MODES OF OCCURRENCE
OF TRACE ELEMENTS IN COAL

by

Robert B. Finkelman

This report was originally submitted to the Chemistry Department, University of Maryland, in partial fulfillment of the requirements for the degree of Doctor of Philosophy, 1980.

81-99

U. S. Geological Survey. OPEN FILE REPORT. This report is preliminary and has not been edited or reviewed for conformity with Geological Survey standards or nomenclature. Any trade names are used for descriptive purposes only and do not constitute endorsement by the U. S. Geological Survey.

ABSTRACT

Modes of Occurrence
of
Trace Elements in Coal

by

Robert Barry Finkelman

The chemical and physical environment (mode of occurrence) of the trace elements in coal can influence their behavior during the cleaning, conversion, or combustion of the coal, and during the weathering of leaching of the coal or its by-products. Information on the mode of occurrence of the trace elements is, therefore, essential for the efficient use of our coal resources.

Previous attempts to determine the mode of occurrence of the trace elements in coal have been largely indirect. Results of the most commonly used appproach, sink-float separation, is often contradictory. Evidence obtained from this study indicate that results from sink-float separations are susceptible to gross misinterpretations.

In order to directly determine the mode of occurrence of the trace elements in coal, a tehcnique was developed using the scanning electron microscope (SEM) with an energy dispersive (EDX) detector. This analytical system allows the detection and analysis of in-situ, micron-sized minerals in polished blocks of coal. In addition, mineralogical data were obtained from individual particles extracted from the low-temperature ash of the coal.

These techniques were applied in an in-depth study of the Waynesburg and Upper Freeport coals, both bituminous coals from the Appalachian Basin. In addition, brief studies were conducted on about 80 coals representing every rank and type, and every major coal basin in the United States plus about 20 coals from worldwide locations.

The results indicate that many trace elements in coal can occur quantitatively in micron-sized accessory mineral grains scattered throughout the organic matrix (macerals). For example, Zn and Cd occur predominantly in the mineral sphalerite; Cu in chalcopyrite; Zr and Hf in zircons; the REE, Y, and Th in monazite and xenotime. In Appalachain Basin coals, lead selenides are dominant over lead sulfides, whereas outside the Basin, lead sulfides are far in excess over the selenides. The majority of the lead in coal, however, may be substituting in barium-bearing minerals. Some elements, such as As and Hg, occur in solid solution with pyrite. The difference in the mode of occurrence between As and Hg and the other chalcophile elements is reflected in their behavior during sink-float separation of the coal; those elements forming micron-size minerals within the macerals are concentrated in the lighter Sp. G. fractions; whereas, those elements associated with pyrite are concentrated in the heavier Sp. G. fractions.

Organic associations constitute a major mode of occurrence for several trace elements. Although Ti-bearing minerals are common in many coals, no more than about 50 weight percent of the Ti can be accounted for in this manner. The remainder is probably bound to the organics. Similarly, significant amounts of Se and Br appear to be organically bound. The mode of occurrence of uranium is quite complex; in one sample, virtually all the U occurred as micron-sized grains of uraninite; in another a significant amount of the U was associated with detrital accessory minerals such as zircon; in other coals, the bulk of the U appeared to be organically bound.

This study demonstrated that the SEM-EDX system can be used to rapidly characterize the accessory minerals in most coal samples. The information so generated provides direct knowledge of the modes of occurrence of many trace elements in coal. Some of these trace elements appear to have been quite mobile at some time during the coalification process. This study also demonstrated that, although some elements are inoganically bound in coal, during fractionation, they behave as if they are organically bound.

It is evident that this type of detailed analytical approach is essential if we are to anticipate accurately the effects of the trace elements on the various technological processes that coals will undergo.

Acknowledgements

I owe a deep debt of gratitude to Harry J. Rose, Jr., and Irving A. Breger both of the U. S. Geological Survey and the Univerity of Maryland. They freely offered much needed advise and encouragment through the duration of this study.

I would also like to extend my sincere thanks to the many individuals who have rendered assistance at various stages of this study. Among these are: Drs. Isidore Adler and Sheldon Sommer of the University of Maryland; Peter Zubovic, C. Blaine Cecil, and Ronald W. Stanton, of the U. S. Geological Survey.

My deepest appreciation is reserved for my wife and children, whose unwavering support has been invaluable.

Table of Contents

List of Tables

List of Figures

1. INTRODUCTION

Whenever coals are burned, gasified, liquified, or leached, the inorganic trace elements incorporated in the coal are often released into the environment with potentially deleterious effects. A knowledge of the mode of occurrence of these trace elements, that is the manner in which they are chemically bound and distributed within the coal, is essential in order to predict their behavior in these processes. It is the primary objective of this study to determine the modes of occurrence in coal of as many inorganic trace elements as possible.

The modes of occurrence of the major elements are reasonably well known. Although some occur in a score or more of different compounds in the coal, the bulk of each element is found in no more than one or two forms. Thus, silicon is primarily found in the clay minerals; quartz, calcium and much of the magnesium in carbonates; iron in pyrite and marcasite; and aluminum and potassium in the clays. These minerals are generally present in sufficiently high concentrations so that they can be isolated and analyzed by conventional mineralogical techniques.

In contrast to the major inorganic elements, the modes of occurrence of trace elements are poorly understood, despite the fact that many of them are of rather important geological, geochemical, environmental, and economic significance.

It is common knowledge that most trace elements in coal, such as Zn, Cu, Cr, and Sn, are largely associated with the inorganic fraction. Gluskoter et al. (1977) cite only four trace elements with predominant organic affinities (Ge, Be, B, and Sb). Thus an understanding of the modes of occurrence of the trace elements in coal requires a detailed knowledge of the variety of minerals that occur in coal and an understanding of compositional variation of these minerals.

There have been many attempts to determine the mode of occurrence of trace elements in coal. These will be described in detail in later sections. However, as we will see, these efforts have generally resulted in a qualitative, or at best, a semiquantitative assessment of the organic/inorganic affinity for an element. Furthermore, it will be shown that without a knowledge of the mineral type in which the element occurs, the grain size of the mineral, and its maceral associations, the analytical results generated in these studies may be misinterpreted.

Adequate techniques exist for the analysis of the major mineral species in coal, and many papers on this subject have been published. There is, however, a paucity of information on the accessory minerals in coal. Very early in the present study attention was focused on these minerals, and it was found that they exert an influence far in excess of what their small mass would indicate. As a result, it can now be demonstrated that the accessory minerals may have a greater impact than the major minerals on the distribution of most trace elements in coal. Thus, a major aspect of this study is concerned with the elucidation of the relationships between the accessory minerals and the trace elements.

1.1 Samples

The purpose of this study is to determine the modes of occurrence of trace elements in coal. This can be accomplished with a survey of coals of different type, rank, grade, age, geographic location, etc., or with a detailed study of a few selected coals.

The mode of occurrence of an element is a response to a complex and variable set of physio-chemical conditions. These conditions very likely varied from one coal to another. Thus, the mode of occurrence of an element undoubtedly will show some variation between different coals. It is unlikely that a survey approach would shed light on the underlying factors controlling the mode of occurrence. A detailed investigation of a single sample would allow for a better understanding of the geochemical principles governing the form and distribution of the trace elements in coal. The Waynesburg Coal was selected for this purpose. (See Stanton, 1975, for comments on the geology.)

From a technological viewpoint it can be argued that a knowledge of the distribution of the various inorganic phases is at least as important as understanding why these phases exist. For this purpose a survey approach is essential. Samples of over 70 coals from around the world were studied. Samples were obtained from most major coal producing countries (Table 1A) and most of the coal regions in the U. S. (Table 1B, Figure 1). Coals from the

Table 1. List of Samples*

1A. Foreign Coals

	Country	Rank	Age	Formation or bed	Location/ Comments
1.	Australia	Bituminous	Permian	Bulli	N.S.W.
2.	Brazil	Sub-Bit.	Permian	Barro Branco	
3.	Canada	--	Devonian		Quebec
4.	Canada	Bit.	Penn.		Nova Scotia
5.	Canada	Sub-Bit.	Eocene	Hat Creek	British Columbia
6.	China (P.R.)	Bit.(?)	Paleocene (?)		Marine (?)
7.	England	Bit.	Carb.	Hem Heath	
8.	England	Bit.	Carb.	Ollerton	
9.	England	Bit.	Carb.	Thorsby	
10.	Germany	Bit.	Carb.	Floz Erda	Ruhr
11.	Germany	Bit.	Carb.	Floz Johann	Ruhr
12.	India	Bit.		J/3	
13.	India	Bit.		J/8	
14.	New Zealand	Bit.	Up.Eocene	Brunner	South Island
15.	Norway	Bit.	L. Cret.		Spitzbergen
16.	Scotland	--	Carb.		Boghead
17.	South Africa	Bit.	Perm.		Natal
18.	Taiwan	Bit.	Miocene	Shihti Form.	
19.	USSR	Bit.	Carb.		Donets Basin
20.	Venezuela	Bit.	Tertiary	Naricual	Anzoategin
21.	Venezuela	Bit.	Tertiary	Lobatera	Tachira

* See Table 1D for explanation of abbreviations used in Tables 1 and 2.

1B. U.S. Coals (Exclusive of the Appalachian Province)

Interior Province Coals

Eastern Region

Coal Bed	State	County	Rank	Age; Comments
1. Block	Indiana	Clay	Bit.	Penn.
2. Breckenridge	Kentucky	Hancock	Bit.	Penn; Cannel
3. Illinois No. 6	Illinois	St. Clair	Bit.	Penn.
4. Kentucky No. 11	Kentucky	?	Bit.	Penn.
5. Nolan	Kentucky	Butler	Bit.	Penn.

Western Region

6. Cavanal	Oklahoma	Leflore	Bit.	Penn.
7. Croweburg	Oklahoma	Okmulgee	Bit.	Penn.
8. "Iowa"	Iowa	Taylor	Bit.	Penn.
9. Iron Post	Oklahoma	Rogers	Bit.	Penn.
10. Laredo	Missouri	Adair	Bit.	Penn.
11. Rowe	Oklahoma	Rogers	Bit.	Penn.
12. Stigler	Oklahoma	Haskell	Bit.	Penn.
13. Tebo	Missouri	?	Bit.	Penn.
14. Upper Hartshorne	Oklahoma	Leflore	Bit.	Penn.

Northern Region

15. Randell Lump	Michigan	Bay	Bit.	Penn.

Rocky Mountain Province

Denver Region

1. "Denver Lignite"	Colorado	Adams	Lignite	Paleocene

San Juan River Region

2. Fruitland	N. Mexico	San Juan	Sub-Bit	Up. Cret.

Table 1B, continued

Green River Region				
3. Vermillian Creek	Wyoming	Sweetwater	Sub-Bit.	Cret.?; Lacustrian
Uinta Region				
4. "Ferron"	Utah	?	Bit.	Cret.; Emery Field
Wind River Basin				
5. "Wind River-7A"	Wyoming	Fremont	Sub-Bit.	Cret.
6. "Wind River-11"	Wyoming	Fremont	Sub-Bit.	Cret.
Northern Great Plains Province				
Fort Union Region				
1. Beulah	N. Dakota	Mercer	Lignite	Cret.
Powder River Basin				
2. Monarch	Wyoming	Sheridan	Sub-Bit.	Tertiary; Cannel
North Central Region				
3. "Montana"	Montana	Gallatin	Lignite	Cret.-Tert.
Gulf Province				
Texas Region				
1. "Texas Lignite"	Texas	Wood	Lignite	Tertiary
Alaska Province				
Northern Alaska Fields				
1. "Alaska"	Alaska	Dist. 21	Bit.	Cret.

1C. Appalachian Province Coals

Appalachian Region

Coal Bed	State	County	Rank	Age; Comments
1. Alma	Kentucky	Martin	Bit.	Penn.
2. Coalburg	Kentucky	Martin	Bit.	Penn.
3. Dade	Georgia	Walker	Bit.	Penn.
4. "Deer Park"	Maryland	Garrett	Bit.	Penn.
5. Elk Lick (?)	W. Virginia	Mineral	Bit.	Penn.
6. Harlem	Ohio	Jefferson	Bit.	Penn.
7. Lower Freeport	Ohio	?	Bit.	Penn.
8. Lower Kittanning	W. Virginia	Kanawha	Bit.	Penn.; Cannel
9. Lower Splint	Virginia	Wise	Bit.	Penn.
10. Middle Pewee	Tennessee	Morgen	Bit.	Penn.
11. Pittsburgh	Penna.	Washington	Bit.	Penn.
12. Pocahontas No. 5	W. Virginia	McDowell	Bit.	Penn.
13. Pocahontas No. 3	W. Virginia	Wyoming	Bit.	Penn.
14. "Raleigh-Barnett"	Penna.	Bedford	Bit.	Penn.; = Kitanning?
15. Raven	Virginia	Wise	Bit.	Penn.
16. Raymond	W. Virginia	Putnam	Bit.	Penn.; = Pittsburgh
17. Sharon	Ohio	Pike	Bit.	Penn.
18. Sewell	W. Virginia	Randolph	Bit.	Penn.
19. "Tupper Creek"	W. Virginia	Kanawha	Bit.	Penn.
20. Upper Cobb	Alabama	Fayette	Bit.	Penn.
21. Upper Freeport	Penna.	Indiana	Bit.	Penn.
22. Washington	Ohio	Belmont	Bit.	Perm.
23. Waynesburg	W. Virginia	Monongolia	Bit.	Penn.

Anthracite Region

Coal Bed	State	County	Rank	Age; Comments
24. "Anthracite I"	Penna.	?	Anthracite	Penn.
25. "Anthracite II"	Penna.	?	Anth.	Penn.

Table 1C, continued

26. "Burnside"	Penna.	North-umberland	Anth.	Penn.
27. "Glen Burn"	Penna.	Luzerne	Anth.	Penn.
28. "Jim Thorpe"	Penna.	Carbon	Anth.	Penn.
29. "Wanamie"	Penna.	Luzerne	Anth.	Penn.

Valley Fields

30. Merrimac	Virginia	Montgomery	Semi-Anth.?	Miss.; Cannel(?)

Deep River Field

31. Comnock	N. Car.	Chatham	Bit.	Triassic

Rhode Island Meta-Anthracite Region

32. "Meta-Anthracite"	Rhode Isl.	?	Meta-Anth.	Penn.

1D. Miscellaneous Samples

1.	Lignite	Brandon Lignite; Vermont
2.	Peat	Ohio
3.	Peat	Florida
4.	Coalified Wood	Fairfax, Va.; Recent
5.	"Coal"	Pennsylvania; Devonian
6.	Coal Pellet	Maryland; detrital meta-anth. ?
7.	Asphasltite	Cucuta, Venezuela

Explanation of Abbreviations

Anth. = Anthracite

Bit. = Bituminous

Carb. = Carboniferous

Cret. = Cretaceous

Table 1D, continued

L. = Lower
Miss. = Mississippian
Penn. = Pennsylvanian
Perm. = Permian
Up. = Upper

Table 2. General Stratigraphic Sequence of Appalachian Coals

Age	Coal Bed
Lower Perm.	Washington
Upper Penn.	Waynesburg
	Pittsburgh (No. 8) ≈ Raymond
	"Tupper Creek"
	Elk Lick
	Harlem
Middle Penn.	Upper Freeport
	Lower Freeport
	"Raleigh-Barnett"
	Lower Kittanning
	Coalburg
	Lower Splint
	Alma
Lower Penn.	Raven
	Sharon
	Sewell
	Pocahontas No. 5
	Pocahontas No. 3
Miss.	Merrimac

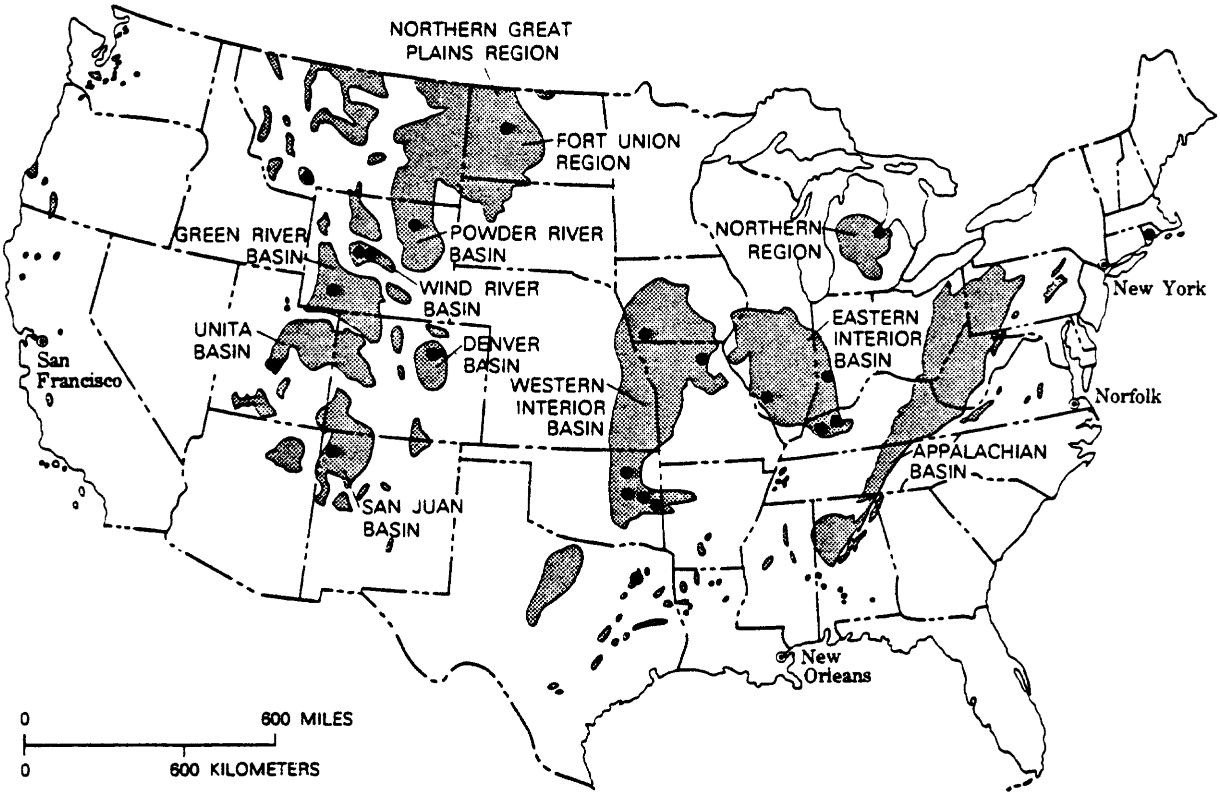

Figure 1. Distribution of samples within the coal fields of the conterminous United States. See Figure 2 for the distribution of samples in the Appalachian Basin.

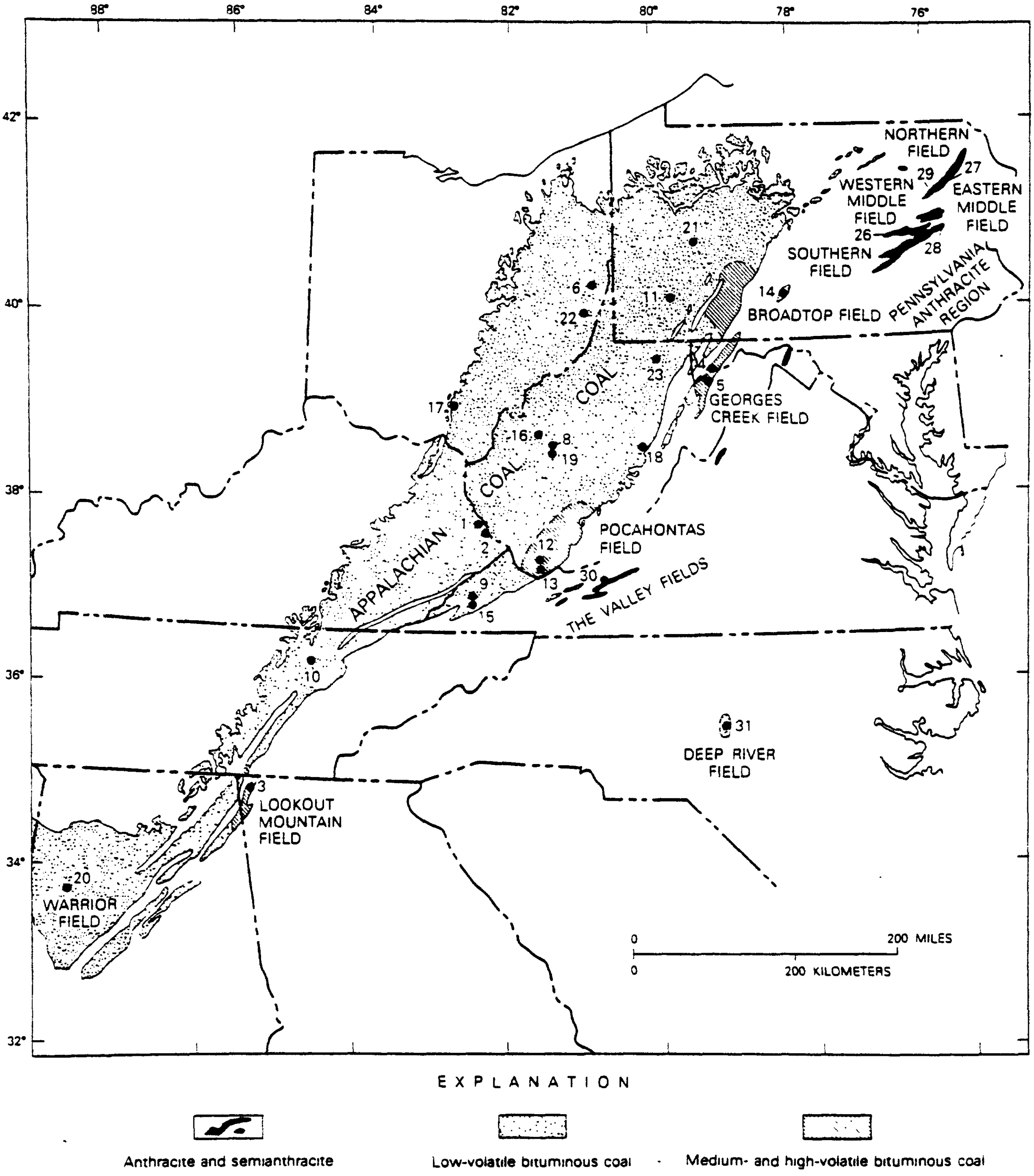

Figure 2. Distribution of samples within the coal fields of the Appalachian Region. Numbers are keyed to Table 1C.

Appalachian Region constitute the single largest group studied (23 samples). Geographically and stratigraphically these samples cover virtually the entire coal-bearing sequence of the Appalachian Region (Figure 2; Tables 1C and 2). Table 1D lists several miscellaneous samples studied for this report.

It is, of course, unrealistic to expect a single sample of coal to be representative of an entire coal bed, much less all of the coal beds in a basin or a country. At this early stage in the gathering and evaluation of geochemical information from coal, there may be no reasonable alternative to a shotgun type approach.

For the most part the samples analyzed were randomly selected fragments of coal samples made available from various sources. Whenever possible, fresh unweathered samples were selected. Samples containing cleat or fracture fillings were avoided. These fillings were clearly introduced after the onset of coalification and are relatively easy to separate from the coal. Moreoever, the syngenetic minerals in coal generally are much more abundant than the epigenetic minerals (Mackowsky, 1968). Thus, the minerals in these cleats are of less geochemical and technological interest than the minerals that are intimately admixed with the organic matter.

1.2 Analytical Techniques

1.21 Scanning Electron Microscopy (SEM)

Most attempts to study the minerals in coal are initiated by removing the organic matter either by ashing (Soong and Gluskoter, 1978; Augenstein and Sun, 1974; O'Gorman and Walker, 1971), by chemical attack (Nalwalk et al., 1974; Ward, 1974) or by grinding followed with float-sink separations (Paulson et al., 1972). Thus, the potentially valuable information on the mineral-maceral[*] relationships have been destroyed. Sample preparations traditionally used for transmitted or reflected light optical microscopy preserve this relationship. However, the ability to resolve many of the extremely fine-grained mineral occurrences is restricted by the resolution of the light optics system. Furthermore, the ability to identify and chemically characterize the mineral grains by optical microscopy is sharply limited.

An approach was sought that would allow the fine-grained minerals in the coal to be observed and analyzed and that would simultaneously preserve the relationship of the minerals and the organic constituents.

The scanning electron microscope (SEM) equipped with an energy dispersive X-ray detector (EDX) proved to be an ideal system for this purpose.

The SEM has a wide range of useful magnifications (∿10X-20,000X), a great depth of focus, and good resolution (∿200 Å). The EDX system is capable of detecting all elements with atomic numbers 11 (sodium) and greater that are present in concentrations down to about 0.5 weight percent.

With the combination of these two instruments, individual, in-situ mineral grains with diameters as small as 0.5 micrometers could

---

[*] See Appendix I for definitions of coal petrographic terms.

routinely be observed and analyzed.

Dutcher et al. (1973) were among the first to apply the SEM with analytical capability to the study of minerals in coal. They suggested using the SEM for the determination of the sizes, shapes, and orientations of specific minerals. Other published reports utilizing a SEM to study coal minerals include Nandi et al., 1970; Vassamillet, 1972; Gluskoter and Lindahl, 1973; Ruch et al., 1974; Augustyn et al., 1976; Finkelman et al., 1976; Finkelman, 1978; Lee et al., 1978; and Finkelman and Stanton, 1979.

In addition to the good visual resolution of the SEM and the analytical capability of the EDX, the system has another feature that proved to be of immense value in this study. Most SEMs display secondary electron images on the cathode ray tube. The low-energy secondary electrons are generated when the primary electron beam excites loosely bound atomic electrons in the sample. These images are well suited for surface topography studies (Goldstein, 1975). The system used in this study was equipped with a back-scattered electron detector. These relatively high-energy electrons are generated by elastic scattering events. The images produced are very sensitive to variations in the mean atomic number of the elements in the sample, much more so than the secondary electron images which are strongly influenced by topography. This feature greatly facilitated the search for mineral grains containing heavy elements. By adjusting the contrast on the back-scattered electron image, minerals such as rutile whose mean atomic number (14) is only slightly higher than minerals such as quartz (10) and most clays (8-10) could be made to appear relatively bright. Thus, large areas on a polished block could be rapidly scanned in search of these highly reflective phases.

