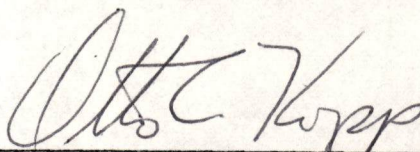


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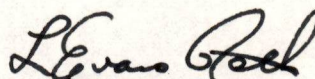
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PALEOENVIRONMENTALLY DETERMINED MACERAL, LITHOTYPE, AND
ELEMENTAL RELATIONSHIPS IN TWO COALS OF THE
CUMBERLAND PLATEAU, TENNESSEE

A Thesis
Presented for the
Master of Science
Degree
The University of Tennessee, Knoxville

Harold Elliott Barrett, Jr.

August 1979

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ABSTRACT

Samples comprising vertical sections of two coal horizons have been analyzed for major and minor elements, maceral contents, and lithotypes. The coals studied are the Middle Pennsylvanian Pewee of the uppermost Redoak Mountain Formation, and the Grassy Spring of the lowermost Cross Mountain Formation that are exposed in stripmine highwalls on the Cumberland Plateau near Caryville, Tennessee. The Pewee coal was deposited in an upper delta plain environment and the Grassy Spring coal was deposited in a lower delta plain environment. These coals were chosen because their different paleoenvironments were expected to provide a contrast by which to elucidate controls on the distribution of major and minor elements, maceral contents, and lithotypes.

This study concludes that: (1) the elemental relationships established during the existence of the respective swamps are indicative of their environments of formation; and (2) the maceral contents and lithotypes of the two coals reflect the sedimentological and geochemical conditions under which they were formed. These results suggest that: (1) future studies of the elemental contents of coals must consider a coal's environment of deposition if the data collected are to be of use in predicting coal quality; and (2) the field study of a coal can significantly augment the interpretation of the coal's depositional environment which is usually based solely on the consideration of the coal's associated strata.

ACKNOWLEDGMENTS

The author would like to recognize the support and encouragement he has received from the faculty and students during the course of his studies.

In particular, he would like to acknowledge Dr. Otto C. Kopp for his unfailing optimism, devotion, and integrity; Dr. Garrett Briggs on whose authority the author entered the department, and whose patient instruction in the field fostered the interest in the thesis topic; Dr. Larry A. Taylor for his perspicacious questions; Ben K. Bowlin for his preparation of the polished sections from the Pewee coal and assistance in the beginnings of this thesis; Thomas A. McWhorter for his help in the field; Thomas A. Roberts for his explanations of Pennsylvanian paleoenvironments; and Bradner D. Wheeler, Nancy C. Jacobus, and Dr. Dan Bartell of EG&G ORTEC for their assistance in using their firm's TEFA 6110 x-ray fluorescence unit.

Support for this work was obtained in part from a grant from Sigma Xi.

Most especially, the author would like to express appreciation to his wife, Mavis H. Barrett, for supporting him in this life; and to his parents, The Reverend Harold E. Barrett and Margaret L. Barrett, for having brought him into it.

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CHAPTER I

PURPOSE

The purpose of this investigation is to compare the vertical distributions of major and minor elements, maceral contents, and lithotypes in two coals which were deposited under different sedimentological conditions. It is believed that this approach, which was suggested by Nichols (1968), will allow a better understanding of the relationships between a coal's characteristics and its environment of formation.

The approach taken in this study differs from those involving random samples taken from wide geographic regions or specific coal fractions. Such studies provide general ranges of elemental compositions of a region or within a coal fraction; however, they generally do not permit the determination of the influence of the environment of formation on a coal's geochemical and lithotypic characteristics.

In the present study, two coal seams—one thought to be terrestrial, the other influenced by marine conditions—were sampled in their entirety in an attempt to eliminate sampling bias. The results demonstrate that important relationships do exist.

Maceral and elemental analysis methods were chosen in part because of equipment accessibility. Although there are techniques extant which permit better determinations (e.g., photometric microscopy, atomic adsorption, or neutron activation), none was readily available for the large number of analyses to be made in a reasonable amount of time.

This study does not purport to detail all the relationships which may exist or the mechanisms which establish them. Nor was any attempt made to identify any of the detrital silicate phases which might be present in either coal. The monumental treatment required by such a study is beyond that intended of this work.

The samples and data are on file in the Department of Geological Sciences.

CHAPTER II

METHODS

I. LOCATION AND CHARACTER OF SAMPLING SITES

The coal samples studied were obtained from exposures of the Pewee and Grassy Spring horizons located on the Cumberland Plateau near Caryville, Tennessee. These two coals were chosen because they have been studied in the field and their environments of deposition interpreted by previous workers (White, 1975; Minkin, 1977; Roberts, 1978). Also, they were being actively mined, which facilitated the collection of fresh samples.

The Pewee coal is the most extensively mined coal in the study area and the frequent exposures have allowed the determination of the environments in which the coal formed (Roberts, 1978). This coal developed in a stable backswamp which was associated with a major distributary of an upper delta plain system. Recent upper delta plain peat-forming swamps are characterized by a fresh water environment and are not subject to active inorganic sedimentation (Frazer and Osanik, 1969).

The Pewee horizon, its underclay, and overburden were sampled at a drift mine operated by the Dan Branch Mining Company. The mine is located at the 2520' level on Ash Log Mountain 3000' SE of Ash Log Gap. Map coordinates on the Block, Tennessee 7.5 minute quadrangle no. 128-SE for this location are 687,000 feet and 2,495,000 feet (Figure 1). The

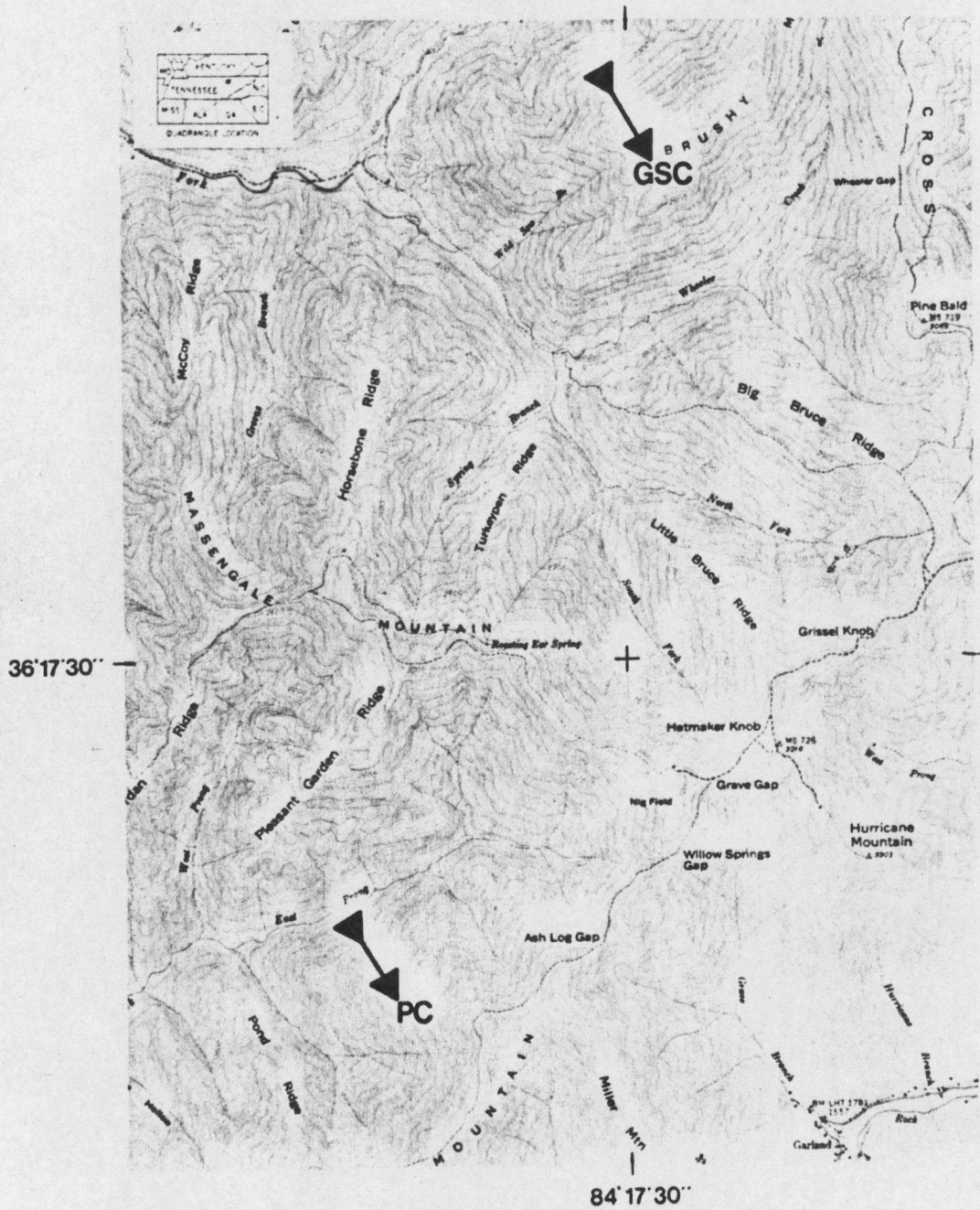


Figure 1
Location Map of Sampling Sites

Pewee coal is 100 cm. thick at this location. Oriented, full-faced samples were taken at this location. The exposure was free of iron-oxide staining and calcium sulfate, suggesting that it had not undergone extensive weathering.

The Grassy Spring interval contains two coals, the upper and lower Grassy Spring. The lower coal developed in a backswamp environment which was terminated by an influx of clastics brought in by channel migration (Roberts, 1978). At some localities the upper coal is overlain by marine bayfill sediments which contain marine fossils and is thought to represent a coal which developed under the influence of marine waters in a lower delta plain environment (Minkin, 1977). The upper Grassy Spring coal was sampled for study because the marine influence would provide a contrast to the Pewee coal which developed under fresh water conditions.

Oriented, full-face samples were taken from a strip mine operated by Long Pit Mining Company at the 2720' level on Bushy Mountain one mile west of Wheeler Gap. The underclay and overburden were also sampled. The upper Grassy Spring is 72 cm. thick at this location. Map coordinates on the Block, Tennessee 7.5 minute quadrangle, no. 128-SE for this location are 703,000 feet and 2,498,750 feet (Figure 1). This coal had been exposed less than ten days when the samples were taken and therefore had not undergone extended weathering.

II. PETROGRAPHY

Polished sections (approximately 2.5 centimeters in diameter) were made from the samples of the two coals, including sixty from the Pewee

and thirty-eight from the Grassy Spring. They were cut perpendicular to bedding and represent a complete and continuous sampling of the seams, the continuity being preserved by careful sample handling and preparation. The corresponding offcuts were retained for x-ray fluorescence analysis.

Examination of each of the polished sections was conducted using a 25X oil objective in reflected light. Point count data for the constituents, vitrinite, exinite, inertinite, pyrite, and other mineral matter, were obtained during the examination using a Swift point counting stage. The point to point and line to line distances of the counting traverses for a maceral analysis are usually 0.3 to 0.5 millimeters (Stach et al., 1975). Since the available stage only moved in increments of 0.33 millimeters and 0.66 millimeters, the former was chosen, and resulted in approximately 1850 points per polished section. The point count analyses are subject to an error of $\pm 2\%$.

Polished sections are usually made from crushed coal (Stach et al., 1975). Because the polished sections used in this study were not made from crushed coal and since the coal exhibited a pronounced bedding, good practice required that traverses across the sections were made at a specific angle to the bedding in an effort to minimize errors. The chosen angle, 39° , has a percentage of error versus inclination of zero (Chayes, 1956).

III. X-RAY FLUORESCENCE

Each sample to be analyzed by x-ray fluorescence was crushed to pass 60 mesh and was then dried at 98°C in air for 24 hours. Samples of $5.0000 \pm .0001$ grams were placed in a Spex Industries Shatterbox (a

tungsten carbide mill) with $1.0000 \pm .0001$ grams of boric acid (a binder) and five drops of acetyl anhydride (a grinding agent). This mixture was milled for six minutes. After processing, each sample was placed in a dessicator for storage. Just prior to analysis, a pressed pellet was made from each sample using a hydraulic press operated at 30,000 psi for 10 seconds. The sample cup was formed from boric acid.

The representative samples were analyzed for major and minor elements using an EG&G ORTEC 6110 tube-excited fluorescence analyzer owned by EG&G ORTEC, INC., Oak Ridge, Tennessee.

Major element concentrations were calculated from a working curve derived from a linear least squares fit of the intensity versus concentration of standards of known concentration. The computer program, CALC, which controls the data taking also stores the x-ray spectra on floppy disk. Excitation conditions for these analyses were: Rh anode, no filter, 10 KV, 100 μ A, 0-10 Kev, 200 sec. Matrix corrections for absorption and enhancement effects were applied to the CALC data using another computer program, FLINT. The FLINT matrix correction program is based on an exponential formula (Beers' Law) as described by Hasler and Kemp (1957). The applied corrections were: Mg for S, P for S, K for Ca, Ca for K, Al for S, and Si for S. An analytical summary of the four standards used for the major element analyses is shown in Table 1. These standards were supplied by the Canadian Bureau of Mines and will be subject to a round robin analysis.

Minor and trace element analyses were obtained using a specially modified version of the CALC software program. Excitation conditions for the analyses were: (Mn) Rh anode, no filter, 20 KV, 10 μ A, 0-20 Kev,

Table 1
Analytical Summary for Major Element Standards

Element	Standard Deviation	Mean Absolute Error	Mean Statistical Error	Concentration Range	
Mg	.0545	.0245	.0208	.090	.490
Al	.0393	.0167	.0323	1.940	5.500
Si	.0507	.0210	.0270	3.090	8.020
P	.0197	.0082	.0040	.0020	.1110
S	.7978	.4324	.0011	.3400	1.4900
K	.0681	.0258	.0024	.0400	.6900
Ca	.0162	.0079	.0023	.1000	1.7300
Ti	.0330	.0181	.0007	.1000	.1600
Fe	.3243	.1959	.0006	.8800	5.3900

100 sec, and (Ni, As, Rb, and Sr) Rh anode, Rh filter, 50 KV, 10 μ A, 0-40 Kev, 100 sec. National Bureau of Standards 1962b was used as a standard.

CHAPTER III

PETROGRAPHY

I. MICROPETROGRAPHY

Coal petrography has developed along two different lines. In America, Theissen (1913) pioneered and developed transmitted light techniques while Europeans (e.g., Stach, 1927) utilized oil immersion, reflected light microscopy. The latter method is used almost exclusively today because polished sections are much easier to make and because one of the groups of organic particles which constitute coal is opaque in visible light. In addition, reflected light microscopy permits the examination of particle surfaces to determine the degree of degradation during the coal forming process (Francis, 1961).

Examination of a polished section of coal in reflected light will reveal distinct bands and particles. These constituents can be divided into groups based on their morphologies, colors, and relative reflectivities. The organic constituents, referred to as macerals, are divided into three major groups (Stopes, 1935): vitrinite, exinite, and inertinite. Since these divisions form the basis for the petrographic characterization of coal, they will be discussed individually in subsequent paragraphs.

