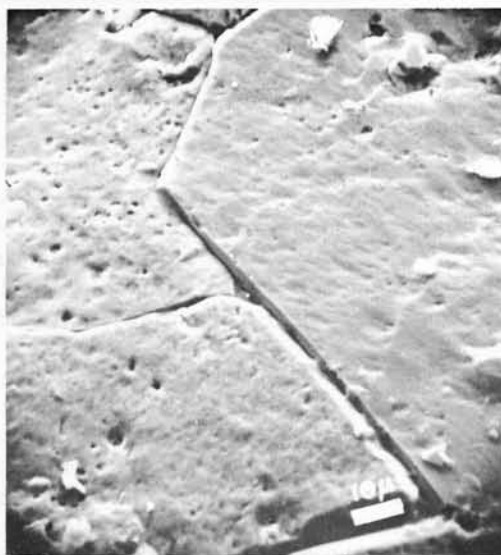
Much of the previous work on carbonate minerals has been chiefly concerned with those of the strata associated with coal seams. The carbonate minerals in coal have been classified broadly as "ankerites" or "brass-stones" (King, Maries, and Crossley, 1936). Ankerite is considered as the type mineral $2\text{CaCO}_3 \cdot \text{MgCO}_3 \cdot \text{FeCO}_3$, whereas brass-stone is a mixed iron-magnesium carbonate containing much smaller amounts of calcium than is contained in ankerites. In British coals (King, Maries, and Crossley, 1936), carbonates generally occur as ankerites; in the coals of South Wales, ankerites occur only in small amounts and brass-stones are the predominant form of carbonates. Small amounts of MnCO_3 , up to 5 percent, are reported in ankerites.

Pringle and Bradburn (1958) analyzed about 80 samples collected from all the major coal fields in Britain and reviewed the literature on coal seam "ankerites." Besides calcite and siderite (chalybite), they observed two classes of ankeritic carbonates (dolomitic ankerites and sideritic ankerites). They believed the variation in composition of carbonates in British coals resulted from calcite having been deposited and then altered to various types of carbonate minerals, depending on the composition of the infiltrating solution.

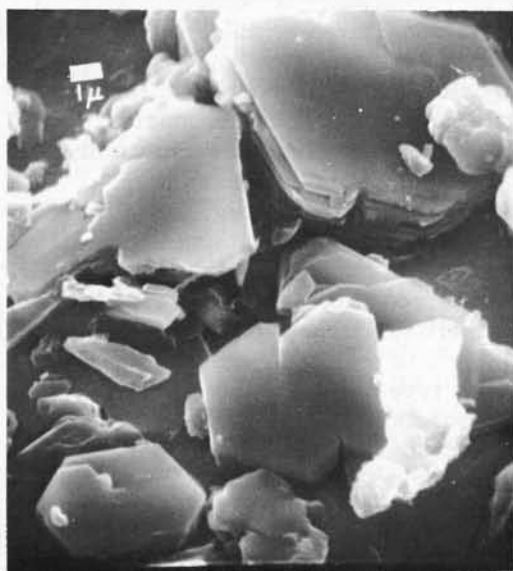
The carbonate minerals filling vertical fractures, or "cleats," in East Midlands coals of Great Britain were studied by optical, specific gravity, and acid-extract techniques (Dixon, Skipsey, and Watts, 1970). This study confirmed the occurrence of "ankerite" and calcite but noted that the iron content of "ankerite" is lower than that reported by Pringle and Bradburn (1958). Dixon, Skipsey, and Watts (1970) suggested that this difference may have been attributable to the inclusion of iron from pyrite in the cleat or of siderite in the coal due to the vigorous acid-extraction technique used by Pringle and Bradburn (1958). No dolomite, magnesite, or siderite was observed in the cleat carbonates, nor was there evidence of extensive interaction, of solid solution, or of the formation of isomorphous mixtures.



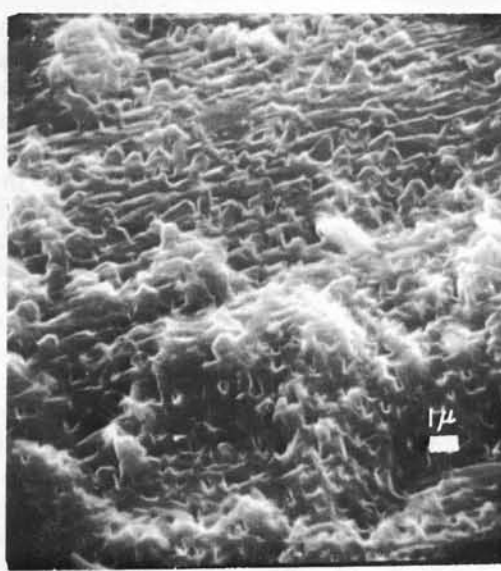
A



B



C



D

Plate 1 - Scanning electron photomicrographs of mineral matter in coal. A. Euhedral pyrite crystals in Colchester (No. 2) Coal Member; B. Subhedral pyrite crystals filling cleat (vertical fracture) in Opdyke Coal Member; C. Kaolinite associated with pyrite in cleat filling in Harrisburg (No. 5) Coal Member; D. Calcite from cleat in Opdyke Coal Member.

Siderite, ankerite, and calcite are commonly occurring carbonate minerals in Australian coals, as determined both by microscopic observations (Kemežys and Taylor, 1964) and by chemical analyses (Brown, Durie, and Schafer, 1960). The chemical analyses of 24 seam composites (excluding dirt bands) of Australian coals revealed that the carbonates vary widely from a composition approaching calcite to one of almost pure siderite (Brown, Durie, and Schafer, 1960). This range suggested that the variation in carbonate mineralogy is due to the exchange between calcium and ferrous ions in the mixed carbonate (ankerite) lattice. Siderite in Australian coals was observed to occur predominantly as nodules (1-5 mm in size) and lenticular masses (up to 6 feet across) in seams that were overlain by fresh-water rather than marine rocks. Siderite and pyrite usually do not occur together in significant amounts in coal. Unlike siderite, both ankerite and calcite occur as veins, infilling cellular structures and actually replacing coal (Kemežys and Taylor, 1964, p. 393). Occasionally, ankerite and calcite also occur as nodules and lenticular masses. Such nodules are usually very small (about 100 to 400 microns across). Ankerite and calcite occur in seams overlain by both fresh-water and marine rocks.

The composition of carbonate minerals reported in the literature is based mostly on the analyses of an acid extract of coal (Pringle and Bradburn, 1958; Brown, Durie, and Schafer, 1960). The Ca, Mg, Fe, and Mn in the extract were determined and the results were corrected for the presence of interfering ferrous sulfate and any additional acid-soluble salts. The acid-extract method is not only destructive to the minerals present, but the extractable material may come from sources other than carbonates. Reconstructing the carbonate mineralogy in the coal from chemical analyses may result in errors because the cations identified may have been present in a mixed-carbonate mineral or may have occurred in other separate mineral phases.

The carbonate minerals in Illinois coals are distinctly different from those in Australian or-British coals. The X-ray study of all the Ita samples from composite face-channel samples (samples in which mineral bands of more than 3/8 inch in thickness are not included) of Illinois coals from six different coal seams and from widely separated locations did not suggest any wide variations in carbonate minerals. Calcite is the dominant carbonate mineral in Illinois coals. Siderite and dolomite are observed in a few samples and only in trace amounts. Neither magnesite nor ankerite are detected in the X-ray diffractograms of the investigated samples. The strongest reflection (211) of most of the carbonate minerals is very sensitive to isomorphous substitution of cations, and variations of the composition produce a shift in this peak on the X-ray diffractogram. However, in our investigations, the distance between the (211) calcite peak and the (111) peak of the internal standard, fluorite, did not deviate appreciably enough to suggest any substitution. Calcite in coal is similar to calcite in sedimentary carbonates, which consist chiefly of low-magnesian calcite with less than about three mole percent MgCO_3 in solid solution (Chave, 1954; Goldsmith, Graf, and Joensuu, 1955; Tennant and Berger, 1957; Peterson, 1962; and Fisher, 1968). Though the present investigation emphasizes the bulk composition of mineral matter in Ita, observations of many of these coal samples indicate that a major proportion of the carbonate minerals in Illinois coals seems to occur as cleat (vertical fracture) fillings or as infillings of cellular plant structures. A lesser portion of the carbonate minerals may occur as very small nodules or lenticular masses, and nodular carbonate

petrifications ("coal balls") are also a common mode of occurrence of carbonate minerals in Illinois coals (Cady, 1937; Noé, 1932; Andrews, 1951; Rao, in preparation).

Calcite in the lta can be readily altered by the addition of water. A drop or two of water is sufficient to dissolve iron sulfate and iron sulfide minerals, forming sulfuric acid, which immediately reacts with calcite and produces gypsum (fig. 1).

The percent of calcite in all samples studied ranges from 0 percent to a maximum of 23 percent. The mean calcite percentages of 37 lta samples from the Herrin (No. 6) Coal Member is 8.7 percent, and the mean value for all samples is 9.0 percent. Only five samples of Illinois coals had a calcite content greater than 15 percent (fig. 10).

Quartz

Quartz is present in all the samples investigated. The percentage of this mineral in lta ranges from a low of 2 to a maximum of 28 percent. The mean and standard deviation are 15.3 percent and 6.0, respectively. The frequency distribution of quartz in Illinois lta samples depicted in the histogram (fig. 11) seems to be polymodal. Samples containing less than 5 percent quartz are rare.

Sulfides and Sulfates

Pyrite is the dominant sulfide mineral in Illinois coals. It is present in all the lta samples investigated. In a few of these samples, marcasite and sphalerite occur in trace amounts. Pyrite and marcasite are dimorphs, minerals that are identical in chemical composition (FeS_2) but differ in crystalline form. Pyrite is isometric and marcasite is orthorhombic. Sphalerite (ZnS) and gypsum (CaSO_4) are only rarely observed. Galena (PbS) has been identified by electron microscopy but has not been observed in X-ray diffraction analyses.

Pyrite is very susceptible to oxidation and decomposes to various phases of iron sulfate minerals at room temperature. The following iron sulfate mineral phases are reported to be associated with Illinois coals which had been subjected to oxidizing conditions (Gluskoter and Simon, 1968):

Szomolnokite	$\text{FeSO}_4 \cdot \text{H}_2\text{O}$
Rozenite	$\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$
Melanterite	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
Coquimbite	$\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$
Roemerite	$\text{FeSO}_4 \cdot \text{Fe}_2(\text{SO}_4)_3 \cdot 12\text{H}_2\text{O}$
Jarosite	usually a sodium jarosite $(\text{Na}, \text{K})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$

In the present study, szomolnokite and coquimbite are observed to occur together in most of the investigated lta samples. It is known that melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) dehydrates to rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$) and then to szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) in the laboratory. The dehydration of melanterite to rozenite is rapid, occurring in just a few minutes (Gluskoter and Simon, 1968).

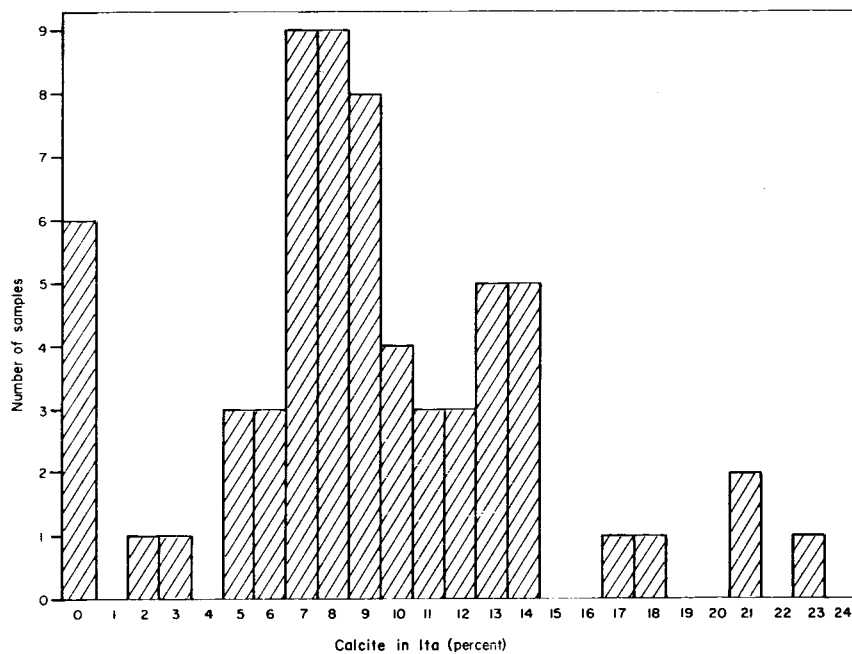


Fig. 10 - Distribution of calcite in mineral matter of Illinois coals.

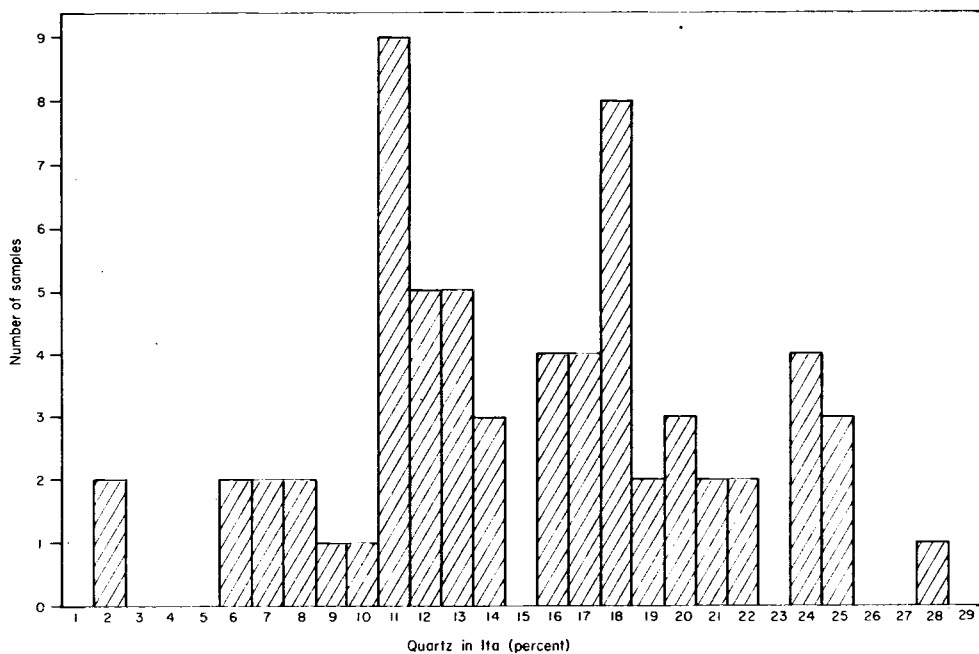


Fig. 11 - Distribution of quartz in mineral matter of Illinois coals.