By examining a variety of minerals on a polished block, it was determined that peak height measurements of back-scattered electron image intensities can give at least a qualitative indication of the mean atomic number of the elements composing the minerals. This feature (atomic number contrast, Newberry, 1975) is useful, for example, in determining whether a phase is metallic or an oxide, sulfide or sulfate, hydrated or anhydrous.

In the present study an ETEC Autoscan model U1 SEM was used. In general, the SEM was operated at an accelerating potential of 20-30 kV; a condenser current of $\leq$ 2.0 Å, and a working distance of about 10 mm. The SEM photomicrographs used in this report are of secondary electron images unless otherwise noted.

In conjunction with the SEM an EDAX model 707A multichannel analyzer was used. It had a lithium drifted silicon detector with a resolution of about 180 electron volts. In general, the elemental data obtained from 20-40 second count intervals were sufficient to characterize most particles (Figure 3). Identifications based primarily on major element data appear in quotation marks in this report. The mineral name used within the quotation marks is considered to be the most likely of the possible polymorphs. X-ray diffraction analyses of individual grains and fragments of coal containing mineral matter has confirmed that the mineral name given in quotes is indeed the dominant polymorph in the coal samples studied. Table 3 lists various polymorphs for the more common minerals appearing in quotation marks.

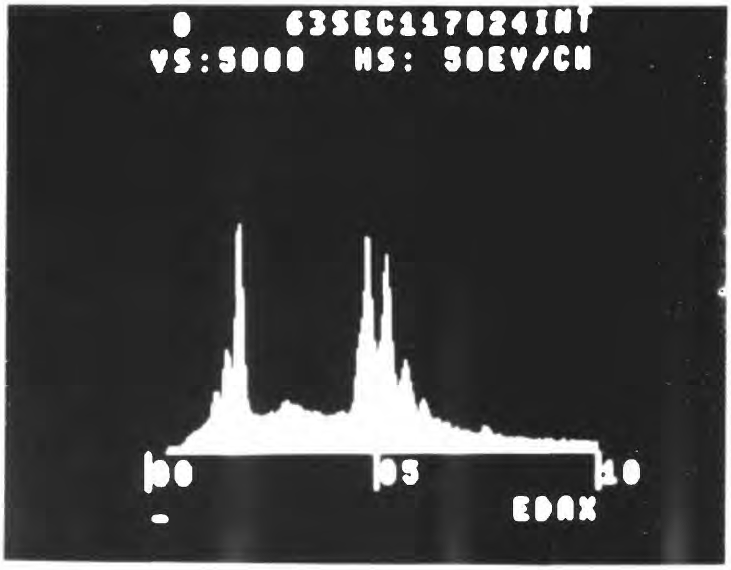

Figure 3. Energy-dispersive spectrum of "monazite" particle in Figure 4.

Figure 4. SEM photomicrograph of a bright "monazite" grain in a polished block of Waynesburg coal: Q = quartz, C = clay. Scale bars are in micrometers.

Table 3. Polymorphs of the More Common Minerals Found in Coal

Elemental Composition Major/minor/trace	Category	Possible Polymorphs
Fe, S//	"pyrite"	pyrite, marcasite, and perhaps melnikovite
Si//	"quartz"	Quartz, chalcedony, opal
Si, Al//	"kaolinite"	kaolinite, halloysite, dickite, allophane, nacrite
Si, Al/K/Fe, Ti	"illite"	illite, sericite, muscovite, mixed-layer clays, feldspars (?)
Ti//	"rutile"	rutile, anatase, brookite
Ca//	"calcite"	calcite, aragonite
Si, Al, K//or Si, Al, Ca/Na/	"feldspar"	potash feldspar, plagioclose, feldspar, clay (?)

1.211 Sample Preparation for SEM

A number of different sample preparation techniques were tested in the course of this study. Initial efforts were conducted on polished pellets prepared from -20 mesh coal particles. These 25 mm diameter mounts prepared by standard procedures (ASTM, 1977) are widely used for petrographic analyses of coal. They can be easily examined by various techniques (SEM, reflecting light optical microscopy, electron microprobe, ion microprobe). The major disadvantage is that the individual coal particles are small (<840μm) and therefore lack textural continuity. Also, in the SEM it is sometimes difficult to distinguish between the epoxy binder and the coal fragments. This point is discussed more fully by Moza et al. (1978). In addition, isolated mineral grains in the binding medium may be either particles released from the coal during grinding or contaminants.

Polished thin-sections on 25 mm diameter microscope slides are the most versatile method of sample preparation. These sections can be studied by transmission light microscopy in addition to the methods noted above. Thin-sections can be prepared from pellets or from oriented blocks of coal. Coal, however, requires thinner than normal thin sections (~10μm) to permit light transmission. These slides are difficult and time consuming to prepare, particularly without plucking mineral grains from the mount.

Oriented polished blocks (10-20 mm on edge) were found to be the most convenient sample form. Most of the SEM data in this report were generated from this type of sample. The oriented blocks are easy to prepare and provide most of the advantages of the thin sections. The relatively large size of the coal fragments allows for a more thorough examination of the mineral-maceral relationships. One drawback of the polished blocks is that they may not be as representative as the pellet mounts.

A limited attempt was made to study freshly fractured surfaces of coal. These samples are easily prepared and they allow observation of surface characteristics and three-dimensional features of minerals and macerals. Greer (1977), Hughes (1971), Augustyn et al. (1976), and Boateng and Phillips (1976) have all used this approach. The extreme relief of the fractured surfaces makes it difficult ot see fine details. Furthermore, the ability to identify macerals on fractured surfaces is severely limited, since the optical properties of the macerals, in reflected light, are the diagnostic characteristics.

Minerals extracted from the LT ash residues can also be prepared for the SEM in several ways. Individual hand-picked grains or bulk samples can be mounted on SEM stubs using a variety of fixatives, such as double-sticky tape, collodion, Duco cement, etc. A technique developed for study of the lunar soil (Finkelman, 1973) was found to be effective for the LT ash. The ash is sprinkled onto 25 mm diameter microscope slides, then covered with epoxy. After hardening, the mount is carefully ground until individual grains are exposed at the surface. The mount is then polished with successively finer polishing compounds until an adequate number of polished grains are available for analysis. This preparation has all the versatility of the polished thin-sections. In addition, individual grains can be removed from the mount for X-ray diffraction analyses.

1.22 Low-Temperature (LT) Ashing

Gluskoter (1965) revolutionized the study of minerals in coal by electronically ashing coal at temperatures less than 200°C. This procedure minimizes the alteration of minerals that may occur during the high temperature ashing processes. In the device used by Gluskoter, and in the low-temperature ashers used in this study, a stream of oxygen is passed through an electromagnetic field produced by a radio-frequency oscillator. A discharge takes place in the gas producing activated oxygen which Gluskoter (1965, p. 285) defines as "a mixture of atomic ionic species as well as electronically and vibrationally excited states." The activated oxygen is then passed over the ground coal, where it oxidizes the organic constituents without significantly heating the sample.

There are some relatively minor disadvantages associated with this procedure:

- It generally requires several days to completely ash a few grams of finely ground coal;
- Metallo-organic complexes;
- Artifacts such as calcium and sodium sulfates and perhaps iron sulfates and oxides can be created in the ashing process (Gluskoter, 1965).

All in all, though, for the study of minerals in coal, the advantages of the LT ashing technique far outweight the disadvantages.

1.23 X-ray Diffraction

X-ray diffraction analyses were conducted on several bulk LT ash samples and on polished pellets of coal using a conventional diffractometer. Individual particles from the LT ash and chips of mineral rich coal were analyzed by the powder method using 114.6 and 57.3 mm Debye-Scherrer powder cameras.

Special handling techniques had to be used for the very small particles. Manipulation of the individual grains was done under a binocular microscope with an electrolytically etched tungsten needle. Particles $\geq$ 20μm were placed in a droplet of a 1:1 collodion:amyl acetate solution on a clean microscope slide. A second slide was placed on top and pressure gently applied until the particle was crushed. The slides were then separated and the collodion:amyl acetate solution was allowed to dry. When dry, the film containing the powdered grain was scraped from the slide and formed into a rough ball. An X-ray spindle was then prepared from a fine glass fiber made by extruding a heated glass capillary tube. The fiber, only a few μms in diameter, was dipped into a drop of the collodion: amyl acetate solution and touched to the rough ball. By holding the collodion ball over a drop of amyl acetate, the ball was moistened by the fumes and formed a compact sphere containing randomly oriented grains. The sample was then mounted in a 57.3 mm camera and exposed to X-rays for up to 48 hours.

Individual grains smaller than 20μm were picked up directly on a collodion moistened fiber. The resultant spotty film can be read with the aid of a templet or a Gondolfi camera can be used to generate a line pattern.

1.24 Electron Microprobe (EMP) X-ray Analysis

Analytical data generated by the SEM-EDX system are generally semi-quantitative. The data are usually adequate for identification purposes, but for quantitative results and for the ability to detect trace constituents in coal minerals and macerals, an EMP is required.

Dutcher et al. (1964) were the first to use the EMP to study the distribution and composition of coal minerals and macerals. More recently, Raymond and Gooley (1978), Raymond (1979), and Minkin, Chao, et al. (1979) have applied the EMP to coal.

Two EMP units were utilized in this study, a Materials Analysis Corporation (MAC) microprobe with three wavelength spectrometers and an EDX unit, and a fully automated American Research Laboratory (ARL) microprobe with three wavelength spectrometers.

1.25 Transmission Electron Microscopy (TEM)

The principle application of the TEM in the study of coals has been its use in determining the size-frequency distribution of pores (see for example McCartney et al., 1966). Harris and coworkers (Harris et al., 1977; Lin et al., 1978; Strehlow et al., 1978) have recently applied the TEM to the study of sub-micron size minerals in coal. They have found numerous mineral grains down to the limit of detection (∿2nm) dispersed in various macerals.

In this study a 100 kV JEOL TEM was used. Portions of the LT ash were suspended in vials of distilled water. The suspensions were then pipetted onto formvar coated TEM grids and allowed to dry before viewing in the TEM.

1.26 Ion Microprobe (IMP)

The ion microprobe is a relatively new and powerful analytical instrument for detecting trace constituents in small samples. Colby (1975) notes that compared to the EMP, the IMP has (1) better detection sensitivities, typically less than 1 ppm (compared to 500-1000 for the EMP); (2) greater sensitivity to the light elements, such as B, C, O, even H; (3) ability to be used for isotopic analysis. Quantification of IMP data has not yet been perfected. Other minor drawbacks of the IMP are the broad beam size (>30 μm vs <1 μm for the EMP) and the destructive nature of the analysis.

Ribbe (1975) has used the IMP to determine trace and minor elements in coal minerals and macerals.

In this study an ARL IMP from the National Bureau of Standards in Gaithersburg, Maryland, was used for the analysis of both minerals and macerals.

1.27 "Lexan" Technique

Finkelman and Klemic (1976) described an extremely sensitive technique for detecting uranium bearing particles in a fine grained sample. This procedure, a variation of the "Lexan" technique of Fleischer et al. (1964), was applied to the LT ash of several coals.

The LT ash was dispersed in a 1:1 collodion:ethyl alcohol solution and spread on several 1- by 2-inch strips of 10-mil (0.01 inch) "Lexan." After irradiation in a flux of 10^{15} neutrons per square centimeter per second, the collodion film containing the sample was stripped from the "Lexan." The "Lexan" was then etched in a 7N sodium hydroxide solution at 70°C to make the fission-track damage more visible. The "Lexan" slides were then washed, dried, and the collodion film replaced. The film can be repositioned to within a few micrometers of its original position by utilizing scratches or pits in the "Lexan" that have been replicated in the collodion film or by other registration marks made in the collodion and "Lexan" before stripping. Once the collodion is properly repositioned, the particle from which the fission tracks were generated could be easily found, either by the similarity in shape of the particle and the area damaged by fission tracks (generally for grains greater than 20 micrometers in diameter) or by the proximity of tracks and the particle from which they were generated to the registration marks. This is done by measuring bearing and distance with a micrometer ocular. With this technique, individual micrometer size particles containing a few ppm uranium can be located.

1.28 Chemical Analysis

Analyses of whole coal, high temperature ash, and LT ash samples were obtained from the U.S. Geological Survey's Analytical Laboratories Branch. Unless otherwise noted, the analytical methods, limits of detection, accuracy, precision, etc., are detailed in Swanson and Huffman (1976).

1.3 Separation Techniques

The problem of relating trace element data to mineralogy would be a simple matter indeed, if clean, quantitative concentrates of the minerals could be extracted from the LT ash. Unfortunately, obtaining clean concentrates of clays, carbonates, phosphates, sulfides, feldspars, etc., is far easier said than done.

Most separation techniques are based on the physical properties of the minerals: optical and morphological characteristics for hand-picking; differences in magnetic susceptibility for magnetic separations; differences in density for separation by heavy liquids; or differences in grain size for sieving or settling techniques. All of these approaches were attempted on the Waynesburg LT ash, but clean, quantitative concentrations of the minerals could not be achieved.

1.31 Size Separations

A 200 mg sample of LT ash was dispersed in water with .01N Na_2CO_3 as a deflocculent. The suspension was ultrasonerated, then passed through a stack of 3-inch stainless steel sieves (mesh sizes 30, 60, 90 μm). Very little material was retained on the 60 and 90μm sieves. The few larger grains were predominantly particles of pyrite. Most of the material retained on the 30μm sieve consisted of clays clogging the fine pores.

It is apparent that the bulk of the minerals in coal are very fine-grained. Sarofin et al. (1977) found the median size of the minerals in two coals to be about 2μm. This fine-grain size is the major deterrent in obtaining good separations of the minerals. Obviously, hand picking would be of limited value with such fine-grained material. Nevertheless, mineral grains varying in size from a few μm to several hundred μm were extracted by hand from the LT ash for mineralogical characterization.

An attempt was made to separate the minerals in a 40 cm settling column. Despite the presence of the deflocculent, the LT ash coagulated and sank almost immediately.

The most successful separation was obtained by allowing a gentle stream of water from a small tube to flow into the bottom of a beaker containing the LT ash. The flow was carefully adjusted so that the current brought the visible mineral grains about 2/3 of the way up the beaker before they settled back towards the bottom. An excellent concentration of carbonate laths was achieved in this manner.

1.32 Magnetic Separations

Attempts to use a Franz Isodynamic Magnetic Separator were frustrated by the tendency of the LT ash to aggregate. A few moderately large (~100 μm) grains were separated from the bulk sample by this technique. These grains included ilmenite and pyrite. As pyrite is nonmagnetic, these iron sulfide particles must also contain pyrrhotite, a magnetic iron sulfide.

Strongly magnetic particles as small as a few μm could be observed by waving a hand magnet over a petrie dish containing the LT ash dispersed in alcohol. The rhythmic movement of the magnetic grains was quite obvious. These particles could then be removed from the dish with a capillary pipette. All the particles extracted in this way proved to be magnetite.

1.33 Heavy Liquid Separations

A number of attempts were made to separate the minerals by using heavy liquids. Generally, mixtures of NN-diiodomethane {Specific Gravity (Sp.G.) = 3.3} and NN-dimethylformamide (Sp. G.

= 0.947) were used. Several different centrifuge tube designs were tried. These included the tube-within-a-tube apparatus described by Woo (1964) and a 13 cm long Hutton type centrifuge tube (constricted waist). The latter proved to be the more practical. Centrifuge speeds and times were adjusted so that a 1 μm particle with a density of 3 should travel the full length of the tube in twenty minutes (see Allman and Lawrence, 1972, for details of the procedure).

Despite these attempts, separations by heavy liquids were only marginally successful. In an effort to obtain a quantitative separation of pyrite, the LT ash floating on the diiodomethane was vigorously ultrasonerated for several minutes. This was followed by centrifugation at 10,000 rpm for one hour. The procedure was repeated three times with substantial amounts of finer and finer pyrite grains sinking with each successive attempt.

Despite the problems, heavy liquid separation of coal minerals is an area that deserves further attention. It would, therefore, be worthwhile to document some of the difficulties encountered.

The small particle size of the LT ash is probably the most difficult problem to overcome. Muller (1967) states that the limiting size for separation of particles 10 μm. However, Allman and Lawrence discuss procedures for concentrating particles less than 1 μm in diameter. These procedures generally require high centrifugation speeds (>10,000 rpm), long centrifugation times (hours to days), and differences in density between the grains and the heavy liquids of only 0.01. They also note that these techniques are most efficient if all the particles in the sample are the same size. In the LT ash grain sizes for quartz, pyrite, clays, etc., range from less than 1 µm to greater than 100 µm.

Flocculation of clays is a major problem, since the ash of most coals consists predominantly of clays and clay-sized minerals. In aqueous solutions the problem can be overcome by use of one of several deflocculating agents such as sodium carbonate or a metaphosphate, which neutralizes the surface charge on the clay grains. Unfortunately, these chemicals are immiscible in organic heavy liquids. Francis et al. (1972) recommend the use of a nonionic vinylpolymer (PVP K-30, polyvinylpyrrolidone) dissolved in 200-proof ethanol as a deflocculating agent in organic liquids. This compound was tried, but it left an unacceptable waxy residue that obscured the sample.

A more promising approach to reducing the caking problem caused by flocculation was suggested by Henley (1977). He recommended creating a density gradient column spanning the specific gravity range of the light minerals, this gradient to be created above the heavy liquid used for separating the high Sp. G. minerals. This procedure did indeed spread the light minerals throughout a finite volume of heavy liquid, allowing more efficient separation of the heavy minerals.

The ideal separation system should result in multiple discrete bands of homogeneous minerals concentrated in a density gradient. This may not be possible because most accessory minerals in coal, such as the carbonates, micas, spinels, pyroxenes, etc., are members of isomorphous series that exhibit wide ranges in density. Moreover, the density of some of these minerals overlap with that of the clays.

It would appear that Nelson (1953) may have been prophetic in his remark that the detection and estimation of the accessory minerals in coal is never likely to become a straightforward or routine matter.

A word of caution is in order: the small size of the accessory minerals in coal requires extra precautions to avoid contamination. All solvents should be passed through filters with submicron pore sizes. This is particularly important for the diiodomethane. Copper wire is generally used to inhibit oxidation of this liquid; the wire apparently reacts with the solution to form a myriad of minute copper iodide crystals.

2. RESULTS

2.1 Minerals in Coal

2.11 Introduction

Gluskoter (1975) noted that the term "mineral matter in coal" has often been liberally interpreted so as to include all inorganic non-coal material found in coal. This broad usage thus combined in a single category mineral matter in the true sense and all elements classically considered inorganic, although they may be organically bound in the coal. In this report the term "inorganic constituents" will be used for all elements, regardless of their mode of occurrence in the coal, except for carbon, oxygen, nitrogen, hydrogen, and organic sulfur. The terms "mineral matter" and "minerals" will be used in the strict mineralogical sense, i.e. any naturally occurring homogeneous solid, inorganically formed, with a definite chemical composition and an ordered atomic arrangement (Berry and Mason, 1959).

The literature on coal minerals is voluminous. Watt (1968) has cited over 450 references in his comprehensive survey of literature on the origin, identity, and distribution of minerals in British coals. Akers et al. (1978) recently compiled a bibliography of coal minerals. Their survey, although restricted to articles dealing only with North American coals, yielded 439 references.

The majority of these publications deals with the major mineral species in coal, while relatively few were concerned with the accessory minerals.

The studies of Ball (1935) and of Sprunk and O'Donnell (1942) are unsurpassed in their comprehensive treatment of minerals in coal and deserve special attention.

Ball (1935) separated minerals from the Illinois No. 6 coal bed by crushing to three size fractions (48 X 100 mesh, 100 X 200 mesh, and 200 mesh X 0). After rinsing each fraction in HCl, he separated each split in a 1.70 Sp. G. liquid. The sink fractions were further separated in 2.85 Sp. G. liquid. The resultant mineral concentrates were studied petrographically. Only one page of his 106-page report was devoted to the accessory minerals. This page consisted primarily of a table documenting the occurrence of the accessory minerals in the various splits.

In contrast to Ball, Sprunk and O'Donnell (1942) petrographically examined over 3,000 thin sections from about 100 coals. They presented a detailed and well illustrated account of the modes of occurrence of the major mineral species but devoted only a few brief comments to the accessory minerals.

The absence of systematic studies of the accessory minerals in coal has been noted by Mackowsky (1975), Miller (1978), and Falcon (1978). Falcon (1978, p. 33) states that the "Systematic studies of heavy mineral associations in coal have not been made although they should give detailed insight into source rocks, and they are necessary for the understanding for the behavior of coal in certain technological processes such as gasification."

Why has this important phase of coal research been neglected?

In part, the neglect is related to the difficulty of analyzing these exceedingly fine-grained and widely dispersed phases. But equally to blame for this neglect is the common misconception that the accessory minerals occur in amounts too small to be of much practical importance. Ball (1935, p. 22) states that "the non-clay detrital minerals, although always present, are quantitatively of little importance." This sentiment was echoed by Watt (1968. p. 47) who also cited quartz (p. 62) as the only accessory mineral found in amounts large enough to have a significant influence on the utilization of a coal.

We will see that the results from this present study indicate that the accessory minerals may indeed be inconspicuous, but they are certainly not insignificant.

2.12 Variety of Accessory Minerals in Coal

Over 125 minerals have reportedly been found in coal. Appendix II is a comprehensive but undoubtedly incomplete list of these minerals. The frequency of occurrence of the accessory minerals varies from minerals, such as quartz, that are mentioned in virtually every report on the subject, to minerals that have been reported from only a single source.

The study of the Illinois No. 6 coal by Ball (1935) represents the only detailed investigation of the variety of accessory minerals in a single coal. It would therefore be desirable to obtain such information on other coal samples using modern mineralogical techniques.

2.121 Accessory Minerals in the Waynesburg Coal

Samples of the Waynesburg coal collected from two mines in Mongolia County, West Virginia, were studied to determine the variety of accessory minerals that may be found in a single coal.

2.1211 Results from SEM Study of Polished Blocks: Table 4 lists the accessory phases found in the Waynesburg Coal by SEM examination of eight polished blocks. Most of the minerals were discerned because of their relatively high reflectivity in the SEM (Figure 4). The list is, therefore, biased towards those minerals containing relatively heavy elements and those minerals that are not hydrated.

One of the most unusual accessory phases consisted of small (1-5 μm) iron-chromium-rich particles that almost invariably formed thin rims on quartz grains in two polished blocks. Figure 5 shows four such grains in one field of view. Counting times of several minutes at 30 kV accelerating potential did not reveal the presence of any other elements heavier than sodium. The mean atomic number of this mineral was determined to be approximately 20. Chemistry of the grains and the mean atomic number are consistent with the conclusion that these particles are iron-rich chromites.

A curious feature of the Fe-Cr rims is that they are concentrated about a hairline fracture parallel to the bedding in the coal and always adhere to the sides of the quartz grains facing the fracture (in Figure 5, the fracture is to the right). One possible explanation for this feature is that iron- and chromium-bearing

Figure 5. SEM photomicrograph of the Waynesburg coal, showing four "chromite grains (bright) adhering to "quartz" particles.

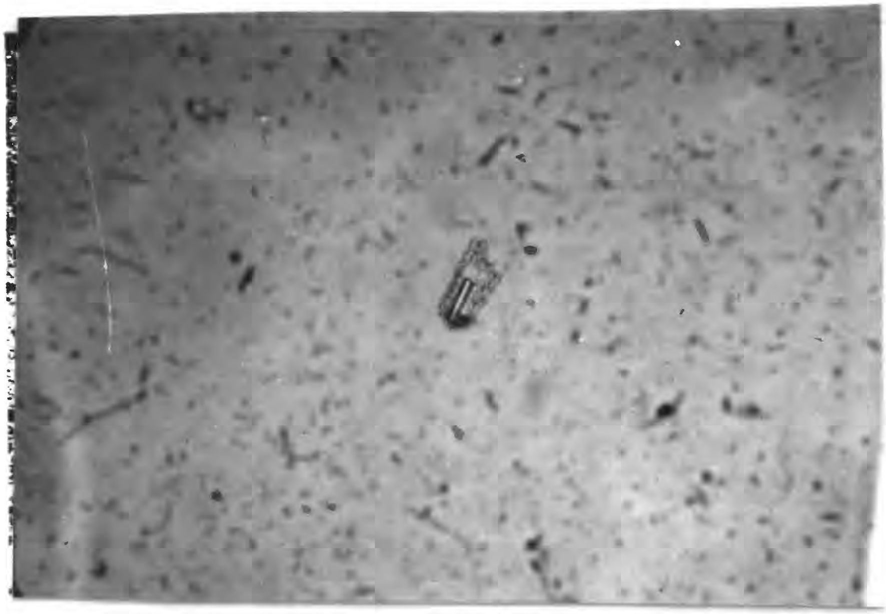

Figure 6. Optical photomicrograph of a 7 µm long tourmaline crystal extracted from the LT ash of the Waynesburg coal.

fluids diffused out from the fracture and concentrated along impermeable barriers. In what may be an analogous situation on another polished block, 1-3 µm wide rims of a nickel silicate were found on dozens of quartz grains in a single band of detrital material.

Table 4. Accessory Phases in the Waynesburg Coal Determined by SEM-EDX Study of Polished Blocks

(Major constituents are to the left of the slashes, minor are between, trace constituents to the right. Re = rare-earth elements. Quotation marks indicate identification based primarily on major element data.)

"Allanite" (Si, Re//)
"Apatite" (Ca, P//)
"Barite" (Ba, S//)
"Chalcopyrite" (Fe, Cu, S//)
"Clausthalite" (Pb, Se//)
"Epidote" ? (Si, Al, Pb, Ca//)
"Feldspar" (Se, Al, K or Ca//Ba, Na)
"Gold"
Goyazite (Sr, Al, P//Ca, Re, Fe)
"Ilmenite" (Fe, Ti//)
"Monazite" (Ce, P//Th)
"Rutile" (Ti//)
"Sphalerite" (Zn, S//)
"Sphene" (Ca, Ti, Si//)
"Xenotime" (Y, P//)
"Zircon" (Zr, Si//)
________ Ca-silicates
________ Cu//
________ Fe//
________ Fe, Cr// (Chromite?)
________ Fe, Mg-silicates
________ Na, S/Cl, K, Mg/
________ Ni, Si//
________ P, Si, Al/Re/
________ Si, Al/Fe/
________ Sr, Ba, Al, Si/K/
________ Sn, Si, Al/Mo, Fe/
________ W, Pb//

2.1212 Results from LT ash Residues: Splits of the Waynesburg coal were ground to -120 mesh and ashed in an LT ashing unit. The resultant ash was separated into several density fractions by use of heavy liquids. Individual grains were selected for analysis from the bulk residue and from the heavy liquid concentrates.

