

## OCCURRENCE OF SULFUR IN ILLINOIS COALS

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## Introduction

Sulfur in its several forms is prominent among the species of mineral matter known to occur in coal. Not only is its presence widespread but its effects may be very detrimental, particularly in specialized uses. The many problems associated with the presence of sulfur in coal include those involving air pollution, restrictions on amount of sulfur allowed in metallurgical coke, boiler corrosion and deposits, difficulties in mining, acid drainage from mines and spoil piles, and spontaneous combustion of coal.

Because of the recognition of the importance of sulfur in the utilization of coal, investigations concerning sulfur in coal have been pursued at the Illinois State Geological Survey since founding more than 50 years ago. This paper attempts to summarize the pertinent data concerning the occurrence of sulfur in Illinois Coals from this long term study. These data have been acquired by many members of the Survey staff.

Except when specifically stated to the contrary, all data discussed in this paper were obtained from analyses of face channel samples of coal. These samples were taken in the mines by Survey personnel following recommended United States Bureau of Mines methods of sampling, which provide for exclusion of mineral bands over 3/8 inch in thickness (Holmes, 1911).

## Distribution of Sulfur Within Illinois Coals

It has long been recognized that sulfur occurs in coal in both inorganic and organic forms. It occurs inorganically as sulfides and sulfates, but the exact mode of occurrence of the organic sulfur is not known. Given and Wyss (1961) state that it is usually assumed that sulfur is in one of the following four forms:

1. mercaptan or thiol, RSH
2. sulfide or thio-ether, RSR'
3. disulfide, RSSR'
4. aromatic systems containing the thiophene ring,



Free sulfur or native sulfur has been reported in coal (Yurovski, 1959; Berteloot, 1947). However, its occurrence is rare, and small enough an amount to be disregarded for most purposes. It has not been reported from Illinois coals.

Sulfate Sulfur. Sulfate sulfur is present in minor amounts in nearly all of the samples analysed. The sulfate sulfur values range from a high of 0.57 percent to a low of 0.00 percent. The mean, calculated from sulfate sulfur analyses of 300 face channel samples of Illinois coals is 0.071 percent and the mode, although not calculated, would be lower than the mean.

Organic Sulfur. Organic sulfur values ranged from a low of 0.27 percent to a high of 2.98 percent in Illinois coals sampled to date. The distribution of organic sulfur for all face channel sample analyses of No. 2 Coal, No. 5 Coal, No. 6 Coal and No. 7 Coal are given in the histograms on figure 1. None of the histograms have the shape of a normal distribution. The organic sulfur values of No. 2 Coal and No. 5 Coal are rather evenly distributed and are between 0.4 percent and 2.4 percent. It is probable that these diagrams would show a normal distribution if additional data were included. Too few analyses of samples from No. 7 Coal are available to draw any conclusions from the histogram. Organic sulfur from No. 6 Coal shows a distinct bimodal distribution with one peak between 0.2 and 0.8 percent and the second peak between 1.6 and 2.2 percent.

Pyritic Sulfur. The range in values of pyritic sulfur in face channel samples is even greater than the range in organic sulfur. The range is from a low value of 0.10 percent to normally high values of 4.5 percent to 5.0 percent with a few extreme values approaching 9.0 percent. Histogram depicting the distribution of the pyritic sulfur values for each of four coals are given in figure 2. The histogram of pyritic sulfur values in No. 5 Coal shows the most nearly normal distribution and that for No. 6 Coal shows a bimodal distribution. Again it must be emphasized that these data are obtained from face channel samples and any mineral bands in the coal, including iron sulfides, over 3/8 inch thick were excluded from the sample.

Total Sulfur and Relationship Between Pyritic and Organic Sulfur. Total sulfur in face channel samples ranges from low values of less than 0.5 percent to high values of 5.5 percent with a few extreme cases of nearly 10 percent. Sulfur in these few very-high-sulfur channel samples is predominantly pyritic.

Four graphs showing the relationships between organic and pyritic sulfur for four Illinois coals are given in figure 3. Each point on graphs 3a and 3b (No. 2 Coal and No. 7 Coal) represents sulfur values from a single face channel sample analysis, whereas each point on graphs 3c and 3d (No. 5 Coal and No. 6 Coal) represent average sulfur values for a single mine. Using mine averages rather than individual analyses does not alter the overall picture but does facilitate handling of the data.