Vitrinite

The most common maceral group occurring in bituminous coals is vitrinite. Some examples are shown in Figure 2. It develops from the

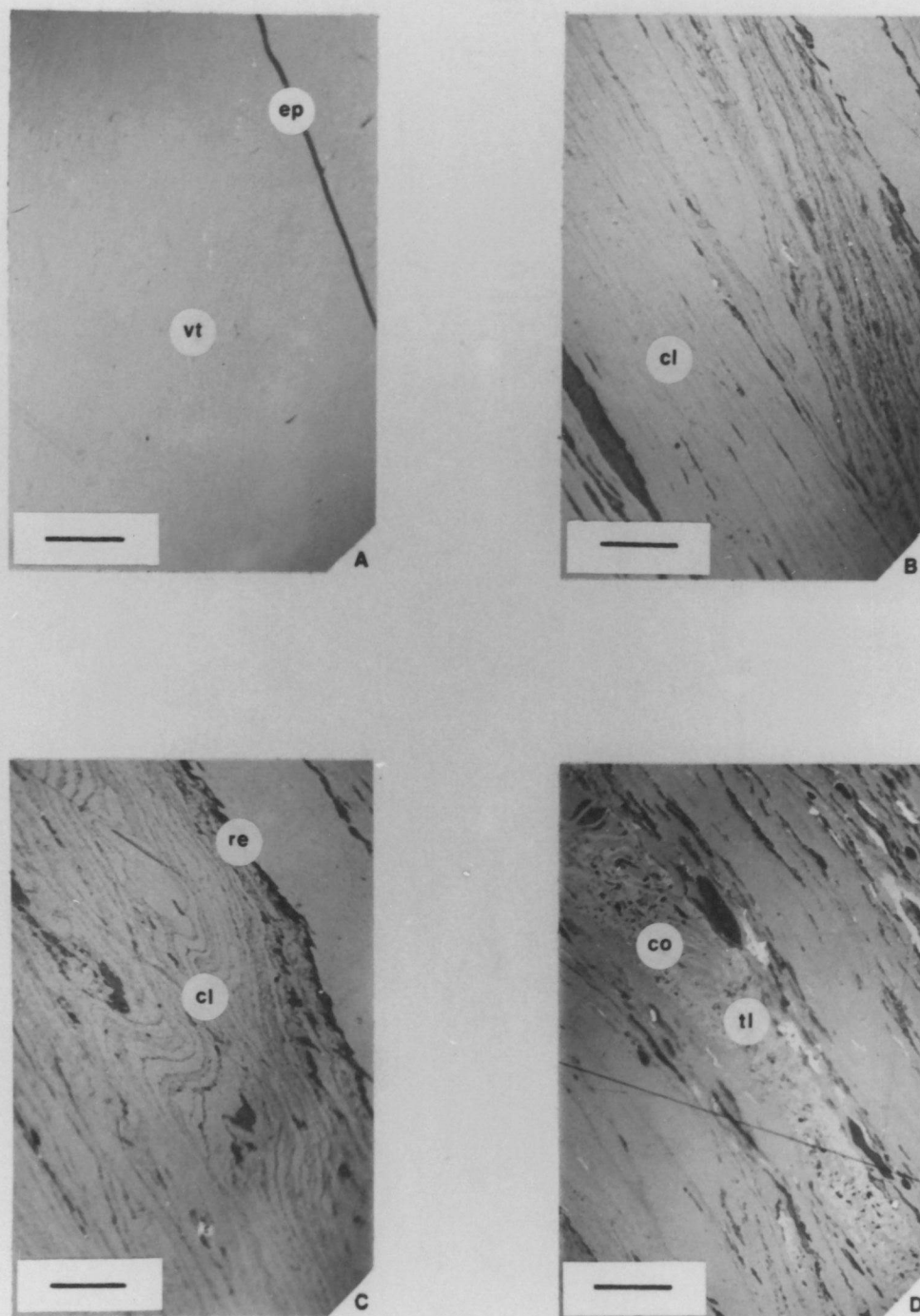


Figure 2. Reflected light photomicrographs of vitrinites. (A) Structureless vitrinite (vt) with epoxy (ep) fissure filling; (B) clay laminae (cl) in vitrinite; (C) clay laminae (cl) with resinous exinites (re) which show deformation structures in vitrinite; (D) tellinite (tl) which is lighter and collinite (co) which is darker of a structured vitrinite. Scale: bar equals 70 microns.

humic gels which result during the bacterial disintegration of the woody parts (lignin) of plants (Flaig, 1968). Under reflected light, it appears medium grey and is usually featureless except for occasional clay partings. Less commonly, a subtle structure is seen when the cell walls (tellinite) are distinct from the cell material (collinite). The reflectivity of vitrinite varies with the rank of the coal and has been used to determine the temperature and pressure conditions of coal metamorphism (Teichmuller and Teichmuller, 1968). Relative to the other maceral groups, vitrinite has more oxygen with less hydrogen and carbon (Dormans et al., 1957).

Exinite

The second maceral group, called the exinite group, is composed of coalified spores, cuticles, waxes, and resins of plants which are dark grey in reflected light. Because their reflectivity is nearly identical to the epoxy mounting medium, care must be exercised so that infilled cracks and fissures are not confused with this maceral group. The morphologies exhibited by this class are distinctive and aid greatly in identification. Typical examples are shown in Figure 3. Spores are the most common contributor to this maceral group and exhibit numerous variations in their characteristic collapsed-sphere shapes. Their sizes range from 3 millimeters for some megaspores to 20 microns for microspores and pollen. Because they cannot be distinguished in reflected light, microspores and pollen are collectively referred to as miospores (Guennel, 1952). Cuticular exinite resembles a fine-toothed blade in some cases, but most often it appears as irregular, black laminae in

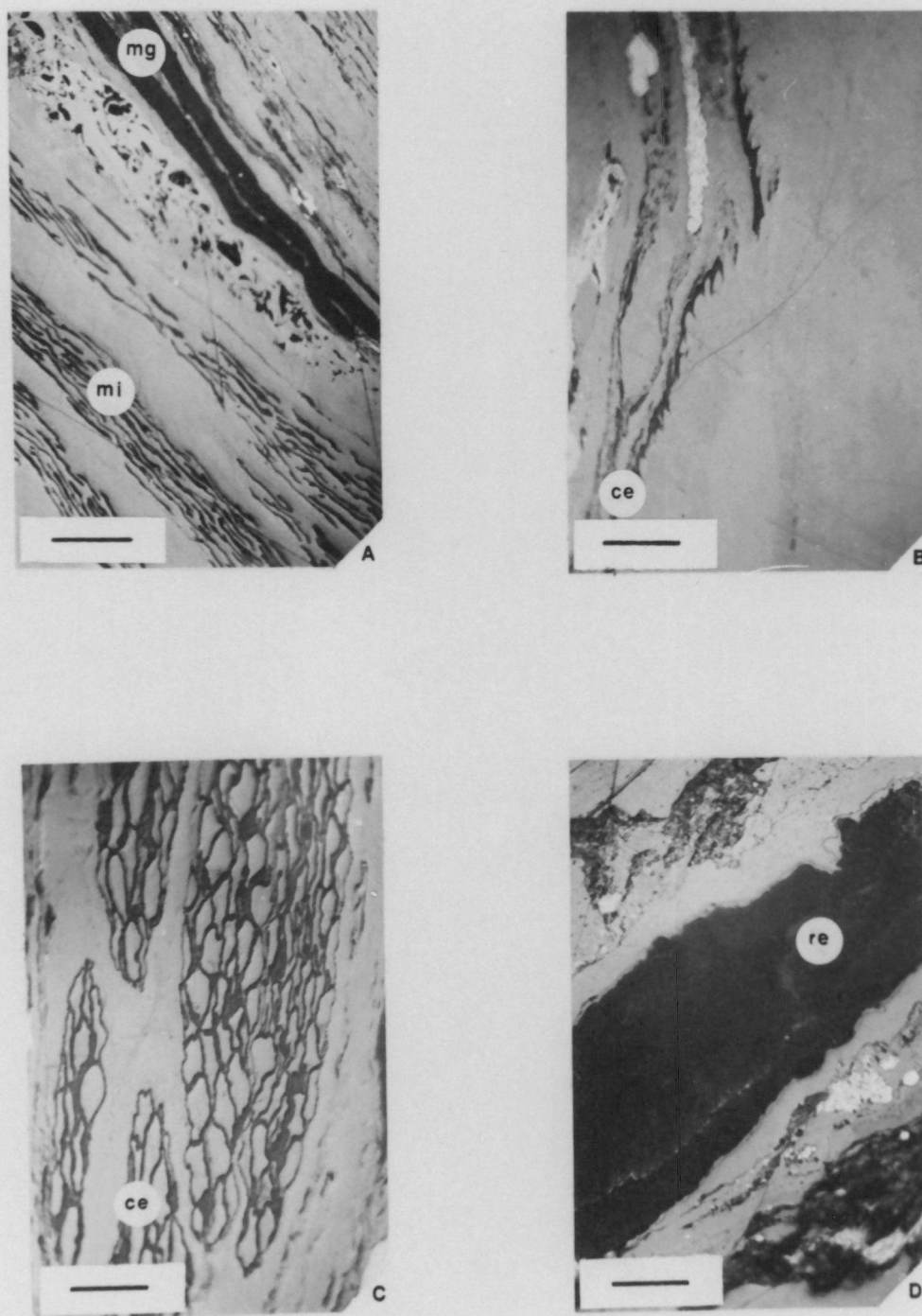


Figure 3. Reflected light photomicrographs of exinites. (A) Megaspores (mg) and miospores (mi) in vitrinite; (B) serrated cuticular exinite (ce) in vitrinite; (C) cuticular exinite (cd) cut parallel to the leaf surface; (D) resinous exinite (re). Scale: bar equals 70 microns.

vitrinite layers. This material is derived from the skin of the plant leaves. The last kind of exinite common in bituminous coals is formed from resins. It appears as ovoids suspended in vitrinite. Care must be taken because it often fills cavities and may be mistaken for inorganic minerals or epoxy. The exinites as a group are responsible for much of the initial formation of methane during coalification due to their high H content relative to the other maceral groups.

Inertinite

The last maceral group is called the inertinite group. Some typical ones are shown in Figure 4. For the most part, it is made up of organic particles which have undergone extensive oxidation prior to coalification. Although not all inertinite results from fires, recent studies of peat bogs have shown that fires can result in significant contributions of preinertinite to the swamp environment (Casagrande et al., 1976). A very distinctive example of inertinite results from the crushing of highly carbonized woody material reminiscent of volcanic glass shards. This is called Bogen structure. Equally distinctive are nearly spherical particles of high reflectance and relief, called schlerotinite. These are recognized from Tertiary coals as being of fungal origin (Stach et al., 1975). All inertinites exhibit a high reflectance and in most cases are featureless and white. Of the three maceral groups, they contain the most carbon and the least hydrogen and oxygen.

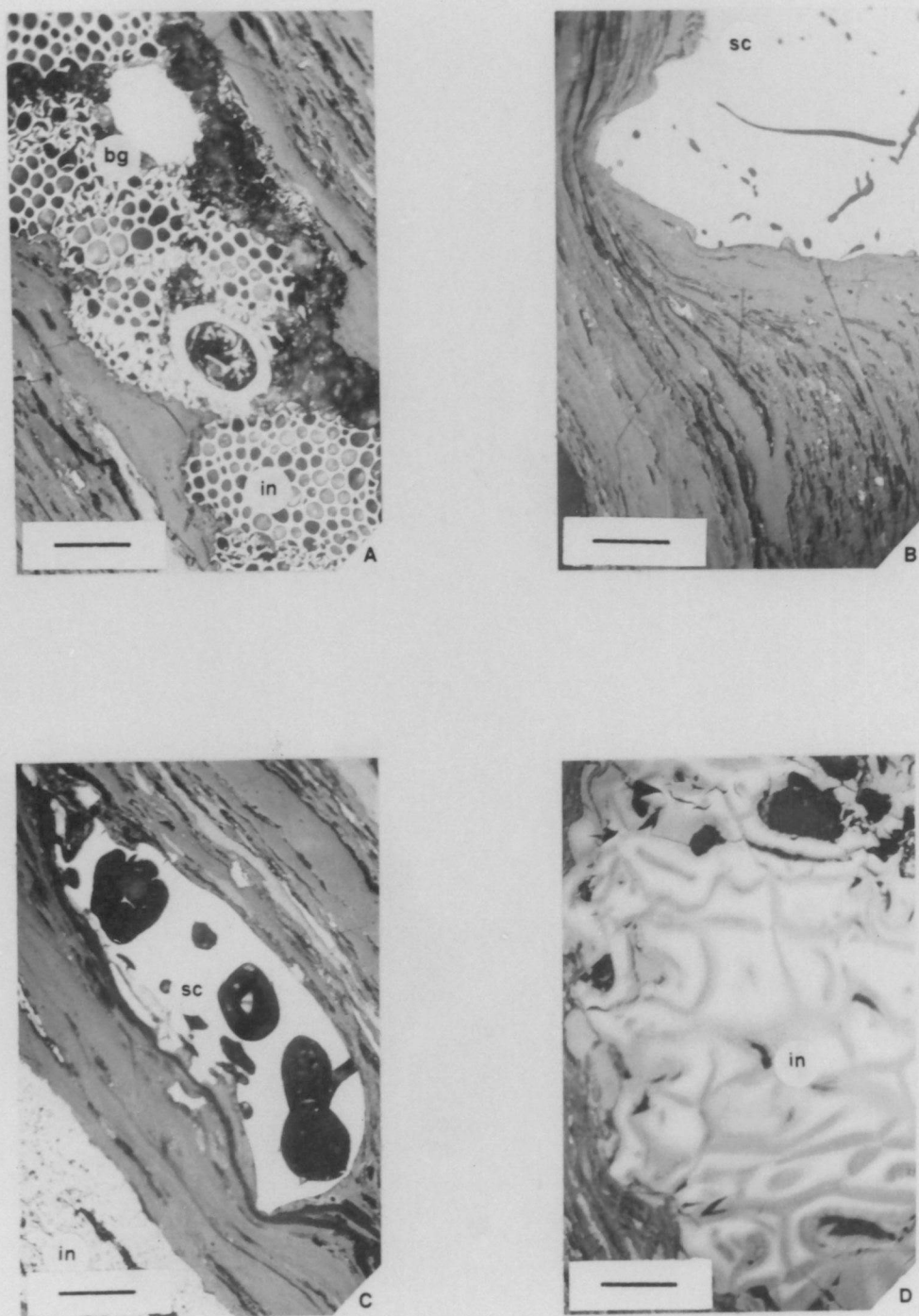


Figure 4. Reflected light photomicrographs of inertinites. (A) Cell walls preserved as inertinite (in) with Bogen structure (bg) in upper left-hand corner; (B) sclerotinite (sc) with sporinite deformed due to compaction; (C) inertinite (in) and sclerotinite? (sc); (D) inertinite showing the effects of selective oxidation. Scale: bar equals 70 microns.

Inorganic Minerals

In addition to the organic material, there are also inorganic mineral components in coal. These are most commonly pyrite, quartz, carbonates, kaolinite, and illite (Mackowsky, 1968; Ward, 1977). Except for pyrite, the similar reflectivities make the identification of these phases difficult. The pyrite occurs in two dominant morphologies. Examples of each are shown in Figure 5. Most commonly it occurs as 20 micron spheres, called framboids, which have a porous surface. This type of pyrite is thought to have formed early, as evidenced by the compression of clay laminae and macerals. Framboidal pyrite is usually associated with the vitrinite bands (Thiessen, 1913). The second type of pyrite occurs as a void filling and may sometimes be euhedral. It is most commonly associated with fractures and fusain layers.

II. MACROPETROGRAPHY

Coal can also be examined macroscopically, either in hand specimen or on outcrop. Such examinations were made before the microscopic techniques were well developed (Stopes, 1919). Although macroscopic studies have not been used extensively in this country, they still have great potential for characterizing coals and determining the particular swamp conditions under which those coals formed.

Four macroscopically distinct lithotypes are recognized in bituminous coals. They are called durain, vitrain, clarain, and fusain (Stopes, 1919). The first three descriptive names were derived from the Latin roots duro, clareo, and vitre (which mean, respectively, dull, bright, and glassy). The fourth is derived from the French word for a drawing

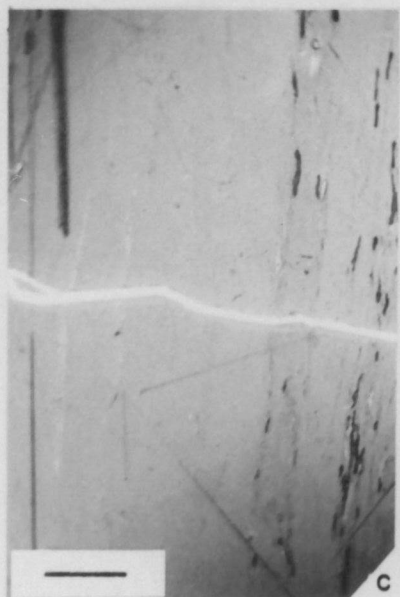
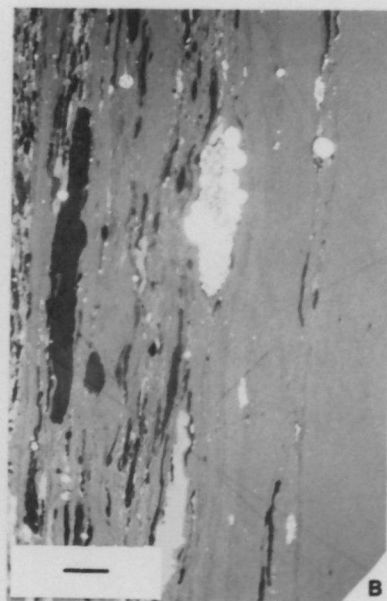
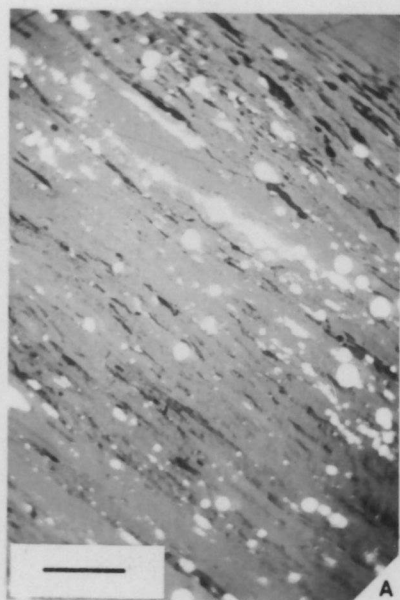


Figure 5. Reflected light photomicrographs of pyrites. (A) Framboidal pyrite seen as myriad spheres in vitrinite; (B) framboidal pyrite with compaction structures; (C) fissure-filling pyrite; (D) inertinite which has been pyritized. Scale: bar equals 70 microns.

charcoal. Examples of hand samples and polished sections are shown in Figure 6.