Although clays and quartz predominate in the light fraction (Sp. G. <3.3), a cursory optical scan indicated the presence of numerous small ($\sim 5\mu m$) crystals of tourmaline (Figure 6). Identification of the grains was confirmed by X-ray powder patterns, optical characteristics, and energy-dispersive analysis. Several interesting grains were observed in a dense (Sp. G. >3.3) fraction of the ash, which was further separated on the basis of its magnetic properties. Figure 7 shows a nearly perfect octahedron of magnetite; identification was confirmed by an X-ray powder pattern. It is hard to conceive of a large ($\sim 70\mu m$) euhedral crystal such as this as being anything but authigenic in origin. In the same heavy magnetic fraction, we also noted a lustrous, black sphere (Figure 8). Energy-dispersive analysis indicated that it consisted essentially of iron with a trace of nickel. An X-ray powder pattern of magnetite was obtained from this $5\mu m$ particle. The surface morphology, chemistry, and mineralogy are all consistent with identification of the particle as a meteorite ablation product (Finkelman, 1972).

The most interesting minerals in the heavy, nonmagnetic fraction of the Waynesburg LT ash were large olive green particles (Figure 9). About a dozen of these grains, ranging from 50 to 200 μm in length, were observed. An X-ray powder pattern obtained from one of these

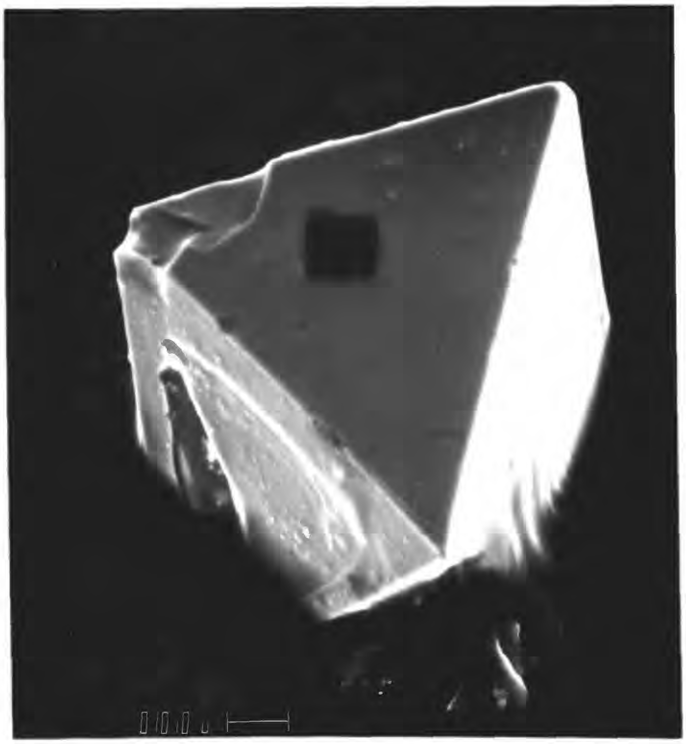

Figure 7. SEM photomicrograph of a euhedral octahedron of magnetite extracted from the heavy (Sp. G. >3.33) magnetic split of the Waynesburg low-temperature ash. The dark patch on the surface was caused by the stationary electron beam during energy-dispersive analysis.

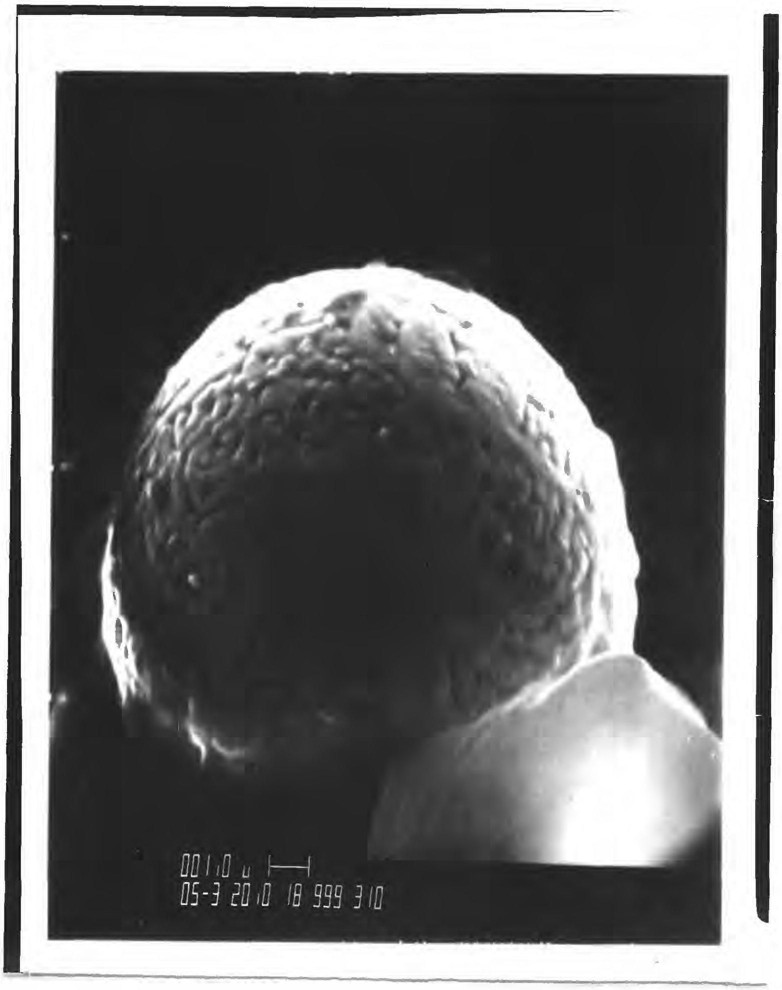

Figure 8. SEM photomicrograph of a probable meteorite ablation sphere found in the heavy (Sp. G. >3.33) magnetic split of the Waynesburg LT ash.

Figure 9. A SEM photomicrograph of a large subhedral crystal of amphibole from the heavy (Sp. G. >3.33) portion of the low-temperature ash from the Waynesburg coal.

Table 5. Accessory Phases in the Low-Temperature Ash of the Waynesburg Coal

Accessory Phase	Comments
Amphibole	See text
Biotite	
Bloedite	$Na_2Mg(SO_4)_2 4H_2O$ associated with sylvite
Calcite	Some have detectable Mg and Fe
Calcium Sulfate (?)	Probably gypsum created during ashing process
Chlorite	
Diopside	
Hypersthene	
Ilmenite	
Iron Oxides	Amorphous to X-rays (?)
Magnetite	Authigenic, detrital, and extra-terrestrial
Marcasite	Framboid, irregular
Microcline	
Plagioclase	
"Pyrrhotite"	Magnetic iron sulfide
Rutile	
Siderite	Some have detectable Mn
Staurolite	
Sylvite	KCl, associated with bloedite
Talc	
Thenardite	Probably created in ashing process
Tourmaline	Most less than 10μm in length
Zircon	
Sn/Fe, Cu, S/	Amorphous to X-rays (?)

green particles was virtually identical with that of magnesioarfvedsonite, described by Milton et al., 1974, from the Green River Formation as the only known low-temperature authigenic amphibole. The large size of these green amphiboles (for comparison, the largest detrital quartz grain observed was about 100μm), their subhedral forms, and the analogy to the magnesioarfvedsonite of the Green River Formation suggest that this amphibole from the Waynesburg coal may be authigenic. However, quantitative microprobe analysis of the LTA-derived minerals indicates a composition more consistent with that of hornblende $\{(Ca,Na,K)_{2\cdot5}(Mg, Fe, Ti, Al)_{5\cdot5}Si_6(Si,Al)_2O_{22}(OH,F)_2\}$, a not uncommon detrital mineral. Though the question of an authigenic or a detrital origin for the Waynesburg amphibole remains unanswered, the presence of fluorine in this mineral raises questions about the distribution of fluorine in the Waynesburg coal.

It has generally been assumed that, in coals, fluorine is associated with apatite (Francis, 1961). In the Waynesburg coal, however, far more fluorine may be associated with this amphibole ($\sim$0.2 weight percent F) than with the rare apatite, of which only three minute grains (<5μm) were observed (see discussion of F in Section 3.22).

Table 5 lists the accessory phases found in the LT ash residues of the Waynesburg coal. Virtually all the minerals in this table were identified by X-ray diffraction patterns.

2.122 Comparison of Waynesburg Coal Data to Data from Other Coals

Accessory mineral data for the Upper Freeport coal and for the

Pittsburgh No. 8 coal appear in Tables 6 and 7, respectively. The study of the Upper Freeport coal was somewhat less intense than that of the Waynesburg coal, and the study of the Pittsburgh No. 8 coal less intense than that of the Upper Freeport. It would appear that the number of accessory phases detected in a coal sample is proportional to the time devoted to the search. This may be true only for coals with similar geochemical histories. Certain coals, generally those with little detrital influx (see Section 3.1), have very simple mineralogies, often containing less than 5 or 6 different minerals.

It is also evident that, when making comparisons, the data should have been obtained by the same analytical procedure. For example, the following accessory minerals were observed in a detailed scan of two polished blocks of the Illinois No. 6 coal: barite; chlorite; quartz; rare-earth phosphates and silicates (?); rutile; sphalerite; and zircon. Of these eight minerals, only chlorite, quartz, rutile and zircon were reported by Ball (1935). Thus, only 4 of the 15 accessory minerals noted by Ball were observed in the present study, while 4 accessory minerals not found by Ball were detected here.

The disparity in the data may in part be due to inhomogeneity in the distribution of the accessory minerals. More likely, the disparity is due to the differences in analytical technique. Most of the minerals observed by Ball but not detected in the present study have relatively low mean atomic numbers (less than or similar to quartz and the clays) and nondistinctive chemical compositions which would account for their not being readily detected in the SEM. As a matter of fact, nine of these minerals (biotite, garnet, horn-

Table 6. Accessory Phases in the Upper Freeport Coal
As Determined by the SEM-EDX Study of Polished Blocks and LT Ash

(Quotation marks indicate identifications based primarily on major element data. Other phases identified by X-ray diffraction patterns or optical characteristics.)

- "ankerite"
- apatite
- "argentite"
- "barite"
- calcite
- chalcopyrite
- "clausthalite"
- chlorite
- crandallite
- diaspore
- feldspar (potash)
- "galena"
- magnetite
- elemental gold
- halite
- ilmenite
- monazite
- neodymium monazite
- olivine
- opal
- pyrrhotite
- quartz
- rutile("anatase")
- siderite
- sphalerite
- manganese silicate
- calcium sulphate
- xenotime
- zircon

Table 7. Accessory Phases in the Pittsburgh Coal
As Determined by SEM-EDX Study of Polished Blocks

- "barite"
- "calcite"
- calcium & iron-magnesium silicates
- calcium sulfate
- "chalcopyrite"
- "chlorite"
- "chromite"
- "goyazite" ?
- "ilmenite"
- "monazite"
- nickel silicate (?)
- potash feldspar
- quartz
- "rutile-anatase"
- "siderite"
- "sphalerite"
- "xenotime"
- "zircon"

blende, muscovite, staurolite, topaz, and tourmaline) have not been observed by the SEM in any of the coals examined in this study.* Furthermore, those minerals detected in this study but not by Ball -- barite, rare-earth phosphates and silicates, and sphalerite -- all have relatively high mean atomic numbers and distinctive chemical compositions.

2.13 Frequency of Occurrence of Accessory Minerals

The large number of coals examined (-80) made it possible to estimate the frequency of occurrence of many accessory minerals (Table 8). These data are based primarily on SEM-EDX analyses of polished blocks, thus suffering the usual bias towards those minerals containing the heavier elements. The values in Table 8 represent the percentage of coal samples in which the tentative identification of that mineral was made. The values do not reflect the abundance of the minerals, an aspect that will be discussed below. Furthermore, the values must be considered as minima, since the minute accessory minerals may easily be overlooked or may not have been present on the surface examined.

With these limitations in mind, the high frequency of occurrence of some of the minerals is indeed impressive. Quartz, not surprisingly, has the highest frequency of occurrence, having been detected in most of the coal samples studied. The observation that monazite occurs in about 50 percent of the coals is especially surprising, since it

---

* A lead-bearing epidote was tentatively identified in the Waynesburg coal.

was not reported from coal until 1976 (Finkelman et al., 1976). Aside from several papers by Finkelman and coworkers, only Lee et al. (1978) have reported this apparently commonly occurring coal mineral. In view of the lack of previously reported occurrences, the following minerals have surprisingly high frequencies: xenotime, crandallite group, and some of the accessory sulfides (these will be discussed in detail below).

Table 8. Frequency of Occurrence Of Accessory Minerals in Coal

(Primarily from SEM-EDX analyses of polished blocks)

Frequency in 79 Coals	Mineral
>50%	quartz
∿50%	monazite
∿33%	rutile-anatase barite siderite zircon chalcopyrite sphalerite
∿25%	calcite xenotime galena clausthalite
∿10%	feldspar apatite diaspore crandallite group barytocalcite-witherite iron-calcium-magnesium silicates strontionite linnaeite group magnetite & other iron oxides chlorite

2.131 Minerals Not Previously Reported in Coal

The detailed approach and sophisticated analytical equipment has allowed the detection of several minerals not previously reported in coal.

Predominant in this category are the rare-earth minerals monazite and xenotime. Several rare-earth silicates have also been observed. From an environmental point of view, the most significant mineral found is the lead selenide, which will be discussed in detail in Section 2.18.

Other minerals that were observed in coal for the first time include diopside, hypersthene, magnesioarfvedsonite(?), olivine (fayalite), chromite(?), bloedite, strontionite, bismuthinite(?), native gold, copper sulfide, and tin oxide and sulfide.

2.14 Comparison of Accessory Minerals by Coal Rank, Age, and Type

At this point there is insufficient data to provide significant comparisons of the accessory minerals in coals of different rank, age, or type. Variations within the subdivisions of these categories appear to be as great as the variations between the subdivisions. There is, therefore, little basis to determine whether these mineralogical differences are characteristic of the subdivisions or are due to differences in mineral source or geochemical environment. Therefore, only a few general comments will be offered on each category.

2.141 Comparison by Rank

Although the data in Table 8 contain information from all the samples studied for this report, they are dominated by the bituminous coals and may serve as a standard for comparison to data from other ranks.

Six anthracites and a meta-anthracite were analyzed. It is interesting to note that five of these samples had "siderite," one contained "witherite," and only one problematical grain (high iron) of "calcite" was detected. Linnaeite group minerals were found in three of these samples and in only two of the remaining 70-plus samples. Perhaps these minerals may be characteristic of high rank coals.

Seven sub-bituminous coals were examined. No distinguishing mineralogical characteristics were noted.

Four lignites were studied. All four contained barite. Two of these samples contained PbSe grains. This is unusual in that this mineral appears to be exceedingly rare outside the Appalachian Region.

Two peat samples were examined. The peat from Ohio had a mineral assemblage similar to that of most coals (clays, "pyrite," "apatite," "zircon," "K-feldspar," "pyroxene," and a Pb-bearing "crandallite"). The mineral assemblage of the Florida peat was much more restricted, being dominated by carbonates, silica, and iron sulfides.

The clear difference in the mineral asemblages of these peats undoubtedly reflects the differences in source area.

2.142 Comparison by Age

The geologic age of the samples studied ranged from Devonian to Holocene, the vast majority of samples coming from Carboniferous (Pennsylvanian) deposits. Permian, Cretaceous, and Tertiary coals were well represented. No relationships between mineralogy and geologic age were recognized.

2.143 Comparison by Coal Type

Three sapropelic coals were studied (the rest being humic coals). Two of these were classified as cannel coals, the third as a boghead coal. Too few data are available to draw any conclusions, although in one sample some of the minerals may have been derived from volcanic ash fallout (see Section 3.12).

2.15 Comparison of Accessory Minerals by Geographic Region

A brief SEM scan of one small sample from a single coal or even a few coals cannot possibly be representative of an entire geographic region. A large number of samples from a single area may begin to reveal certain mineralogical characteristics of the area. Unfortunately, with the possible exception of the Appalachian Coal Province, there is, as yet, insufficient data to provide this insight. Nevertheless, in contrasting the frequency of occurrence of minerals within Appalachian Province coals to the minerals in coals outside this

Province, certain differences have emerged. In Appalachian Province coals, lead selenides appear to be far more common, and lead sulfides less common than in coals from outside this Province (Table 9). Apatite and perhaps barite appear to be more common outside the Appalachian Province.

These differences may be due to differences in the source of the minerals (for example, volcanic ash falls are unknown in the Appalachian Province but are important in Western coals), or they may be due to differences in the geochemical environments during coal formation.

No significant differences were discerned between U.S. coals and foreign coals.

According to Chandra and Taylor (1975), there is a broad similarity between minerals in Gondwana coals and the European Carboniferous coals. However, they note that there are marked differences in the total mineral content and in the proportion of particular classes of minerals. Seven Gondwana coals were studied for this report. Other than an apparent high frequency of occurrence of siderite, these coals had no distinguishing mineralogical characteristics.

2.16 Variation of Accessory Minerals Within a Coal Column

It takes little more than a cursory glance at a slab of coal to recognize its inhomogeneity. Bright and dull bands of varying thinkness alternate at irregular intervals, even on the microscopic level. However, there have been few attempts to study the vertical variation of accessory minerals within a bench or a column of coal.

Finkelman and Stanton (1979) conducted a detailed study of a 127 cm long column of the Upper Freeport coal bed. They showed that sphalerite was uniformly distributed throughout the entire column. Chalcopyrite was found only in the lower 3/5 of the column, whereas lead selenides were found to be restricted to a 10 cm thick shaly interval about 40 cm from the base of the column.

2.17 Concentration of Accessory Minerals in Coal

2.171 Introduction

The concentration of individual minerals in coal can vary widely among samples. Rao and Gluskoter (1973) noted the range of quartz concentrations in the ash of Illinois coals to be 2-28 percent, and that of calcite as 0-23 percent. Even larger variations are known. For example, O'Gorman (1971) reported a coal from Colorado to contain 20-30 percent plagioclase in the ash. This coal was the only one of 57 coal samples in which plagioclase was above the limit of detection. In the present study, barite, a trace constituent in many coals, was the major phase in the Beulah lignite.

There have been no attempts specifically to determine the abundances of accessory minerals in coal. Perhaps O'Gorman (1971) and O'Gorman and Walker (1975) came closest to achieving this in their analyses of the LT ash from 57 coal samples by X-ray diffraction. Semiquantitative mineral analyses were reported for kaolinite, illite, muscovite, chlorite, montmorillonite, mixed-layer clays, calcite, aragonite, dolomite, ankerite, siderite, quartz, gypsum, pyrite, jarosite, hematite, rutile, thenardite, and plagioclase. Many of the accessory phases were below the limits of detection in most samples. This points up a limitation in the use of X-ray diffraction for quantifying mineral concentrations. X-ray diffraction may be an acceptable technique for semiquantitative determination of minerals present in concentrations >5 weight percent. However, it is not sensitive to concentrations below this value and may not even detect minerals present in concentrations below one percent.

2.172 Relative Abundance of Accessory Minerals

Although some of the minerals considered here as accessory phases can indeed be locally abundant (especially quartz and calcite), most are generally present in concentrations far below one weight percent of the ash. The relative concentrations of the minerals, including the accessory minerals, from three horizons of the Pittsburgh coal were determined in this study by analyzing 250-500 randomly selected mineral grains from each sample. The results presented below indicate that the total accessory minerals (other than quartz) constitute less than one percent of the minerals (values are in percent of total):

Sample	"Pyrite"	"Illite"	"Kaolinite"	"Quartz"	Accessory	No. of Grains
PAS 44	60	14	16	10	0.6	500
PAS 45	30	7	51	11	1.2	250
PAS 46	33	26	16.5	24	0.8	250
					(avg. 0.8)	

A similar effort was made to determine the relative concentrations of the minerals in a carbominerite band (lithotype sample) of the Waynesburg coal. Two blocks, representing sections of the band about 30 feet apart, were analyzed. The results were as follows (values are in percent of total):

Sample	"Pyrite"	"Illite"	"Kaolinite"	"Quartz"	Accessories	Total No. of Grains
Waynesburg I*	13.5	30	7	45	4.5	377
Waynesburg II	5	20	15	45	6	150

As the data for the Pittsburgh coal are essentially on a whole coal basis, while the Waynesburg data are derived from a single carbominerite band, these data sets are not directly comparable. Nevertheless, certain differences are apparent.

The relative concentration of the accessory minerals in the two Waynesburg blocks are similar, although both are somewhat higher than the value obtained for the accessory minerals in the Pittsburgh coal. The significantly higher quartz and illite content of the Waynesburg lithotype is indicative of a higher influx of detritus. We shall see (Section 3.1) that many of the accessory minerals appear to have a detrital origin. Thus the higher proportion of detritus in the Waynesburg microlithotype would account for part of the difference in the proportion of the accessory phases. Furthermore, the minerals found in the extensive areas of vitrinite in these samples consist largely

---

* These data were obtained after the back-scattered electron detector was installed on the SEM. The apparent higher proportion of pyrite may be due to its greatly enhanced brightness in this mode.

of kaolinite and pyrite. If the Waynesburg data were to be calculated on a whole coal basis, these minerals would tend to dilute the proportion of the accessory phases further.

2.173 Quantification of Accessory Phases and Their Relationship to Trace Elements

In Section 2.1212, it was suggested that the fluorine in the Waynesburg coal may be associated with the fluorine-bearing amphibole observed in the LT ash. Finkelman and Stanton (1978) suggested that a significant percentage of the chromium in the Waynesburg coal is in the iron-chromium particles and that the rare-earth elements appear to be accounted for in the relatively large proportion of rare-earth bearing minerals. It seemed clear that more than a casual relation exists between the accessory minerals and certain trace elements in coal.

One way to test this observation is to compare the analytical values of the trace elements to their concentrations calculated from the abundance of the accessory minerals in which the elements occur.

In Section 1.21 it was indicated that in the back-scattered electron mode the SEM is able to discriminate between the "lighter" minerals such as clays and quartz, and the accessory minerals containing the heavy elements. Using this capability of the SEM, an attempt was made to determine the relative concentrations of the accessory minerals in the Waynesburg coal.

Several estimates and assumptions had to be made in order to relate the occurrences of accessory minerals in the coal to the trace element data. These are:

1. The polished blocks examined in the SEM are representative of the chemically analyzed ash. A mineral rich zone (carbominerite) 0-6 in. below a prominent parting in the Waynesburg coal was selected for this study. Three polished blocks were prepared, and portions of the sample were ashed in a LT asher; the resultant ash was analyzed by optical emission spectrographic (OES) and instrumental neutron activation analysis (INA).

2. The mineral matter in the polished blocks covers one third of the surface area of the carbominerite. Most of the accessory minerals in the Waynesburg coal are in concentrated bands of mineral matter referred to as carbominerite. These bands may contain as much as 75 percent of the total mineral matter and 90 percent of the accessory minerals. The search for accessory minerals was confined to these bands of carbominerite. At 500X the area in a field of view is approximately 30,000 μm^2. It was estimated that the mineral matter occupies about one third of this area, or 10,000 μm^2.

3. The mean diameter for the accessory minerals is 5 μm. This value was established by measuring the diameters of 20-30 accessory minerals and estimating the diameters of the remaining accessory grains. Although sub-micrometer sized particles could be resolved with the SEM-EDX system, a minimum diameter of 2 μm was imposed. This greatly expedited the survey without sacrificing accuracy (it would require 125 1-μm particles to have the elemental concentration equivalent to one 5-μm grain).

4. Each accessory grain represents about 2500 ppm of the total mineral matter in each field of view. From items 2 and 3 it can be determined that each 5-um accessory mineral grain represents 0.0025 percent (2500 ppm) of the mineral matter per unit area. When we assume that the relative proportions of these phases are similar in the third dimension, each accessory grain would represent 2500 ppm of the mineral matter volume. In order to convert these data into weight percentages, the relative densities of the accessory minerals and the major mineral phases (clays, quartz, pyrite) have to be considered. The accessory minerals are clearly denser than the clays and quartz (about 30 to 50 percent) but many are less dense than pyrite, which accounts for about 20 weight percent of the mineral matter. Perhaps an increase of 20 to 30 percent is justifiable in converting the volume percent to weight percent for the accessory minerals. However, the carbominerite bands probably represent 70 to 80 percent of the mineral matter in the sample, the rest of the mineral matter being virtually free of accessory minerals.

These two factors tend to cancel each other, and it is assumed that each 5-μm accessory mineral represents about 2500 ppm of the weight of the mineral matter per unit area.

In view of the inherent errors involved in the preceding assumptions and estimates, the calculated elemental concentrations should be considered as semiquantitative. The calculated value for each element is derived by the following formula:

$$C = \frac{N \cdot We \cdot Wm}{A}$$

C = calculated weight concentration for the element in ppm

N = total number of the primary accessory mineral grains observed

We = weight percent of the element in the accessory mineral

Wm = weight percent of the total mineral matter per unit area represented by each accessory mineral grain (= 2500 ppm)

A = total number of areas scanned (= 200)

The results of the survey appear in Table 9. Until further similar studies are made, the conclusions drawn from these data pertain only to the specific sample studied. Data for the rare earth elements (REE), chromium, yttrium, zirconium, zinc, and nickel show an excellent agreement between the analytical values and the values calculated from the abundance of the accessory minerals noted in Table 9. This agreement suggests that, in the Waynesburg coal, these elements are predominantly bound in the specific mineral phases indicated in Table 9.

About one third of the titanium can be accounted for as titanium dioxide (major titanium the only element detected). Some titanium is bound in the clays (estimated from energy dispersive X-ray analysis to be 500-1000 ppm) as well as other accessory minerals (sphene, ilmenite, pyroxene). However, even when we take these estimates into account, a large discrepancy remains between the analytical and calculated values for titanium. There are several possible explanations for this discrepancy. When semiquantitative OES analysis is used, the potential error is as much as 50 percent of the amount reported. However, the value for titanium reported here (3400 ppm) is lower than the values reported by Swanson et al. (1976) for Waynesburg coal samples. Some of the titanium may be bound in micrometer-size grains which could have been overlooked; to compensate totally for the difference would require almost 100 unobserved TiO_2 grains per field of view. This seems unlikely.