Correlation coefficients for the four graphs vary considerably. The correlation is poor for Coal No. 5 (correlation coefficient .24) and non-existent for Coal No. 7 (correlation coefficient -.09). However, coals No. 2 and No. 6 do show a fairly good correlation between pyritic and organic sulfur (.76 for No. 6 Coal and .75 for No. 2 Coal). Both of these latter values demonstrate a high degree of significance, well over the 99.9 percent level. The rate of increase of pyritic sulfur with an increase in organic sulfur is much greater for No. 6 Coal than for No. 2 Coal. The one graph showing negative correlation (No. 7 Coal) is not statistically significant because of the small number of analyses.

Differing conclusions have been drawn by various workers as to the relation of pyritic to organic sulfur in coals. A number of researchers have reported such a correlation (Rose and Glenn, 1959; Leighton and Tomlinson, 1960; Wandless, 1959) whereas others have not observed the correlation in their studies (Yancy and Fraser, 1921; Brooks, 1956).

Discounting No. 7 Coal because of lack of sufficient data, the Illinois coals do show a positive correlation between organic and pyritic sulfur. This correlation is much better for No. 2 Coal and No. 6 Coal than for No. 5 Coal.

The fact that a correlation does exist, suggests that in a coal-forming-swamp environment which was relatively high in sulfur, the sulfur contribution to the plants would be high and that sulfur in the environment also would be available for the formation of pyrite during the early stages of peat formation. The correlation exists even though much secondary inorganic pyritic sulfur has been added to the coal as veins and deposits along fractures which occurred subsequent to the peat formation and possibly very late in the history of the coal bed. It is also conceivable that much of the late secondary pyrite may represent a reorganization of the sulfur that was introduced into the environment at a very early stage of coal formation.

The bimodal distribution of both pyritic sulfur and organic sulfur shown in figures 1 and 2 also might suggest a close correlation between the two forms. However, the low sulfur coals in Illinois have been mined extensively and therefore have also been of much interest to the Survey and have been sampled heavily. The low sulfur peaks in the bimodal distribution may simply represent preferential sampling.

#### Mineralogical Occurrence of Sulfur

Sulfate Sulfur. The small amount of sulfate sulfur that occurs in nearly every face channel sample of Illinois coal is contained primarily within the mineral gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) which occurs as a secondary vein and cleat filling.

The amount of sulfate sulfur increases rapidly upon weathering of the coal as the oxidation of pyrite ( $\text{FeS}_2$ ) gives rise to ferrous and ferric sulfates. The following minerals have been identified from samples collected in deep mines from old mined-out areas and from samples of coal which have weathered from exposure at the surface either in outcrop, mine dumps, or in the laboratory:

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	possibly the hydronium jarosite (carphosiderite) $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_4 \cdot 7\text{H}_2\text{O}$

More than one of these phases often occur in a single sample. It is also difficult to know exactly which phases occur in the mines since 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 is very rapid; occurring in a few minutes time in the case of melanterite → rozenite.

**Pyritic Sulfur.** Iron disulfide can occur as either pyrite which forms in the isometric crystal system or as marcasite which is orthorhombic. Pyrite is the most commonly reported dimorph although marcasite is often mentioned as occurring in lesser amounts. Marcasite has only rarely been reported in Illinois coals and pyrite is apparently the dominant sulfide.

The macroscopic forms of pyrite in coal were systematically described by Yancy and Fraser (1921). A summary of their description follows: 1) fine pyrite, as small disseminated particles or thin film-like coating on joint planes (cleat) or along the bedding; 2) lenses, from 1 to 2 inches long and a fraction of an inch thick to those 3 or 4 feet thick and hundreds of feet long; 3) nodules, roughly spherical in shape, may also be either inches or several feet in diameter; 4) beds or continuous bands of pyrite, often may include coal or bony coal and/or may be intimately associated with argillaceous sediments.

The finely disseminated pyrite grades downward in size to the microscopic forms of the mineral. Microscopic pyrite is very widespread in coal and has been observed in all coal macerals except massive micrinite. A complete range from euhedral crystals to irregular anhedral aggregates may be observed microscopically in Illinois coals (J. A. Harrison, personal communication). Observations similar to those preceding were made for the Pittsburgh coal by Gray, Schapiro and Coe (1963).