Although pyrite is very easily oxidized, no appreciable alteration of this mineral is detected in the lta of fresh coals. Sulfate minerals have been reported formed by the fixing of a portion of the organic sulfur in the low-temperature ash (Gluskoter, 1965).

The sulfate minerals observed formed either in this manner, or in the coal seams prior to collection of the samples, or during the time the samples were stored in the laboratory. Since care is generally taken in originally collecting the sample to obtain fresh (unaltered) coal, it is likely that most of the iron sulfate minerals observed formed in the coal in sealed sample containers prior to ashing.

The percentage of pyrite in lta, based on the amount of pyritic sulfur in coal, has been plotted against the (311) pyrite peak heights on the X-ray diffractograms (fig. 12). Samples free of iron sulfate minerals generally show a linear relationship between the pyrite peak heights and the percents of pyrite as calculated from the chemical analyses, whereas scattering of points seems to suggest oxidation of pyrite to various phases of iron sulfate minerals. The amount of iron sulfate minerals in lta is assumed to be the difference between the pyrite calculated from chemical analysis and that determined by X-ray analysis. Since the molecular weights of the iron sulfates are greater than the molecular weight of pyrite, this value is not the true sulfate percent. The number in the column headed "Pyritic sulfur" on the appendix is the pyrite equivalent of the iron sulfates in the lta.

The histogram illustrating the distribution of pyrite (fig. 13) originally present in the samples shows an almost normal distribution of this mineral in lta. The pyrite percentages range from a low of 7 percent to a high of 48 percent. Values less than 10 percent and greater than 32 percent are relatively rare. The mean and standard deviation of 65 samples are 22.47 percent and 8.44 respectively. The X-ray determined pyrite content has a mean of 18 percent and a standard deviation of 7.65.

The distribution of iron sulfate minerals in the low-temperature ash, as shown in the histogram (fig. 14), ranges from 0 percent to a maximum of 32 percent; the mean and standard deviation are 5.46 percent and 5.99, respectively. In general, the iron sulfate minerals rarely comprise more than 7 percent of the total lta mineral matter. Most samples contain less than 4 percent iron sulfate minerals in the low-temperature ash immediately following the ashing

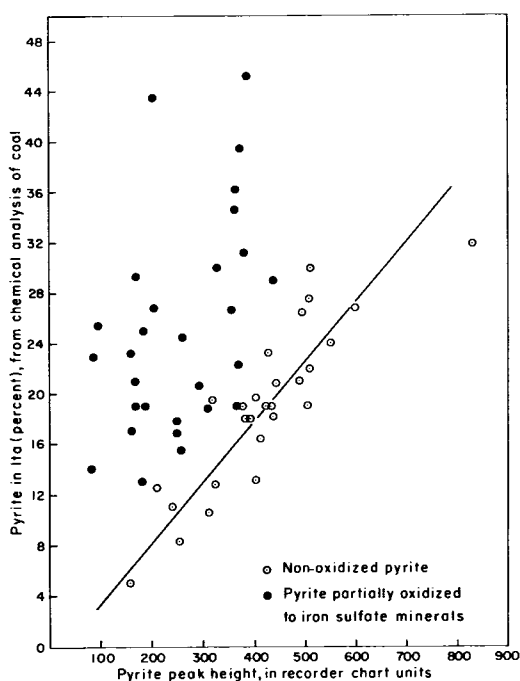


Fig. 12 - Oxidation of pyrite to iron sulfate minerals. Oxidation occurred prior to low-temperature ashing.

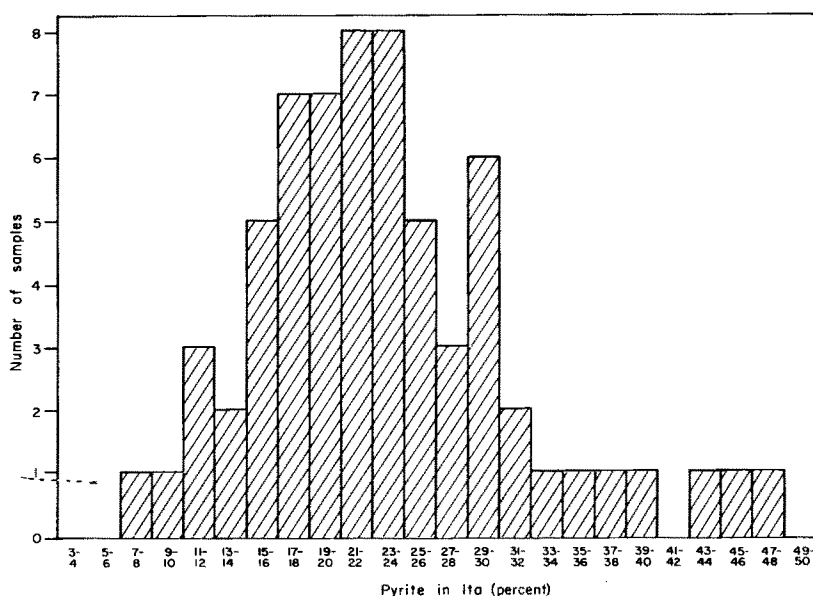


Fig. 13 - Distribution of pyrite in mineral matter of Illinois coals.

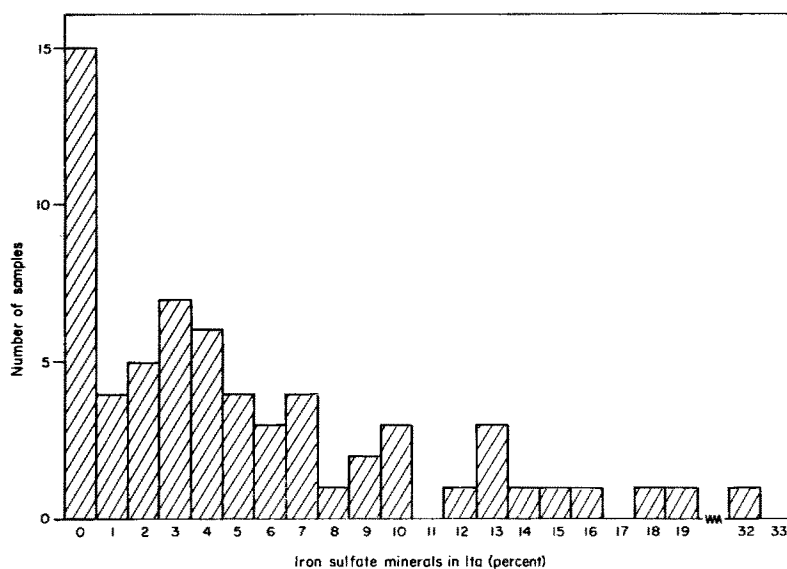


Fig. 14 - Distribution of iron sulfate minerals in low-temperature ash of Illinois coals.

of the coal. The higher percentage of iron sulfate minerals is generally found in older samples that were originally high in pyritic sulfur. Of all the samples analyzed, the sample observed to have the maximum amount of iron sulfate minerals (32 percent) had the maximum peak height of szomolnokite. It also had a comparatively high coquimbite peak height. It is possible that the alter-

ation of pyrite to iron sulfate minerals may occur in the ash during storage subsequent to ashing. This oxidation subsequent to low-temperature ashing is probably of little importance, because the low-temperature ash contains practically no moisture whereas the original coal sample was high in moisture content.

Clay Minerals

Clay minerals are the most commonly occurring inorganic constituents in coal and in the strata associated with coal. Much of the previous work on these minerals has been from strata associated with coals and not from the coals themselves.

The clay minerals in, or associated with, British coals have been reported upon from East Midlands and South Wales. The kaolinite and mica groups of clay minerals, and generally quartz, are the major minerals from roofs, floors, and clay bands associated with East Midlands coals (Dixon, Skipsey, and Watts, 1970). However, the clay minerals are not the dominant inorganic constituents in these coals. They are next in quantity to carbonates and pyrite, which each account for 20 to 90 percent of the mineral matter in coal. Kaolinite is the principal clay mineral in these coals. In South Wales, quartz and illite are the major minerals from the roof strata immediately above the coal whereas kaolinite and illite are the principal mineral constituents in the coals (Hicks and Nagelschmidt, 1943). In general, in the clay minerals reported from British coals, the roof and floor strata contain more mica than kaolinite, whereas in coal, kaolinite predominates. Dixon, Skipsey, and Watts (1970) believe that the muscovite type of mica is unstable in the reducing conditions associated with coal formation, that it does not form in that environment, and that, if present as a detrital mineral, it alters to illite and kaolinite, which are more stable.

Australian coals contain a wide range of clay minerals: kaolinite, halloysite, montmorillonite, illite, chlorite, muscovite, and biotite (Kemežys and Taylor, 1964). Clay minerals, sulfides, and carbonates account for more than 95 percent of the mineral matter associated with coal, and kaolinite is the dominant clay mineral in coal from New South Wales (Brown, Durie, and Schafer, 1959). Montmorillonite is generally the major clay mineral in the Australasian seam (in the Sydney Basin) and it occurs in association with kaolinite, quartz, and montmorillonite-illite mixed-layer minerals (Grim, in Brown, Durie, and Schafer, 1959). This unusual predominance of montmorillonite is believed to be the result of volcanic activity in the basin. Most of the clay minerals in Australian coals occur as layers interbedded with coal; however, some occur as single particles, crystals, or aggregates ranging from 1 μ m to 100 μ m across and a few as kaolinite petrifications (Kemežys and Taylor, 1964). Clay minerals of possibly recent origin occur in veins and as thin films on cleat and joint planes in coals.

Clay minerals in strata intimately associated with Illinois coals have been extensively studied at the Illinois State Geological Survey (Spencer, 1955; White, 1956; Woltman, 1956; Wahl, 1957; Parham, 1958, 1964; Odom, 1963; Odom and Parham, 1968; and Hughes, 1971). Odom and Parham (1968) compiled various mineralogic and textural data of underclays associated with Illinois coals and prepared regional variation maps for the underclays below the Colchester (No. 2), the Harrisburg-Springfield (No. 5), and the Herrin (No. 6) Coal Members. These maps indicate that underclays are developed in a series of

lateral mineral zones representing different admixtures of kaolinite, illite, illite-montmorillonite, and chlorite. The zonal pattern is the result of selective transportation, deposition, and alteration of clay minerals in the aqueous environment. Hughes (1971) recently studied the underclays of Illinois coals to determine the relationship of nonclay minerals to the distribution pattern of clay minerals. This investigation confirmed the clay-mineral distribution pattern of underclays previously described by Parham (1964) and Odom and Parham (1968). The kaolinite was observed to vary from a poorly crystallized, halloysitic kaolinite to well-crystallized kaolinite that resulted from acid and oxidizing conditions in the Illinois Basin. The amount of feldspar minerals is inversely related to the amount of kaolinite. Pyrite, feldspar, calcite, dolomite, siderite, and gypsum are well preserved only in illite-chlorite underclays. Hughes (1971) interpreted these results as a suggestion of development of underclays by flooding of distributary channels into nonmarine regions of a deltaic province.

The roof rock of Illinois coals is commonly a black or gray shale or a gray to dark gray limestone. The roof shales consist principally of kaolinite, illite, chlorite, and a mixed layer of illite-montmorillonite (Webb, 1961; Odom, 1963; Hughes, 1971). Kaolinite is commonly found immediately overlying the coal. However, the most abundant clay minerals of roof shales are the illite-chlorite type. Sedimentary apatite, carbonate minerals, concretions, and commonly a few fossils are also present in the roof shales.

Gluskoter (1967) found, on the basis of the X-ray analyses of the less than 2 μm fraction of lta samples, the clay minerals in Illinois coals to be illite, kaolinite, a random mixed-layer illite-montmorillonite, montmorillonite, and chlorite. Montmorillonite as a separate phase was observed only rarely. Chlorite was observed in only one sample and in trace amounts and is thought to be rare in coal because it is unstable in the acid coal swamp environment. Authigenic kaolinite was observed in almost all samples.

An X-ray study of smear lta samples (Hughes, 1971) identified a significant amount of well-crystallized kaolinite, illite, and "expandable" clay minerals in every sample, confirming Gluskoter's (1967) $<2 \mu\text{m}$ clay mineralogy of Illinois coals. The "expandable" clay minerals were found to vary in d-spacings and in degree of crystallinity.

Scanning electron microscopic examination (Hughes, 1971) shows that kaolinite occurs both as a disseminated and as a cleat-filling mineral in Illinois coals. Disseminated kaolinite occurs as euhedral, vermicular individuals similar to the cleat-filling type. Rarely it occurs as small pods and as petrifications. Hughes (1971) concluded that disseminated kaolinite, vermicular kaolinite, and petrifications of kaolinite are authigenic in origin as are cleat or other vertical fracture fillings. Pods may be either authigenic or transformational, but X-ray properties suggest authigenic origin.

In general, the total clay-mineral content in lta dominates the rest of the mineral assemblages in Illinois coals. The mean and standard deviation of total clay content are 52 percent and 9. The distribution of total clay shown in the histogram of all samples (fig. 15) is observed to be polymodal as are the distributions of calcite and quartz. The total clay-mineral content varies from a low of 24 percent to a maximum of 71 percent.