Table 9. Comparison of Calculated and Analytical Concentrations

For Selected Trace Elements in the Waynesburg Coal

Element	Primary Accessory Mineral	No. of Grains (N)	Proportion of element in the mineral (We)	Calculated Value (C)	Analytical Value*	
Ti	"rutile"	139	0.6	1000 ppm	3400 ppm	OES
REE	various	31	∿0.6	230	∿200	INA
Cr	Fe-Cr oxide	18	∿0.4	90	80	INA
Zr	zircon	20	0.5	120	110	OES
Zn	"sphalerite"	8	0.75	70	70	INA
Cu	"chalcopyrite"	8	0.33	30	47	OES
Ni	Ni-silicate	5	∿0.5	30	26	OES
Pb	various	3	∿0.5	20	31	OES
Ba	feldspars	6	variable	∿100	600	INA
Sr	"strontionite"	2	0.7	10	240	OES
Y	"xenotime"	4	0.5	20	18	OES

* OES = optical emission spectrography; INA = instrumental neutron activation.

Another explanation is that titanium may be organically bound, which would be in agreement with the suggestions of Horton and Aubrey (1950), Zubovic et al. (1960), and Brown and Swaine (1964). A similar discrepancy exists for barium and strontium; both are relatively heavy elements and easily detected in the SEM. There are, however, major differences between their analytical and calculated values (Table 9). Both barium and strontium have low ionic potential, and thus, in contrast to titanium, both have low organic affinity (Zubovic, 1976). Finkelman (1978) speculated that these elements are perhaps present in trace amounts (as much as 0.5 percent) in carbonates, feldspars, and clays. Or they may be bound in hydrated phases with low mean atomic numbers that would not easily be detected by the SEM in polished blocks of coal. Subsequent study has revealed the presence of barite ($BaSO_4$) in many coal samples, although generally not in the carbominerite (see Section 2.23). Barytocalcite(?) ($BaCa(CO_3)_2$), witherite ($BaCO_3$), strontionite ($SrCO_3$) and celestite ($SrSO_4$) have been observed in the vitrinite of various coals. Authigenic minerals of the crandallite group (Ca, Ba, Sr) Al_3 $(PO_4)_2$ $(OH)_5 \cdot H_2O$, including gorceixite and goyazite, the barium and strontium end members, respectively, have been found in a number of samples. Thus the discrepancy in Table 9 between the analytical values and the calculated values of barium and strontium probably reflects the fact that most of the Ba and Sr minerals do not occur in the carbominerite but rather they are authigenic phases in other macerals (see discussion of Ba in Section 3.22).

2.18 Mode of Occurrence of Accessory Sulfide and Selenide Minerals

2.181 Introduction

The accessory sulfides (those other than pyrite and marcasite) are among the more important inorganic phases in coal because they contain many elements of environmental and economic interest, such as arsenic, bismuth, cadmium, copper, lead, mercury, molybdenum, selenium, silver, tin, and zinc.

Accessory sulfides are not uncommon in coal. Mackowsky (1975, p. 128) states that "most coal seams contain small quantities of sphalerite, galena and chalcopyrite, in particular if hydrothermal veins are found close to the seams." Nevertheless, relatively little has been written about their modes of occurrence (mode of occurrence should include information on grain size distribution, morphology, mineral and maceral associations, frequency of occurrence, etc.).

Sphalerite has often been observed in cleats and fractures in coal (Gallagher, 1940; Hatch et al., 1976; Sprunk and O'Donnell, 1942; Kemezys and Taylor, 1964). Hatch et al. (1976) suggested that cleat sphalerite in coals of the Illinois Basin is the product of epigenetic mineralization. Boctor et al. (1976) noted that sphalerite in an Indiana coal occurs exclusively in fusinite, where it is occasionally associated with pyrite as a filling mineral in cleats. In rare cases sphalerite filled cell cavities in fusinite. In addition to its occurrence in veins in Australian coals, Kemezys and Taylor (1964) also reported that isolated grains of sphalerite occur in coal and as infillings of cell lumina in semifusinite. They also noted a unique occurrence of sphalerite nodules. Smyth (1966) observed that sphalerite was exclusively associated with vitrinite and semifusinite in the Australian coals she studied. Mackowsky (1968) cited an earlier report describing concretions of pyrite in which concentric scales of pyrite alternated with sphalerite or chalcopyrite.

Less is known of the modes of occurrence of the other accessory sulfides. Kemezys and Taylor (1964) reported galena to occur mostly in veins but also as fillings of cell lumina in semifusinite. They noted one occurrence of chalcopyrite that was associated with pyrite, sphalerite and galena. Taylor and Warne (1960) noted that galena and sphalerite occur most often in narrow veins but also as infillings in fusite and occasionally as euhedral crystals in shaly coal. Several other accessory sulfides have been noted in the literature, generally without discussion of their modes of occurrence.

2.182 Results from Current Study

Because the accessory sulfide minerals contain elements of high atomic number, they can be readily detected in the back-scattered mode of the SEM.

Table 10 shows the distribution of the accessory sulphides by geographic region. The values indicate the number of samples in which the phase was observed; they do not reflect the relative abundance of the minerals.

Chalcopyrite: Chalcopyrite is the most widespread of the accessory sulfides, occurring in most of the Appalachian Region coals and in many of the coals outside of the Appalachian Region. It is

Table 10. Occurrence of Accessory Sulfides

(values indicate number of samples in which the phase was observed)

Geographic location	No. of Samples	ZnS	$CuFeS_2$	PbSe	PbS	Linnaeite Group	Others
Eastern Province							
Appalachian Region	23	12	17	13	2		As-Co-Ni-Fe-Se-S; CuS; SnS; AgS; HgS; CuFeZnS
Anthracite Region	6	2	5	2	2	2	
Valley Fields	1	1	1		1		
Meta-anthracite	1					1	
Deep River Field	1		1				
Interior Province							
Eastern Region	5	2	1		1		CuFeZnS
Western Region	9	1			1		SnS
Northern Region	1	1					
Rocky Mountain Province							
Denver Region	1	1		1	1		
San Juan River Region	1		1				
Green River Region	1				1	1	HgCuS
Uinta Region	1						
Wind River Basin	2						
Northern Great Plains Province							
Fort Union Region	1			1			
North Central Region	1						
Powder River Basin	1						
Gulf Province							
Texas Region	1						
Alaska Province							
Northern Alaska Fields	1						
Foreign Coals	21	8	10	2	8	1	CuS; SnS; CuFeZnS; AgS; BiS

found as grains up to about 30 µm in diameter, predominantly in pores of inertinite macerals (Figure 10) and as micrometer-size grains in vitrinite. Intergrowths of chalcopyrite and sphalerite have been observed. The micrometer-size grains containing copper, zinc, iron, and sulfur (Table 10) may be unresolved intergrowths of these minerals. Less commonly, chalcopyrite is found associated with kaolinite and siderite, which are generally considered to be authigenic (Stanton and Finkelman, 1979; Mackowsky, 1968).

Sphalerite: Sphalerite was noted in twelve Appalachian coals and in sixteen coals outside the Appalachian Region. Energy dispersive analysis and electron microprobe analysis (J. Minkin, personal communication, 1979) indicate that some sphalerite particles in the Appalachian Region coals contain as much as two weight percent cadmium. Gluskoter and Lindahl (1973) previously suggested that most of the cadmium in coal occurs in solid solution in sphalerite.

In this study, sphalerite was found to occur predominantly in pores of inertinite; like chalcopyrite, it rarely fills an entire pore. Less commonly, sphalerite was found to occur as discrete grains in vitrinite. Morphology in polished sections ranged from various polygonal (Figure 11) to circular (Figure 12) forms. In particles isolated from LT ash residues, the morphology varies from subhedral forms (Figure 13) to tapering cylinders (Figure 14), and color from yellow to brown to black. The largest grain in the polished section had a diameter of 30 µm. Sphalerite was rarely associated with kaolinite and siderite, and in only one occurrence with a potassium aluminum silicate. Sphalerite and chalcopyrite have not been found in association with pyrite.

Figure 10. SEM photomicrograph of "chalcopyrite" replacing "kaolinite" in a semifusinite pore.

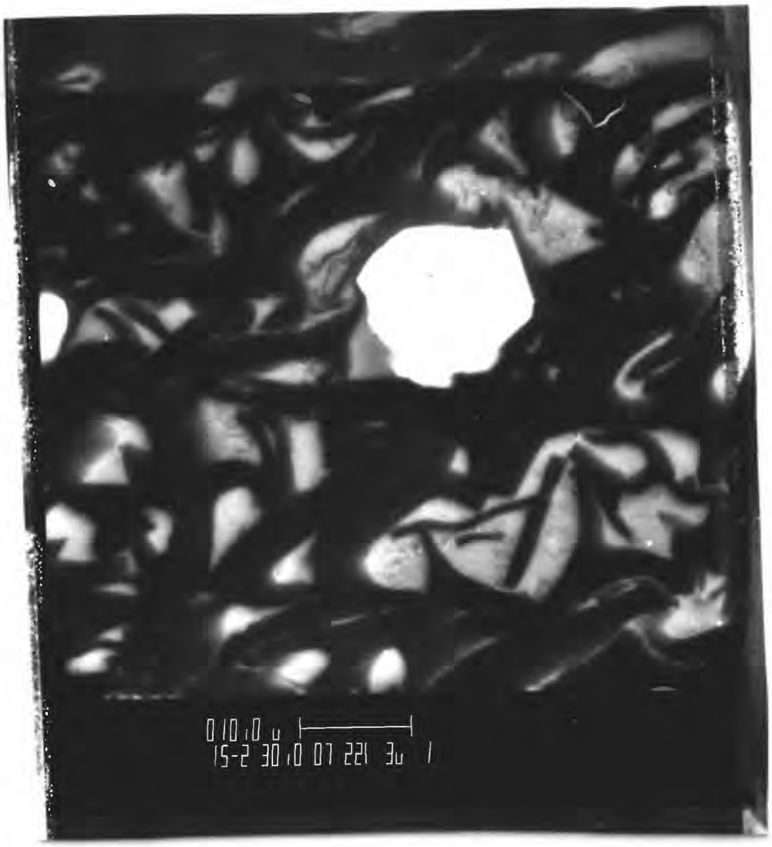

Figure 11. SEM photomicrograph of a "sphalerite" crystal in inertinite.

Figure 12. SEM photomicrograph of "sphalerite" in an organic particle in an ash-rich zone of the Upper Freeport coal.

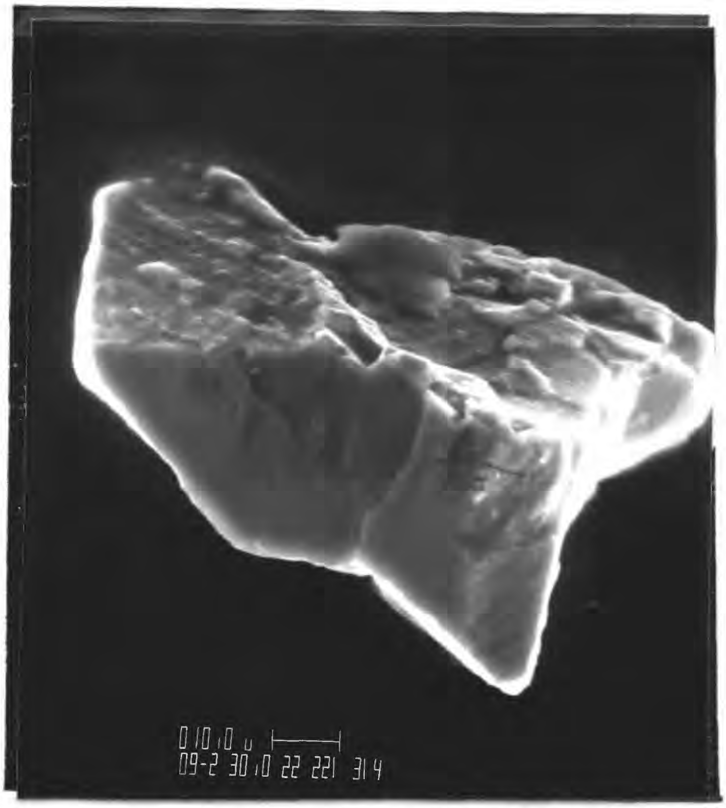

Figure 13. SEM photomicrograph of a subhedral sphalerite crystal extracted from the LT ash of the Upper Freeport coal.

Figure 14. SEM photomicrograph of a cylindrical sphalerite grain from the LT ash of the Upper Freeport coal.

PbSe: A lead-selenium bearing phase, up to 3 μm in diameter, was observed in nineteen coals. The intensity of the back-scattered electron image indicated a mean atomic number considerably higher than that of sphalerite (∿23). It is believed that this phase is a lead selenide (mean atomic no. ∿58), probably the mineral clausthalite (PbSe). In all but one instance, the PbSe is found in the pores of inertinites and in vitrinite. In the lone exception it occurred as an overgrowth on a doubly terminated quartz crystal (see Figure 5 of Finkelman, 1978). Even in ash-rich zones (90 weight percent ash), PbSe is found encapsulated in organic inclusions. PbSe is commonly intergrown with sphalerite (Figure 15), but rarely with chalcopyrite. Several complex crystals consisting of PbSe, chalcopyrite and sphalerite have also been observed (Figure 16).

Experiments by Bethke and Barton (1971) on the chemical partitioning of selenium between sphalerite, galena, and chalcopyrite suggest that the sphalerite-chalcopyrite-clausthalite assemblage would be thermodynamically stable at low temperatures (<300°C).

If we consider the reaction describing the distribution of selenium between sphalerite and galena:

$$PbS + ZnSe \rightleftarrows PbSe + ZnS$$

the distribution coefficient is given as:

$$K_{Se} = \frac{N_{(PbSe\ in\ galena)} \cdot N_{(ZnS\ in\ sphalerite)}}{N_{(PbS\ in\ galena)} \cdot N_{(ZnSe\ in\ sphalerite)}}$$

where N = mole fraction.

The equil ibrium constant is strongly positive at 900°C and increases rapidly with decreasing temperature, indicating that

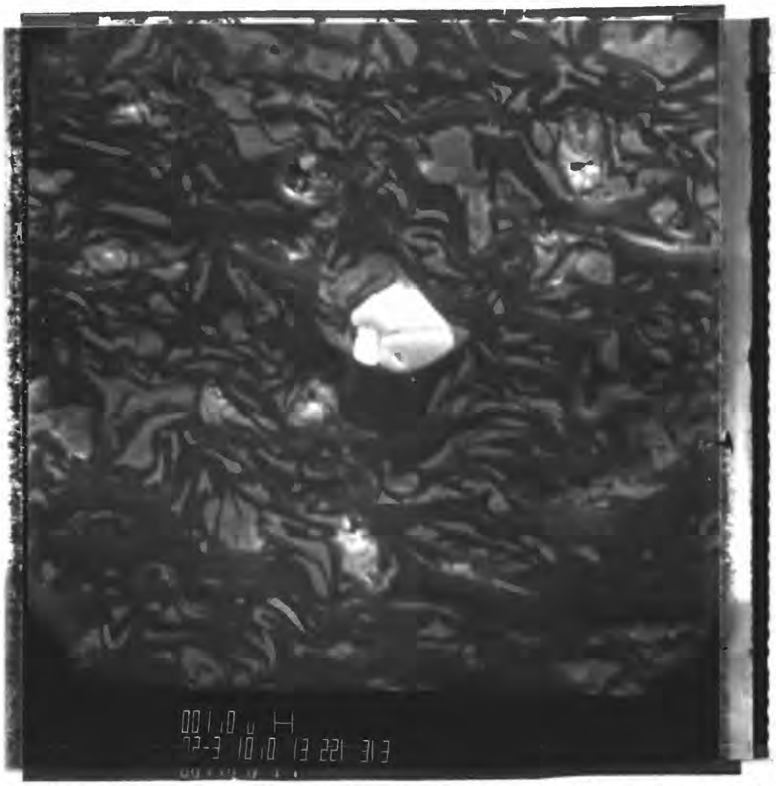

Figure 15. SEM photomicrograph of "sphalerite" (light grey) with a PbSe inclusion (white) in a crushed inertinite particle.

Figure 16. SEM photomicrograph of a grain consisting of "sphalerite" (right tim), "chalcopyrite" (left rim), and lead selenide (bright cap).

clausthalite and sphalerite are the stable phases.

Bethke and Barton (1971) determined the formula for deriving the distribution coefficient at any temperature to be:

$$\text{Log } K_{Se} = \frac{2850}{T^{o}K} - 1.24$$

at 300^{o}K Log K_{Se} = 8.26, assuming equillibrium.

If the sphalerite contained as much as 1/10 mole percent ZnSe (this appears to be a generous estimate, as no Se has been detected in the sphalerite), it would be in equillibrium with clausthalite containing only one part in 20,000,000 of PbS. A similar situation exists with the distribution of selenium between chalcopyrite and sphalerite (Bethke and Barton, 1971). Thus, the clausthalite in this assemblage must be end member PbSe.

Although lead selenide has never previously been reported in coal, it appears to be nearly ubiquitous in samples from the Appalachian Region occurring in thirteen of the twenty-three samples examined (Table 10). Curiously, PbSe was detected in only six of the fifty-six samples outside the Appalachian Region. It is not clear why the Appalachian Region should be so different.

<u>"Galena" (PbS):</u> In contrast to the other accessory sulfides, "galena" (quotation marks indicate tentative identification based primarily on major element data from the energy dispersive system) is often physically associated with pyrite (Figure 17). The "galena" crystals were possibly exsolved during crystallization of the pyrite. "Galena" crystals rarely exceed 3 μm in diameter. Abundances range from one particle to several hundred in a pyrite-rich coal sample from

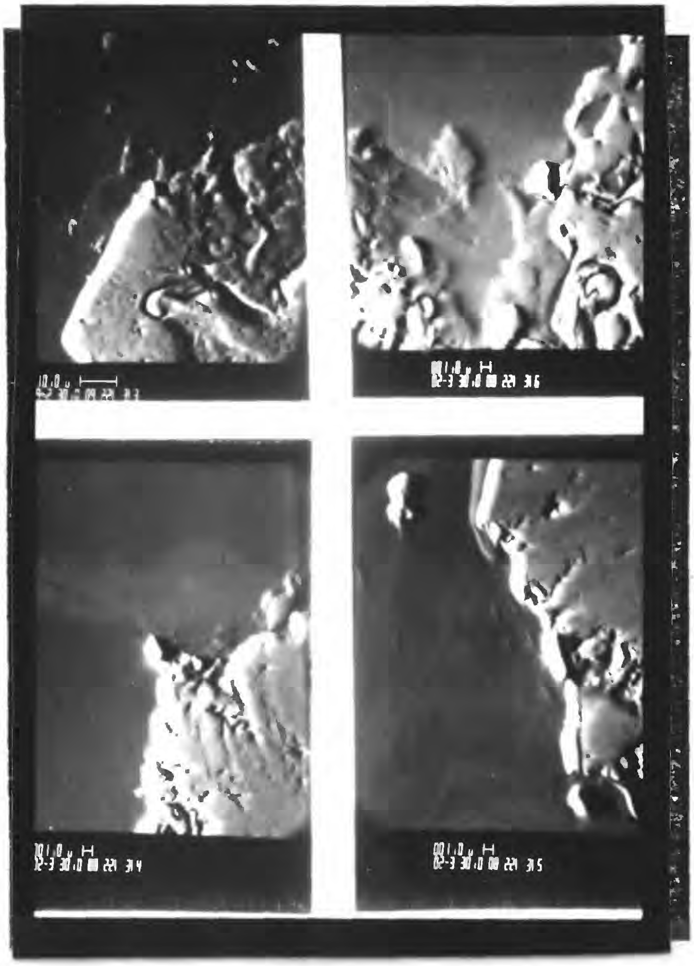

Figure 17. SEM photomicrographs of "galena" (white) on pyrite (grey).
Backscattered-electron image.

Nova Scotia (790 ppm Pb in the ash). In this sample the "galena" also occurs with kaolinite in the pores of inertinites. In a sample of the Merrimac coal from Virginia, "galena" is associated with sphalerite in siderite. "Galena" is seldom found in vitrinite.

Linnaeite group: Copper-cobalt-nickel-iron sulfides were detected in five samples including two anthracites and the meta-anthracite. They occur as micrometer-size grains in vitrinite, although one particle from one of the anthracites was associated with kaolinite. Identification of the linnaeite group was confirmed by an X-ray powder pattern obtained from a 10-μm crystal isolated from the LT ash of the meta-anthracite.

Other Accessory Sulfides: Micrometer-size grains of several other accessory sulfides were observed. Unless otherwise noted, they occur in an organic matrix. They include copper sulfide (found in two samples), bismuth sulfide (in one sample), silver sulfide (in two samples) (also reported by Lee et al., 1978), mercury sulfide (in one sample) and mercury-copper sulfide (in one sample) (Stutzer, 1940, reports the occurrence of cinnabar in coal), an arsenic-cobalt-iron-nickel-selenium sulfide (in one sample), tin sulfides (in three samples), some of which contain iron. Several tin-iron-copper sulfides of questionable origin were isolated from the LT ash of the Waynesburg coal; possible occurrence of a nickel sulfide (millerite has been reported by Lawrence et al., 1960) and a molybdenum sulfide.

Although arsenic-bearing pyrite has been observed (Minken et al., 1979), no occurrence of arsenopyrite was noted.

2.183 Discussion

The accessory sulfides probably formed during the early stages of coalification, at a time when it was relatively easy for solutions to percolate through the brittle, porous inertinites and to permeate the vitrinite. The complex particle in Figure 16 has incorporated kaolinite as well as some organic matter in its hollow center, indicating that the accessory sulfides may have formed after the inertinite pores filled with kaolinite or carbonates. Where the accessory sulfides are encased in a crushed or distorted inertinite particle, it is not clear whether their formation predated the deformation.

Hatch et al. (1976) suggest that the large size of the sphalerite in cleats is indicative of relatively slow deposition. The small size (and the morphology) of the accessory sulfides may, however, be the result of physical constraints of the enclosing maceral. Those accessory sulfides in the vitrinite rarely exceed 2μm, and all appear to be anhedral, whereas those in the pores of the inertinites have diameters generally in the range of 5-10 μm with a maximum diameter of about 30 μm (roughly the size of the larger pores); the length of these grains may exceed 100 μm (Figure 14). Sulfides that completely fill the pores of the inertinite generally have elliptical or circular cross-sections (Figure 12; and Figure 8 of Finkelman and Stanton, 1978). Smaller sulfide grains in the inertinite often exhibit crystal faces (Figure 11).

Cecil et al. (1979) have presented results from statistical analyses of analytical data from 96 samples of the Upper Freeport coal. The data indicate positive correlations between Cd, Cu, Pb, Se, Sn, and Zn with total ash, SiO_2, Al_2O_3, MgO, Na_2O, K_2O, TiO_2, etc. They refer to these as the ash-related elements and suggest that plant inorganic matter must be the major source of these elements. It is likely that some, perhaps many, trace elements are cycled through an organic phase. However, it is possible that most of the trace elements enter the depositional basin in solution, as organo-metallic complexes, or associated with minerals. Indeed, in many of the coals studied, a significant percentage of the minerals occur in distinct bands containing a typically detrital mineral assemblage.

The most important process during the early stages of coalification is humification (Teichmuller, 1975). This is the generation of humic substances, such as humic acids, and their salts, the humates. The ability of humates to leach minerals and mobilize certain metals is well known (Nissenbaum and Swaine, 1976). Nissenbaum and Swaine (1976) argue that the metals enriched in marine humates are derived from the dissolution of the metals from various mineralogical phases. They cite as evidence indications that several metals including Cu, Zn, Co, Ni and Fe can be mobilized from soils and sediments by the leaching action on organic substances under reducing conditions.

The generally acidic conditions created by the degradation of the plant material would tend to break down most clays and ferromagnesian minerals. Any available $S^=$ or $Se^=$ would quickly precipitate the chalcophile elements released in this process as well as those in solution. This would prevent the elements from migrating out of the depositional basin and thus retain the original correlations between the chalcophiles and the other ash-forming components.

Nissenbaum and Swaine (1976) note that in recent sediments Cu and most of the Zn remain associated with the humic acid, whereas Co, Ni and Fe have become bound as sulfides. Experiments by Rashid (1974) on the absorption of metals on sedimentary humic acids and on peat suggest that the "metal-holding capacity" is greater for Cu and Zn than for Fe. These data are consistent with the observation of Zubovic (1976) that stability constants for organic ligands indicate that copper and zinc form more stable organometallic bonds than does ferrous iron. Perhaps this may explain why sphalerite and chalcopyrite were not found associated with pyrite in the coals. Iron sulfide would precipitate out first, perhaps coprecipitating the lead and probably removing any available $Se^{=}$. At a later time, when conditions (lower pH?, lower Eh?) favored breaking the stronger metal-organic bonds, the Cu and Zn would precipitate.

Alternatively, if iron initially formed an insoluble ferric hydroxide layer, the zinc, copper, and lead sulfides and selenides would precipitate first, forming the observed sphalerite-chalcopyrite-clausthalite intergrowths. In this regard it is interesting to note that in a detailed study of a column of the Upper Freeport coal, Finkelman and Stanton (1979) found that the accessory sulfides, particularly clausthalite, were concentrated in a 10 cm shaly zone, which probably represents the most oxidizing environment encountered in the column, perhaps sufficiently oxidizing for trivalent iron to have formed.

Further support comes from the common association of the accessory sulfides with fusinites and semifusinites which may require oxidizing conditions for their formation (Teichmuller, 1975, p. 219; Navale, 1979).

According to the data of Barnes and Czamanske (1967), differentiation of these elements can also occur in low-temperature aqueous solutions if bisulfide complexes such as $Zn(HS)_3^-$ or $Cu(HS)_3^-$ are formed. In contrast, iron does not as readily form bisulfide complexes and lead may form stable chloride complexes. Oxidation is the most likely and effective cause of deposition from solutions carrying the bisulfide complexes. Decrease in pH would also lower the bisulfide concentration and cause deposition.

2.2 Relationship Between Minerals and Macerals

2.21 Introduction

Information on the physical relationships between the minerals and the macerals can be an asset in determining the parageneses of the minerals. Furthermore, we will see in Section 2.3 that a knowledge of these relationships may be of value in predicting the behavior of certain trace elements during coal cleaning processes.