#### Sulfur in the Banded Ingredients of Coal

A study was made by Survey personnel into the distribution of the forms of sulfur in the megascopically distinguishable banded ingredients (Cady, 1935a). The banded ingredients sampled were vitrain, clarain and fusain. Durain or dull splint coal is very rare in Illinois coals and none was sampled. Figure 5 summarizes the sulfur analyses of approximately 100 samples of banded ingredients.

In general the pyritic sulfur content is greater in the fusain than in the other bands, although it does show a wide range in the different fusain samples. This is due to the degree to which the cavities in the fusain are filled with pyrite. Vitrain and clarain have a higher organic to pyritic ratio with ratios generally greater than one. The organic sulfur content of vitrain is usually lower than of clarain from the same coal. The preceding generalizations not withstanding, Cady (1935a) concluded that the variations in organic sulfur content of Illinois coals cannot be ascribed only to variation in relative amounts of banded ingredients.

#### Occurrence of Low-Sulfur Coal in Illinois

There are three known areas in the state where there has been significant production of low-sulfur coal, most of which contain less than 1.5 percent sulfur. These areas, outlined in figure 6, are highly generalized and are subject to appreciable modification.

The largest of the three low-sulfur areas, and the most important on the basis of tonnage of coal produced, is in No. 6 Coal in Franklin County and

adjacent portions of Jefferson County to the north and Williamson County to the south and is similar to the area reported by Cady (1919). The delineation of the low sulfur area has been based on the following information:

- 1) Data from the files of the Illinois State Geological Survey on face channel samples of mines, most of which have been published by Cady (1935b, 1948).
- 2) Evaluation of a few miscellaneous coal samples from mines in the general area and from diamond drill core analyses.
- 3) Interpretation of drill logs based on character of overlying strata.

Utilization of the data in 1) and 2) above is self-explanatory, but 3) should be more fully explained. The interpretation of drill logs is based on the observation that in this general area where No. 6 Coal has a thick gray shale overlying the coal, the sulfur content is relatively low. Conversely, where the black "slaty" shale and marine limestone lie close to the top of the coal, the sulfur content is substantially higher. This association of high sulfur coal and overlying marine beds has also been reported for Russian and British coals (Yurovski, Mangubi, and Zyman, 1940; Wandless, 1959; Williams and Cawley, 1963).

The low sulfur area in Franklin, Williamson and Jefferson Counties is outlined primarily by analyses of mine samples. However, details of the configuration of the "low-sulfur" line are based on interpretations of drill hole logs of variable quality including electric logs of oil test holes. The presence of more than 20 feet of gray shale immediately above the coal has been used as indicating low sulfur content and less than 10 feet between the coal and the overlying black shale and limestone as indicating higher sulfur area. Intermediate thicknesses of gray shale have been variously interpreted depending in large measure on the geographic relationship of such datum points.

All of the low sulfur lines on the map indicate areas in which the sulfur content is believed to average 2 percent or less. The analytical data within the Franklin-Williamson-Jefferson Counties area indicate that most of the area outlined contains coal with less than 1.5 percent sulfur (as received basis, face channel sample), and a substantial part of the area has included coal, now largely mined, which averaged less than 1 percent sulfur.

In the western part of this low-sulfur area there is a portion mapped as containing "split coal." The split consists of beds of shale and siltstone interbedded between coal benches. It is believed that most of the coal in the "split-coal" area is probably of low-sulfur content. As shown on the map (fig. 6), the low sulfur area extends locally a relatively short distance west of the "split coal" area.

A second important area of low-sulfur coal occurs in the Harrisburg (No. 5) Coal in Saline County. Coal with less than 1 percent sulfur has been mined in this area and there is a substantial area in which the coal probably averages less than 2.5 percent sulfur as shown in Figure 7. This area is much less well defined than the previously described low-sulfur area of No. 6 Coal because much less data concerning it are available.

A third substantial area of low-sulfur No. 6 Coal lies in parts of Madison and St. Clair Counties in the vicinity of Troy, Illinois, and is shown

in figure 6. Although less is known of this area than the areas described previously, there is perhaps up to 70 square miles of coal with a sulfur content less than 1.5 percent. Analyses of face channel samples from one mine which operated in this low-sulfur area, reported by Cady (1948), showed the coal to average less than 1 percent sulfur.