The amounts of kaolinite, illite, and "expandable" clay minerals in lta are analyzed from 44 samples. The distribution of these minerals is shown in histograms (figs. 16-18). Greater spread in composition is observed for illite

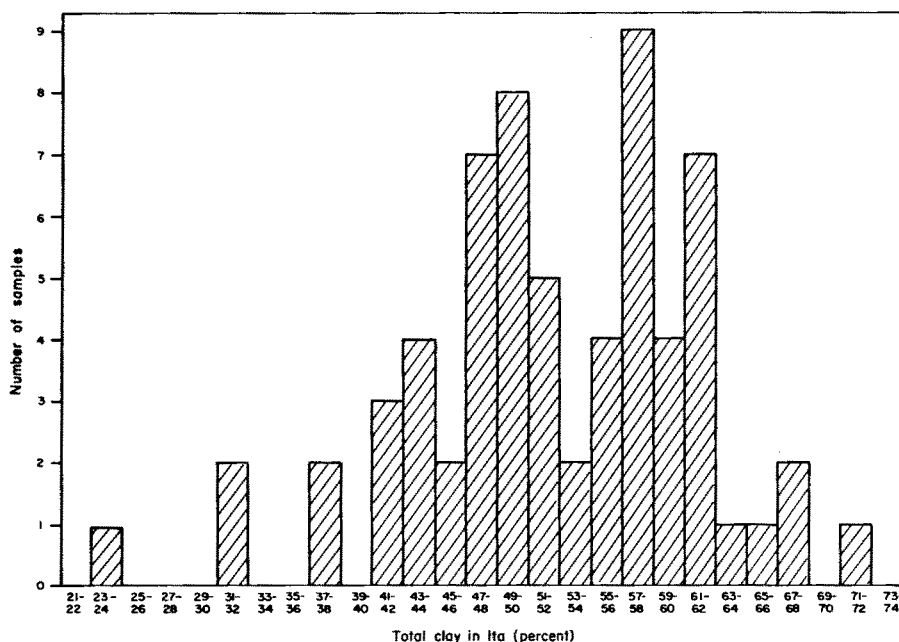


Fig. 15 - Distribution of total clay minerals in mineral matter of Illinois coals.

(8 to 36 percent) and "expandables" (4 to 31 percent) than for kaolinite (7 to 21 percent). More than 50 percent of the Ita samples analyzed contain less than 12 percent kaolinite, and in all of these samples, illite and "expandables" are more abundant than kaolinite. The mean illite content is 21.13 percent, mean "expandables" is 18.18 percent, and mean kaolinite is 12.63 percent. Illinois coals therefore differ from British and Australian coals, in which kaolinite is the predominant clay mineral. The clay-mineral contents of Illinois coals are illustrated by a triangular coordinate diagram of the relative percents of clay minerals in the total clays (fig. 19). Gluskoter, 1967, observed that samples containing relatively more illite than mixed-layer clays also contained more kaolinite than the samples in which mixed-layer clays were dominant over illite.

Stratigraphic Variation of Mineral Matter in Illinois Coals

It would be desirable to compare and contrast the mineral-matter content of the eight different coal seams sampled in this study. However, of the 65 samples, 41 are from the Herrin (No. 6) Coal Member, 14 are from the Springfield-Harrisburg (No. 5) Coal Member, and of the 10 remaining samples, no other coal seam contributed more than 4. With the limited data available, no valid comparison can be made of mineral-matter distributions between individual seams, but two striking differences are apparent when the data from the four older and four younger seams are grouped (table 6). The mean quartz content

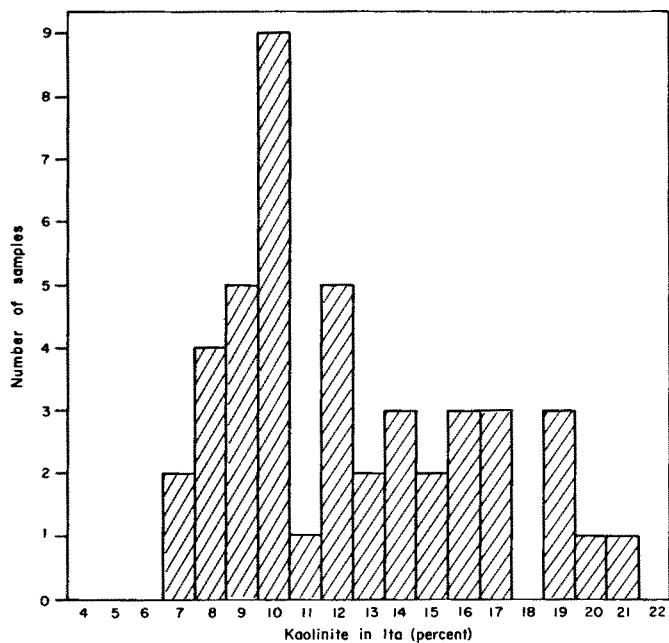


Fig. 16 - Distribution of kaolinite in mineral matter of Illinois coals.

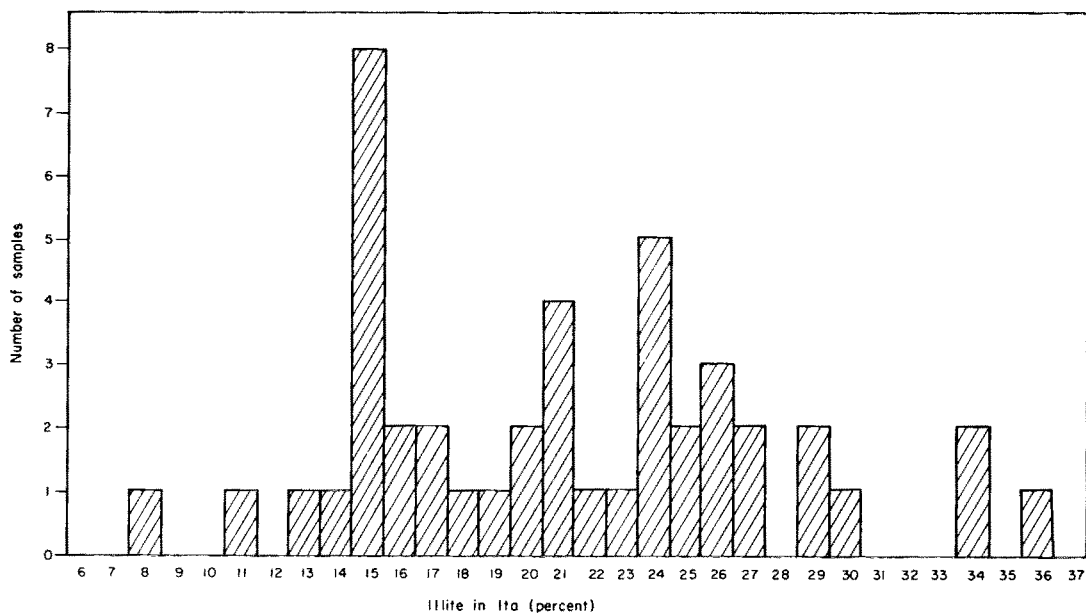


Fig. 17 - Distribution of illite in mineral matter of Illinois coals.

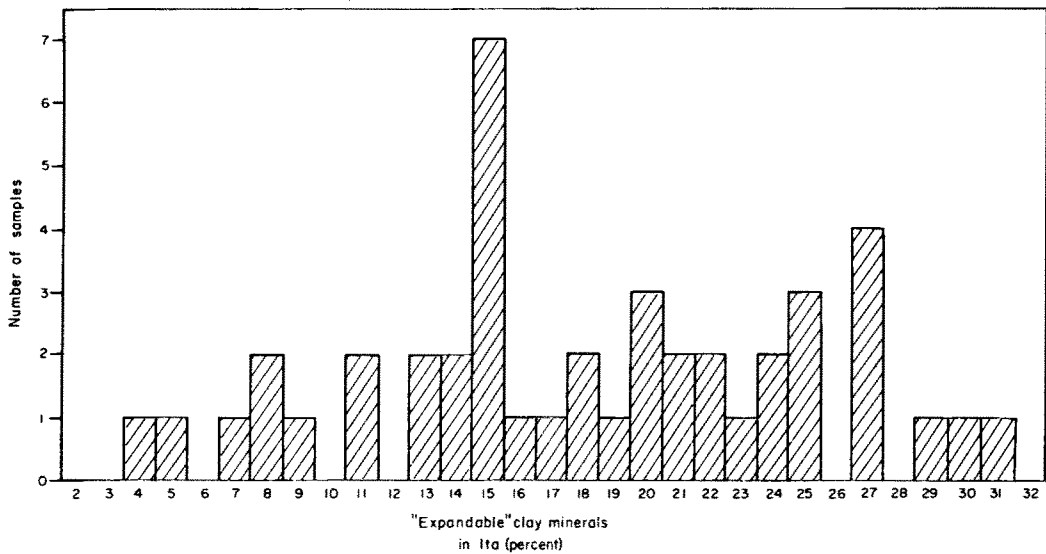


Fig. 18 - Distribution of "expandable" clay minerals in mineral matter of Illinois coals.

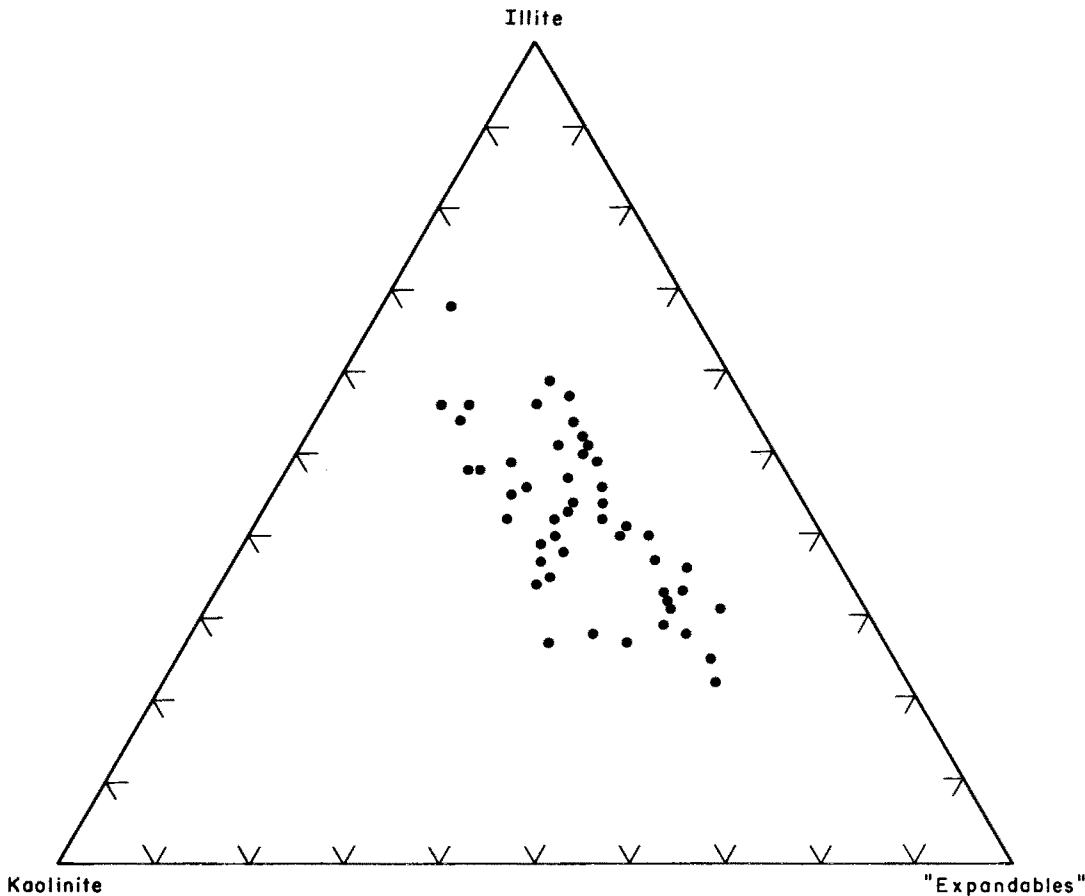


Fig. 19 - Relative percent of illite, kaolinite, and "expandable" clay minerals in Illinois coals.

TABLE 6 - MEAN VALUES OF QUARTZ AND PYRITE IN
LOW-TEMPERATURE ASH OF ILLINOIS COALS

Coal member	Number of samples	Quartz (%)	Pyrite (%)	Low-temperature ash (%)
Danville (No. 7)	2	23.00	16.50	12.27
Herrin (No. 6)	41	15.12	20.68	15.51
Springfield- Harrisburg (No. 5)	13	18.36	24.93	15.47
Sumnum (No. 4)	1	<u>24.00</u>	<u>20.00</u>	<u>12.63</u>
	mean	16.32	21.55	15.33
Colchester (No. 2)	4	8.75	38.25	14.35
Dekoven	1	8.00	32.00	17.50
Davis	1	7.00	41.00	13.23
Murphysboro (Southern Illinois) or Rock Island (No. 1) (Northern Illinois)	2	<u>4.00</u>	<u>44.00</u>	<u>14.92</u>
	mean	6.75	39.25	14.74

of the low-temperature ash from the four younger seams [Danville (No. 7), Herrin (No. 6), Springfield-Harrisburg (No. 5), and Sumnum (No. 4) Coal Members] is 16.32 percent. This value is 2.42 times the mean value of the quartz content (6.75 percent) of the lta of the four older coals [Colchester (No. 2), Dekoven, Davis, and Murphysboro or Rock Island (No. 1) Coal Members]. There is also a significant difference in the pyrite content of the low-temperature ash of these two groups of coal seams. The lta of the four younger coals contains an average of 21.55 percent pyrite, whereas the pyrite content of the four older seams averages 39.25 percent.

The higher quartz content of the lta of the younger coals suggests a greater detrital contribution to the mineral matter, possibly by nearby penecontemporaneous streams. The influence of such streams upon the depositional environments in the coal swamp will be discussed later. If this interpretation is correct, the coals having high quartz contents are those most closely associated with fresh waters. Pyrite in Illinois coals is thought to be concentrated in those areas influenced by marine conditions (Gluskoter and Hopkins, 1970, p. 95); therefore the negative correlation between pyrite and quartz in the lta of the two groups of coals would be expected.

DISTRIBUTION OF MINERAL MATTER IN THE HERRIN (NO. 6) COAL MEMBER

The composition of mineral matter in the Herrin (No. 6) Coal Member is very similar to the previously described overall composition of mineral matter in Illinois coals. The major minerals also occur in the same relative order of abundance: the total clays (54 percent), pyrite and its altered iron sulfate minerals

(20.7 percent), quartz (15 percent), and calcite (9 percent). Marcasite, sphalerite, siderite, dolomite, and feldspar occur only as trace minerals.