Here, too, relatively little information has appeared in the literature that might be used to elucidate these relationships. Sprunk and O'Donnell (1942) give an excellent account of the occurrence, characteristics, and maceral associations of the major mineral species in coal. Smyth (1966) recognized a need for this information and conducted a comprehensive study of 80 Australian coals. She documented the association of clay, quartz, carbonates, pyrite, apatite and sphalerite with maceral and microlithotype constituents. Graphs and tables were presented to illustrate the associations of the minerals with the macerals and microlithotypes. The distribution of minerals was found to be complex and to vary among different types of coal, and even occasionally within similar coals.

In contrast to the statistical approach of Smyth (1966), Kemezys and Taylor (1964) used a descriptive approach for the occurrence and distribution of the minerals in 52 Australian coals. These authors reported on silica (quartz and chalcedony), clays, feldspars, carbonates (siderite, ankerite, calcite), pyrite, marcasite, sphalerite, galena, chalcopyrite, millerite, gypsum, barite, fluorapatite, zircon, goethite, and limonite. Their report is entirely descriptive; no conclusions were drawn or theories offered.

Most other papers that deal with the relationship between minerals and macerals are concerned with the more general organic constituents, the microlithotypes (Marshall and Tompkins, 1967) or with individual minerals such as apatite (Beeston, 1974).

2.22 Application of the SEM

The SEM-EDX system is uniquely suited to study the mineral-maceral relationships in coal. By applying this approach to polished blocks or pellets of coal, in which these relationships are preserved, a more complete picture of coal petrography can be obtained.

The value of the SEM-EDX system in studying the fine-grain accessory phases in coal has already been discussed. It was clear from the beginning of this study that it would be necessary to obtain information on the minerals and the macerals with which they are associated. Ideally, this should be done with a single analytical tool -- the SEM. However, macerals are not easily studied by using the SEM; Stanton and Finkelman (1979) have pointed out some of the difficulties in using the SEM for this purpose. They note that macerals are not easily studied in the SEM because they are composed of elements having generally low mean atomic numbers and thus appear relatively dark on the SEM screen. Moreover, macerals do not have distinguishing crystallographic or chemical characteristics that can be determined by the SEM-EDX system. Furthermore, the characteristics by which macerals are identified are defined by optical properties. However, Stanton and Finkelman (1979) achieved an insight into relationships between macerals and minerals by optically photomapping a sample to identify the macerals prior to SEM analysis; then the minerals can be readily identified on the SEM image and the macerals can be identified by correlating the SEM image with the photomap. Such correlation between an optical photomap and an SEM image is not always possible; maceral identifications commonly must be made from the SEM image alone. Stanton and Finkelman state that all maceral groups and some individual macerals can indeed be identified in the SEM by relying on (1) the shape of the maceral (often enhanced by the surrounding or incorporated minerals), (2) the mean atomic number, and (3) polishing relief that is apparent in the secondary electron image. These general criteria are summarized in Table 11. Various macerals are illustrated in Figures 18, 19, and 20.

The use of the SEM to study the plant constituents of coal is being investigated by Finkelman and Lyons (Lyons et al., 1980). They are attempting to identify specific plant parts in polished sections of bituminous coal.

2.23 Results from Current Study

SEM-EDX analysis was conducted on random mineral grains associated with various macerals and microlithotypes in the Waynesburg coal. The results indicate a clear difference in the mineral-maceral distribution. The greatest variety as well as the highest concentration of minerals is in the carbominerite bands (Table 12). Figure 21 illustrates a typical mineral concentration in the carbominerite. More than 20 different accessory minerals were observed in this microlithotype. The relative concentration of minerals per unit area is: carbominerite>>fusinite, semifusinite>vitrinite.

Table 11. Appearance of Macerals in the SEM†

Maceral Group	Maceral Varieties	Morphology	Relief*	BSE Contrast*
Vitrinite	telenite collinite	generally smooth and nontextured	———	———
Inertinite	fusinite sclerotinite macrinite	---porous ---subrounded, porous ---subrounded	modest relief	little or no difference
Exinite	resinite sporinite cutinite	--rounded bodies --elongated, has central canal --elongated, has serrated edge	positive	darker

* Relief and BSE contrast relative to relief and contrast of vitrinite.

† From Stanton and Finkelman (1979)

Figure 18. SEM photomicrograph of megaspores in an Alaskan coal. Backscattered-electron image.

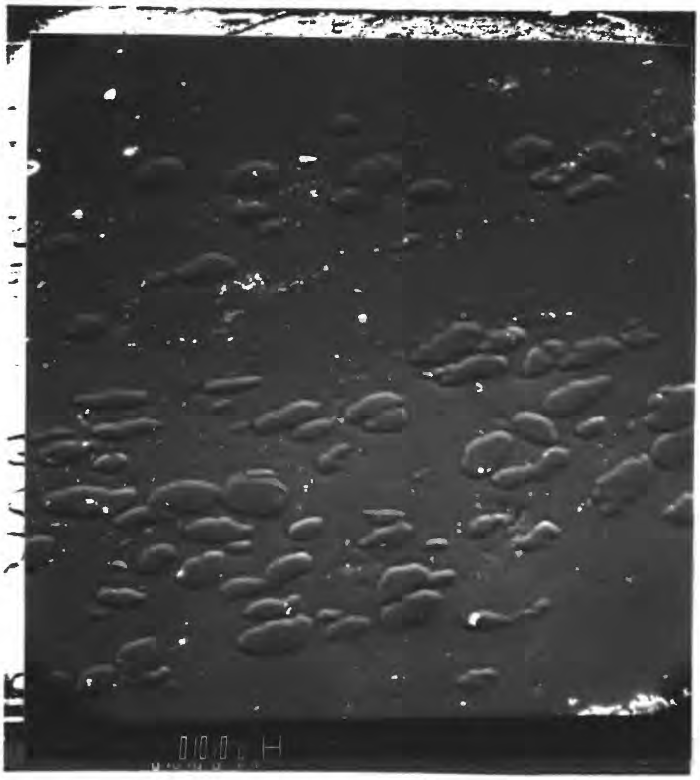

Figure 19. SEM photomicrograph of resin bodies in the Ferron coal.

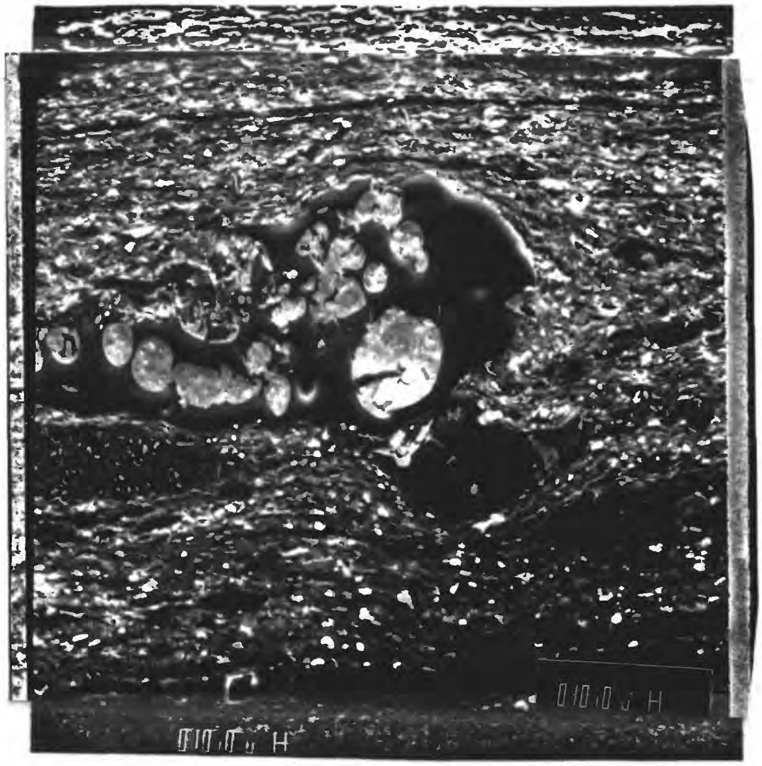

Figure 20. SEM photomicrograph of a large inertinite particle in an ash-rich zone of the Upper Freeport coal. Note the "chalcopyrite" crystal in the large pore.

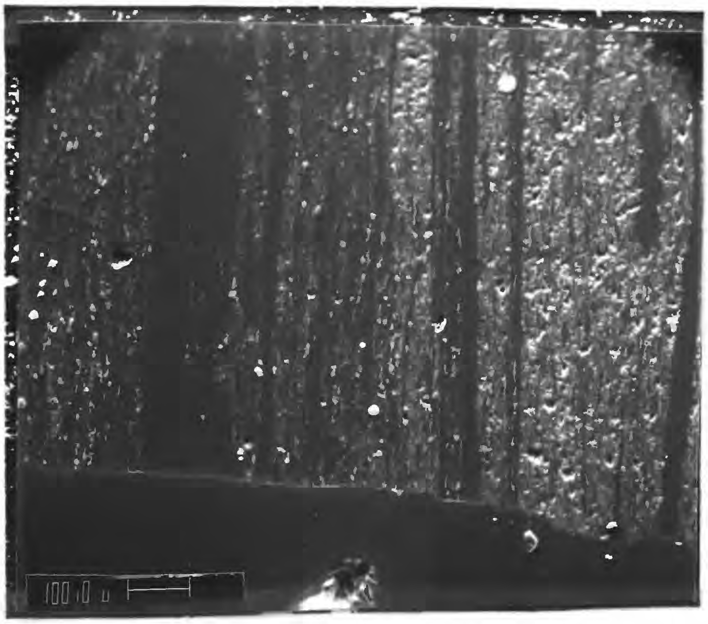

Figure 21. SEM photomicrograph of alternating bands of carbominerite and vitrinite.

Table 12. Percent of Total Mineral Matter

Associated with Waynesburg Coal Macerals

(* = Total number of mineral grains analyzed. Quotation marks indicate that mineral name signifies a mineral group rather than a specific mineral.)

	"Pyrite"	"Illite"	"Kaolinite"	"Quartz"	"Rutile"	"Calcite"	Accessories
Vitrinite (25)*	56	0	24	0	0	4	16(1)
Fusinite (150)*	10	0	85	0	0	1	4(2)
Semifusinite (50)*	0	0	90	8	0	0	2(2)
Carbominerite (150)*	5	29	15	45	5	0	1(3)

(1) iron aluminum silicate

(2) "siderite," "barite," "diaspore"

(3) "zircon," "barite," "monazite," "rutile," K-feldspar, "chromite," "chlorite"

Image analyses of an area having a longitudinal and a cross section of mineralized inertinite (Figure 22) indicated that approximately one third of the area is occupied by the minerals.

Table 13 lists the various minerals commonly associated with the three maceral types and with carbominerite.

Two distinct suites of accessory minerals are evident in most coal samples. The first suite is observed predominantly in pores of inertinite and less commonly in vitrinite, resinite, and sporinite. This suite includes chalcopyrite, sphalerite, "clausthalite," crandallite, rare-earth phosphates (in part), "anatase-brookite," apatite, and barite. Because these minerals commonly exhibit crystal faces and are intimately intergrown with one another, and as they occur exclusively within organic components, an authigenic origin is indicated. The second group of accessory minerals occurs exclusively in quartz-illite rich bands (carbominerite) composed of intermixed macerals and randomly oriented, subangular, to sub-rounded mineral grains that are probably of detrital origin. This suite includes quartz, rutile, zircon, and the rare-earth bearing phases (in part).

Although the division of the accessory minerals into authigenic and detrital suites based on their textural relationships, as seen in the SEM, is fairly clear cut, there are some exceptions. The rare-earth phosphates appear to occur with equal abundance in either suite, and grains with authigenic and detrital origins may both be present in the same sample. Titanium dioxide appears to be predominantly detrital in many Appalachian coals. Grains removed from the detritus-rich Waynesburg coal gave rutile powder patterns. In several coals,

Table 13. Association of Minerals and Macerals

(in roughly decreasing frequency of association)

Inertinite	Vitrinite	Exinites	Carbominerite
Kaolinite	Pyrite	Barite	Illite
Siderite	Kaolinite	Chalcopyrite	Mixed-layer clays
Pyrite (marcasite)	Sphalerite	Sphalerite	Quartz
Calcite	Chalcopyrite		Zircon
Sphalerite	Clausthalite		Rutile
Chalcopyrite	Witherite		Rare-earth phosphates
Rare-earth phosphates	Strontionite		Feldspars
Clausthalite	Barytocalcite		
Crandallite			
Silica			
Titanium oxides			
Ilmenite			
Apatite			

Figure 22. SEM photomicrograph of transverse and longitudinal sections of fusinite with "kaolinite" pore fillings.

Figure 23. SEM photomicrograph of titanium oxide (grey) and "ilmenite" (white) pore fillings from the Bulli coal.

however, the titanium dioxide phase appears to be authigenic, occurring as infillings in fusinite (Figure 23). A splintery (fusinite pore fillings?) brown titanium mineral removed from the LT ash of the Ollerton coal yielded an X-ray pattern of brookite. Anatase, a low temperature polymorph of TiO_2, has been detected in the Upper Freeport coal (Finkelman, Dulong et al., 1979).

Although most of the silica minerals appear to have a detrital origin, authigenic silica minerals are not rare. Chalcedony has been reported (see Appendix II), and particles of opal have been isolated from the Upper Freeport coal. Authigenic silica has been observed in the SEM as fracture fillings, euhedral crystals (Figure 24), secondary overgrowths (Figure 25), intergrowths with pyrite (Figure 26) and as pore fillings in inertinite. One sample (Pittsburgh No. 8 coal bed, Washington County, Pennsylvania) was unique in that all of the silica phases in the lowermost part appeared to be authigenic. The bulk mineralogy and major-element chemistry of this sample are similar to those of stratigraphically higher samples. Only by observations of the morphology and intergrowths of the quartz has it been possible to recognize that the minerals in the lowermost horizon have been altered.

Other characteristically detrital phases that appear, from textural evidence, to have formed in-situ in some coals include ilmenite (Figure 23), zircon, and magnetite (Figure 7).

The carbonate minerals (calcite, siderite and ankerite) all appear to have formed authigenically, occurring primarily in the pores of the inertinites as well as in cleat and parting fillings.

Figure 24. SEM photomicrograph of a euhedral "quartz" crystal in the Pittsburgh No. 8 coal.

Figure 25. SEM photomicrograph of a secondary overgrowth on a "quartz" crystal. Note bright PbSe grains along left edge of the "quartz".

Figure 26A. SEM photomicrograph of "quartz" overgrowth on "pyrite".

Figure 26B. SEM photomicrograph of "quartz" inclusion in "pyrite".

Pyrite (and marcasite) is ubiquitous, occurring within the inertinite pores, in cleats and partings, in the vitrinite, in bands of detrital matter (although it appears to be authigenic), etc. Galena, generally associated with pyrite, is formed probably by epitaxial growth or by exsolution.

Other accessory minerals for which there are skimpy data include feldspars (generally detrital), chlorite (detrital?), celestite (authigenic), witherite (authigenic), diaspore (authigenic alteration product, commonly associated with kaolinite; Figure 28), linnaeite group (authigenic), crandallite group (authigenic), ilemnite (authigenic, Figure 23; and detrital), magnetite (authigenic, Figure 7; extraterrestrial, Figure 8; and detrital).

These observations are summarized in Table 14.

2.24 Mineralogy of Microcleats

The mineralogy of cleats and partings was not considered in this study because it is easily studied by conventional techniques and because the minerals in cleats and partings are more readily removed from coal than are the finely dispersed mineral grains.

"Microcleats" were encountered in a number of samples. These are short (several 10s of μm) narrow gashes in the vitrinite. They are always perpendicular to the bedding and generally pinch out on approaching mineral rich bands (Figure 29). In all probability, they are tension gashes (Hills, 1963) formed by compressional forces. Ball (1934) describes them as desiccation cracks, but Sprunk and O'Donnell (1942) have questioned this interpretation, suggesting that they are

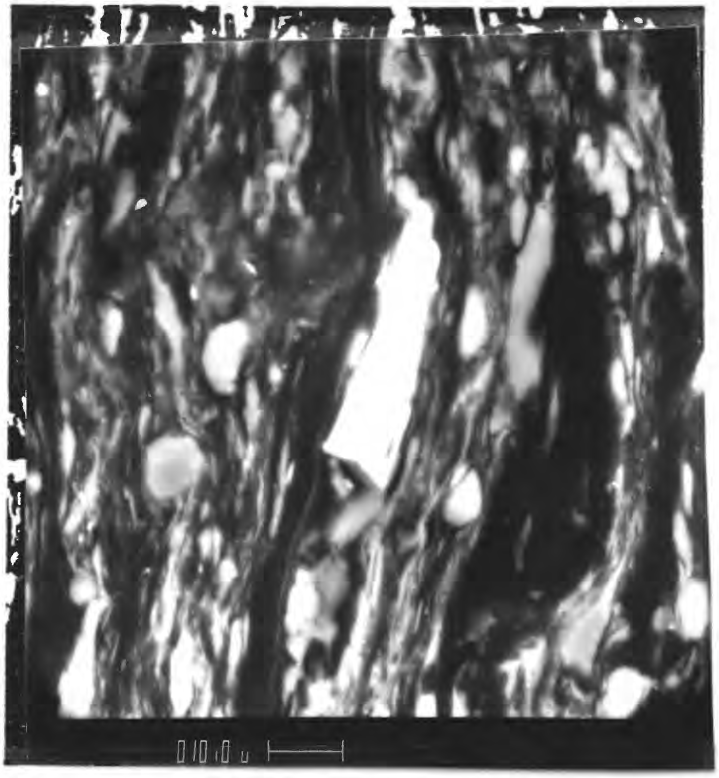

Figure 27. SEM photomicrograph of an angular titanium oxide crystal.

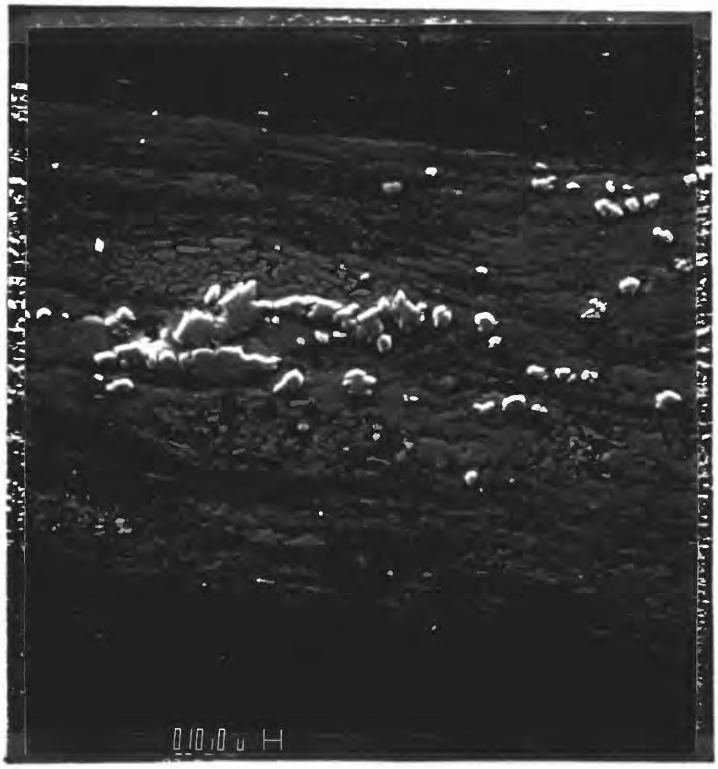

Figure 28. SEM photomicrograph of "diaspore" on "kaolinite".

Table 14. Major and Accessory Minerals*

And Their Apparent Origin†

		Detrital (Transported material)	Authigenic (Formed in place)
Major	Quartz SiO_2	++	-
	Siderite $FeCo_3$		++
	Calcite $CaCO_3$		++
	Illite (See 1)	++	
	Kaolinite $Si_2Al_2O_5(OH)_4$	- (?)	++
	Pyrite FeS_2		++
	Marcasite FeS_2		++
Accessories	Sphalerite (Fe,Zn)S		++
	Apatite $Ca_5(PO_4)_3(OH)$	+	+
	Barite $BaSO_4$		++
	Chalcopyrite $CuFeS_2$		++
	Clausthalite PbSe		++
	Crandallite Group $(Ca,Ba,Sr)Al_3(PO_4)_2(OH)_5 \cdot H_2O$		++
	Diaspore AlO(OH)		++
	Galena PbS		++
	Gold Au	++	
	Halite NaCl		++
	Magnetite Fe_3O_4	+	+
	Monazite $CePO_4$	+	+
	Rutile TiO_2	++	-
	Xenotime YPO_4	+	+
	Zircon $ZrSiO_4$	++	- (?)

++ very predominant + less predominant - rare

Note 1: $(KH_3O)(Al,Mg.Fe)_2(Al,Si)_4O_{10}\{(OH)_2H_2O\}$

* Other minerals have been identified, but data are insufficient to classify them in above scheme.

† From Stanton and Finkelman (1979)

Figure 29. SEM photomicrograph of microcleat in vitrinite.

fractures formed by pressure. Kaolinite is the only mineral cited by these authors as filling the cracks. Parks (1952) attributed the formation of the tension fractures to shrinkage caused by expulsion of water by compressive forces. He indicated that calcite and pyrite, in addition to kaolinite, commonly fill these cracks.

During the course of the current study a number of minerals have been observed filling the tension gashes. These include kaolinite, siderite, pyrite, calcite, barite and silica. The most common gash filling, however, was aluminum silicates with varying amounts of calcium, magnesium, and iron.

Minerals with these compositions are not common syngenetic phases in coal and are unknown as late epigenetic material filling the larger cleats. Their occurrence in the microcleats can best be explained as an early diagenetic formation. They are, perhaps, products from the breakdown of detrital ferromagnesian minerals. Huang and Keller (1970) noted that the solubilities of Si, Al, Fe, Ca, and Mg were enhanced by the presence of organic acids such as humic acids. Thus, these components may have been leached from the ferromagnesian minerals in the coal and deposited in the more favorable environment of the microcleat.

2.3 Sink-Float Experiments

2.31 Introduction

Traditionally sink-float separations of coal have been the most frequently used approach to elucidate the mode of occurrence of the chemical elements. The procedure involves separating ground coal into several Sp. G. fractions. Analyses of these splits reveal how the various elements have been fractionated during the density separation. It is presumed that those elements concentrated in the lighter Sp. G. fractions are organically bound. Those elements concentrated in the heavier Sp. G. fractions are presumed to be inorganically bound.

At best this is an indirect approach to the mode of occurrence, and as we shall see, the results are readily susceptible to misinterpretation. Further discussion of the limitations of this approach appears in Section 3.211.

Despite the potential problems and the limitations inherent in this approach, sink-float experiments can still offer valuable insights into the modes of occurrence of many elements.

Two such experiments were conducted for this study, a separation of the Waynesburg coal (Section 2.32), and a separation of the Waynesburg LT ash (Section 2.33). A third experiment, on the Upper Freeport coal, which was done as part of another program, is discussed in Section 2.34.

2.32 Sink-Float Separation of the Waynesburg Coal

A sample of the Waynesburg coal was ground in a tungsten carbide mortar and separated into four size-fractions (>10, 10-20, 20-80, and <80 mesh). Using commercial Sp. G. liquids (Centrigrav), the three coarser size-fractions were separated into four Sp. G. fractions (float 1.30, 1.30-1.50, 1.50-1.70, and sink 1.70). The resultant size-density fractions, as well as the bulk sample, were analyzed by INA (whole coal), and OES (550°C ash). The analyses appear in Appendices III A and B.

2.33 Sink-Float Separation of the Waynesburg LT Ash

Sink-float separation of the LT ash of a coal should allow the fractionation of the elements to be observed without the interferences and anomalies created by the organic matter. No similar experiment appears in the literature. The major drawback to this approach is the difficulty to effect a quantitative separation of the fine grained phases in the ash (see Section 1.3).

The LT ash from the Waynesburg coal was separated into three Sp. G. fractions (float 2.5, 2.5-3.3, and sink 3.3) using the procedure described in Section 1.33. Results appear in Appendix III C and D.

A major unresolved question is how the elements that were organically bound would behave during the sink-float separation of the ash. Many of these elements probably form oxides or sulfates upon LT ashing. Mass transfer in this dry, relatively low-temperature process would be limited, so that the phases created should be relatively small, perhaps small enough (<10 μm) that the physical laws governing density separations do not apply. If this situation prevails, there would be no way to predict to which Sp. G. fraction these elements would report. In this context it is interesting to note that relatively large (up to 100 μm) crystals of anhydrite have been created during the LT ashing of coals for this study. The large size of these crystals may be attributable to the relatively high concentration of calcium in most coals.

2.34 Sink-Float Separation of the Upper Freeport Coal

As part of an EPA sponsored research program on the contaminants in coal, sink-float experiments were conducted on the Upper Freeport coal.

Four size-fractions were obtained (+¼", ¼" x 8 mesh, 8 x 100, <100 mesh). The coarser three fractions were separated into seven Sp. G. fractions (float 1.275, 1.300, 1.325, 1.400, 1.600, 1.80, sink 1.80). Sample preparation and separation was performed by Pedco, Inc. Analyses of the splits were performed by the U.S. Geological Survey.

Preliminary interpretation of the data appeared in Finkelman et al. (1979).

2.35 Discussion of Sink-Float Separations

It is evident from the data in Appendices III A and B that on a relative basis, the higher concentrations of many elements are found in the various sink fractions. Figure 30 illustrates the concentrations of Zn in a size-gravity separation of the Upper Freeport coal. Similar results were obtained for Cd, Cu, and Pb on six samples of that coal, and also for Co, Ni, and Zn from the Waynesburg coal. These data may be misleading because most of the coal generally floats in the lower Sp. G. fractions.* The data from Appendices III A and B

---

* It is worth noting that not all samples demonstrate this type of behavior. Finkelman et al. (1979) found, in several Upper Freeport samples, that more than 50 weight percent of the coal sank in the 1.6 Sp. G. fractions. The coal carried with it as much as 85 percent of the trace elements.