#### Vertical and Lateral Distribution of Varieties of Sulfur

The variations in both pyritic and organic sulfur in the individual coal seams are very large when considering the state as a whole, as can be seen from figures 1 and 2. There have been, however, differences of opinion as to the amount of local variation which exists in the organic sulfur content. There are no such differences of opinion concerning the pyritic sulfur distribution inasmuch as extremely localized concentrations of secondary pyrite are common.

Cady (1935a, p. 30, 31) observed, "Local variation in organic sulfur is rarely more than 1 percent..." "...and generally not more than 0.5 percent irrespective of the locality.", and "...the organic sulfur is the best index of the sulfur content and the organic sulfur content is regionally consistent for each coal bed." Yancy and Fraser (1921) studied extensively the variations in varieties of sulfur both vertically and laterally within a single mine in southern Illinois. Concerning the lateral variation in organic sulfur they concluded that uniformity in organic sulfur distribution is confined to very limited areas in the coal seam (Yancy and Fraser, 1921). They found this variation to be large within a single mine, although not as large as variations in pyritic sulfur. Within the mine studied, the organic sulfur in the face channel samples (No. 6 Coal) ranged from .69 to 1.90 percent and the pyritic sulfur from .66 to 3.17 percent. It has been suggested (Cady, 1935a, p. 31) that the wide range in organic sulfur observed by Yancy and Fraser (1921) may be attributable in some way to the location of the sampled mine on the margin of the area of low sulfur coal in Franklin County.

Yancy and Fraser (1921) also analyzed individual benches of face channel samples for varieties of sulfur. They took 12 face channel samples from a mine in southern Illinois, six samples from a mine in west Kentucky in No. 7 Coal, and two samples from a mine in Kentucky No. 8 Coal. The organic sulfur content was relatively uniform between benches of the individual face channel samples. The greatest variation in any single section was a minimum of 0.57 percent and a maximum of 1.25 percent. Most of the benches in a single face channel had an organic sulfur content within 25 percent of each other.

The vertical variation in pyritic sulfur was found to be very large between different benches in the same face channel sample, ranging, in two instances, from 0.81 percent to 5.54 percent and from 0.02 percent to 2.09 percent. Yancy and Fraser (1921) reported that in nearly every section (face channel sample) the pyritic sulfur, and thereby also the total sulfur, were much higher in uppermost and lowermost benches. This conclusion was found to be true for their samples of Illinois No. 6 Coal and for the Kentucky No. 7 Coal. The two samples of the Kentucky No. 8 Coal had the highest pyritic sulfur in the lowest benches but the uppermost benches were relatively low in sulfur. Wandless (1959) in a general discussion of the occurrence of sulfur in British coals reached conclusions which support Yancy and Fraser in recognizing the concentration of pyrite at the top

and bottom of the coal and also in the rather uniform organic sulfur composition in a single section. However, Wandless' (1959) observation that organic sulfur is uniform over a wide area in a single seam is in better agreement with the similar observation for Illinois coals by Cady (1935a).

Further studies on the varieties of sulfur and their vertical and lateral variation are in progress. Preliminary results suggest that a concentration of pyritic sulfur at the top and bottom of the coal tends to occur in No. 6 Coal samples obtained from southern Illinois, and that the vertical distribution of organic sulfur within these coals is relatively uniform. Further data will allow more definite conclusions to be drawn concerning the local variation laterally in organic sulfur.

Wandless (1959) in a review article on sulfur in British coals stated an admonition with which we heartily concur. Concerning conclusions drawn from chemical analyses of sulfur in coal he wrote, (Wandless, 1959, p. 259) "Unfortunately the number of exceptions to these generalizations is sufficient to render them non-specific in individual cases. Here, as elsewhere, the examination of very large numbers of samples provides a graveyard for promising generalizations; nevertheless, the trends noted are interesting and can, with proper caution, prove useful on occasion."