Though the mineral assemblages are similar in composition, the X-ray analyses of 41 lta samples from different locations in Illinois show wide variations in the absolute amounts of the minerals. In order to explain the depositional or diagenetic environments, variation maps for each of the major minerals have been prepared. Unless otherwise stated, all the percentages given are in terms of the minerals' contents in the low-temperature ash (lta) and do not correspond to absolute amounts in coal. Histograms showing the distribution pattern of each of these minerals have also been prepared (figs. 20, 22, 27, and 29). The maps showing regional variations of these minerals (figs. 21, 23, 28, and 30) were made using compositional ranges suggested by groupings on the histograms, and boundaries were drawn to separate areas of different mineral content. In most instances the lateral mineral variations are gradational over several miles. However, the data are limited mostly to southern and southwestern Illinois, where the majority of the mines sampled are located. Although the compositional zones observed in southern Illinois are extended to the northwestern part of the state with a liberal amount of interpretation and subjectivity, only the regional variations in southern Illinois are discussed. Changes in the interpretations are to be expected as more data become available, especially in the deeper part of the Illinois Basin.

In the lta samples of Herrin Coal, calcite ranges from a low of 0 percent to a maximum of 21 percent. The mean and standard deviation of 41 samples are 9.27 percent and 4.54, respectively. The distribution of this mineral in lta of Herrin Coal, shown in the histogram (fig. 20), suggests a regional variation of calcite which can be divided into four compositional ranges: 0-5 percent, 6-10 percent, 11-15 percent, and greater than 15 percent. The regional variation map (fig. 21) not only confirms this observation but shows a progressive increase of calcite from east to west, which may have resulted from an increas-

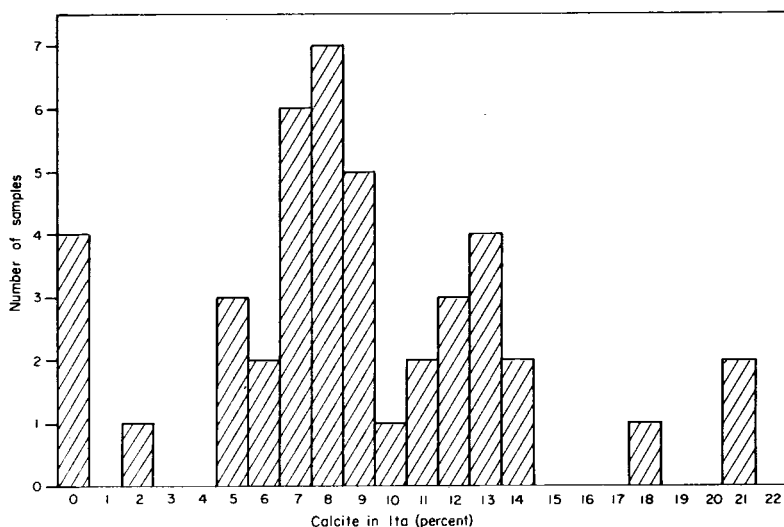


Fig. 20 - Distribution of calcite in mineral matter of Herrin (No. 6) Coal Member.

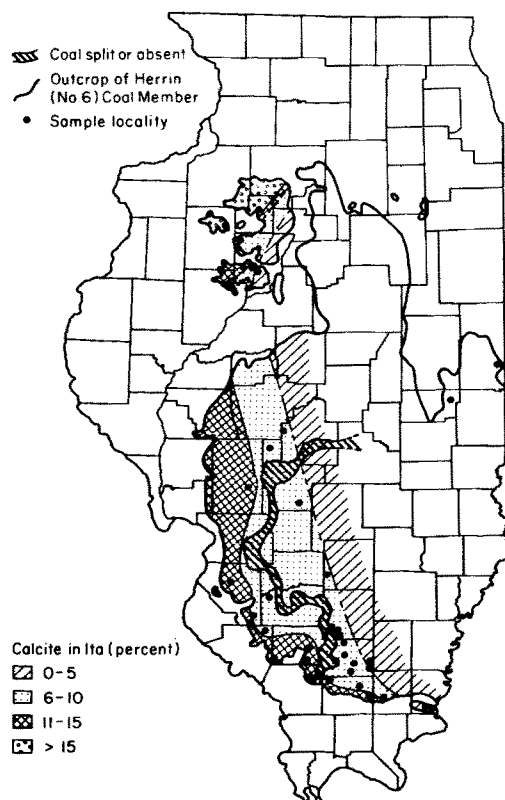


Fig. 21 - Regional variation of calcite in mineral matter of Herrin (No. 6) Coal Member.

ingly open-marine environment in the same direction. The four arcuate zones of calcite are parallel and do not seem to be related to the influence of a penecontemporaneous sandstone channel partially of Herrin Coal age.

Clays dominate the Ita mineral assemblages in the Herrin Coal, and have a mean and a standard deviation of 55 percent and 9.4, respectively. The range of total clays is from a low of 36 percent to a maximum of 68 percent and may easily be separated into three compositional ranges (36-52 percent, 53-62 percent, and 63-68 percent) as indicated by the histogram (fig. 22) of the total clay distribution in Ita.

The regional variation of total clays is gradational (fig. 23). The maximum concentration of clay minerals in Ita is in the samples lying farthest eastward, and the clay concentration progressively decreases from east to west, unlike calcite, which increases in this direction. Such a distribution pattern seems to indicate the introduction of a source sediment rich in clay minerals from the east and northeast into the Illinois Basin. The three arcuate zones of total clay content are parallel and correspond approximately to the calcite zones previously discussed. The amount of total clays did not change appreciably in the vicinity of the penecontemporaneous (in part) sandstone channel of Herrin Coal age.

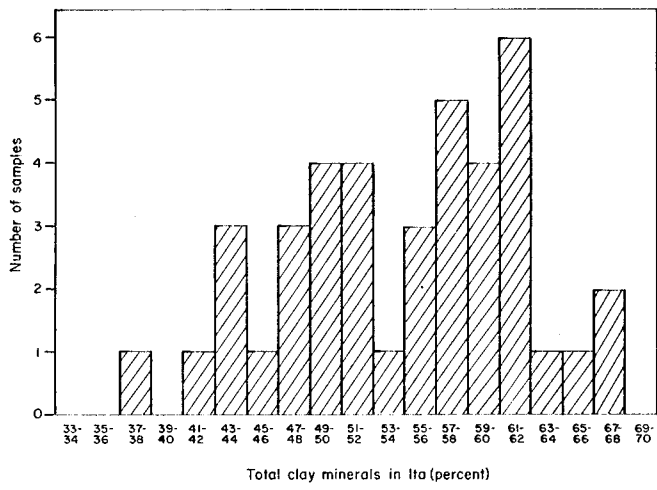


Fig. 22 - Distribution of total clay minerals in mineral matter of Herrin (No. 6) Coal Member.

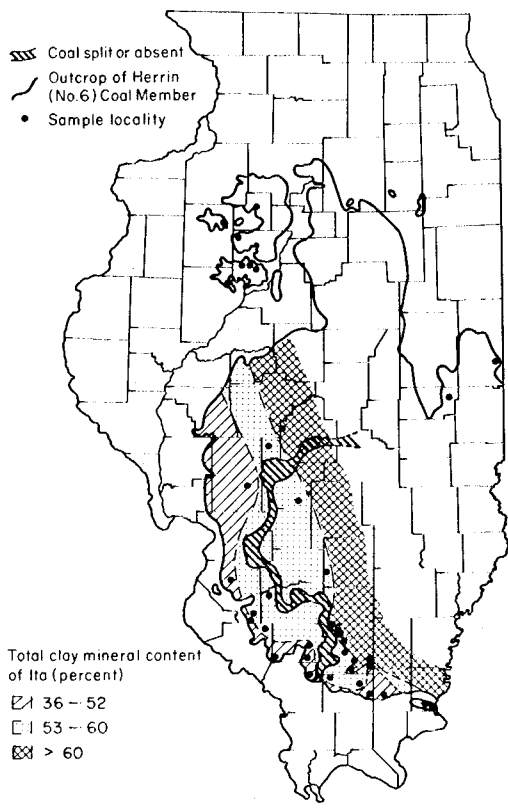


Fig. 23 - Regional variation of total clay in mineral matter of Herrin (No. 6) Coal Member.

The dominant clay minerals are illite, random mixed-layer illite-montmorillonite, and kaolinite. Well-crystallized authigenic kaolinite is commonly observed in almost all the coal samples that have been investigated (Gluskoter, 1967; Hughes, 1971). The regional distribution of illite, kaolinite, and "expandable" clay minerals is shown in figures 24, 25, and 26. In the present study the "expandable" clays represent all clay minerals except kaolinite and illite. Odom and Parham (1968) observed a large area of "P" and "Q" type underclays (abundant in "expandables" containing some illite and kaolinite) below the Herrin Coal in south-central and southwestern Illinois. Larger amounts of expandable clay minerals are found in the Ita from the Herrin Coal in this area (20-30 percent, mean 24.1 percent) than are found in other parts of the Illinois Basin (7-17 percent, mean 13.3 percent).

The lowest range of illite (13-19 percent, mean 15.8 percent) is also found in this region, while the illite progressively increases eastward, grading through two compositional zones (20-25 percent, mean 23.0 percent; and 26-29 percent, mean 28.2 percent). Relatively much lower amounts of kaolinite are present in this area (8-12 percent, mean 9.9 percent) than in other areas of the state (13-21 percent, mean 17.6 percent). Maximum amounts of kaolinite are found in the coals in close proximity to the major channel.

Quartz is present in all of the investigated samples of Ita from the Herrin Coal. Its mean and standard deviation are 15.12 percent and 4.48 respectively.

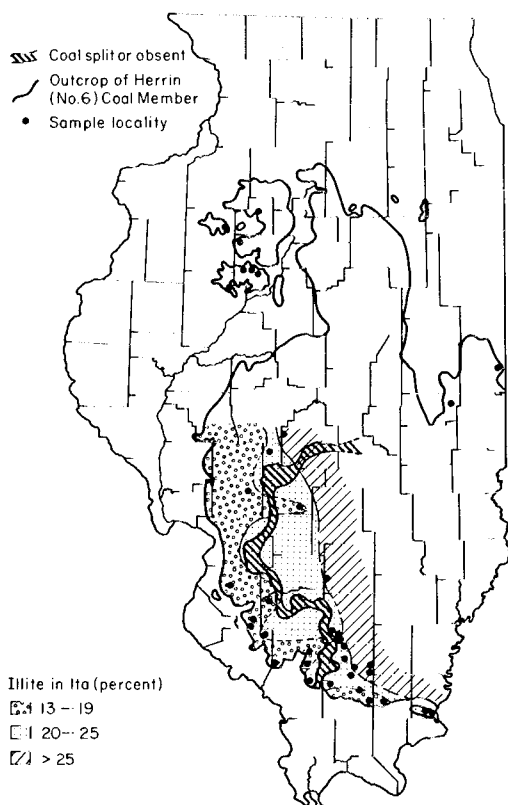


Fig. 24 - Regional variation of illite in mineral matter of Herrin (No. 6) Coal Member.

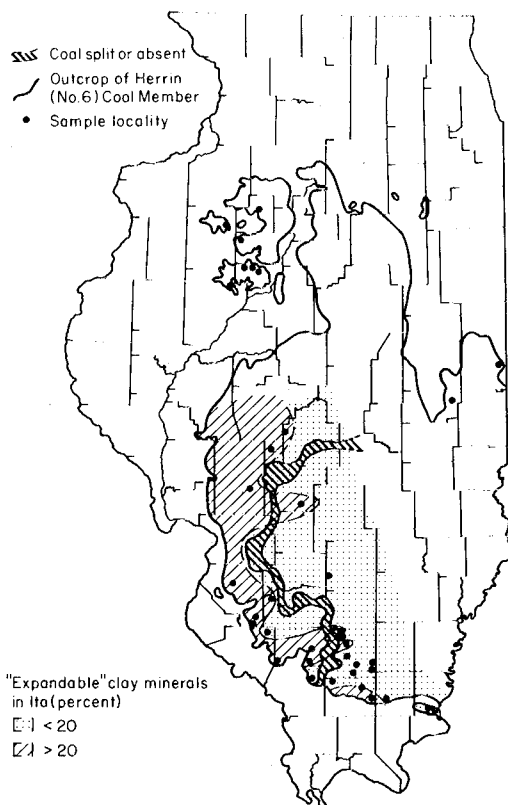


Fig. 25 - Regional variation of "expandable" clay minerals in mineral matter of Herrin (No. 6) Coal Member.

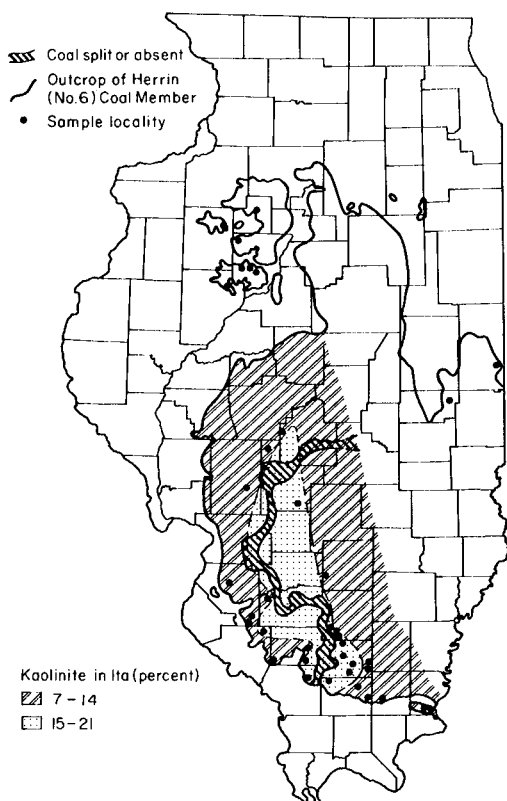


Fig. 26 - Regional variation of kaolinite in mineral matter of Herrin (No. 6) Coal Member.

The distribution of quartz, illustrated in the histogram (fig. 27), ranges from a low of 6 percent to a maximum of 25 percent in four compositional ranges (0-10 percent, 11-15 percent, 16-19 percent, and 20-25 percent). The regional variation pattern of these four compositional ranges of quartz in Herrin Coal is different from the distribution patterns of calcite and of clay minerals (fig. 28). The zone of maximum quartz content is adjacent to the penecontemporaneous sandstone channel. Away from this zone, on both sides, the quartz decreases. This distribution pattern is more closely related to the specific geography of the sandstone channel rather than to the broader pattern of northeast to southwest introduction and transportation of sediment into the Illinois Basin. A similarly high quartz content of Ita in a sample from eastern Illinois may be due to its proximity to the source area or to its position along an eastern extension (yet unmapped) of the same channel system.

Pyrite is the dominant sulfide mineral and is present in all the investigated Ita samples of Herrin Coal.