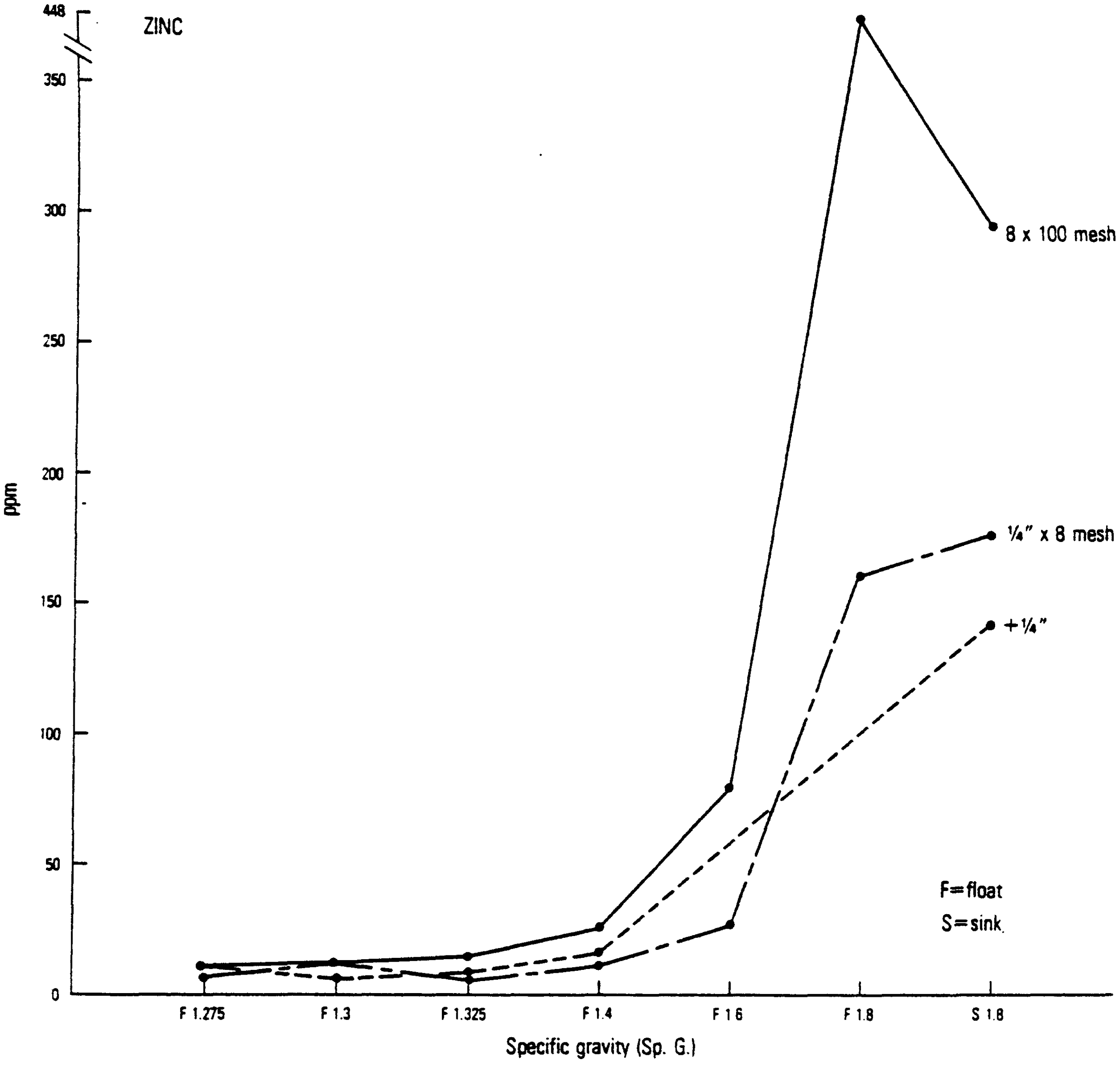

Figure 30. Concentration of zinc (whole-coal basis) in size-gravity separates of an Upper Freeport coal sample. (From Finkelman et al., 1979).

have been recalculated to show the proportion of each element in each Sp. G. fraction (Table 15). This approach reveals that substantial amounts of these elements are retained in the lighter Sp. G. fractions. Similar results were obtained in a washability study of these coals by Cavallaro et al. (1978).

Certainly, the proportion of these elements that reported to the heavier Sp. G. fractions probably has an inorganic association. But what of the elements in the lighter Sp. G. fractions? Are they predominantly organically bound? For most elements the answer appears to be no. The detailed SEM-EDX analyses of the Waynesburg and Upper Freeport coals has revealed that many of the trace elements in question occur quantitatively in micron-size accessory mineral phases that are generally dispersed throughout the organic matrix. Grinding to the particle sizes normally used in cleaning coal ($\sim\frac{1}{4}$") is ineffective in quantitatively releasing these phases from their matrix. The divergence of the curves in the high Sp. G. range (Figure 30) is consistent with the observation that Zn (and Cu, Cd, Pb, etc.) occur as fine grained minerals which are increasingly released from their organic matrices only upon grinding to very fine particle sizes.

The relatively small masses of the fine grained inclusions would not be sufficient to affect the density of the encasing organic particle. Thus, in the sink-float separation, the included accessory phases would be rafted up to the lighter Sp. G. fractions. This theory is supported by SEM analysis of a pellet prepared from the float 1.30 Sp. G. fraction of the Waynesburg coal (Table 16). In this pellet micron-size sphalerite, chalcopyrite, and over a dozen other minerals were found to be included in the organic fragments.

Table 15. Trace element concentrations in size-gravity splits of two Appalachian coals. Values are in percentages of the element in each Sp. G. fraction of a size split.

Upper Freeport (H2-42P-1.1)

Mesh size / Sp. G.	Cd			Cu			Pb			Zn			Hg			As		
	+1/4"	1/4"x8	8x100	+1/4"	1/4"x8	8x100	+1/4"	1/4"x8	8x100	+1/4"	1/4"x8	8x100	+1/4"	1/4"x8	8x100	+1/4"	1/4"8	8x100
Float 1.275		36	9	3	20	10		19	13	5	28	21	0.5	8	6	tr	5	5.5
1.300		17	16.5	33	30	21		18	9	12.5	27	13	3.5	10.5	6	tr	8	6.5
1.325		10	0.5	18	12	4		16	2	11	4	2	3.5	7	1	tr	4	1
1.400		6	6.5	13	12	10		18	9	7.5	4.5	4	5	8	2.5	tr	5.5	2
Cumulative percent		(69)	(42.5)	(67)	(74)	(45)		(71)	(33)	(35)	(63.5)	(40)	(12.5)	(33.5)	(15.5)	(1)	(22.5)	(15)
1.600		9	4		11	8.5		14	10		5	7		10	4		6	3
1.80		9	14.5	32	5	4		5	4	65	9	15	87	10	4	99	2.5	4
Sink 1.80		12.5	49.5		10	42		10	53		21	40		46.5	75		69.5	78

Waynesburg

Mesh size / Sp. G.	Mo		Cu			Pb			Zn			Ni			As*		
	>10	10-20	>10	10-20	20-80	>10	10-20	20-80	>10	10-20	20-80	>10	10-20	20-80	>10	10-20	20-80
Float 1.30	36.5	16	33	18	38	34	15.5	28.5	27	15	34.5	31	16.5	36	<150	<150	<150
1.50	45.5	55	65.5	79	53	60.5	69.5	41.5	59.5	62.5	33	60.5	67.5	41.5	<150	<150	<150
Cumulative percent	(82)	(71)	(98.5)	(97)	(91)	(94.5)	(85)	(70)	(86.5)	(77.5)	(67.5)	(91.5)	(84)	(77.5)			
1.70	2	5	0.5	1.5	3	1.5	4.5	9	2.5	6	7	1.	3.5	4.5	<150	<150	<150
Sink 1.70	16	24	0.5	1.5	6	4	10	21	11	17	25	7.5	12.5	17.5	1500	990	610

*ppm

tr = trace

Table 16. Minerals in the Waynesburg Float

1.3 Sp. G. Fraction

"Barite"
"Calcite"
"Chalcopyrite"
"Illite"
"K-feldspar"
"Kaolinite"
Marcasite
"Monazite"
"Pyrite"
"Quartz"
Rare-earth carbonate(?)
"Rutile"
"Siderite"
"Sphalerite"
"Xenotime"
"Zircon"

The retention of the fine-grained minerals, such as the accessory sulfides, in the lighter Sp. G. fractions is reflected in the analyses of the ash. Figure 31 illustrates the relatively high concentrations of the chalcophile elements in the ash of the lighter Sp. G. splits. Here too, similar results have been obtained for Cd, Cu, and Zn in many of the Upper Freeport samples and also for these elements in the Waynesburg coal. The high concentrations in the sink 1.8 fractions are probably due to the release of some of these minerals during grinding.

Conventional thinking might lead to the suggestion that the high concentrations in the low-ash low-Sp. G. fractions were due to the contribution of organically bound elements to the "extraneous" ash. However, the observations described herein strongly argue in favor of attributing the high elemental concentrations in the ash of the

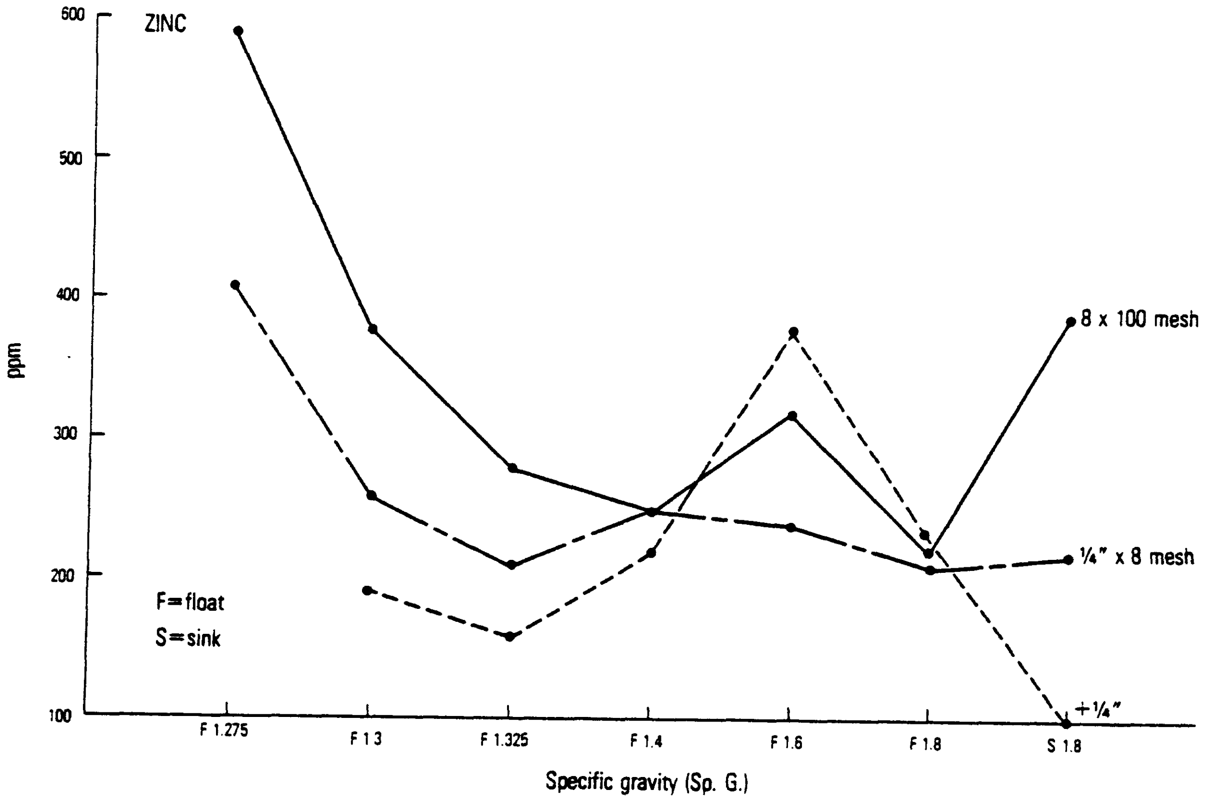

Figure 31. Concentration of zinc in the ash of size-gravity separates of an Upper Freeport coal sample. (From Finkelman et al., 1979).

lighter Sp. G. fractions to discrete mineral grains being rafted into these fractions by the encasing organic matter.

Not all the elements behave in this fashion. From Table 15 it can be seen that the bulk of As and of Hg are found in the higher Sp. G. fractions. The difference in behavior between As and Hg and the other chalcophile elements is attributable to the differences in the modes of occurrence. Arsenic and mercury do not occur as micron-sized accessory sulfide grains dispersed in an organic matrix. Rather, they occur in solid solution with pyrite. Thus, their sink-float behavior is dictated by the behavior of pyrite. This dependence is clearly reflected in the similar values for the percentages of pyrite, As, and Hg in the various fractions.

Results from the sink-float separation of the Waynesburg LT ash were difficult to interpret. Elements such as Ba, Th, REE, and Zn, which are believed to be associated with minerals having high Sp. G., were found to be concentrated in the float fractions. Bromine, which is believed to be dominantly bound to the organic fraction of the coal, did not demonstrate the expected strong organic affinity.

The problems with interpreting the results likely stems from the difficulty in obtaining quantitative separations of the minerals. This problem is discussed more fully in Section 3.211.

The behavior of individual elements will be discussed in Section 3.22.

3. DISCUSSIONS

3.1 Sources of Inorganic Elements and Minerals in Coal

3.11 Introduction

Sources of the inorganic elements and minerals in coal have been the subject of considerable speculation. Goldschmidt (1935) suggested three methods by which organic matter in coal can be enriched in trace elements:

(1) concentration by living plants

(2) concentration during decay of the organic matter

(3) concentration after burial

In order to complete the list of methods by which elements can be introduced into the basin of deposition of the coal, we must add those elements introduced by:

(4) the influx of detrital material

(5) mineralization subsequent to coalification

Although the sources of the minerals in coal closely parallel those of the inorganic elements, a distinction between them should be made. Many references lump them together as "ash-forming substances" (Parks, 1952; Deul, 1955), thus obscuring the differences.

Minerals can be introduced into a depositional basin as:

(1) detritus brought in by running water

(2) airborne dust (including cosmic dust)

(3) post-coalification mineralization, generally deposited in cleats and partings

(4) organically formed crystals within the living plants. Although these are not minerals in the strict sense, the products would be impossible to differentiate from chemically similar inorganically formed phases.

(5) authigenically precipitated phases formed from elements in solution or organometallic complexes.

(6) alteration products of preexisting minerals.

Mackowsky (1968) categorized the formation of minerals in coal by the stage in the coalification process in which the minerals were introduced. Inasmuch as the presence of minerals in coal results primarily from the action of water, Mackowsky used the term "syngenetic" for all minerals formed or introduced into the precursors of the coal, that is, into the swamps or peat, or during the early diagenetic stages. The other major category, the "epigenetic" minerals, are those minerals deposited in cracks, fissures, or bedding planes of a coal bed. These major categories are further subdivided by Mackowsky, but it is evident from her data (Mackowsky, 1968, Table 1) that many minerals can occur in several, if not all, of her categories.

Watt (1968) has suggested that a distinction between "syngenetic" and "epigenetic" origins for minerals, although of scientific value, is often not possible to accomplish in practice. Rather, he recommended the use of the terms "inherent mineral matter" for material too closely associated with the coal substance to be readily separated from it, and "adventitious mineral matter" for material readily separated from the coal. This latter category is also referred to as "extraneous mineral matter."

Watt's definition of "inherent mineral matter" combines the organically bound trace elements with the finely divided mineral matter. Material included in this category would vary with the method used for effecting the separations. Furthermore, it would be difficult to categorize those minerals observed with the petrographic microscope or with the scanning electron microscope, as this definition requires a judgment as to how readily separable the minerals would be from the coal.

Evidence from the current study suggests that there has been significant remobilization and reprecipitation of many trace elements. Thus, the question of how the elements originally became associated with the coal is a moot one, although the manner in which the elements are now chemically bound in the coal is still of paramount importance.

3.12 Origin of Minerals in Coal

Studying minerals in coal with the SEM provides an opportunity for determining the origin or source of the minerals, as well as for evaluating the relative significance of each of the sources. Again, it should be noted that epigenetic minerals were not considered in this study.

Textural evidence, that is, the relationships between different minerals and between minerals and macerals (see Section 2.2), indicates a detrital source for substantial amounts of the minerals in coal. The evidence includes a typically detrital mineral suite occurring in coherent bands (carbominerites), a very sharp mineralogical difference between this mineral suite and those minerals that are clearly authigenic, the occurrence of mineral intergrowths such as rutilated quartz and flecks of elemental gold in quartz.

Although a detrital source appears to account for about half of the minerals in the Waynesburg and Upper Freeport coals, many coals appear to have had little or no detrital influx. In some instances, this may be due to subsequent diagenesis obscuring the relationships. In many of the coals where there is an undeniable absence of detrital minerals, the coals had formed far from a detrital source (for example, the Indiana Block coal; see Zubrovic 1966 B).

Intuitively, it seems reasonable to assume that the detritus was introduced during the peat stage by running water. However, it has been suggested (E. C. T. Chao, personal communication, 1980) that some of the clays in the Upper Freeport coal were transported by wind. Finney and Farnham (1968) also conclude that most of the minerals in a Minnesota peat bog were transported there by wind.

In a major departure from conventional thought, Renton and Cecil (1979) have suggested that most of the minerals in coal, including some of the major partings, are of authigenic origin. They argue that there is sufficient inorganic matter inherent in peat-forming plants to account for all the ash in coal. Degradation of the plant material leaves behind the inorganic constituents which are reconstituted into the minerals found in coal. Partings can result from extensive degradation.

It is difficult to reconcile the suggestion of Renton and Cecil with the textural evidence outlined above and discussed in Section 2. Furthermore, there appears to be ample data clearly indicating that trace element ratios obtained from coal ash are identical to those of detrital sedimentary rocks. Those elements such as Zr, Ta, Nb, Hf and the RE are generally associated with the more resistive minerals, that is, those minerals that are found in detrital sediments. These data are presented in the discussions of the individual elements in Section 3.22. The argument of Renton and Cecil would appear to be further weakened by the observations of Austin (1979) who traced a shaly mudstone that split into six partings which passed into a coal bed. Some of the partings graded into bone coal bands.

The intention here is not to imply that there is no merit to the suggestion of Renton and Cecil or that authigenic minerals in coal are not significant. There are clearly significant amounts of authigenic minerals in most coals. The criteria used to distinguish authigenic minerals are discussed in Section 2. The minerals in some low ash coals appear to be exclusively authigenic. In general, at least 50 percent of the minerals in coal appear to be of authigenic origin. The ubiquitous nature of the authigenic sulfides has been discussed in detail in Section 2.18.

Another source of minerals that may be of significance in certain coals is the fallout from volcanic eruptions. These ash deposits, generally referred to as tonsteins or kaolinitic bentonites, have been recognized in coals from many parts of the world (Williamson, 1970). They have been most intensively studied in Europe and the

Western U. S.; none has been recognized in the Appalachian Basin.

Microscopically, these deposits are characterized by relatively large, angular to euhedral crystals, and by their distinct mineralogy. From the comments of Williamson (1970) and Bohor et al. (1979), a characteristic feature of ash falls is the abundance of accessory minerals such as zircon, apatite, sphene, anatase, magnetite, sanadine, goyazite, and ilmenite. Volcanic glass has also been reported (Appendix II).

Two samples reportedly (B. Bohor, personal communication, 1977) associated with tonsteins were studied for this report. The Denver Lignite contained abundant kaolinite, large authigenic quartz crystals, angular grains of "sphene" and "ilmenite," abundant "zircon" crystals, "apatite," and authigenic Ti-oxides. The Fruitland coal also contained abundant kaolinite, large angular quartz grains, "apatite" and zircon crystals, angular Ti-oxides, "crandallite," and barite. Crystals of zircon, monazite, and a pyroxene were extracted from a kaolinitic parting associated with this coal.

In the course of this study, several other coals were encountered that had mineral assemblages virtually identical to those just described. These include the India J3 coal, the Hem Heath coal from England, and the coal (7A) from the Wind River Basin (tonsteins have been reported from this Basin, J. Windolph, personal communication, 1980). It is likely that all of these samples received fallout from volcanic eruptions.

Two other possible occurrences of volcanic material in coal were found in Appalachian Basin samples. A single horizon in the Waynesburg coal contained an anomalous amount of large "quartz" grains and large angular Ti-oxides (Figure 27). A cannel coal from West Virginia (possible equivalent to the Lower Kittanning) contained abundant "kaolinite," "ilmenite," "zircon" crystals, "monazite," and Ti-oxide crystals. This sample differed from the other in that all the minerals were very fine grained, and quartz was virtually absent. Perhaps this is characteristic of volcanic fallout far from the source.

If these latter two samples contain valid occurrences of volcanic ash, it would be the first such material reported from the Appalachian Basin coals. This may have significant application in correlating and age-dating these coals. This is certainly an area of research that deserves further attention.

An important class of minerals in coal are those that have been formed by the alteration of preexisting minerals. Certainly some of the clays may be alteration products of other clays or feldspars (Karner et al., 1979). Some of the silica minerals may have a similar origin. Iron oxides are rarely reported in coal, yet they were present in many of the LT ash residues examined in the course of this study. Most of the iron oxides had the red to brown color characteristic of ferric iron, and all of these appeared to be amorphous to X-rays. It is possible that these iron oxides are produced by the LT ashing process. However, they may be natural alteration products of pyrite or siderite and their presence in coal may be underestimated. Other probable diagenetic minerals noted in this study include diaspore (AlOOH) which can form by hydrolysis of silicates and by hydrothermal alteration of aluminous minerals (Deer et al., 1962); leucoxene, a characteristic alteration product of ilmenite; and crandallite minerals which may have formed by lateritic alteration of apatites and clays (Altschuler, 1973).

Relatively little has been written about diagenetic minerals in coal. This is in part due to the difficulty in differentiating these minerals from minerals having other sources, and in part due to the diffuse boundaries of the subject. Transformations of minerals begin with weathering in the source rocks, are undoubtedly accelerated in the acidic swamp environments, proceed through all stages of coalification, and continue right up to the analysis in the laboratory. The latter phenomenon is evidenced by the formation of sulfates on coal surfaces shortly after polishing. The formation of secondary hydrated sulfates in a Nova Scotia coal field has been studied in detail by Zodrow and McCandlish (1978) and Zodrow et al. (1979). The effects of metamorphism on coal minerals other than clays has not been systematically studied. (See Raben, 1979; Teichmuller and Teichmuller, 1979.)

Another source of authigenic crystalline material are the organometallic complexes such as nitrates, acetates, oxylates, porphyrins, etc., formed within living tissues. Some of this material may be preserved in the coal (Firth, 1971). Unfortunately, the techniques used in this report would either destroy (LT ashing) or be insensitive (back-scattered electron images) to these phases. Although no definitive statement can be made concerning these phases, it is believed that they are not numerically significant.

In the course of this study, meteorite ablation products were recognized in coal for the first time (Finkelman and Stanton, 1979). Subsequently, Alexander et al. (1979) have also recognized these extraterrestrial objects in coal. Nevertheless, the contribution of cosmic dust in coal does not appear to be significant (see discussion of Ni in Section 3.22).

3.2 Modes of Occurrence of Trace Elements

3.21 Introduction

In this section, an attempt was made to bring together all of the information pertinent to the mode of occurrence of trace elements in coal. For many elements, this required a synthesis of the data in the literature and the data generated in this study. Wherever possible suggestions have been offered as to the most likely modes of occurrence.

Data for this synthesis were obtained from many different sources. The various authors who have been cited used different assumptions, approaches, and analytical techniques, while working with samples of different geographic location, geologic age, coal rank and type, geologic history, and geochemical environment. There should be little wonder that these authors failed to achieve a consensus on the mode of occurrence of many elements. However, if allowances are made for the intimately dispersed accessory minerals in coal, this diverse mass of data begins to make sense. This really should not be too surprising, since the trace elements in coal, as in other geologic samples, obey basic geochemical principles.

While reading this section, the following points must be kept in mind:

- The primary concern is with the mode of occurrence of the trace element in coal as mined. This may not be the same as the mode of the element entering the depositional basin. Indeed, many trace elements appear to have been quite mobile and may have existed in several different forms at various times during the geologic history of the deposit. Many stimulating discussions on the source of the elements, mode of entry, organometallic complexing, etc., have been set aside as being beyond the scope of this discussion.
- The phrase "associated with the coal substance" used in many reports cited in this section does not preclude an inorganic association for the trace element. Many authors (for example, Bethell, 1962) using this phraseology acknowledge that substantial amounts of fine-grained minerals may not be physically separated from the coal. Thus, the phrase is essentially equivalent

to the "inherent ash" discussed in Section 2.11 which includes both intimately admixed minerals and organically bound elements.

- Many of the conclusions were strongly influenced by this author's familiarity with the Waynesburg and Upper Freeport coals which appear to have large detrital components. (See Renton and Cecil, 1979, for an opposing viewpoint on the origin of the minerals in coal.)
- The conclusions, both tentative and firm, may reflect the author's inorganic geology background. Bias may also be introduced by the analytical techniques utilized which again favor inorganic associations. Nevertheless, the conclusions appear to be consistent with the observations of this author and much of those in the literature.

Before we examine the data, it would be worthwhile to review briefly the approaches that have been used to ascertain the modes of occurrence of trace elements in coal.

3.211 Sink-Float Separations - Literature Review

The most widely used approach involves sink-float separation of raw coal followed by analysis of the various Sp. G. fractions. Those elements concentrated in the heavier Sp. G. fractions are presumed to have inorganic affinities, whereas, those elements concentrated in the lighter Sp. G. fractions are presumed to have organic affinities. The organic/inorganic affinity or association of an element is a general form of the mode of occurrence. The determination of an element's affinity (association) relies largely on indirect or circumstantial evidence.

Horton and Aubrey (1950) conducted the first experiment to determine the organic/inorganic affinity of the minor elements in coal. They handpicked pure vitrain samples from three coals and separated them into at least five Sp. G. fractions. They then plotted the concentrations of 16 elements in each of the Sp. G. fractions and compared the resultant curves to idealized curves illustrating the proportion of an element contributed by the organic material.

Zubovic and co-workers (Zubovic et al., 1960, 1961; Zubovic, 1966, 1976) followed with a series of papers based on the separation of thirteen coals into two density fractions. By comparing the recovery of each of the elements against the proportion of organic/inorganic matter in each of the fractions, they were able to calculate the degree of organic/inorganic association of each element. In general, there is good agreement between their data and those of Horton and Aubrey (1950).

Ratynskiy and Glushnev (1967) looked at the organic/inorganic associations of eleven elements by separating forty-four coal samples into a number of Sp. G. fractions and spectrographically analyzing the coal and the coal ash. They reported their results in terms of the ratio of the concentration of each element in the <1.40 Sp. G. fraction over the concentration of the element in the >1.60 Sp. G. fraction.