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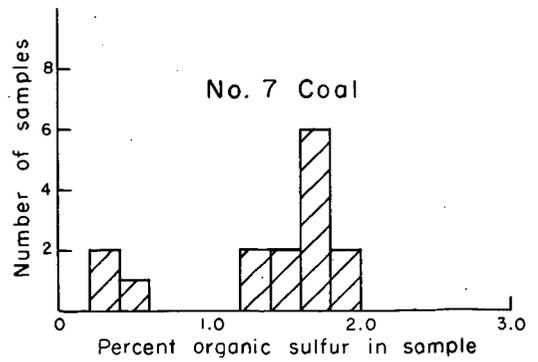
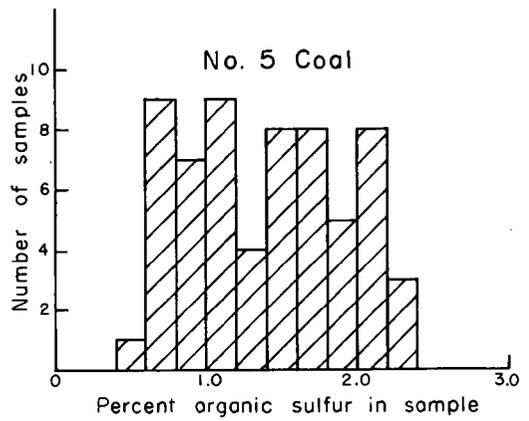
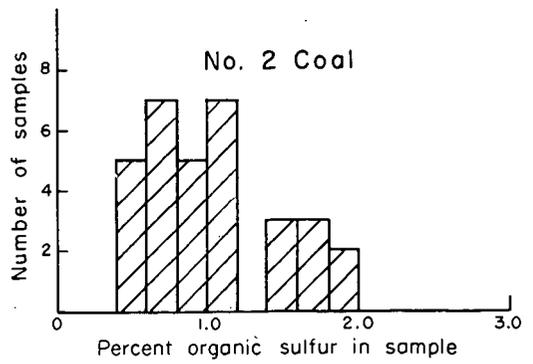
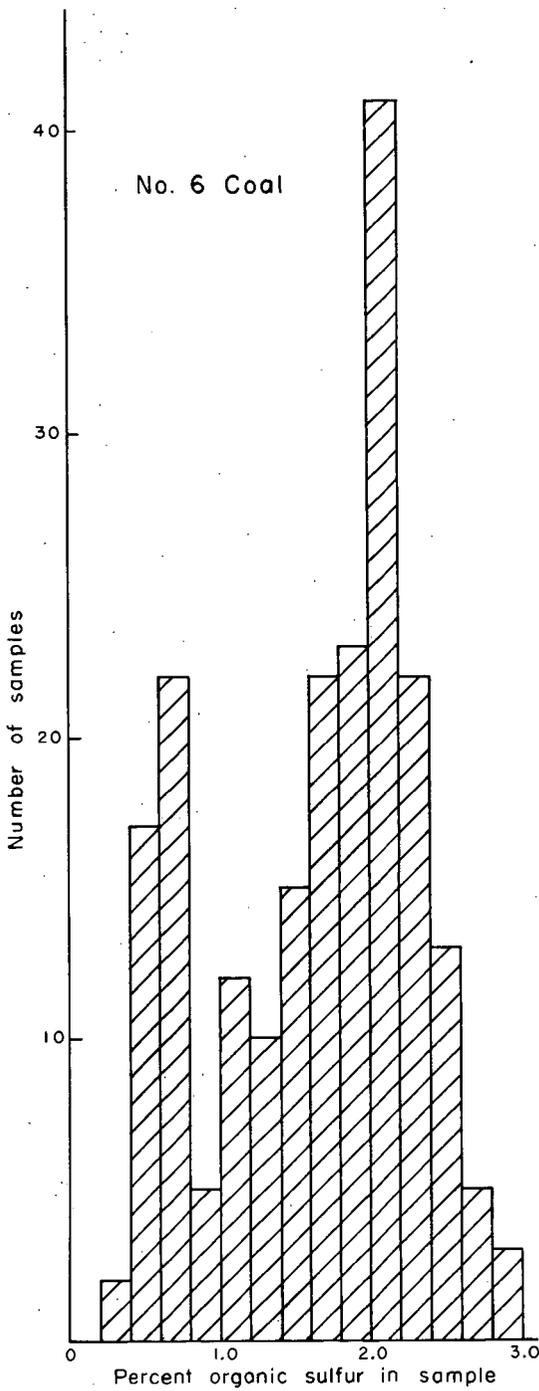