The durain bands are hard and dull, with a granular texture. Clarains exhibit a satin luster. This luster is due to the very fine banding of the three maceral types which comprise clarains. The glassy bands which generally show blocky fracture but often exhibit a conchoidal fracture are the vitrains. The fusain layers are made of fibrous carbon which have a distinctive silky sheen. It is this material which soils one's hands when handling bituminous coal.

III. SEAM FORMATION PROFILE

According to Tasch (1960), the lithotypes result from different subsidence rates in the swamp environment. Fusain develops under the driest conditions representing slow subsidence. Vitrain, clarain and durain develop under increasingly deeper water, respectively, representing greater subsidence rates. A typical profile of a coal seam may be constructed using the lithotypes of a coal determined at 1 centimeter intergals. This curve depicts the changes in the subsidence of the swamp in which the coal formed. Tasch (1960) called this curve the "seam formation profile." Examples drawn for the Pewee and Grassy Spring coals are shown in Figure 7.

IV. FACTORS WHICH INFLUENCE THE ABUNDANCE AND DISTRIBUTION OF MACERAL GROUPS AND MINERAL MATTER

The development and preservation of a peat in a particular swamp environment is dependent on many factors including its flora, climate,

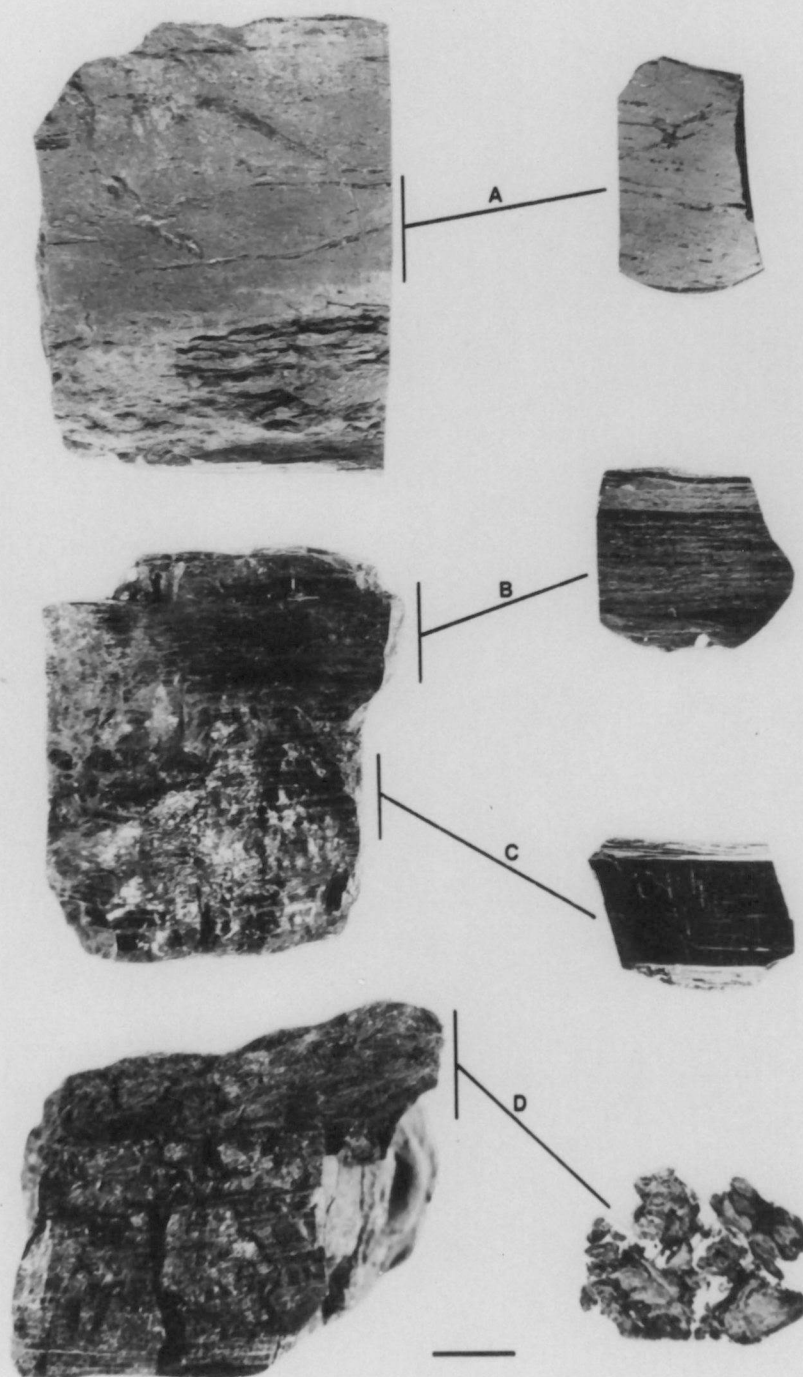


Figure 6. Photographs of hand specimens (left) and polished sections (right). (A) Durain; (B) clarain; (C) vitrain; (D) fusain. Scale: horizontal bar equals 1 cm.

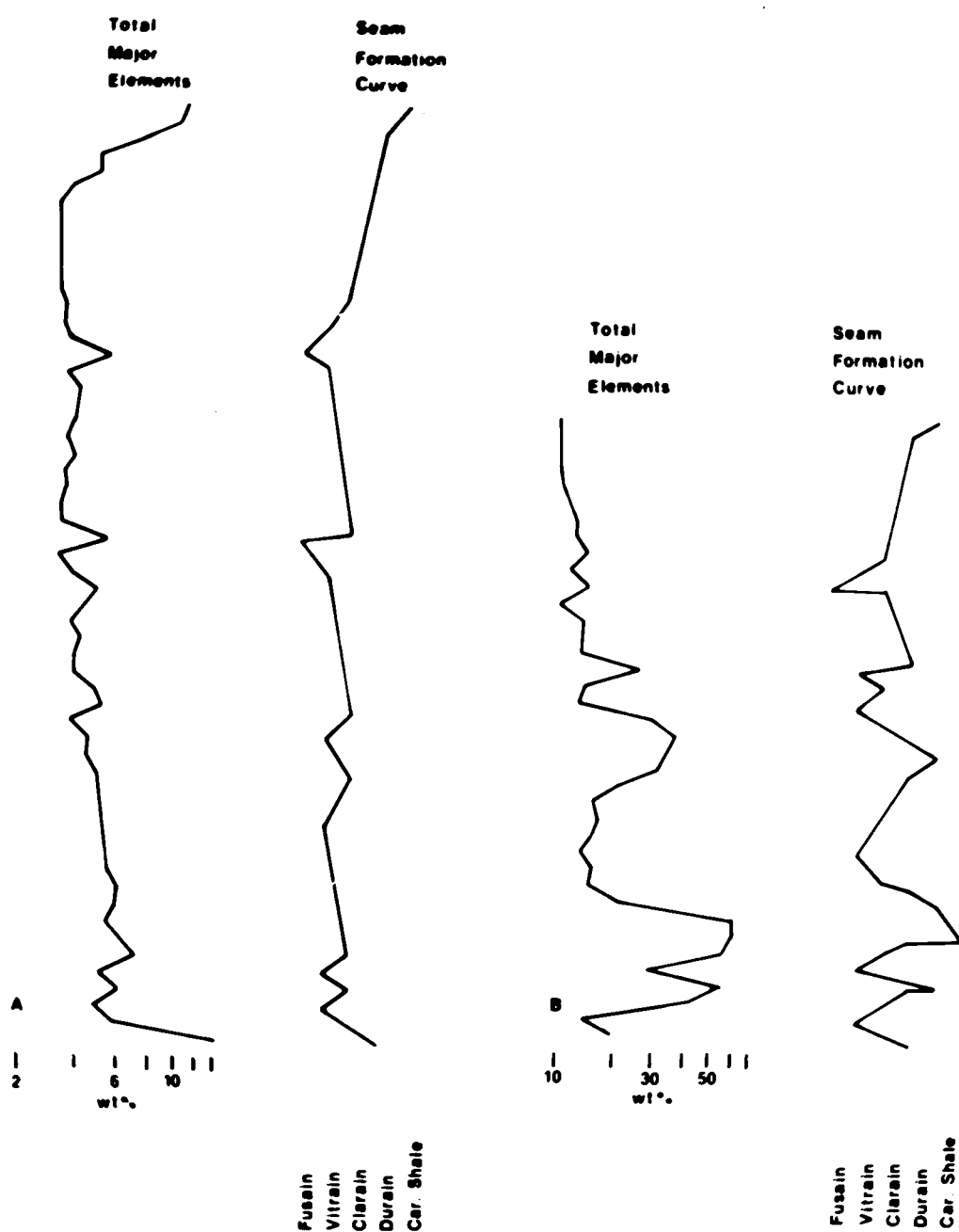


Figure 7. Total major element and seam formation curves. (A) Pewee coal; (B) Grassy Spring coal.

nutrient supply, water table stability, detrital sediment supply, pH, and Eh conditions. These controls will be reflected in the abundance and distribution of the maceral groups and mineral matter in a particular coal.

Where flora reach maximum diversity and development under conditions of a warm climate and eutrophic nutrient supply, large quantities of woody material are produced. If the water table remains just high enough to cover this material, it will be preserved to form a vitrinite-rich coal. Such coals are often referred to as "bright coals." With increasing elevation of the water table in the swamp, exinite, inertinite, and mineral matter will increase in the coal due to the more open water conditions. The resultant coals will be clarains and durains of a semi-bright to dull coal.

Change in the height of the water table will affect the maceral distribution and lithotype because it exerts significant control over Eh conditions. Oxidizing conditions exist when the peat surface is exposed or when there is active flow of water through the swamp. Under these conditions, the woody materials are oxidized to form preinertinites (Stach et al., 1975). The increased flow of water also increases the detrital sediment supply. The activity of hydrogen ions (pH) also influences the development of the swamp. Elevated alkalinity typical of brackish to marine waters will increase anaerobic bacterial decay of the peat. The increased bacterial decay reduces the amount of vitrinite material which ultimately develops. The effects of increased bacterial activity can be seen in the vitrinites which retain structure. Those developed under low pH conditions more frequently retain structure than

those vitrinites developed under marine conditions (Francis, 1961; Stach et al., 1975).

V. USES OF PETROGRAPHY

Point count analyses of macerals from polished sections and lithotype determinations from hand specimens permit the recognition of the three primary swamp subenvironments of the Carboniferous. These are: (1) open water areas characterized by subaquatic deposits of mud and allochthonous detritus which result in sporinite-rich durains and micro-layered clarains (Reidenouer et al., 1967), (2) calamitian reed marshes which form sporinite-rich clarains, and (3) forest swamps inhabited by lepidophytes and pteridosperms which are rich in previtrinite woody material and give rise to vitrains and sporinite-poor clarains (Stach et al., 1976). The macroscopic and microscopic analyses also permit establishment of a seam profile which can be useful in correlating coal horizons. It has been demonstrated by extensive studies of Smith (1968) that a seam profile for a particular coal retains a striking similarity over wide geographic areas. Relative subsidence rates in the coal swamps can also be estimated from the seam formation profile (Tasch, 1960).

Thus, it would be useful to establish profiles for the coals of our region as they are investigated. Such data could give the geologist an additional tool for establishing the identity of a coal horizon in a particular geographic area. The subsidence curve could also supplement data derived from associated sediments which are used to locate the placement of these sediments in a deltaic model.

CHAPTER IV

GEOCHEMISTRY

I. MAJOR ELEMENTS

The major elements found in coal (Mg, Al, Si, P, S, K, Ca, Ti, Mn, and Fe) have received the most attention because they comprise most of the inorganic minerals in coal. Unless they are first removed by separation, these minerals form ash, gases, and particulate matter when the coal is burned. The amount of this material industry has to contend with is astounding. Gluskoter (1975) estimates that in 1973, 15% (or 89×10^6 tons) of the coal mined was unwanted mineral matter. Additional problems are created by the noxious oxides of sulfur also formed when the coal is burned, and by the oxidation of the mineral matter associated with the refuse of mining operations.

Most investigations of this mineral matter have been directed to determine the mineral phases present and how they react in or influence industrial processes (Kemezys and Taylor, 1964; Warne, 1965, 1970; Watt, 1968; O'Gorman and Walker, 1971, 1972; Rao and Gluskoter, 1973). Little attention has been given the spacial occurrence of the minerals in the coal and their relationships to paleoenvironments. Clearly a better understanding of the distribution of these elements in coal could contribute to a more cost-effective utilization of our major fossil energy resource.

The distribution of the major elements in coal is influenced by factors such as the kinds of inorganic detritus, water solutes, bacteria, pH, and Eh conditions of the swamp. Inorganic detritus in coal consists primarily of clay-sized particles of quartz and phyllosilicates. This material enters the swamp through aqueous and aerial transport, and as such is controlled by the sedimentological regime. However, some geochemical controls may also operate. Meyers and Quinn (1973) have shown that flocculation of clays due to the adsorption of fatty acids dramatically increases as salinity rises from 0% to 4%. Similar salinity effects on flocculation were reported by Sholkovitz (1976). Since the upper limit of fresh water salinity is 1% (Degens, 1965), these studies imply the possibility of an influence on phyllosilicate sedimentation by the transport medium's geochemistry. This suggests that the precipitation of suspended clay minerals would be greater in brackish to marine waters.

The mechanisms controlling Fe and S distributions are complex and interrelated. Early workers suggested that coal overlain by marine sediments were higher in sulfur due to the influence of marine waters during peat formation (Ashley, 1920; Yancey and Fraser, 1921; Williams and Keith, 1963; Reidenour et al., 1967). Confirmation of this relationship can be seen in several studies of modern sediments. Matsuyama (1975) reported an increase in sulfur from 0.1-0.2% to 4.0-6.0% in sediments of Lake Suigetsu coincident with a permanent marine incursion. Similar relationships have been reported for sulfur in peats of the Okefenokee Swamp and the Florida Everglades (Casagrande et al., 1977). It was assumed by early workers that sulfate available in marine waters provided an oxygen source for anaerobic bacteria which in turn facilitated pyrite

production. The sequence of events in pyrite formation in sediments has been investigated in detail by Berner (1970). He demonstrated that pyrite formed in sediments by a step process in which bacteria reduce sulfate and produce H_2S . This H_2S then reacts with iron minerals to form monosulfides, and finally the monosulfides react with elemental sulfur to form pyrite. The limiting factor significant to pyrite formation is the diffusion of sulfate in the sediments and the availability of elemental sulfur. The much greater sulfate concentration of marine waters contributes to the greater production of pyrite in associated sediments.

Although recent work suggests that framboidal pyrite formation can occur in abiotic systems (Sweeney and Kaplan, 1973), bacterial activity (which is controlled by pH and Eh conditions) still appears to be the most significant contributor to sulfide formation and its preservation in sediments. Two types of bacteria operate to influence pyrite formation. The group which is most often considered is the sulfate-reducing bacteria. Their activity under conditions of high pH and low Eh generate the H_2S necessary for pyrite formation. It is important to note the pH range under which these bacteria thrive, 6.5-8.0 (Baas-Becking et al., 1960), because it is coincident with marine conditions. The other type of bacteria is the iron bacteria. They are most active when pH is low and Eh is high. Under these conditions they oxidize pyrite to form sulfate (Moss and Anderson, 1968). This mechanism is operating in many mining refuse piles, and serves to increase pyrite oxidation by a factor as large as 10^6 (Singer and Stumm, 1970). Low pH conditions are typical of fresh water in which the suspended organic matter is greater

than the inorganic matter, and where influence by underlying carbonate rocks is minimal. The highest pH measured in some coastal plain rivers of the southeastern U.S. was 4-5, with associated ponds having a typical pH of 3.8 (Beck et al., 1974). These data are consistent with values reported for the waters of Okefenokee Swamp (Casagrande et al., 1976). Therefore it is not surprising that the conditions of low pH which inhibit sulfate-reducing bacteria and stimulate pyrite-oxidizing bacteria are coincident with low pyritic sediments.