More recently, Gluskoter et al. (1977) conducted a series of sink-float experiments, in which they separated eight coals into at least six Sp. G. fractions and a ninth coal into three Sp. G. fractions. They analyzed for up to 48 elements in each fraction. Gluskoter et al. devoted several pages (110-112) to a discussion of the calculation of organic affinities and to a table displaying the resultant values (Gluskoter et al., 1977: Table 25, pp. 116-117). However, in the summary of the elements' affinities, the data are presented (Gluskoter et al., 1977: Table 26) in purely qualitative groupings ("organic"; "intermediate-organic"; "intermediate-inorganic"; "inorganic"). The calculated organic affinity values are used merely as arbitrary cutoff points for these groups. Gluskoter et al. (1977, p. 115) emphasize that the elements in their Table 26 "were placed in these groups in a somewhat arbitrary manner and not strictly on the basis of the value for organic affinity."

In earlier papers based on the same set of analytical data (Gluskoter, 1975, p. 12; Ruch et al., 1974, p. 36), the following statement was made: "The numerical values thus determined (the organic affinities) are not given since they will vary with the particle-size distribution of the coal, the specific gravity of the liquids used to make the first (lightest) separation, and the size distribution of the mineral fragments in a single coal." They do not elaborate further on this significant point. However, it is worthwhile emphasizing the potential difficulties encountered in this approach.

Horton and Aubrey (1950) recognized these problems and stipulated that certain assumptions must be accepted for the conclusions based on fractionation of the trace elements by density separation to have validity. These assumptions are:

1. The variations in the relationship between total mineral matter and ash throughout any series of density fractions are negligible.
2. Negligible errors are introduced by regarding the total ash as indicative of the adventitious mineral matter in the fractions, thereby neglecting entirely the inherent ash.
3. The concentrations of the minor elements associated with the pure coal substance and with the adventitious mineral matter vary only to a negligible extent from one fraction to another.

In discussing these assumptions, Horton and Aubrey acknowledge that variations in trace element distribution would be expected owing to differences in mineral grain size and density.

Further complications in interpreting the sink-float data arise if minerals that concentrate particular elements behave differently than the bulk of the mineral matter. This is precisely what occurs with the fine-grain accessory minerals that are intimately admixed with the organic constituents. These minerals are rafted up to the lighter Sp. G. fractions by the organic material in which they are encased. Thus, the appearance of an "organic" association for the element is created (see Section 2.3).

In short, caution must be exercised in interpreting sink-float data. The results may not reflect the chemical environment of the element but rather the physical behavior of the minerals they are associated with.

The sink-float approach has also been used by Otte (1953), Hawley (1955), Ford (1977), Schultz et al. (1975), Fiene et al. (1979), and Kuhn et al. (1978); and probably by Leutwein and Rosler (1956) and Bogdanov (1965).

3.212 Variation of Trace Element Concentration with Ash Content

Nicholls (1968) noted that for an element entirely associated with the organic fraction of a coal, the concentration of that element in the whole coal is nearly constant with rising ash content, but the concentration of the element in the ash falls sharply with rising ash content. For an element associated with the inorganic fraction, the concentration of that element in the whole coal rises with increasing ash content, but its concentration in the ash content remains constant. Nicholls plotted the analytical value of an element in a coal or in coal ash against the ash content of the coal. He then interpreted the resultant diagram for degree of organic or inorganic affinity.

In a report on the distribution of trace elements in Indian coals, Chattergee and Pooley (1978) arranged the following twelve elements from thirteen samples by decreasing organic affinity:

Cu>Mo>Be>Co>Ni>Pb>Mn>Sb>Zn>Cd>Ti>Cr. This list is apparently derived from the correlation coefficient of each element with the ash content of each sample. The more positive the correlation coefficient, the lower the organic affinity.

Szilagyi (1971) used this approach to help elucidate the mode of occurrence of Mo, V, and Cr in Hungarian coals. Gindy et al. (1978) also used this approach on Egyptian coals, and Mukherjee and Ghosh (1976) on Indian coals. In the following discussions of the individual elements, several studies are cited in which attention is called to the relationship between the concentrations of the element and the ash content of the coal.

One assumption, basic to the premise outlined by Nicholls, is that the concentration of every element is uniform in each increment of ash content. That this premise may not necessarily hold true is evidenced by the extent of epigenetic, diagenetic, and authigenic mineralization in coal. If epigenetic solutions were to deposit, in coal, small quantities of a mineral containing one of the trace elements as a major constituent, there would be no appreciable change in the ash content. Instead, a substantial change in the content of the trace element with respect to the ash would occur. Conversely, elements can be selectively leached from the ash. Again, there would be no detectable change in ash content, but an obvious change in ash chemistry would occur. The abundance of authigenic minerals in coal is a testament to the mobility of the elements. It is this mobility that could undermine the basic premise of the approach used by these authors.

3.213 Leaching Characteristics

The behavior of an element during chemical attack of the coal by various solvents can offer insight into its mode of occurrence.

Miller and Given (1978) examined the leaching behavior of up to thirty elements in Sp. G. fractions of several lignites treated with ammonium acetate and 1 N HCl.

Filby et al. (1977) assumed that the pyridine insoluble fraction of coal consists purely of inorganic material. They also assumed that K is present only in an inorganic form. The inorganic and organic fractions of 21 elements in a coal were then calculated from the elemental data on the raw coal, solvent refined product, and pyridine insolubles normalized to K.

In the discussions of the individual elements, experiments are cited in which the leaching characteristics of a particular element were examined. See, for example, Dalton and Pringle's (1962) study of Ga and the extraction of F from coal by Lessing (1934).

In an interesting experiment, Kuhn et al. (1978) "demineralized" coal by leaching samples in HNO_3, HF, HCl, and H_2O. Based on the organic affinity estimates for 41 elements obtained from the sink-float data, Kuhn et al. calculated the concentrations to be expected in "demineralized" coal. It was found, for the Pittsburgh No. 8 coal, that the calculations based on the organic affinities over-estimated the amount to be anticipated in the "demineralized" coal for virtually every element! This result strongly suggests that the organic affinity estimates based on sink-float data may, in many instances, be greatly inflated.

The Rosebud seam, a lower rank coal than the Pittsburgh No. 8, contains more ion exchangeable cations. With this sample Kuhn et al. found the discrepancy between the calculated and analytical values for the "demineralized" coal not to be as dramatic. Nevertheless, for those elements with relatively high (>.5) organic affinities, the calculated values exceeded the analytical values in about two-thirds of the cases.

Kuhn et al. concluded that elements such as Si, Al, Li, K, Rb, Cs, and Be, which have high organic affinities based on sink-float data, may occur as finely disseminated minerals in the coal.

In all the leaching experiments it is assumed that the solvents are quantitatively effective. This assumption is suspect. Greer (1977) has demonstrated that substantial amounts of fine-grained pyrite in coal escape attack by nitric acid.

3.214 Correlation Coefficients

There appears to be a tendency to attribute similar modes of occurrence to elements that exhibit strong positive statistical correlations and to deny a similar mode to those elements that have negative correlations (see section on phosphorus).

This procedure is dangerous, particularly when bulk samples or multiple samples are used. It is the opinion of this author that positive correlation coefficients generally indicate a common source for the elements rather than a common mode of occurrence. This is illustrated nicely by the data of Cecil et al. (1979 A). Although there is an excellent positive correlation between many trace elements and the ash forming components, micromineralogical analyses indicate that these elements are not physically associated (Cecil et al., 1979 B). This situation could be brought about if the elements had a common source but were remobilized and reprecipitated in the depositional basin. For example, the chalcophile elements may have originally been associated with the clays or the ferromagnesium silicates. These minerals will readily break down in the generally acidic conditions in the swamp, thus releasing the associated chalcophile elements which would be rapidly precipitated by any available $S^=$ or $Se^=$. (See Section 2.18 for more complete discussion of this process.) This scenario requires a closed system for the elements with positive correlations; no unique source, no selective removal.

That the positive correlation coefficients are indicative of a common source is supported by the data on As and Hg in the Upper Freeport coal. These elements do not correlate with the majority of other elements, though they do correlate well with each other. In the discussion in Section 2.3, it was pointed out that As and Hg appear to have a common source.

Significant universal correlations among trace elements may not exist. The many strong positive correlations found by Cecil et al. (1979A) were obtained from samples of a single coal, the Upper

Freeport, whereas the data of Gluskoter et al. (1977), which displayed few strong correlations, were obtained from 114 coals from throughout the Illinois Basin. Many of these coals undoubtedly had different source areas reflecting different geochemical association.

Correlation coefficients obtained from sink-float separation of a single coal should have some relevancy in indicating common modes of occurrence for the trace elements. Unfortunately, few such data exist. Kuhn et al. (1978) found many strong positive and negative correlations in their data on separates from the Pittsburgh No. 8 and Rosebud coals, but no discussion of the significance of these correlations was offered.

3.22 Modes of Occurrence of Individual Elements

Antimony: Swanson et al. (1976) indicate the mean value for Sb in 799 U. S. coals of different ranks is 1.1 ppm on a whole-coal basis.

In the sink-float study of Gluskoter et al. (1977), Sb displayed a strong organic tendency in four samples and an intermediate affinity in four. In the study of Kuhn et al. (1978), Sb showed an inorganic tendency in one sample and an organic inclination in the other. Leutwein and Rosler (1956) and Otte (1953) found Sb to have an intermediate affinity, whereas Bogdanov (1965) lists Sb with those elements associated with the "organic substance." Filby et al. (1977) estimated that, in the coal sample they studied, 79 percent of the Sb was inorganically bound.

Antimony is considered to have strong chalcophile tendencies (Goldschmidt, 1954) and would likely be associated with the sulfides. Solid solution of Sb in pyrite is certainly possible in some samples. Dvornikov and Tikhinenkova (1973) found certain epigenetic pyrites in coal to be richer in Sb than epigenetic and diagenetic pyrites from other areas. No values for Sb in pyrite were given. This mode of occurrence is not likely to be significant. If all the Sb were to occur in this form, the pyrite would have to have a mean value of 100 ppm Sb. But in a survey of minor elements in sulfides, Fleischer (1955) found that in only 14 percent of the analyses reporting Sb did the concentration exceed 100 ppm. Cambel and Jarkovsky (1967) found no detectable Sb in pyrites from Czechoslovakian coals.

Minkin (personal communication, 1978) detected by EMP analysis low concentrations (up to 0.2 weight percent) of Sb in sphalerites from the Upper Freeport coal. Assuming all the Zn to be in sphalerites, the Zn/Sb ratio of this sample indicates that no more than 10 percent of the antimony can be accounted for in this association.

The only antimony mineral reported from coal are crystals of ullmannite (NiSbS) found by Spencer (1910) in a carbonate vein in a British coal.

No Sb-containing minerals were detected in any of the coal samples examined in the current study. However, in the sink-float experiments on the Waynesburg coal (Section 2.32) as well as on the Upper Freeport coal (B. Cecil, personal communication, 1979), Sb is concentrated, on a relative basis, in the sink fractions. This is characteristic of the behavior of the chalcophile elements associated with the accessory sulfides (see Section 2.18). It thus seems probable that a substantial amount of the Sb in these coals occurs in minute grains of Sb_2S_3 (stibnite) dispersed throughout the organic matrix. This mode of occurrence may well account for the apparent organic affinity displayed by Sb in the sink-float experiments. It is not surprising that grains of Sb_2S_3 have not been encountered; sphalerite is a trace constituent of the Waynesburg coal, yet Zn is 100 times as abundant as Sb in this sample.

Arsenic: The mean value for arsenic in coal is 15 ppm (Swanson et al., 1976).

Arsenic displayed inorganic tendencies in all the samples studied by Gluskoter et al. (1977), Kuhn et al. (1978), and by Ford (1977). Hawley (1955) found that As was concentrated in both the light and heavy Sp. G. fractions of a Nova Scotian coal. Leutwein and Rosler (1956) suggest that As may be associated primarily with the "organic substance." Bogdanov (1965) also found As to have a strong organic association. Filby et al. (1977) estimated that 52 percent of the As in their sample was inorganically bound.

According to Brown and Swaine (1964), arsenic commonly occurs either as or associated with sulfides. He found one percent As in pyrite separated from a mudstone in an Australian coal, equivalent to the total As in the section. Brown and Swaine suggest that the As in this sample may occur as arsenopyrite.

There appears to be little consensus on the mode of occurrence of arsenic in coal. It has variously been suggested that arsenic in coal is (1) associated with pyrite (Chapman, 1901; Crossley, 1946); (2) occurs as arsenopyrite (Duck and Himus, 1951; Wandless, 1959); (3) is organically combined (Noble, 1972; Duck and Himus, 1951); and (4) is associated with clay minerals (Kirsch et al., 1968). Much of the evidence in these earlier reports is circumstantial; some is contradictory (Kunstmann and Bodenstein, 1961).

The association of arsenic with pyrite seems to be well documented. Fleischer (1955) found about 10 percent of those studies reporting As in pyrite recorded values of one weight percent or more. There is no indication, however, if these were primarily high temperature phases. The possibility of admixed arsenopyrite must be considered in view of the fact that Cambel and Jarkovsky (1967) found essentially no As in pyrite from Czechoslovakian coals.

Nicholls (1968) believes arsenic to be mainly in the inorganic fraction, probably enriched by post-depositional reaction between sulphides and circulating groundwater. Dvornikov and Tikhinenkova (1973) found epigenetic pyrites in certain coals to have considerably higher As values than the epigenetic and diagenetic pyrites from other areas. Hokr (1978) reports both epigenetic and syngenetic arsenic in Czechoslovakian coals; the epigenetic As was associated almost exclusively with pyrite.

Minkin, Finkelman and others (1980) used optical, electron microprobe, and scanning electron microscope techniques in a detailed investigation of the mode of occurrence of arsenic in pyrite in Upper Freeport coal from the Homer City area, Pennsylvania. Polished blocks were prepared from columnar samples of the coal bed to represent particular vertical zones continuously from top to bottom. The initial selection of zones was based on chemical analysis of bench-channel samples. The electron microprobe data indicate that small amounts of arsenic (highest observed concentrations about 0.1 weight percent) are present at isolated points within pyrite grains at various strata of the coal bed, perhaps in small mineral inclusions formed and incorporated into the pyrite at the time of crystallization. Most of the arsenic (concentrations as great as 1.5 weight percent determined by electron microprobe analysis) is apparently in solid solution in pyrite, probably having been emplaced later as a result of reaction of pyrite with epigenetic arsenic-bearing solutions that pervaded the coal along fractures. In most pyrite grains the arsenic was found in pitted areas adjacent to fractures (Figures 32 and 33). In the two samples studied, from locations 1.8 km apart, arsenic in apparent solid solution in pyrite is found at comparable limited stratigraphic intervals below the top of the coal bed. This lateral consistency reinforces the concept that such arsenic was brought into the coal bed by water transported during a limited period (or periods) after the coal had formed and been fractured.

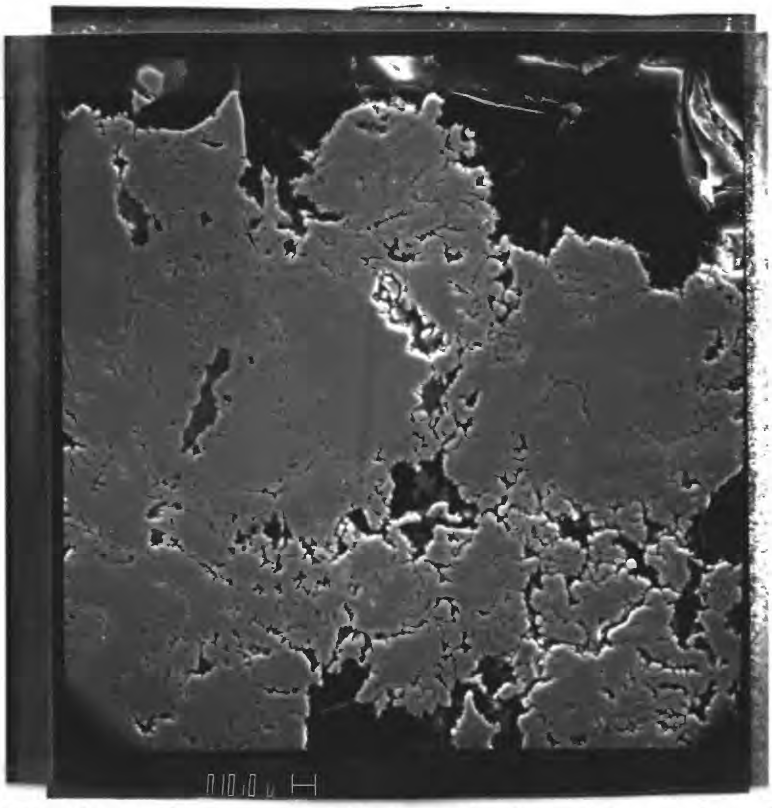

Figure 32. SEM photomicrograph of arsenic-bearing pyrite in the Upper Freeport coal. Smooth pyrite is arsenic-free. The series of spots down the center of the photograph marks the traverse of the EMP beam. (From Minkin, Finkelman et al., 1979).

Figure 33. SEM photomicrograph of arsenic-bearing pyrite in the Upper Freeport coal. The outer rim contains arsenic, the core is arsenic-free.

Because arsenic in the Upper Freeport coal bed seems to be totally associated with the pyrite, most arsenic in this coal should be removed during the physical cleaning process if fine grinding and gravity separation succeeds in removing most of the pyrite. Data on size-gravity splits (Finkelman et al., 1979) confirm this suggestion.

These data do not preclude the possibility of arsenic occurring in other associations, but it does represent the first definitive study on the mode of occurrence of this element in coal.

In the current study low levels of arsenic ($\lesssim$1 weight percent) were detected by the SEM-EDX system in pyrite grains from several different coals. No grains approaching arsenopyrite compositions were observed. Trace amounts of As were also detected in a chalcopyrite particle, a linnaeite grain, and in a strontium aluminum-bearing particle. The only particle observed in which arsenic was a major component was an As-Co-Ni-Fe-Se sulfide in the Pocahontas No. 3 coal.

Barium: The mean value for barium in coal is 150 ppm (Swanson et al., 1976).

In the sink-float study of Gluskoter et al. (1977), Ba displayed an organic affinity in three samples, an inorganic affinity in one, and an intermediate behavior in another. In the study of Kuhn et al. (1978), Ba behaved as if it were organically bound in the Pittsburgh No. 8 coal and as if it were inorganically bound in the Rosebud coal. Leutwein and Rosler (1956) found Ba to have an inorganic affinity, whereas in the study of Bogdanov (1965), Ba displayed an intermediate affinity.

Filby et al. (1977) estimated that 76 percent of the Ba in their sample was inorganically bound.

Nicholls (1968) found Ba to be associated with the inorganic fraction in the coals studied. He speculates that authigenic barium minerals or detrital barite may be responsible for the high barium content of some coal ashes. Nicholls suggests that the virtual restruction of barium to the heavy fraction of the coal studied by Hawley (1955) must mean that Ba is almost entirely located in Ba minerals and that no significant amount is associated with clay or the organics.

Barium is one of several elements (B and Sr are the others) that exhibit a distinct variation of concentration with rank, although Hildebrand and Hatch (1977) state that no general trend of Ba concentration with coal maturity was observed in the western coals. O'Gorman and Walker (1971) suggest that the high concentrations of Ba and Sr in low-rank coals are related to ion exchange with carboxyl groups. Miller and Given (1978), however, found that most of the barium in a North Dakota lignite was present in association with minerals. In the Wall seam, a subbituminous coal from the Powder River Basin, Wyoming, they found barium (and strontium) to be mainly in an acid insoluble form, perhaps as barite, in the lower half of the seam, whereas in the upper half, these elements were present primarily in the ammonium acetate soluble fraction, which is suggestive of an organic association.

O'Gorman and Walker (1971) found barium to be concentrated in lithotypes which had low ash contents. They speculate that finely divided barite might be the source, although they also suggest the possibility that both barium and strontium can be absorbed by illite. Leutwein (1966) found a positive correlation between the Ba content and the amount of clays in a profile of brown coal. This, of course, does not prove a cause and effect relationship.

Barium minerals (barite, $BaSO_4$ and witherite, $BaCO_3$) have been observed in coal and may be locally abundant (Reynolds, 1939). In addition, barytocalcite (?), alstonite (both $BaCa(CO_3)_2$) and witherite ($BaCO_3$) have been observed in several coals.

In the present study it was found that barium-bearing feldspars accounted for as much as one-sixth of the barium in the detritus rich carbominerite from the Waynesburg coal (Table 9).

Barite was observed as both an early and late (fracture fillings) authigenic phase in many coals. Gorceixite and other barium-bearing crandallite group minerals were found in all ranks of coal (peats through anthracite). The mode of occurrence of barium differed in the two samples with the highest barium contents (both >3200 ppm Ba in the ash). Barium occurred predominantly in the carbonates in the bituminous Alaskan coal, whereas in the

Beulah lignite, barium occurred exclusively as the sulfate. The abundance of barium minerals, as detected by the SEM, suggests a predominant inorganic association for barium in all ranks of coal. In this regard it is interesting to note that although barite was observed in roughly one third of all the coals studied, it was found in all six of the lignite samples (Section 2.141). The presence of some organically associated barium (attached to carboxyl groups) is certainly a possibility, particularly in lower rank coals.

Boron: The mean value for boron in coals is 50 ppm (Swanson et al., 1976). Boron (atomic no. 5), like beryllium, cannot be detected by the EMP or the EDX systems.

In the samples analyzed for this report, boron was found to be concentrated in the lighter fractions of the Waynesburg coal and LT ash (Appendix IIIA). The highest values for boron were detected in the low-rank Beulah lignite and in the low-ash Alaska and Indiana coals (Appendix IIIE).

Goldschmidt (1935) notes that of all the elements, boron demonstrated the greatest factor of enrichment when comparing the average percentage of the element in "rich" coal ash to the percentage in the earth's crust. He attributes the enrichment to the uptake by plants. Deul and Annell (1956) suggest that the high boron contents in the ashes of low rank coals were due to retention of plant boron. They state (p. 164) that boron is "perhaps the only element in coal ash which is directly attributable to the living plants which were the progenitors of coal."

Brown and Swaine (1964) could find no boron-containing minerals in Australian coals. Acknowledging that there was no direct evidence, they suggested that boron may be in part organically bound. In a detailed study of the mode of occurrence of boron in Bowen Basin coals, Swaine (1971) concluded that boron is mainly organically bound. He examined several possibilities for the occurrence of inorganic boron. He found no illite in the coals and a maximum of 17 ppm B in the kaolinite. No discrete boron minerals were detected, nor was boron detected in the pyrite, calcite, siderite, quartz or apatite.

In an attempt to determine paleosalinity, Bohor and Gluskoter (1973) studied the boron content of illites from Illinois coals. The concentration of boron in the illites ranged from 76 to 200 ppm. According to the tabulated data of Bohor and Gluskoter, illites in their samples represented about 25 percent of the mineral matter, which in turn represented about 15 percent of the coal. Thus, the boron in the illites would contribute no more than about 4 ppm B on the whole coal basis. Although Bohor and Gluskoter (1973) do not present data for boron on a whole coal basis, Gluskoter et al. (1977), using many of the same samples, reported a mean of 110 ppm for boron. It is clear that association with illites is not a major mode of occurrence for boron in these coals.

O'Gorman (1971) notes that there is a decrease of boron content with increasing rank of the coal. Bethell (1962) speculates that boron may be gradually removed with time or that there is a decrease in boron holding capacity of the coal with maturation. In this context it is interesting to note that Valiev (1977) found the proportion of silicate-bound B increased with the degree of coal metamorphism. Perhaps the decreased boron with rank may reflect the limited ability of clays to adsorb the B being released by the organic matter.

The sink-float experiments of Horton and Aubrey (1950), Hawley (1955), and Zubovic et al. (1961), show boron to have organic affinities. Boron exhibited a very strong organic affinity in most samples studied by Gluskoter et al. (1977) but demonstrated an equally strong inorganic affinity in one sample. Ford (1977) found B to concentrate in the lighter Sp. G. fractions of some samples and in the heavier Sp. G. fractions of other samples. As with beryllium, there appears to be an inverse relationship between boron and ash contents (cited in Bethell, 1962). This is clearly suggestive of an organic association. Nicholls (1968) states that it appears likely that in most coals the bulk of the boron is associated with the organic fraction. However, he cites a Jurassic coal from Montana in which much of the boron appears to be associated with the inorganic fraction.

The conclusion of Nicholls (1968) seems reasonable, but it is intriguing to speculate on the mode of occurrence of boron in those coals in which it appears to be inorganically bound.

Tourmaline, a complex boro-silicate with up to 3 weight percent boron, has been reported in several studies of coal minerals (see Appendix II). Optical characterization of the light fraction of the LT ash from the Waynesburg coal revealed numerous minute (∿10μm) tourmaline crystals (Figure 6). Detrital tourmaline crystals this size have been known to survive several cycles of sedimentation (Krynine, 1946), nor are authigenic tourmalines uncommon in sedimentary deposits. Regardless, it seems that tourmaline may be more abundant in coals than heretofore suspected. Nevertheless, the small size of the crystals and, more importantly, the low concentration of the boron, argue against this being a major mode of occurrence of boron in coal. Nor does there appear to be any evidence to substantiate the suggestion of Wandless (1957) that borates may be present in coal. The most likely solution seems to be in the boron content of the clays. Saline clays can contain several thousand ppm B, averaging about 1000 ppm (Wedepohl, 1974). Thus, in an ash-rich, illite-rich coal with a strong marine influence, significant amounts of boron may be inorganically associated.

Beryllium: The mean value for beryllium in coal is 2 ppm (Swanson et al., 1976). Neither the EMP or the EDX systems can detect beryllium (atomic no. 4). Thus, beryl ($Be_3Al_2Si_6O_{18}$), the only major Be bearing mineral, would appear to be an aluminum silicate in the SEM or in the EMP.

There is abundant evidence in the literature to suggest a strong organic affinity for Be. Few other elements so consistently report to the organic fraction in float-sink experiments (Horton and Aubrey, 1950; Otte, 1953; Hawley, 1955; Leutwein and Rosler, 1956; Miller and Given, 1978; Gluskoter et al., 1977; Zubovic et al., 1960). Only Bogdanov (1965) found this element to have a strong inorganic affinity. According to Ratynskiy and Glushnev (1967), the concentration of Be in Sp. G. splits shows little variation. They suggest that accumulation of Be in coal is due to both concentration by organic matter and to inflow of terrigenous material.