Fig. 1- Organic Sulfur - Distribution in Illinois Coals

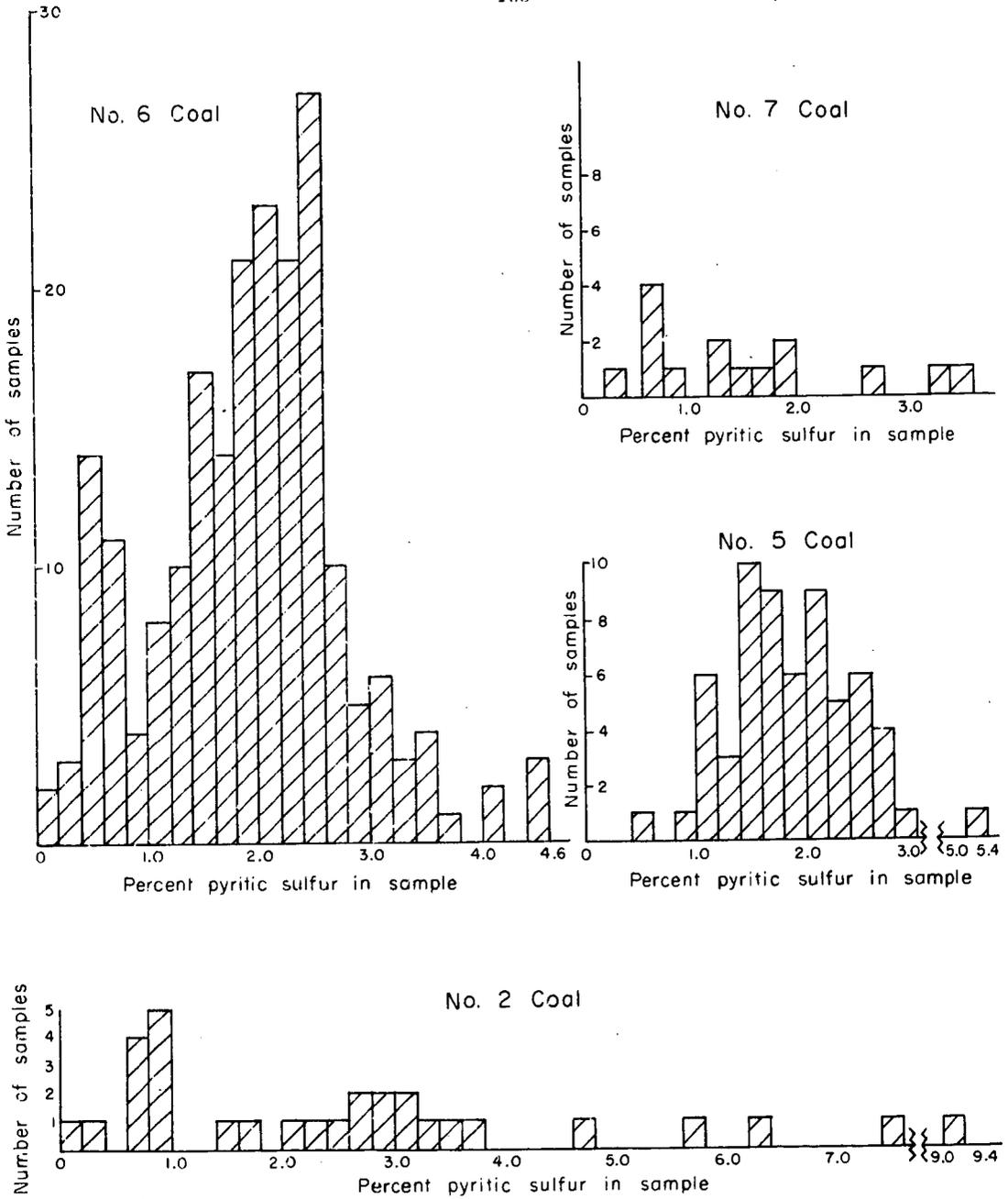


Fig. 2 - Pyritic Sulfur - Distribution in Illinois Coals

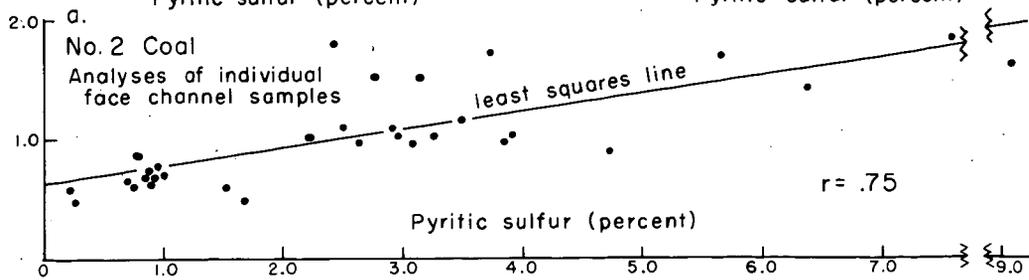