II. MINOR AND TRACE ELEMENTS

The first detailed examination of trace elements in coal was reported by Goldschmidt and Peters (1933). They investigated the trace element concentrations of selected coal ashes and reported anomalous values for 19 elements. Since this initial study, extensive surveys have been conducted of the U.S. coal provinces (Zubovic et al., 1961, 1964, 1966, 1967; Gluskoter, et al., 1976). Further study of trace elements in coal is important because, as Goldschmidt (1954) suggested, coal ashes could be an important source for certain elements, notably beryllium and germanium. Additionally, and perhaps of greater social impact, knowledge of trace element distributions in coal may allow us to anticipate and prevent environmental problems associated with the predicted massive utilization of coal.

The controls on the distribution of trace elements in coal are not well understood. The majority of studies suggest that the distributions are random in space. While this may be the case, most studies of trace

element distribution do not consider the particular coal's environment of formation.

Zubovic et al. (1966a) made extensive studies of the inorganic geochemistry of U.S. coals. They concluded that the concentrations of trace elements were controlled by the availability of the elements to the swamp in which the coal was formed and that these distributions reflect orogenic history and mineral stability under weathering conditions. While this study contributes to an understanding of the distribution of trace elements through time, it does not address the problem of their distribution in space. In order to better understand the spacial distribution, one must consider the manner in which an element enters the swamp and what happens once it is there.

Elements may enter a swamp as detritus, solutes, or adsorbed on suspended mineral matter. Studies of sediment-aqueous systems indicate that significant transport occurs via the clay minerals and the hydroxides of Fe and Mn (Degens, 1965; Steele and Wagner, 1975). If these transport mechanisms control the distribution of the trace elements, areas of a swamp subject to a greater sediment load would be expected to contain higher concentrations of trace elements. However, coals containing high amounts of inorganic detritus do not always exhibit high trace element contents. This suggests that once trace elements enter the swamp, other processes, like concentration by biological systems or by organic acids, may control the distributions of trace elements.

Trace elements also may be concentrated in the swamp during the life of the plants or the decay of the plant debris. The ability of living things to concentrate trace elements has been demonstrated by many

workers. Goldschmidt (1954) analyzed living trees, forest litter and soil humus. He demonstrated that the trees were actively removing metals from the soil and that these metals were concentrated in the forest litter. Similar results were demonstrated for the Okefenokee Swamp by Casagrande et al. (1976, 1977). There is also good documentation of enrichment of trace metals in marine organisms. Goldberg (1957) indicated that enrichment factors of several hundred to hundreds of thousands are possible in certain marine organisms. This is not included to suggest that these concentrations are necessarily reflected in the marine sediments, but rather it is intended to substantiate the idea that biota can concentrate trace elements.

It was noted some years ago that certain elements had organic affinities (Goldschmidt, 1954; Krauskopf, 1956; Mothersill, 1975; Nissenbaum and Swaine, 1976). The fact that particular elements such as Br, B, Ge, Ga, Ni, V, Ti, Sb, P, Co have been found to be associated with the vitrain-rich parts of coal suggests the element's organic affinities (Ingerson, 1954; Zubovic et al., 1964d; Gluskoter et al., 1976). Since the organic acids are the chemical precursors of vitrain, the observed affinities take on special meaning because they lend credence to the idea that humic acids may influence trace element distributions in coal. Recent work on organic acids indicates that they are effective binders of metals (Ahren et al., 1975; Eskenazy, 1967; Picard et al., 1976) and in some cases are effective concentrators of metals (Szalay et al., 1976). However, the mechanism by which the interactions take place remains to be completely defined. Szilagyi (1974) has compiled data from the literature and combined it with data from her

own laboratory studies. The study indicates that certain elements link with humic acids when they change valency. She writes:

. . . we may conclude that, in aqueous media, humic acids can be considered as reversible redox systems which—depending on circumstances—may reduce or oxidize reaction partners.

Remembering that the swamp milieu is dominated by organic debris, the above discussion suggests that it must play a major role in trace metal distributions.

This affinity of metals for organic acids has been shown to be pH dependent. This is significant because one can anticipate a change in trace element geochemistry with environment. The complexing by organic compounds of Hg is 3X greater in the Everglades than in the Mississippi (Ahren et al., 1975). Organic complexes with cobalt and iron are significantly more stable under marine conditions (Malcolm, 1972). He also noted that metallo-organic compounds are not affected by alkalis, but are leached by acids. Picard et al. (1976) have also shown that humic acids are effective complexors of iron under marine conditions.

The accumulation of metals by living organisms would not be important to coal quality unless there was a mechanism for maintaining or increasing the concentration after the plants perish. While it appears that the humic acids may serve this purpose and be dominant in controlling trace element distributions, Nissenbaum and Swaine (1976) suggest that, "The detailed role of humic substances in trace element geochemistry of sediments remains to be elucidated. This is pertinent, inter alia, to ore genesis and environmental chemistry."

CHAPTER V

DISCUSSION OF DATA

I. PEWEE COAL

The data from the Pewee coal suggests that it developed in an undisturbed terrestrial forest swamp where peat production kept pace with subsidence. These conditions produced a thick, bright coal which is low in sulfur, pyrite and other mineral matter.

The seam sections (Figure 8) determined from the maceral and macrolithotype data presented in Table 2 suggest that the Pewee swamp developed as a patchwork of densely forested and more open water areas. The high content of vitrain which accounts for almost 30% of the seam is indicative of a well-developed terrestrial, forest swamp. The clarain bands represent a more open water environment. These areas are less rich in vitrinite and contain greater proportions of exinite and inertinite. Although they have the characteristics of more open water area (higher exinite and inertinite) they do not represent a reed marsh facies. A reed marsh is characterized by strongly decomposed vitrinites and an exinite content about 10 times higher than a forest swamp (Stach et al., 1975). The stability of the environment is evidenced by the continuity of the lithotypic profile and the absence of durains. This indicates that vegetation was able to keep pace with subsidence.

In the top half of the coal seam, there are periodic occurrences of an unusual maceral association which was noted during the petrographic

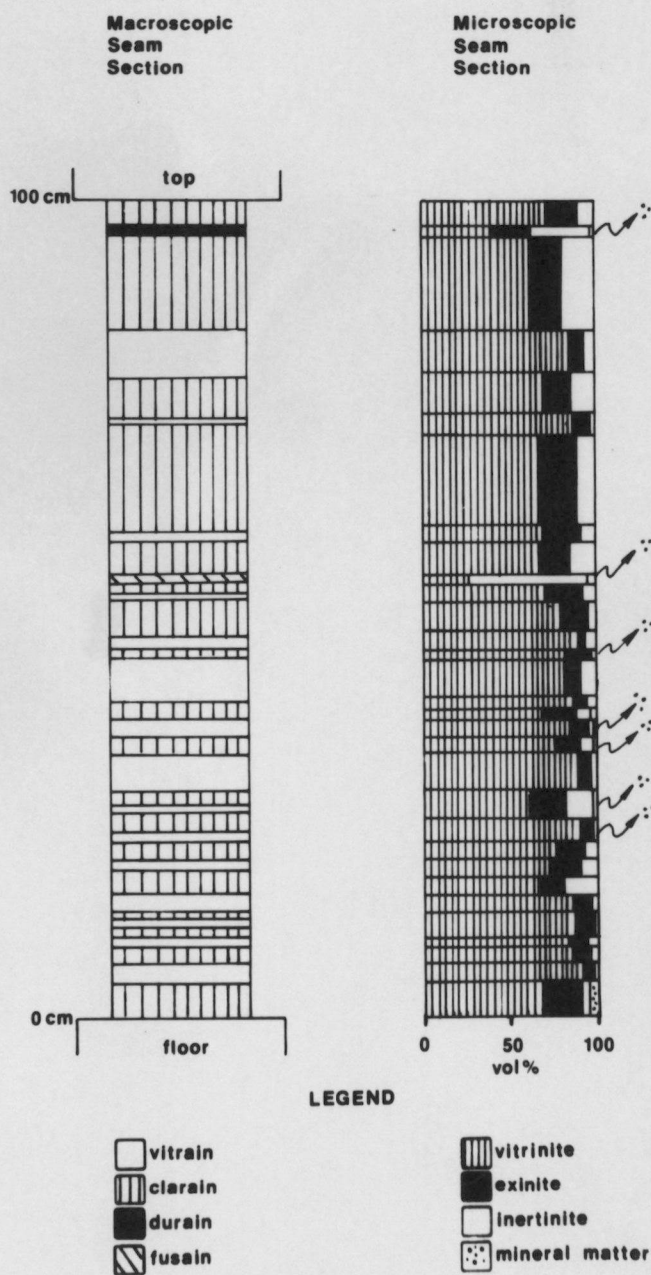


Figure 8. Seam sections of the Pewee coal. (A) Macroscopic seam section; (B) microscopic seam section.

Table 2
Point Count and Lithotype Analyses of the Pewee Coal

Sample Number	Volume Percent $\pm$ 2					Lithotype	
	Vitrinite	Exinite	Inertinite	Pyrite	Mineral Matter	First cm	Second cm
10E	78	7	< 1	4	10	Clarain	Clarain
10D	58	35	6	< 1	1	Clarain	-
10C	82	11	7	-	-	Clarain	Vitrain
10B	93	6	< 1	< 1	-	Vitrain	Clarain
10A	89	11	< 1	-	-	Clarain	-
9E	83	12	5	-	-	Vitrain	Clarain
9D	86	13	1	-	-	Vitrain	Clarain
9C	85	11	4	-	-	Vitrain	Vitrain
9B	65	15	20	< 1	-	Clarain	Clarain
9A	72	18	10	-	-	Clarain	Vitrain
8B	77	18	5	< 1	-	Clarain	Clarain
8A	90	7	3	-	-	Vitrain	Clarain
7E	62	21	17	-	< 1	Clarain	Vitrain
7D	40	40	20	-	-	Clarain	Vitrain
7C	69	19	13	-	-	Clarain	Clarain
7B	72	15	13	-	-	Clarain	Vitrain
7A	93	4	3	-	-	Vitrain	-
6G	98	< 1	1	-	-	Vitrain	-
6F	81	12	7	-	-	Vitrain	-
6E	76	12	12	-	< 1	Clarain	-
6D	80	12	8	-	-	Clarain	-

Table 2 (continued)

Sample Number	Volume Percent $\pm$ 2				Mineral Matter	Lithotype	
	Vitrinite	Exinite	Inertinite	Pyrite		First cm	Second cm
6C	83	11	5	-	< 1	Vitrain	Vitrain
6B	68	19	11	-	2	Clarain	Clarain
6A	86	8	6	-	< 1	Vitrain	-
5G	70	12	18	-	-	Vitrain	-
5F	93	3	4	-	-	Vitrain	Vitrain
5E	79	9	12	-	-	Vitrain	Vitrain
5D	82	13	5	< 1	-	Clarain	Vitrain
5C	88	4	7	< 1	-	Clarain	-
5B	79	15	5	< 1	< 1	Clarain	Clarain
5A	76	13	10	1	-	Clarain	Vitrain
4	71	11	18	-	-	Clarain	-
3/4	25	-	70	-	5	Fusain	-
3J	79	14	7	-	-	Clarain	Clarain
3I	67	16	18	-	-	Clarain	Clarain
3H	64	14	22	-	-	Vitrain	-
3G	74	20	6	-	-	Clarain	Clarain
3F	84	15	1	-	< 1	Clarain	Clarain
3E	71	18	11	-	-	Clarain	-
3D	41	29	30	-	-	Clarain	Clarain
3C	37	24	39	-	-	Clarain	Clarain
3B	52	20	27	-	-	Clarain	-
3A	63	20	17	-	-	Clarain	-

Table 2 (continued)

Sample Number	Volume Percent $\pm$ 2				Mineral Matter	Lithotype	
	Vitrinite	Exinite	Inertinite	Pyrite		First cm	Second cm
2F	89	11	< 1	-	-	Clarain	Clarain
2E	87	11	2	-	-	Vitrain	-
2D	87	11	2	-	-	Clarain	Clarain
2C	84	14	2	-	-	Clarain	Clarain
2B	60	20	20	-	-	Clarain	Vitrain
2A	84	8	9	-	-	Vitrain	Vitrain
1K	87	4	7	-	-	Vitrain	-
1J	84	8	8	-	-	Vitrain	-
1I	63	19	18	-	-	Clarain	Clarain
1H	74	13	13	-	-	Clarain	-
1G	70	15	16	-	-	Clarain	Clarain
1F	57	16	26	-	-	Clarain	-
1E	63	14	23	-	-	Clarain	Clarain
1D	46	23	31	-	-	Clarain	-
1C	42	22	36	-	-	Clarain	Clarain
1B	47	19	33	1	-	Clarain	Clarain
1A	73	17	6	4	-	Clarain	-

study. These areas are composed almost entirely of exinite and inertinite. A significant amount of the inertinite is sclerotinite (Figure 9). These sclerota are the result of increased fungal and aerobic bacterial activity due to oxidizing conditions in the swamp (Francis, 1961). This association could have resulted from exposure of the peat surface and may indicate a decrease in the rate of subsidence (or a fall in the water table). The increasing occurrence of this association toward the top of the seam probably indicates dessication in the swamp environment. Similar sequences have been described by Smith (1970).

The amount of inorganic mineral matter in coal is usually determined by various ashing techniques. Since these methods were not used in this study, there was no direct way to represent the total inorganic mineral content of the samples. The sum of the elements Mg, Al, Si, P, S, K, Ca, Ti, and Fe is used to represent the amount of mineral matter present in the samples. This sum will be referred to as the total major element concentration. Although this method does not provide absolute percentages, it does provide relative abundances which can be used for comparison purposes.

The major element curves determined from data in Tables 3 and 4 indicate that the Pewee coal is very low in inorganic constituents (Figure 10 (A)). The average major element content is 4.8 weight percent. The petrographic examinations revealed infrequent and barely discernible laminae in the vitrinites of the clarains. These may be phyllosilicate minerals. The general lack of mineral matter indicates that the swamp was not subject to active siltation. Sedimentation would have taken

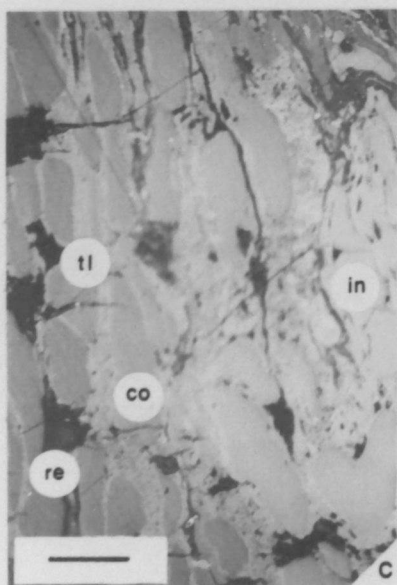
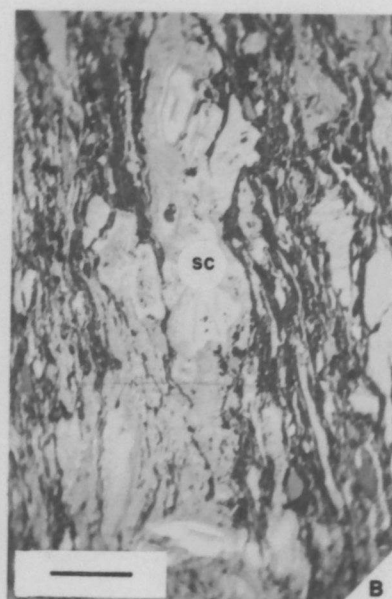


Figure 9. Reflected light photomicrographs of sclerotinite and inertinite with exinite which suggests dry conditions in the swamp. (A) Inertinite and exinite; (B) sclerotinite in vitrinite with reflectivity decreasing away from the sclerota; (C) unusually well-preserved tellinite and collinite which grade into inertinite; (D) sclerotinite and exinite with little or no vitrinite. Scale: bar equals 70 microns.