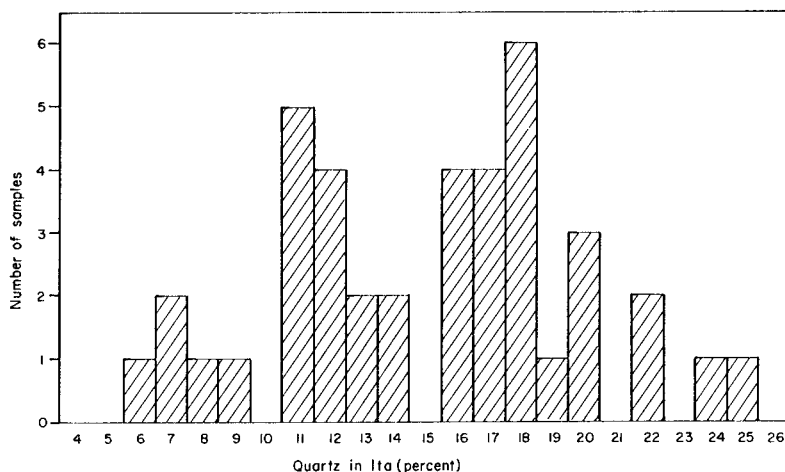


Fig. 27 - Distribution of quartz in mineral matter of Herrin (No. 6) Coal Member.

Marcasite and sphalerite are detected in trace amounts in a few samples. Coquimbite and szomolnokite are the most common iron sulfate minerals. Gypsum is only rarely observed.

The histogram illustrating the distribution of pyrite (fig. 29) shows a near normal distribution of this mineral in Herrin Coal lta. The pyrite percentages range from a low of 7 percent to a maximum of 30 percent, and the mean and standard deviations are 19.61 percent and 4.54, respectively. Only two samples have less than 10 percent pyrite in lta. The pyrite detected in the X-ray analyses has a mean value of 15.83 percent and a standard deviation of 5.91.

The regional variation pattern of pyrite in the lta of Illinois Herrin Coal (fig. 30) shows a relationship to the channel as does that of quartz, but it is different from those of calcite and the clay minerals. The low-pyrite zone, ranging from a low of 11-20 percent pyrite in lta (mean 15.9 percent), encloses most of the sandstone channel and extends to north-western Illinois. A small area with this compositional range occurs in

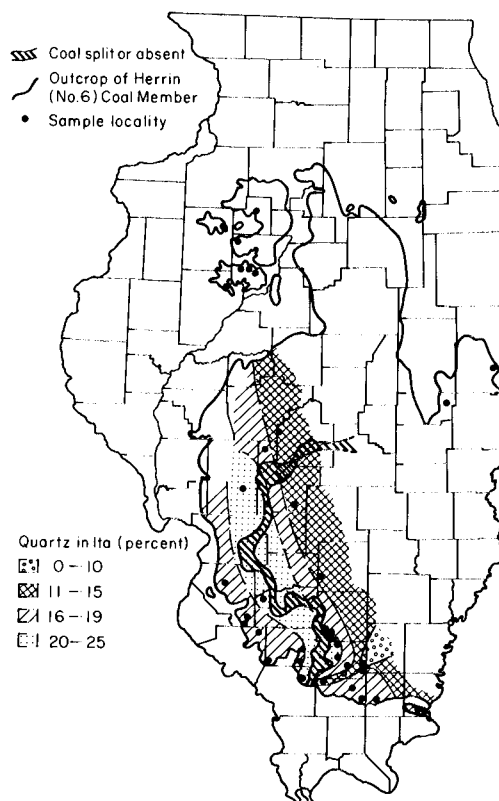


Fig. 28 - Regional variation of quartz in mineral matter of Herrin (No. 6) Coal Member.

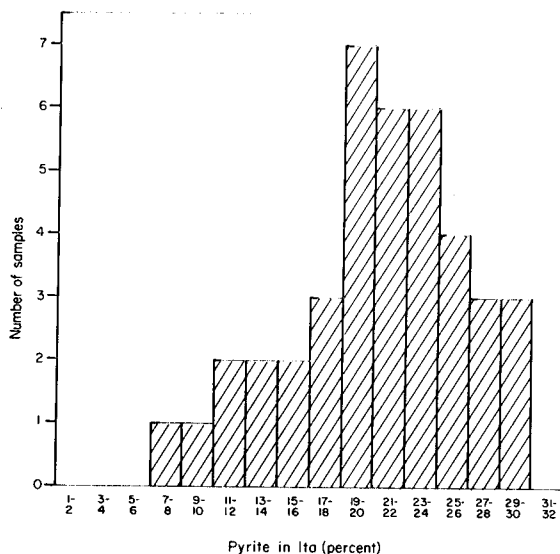


Fig. 29 - Distribution of pyrite in mineral matter of Herrin (No. 6) Coal Member.

eastern Illinois. Away from this channel, on either side, pyrite increases (21 to 30 percent, mean 24.7 percent). The quartz content is also related to the position of the channel; it is highest in concentration along the channel and decreases away from it.

Low-sulfur coals in the Herrin Coal occur in southern Illinois (Gluskoter and Simon, 1968, and Gluskoter and Hopkins, 1970). The three areas of low-sulfur Herrin Coal in southern Illinois that have been mapped average approximately 1.5 percent total sulfur and are associated with the sandstone channel, where there is 20 feet or more of nonmarine or transitional gray shale between the coal and the overlying marine black shale or limestone.

The low-sulfur Harrisburg Coal Member in southeastern Illinois, an associated gray shale roof, and a related sandstone channel have been described by Hopkins (1968). Hopkins and Nance (1970) also described similar relationships in the Colchester (No. 2) Coal Member. The amount of pyrite is found to decrease in the Colchester Coal, at Banner Mine, with the increase of the thickness of the overlying gray Francis Creek Shale Member. The relationship of stratigraphic variation to low sulfur will be explained later, along with the environmental model.

Gluskoter and Simon (1968) studied the relationship between pyritic sulfur and organic sulfur based on chemical analyses of 473 face-channel samples of Illinois coals. The correlation coefficient between them for the entire data is 0.31, and the mean value for the ratio of pyritic to organic sulfur is 1.56. The best correlation coefficient observed was 0.55 in 230 Herrin Coal samples. Because of this correlation, a possible relation between the modes of formation of the two forms of sulfur was suggested.

The regional variation map of the ratio of pyritic to organic sulfur in the Herrin Coal samples investigated by Ita procedures is shown in figure 31. A numerical value greater than 1 indicates relatively more pyritic sulfur than organic sulfur. This ratio varies from a low of 0.50 to a maximum of 2.75 in the present study. The zone of relatively high organic to pyritic sulfur (numerical values less than 1) extends north-south in west-central Illinois and encloses the sandstone channel. To the east of this zone of relatively high organic sulfur and in some areas around the southern margin of the basin, pyritic sulfur dominates over organic sulfur.

In order to study the relationship between pyrite and calcite, relative amounts of these minerals are calculated by using the previously described

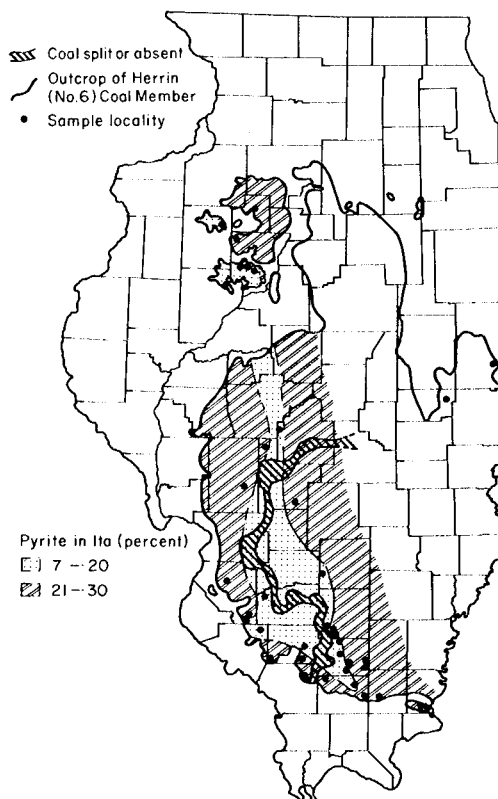


Fig. 30 - Regional variation of pyrite in mineral matter of Herrin (No. 6) Coal Member.

method of Tennant and Berger (1957). The relative percent of calcite in the total of calcite plus pyrite is highest in the zone where the pyrite content of lta is low (20-36 percent, mean 28.3 percent) (fig. 32). East of this zone the relative calcite percent is the lowest (0-9 percent, mean 4.5 percent), whereas west of the channel, calcite ranges from 8-15 percent and has a mean value of 12.5 percent. Though the amount of calcite varies, these relationships confirm that there is appreciably more pyrite than calcite in coals throughout the state.

Figure 33 is a histogram illustrating the distribution of weight percent of low-temperature ash in the Herrin Coal. The lta ranges from a low of 9 percent to a maximum of 22 percent and the mean and standard deviations, respectively, are 15.51 percent and 2.87. Only two samples contain less than 11 percent and two more than 19 percent lta. Though the regional variation map of lta (fig. 34) shows a general decrease of lta weight percent in this coal from east to west, the lowest weight percent of lta is along the channel. The lta regional distribution pattern is, in part, a function of the densities of minerals in Illinois coals. Because the specific gravity of pyrite is almost twice that of other minerals in Illinois coals, the regional distribution of the amount of lta is related to pyrite concentration. The zone of lowest lta content, along the channel, corresponds to the low-pyrite zone.

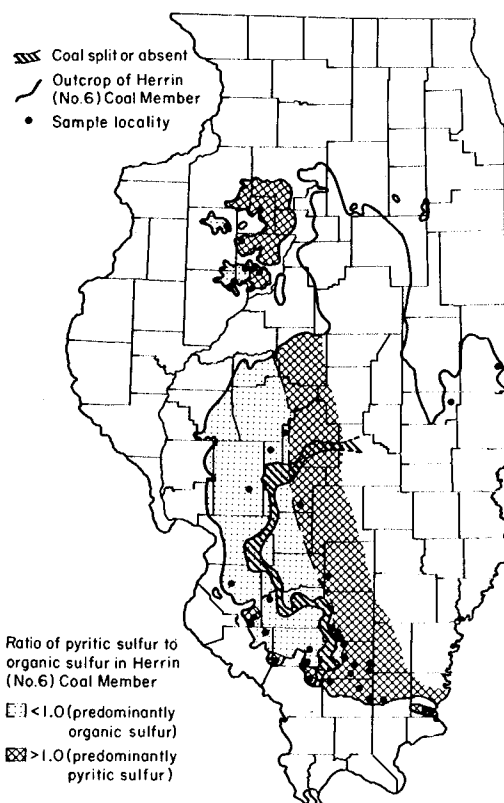


Fig. 31 - Regional variation in ratio of pyritic sulfur to organic sulfur in Herrin (No. 6) Coal Member.

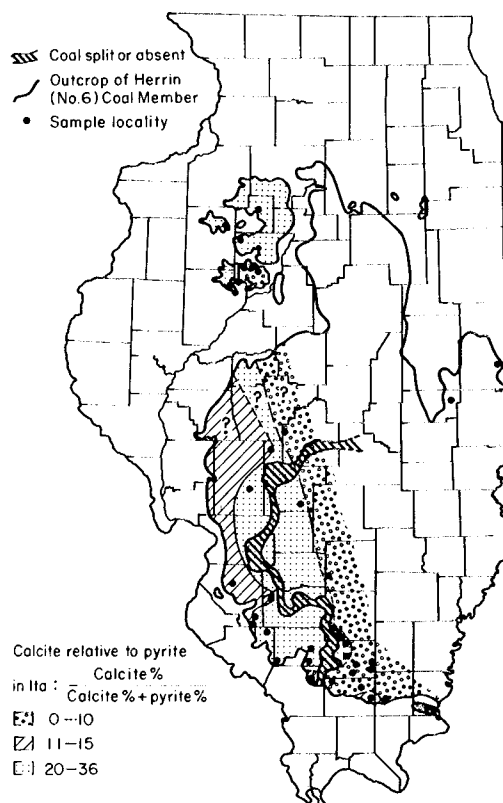


Fig. 32 - Regional variation of calcite relative to pyrite in mineral matter of Herrin (No. 6) Coal Member.

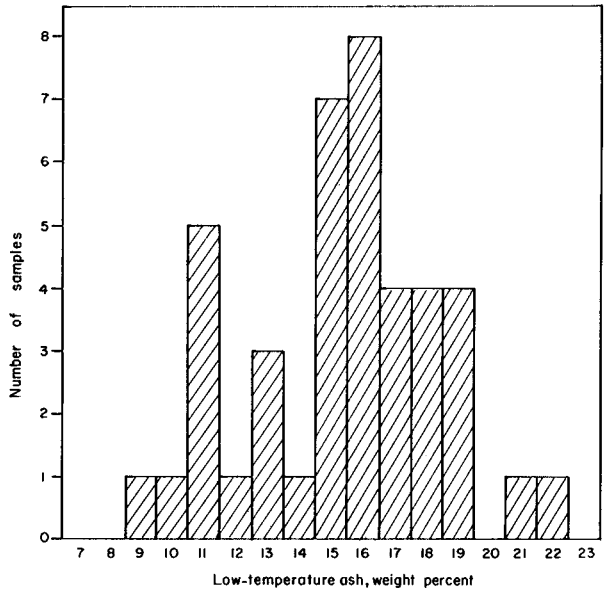


Fig. 33 - Distribution of low-temperature ash in Herrin (No. 6) Coal Member.

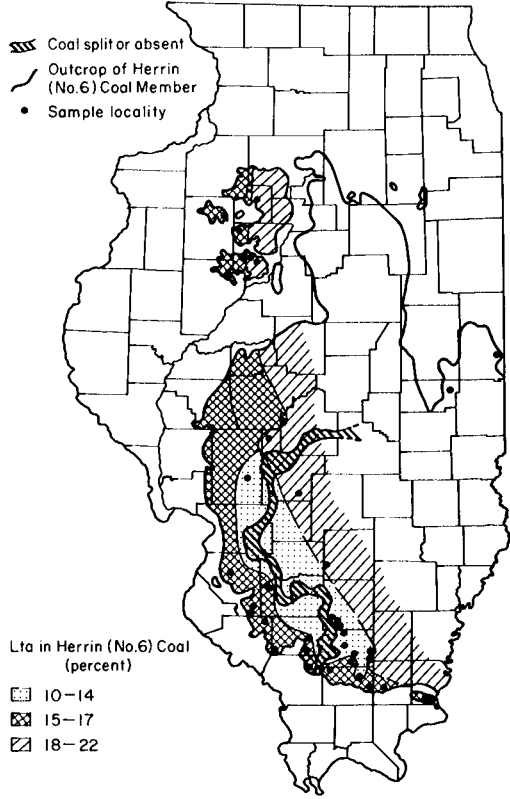


Fig. 34 - Regional variation of low-temperature ash in Herrin (No. 6) Coal Member.