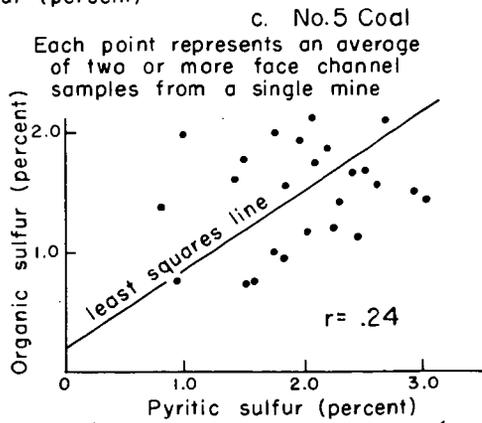
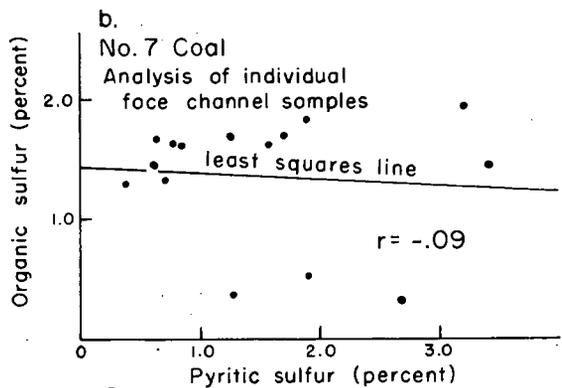
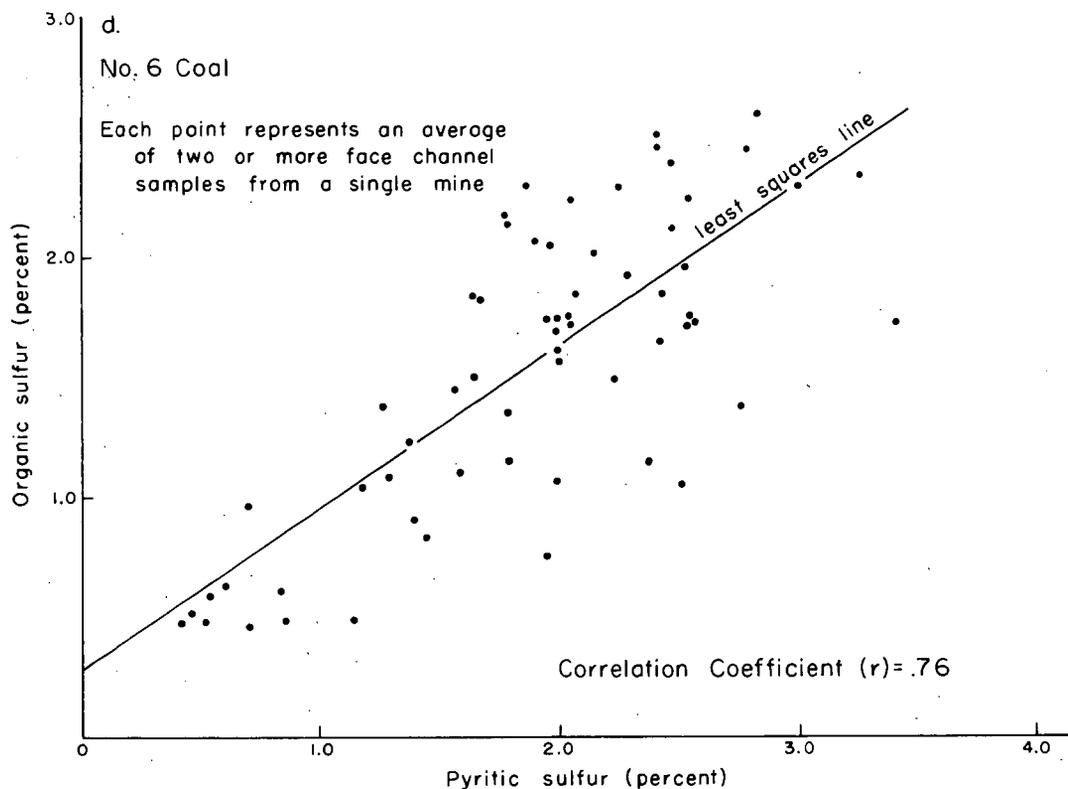
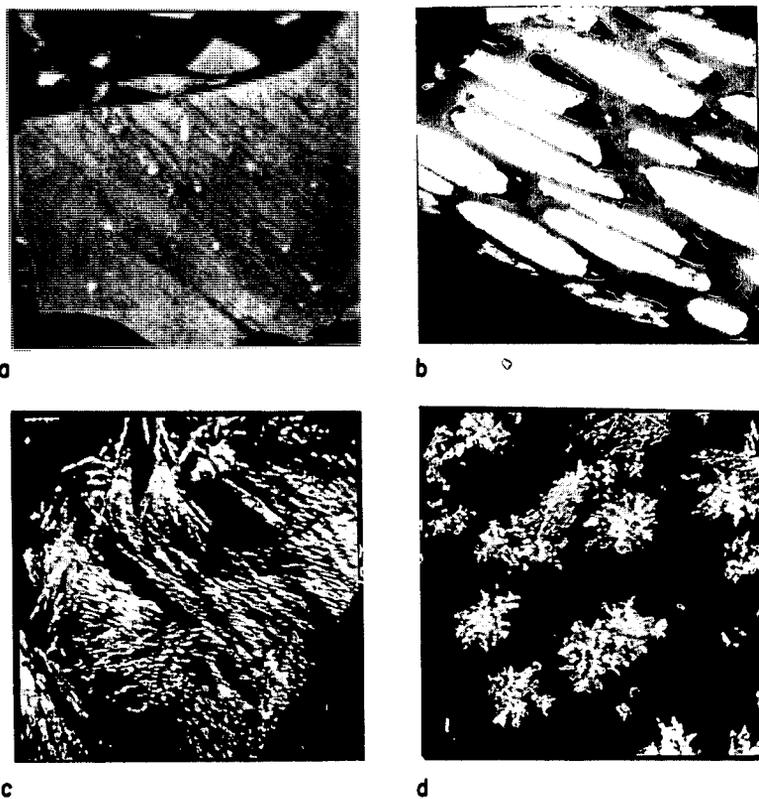