Table 3

Major and Minor Element Contents of the Pewee Coal

Sample Number	Weight Percent							Parts Per Million						
	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Ni	As	Rb	Sr	Mn
10E	.26	4.20	6.88	.05	.90	.70	.21	.25	.76	32	8	115	1468	16
10D	.04	1.48	2.22	.12	.90	.08	.44	.12	.49	64	4	19	4344	--
10C	.06	1.09	1.45	.14	.89	--	.53	.10	.49	15	2	--	5062	2
10B	.08	1.43	2.08	.11	.91	.11	.48	.13	.77	9	6	--	3313	4
10A	.08	1.20	1.66	.12	.90	.07	.47	.12	.53	45	2	--	3856	1
9E	.12	1.63	2.62	.23	.87	.10	.57	.13	.78	--	2	13	4006	--
9C	.02	1.21	1.85	.17	.85	.03	.54	.12	.51	--	2	11	2876	5
9B	.08	1.41	2.13	.17	.86	.04	.49	.13	.49	37	1	6	4632	--
9A	.09	1.31	2.31	.23	.84	.04	.50	.14	.47	18	4	3	5741	--
8B	.06	1.19	2.06	.12	.85	.06	.45	.12	.50	24	3	35	2630	2
8A	.05	.99	1.66	.14	.85	.01	.56	.10	.50	10	2	--	1828	19
6G	.02	.70	1.62	.02	.83	.04	.44	.13	.54	--	1	11	721	--
6F & E	.01	.78	1.67	.04	.83	.04	.42	.13	.50	10	2	11	1201	9
6D	--	.61	1.09	.02	.84	--	.47	.10	.52	--	2	7	861	--

Table 3 (continued)

Sample Number	Weight Percent							Parts Per Million						
	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Ni	As	Rb	Sr	Mn
6C	.06	1.00	2.03	.11	.81	.06	.41	.14	.45	17	4	20	3451	--
6B	.06	.70	1.96	.02	.81	.06	.42	.15	.47	39	3	4	753	17
6A	.01	.59	1.47	.02	.82	.03	.37	.12	.44	20	2	18	728	--
5G	--	.61	1.47	.02	.82	.02	.35	.12	.41	10	2	5	958	28
5F & E	.01	.69	1.37	.03	.83	.03	.41	.10	.51	26	2	6	568	7
5D	--	.54	1.15	.02	.82	--	.43	.10	.50	52	2	--	325	7
5C	.02	.65	1.37	.03	.83	.02	.42	.11	.56	30	1	6	601	6
5B	.02	.49	2.37	.03	.81	--	.38	.17	.48	40	2	0	477	--
5A	--	.49	1.22	.02	.82	.07	.45	.12	.51	40	1	1	527	6
4	--	.26	1.11	.01	.81	--	.41	.11	.48	8	2	9	535	13
3/4	--	.76	2.55	.01	.78	.12	.40	.12	.59	47	--	19	352	49
3J	--	.50	.87	.01	.82	--	.45	.09	.52	45	2	2	687	31
3I	--	.28	.98	.02	.82	--	.45	.11	.50	28	--	--	560	--
3H	--	.40	1.13	--	.81	--	.44	.11	.49	21	1	--	543	10
3G	--	.46	1.00	--	.82	--	.41	.09	.55	6	1	12	752	11

Table 3 (continued)

Sample Number	Weight Percent							Parts Per Million						
	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Ni	As	Rb	Sr	Mn
3F	.01	.38	1.07	.03	.81	--	.70	.11	.62	18	2	4	691	13
3E	--	.30	1.09	.02	.81	--	.57	.11	.58	37	1	4	476	44
3D	--	.26	1.19	.02	.81	--	.72	.12	.58	33	2	3	446	15
3C	--	.20	1.69	.01	.80	--	.52	.14	.48	42	1	32	481	--
3B	--	.30	1.63	.01	.80	--	.48	.13	.53	23	1	6	526	21
3A	--	.23	1.31	.01	.81	--	.44	.12	.51	31	2	6	579	3
2F & E	--	.79	2.29	.04	.84	.04	.49	.20	.62	56	4	--	938	21
2D	--	.46	1.04	.00	.83	--	.50	.11	.59	39	2	7	518	48
2C	--	.31	.90	.01	.83	--	.54	.11	.56	15	1	7	445	--
2B	--	.38	1.08	.01	.82	--	.42	.12	.51	28	1	--	574	--
2A	--	.24	1.01	.03	.82	--	.41	.11	.50	63	--	--	607	--
1G	--	.35	.90	-	.82	--	.41	.10	.45	36	1	--	477	3
1F	--	.39	1.20	.01	.82	--	.48	.12	.51	41	2	--	505	14
1E	.01	.75	2.05	.02	.82	--	.46	.14	.48	44	--	12	528	36
1D	--	.64	2.09	.02	.83	--	.44	.15	.46	80	2	4	693	14

Table 3 (continued)

Sample Number	Weight Percent						Parts Per Million							
	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Ni	As	Rb	Sr	Mn
1C	--	.98	4.39	.08	.81	--	.39	.21	.36	52	--	--	2071	17
1B	.04	1.74	5.99	.04	.85	--	.35	.21	.75	70	6	10	1270	--
1A	.16	2.27	4.70	.04	.93	.28	.28	.16	1.38	213	24	33	680	--
UC	1.94	22.41	30.72	.00	.66	2.36	--	.31	1.24	6	3	309	1022	16
OB	2.38	20.55	35.51	.01	.65	2.37	--	.28	1.45	23	3	287	1006	150
Mean														
Statistical														
Error	±.02	±.02	±.02	±.01	±.01	±.01	±.01	±.01	±.01	±17	±1	±6	±46	±21

Table 4

Major and Minor Element Contents of the Grassy Spring Coal

Sample Number	Weight Percent							Parts Per Million						
	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Ni	As	Rb	Sr	Mn
A2	.38	6.69	8.96	.05	.97	.51	.19	.17	2.54	36	10	72	2001	2
A1	.26	4.22	5.72	.15	1.03	.26	.42	.16	2.44	38	12	52	7099	12
B2	.95	14.61	24.55	.24	.75	.94	.06	.32	.65	7	5	153	8607	44
B1	1.31	18.01	33.84	.22	.69	1.12	--	.39	.39	3	5	172	9183	36
C2	.48	8.39	12.55	.08	1.18	.53	.12	.22	5.41	--	9	72	4239	53
C1	1.33	18.37	34.84	.28	.69	1.11	--	.39	.42	--	3	178	11,651	30
D	1.36	19.00	37.75	.08	.69	1.26	--	.38	.45	17	4	195	3935	27
E	1.58	20.49	35.18	--	.68	1.43	--	.36	.89	6	6	203	617	65
F9	.39	6.14	9.34	.04	1.12	.49	.18	.20	4.49	25	12	65	1220	10
F8	.19	3.54	3.59	.12	1.31	.05	.51	.11	5.80	6	15	8	8154	11
F7	.29	5.09	6.12	.37	.10	.24	.61	.15	1.92	8	5	58	13,493	26
F6	.25	4.12	4.81	.31	1.03	.17	.69	.14	2.09	7	8	35	11,669	1
F5	.27	4.59	5.56	.24	1.08	.18	.56	.14	3.13	6	11	35	10,119	27
F4	.20	4.03	4.67	.10	1.38	.09	.50	.14	6.23	--	18	18	6391	1

Table 4 (continued)

Sample Number	Weight Percent							Parts Per Million						
	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Ni	As	Rb	Sr	Mn
F3	.29	4.90	5.50	.31	1.14	.08	.67	.18	3.54	1	13	10	13,986	46
F2	.38	7.05	10.73	.80	.88	.14	.86	.30	.21	6	6	--	22,645	29
F1	.46	9.28	19.67	.17	.85	.21	.24	.44	.80	6	6	22	5147	109
G9	.79	12.07	19.70	.01	.87	.99	--	.26	2.29	14	7	143	544	24
G8	.54	9.19	14.44	.01	1.11	.87	.01	.21	3.86	--	8	128	528	12
G7	.12	2.32	3.57	--	1.45	.18	.27	.12	5.55	6	7	38	404	23
G6	.17	3.16	5.12	--	1.28	.26	.26	.14	4.09	18	8	71	452	6
G5	.50	8.64	13.27	.02	.97	.85	.05	.20	1.94	11	5	162	665	20
G4	.17	3.24	5.34	.01	1.18	.31	.26	.14	3.42	3	5	66	440	17
G3	.08	1.95	2.87	--	1.50	.09	.25	.10	7.19	1	8	24	291	54
G2	.05	1.73	2.40	--	1.68	.05	.24	.09	8.26	--	14	17	203	46
G1	.12	1.67	3.10	--	1.25	.12	.40	.12	4.32	5	9	39	429	20
H11	--	1.00	.97	--	2.49	--	.12	.05	10.83	15	32	--	7	--
H10	.052	.98	1.30	--	1.61	--	.31	.08	7.91	--	45	10	277	--
H9	--	1.04	1.13	--	2.16	--	.18	.06	10.02	3	97	3	121	20

Table 4 (continued)

Sample Number	Weight Percent						Parts Per Million							
	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Ni	As	Rb	Sr	Mn
H8	--	1.00	1.16	--	1.82	--	.26	.07	9.03	3	52	6	153	35
H7	--	1.00	1.16	--	1.82	--	.26	.07	9.03	2	45	8	237	33
H6	.04	.93	1.21	--	1.61	--	.31	.08	7.94	--	48	13	298	13
H5	.04	.81	1.10	--	1.54	--	.37	.08	7.14	9	30	4	348	--
H4	.06	.78	1.05	--	1.46	--	.41	.08	6.79	1	23	4	354	9
H3	.09	.81	1.07	--	1.40	--	.42	.08	6.44	--	21	11	300	21
H2	.09	.76	1.03	--	1.41	--	.44	.08	6.49	--	21	5	372	19
H1	.06	.77	1.05	--	1.37	--	.43	.08	6.30	10	14	6	246	70
UC	1.71	24.72	32.15	--	.67	2.33	--	.27	.93	6	4	268	1047	47
OB	2.17	20.51	35.45	.04	.67	2.65	--	.24	2.19	15	5	262	1198	121
Mean														
Statistical														
Error	± .02	± .04	± .03	± .01	± .01	± .01	± .01	± .01	± .01	± 6	± 1	± 5	± 45	± 22

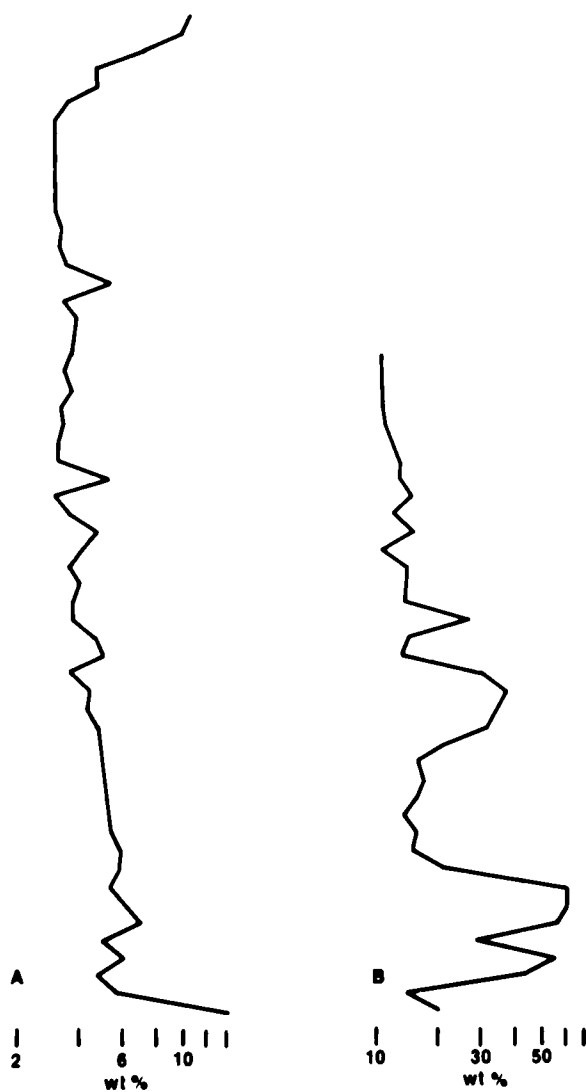


Figure 10. Total major element curves. (A) Pewee coal; (B) Grassy Spring coal.

place if there was active channeling in the swamp or if the swamp was located on the flank of a tributary where seasonal flooding of the river would have increased major element content markedly. It is likely that water movement proceeded en masse throughout the entire swamp without specific channels and minimal sedimentation, similar to water movement in the recent swamps of Florida (Casagrande et al., 1977). The low concentrations of major elements and the dominance of vitrains and clarains suggests that the Pewee swamp developed in the proximal portions of a deltaic system away from areas of active sedimentation. Such an area would provide a substratum upon which a dense forest could be developed and maintained for the 6000-9000 years required to produce the thickness of coal studied (Frazier and Osanik, 1969).

The petrographic examination of the Pewee coal seam revealed the occurrence of an iron sulfide at its top and bottom (see Figure (B), page 15). These sulfides were identified as pyrite by x-ray diffraction of a corresponding sample. Similar increases in pyrite have been described by Ashley (1920), Williams and Keith (1962), and Reidenour et al. (1967). The pyrite is framboidal and compaction structures about the framboids indicate they were formed early. Stach et al. (1975) state that peats overlying clay substrata exhibit a higher pH near the contact. It is likely that the increase in anaerobic bacterial activity in response to the higher pH resulted in the development of conditions conducive to pyrite formation. The pyritization in some areas is confined to the interior of distinct ovoids (Figure 11). These may represent cross sections through rootlets and suggest biological control on the local microenvironment which resulted in pyritization. The

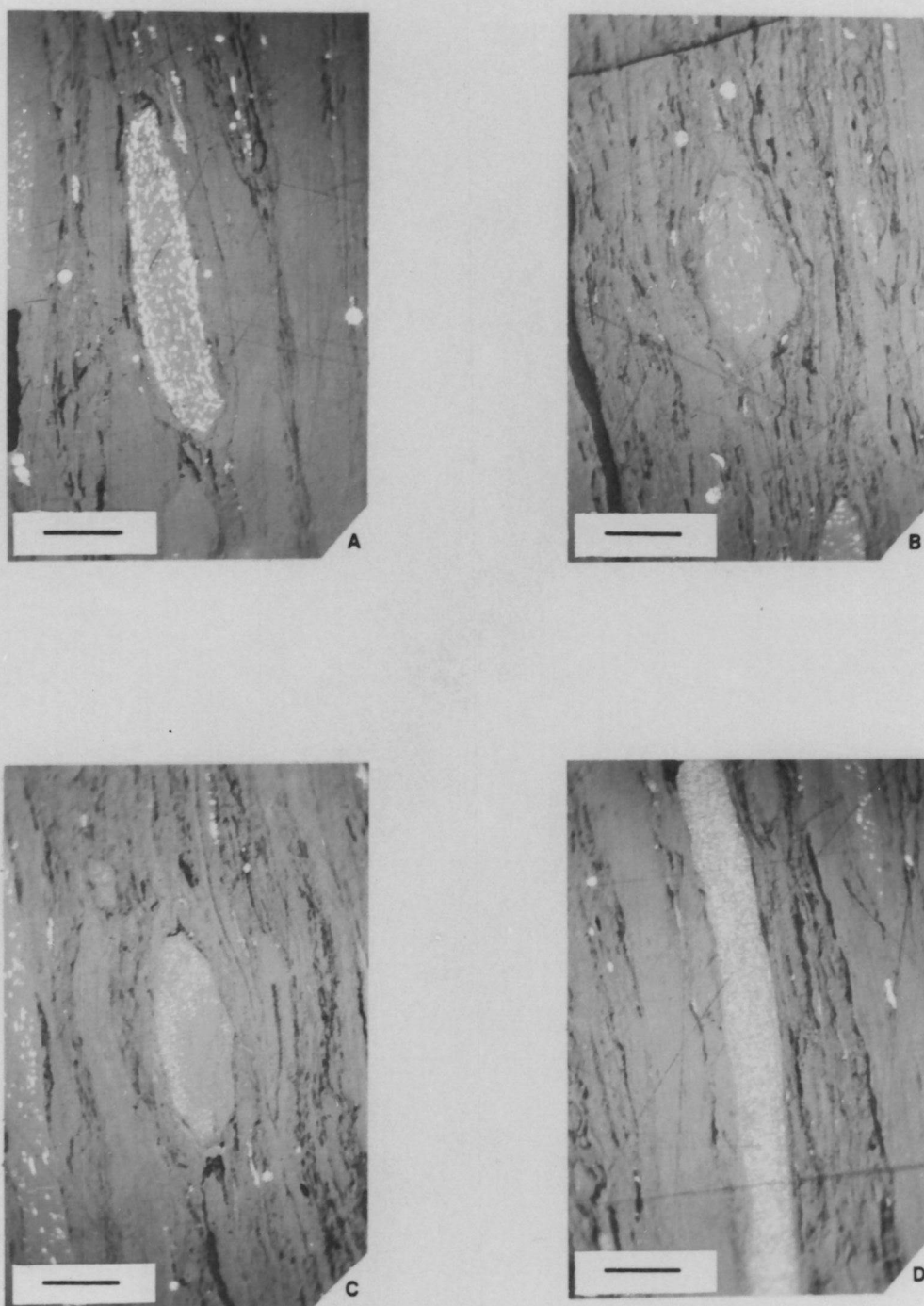


Figure 11. Reflected light photomicrographs of pyritized ovoids from the Pewee coal. (A-C) Transverse sections; (D) longitudinal section. Scale: bar equals 70 microns.

limited development of pyrite in the top of the terrestrial Pewee seam is in contrast to the extensive pyritization typically reported in coals directly overlain by marine sediments. The restriction of this syngenetic mineralization to the upper few centimeters of the seam indicates that Pewee coal is not overlain by marine sediments. Had the Pewee swamp been terminated by a permanent marine incursion, pyritization should have been more pervasive in the seam.