DEPOSITIONAL ENVIRONMENTS OF THE
HERRIN (NO. 6) COAL MEMBER

Previous Interpretations

The conditions of deposition of Pennsylvanian coal beds have been recently reviewed by Wanless, Baroffio, and Trescott (1969). Their study confirmed that most Pennsylvanian coals in Illinois accumulated in situ and that accumulation of very widespread peat occurred at the same time throughout most of the areal extent of each of the present-day coals. Coal swamps in the Illinois Basin during the Pennsylvanian Period were near sea level and, like many of the present-day coastal marshes of the Atlantic coast of the United States, were inundated when there was a slight rise in sea level. The detrital sediments were introduced into the Illinois Basin from source areas north and northeast of the Illinois Basin (Potter and Pryor, 1961). The marine transgressions and regressions were frequently interrupted by the more rapid introduction of deltaic sediments, the effects of which resulted in the formation of clastic wedges of mud (gray shale) and sand (channel sandstone). Wanless et al. (1969, p. 112) concluded:

Those parts of the delta complex above sea level should have supported a dense growth of vegetation, largely in swampy, water-logged soil. Preservation or decay of the vegetable detritus depended to an important degree on the position of the water table with reference to the plant-growing surface. Sporadically, the greater part of the subaerial delta would become an immense coal swamp, much like the delta flats of the Mississippi River in Louisiana, except that (1) the vegetation was principally forest rather than grassland, and (2) probably no trees as tolerant to salt water as the mangrove occurred. The margins of this delta swamp were probably the upper apex of the delta, where ground water would have permitted nearly complete plant decay, and the seaward margin, where depth and salinity of water would prevent tree growth. Rise in sea level just prior to swamp development extended peat deposition above the delta apex into the valley and alluvial plains. Lowering of sea level prevented part or all coal accumulation over the major part of the delta and allowed maximum accumulation along the arcuate front of the now-exposed prodelta, where substrata of the coal generally would be shaly. Growth of the delta might continue through the major period of peat accumulation. Under such conditions the coal bed would be interrupted by channels (or "wash-outs," as they are called in England), the channel fill being contemporary with the coal. Such channels probably would be bordered by natural levees, similar to those marginal to distributaries of the Mississippi, which would prevent frequent flooding of the swamp and introduction of clay or sand splitting the coal deposit. In the Illinois Basin such channels contemporary with the coal appear to be uncommon, though at least two examples are known.

The delta complex below the Herrin (No. 6) Coal Member (fig. 35) in the southern part of the Illinois Basin (Tubb, 1961; Potter and Pryor, 1961; Wanless, 1965; and Wanless, Baroffio, and Trescott, 1969) shows that the major distributary pattern of channels was directed south-southwestward and resulted in a composite delta sand and mud. Marine waters extended beyond the delta margins and formed marine shale encircling the composite delta area. Though the Herrin Coal is the thickest coal in southern Illinois, its local thickness varies (fig. 36). Wanless et al. (1969, p. 120; 1970, p. 222) believe that the formation of the Herrin Coal follows marine regression and thus that the thinnest coal is over the apical part of the preexisting and now exposed delta and the thickest over what had previously been the distal margin and the area beyond.

Two views of the origin of underclays beneath Illinois coals have been proposed recently. Odom and Parham (1968) attributed most of the mineralogic characteristics of underclays to original sedimentation and to chemical regradation of mixed-layer material in a basinward direction. Hughes (1971) observed similar clay-mineral patterns but interpreted the clay-mineral variations as a result of alteration by humic acids associated with peat accumulation and/or effects of leaching and oxidizing conditions on the source material.

The clay-mineral facies map of underclays below the Herrin Coal (fig. 37), prepared by Odom and Parham (1968), is based on the progressive decrease basinward in kaolinite content. They interpreted that the larger particle size of kaolinite caused it to be deposited first, while the finer grained, mixed-layer material was carried farther out into the basin. Some of the mixed-layer material was regraded into illite and a little chlorite and then deposited. Finally, only highly disordered, nonregradable weathered material was deposited in the

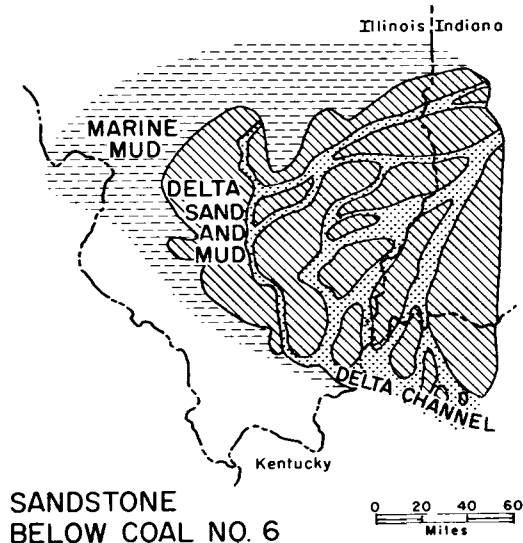


Fig. 35 - Delta complex in southern Illinois Basin between Briar Hill (No. 5a) Coal and Herrin (No. 6) Coal Members, No. 11 Coal of Kentucky. (After Wanless, 1965, and Wanless, Baroffio, and Trescott, 1969; used with permission of the Geological Society of America.)

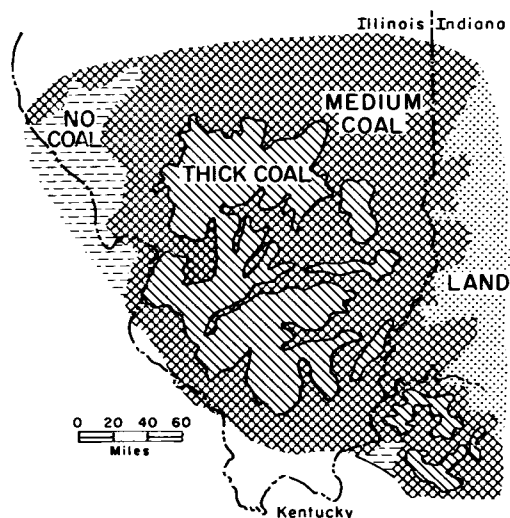


Fig. 36 - Distribution of medium and thick coal in southern Illinois Basin of Herrin (No. 6) Coal Member and correlatives. (After Wanless, 1965, and Wanless, Baroffio, and Trescott, 1969; used with permission of the Geological Society of America.)

most basinward areas. Because kaolinite can occur as an authigenic mineral, the abundance of kaolinite in coal does not necessarily represent a nearshore area. Hughes (1971) observed selective occurrence of feldspar and pyrite, and two types of kaolinite (poorly crystallized and well-crystallized) in the underclays. On the basis of these observations, he concluded that in shallow-water or positive areas near distributary channels, source materials were severely altered by acid oxidizing conditions, resulting in a deposit of poorly crystalline kaolinite with a residual detrital quartz. More distant from the distributary channels, a region of little alteration was present in which source materials were preserved. Still farther from distributary channels, underclay sediments were subjected to acid and reducing conditions and thus the underclay is composed of crystallized authigenic kaolinite and an expandable clay mineral derived from the source material.

Sandstone channel deposits have been mentioned previously and are significant in the interpretation of the depositional environments during the Pennsylvanian Period in the Illinois Basin.

Hopkins (1958) mapped one of these sandstone units (the Anvil Rock Sandstone Member) across the southern part of the state and found it to be present throughout much of the deeper portion of the Illinois Basin. He distinguished between the thicker "channel phase" and a thinner "sheet phase" in the unit. Only the channel phase was present to the west of the Du Quoin-Centralia Monocline. From the pattern of channel phase deposition and from cross-bedding directions measured in outcrop, Hopkins concluded that the drainage pattern that produced the Anvil Rock Sandstone had a general southwestward orientation.

The mapping of the Anvil Rock Sandstone was extended to the north and west by Potter and Simon (1961). They mapped not only the area in which the Herrin Coal was cut out by the sandstone but also areas in which the coal was split, thin, or missing. Potter and Simon (1961) concurred with Hopkins (1958) and concluded that the cutouts are related to a stream drainage pattern of late Pennsylvanian age. Some uncertainty exists as to the designation of the sandstones mapped by Hopkins (1958) and Potter and Simon (1961) as Anvil Rock,

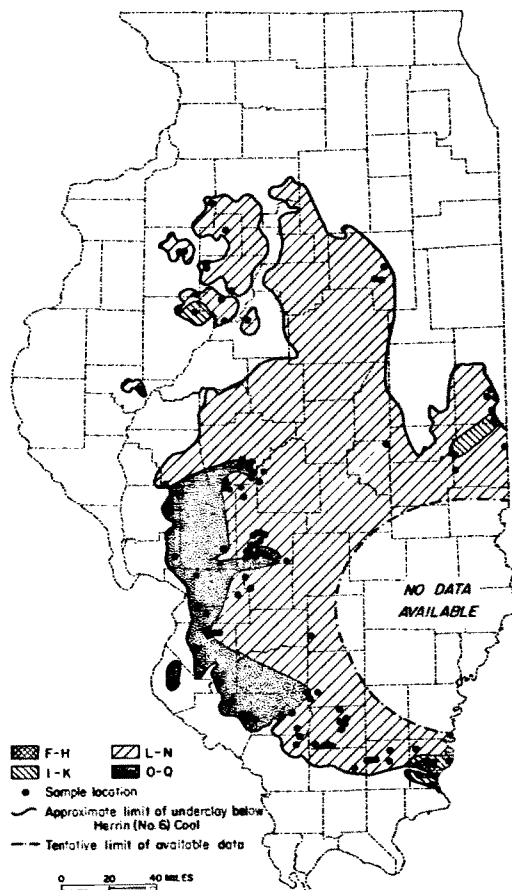


Fig. 37 - Generalized distribution of similar clay-mineral assemblages in underclay below Herrin (No. 6) Coal Member. (From Odom and Parham, 1968.)

especially the sandstone occupying the large channel in southern and southwestern Illinois associated with low-sulfur Herrin Coal. This sandstone does appear to be the same age as the associated gray shale, which itself can be shown to be in part equivalent in age to the Herrin Coal and in part younger. But nowhere is this shale or the associated sandstone known to be the same age as, or younger than, the black "slaty" shale which, over much of Illinois, occurs immediately above the Herrin Coal. Therefore the stratigraphic designation of this sandstone as Anvil Rock is probably wrong. In Illinois, this term should be confined to the sandstone developed between the Conant Limestone and the Bankston Fork Limestone Members, or in the absence of the Conant, between the Brereton and the Bankston Fork Limestone Members. In the same general vicinity as the large sandstone cutout, there are small channels of Anvil Rock Sandstone (restricted sense) along which, in some places, the Herrin Coal and the overlying black shale and the Brereton and Conant Limestones have been removed. The compositional character of the coal, in these areas, does not bear any relation to the presence of the cutout.

The stratigraphic relationships between the two sandstones and their distributions have been studied at the Survey by Donald O. Johnson (1972).

In recent studies of late Paleozoic deltas in the United States, Wanless et al. (1970, p. 220) concluded:

... the geometry of many of the lenticular sand bodies strongly suggest that the divergent channels in Illinois are distributaries of a digitate delta, rather than tributaries. If this is true, the channels may have been cut near sea level by distributaries traversing recently deposited sediment of a lengthening delta front. Under these conditions, in explaining the channels, there is no necessity to assume emergence of the area due to regional uplift. This interpretation would be more logical, because in most cases the sea later buried the recently formed sands with limy mud, now fossiliferous limestone. If this interpretation is made, the underlying shale is part of the same delta complex as the overlying sand

It has long been recognized that the low-sulfur coals in Illinois are associated with gray shale roofs. Hopkins (1968) and Gluskoter and Simon (1968) pointed out that the association is not with merely any gray shale, but that it is specifically with the gray shale occupying the particular stratigraphic position above the coal but beneath the overlying black "slaty" shales and/or marine limestones normally associated with the coal. Gluskoter and Simon (1968) indicated three such low-sulfur coal areas in southern Illinois, and, because a gray shale roof was present in a fourth area somewhat farther north, they suggested that the coal there also could be low in sulfur. Gluskoter and Hopkins suggested (1970, p. 95) that "the deposition of gray shale took place at a relatively rapid rate and preceded all, or at least most, of the black shale deposition."

Roof shales (shales overlying coals) have been studied by Webb (1961), Odom (1963), and Hughes (1971). The clay minerals in these shales are generally illite, chlorite, well-crystallized kaolinite, and a mixed-layer illite-

montmorillonite. Generally, well-crystallized kaolinite occurs near the coal. The predominant clay minerals are of the illite-chlorite type. The relative abundances of illite and mixed-layer clay minerals were closely related to the amount of illite, which decreases as the amount of mixed-layer material increases. The gray and black shales are similar in clay-mineral composition and contain pyrite and calcite. However, pyrite is relatively more abundant in black shale than in gray shale (Hughes, 1971).

Odom (1963, p. 44) concluded that the distribution patterns of clay minerals in the roof shales largely reflect the mineralogy of the source material and the effects of current action, particle size, flocculation tendencies, and position of the site in the depositional basin. However, the close correlation between the abundances of illite and mixed-layer minerals indicates that some diagenetic regrading of mixed-layer material or degrading of illite has occurred.