Fig. 3- Pyritic Sulfur-Organic Sulfur Relationships in Face Channel Samples of Illinois Coals



Scale  
0.2 mm

Figure 4. Microscopic pyrite in coal. All photomicrographs are of samples of No. 6 Coal taken in reflected light.

- a. Discrete grains in vitrinite
- b. Cavity fillings in fusinite
- c. Crystalline "fiber-bundles" in vitrinite
- d. Crystalline aggregates in vitrinite

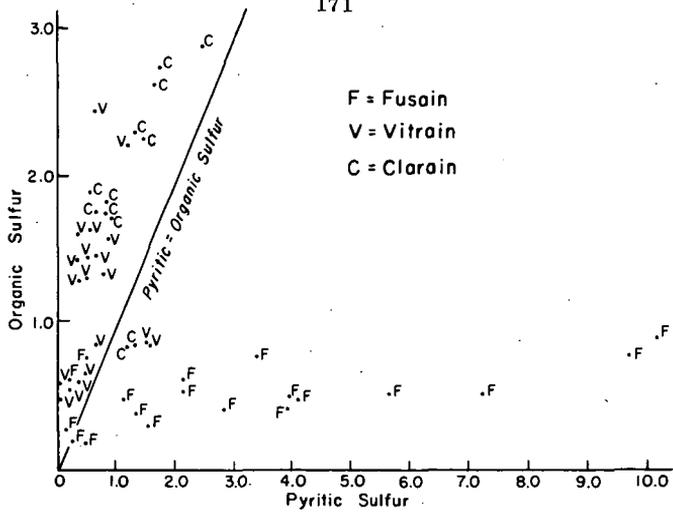


Figure 5 — Pyritic and Organic Sulfur content of Banded Ingredients modified from Cady (1935a, p.34)