Sparsely disseminated framboidal pyrite also occurs in a sample in which the total weight percent major elements is 1.8 weight percent greater than adjacent samples. Whether the formation of the framboids resulted from a change in pH in the peat due to the influence of water-borne clays or due to a brief incursion of brackish waters resulting from a severe storm cannot be determined. Even less frequent was the occurrence of fracture and fusain filling pyrite. In all cases, the mineralization was incomplete and was generally associated with samples which exhibited clay laminae. This association, like the previous one, suggests that either the clay or the fluids which brought the clay influenced the formation of the pyrite.

In one other sample, an increase in total major elements of 2.1 weight percent over adjacent samples was noted. This particular occurrence (unlike those previously discussed) corresponds to a time when the peat surface was exposed to the atmosphere. Oxidation of the peat surface resulted in a layer of fusain. The increase in major elements is caused by the incorporation of oxidation products locally in the peat and by epigenetic mineralization commonly reported in fusains. Similar samples have been described for recent peats by Francis (1961).

Boatneg and Phillips (1976) demonstrated that although coal is heterogeneous, organic sulfur is fairly evenly distributed with random variations in the distribution of sulfur due to pyrite. The mean weight percent sulfur in the Pewee seam is 0.83 with a standard deviation of 0.03. The constancy of sulfur through the seam with the previously discussed paucity of pyrite suggests that the majority of the sulfur is organically bound. The lack of significant variation in sulfur also supports the contention that the Pewee swamp developed on the upper delta plain above the influence of marine waters.

II. CORRELATION COEFFICIENTS

The correlation coefficients, r , for (X, Y) pairs of elemental data were determined for the least squares linear regression of those pairs. The computations indicate whether there are significant positive or negative relationships between various elemental pairs. This mathematical treatment has replaced graphical displays where large amounts of data are compares. The correlation coefficient matrix is shown in Table 5.

Silicon

Silicon, Mg, Al, K, Ti, and Rb exhibit coefficients which suggest that these elements are related, presumably in silicate minerals. Sulfur, Fe, and As correlate moderately well with the aforementioned "silicate elements." Since the greatest concentrations of pyrite and total major elements occur at the top and bottom of the seam, it is likely that these correlations reflect changes in the swamp environment associated with the influx of clay minerals.

Table 5

Correlation Coefficients for the Pewee Coal

	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Ni	As	Rb	Sr	Mn
Mg	1	.93	.70	.50	.74	.86	-.34	.49	.58	.24	.62	.72	.48	-.21
Al	.93	1	.84	.47	.75	.88	-.45	.62	.53	.26	.59	.76	.45	-.10
Si	.70	.84	1	.23	.46	.71	-.53	.87	.51	.42	.56	.65	.19	.04
P	.50	.47	.23	1	.53	.14	.22	.08	.06	-.16	.11	.04	.93	-.33
S	.74	.75	.46	.53	1	.54	-.19	.20	.63	.34	.67	.35	.55	-.31
K	.86	.88	.71	.14	.54	1	-.50	.56	.52	.24	.55	.89	.13	0
Ca	-.34	-.45	-.53	.22	-.19	-.50	1	-.45	-.20	-.36	-.39	-.48	.15	.05
Ti	.50	.62	.87	.08	.20	.56	-.45	1	.27	.31	.36	.53	.05	.06
Fe	.58	.53	.51	.06	.63	.52	-.20	.27	1	.64	.87	.35	-.02	-.03
Ni	.24	.26	.42	-.16	.34	.24	-.36	.31	.64	1	.73	.14	-.16	.04
As	.62	.59	.56	.11	.67	.55	-.39	.36	.87	.73	1	.40	.09	-.15
Rb	.72	.76	.65	.04	.35	.89	-.48	.53	.35	.14	.40	1	.04	0
Sr	.48	.45	.19	.93	.55	.13	.15	.05	-.02	-.16	.09	.04	1	-.35
Mn	-.21	-.10	.04	-.33	-.31	0	.05	.06	-.03	.04	-.15	0	-.35	1

Calcium

There are no significant, positive relationships between calcium and the other elements studied. This suggests that calcium occurs as a carbonate which is not associated with other carbonate or phosphate minerals.

Sulfur

Sulfur correlates with Mg, Al, Fe, and As, which suggests the formation of sulfide minerals associated with clay minerals. The lack of correlation between S and Ca indicates that calcium sulfate is not a significant contributor of either element.

The possible significance of the elemental relationships determined for the Pewee coal is discussed in a comparison with the Grassy Spring coal in the concluding chapter of this work.

III. GRASSY SPRING COAL

This study of Grassy Spring coal suggests that it developed in an area of rapid initial subsidence as a sparsely forested swamp which was terminated by the incursion of marine waters. These conditions produced a semi-bright clarain coal which is higher in pyritic sulfur and other minerals than the Pewee coal.

Total major element data show that the swamp was subject to the periodic influx of large amounts of detritus during its development. This is indicated by the four major pulses in the total major element curve (Figure 10 (B), page 44). The average weight percent of the major elements present in the coal is 14.8. This average does not include data

from those samples which contain over 25 weight percent total major elements. This high figure indicates that there was sufficient movement of water in the swamp throughout its development to transport the mineral matter. The movement of water also created locally oxidizing conditions which resulted in the high content of inertinite (17 volume percent) similar to that described by Ammonsov (1964). These facts suggest that there was active channeling in the swamp and that it was subject to periodic flooding. The general decrease in the major element content toward the top of the Grassy Spring coal probably resulted from the abandonment of the major distributary with which the swamp was associated. This abandonment of the delta lobe not only resulted in decreased inorganic sedimentation in the swamp, but allowed the incursion of marine waters due to subsidence.

The seam sections drawn from the maceral and lithotype (Figure 12) analysis of Table 6 indicate that the Grassy Spring is a clarain-rich coal which contains 18 volume percent exinite (primarily sporinite) and 17 volume percent inertinite. The clarain is microlayered with clay laminae and other mineral matter. There are few continuous vitrain bands and the vitrinites are generally structureless. Telinite and collinite, which evidence a preserved cell structure, were only observed in one sample at the base of the seam.

The high content of major elements and sporinite with lower vitrinite suggest that the swamp was not heavily forested. Sporinite-rich clarains are generally thought to represent more open water conditions than are typical for a well-developed forest swamp (Francis, 1961; Stach et al., 1975). All of these characteristics suggest that

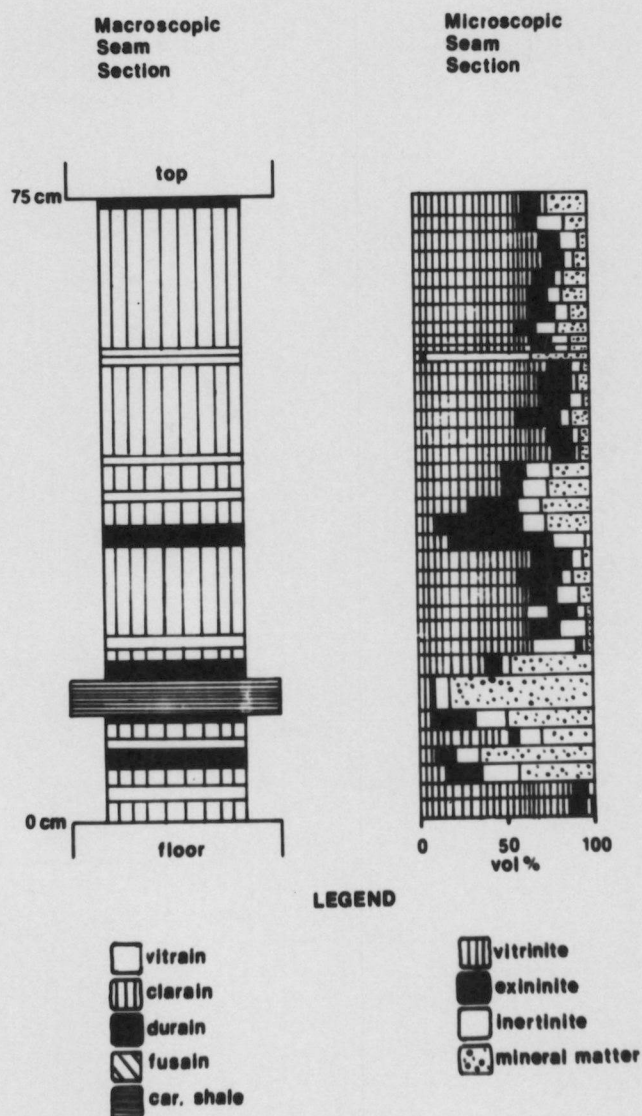


Figure 12. Seam sections of the Grassy Spring coal.
 (A) Macroscopic seam section; (B) microscopic seam section.

Table 6

Point Count and Lithotype Analyses of the Grassy Spring Coal

Sample Number	Volume Percent $\pm$ 2				Mineral Matter	Lithotype	
	Vitrinite	Exinite	Inertinite	Pyrite		First cm	Second cm
A2	83	11	4	2	--	Clarain	Clarain
A1	87	6	2	2	3	Vitrain	Vitrain
B2	14	22	25	2	36	Clarain	Clarain
B1	9	5	17	3	65	Durain	Durain
C2	54	6	12	3	25	Vitrain	Vitrain
C1	6	24	20	3	48	Clarain	Durain
D	6	< 1	6	1	86	Shale	Shale
E	3	1	10	2	84	Shale	Durain
F9	42	5	6	4	42	Durain	Clarain
F8	90	2	1	6	< 1	Vitrain	Vitrain
F7	64	13	19	2	2	Clarain	Clarain
F6	74	15	5	1	5	Clarain	Clarain
F5	63	14	15	5	2	Clarain	-
F4	61	23	5	9	3	Clarain	Clarain
F3	64	19	8	5	3	Clarain	Clarain
F2	20	57	19	1	3	Clarain	Clarain
F1	9	57	14	2	18	Durain	Durain
G10	34	27	14	3	22	Clarain	Clarain
G9	51	11	17	6	15	Clarain	Vitrain
G8	47	14	14	6	19	Clarain	Clarain
G7	81	10	3	6	16	Clarain	-

Table 6 (continued)

Sample Number	Volume Percent ± 2				Mineral Matter	Lithotype	
	Vitrinite	Exinite	Inertinite	Pyrite		First cm	Second cm
G6	78	10	7	4	2	Vitrain	Clarain
G5	59	23	16	2	13	Clarain	Clarain
G4	72	18	7	2	< 1	Clarain	Clarain
G3	71	14	8	7	< 1	Clarain	Clarain
G2	62	19	9	11	< 1	Clarain	Clarain
G1	74	15	7	4	--	Clarain	-
H11	2	< 1	61	37	--	Fusain	-
H10	75	13	9	3	--	Vitrain	Clarain
H9	70	12	14	4	--	Clarain	Clarain
H8	59	13	12	27	--	Clarain	-
H7	69	11	11	8	--	Clarain	Clarain
H6	68	13	12	7	--	Clarain	Clarain
H5	73	14	8	5	--	Clarain	-
H4	77	11	7	5	--	Clarain	Clarain
H3	69	13	11	6	< 1	Clarain	Clarain
H2	60	15	19	7	--	Clarain	Clarain
H1	65	11	3	20	2	Durain	-

the swamp developed in the interdistributary backswamp of a distal deltaic system. Such a location in the lower delta plain would expose the swamp to the high rates of sedimentation due to channel switching and overbank flooding. This area on the delta plain would also be subject to a higher subsidence rate due to dewatering and compaction of the substratum. These characteristics are also significant to the type of forestation which developed because an infirm bottom would not support a heavily forested area (Roberts, 1978).

The swamp developed under fresh water conditions due to the formation of a groundwater lense which was supplied water by the fluvial system (O'Neil, 1949; Teichmuller, 1962a). Peat formation was terminated by sedimentation under marine conditions. This interpretation is based on the distribution of sulfur in the seam. When the weight percent sulfur is averaged for equal intervals in the coal, the sulfur is seen to increase systematically (0.87, 1.06, 1.43, 1.62 weight percent) from the floor to the top of the seam. Casagrande et al. (1977) indicate that a peat which develops under marine conditions will have one to two orders of magnitude more sulfur than a comparable fresh water peat and that sulfur will decrease from bottom to top. The increasing sulfur toward the roof of the Grassy Spring seam indicates that the marine waters which inundated the swamp percolated into the peat, raising the pH and increasing interstitial sulfate. This increased anaerobic bacterial activity which caused H_2S generation resulted in pyritization of the sediments. Point count analyses of pyrite (averaged at equal intervals) show that pyrite increases from the bottom to the top of the seam (2.4, 3.8, 5.3, 11.8 volume percent).

The increase in bacterial activity also affected the vitrinites. As previously mentioned, structured vitrinites were only seen at the bottom of the seam. The peat must have been sealed off quickly by sedimentation, preventing continued circulation of marine water. Recent peats with freely circulating marine waters typically have sulfur contents of 5-10% (Casagrande et al., 1977). Because of the location of the swamp on the flank of a distal tributary, the swamp would inter-finger with higher sulfur marine bay sediments. Sulfur and pyritization can be expected to increase and bed thickness decrease as the Grassy Spring is mined toward its seaward margin.

Possible controls on the location of the previously mentioned syngenetic pyritization are suggested by a comparison of the curves for titanium, iron, pyrite, and vitrinite content (Figure 13). Titanium is used as an indicator of the relative amounts of detritus in the coal because in recent sediments the majority of the Ti occurs as a structural component in the lattice of clay minerals (Hirst, 1962b). When Ti is leached, it immediately precipitates as an hydrated oxide which later alters to an insoluble oxide (McLaughlin, 1958). Thus, the Ti is probably still associated with those elements which formed the detrital carriers of the Ti.