Depositional Environments Interpreted from Mineral-Matter Content of Herrin (No. 6) Coal Member

The depositional environments in southern Illinois during the formation of the Herrin (No. 6) Coal Member are generalized in figure 38. This model depicts a northeast-southwest section with a gentle southwestward slope and represents stratigraphic units deposited before, during, and after the time of deposition of the Herrin Coal. It is based on the synthesis of the data concerned with the Herrin Coal and associated strata, including: X-ray analyses of low-temperature ash, chemical analyses of composite coal samples, mineralogy of underclays and roof strata, and the conditions of sedimentation during the late Paleozoic in the Illinois Basin. This model of depositional environments is essentially a delta distributary system and comprises three parallel contiguous zones from (1) a low positive or shallow-water area to the northeast, to (2) an area encompassing the sandstone channel, and finally to (3) the most open-marine area away from the channel to the southwest. Figure 38 is very similar to a diagrammatic geologic section presented by Gluskoter and Hopkins (1970, p. 94) depicting the general stratigraphic relationships between marine black shales and limestones, gray shales, sandstone bodies, and low-sulfur coals in the Illinois Basin. The relationships depicted by Gluskoter and Hopkins (1970) were further defined by Hopkins et al. (1971), who concluded:

Broad regional changes in mineral matter (clay minerals and calcite) in the coals may reflect transport distance and overall change to open marine conditions to the south and southwest, but do not appear to be related to significant changes in sulfur content of the coals.

A depositional model is suggested whereby sediments, mostly gray muds representing a transitional environment dominated by a deltaic complex, rapidly cover the coal and effectively prohibit infiltration of sulfate ions from sea water, preventing the continued addition of iron sulfides in the low-sulfur areas. A major transgression follows, which results in the deposition of black shale and limestone over most of the Illinois Basin.

SW

NE

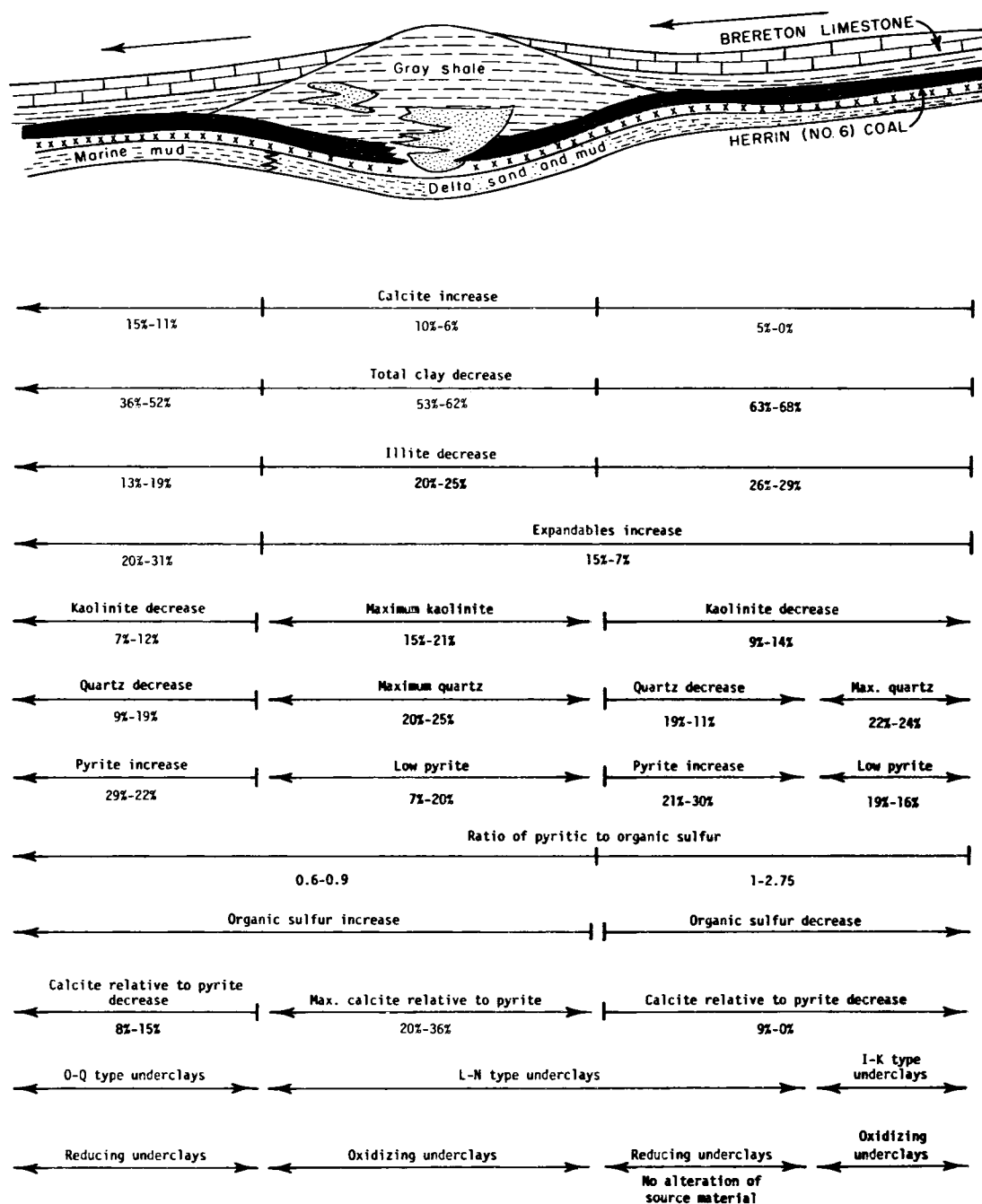


Fig. 38 - General regional interpretation of depositional environments of Herrin (No. 6) Coal Member.

The amount of calcite in the mineral matter of the Herrin Coal progressively increases from northeast to southwest, which is down the normal paleoslope, possibly due to an increasingly open-marine environment in this direction. The amount of calcite does not vary appreciably along the penecontemporaneous sandstone channel of Herrin Coal age. In the Herrin Coal, as in other coal seams in Illinois, calcite is the only dominant carbonate mineral. Siderite and dolomite occur only in trace amounts. Neither ankerite nor magnesite occurs in the investigated samples. There is no evidence of any interaction, solid solution, or formation of isomorphous mixtures. Such a homogeneous carbonate mineralogy reflects that most Illinois coals are overlain by marine rather than fresh-water rocks and that the calcite, after being deposited, did not change appreciably to other carbonate minerals. The homogeneous carbonate mineralogy is possibly a result of the composition of infiltrating solution being very similar to the composition of solution that deposited the carbonate minerals in coal, or of the overlying marine black "slaty" shale or gray shale acting as an impermeable membrane and sealing the coal from access to infiltrating solutions whose compositions were widely different from the carbonate composition in coal.

The maximum concentration of total clay in the low-temperature ash is along the eastern part of the state, and the clay concentration gradually decreases from east to west, in contrast to calcite, which increases in this direction. This distribution pattern seems to indicate the introduction of source sediment, rich in clay minerals, from east and northeast into the Illinois Basin. Like calcite, total clay does not vary appreciably in amount along the channel sandstone.

Gluskoter (1967) observed that, with the exception of chlorite, the clay minerals in ita from the Herrin Coal are similar to those in the roof shales and the underclays of this coal. Chlorite is most abundant in the roof shales, less so in the underclays, and practically absent in the coal. The present study and that of Hughes (1971) confirm his observations. Gluskoter (1967) also noticed variation in clay mineralogy from east to west in the Illinois Basin. The samples to the west contained larger amounts of mixed-layer material in relation to illite than those to the east. In the present study, it is also observed that the concentration of illite gradually decreases from east to west. The "expandable" clay mineral distribution, increasing from east to west, is opposite that of illite. Illite and/or "expandable" clay minerals dominate over kaolinite in most of the samples. Although authigenic kaolinite is commonly observed in Illinois coals (Gluskoter, 1967; Hughes, 1971), the maximum amount of kaolinite in the Herrin Coal occurs along the channel and it decreases away from the channel.

Gluskoter (1967, p. 213) interpreted the clay mineral distribution in this coal to be a result of differential sedimentation and diagenesis:

... kaolinite, illite, mixed layer material, and some chlorite were introduced into the coal swamp and differential sedimentation took place. The chlorite was broken down by the acid environment and kaolinite and illite deposited preferentially in the landward portion of the swamp. The highly degraded mixed layer material was carried farther into the basin and was deposited last. . . .

Recent study by Hughes (1971) indicates that along the channels or in shallow or positive areas an oxidizing type of underclay occurs, characterized by pure,

poorly crystallized kaolinite developed from the alteration of feldspar and residual quartz. A reducing type of underclays (highly degraded "expandables") is concentrated away from the channels. Though some detrital kaolinite was introduced into the basin and preferentially deposited in the landward portion of the swamp, most of the kaolinite in the Herrin Coal is authigenic. The maximum concentration of kaolinite along the channel seems to be due to the introduction of this mineral from the channel deposition. However, the kaolinite variation does not appreciably affect the clay-mineral distribution patterns. The progressive decrease of illite from east to west and the increase of expandables in the same direction support the interpretation that illite was deposited preferentially in the landward portion and the degraded expandable clay minerals were deposited in the seaward direction.

Bohor and Gluskoter (1973) investigated the boron content of illite in low-temperature ash of the Herrin Coal and also correlated their data with a depositional model of a delta distributary pattern. They observed that higher paleosalinity (higher boron) values were located farthest from the mapped delta distributary channels and that the lower paleosalinity (lower boron) values were in those areas influenced by the distributary channels. The higher values are attributed to the proximity to marine water and the lower values to the fresher water introduced along the distributary.

The distribution of quartz is different from the distributions of calcite, total clay, illite, and expandables. The zones of maximum quartz content and of maximum kaolinite content lie adjacent to the penecontemporaneous sandstone channel. Such a distribution pattern seems to be more closely related to the local geographic position of the sandstone channel than to the general areal direction of introduction and transportation of sediment into the Illinois Basin. The high quartz content observed in two samples in eastern Illinois may be due either to the proximity of the sample sites to the source area or to a probable extension of a sandstone channel into eastern Illinois.

The regional variation of pyrite in Illinois Herrin Coal is related to the position of the sandstone channel (fig. 38), and the areas of low pyrite values and of low total sulfur values are in the vicinity of the sandstone channel. Away from this channel, on either side, pyrite increases, whereas quartz decreases. The low-pyrite zone corresponds to the reported occurrences of low-sulfur areas in Herrin Coal (Gluskoter and Simon, 1968). Gluskoter and Simon (1968) and Gluskoter and Hopkins (1970) observed low-sulfur coals where there is 20 feet or more of nonmarine gray shale between the coal and the black shale or limestone. Gluskoter and Hopkins (1970) are of the opinion that the low sulfur content in coal results from rapid deposition of gray mud (shale) that sealed the coal from access to the sulfate-bearing marine waters.

The ratio of pyritic to organic sulfur in the Herrin Coal decreases from east to west. The variation pattern of pyritic to organic sulfur observed in the Herrin Coal in the present study seems to be related to the genesis of these two forms of sulfur. Neavel (1966, p. 292) suggests two factors that control the concentration of organic sulfur: "(1) the availability of sulfur to the local environment, and (2) the rate of sulfate reduction to the sulfide state." The formation of pyrite is also influenced by these two factors, and by the relative availability of iron.

Reducing conditions both east and west of the channel favor the sulfate reduction to sulfide; but the rate at which the sulfate is fixed as iron sulfide depends upon the availability of sulfate-reducing bacterial colonies and of iron in the environment. If the sulfate-reducing bacterial colonies are assumed to be present in sufficient amounts in the reducing environments, then the rate of iron sulfide formation is a function of the amount of iron in the environment. The supply of iron may come from different sources. But, if the iron is obtained mostly from iron adsorbed on clay minerals in coal, as is generally thought to be the case, then the amount of iron is a function of the amount of total clay minerals in coal. The percentage of total clay minerals drops to the lowest value in western Illinois, the distal portion of the swamp, and the amount of iron would be expected to be lowest in this part of the state. For these reasons, it seems that though relatively higher amounts of pyrite are observed in western Illinois than surrounding the channel, the organic sulfur dominates over pyritic sulfur and generally increases away from the channel. The lower concentration of clay minerals, and therefore the smaller amounts of iron that might have been available for pyrite formation, occur in the southwestern part of the Illinois Basin. This is also the area in which the ratio of pyritic sulfur to organic sulfur is the lowest.

SUMMARY

Mineral matter in Illinois coals was liberated by radio-frequency low-temperature ashing and investigated by X-ray diffraction analyses, chemical analyses, and microscopic analyses. Organic carbon, determined on 12 of the low-temperature ash (lta) samples, averaged 1.46 percent. The amount of unoxidized coal in the lta samples, therefore, does not significantly affect the quantitative mineralogical analyses of the lta.

The X-ray diffraction analyses were done on dry cavity mounts, because experimentation with water smears significantly altered the mineral-matter composition. This alteration resulted from the reaction of water and sulfate ion to make sulfuric and sulfurous acids, which reacted with the carbonate minerals. The final result when water was used was a reduction in calcite (CaCO_3) and iron sulfate minerals and the formation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

The most common minerals in Illinois coals are: illite, kaolinite, mixed-layer clay minerals, quartz, calcite, and pyrite and iron sulfate minerals that form upon the alteration of pyrite, namely coquimbite and szomolnokite. Siderite, dolomite, feldspar, and gypsum occur in trace amounts. Marcasite and sphalerite are present as trace sulfide minerals in a few samples. The relative abundances of major minerals are similar in most of the lta samples: the total clays dominate (52.0 percent), followed by the total amount of pyrite and its altered iron sulfate minerals (23.4 percent), quartz (15.4 percent), and carbonates (9.2 percent).

The carbonate mineralogy of Illinois coals differs from that of Australian and British coals, in which carbonates vary widely in composition. In Illinois coals the only dominant carbonate mineral is calcite. There is no evidence of any interaction, solid solution, or formation of isomorphous mixtures. Such a

homogeneous carbonate mineralogy seems to reflect that most of the Illinois coals are overlain by marine rather than fresh-water rocks and that the calcite, once deposited, was not subsequently altered to other carbonate minerals.

The clay mineralogy of Illinois coals is also different from that of Australian and British coals, in which kaolinite is generally the predominant clay mineral; this difference is probably a result of the marine influence on coal deposition in Illinois. In Illinois coals the variation of clay mineralogy is due mostly to variation in illite and "expandable" clay minerals; the authigenic kaolinite is rather uniform in most of the investigated samples. Relatively higher amounts of kaolinite are observed along the channels, where the coal is generally overlain by transitional or nonmarine rather than by marine rocks.

The X-ray determined pyrite content of the Ita is in general agreement with the pyrite content calculated from chemical analyses. Although pyrite is easily oxidized, no appreciable alteration of this mineral is detected in fresh coals ashed in the low-temperature asher. The iron sulfate minerals that were observed most probably formed while the samples were stored in the laboratory. Because conditions in the low-temperature asher favor dehydration, only the final phases of ferrous sulfate (szomolnokite, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$) and ferric sulfate (coquimbite, $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$) are observed. Pyrite in the low-temperature ash ranges from a low of 7 percent to a high of 48 percent, with a mean value of 22.5 percent.