Increases in Fe occur in vitrinites adjacent to high major element areas in the coal. Iron oxides and hydroxides which were adsorbed on the clays were deposited in the swamp with the detritus. Under the acidic conditions prevalent in the swamp during its freshwater development, iron was leached from the clays and was taken up by humic acids in the adjacent peat. The marine inundation at the termination of the

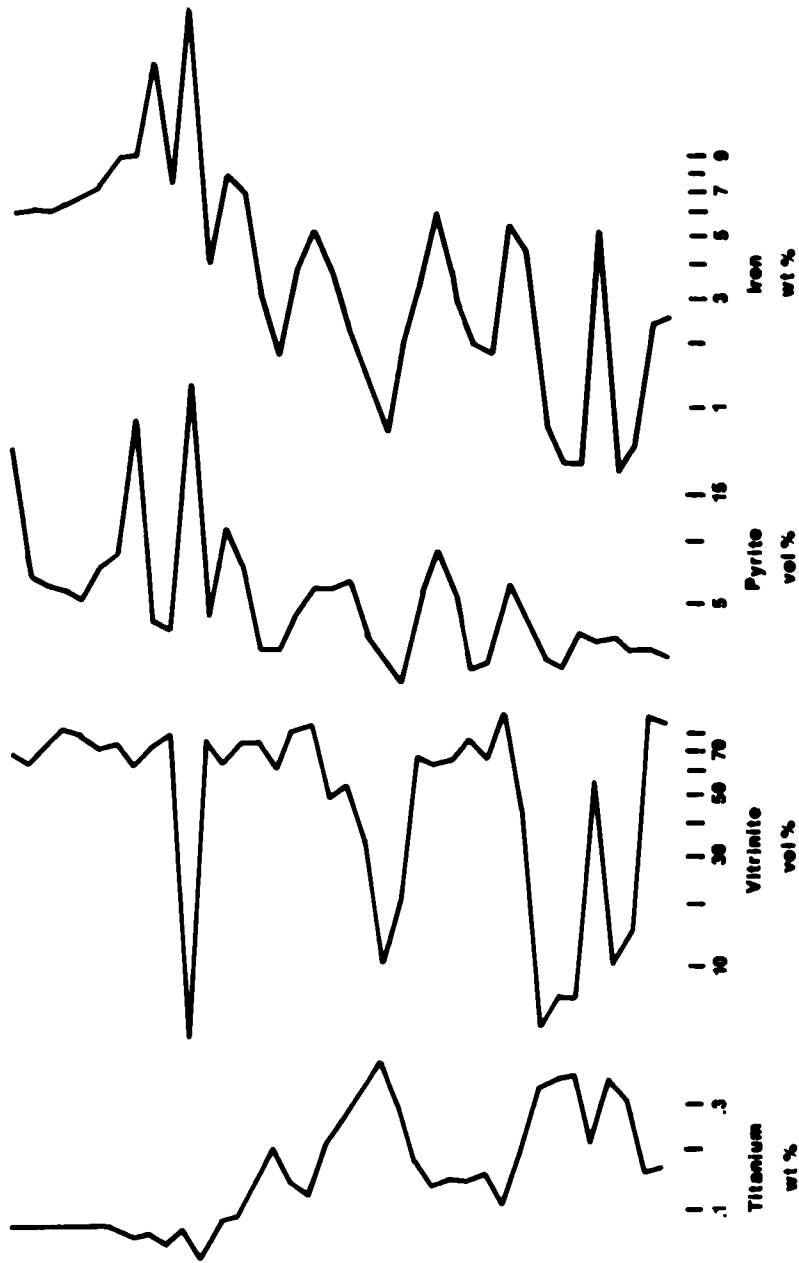


Figure 13. Comparison of curves for the Grassy Spring coal which suggests a control on the formation of pyrite by clay seams.

swamp milieu resulted in the generation of H_2S in the peat which reacted with the iron, eventually resulting in pyrite. In this manner, pyritization was greater adjacent to high clay areas. The highest value for iron is coincident with a fusain (inertinite) layer which has been completely mineralized by epigenetic processes.

Iron is in excess of that required to form pyrite. It is likely that this Fe occurs in the clay minerals, as oxides or hydroxides, and in organic combination due to complexing of the Fe by organic acids. Complexing of Fe by organic acids would have been facilitated by the higher pH which resulted from the marine incursion.

IV. CORRELATION COEFFICIENTS

The correlation coefficients, r , for (X, Y) pairs of elemental data for the Grassy Spring coal were determined for the least squares linear regression of those pairs. The correlation coefficient matrix of all possible elemental pairs are shown in Table 7.

Silicon

Silicon, Mg, Al, K, and Rb exhibit respective correlations of +0.98, +0.99, +0.93, and +0.90. These elements are likely in the clay minerals which are believed to form the bulk of the inorganic detritus. Titanium exhibits correlations with Si, Al, K, and Rb, which suggest that Ti is associated with phyllosilicates. These correlation coefficients are, respectively, +0.84, +0.83, +0.72, and +0.67.

Table 7

Correlation Coefficients for the Grassy Spring Coal

	Mg	Al	Si	P	S	K	Ca	Ti	Fe	Ni	As	Rb	Sr	Mn
Mg	1	.99	.98	.24	.76	.95	-.54	.80	-.74	.09	-.47	.91	.27	.29
Al	.99	1	.99	.28	-.77	.95	-.55	.83	-.77	.10	-.48	.91	.31	.32
Si	.98	.99	1	.24	-.74	.93	-.58	.84	-.74	.08	-.46	.90	.26	.35
P	.24	.28	.24	1	-.46	.08	.52	.38	-.57	-.01	-.32	.03	.97	.11
S	-.76	-.77	-.74	-.46	1	-.72	-.11	-.71	.96	-.21	.75	-.70	-.49	-.28
K	.95	.95	.93	.08	-.72	1	-.68	.72	-.70	.18	-.48	.98	.10	.18
Ca	-.54	-.55	-.58	.52	.11	-.68	1	-.39	.07	-.10	.01	-.69	.53	-.15
Ti	.80	.83	.84	.38	-.71	.72	-.39	1	-.72	.04	-.53	.67	.37	.51
Fe	-.74	-.77	-.74	-.57	.96	-.70	.07	-.72	1	-.27	.74	-.69	-.58	-.25
Ni	.08	.10	.08	-.01	-.21	.18	-.10	.04	-.27	1	-.21	.17	-.02	-.24
As	-.47	-.48	-.46	-.32	.75	-.48	.01	-.53	.74	-.21	1	-.48	-.35	-.21
Rb	.91	.91	.90	.03	-.70	.98	-.69	.67	-.69	.17	-.48	1	.06	.13
Sr	.27	.31	.26	.97	-.49	.10	.53	.37	-.58	-.02	-.35	.06	1	.09
Mn	.29	.32	.35	.11	-.28	.18	-.15	.51	-.25	-.24	-.21	.13	.09	1

Calcium

Calcium has correlation coefficients with P and Sr of +0.52 and +0.53. Phosphorus and Sr have an r of +0.97. These coefficients suggest that the distribution of Ca, Sr, and P are related. The weak correlation between Ca and S, +.11, suggests a minor control on the distribution of these elements by calcium sulfate. This association of Ca and S could have resulted from marine conditions or from the weathering of pyrite on outcrop.

Sulfur

Iron and As have correlation coefficients with S of +0.96 and +0.75, which suggests that these elements are associated as sulfides. The absence of a positive correlation between Ni and S suggests that Ni is not associated with the sulfides.

The possible paleoenvironmental significance of these relationships are discussed in the concluding chapter.

CHAPTER VI

CONCLUSIONS AND SUMMARY

A comparison of the relationships established for these two coal seams reveals several possibly significant findings. In general, these results confirm relationships which could have been anticipated from the geochemical literature. However, serious questions are raised concerning the validity of elemental relationships established by commonly used random and often biased sampling techniques which do not consider the coal's environments of formation.

Tables 5 and 7 (pages 49 and 59, respectively) show the correlation coefficients of silicon and other elements for each seam. In seam, rubidium and potassium exhibit very similar coefficients. The coefficients are higher for the Grassy Spring than the Pewee. This suggests that these elements were removed from aqueous solution by the clay minerals under conditions of different cation availabilities and pH (Carrol, 1959). Potassium and rubidium are found in substantially greater concentrations in sea water than in fresh water (Degens, 1965). Clays exposed to sea water would be expected to fix greater amounts of these elements than clays exposed to fresh water only. This tendency is enhanced by the fact that marine peats exhibit a higher pH than terrestrial peats. Under moderate pH, ≥ 7 , ion exchange reactions are stimulated, so the clays of marine-influenced peats would be expected to fix more cations. It could be argued that rubidium and potassium were brought into the swamp already combined with the clay minerals.

Undoubtedly they were; however, rubidium and potassium have similar exchange affinities (Jenny, 1932, 1936) and similar flow rates through compacted clays (Kharka and Smalley, 1976). The fact that the rubidium and potassium show similar correlations with silicon in each seam suggests that their respective paleoenvironments did act on the clays in a predictable fashion. From the earlier discussion, it would be expected that the silicon of a recent marine-influenced peat would exhibit higher correlation coefficients with rubidium and potassium. It is significant that these environmentally determined relationships have been maintained by the elements of the respective coals with the Grassy Spring coal exhibiting much higher correlations. These higher correlation coefficients suggest that the Grassy Spring swamp was exposed to marine waters.

Titanium exhibits high correlations with silicon, which suggests that it is combined in the structure of clay minerals (Hirst, 1962b) and is not in organic combination as was determined by analysis of coal float fractions (Zubovic, 1966; Ruch et al., 1973). Better understanding of the titanium distributions in coals is important because titanium is a catalyst in combustion processes and because it makes aluminum brittle when the metal is made with titanium-contaminated carbon electrodes (Stach et al., 1975). Persons involved in coal utilization need to consider a coal's paleoenvironment when analyzing coal because if they do not they will continue to erroneously conclude that the distribution of titanium, as well as that of many other elements, is random in space when in fact it is environmentally controlled. The study suggests that titanium, by virtue of its high correlation with silicon (+0.84 and

+0.87), might be used as an indicator of relative amounts of the major elements on coal. An easily determined indicator could be used to substantiate paleoenvironmental interpretations which are made by studying the associated sediments. It is suggested that during future research the coals be analyzed for their titanium content. In order that the sample be representative of the coal, the vitrains and clarains should be sampled during a lithotypic determination of the coal. The material examined should not include durains and carbonaceous shale because they contain unusually high concentrations of titanium.

Examination of Tables 5 and 7 (pages 49 and 59, respectively) show the correlation coefficients for elements which are thought to be controlled by carbonate mineralization. The distributions of iron, magnesium, and manganese are not positively related to calcium. This suggests that other phases controlled the distribution of these elements.

The relationships suggested by the coefficients for calcium, phosphorus, and strontium in Tables 5 and 7 (pages 49 and 59, respectively) may indicate an environmental control on the distributions of these elements. The Ca, Sr, and P of the Grassy Spring coal exhibit correlations which suggest the formation of strontium-rich carbonate apatites. The higher pH resulting from marine conditions is known to promote carbonate apatite formation in recent sediments (Garrels, 1960; Degens, 1965).

Marine conditions are indicated for the Grassy Spring coal by the distribution of weight percent iron and sulfur averaged for four equal intervals (25% of the total thickness of the seam) in each coal (Table 8).

Table 8

Comparison of Sulfur and Iron Contents Averaged for
Equal Intervals in the Pewee Coal and the
Grassy Spring Coal

Pewee Weight Percent		Grassy Spring Weight Percent	
S	Fe	S	Fe
<u>Top</u>		<u>Top</u>	
0.83	0.60	1.70	7.71
0.81	0.55	1.25	5.50
0.82	0.49	1.09	2.89
0.87	0.57	0.82	1.96
<u>Bottom</u>		<u>Bottom</u>	

The increase in sulfur and iron toward the top of the Grassy Spring evidences the percolation of marine waters into the swamp at its termination. This marine inundation resulted in a rise in pH with an increase in available sulfate which contributed to the syngenetic pyritization of the peat. The terrestrial Pewee coal does not exhibit similar increases in iron and sulfur contents.

The correlation coefficients for iron and sulfur in the Pewee and Grassy Spring are, respectively, +0.63 and +0.96. The lower correlation for the former might be expected because there is less iron and sulfur (as pyrite?) in the seam; hence, organically-bound sulfur would diminish the correlation.

The y-intercepts of the least squares linear regressions of the iron and sulfur pairs are +0.76 (Pewee) and +0.65 (Grassy Spring). The first supposition one might make is that these figures represent average organic sulfur in each seam. While there is no direct way to substantiate

this from the data the ratios of the y-intercepts to volume percent vitrinite (corrected so that the three maceral groups equal 100% of the volume) do support the supposition.

The Pewee contains 73 volume percent vitrinite and the Grassy Spring contains 66 volume percent vitrinite. When the Pewee's vitrinite content is ratioed to its y-intercept and is compared as a cross product to the vitrinite content of the Grassy Spring, a y-intercept of +0.69 is calculated. This is very close to the +0.65 value actually determined from the data, suggesting that the y-intercepts do represent the average value for organically-bound sulfur in these coals. Three additional ideas are suggested by these relationships. First, the majority of the organically-bound sulfur is in the vitrinites. Second, the vitrinites of the respective coals developed from similar vegetation which grew and was peatified under fresh water conditions. Third, the Grassy Spring was terminated by a marine transgression which resulted in increased pyrite formation in the peat but not the sulfurization of the pre-vitrinites. This is indicated by the close agreement between the predicted, +0.69, and the calculated, +0.65, value for organic sulfur in the coal.

The data clearly support the paleoenvironmental interpretations made by Minkin (1977) and Roberts (1978). A swamp which develops under marine conditions will have substantial increases in total sulfur. Such a dramatic increase is not seen in the Grassy Spring coal. This indicates that its swamp developed under fresh water conditions, only experiencing marine conditions for a limited time at its termination.

Nickel has received much attention by geochemists studying the genesis of petroleum. Since it tends to neutralize catalysts and contaminate metals, its distribution in coal should receive more attention by coal geologists. The data from the two coals studied do not clearly indicate a control on the distribution of nickel, however, they do suggest areas for further work. The concentration in the underburden and overburden of each coal are 6 ppm/23 ppm and 6 ppm/15 ppm, respectively. Since the Grassy Spring coal contains almost three times the total major elements of the Pewee coal, one might conclude that the Grassy Spring would contain more nickel (Thompson, 1976). This is not the case, however, as the mean nickel content in the Grassy Spring is 7 ppm, while in the Pewee it is 34 ppm. This suggests that some process (or processes) operated during the deposition of the peat or after its burial to concentrate the nickel in the Pewee coal. Since the pyrite mineralization is pervasive in the Grassy Spring and very limited in the Pewee, it is not likely that pyritization is responsible for the increase in nickel. There is one possible hypothesis which could explain high nickel content in the Pewee, although it cannot be supported by quantitative data. Nickel is known to be preferentially complexed by pigments in carbonaceous sediments (Degens, 1965). It could be expected that coals which contain a greater amount of chlorophyll-derived pigments would also contain a greater amount of nickel. Cuticular exinites (which were the covering of pigment-rich herbaceous material) were certainly more prominent in the Pewee coal which would support this argument. These pigments break down under oxidizing (aqueous) conditions. The Grassy Spring coal has a high major element (detritus?) and inertinite content, which indicates active

transport conditions. Such conditions would tend to reduce the amount of chlorophyll available to complex nickel. It may be that the higher levels of pigment-derived compounds in the Pewee coal resulted in its higher nickel content. From this discussion, it would be anticipated that alginite-rich cannel coals would contain substantial amounts of nickel. If nickel (and vanadium) could be shown to vary (proportionately) with the amount of cuticular exinites or some other readily identifiable characteristic, i.e., algae content, an important contribution to the geochemistry of coals would be made.

In summary, this study has examined vertical sections of two coals which were formed in different paleoenvironments. Several geochemical relationships are demonstrated:

1. The relationships established for K and Rb during the development of the swamp were not significantly altered.
2. Titanium is associated with the silicate minerals.
3. Carbonate mineralization alone does not control the distribution of Fe, Mg, and Mn.
4. The relationships between Ca, P, and Sr may be indicative of geochemical conditions in the swamp at its termination.
5. Organic sulfur increases with an increase in vitrinite content.

Insofar as can be determined by this study, several important elemental relationships established during a coal swamp's development were not significantly altered by post-coalification intrastratal solutions. This means that a better understanding of the environment in which a coal formed will allow a geologist to better anticipate coal quality.

6. The lithotypes fusain, vitrain, clarain, and durain, do represent increasingly deeper water conditions in the swamp where the respective lithotype formed. This suggests that the lithotype profile which can be easily determined in the field can be diagnostic of the location of a coal swamp in the deltaic complex. Such data could be used to support paleoenvironmental interpretations which are usually based on the coal's associated sediments. These seam profiles have also been demonstrated to be characteristic of a coal over wide geographic areas, and could be used for correlation purposes. This could have ready application to an area where the coal-bearing strata are structurally deformed and are deeply dissected by stream erosion.

CHAPTER VII

SUGGESTIONS FOR FURTHER WORK

The author would like to suggest several topics which might be examined by other workers.

1. Recent work by Sweeney and Kaplan (1973) suggests that high trace element content in laboratory solutions prevents the formation of framboidal pyrite, causing subhedral to euhedral pyrite to form. Query: Are pyrites of varied composition within a seam and do the changes in composition correlate with changes in morphology?