Quartz is present in all the investigated Ita samples, and is observed to vary from a low of 2 percent to a maximum of 28 percent. Samples containing less than 5 percent quartz are rare.

Stratigraphic variation of relative amounts of minerals in Illinois coals is difficult to interpret because of limited data. However, the four older coals sampled contain higher amounts of pyrite in the Ita than the younger coals do, but the quartz content is appreciably higher in the four younger coals.

The composition of mineral matter in the Herrin (No. 6) Coal Member is very similar to the overall composition of mineral matter in Illinois coals. The major minerals also occur in the same relative order of abundances in Herrin Coal and in the total coals: the total clays (54.7 percent), pyrite and its iron sulfate alteration products (20.7 percent), quartz (15.1 percent), and calcite (9.3 percent). Marcasite, sphalerite, siderite, dolomite, and feldspar occur only in trace amounts.

The synthesis of the X-ray data, combined with chemical analyses of coal, mineralogy of underclays, and previous interpretations of conditions of sedimentation at the time of Herrin Coal deposition, led to a general reconstruction of depositional environments for this coal. This model, a delta distributary system, indicates depositional environments from northeast to southwest in the southern Illinois Basin in three parallel contiguous zones from (1) a low positive or shallow-water area, to (2) an area encompassing the sandstone channel, and finally to (3) the most open-marine area away from the channel. Progressive increase in calcite and decrease in total clay minerals from east to west seem to indicate an increasingly open-marine environment in this direction and the introduction of sediments rich in clay minerals from sources north and northeast of the Illinois Basin. The clay mineralogy of the coal is similar to that of underclays below the coal. The general decrease of illite from east to west and from northeast to southwest and the increase of expandables in the same direction suggest that illite was deposited preferentially in the landward

portion and expandable mixed-layer clay minerals were deposited in the basinward direction. Though some detrital kaolinite was introduced into the basin and preferentially deposited in the landward portion of the swamp, most of the kaolinite is authigenic. The higher concentration of kaolinite and quartz along the channel is probably due to the physical and chemical influences related to the channel. Relatively less pyrite development along the channel and an increase in pyrite away from it seem to be related to oxidizing conditions along this channel and reducing conditions away from it. There is a decrease in the ratio of pyritic to organic sulfur from east to west. This may be the result of a reduced concentration of clay minerals and therefore of the amount of iron on the clays in the southwestern part of the present-day Illinois Basin.

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APPENDIX
ANALYSES OF MINERALS FROM COALS OF THE ILLINOIS BASIN

Coal member	CHEMICAL ANALYSES OF COAL							MINERAL MATTER IN LOW-TEMPERATURE ASH										
	Analysis number	Sulfate sulfur (X)	Pyritic sulfur (X)	Organic sulfur (X)	Total sulfur (X)	Chlorine (%)	Ash (%)	Laboratory number	Low-temperature ash (%)	Quartz (%)	Calcite (%)	Pyrite (%)	Pyrite, calcd. from chem. anal. of pyritic sulfur (X)	Iron sulfate (%)	Total clay (%)	Kaolinite (%)	Illite (%)	Expandables (%)
1 Indiana Danville (VII)	C-15418	.02	.54	.42	.98			600-I-121	12.41	28	Tr.	15	8	Tr.	57			
2 Danville (No. 6)	C-15034	.01	1.16	1.84	3.01	.06	10.0	600-J-65	12.3	18	14	12	18	6	50	12	34	4
3 Herrin (No. 6)	C-14838	.03	1.66	2.56	4.25	.13	12.10	600-J-64	15.81	11	7	16	20	4	62	12	29	21
4 Herrin (No. 6)	C-14574	.04	.94	1.20	2.18	.11	7.34	600-J-67	9.29	24	5	16	19	3	52	14	21	16
5 Herrin (No. 6)	C-12831	.03	1.29	1.28	2.60	.14	10.5	600-II-119	14.54	13	8	12	17	5	62	15	27	13
6 Herrin (No. 6)	C-14684	.02	1.44	1.33	2.79	.28	9.94	600-II-162	12.91	17	7	19	21	2	55	15	27	13
7 Herrin (No. 6)	C-13322	.04	3.58	1.30	4.92	.25	15.8	600-I-143	22.34	18	5	18	30	12	47	14	26	7
8 Herrin (No. 6)	C-13433	.01	2.17	.85	3.03	.42	9.4	600-I-44	11.07	7	2	17	23	6	68	14	27	27
9 Herrin (No. 6)	C-16501	.01	1.21	1.15	2.37	.40	10.3	600-I-199	13.23	24	9	16	17	1	50			
10 Herrin (No. 6)	C-14630	.02	.59	.63	1.22	.40	8.6	600-II-177	11.11	20	9	10	10	0	61	19	21	21
11 Herrin (No. 6)	C-16741	.05	1.54	1.96	3.55	.22	12.89	600-II-164	15.58	8	13	14	19	5	60			
12 Herrin (No. 6)	C-16265	.04	1.22	1.94	3.20	.01	9.50	600-II-172	16.55	17	8	2	14	2	61			
13 Herrin (No. 6)	C-16030	.04	1.87	1.60	3.51	.18	11.92	600-II-140	14.73	12	Tr.	21	24	3	64	15	30	19
14 Herrin (No. 6)	C-9714			4.58		12.3	600-I-190	15.33	11	0	26	29		3	60			
15 Herrin (No. 6)	C-13975	.01	1.82	.71	2.54	.02	11.6	600-II-177	15.73	24	9	20	12	0	56			
16 Herrin (No. 6)	C-15868	.00	.29	.56	.85	.34	8.9	600-II-135	10.80	20	9	7	5	0	62	19	34	9
17 Herrin (No. 6)	C-14613	.01	.65	.77	1.43	.35	9.06	600-I-182	10.84	18	7	9	11	2	64	20	24	20
18 Herrin (No. 6)	C-15791	.02	1.14	.72	1.88	.33	10.34	600-II-124	13.02	16	7	21	16	0	56	12	19	25
19 Herrin (No. 6)	C-16543	.04	1.20	1.91	3.15	.04	11.9	600-II-174	17.00	13	18	12	13	1	56			
20 Herrin (No. 6)	C-15436	.07	1.37	1.89	3.33	.07	10.11	600-J-69	12.40	25	11	23	21	0	41	7	14	20
21 Herrin (No. 6)	C-12540	.05	2.55	1.75	4.33	.43	12.72	600-J-68	17.90	14	9	14	27	13	50			
22 Herrin (No. 6)	C-13464	.67	1.63	1.75	4.05	.44	12.9	600-I-189	17.91	14	8	9	17	8	61			
23 Herrin (No. 6)	C-16139	.11	2.27	2.46	4.84	.07	14.08	600-J-47	17.64	18	8	20	24	4	51	9	20	22
24 Herrin (No. 6)	C-14969	.00	2.37	2.06	4.43	.10	10.7	600-J-33	19.13	11	8	5	23	18	58	21	15	22
25 Herrin (No. 6)	C-16317	.33	.97	1.95	3.25	.02	12.00	600-J-61	14.07	19	20	16	13	0	44			
26 Herrin (No. 6)	C-15079	.07	2.13	1.78	3.98	.02	15.31	600-II-170	20.90	16	5	15	18	3	61			
27 Herrin (No. 6)	C-15117	.08	2.26	1.86	4.20	.03	13.60	600-J-4	15.85	6	9	14	27	13	58	19	24	15
28 Herrin (No. 6)	C-15079	.07	2.13	1.78	3.98	.02	15.31	600-I-176	18.95	12	8	8	21	13	59			
29 Herrin (No. 6)	C-16317	.33	.97	1.95	3.25	.02	12.0	600-II-167	17.35	11	12	10	11	1	66			
30 Herrin (No. 6)	C-14721	.03	1.76	1.94	3.73	.03	10.08	600-II-144	14.76	16	12	19	22	3	50	15	20	
31 Herrin (No. 6)	C-12643	.02	1.67	1.84	3.53	.04	11.85	600-II-111	16.41	17	13	9	19	10	51	10	16	25
32 Herrin (No. 6)	C-15456	.06	2.36	2.03	4.45	.01	12.4	600-I-195	15.02	12	13	13	29	16	46	12	17	17
33 Herrin (No. 6)	C-14982	.01	1.57	2.12	3.70	.05	12.67	600-J-55	15.68	14	9	14	19	5	58	17	26	15
34 Herrin (No. 6)	C-15717	.04	1.59	2.56	4.19	.02	12.15	600-II-125	15.16	17	11	24	20	0	48	10	15	23
35 Herrin (No. 6)	C-15442	.08	1.60	2.13	3.81	.01	13.13	600-J-15	16.22	18	12	14	18	4	52	10	15	27
36 Herrin (No. 6)	C-12479	.04	2.55	1.76	4.35	.05	13.47	600-II-16	18.85	11	7	11	25	14	57	8	18	31
37 Herrin (No. 6)	C-16627	.02	2.07	1.26	3.35	.05	11.41	600-I-188	14.47	16	7	29	27	0	48			
38 Herrin (No. 6)	C-15872	.05	1.81	1.82	3.68	.00	14.44	600-II-129	18.56	9	21	21	18	0	49	17	24	8

APPENDIX CONTINUED

Coal member	CHEMICAL ANALYSES OF COAL							MINERAL MATTER IN LOW-TEMPERATURE ASH										
	Analysis number	Sulfate sulfur (%)	Pyritic sulfur (%)	Organic sulfur (%)	Total sulfur (%)	Chlorine (%)	Ash (%)	Laboratory number	Low-temperature ash (%)	Quartz (%)	Calcite (%)	Pyrite (%)	Pyrite, calcd. from chem. anal. (%)	Iron sulfate (%)	Total clay (%)	Kaolinite (%)	Illite (%)	Expandables (%)
39 Herrin (No. 6)	C-15432	.05	.98	.71	1.74	.10	12.19	600-II-123	14.56	22	13	16	13	0	49	9	26	14
40 Herrin (No. 6)	C-15231	.03	1.69	2.59	4.31	.07	12.45	600-I-192	16.26	20	8	15	19	4	53	10	13	30
41 Herrin (No. 6)	C-12842	.11	2.42	1.38	3.92	.18	12.6	600-J-25	18.04	12	6	17	25	8	57	17	25	15
42 Herrin (No. 6)	C-15038	.01	.99	.53	1.53	.05	10.56	600-J-57	11.43	18	7	16	16	0	59	13	17	29
43 Herrin (No. 6)	C-16692	.02	2.11	1.38	3.50	.14	13.31	600-J-71,72	16.92	18	14	30	23	0	38			
44 Springfield-Harrisburg (No. 5)	C-14735	.02	2.34	1.65	4.01	.31	12.06	600-III-64	18.57	24	10	30	35	5	31	8	15	8
45 Springfield-Harrisburg (No. 5)	C-15125	.01	1.42	2.02	3.45	.03	13.07	600-I-106	14.45	21	14	16	18	2	47	9	24	14
46 Springfield-Harrisburg (No. 5)	C-14774	.02	1.42	2.24	3.68	.02	12.82	600-I-180	17.19	22	11	15	16	1	51	10	30	11
47 Springfield-Harrisburg (No. 5)	C-16264	.05	2.33	2.14	4.52	.01	12.53	600-I-181	15.81	13	14	21	28	7	45			
48 Springfield-Harrisburg (No. 5)	C-15384	.14	2.13	1.63	3.90	.13	12.2	600-I-178	15.20	18	9	22	26	4	47			
49 Springfield-Harrisburg (No. 5)	C-15208	.07	1.96	2.03	4.06	.14	14.77	600-II-88	17.26	25	17	22	21	0	37	7	15	15
50 Springfield-Harrisburg (No. 5)	C-15452	.30	2.06	2.32	4.68	.02	12.7	600-J-119	17.51	11	10	18	22	4	57	9	21	27
51 Springfield-Harrisburg (No. 5)	C-15448	.12	2.56	2.26	4.94	.01	12.64	600-I-125	16.50	13	10	19	29	10	48	12	21	15
52 Springfield-Harrisburg (No. 5)	C-14609	.04	1.81	1.07	2.92	.07	10.40	600-I-186	13.85	11	7	21	24	3	58	16	24	18
53 Springfield-Harrisburg (No. 5)	C-14796	.02	.74	.58	1.34	.02	10.33	600-I-184	13.00	11	6	12	11	0	71	16	36	19
54 Springfield-Harrisburg (No. 5)	C-14646	.06	2.67	1.62	4.35	.18	10.66	600-II-15	21.75	13	7	8	23	15	57	11	21	25
55 Springfield-Harrisburg (No. 5)	C-16729	.04	2.30	.83	3.17	.32	12.2	600-I-197	15.65	25	13	38	28	10	24			
56 Springfield-Harrisburg (No. 5)	C-15012	.02	2.04	1.11	3.17	.06	11.42	600-J-26	12.60	19	10	24	30	6	41	13	23	5
57 Sumnum (No. 4)	C-15496	.05	1.28	2.34	3.67	.03	9.22	600-I-123	12.63	24	8	20	19	0	48	10	11	27
58 Colchester (No. 2)	C-15566	.05	3.38	1.42	4.85	.03	10.12	600-II-113	14.51	11	3	12	44	32	42	9	15	18
59 Colchester (No. 2)	C-14650	.11	3.38	1.32	4.81	.04	9.46	600-I-185	14.00	2	8	26	45	19	43	8	24	11
60 Colchester (No. 2)	C-14646	.04	2.72	2.07	4.83	.03	11.0	600-II-160	15.88	10	9	24	31	7	50	10	16	24
61 Colchester (No. 2)	C-15263	.04	2.27	.85	3.16	.02	8.0	600-II-104	13.04	12	0	33	33	0	55	16	15	24
62 Dekoven	C-15336	.08	2.99	1.98	5.05	.12	14.16	600-J-13	17.50	8	6	25	32	7	54	10	29	15
63 Davis	C-15943	.05	3.02	1.26	4.33	.26	10.5	600-I-189	13.23	7	0	19	41	22	67			
64 Murphysboro	C-16408	.05	3.78	1.07	4.90	.09	11.20	600-J-62	14.61	2	Tr.	39	48	9	50			
65 Rock Island (No. 1)	C-15678	.05	3.21	2.10	5.36	Tr.	10.29	600-I-144	15.22	6	23	40	40	0	31	8	8	15

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