2. Many previous workers have noted the increase in pyritization at the tops and bottoms of coal seams. Classic interpretations rely on post-coalification solutions to explain the peripheral concentrations. Stach et al. (1975) suggest that the overburden and underburden influence the pH conditions in the peat which in turn control pyritization. Query: Where coals are overlain by sandstone, are they lower in pyrite at the contact than where they are overlain by shale? If the sandstone is overlain by marine shales, is pyritization greater than when the sandstone is overlain by terrestrial shales?

3. This study compares a terrestrial coal and a terrestrial coal which was influenced by a marine incursion at its termination. Query: Will the relationships suggested by this study be substantiated by a similar study of a coal influenced throughout its development by marine incursions?

4. The ubiquitous appearance of Ti in coal always leads to an argument as to which phase is its host. Query: Is Ti in the structure of aluminosilicates or in detrital or epigenetic oxides?

5. Mn and Ba are often associated in cryptomelane in what are commonly referred to as "bog ores." Query: Do the relationships between these two elements in coal support other elemental relationships suggested by this study?

6. U-containing compounds are often associated with phosphates and certain heavy minerals. Query: Do U distributions correlate with syngenetic phosphate mineralization?

7. This study relies heavily on the distribution of pyrite in the two coals studied to substantiate the claim that one of the coals was influenced early in its development by a marine incursion. A considerable amount of the pyrite is of the vein filling, nonframboidal variety. The genesis of this pyritic mineralization is not well understood. It is possible that the pyrite formed in the voids after coalification was complete. This vein-filling pyrite may also have resulted from the recrystallization of framboidal pyrite during the coal-forming process. Query: Does vein-filling, nonframboidal pyrite form in the peat in response to paleoenvironmentally controlled geochemical conditions, or does it form after coalification is well advanced in response to a change in geochemical conditions caused by circulating intrastratal solutions?

SELECTED REFERENCES

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- Ahren, A. W., and Harriss, R. C., 1975, Observations on the association between mercury and organic matter dissolved in natural waters, *Geochim. Cosmochim. Acta*, Vol. 39, pp. 1253-1257.
- Ammonsov, I. I., 1964, Composition pétrographique des charbons humiques de l'USSR, *C.R. 5 Contr. Intern. Strat. Géol Carbonifère* 3, Paris, 909-916.
- Ashley, G. H., 1920, Geological aspects of sulfur in coal, *Trans A.I.M.M.E.*, Vol. 63, pp. 732-739.
- Baas-Becking, L. G. M., Kaplan, I. R., and Moore, D., 1960, Limits on the natural environment in terms of pH and oxidation-reduction potentials, *Jour. Geo.*, Vol. 68, No. 3, pp. 243-284.
- Beck, K. C., Reuter, J. H., and Perdue, E. M., 1974, Organic and inorganic geochemistry of some coastal plain rivers of the Southeastern U.S., *Geochim. Cosmochim. Acta*, Vol. 38, pp. 341-364.
- Bermer, R. A., Sedimentary pyrite formation, *Amer. Jour. Sci.*, No. 268, pp. 1-23.
- Boatneg, D. A. D., and Phillips, C. R., 1976, Examination of coal surfaces by microscopy and the electron microprobe, *Fuel*, Vol. 55, No. 4, pp. 318-322.
- Carrol, D., 1959, Ion exchange in clays and other minerals, *Bull. Geol. Soc. Amer.*, Vol. 70, pp. 749-780.
- Casagrande, D. J., and Erchull, L. D., 1976, Metals in Okefenokee peat-forming environments: Relation to constituents found in coal, *Geochemica et cosmochimica, Acta*, Vol. 40, pp. 387-393.
- Casagrande, D. M., Siefert, K., Berschinski, C., and Sutton, N., 1977, Sulfur in peat-forming systems of the Okefenokee Swamp and Florida Everglades: Origins of sulfur in coal, *Geochim. Cosmochim. Acta*, Vol. 41, pp. 161-167.
- Chayes, F., 1956, Petrographic Modal Analysis, John Wiley and Sons, New York, 113 pp.
- Degens, E. T., 1965, Geochemistry of Sediments, A Brief Survey, Prentice-Hall, Englewood Cliffs, New Jersey, 342 pp.
- Eskenazy, G. R., 1967, Adsorption of gallium on peat and humic acids, *Fuel*, Vol. 46, pp. 187-191.

- Flaig, W., 1968, Biochemical factors in coal formation, pp. 197-227, In: Murchison, D., Westoll, T. S., Eds., 1968, Coal and Coal-Bearing Strata, Oliver and Boyd, London, 418 pp.
- Francis, F., 1961, Coal Its Formation and Composition, Edward Arnold Ltd., London, 806 pp.
- Frazier, D. E., and Osanik, A., 1969, Recent peat deposits—Louisiana Coastal Plain, pp. 63-86, In: Dapples, E. C., and Hopkins, M. E., Eds., 1969, Environments of Coal Deposition, Geological Society of America, Special Paper No. 114, 214 pp.
- Garrels, R. M., 1960, Mineral Equilibria at Low Temperature and Pressure, Harper and Brothers, New York, 254 pp.
- Gluskoter, H. J., 1973, Mineral matter and trace elements in coal, pp. 1-22, In: Babu, S. P., 1975, Ed., Trace Elements in Fuel, Amer. Chem. Soc., Washington, D.C., 216 pp.
- Gluskoter, H. J., Ruch, R. R., Miller, W. G., Cahill, R. A., Dreher, G. B., and Kuhn, J. K., 1976, Trace elements in coal: Occurrence and distribution, Ill. Geol. Surv. Cir. 499, 154 pp.
- Goldberg, E. D., 1957, Biochemistry of trace metals, G.S.A. Mem. 67, Vol. 1, pp. 345-358.
- Goldschmidt, V. M. and Peters, C., 1933, Hachr. Ges. Wiss. Göttingen, math.-phys.-chem. Abt. 35.
- Goldschmidt, V. M., 1954, Geochemistry, Oxford Press, London, 730 pp.
- Guennel, G. K., 1952, Fossil spores of the Alleghenian coals of Indiana, Indiana Geological Survey Prog. Rept. No. 14, pp. 1-40.
- Hasler, M. F., and Kemp, J. W., 1957, Amer. Soc. for Testing Materials, A.S.T.M. Committee E-2 SM2-3, Philadelphia.
- Hirst, D. M., 1962b, The geochemistry of modern sediments from the Gulf of Paria—II, Geochim. Cosmochim. Acta, Vol. 26, pp. 309-324.
- Ingerson, E., 1954, Geo-chemical work of the geochemical and petrologic branch of the U.S. Geological Survey, Geochim. Cosmochim. Acta, Vol. 5, pp. 20-39.
- Jenny, H., 1932, Studies of the mechanism of ionic exchange in colloidal aluminum silicates, J. Phys. Chem., Vol. 36, pp. 2217-2258.
- Jenny, H., 1936, Simple kinetic theory of ionic exchange: Ions of equal valency, J. Phys. Chem., Vol. 40, pp. 501-517.

- Kemezys, M., and Taylor, G. H., 1964, Occurrence and distribution of minerals in some Australian coals, *J. Inst. Fuel*, Vol. 37, pp. 389-397.
- Kharaka, Y. K., and Smalley, W. C., 1976, Flow of water and solutes through compacted clays, *Amer. Assoc. Pet. Geol.*, Vol. 60, No. 6, pp. 973-980.
- Krauskopf, K. B., 1955, Sedimentary deposits of rare metals, *Econ. Geol.*, Fiftieth Anniv., p. 411.
- McLaughlin, R. J. W., 1958, The geochemistry of Kaolin clays, *Geochim. et Cosmochim. Acta*, Vol. 17, pp. 11-16.
- Mackowsky, M.-Th., 1968, Mineral matter in coals, pp. 309-319, In: Murchison, D., and Westoll, T. S., Eds., 1968, Coal and Coal-Bearing Strata, Oliver and Boyd, London, 418 pp.
- Matsuyama, M., 1974, Vertical distribution of some chemical substances in surface sediments of meromictic Lake Suigetsu, *J. Oceanogr. Soc. Japan*, Vol. 30, pp. 209-215.
- Meyers, P. A., and Quinn, J. G., 1973, Factors affecting association of fatty acids with mineral particles in sea water, *Geochim. Cosmochim. Acta*, Vol. 37, pp. 1745-1759.
- Minkin, S. C., 1977, Pennsylvanian deltaic sediments of the northern Cumberland Plateau, Tennessee: Unpublished M.S. thesis, University of Tennessee-Knoxville, 141 pp.
- Moss, F. J., and Anderson, J. E., 1968, The effects of environment on bacterial leaching rates, *Proc. Aust. Inst. Min. Met.*, No. 225, pp. 15-26.
- Mothersill, J. S., 1975, Lake Chad: Geochemistry and sedimentary aspects of a shallow polymictic lake, *Jour. Sed. Pet.*, Vol. 45, No. 1, pp. 295-309.
- Nissenbaum, A., and Swaine, D. J., 1976, Organic matter-metal interactions in recent sediments: The role of humic substances, *Geochim. Cosmochim. Acta*, Vol. 40, pp. 806-816.
- O'Gorman, J. V., and Walker, P. L., Jr., 1971, Mineral matter characteristics of some American coals, *Fuel*, Vol. 50, No. 2, pp. 135-151.
- O'Gorman, J. V., and Walker, P. L., Jr., 1972, Mineral matter and trace elements in coal, Office of Coal Research, U.S. Dept. Int., Research and Development Report No. 61, Interim Report No. 2, 184 pp.

- O'Neil, T., 1949, The muskrat in the Louisiana coastal marshes, Louisiana Dept. Wildlife and Fisheries, New Orleans, 152 pp.
- Picard, G. L., and Filbeck, G. T., Jr., 1976, The complexation of iron by marine humic acid, *Geochim. Cosmochim. Acta*, Vol. 40, pp. 1347-1350.
- Rao, C. P., and Gluskoter, H. J., 1973, Occurrence and distribution of minerals in Illinois coals, *Ill. State Geol. Surv. Cir.* 476, 56 pp.
- Reidenouer, D., Williams, E. G., and Dutcher, R. R., 1967, The relationship between paleotopography and sulfur distribution in some coals of Western Pennsylvania, *Economic Geology*, Vol. 62, pp. 632-647.
- Roberts, T. A., 1978, Transitional lower delta plain—upper delta plain sediments in middle Pennsylvanian coal-bearing strata eastern Wartburg Basin, Tennessee: Unpublished M.S. thesis, University of Tennessee, 272 pp.
- Ruch, R. R., Gluskoter, H. J., and Shimp, N. F., 1973, Occurrence and distribution of potentially volatile trace elements in coal, *Ill. State Geol. Survey Environ. Geol. Note No.* 61, 43 pp.
- Sholkovitz, E. R., 1976, Flocculation of dissolved organic and inorganic matter during mixing of river water and seawater, *Geochim. Cosmochim. Acta*, Vol. 40, pp. 831-845.
- Smith, M., 1967, Coal petrology applied to the correlation of some New South Wales Permian coals, *Proc. Aust. Inst. Min. Met.*, No. 221, pp. 11-18.
- Smith, M., 1968, The petrography of some New South Wales Permian coals from the Tobago coal measures, *Proc. Aust. Inst. Min. Met.*, No. 225, pp. 1-9.
- Smith, M., 1970, Type seam sequences for some Permian Australian coals, *Proc. Aust. Inst. Min. Met.*, No. 233, pp. 221-231.
- Stach, E., 1927, *Der Kohlenreliefschliff, ein neues Hilfsmittel für die Angewandte Kohlenpetrographie.*, Mitt. Abt. Gebstein-, Erz-, Kohle- u. Salzunters. Z, 75-94, Berlin.
- Stach, E., Mackowsky, M-Th., Teichmüller, M., Taylor, G. H., Chandra, D., and Teichmüller, R., 1975, Stach's Textbook of Coal Petrology, Gebrüder Borntraeger, Berlin-Stuttgart, 428 pp.
- Steele, K. F., and Wagner, G. H., 1975, Trace metal relationships in bottom sediments of a fresh water stream—The Buffalo River, Arkansas, *Jour. Sed. Pet.*, Vol. 45, No. 1, pp. 310-319.
- Stopes, M. C., 1919, On the four visible ingredients in banded bituminous coals, *Proc. Roy. Soc.*, Vol. 90B, pp. 470-487.

- Sweeney, R. E., and Kaplan, I. R., 1973, Pyrite framboid formation: Laboratory synthesis and marine sediments, *Econ. Geol.*, Vol. 68, No. 5, pp. 618-634.
- Szalay, A., and Szilagyi, M., 1967, The association of vanadium with humic acids, *Geochim. Cosmochim. Acta*, Vol. 31, pp. 1-6.
- Szilagy, M., 1974, Valency changes of metal ions in the interaction with humic acids, *Fuel*, Vol. 53, pp. 26-28.
- Tasch, K. H., 1960, Die Möglichkeiten der Flözgleichstellung unter Zuhilfenahme von Flözbildungsdiagrammen, *Bergbau-Rdsch.*, 12, 153-157.
- Teichmüller, M., 1962A, Die Genese der Kohle, C. R. 4 Congr. Intern. trat. Geol. Carbonifere, Heerlen 1958, 3, Maastricht, 699-722.
- Teichmüller, M., and Teichmüller, R., 1968, Geological aspects of coal metamorphism, pp. 233-263, In: Murchison, D., and Westoll, T. S., Eds., 1968, *Coal and Coal-Bearing Strata*, Oliver and Boyd, London, 418 pp.
- Theissen, R., 1913, The origin of coal, U.S. Bureau of Mines Bull. 38, pp. 187-205.
- Thompson, C. M., 1977, Characterization of the heavy metal content of coal-bearing stratigraphy from the New River Basin, Tennessee; heavy metals released by static leaching: Unpublished M.S. thesis, University of Tennessee, 53 pp.
- Ward, C. R., 1977, Mineral matter in the Springfield-Harrisburg (No. 5) coal member in the Illinois Basin, Ill. State Geol. Surv., Circular 498, 35 pp.
- Warne, S. St. J., 1965, Identification and evaluation of minerals in coal by differential thermal analysis, *J. Inst. Fuel*, Vol. 38, pp. 207-217.
- Warne, S. St. J., 1970, The detection and identification of the silica minerals quartz, chalcedony, agate and opal by differential thermal analysis, *J. Inst. Fuel*, Vol. 43, pp. 240-242.
- White, J. F., 1975, Depositional environments of Pennsylvanian Redoak Mountain formation, Northern Cumberland Plateau, Tennessee: Unpublished M.S. thesis, University of Tennessee-Knoxville, 115 pp.
- Williams, E. G., and Keith, M. L., 1963, Relationship between sulfur in coals and the occurrence of marine roof beds: *Economic Geology*, Vol. 58, pp. 720-729.

- Yancey, H. F., and Fraser, T., 1921, The distribution and the forms of sulfur in the coal bed, Univ. Ill. Eng. Exp. Sta. Bull. No. 125, pp. 1-94.
- Zubovic, P., Stadnichenko, T., and Sheffey, N. B., 1960, The association of minor elements with organic and inorganic phases in coal, U.S. Geol. Surv. Prof. Pap. 400-B, B84-B87.
- Zubovic, P., Stadnichenko, T., and Sheffey, N. B., 1961, Chemical bases of minor element associations in coal and other carbonaceous matter, U.S. Geol. Surv. Prof. Pap. 424-D, D345-D348.
- Zubovic, P., Stadnichenko, T., and Sheffey, N. B., 1961, Geochemistry of minor elements in coals of the Northern Great Plains Province, Geol. Surv. Bull. 1117-A, 58 pp.
- Zubovic, P., Stadnichenko, T., and Sheffey, N. B., 1964, Distribution of minor elements in coals of the Eastern Interior Region, Geol. Surv. Bull. 1117-B, 41 pp.
- Zubovic, P., 1966A, Physio-chemical properties of certain elements as controlling factors in their distribution in coal, In: Gould, R. F., Ed., Advances in Chemistry Series-Coal Science, Vol. 55, American Chemical Society, Washington, D.C.
- Zubovic, P., Stadnichenko, T., and Sheffey, N. B., 1966, Distribution of minor elements in coals of the Appalachian Region, Geol. Surv. Bull. 1117-C, 37 pp.
- Zubovic, P., Stadnichenko, T., and Sheffey, N. D., 1967, Distribution of minor elements in coals of the Western and Southwestern Regions of the interior coal province, Geol. Surv. Bull. 1117-D, 33 pp.

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