Goldschmidt and Peters (1932) note that Be is more highly concentrated in coal than in detrital sedimentary rocks. Stadnechenko et al. (1961) pointed out that beryllium is concentrated in vitrain more than in fusain. They suggest methods of Be transport and accumulation in coal. In a study of the distribution of trace elements in the Illinois Basin, Zubovic (1966 B) found Be concentrated in the near source margins. He attributes this to the chelating properties of the small, highly charged Be ion which would form stable, insoluble organic complexes.

Perhaps the most telling argument for an organic association is that the beryllium content of coals varies inversely with ash content (Jedwab, 1964; Razdorozhnyy, 1967; Miller and Given, 1978).

No attempt was made in this study to determine the mode of occurrence of beryllium, nor were any beryllium-bearing minerals recognized. In the sink-float experiments of both the Waynesburg LT ash and coal, beryllium was concentrated in the lighter Sp. G. fractions.

Although Be can replace Al in a tetrahedral crystallographic site, the Be content of clays is only a few ppm (Wedepohl, 1969). It would not appear likely that this mode would account for a substantial part of the Be coal.

Bismuth: There is little information in the literature on bismuth in coal. Swanson et al. (1976) do not report mean values for bismuth because its concentration, even in the ash, is generally below the limits of detection (∿10 ppm by optical emission spectroscopy).

Wedepohl (1969) cites two studies on European coals and bitumen samples in which the average value for bismuth is about 1 ppm. Goldschmidt (1954) notes that bismuth is concentrated in the ash of some coals, but no values are given. Brandenstein et al. (1960) report a distinct enrichment of Bi in the acid insoluble fractions of coal and bitumen samples but give no further details.

Geochemically, bismuth is distinctly chalcophile, although in magmatic minerals it can substitute for calcium and the rare earths, especially in yttrium minerals (Goldschmidt, 1954). The detection of Bi in xenotime would make a strong argument for a detrital source for this mineral. Apparently, Bi does not readily fit into the pyrite structure. Of the 17 studies reporting Bi in pyrite, only one found more than 50 ppm (Fleischer, 1955). Cambel and Jarkovsky (1967) did not find any Bi in the pyrite from Czechoslovakian coals.

Only one particle containing major amounts of Bi was detected in this study, a bismuth sulfide (perhaps bismuthinite) in the

South African coal. Trace amounts of Bi were detected in a sphalerite grain and a galena particle. Bismuth was not detected in any of the coal samples analyzed for this report.

It is probable that bismuth is associated with the sulfides in coal, perhaps as accessory sulfides (bismuthinite) dispersed throughout the organic matrix. Due to the low concentration of bismuth in coal, it is not surprising that only one such particle was encountered.

Bromine: Neither Swanson et al. (1976) nor Zubovic et al. (1979) report values for bromine. Wedepohl (1974) cites several studies reporting bromine with the average about 10 ppm. Gluskoter et al. (1977) give the following mean values for Br: 13 ppm in Illinois basin coals; 12 ppm in Eastern U.S. coals; and 4.7 ppm in Western U.S. coals. Kuhn et al. (1978) reported Br values of 12 ppm for the Pittsburgh No. 8 coal from West Virginia and 1.6 ppm for the subbituminous Rosebud coal from Montana. The Br content of the Upper Freeport coal varied from 2 to 90 ppm in eight samples.

Gluskoter et al. (1977) and Kuhn et al. (1978) report that bromine consistently had the highest organic affinity of any element. In the sink-float separation of the Waynesburg coal, bromine was concentrated on a relative basis in the sink fractions (Appendix IIIA). Recalculating these data to absolute values, it was found that 70 percent of the Br in each size split was concentrated in the two lighter Sp. G. fractions. Filby et al. (1977)

estimated that 30 percent of the Br in their sample was inorganically bound; this was the lowest value for inorganic association of the 21 elements considered.

Finkelman and Cecil (unpublished data) have recently designed an experiment to evaluate the effect of ashing on the behavior of volatile elements; a sample of whole coal and a sample of the low- and high-temperature ash of that coal were analyzed by instrumental neutron activation (INA). One third of the Br was lost during the LT ashing process. Recalculated on a whole coal basis, this means that about 98 percent of the bromine was volatilized. Lutz et al. (1978) also observed the loss of Br during the LT ashing of a coal. This behavior may be characteristic of organically bound volatile elements (see comments on Se).

Wedepohl (1974) notes that there is a strong correlation between bromine and organic carbon in sedimentary rocks. In Figure 34, the Br contents of several samples from a column of the Upper Freeport coal are plotted against ash content. A correlation coefficient of -0.91 was obtained, which again suggests a strong organic association for Br. It is possible that some Br in low Br coals is inorganically bound. For more detailed discussion, see the section on iodine.

It is interesting to note that the only Br detected by the SEM was associated with a galena particle imbedded in clay (Spitzbergen sample). Nevertheless, it appears that the bulk of the bromine, perhaps as much as 98 percent, is organically associated.

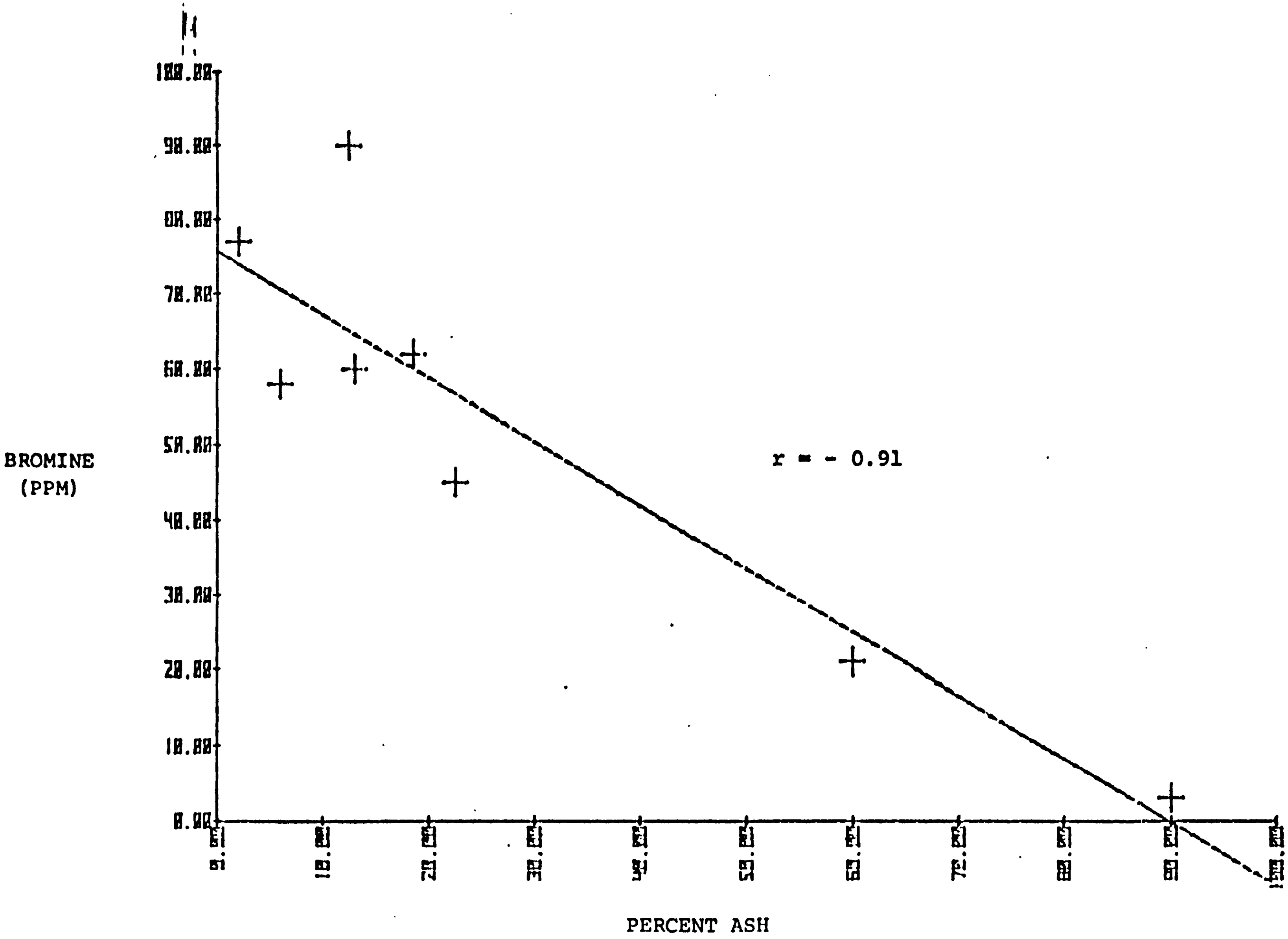

Figure 34. Distribution of bromine with respect to ash content inthe Upper Freeport coal.

Cadmium: The mean value for cadmium in U. S. coals is 1.3 ppm (Swanson et al., 1976).

In the sink-float study of Gluskoter et al. (1977), cadmium displayed a strong inorganic affinity. Gluskoter and Lindahl (1973) convincingly demonstrated that cadmium quantitatively occurs in sphalerite in Illinois Basin coals. Godbeer and Swaine (1979), however, could find no direct relation between cadmium and zinc contents in the low-Cd Australian coals. This observation may indicate that the cadmium content of sphalerites varies from coal to coal. Bogdanov (1965) found Cd (and zinc) to be associated with the "organic substance."

Finkelman et al. (1979) demonstrated that cadmium and zinc behave similarly in the size-gravity separation of the Upper Freeport coal (Table 15). In the present study, cadmium was observed in the energy dispersive spectrum of sphalerite particles from several samples. Minkin (personal communication, 1979) reports as much as 2 weight percent cadmium in sphalerites from the Upper Freeport coal. It seems reasonable to anticipate that the bulk of the cadmium in coal occurs in association with sphalerite.

Cesium: The mean value for cesium in 617 coal samples from the Eastern U.S. is 1.1 ppm (Zubovic et al., 1979). Gluskoter et al. (1977) report mean values for Cs to be 1.4 ppm in Illinois Basin coals, 2.0 ppm in Eastern U.S. coals, and 0.42 in Western U.S. coals.

Geochemically cesium is concentrated in K-bearing minerals such as feldspar and micas. There is little information in the literature on the occurrence of this element in coal. The large size and low charge indicate that cesium should have a low organic affinity. This is substantiated by the data of Gluskoter et al. (1977) in which cesium exhibits one of the lowest organic affinities of any element. Filby et al. (1977) estimated that 96 percent of the Cs in their sample was inorganically bound. Solodov et al. (1975) found that the Cs content of Russian coals increased with increasing ash content. But Razdorozhniy and Petrus (1975) found that Cs in Dnieper Basin brown coals varied inversely with ash and concluded that it is associated with the organic matter.

In this study cesium was detected only in the INA data from the Waynesburg sink-float experiments (Appendix IIIA). In the LT ash cesium was concentrated in the lighter fractions. In the size-density experiment on the coal, cesium was concentrated in the 1.5 - 1.7 Sp. G. splits. Unfortunately, spectroscopic interferences obscured the behavior of K in these samples. Nevertheless, the data is not inconsistent with an inorganic association for cesium, either in the feldspars, micas, or clays.

Chlorine: Given and Yarzab (1978) give the following values for chlorine in U. S. coals:

Samples	Number	Mean Cl (ppm)
All samples	444	580
Interior Province	72	1030
All samples less Interior Province	372	500

X-ray fluorescence analysis of 656 whole coal samples gave a mean value, for Cl in Appalachian coals, of 629 ppm with a maximum value of 2500 ppm (Finkelman, unpublished data).

The chlorine content of coals is affected by marine influence. Coals of the Illinois basin which accumulated under saline conditions have much higher Cl contents than non-marine coals. Gluskoter and Ruch (1971) found that the Cl content of coal was closely related to the Cl content of the associated groundwater. They suggest that the present chlorine content of the coal in the Illinois Basin is the result of an equilibrium between the coal and the groundwater currently in contact with the coal.

Literature on the significance of chlorine in coal is voluminous. Watt (1968), Bethell (1962), Gluskoter and Ruch (1971), and Gluskoter and Rees (1964) summarize various aspects of the research on chlorine and the various suggestions on its mode of occurrence.

Basically, there are two schools of thought on the mode of occurrence of chlorine in coal. The first school believes that chlorine occurs in coal almost entirely as inorganic chlorides, predominantly NaCl. The other school believes that chlorine occurs partially in combination with the organic matter. In his thorough review of the problem, Watt (1968, p. 61) states that, "In spite of the considerable amount of experimental work that has been done on this problem, it cannot be said that it is yet possible to give a clear and sharply defined account of the mode of combination of chlorine in coals."

Gluskoter and Ruch (1971), however, in a detailed study of the stoichiometry of the Cl, Na, and K leached from coal reversed an earlier suggestion by Gluskoter and Rees (1964) that most of the Cl in Illinois coals occurs as inorganic halides, and concluded that substantial amounts of Cl are organically bound.

Evidence from the present study tends to support this conclusion. Efforts were made to isolate the LT ash fraction (Sp. G. <2.2) in which halite (NaCl) would be found. Only a few small crystals (Figure 35) were detected in the coal with the highest chlorine content (an Upper Freeport coal with 2200 ppm Cl). A similar, but unsuccessful, attempt to locate halite crystals was made on the three English coals (Cl reported to be about 0.5 weight percent). In these coals Cl was detected by the EDX system in the vitrinite. No corresponding Na was detected. This is consistent with the observations of J. Minkin (personal communication, 1979). Using an EMP, she found up to 0.3 weight percent Cl in vitrinite from the Upper Freeport coal and up to 4 percent in the Ferron coal. She, too, feels that the Cl is organically associated, as comparable levels of cations such as Na or K were not found.

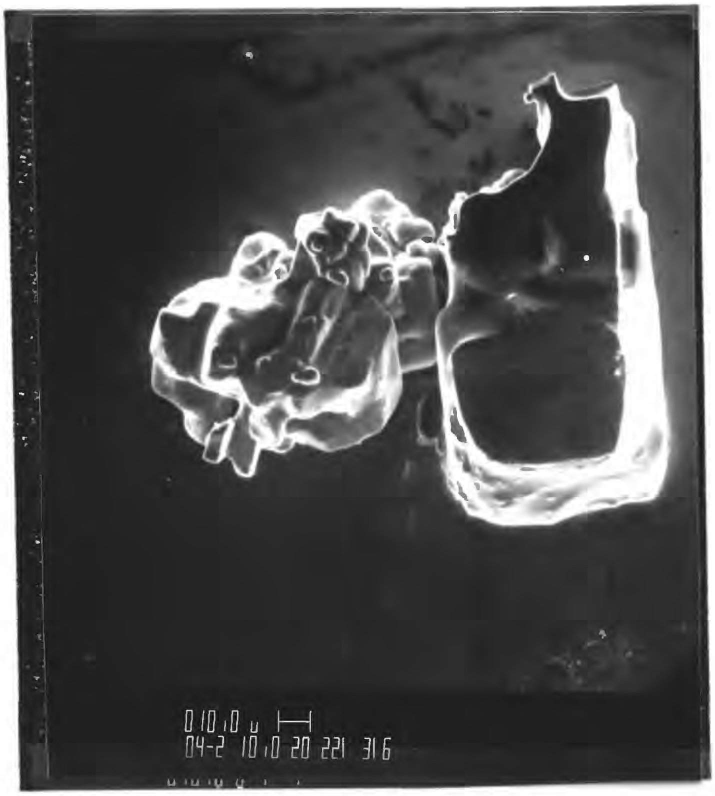

Figure 35. SEM photomicrograph of halite crystals.

Small amounts of Cl were detected by the SEM-EDX system in several clays. It is possible that the Cl detected may have been from the surrounding organic matter. The only other salt grains encountered were an intergrowth of sylvite (KCl) and bloedite $\{Na_2Mg(SO_4)_2 \cdot 4H_2O\}$ from the LT ash of the Waynesburg coal, and a grain of sylvite in the Ferron coal. Several polished sections were prepared using oil based polishing slurries to avoid dissolving the halides, but none was found. Lee et al. (1978), using the SEM, report traces of halite and sylvite from two Appalachian coals.

As part of the study of the Upper Freeport coal, an X-ray fluorescence technique was developed to determine the chlorine content of whole coal. The Cl values for the Upper Freeport coal, plotted against the ash content, revealed a surprisingly strong negative correlation ($r = -0.95$, Figure 36). It is thus evident that Cl is unrelated to the ash in this sample. This relationship and the paucity of apatite grains (frequency of occurrences is <10 percent; see Table 8) shed doubt on the significance of the suggestion by Nelson (1953) that some chlorine may occur as water-insoluble chlorine-bearing minerals such as chlorapatite or sodalite.

It seems probable that much of the chlorine in coal occurs in association with the organic matter. Different types of bonding would account for the differences in the leaching characteristics of Cl. (Bethell (1962) suggests that some Cl may be ionically bonded to nitrogen atoms.) Where Na + K ions are available, halides will form, which may be of local significance.

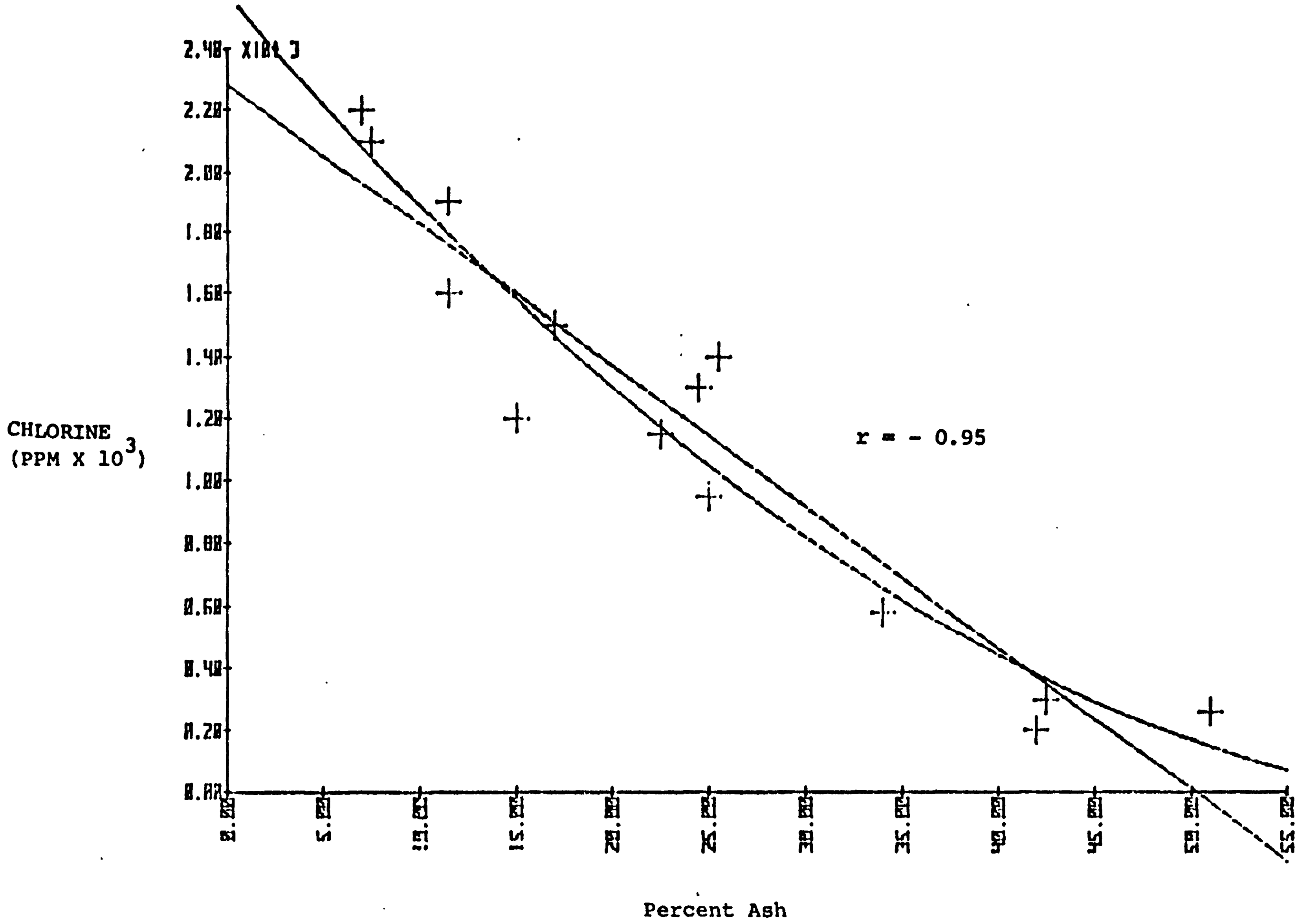

Figure 36. Distribution of chlorine with respect to ash content in the Upper Freeport coal. First and second order regression lines are shown.

Chromium: The mean value for chromium in coals is 15 ppm (Swanson et al., 1976).

Information on the mode of occurrence of chromium in coal is sparse and inconclusive. Based on the irregular variation of chromium content with ash, Szilagyi (1971) concluded that Cr in the Hungarian coals studied was concentrated as a result of groundwater enrichment. Otte (1953), Leutwein and Rosler (1956), and Hawley (1955) found Cr to be predominantly associated with the "coal substance." Miller and Given (1978) found Cr to have a high degree of organic association in the North Dakota lignite. The sink-float data of Gluskoter et al. (1977) show a wide range of organic affinities from a clear inorganic association in one sample to a distinct organic association in another. The data of Horton and Aubrey (1950) also show a wide range of organic association (0-100 percent). Zubovic et al. (1961) report the percent organic affinity for chromium to be 55 percent, an intermediate value. Bogdanov (1965), Schultz et al. (1975), and Ford (1977) all found Cr to behave as if it were inorganically bound. Filby et al. (1977) estimated that 100 percent of the Cr in their sample was inorganically bound.

In this study few chromium-bearing mineral grains were detected aside from the abundant "chromites" from the Waynesburg coal (discussed in Section 2.1211). The "chromites" were sufficiently abundant to account for the chromium in the lithotype sample studied (Table 9). It was suggested earlier that the "chromites" were precipitated from solutions that percolated through fractures in the coal. This is, of course, consistent with the suggestion of Szilagyi (1971); the epigenetic origin accounting for the poor correlation between the Cr and ash contents. Moreover, if Cr occurred in irregularly distributed, finely disseminated particles, it could account for the inconclusive sink-float data.

However, the fact that chromites were not found in any other coal indicates that this may not be a widespread mode of occurrence.

According to Nicholls (1968), chromium is largely associated with the inorganic fraction of coal. He rules out the possibility of detrital chromite because Cr exhibited a tendency for marginal enrichment in several coals. Nicholls notes that chromium is distributed between the light and medium separated fractions of coal and suggests that it is likely that the Cr is associated with finely divided clays intimately mixed with the organic matter. Nicholls further states that the accumulation of Cr in coals is due to post-burial sorbtion by clays.

The observations of Nichols (1968) are in agreement with the data on the Waynesburg coal where Cr is concentrated in the lighter fractions of both the coal and the LT ash (Appendices III A and C).

Nicholls' suggestion that Cr is likely to be associated with the clays seems reasonable, although the possibility that some Cr is associated with finely divided chromites (authigenic or detrital) should not be dismissed.

Cobalt: The mean value for cobalt in coal is 7 ppm (Swanson et al., 1976).

Cobalt is one of the few elements that can easily substitute in the pyrite lattice (Deer et al., 1962), although Goldschmidt (1954) indicates that the incorporation of Co in the pyrite structure is more effective in the high temperature deposits. Brown and Swaine (1964) report that Co was not detected spectrographically in pyrite from Australian coals. Nor was it detected in this study by IMP analysis of pyrite from the Waynesburg coal or by EMP in pyrites from the Upper Freeport coal (J. Minkin, personal communication, 1979). In contrast, IMP analysis of pyrite from the Upper Freeport coal indicated concentrations of several hundred ppm Co. Cambel and Jarkovsky (1967) found 30-50 ppm Co in the pyrites from Czechoslovakian coals.

Reports of discrete cobalt minerals are rare. Des Cloizeaux (1880) refers to the occurrence of linnaeite $\{(Co,Ni)_3S_4\}$ in a Welsh coal. Goldschmidt (1954) also notes the occurrence of distinct crystals of linnaeite in coal seams. Brown and Swaine (1964) could not find cobalt in mineral form in any of the many Australian coals they examined.

In the present study, linnaeite and linnaeite group minerals were found in five coal samples, including two anthracites and the meta-anthracite (see Table 10). It is tempting to suggest that the presence of linnaeite group minerals in coal is characteristic of higher rank coals. More data is, of course, necessary. Swaine (1961) suggests that linnaeite might form under poor drainage conditions where cobalt shows increased mobility.

In the sink-float data of Gluskoter et al. (1977), Co consistently demonstrates a strong organic affinity. In one sample, Co had the highest organic affinity of any element. In the studies of Zubovic (1961), Otte (1953), and Horton and Aubrey (1950), Co had an intermediate behavior. Leutwein and Rosler (1956) found Co to have inorganic tendencies, as did Hawley (1955), who found it to be concentrated in the sink fraction of the Nova Scotia coal. Filby et al. (1977) estimated that 83 percent of the Co in their sample was inorganically bound.

In the sink-float experiment on the Waynesburg LT ash, cobalt was enriched in the sink fraction by a factor of 3. This enrichment, although not as strong as that of Pb and Zn, was stronger than that of Cu (Appendix IIIA). Modest relative enrichments in the heavy fractions were noted in the size-gravity separations of the Waynesburg coal (Appendix A) as well as in the Upper Freeport coal. These data argue for an inorganic association for cobalt. Zubovic (1976) notes that the uniform distribution of Co throughout the Illinois basin is indicative of low organic affinity.

Nicholls (1968) found cobalt in the heavy fraction of an English coal and suggested a sulfide association. He suggests that coprecipitation with iron in sulfides is the most probable mechanism of incorporation of cobalt in most coals with some post-burial enrichment by sulfide reactions. He does not rule out the possibility of some organically bound cobalt.

Notwithstanding some of the sink-float data, there seems to be no direct evidence to suggest an organic association for cobalt.

In all probability, most of the cobalt is associated with the sulfides, perhaps some in solid solution with pyrite. Minkin and Finkelman (unpublished data) found Co to increase with iron in concentrates of pyrite from the Upper Freeport coal. If all the cobalt were associated with pyrite, the pyrite would contain several hundred ppm Co. This concentration should have been detected by the various analytical techniques mentioned above. It therefore seems reasonable to expect that a substantial amount of Co occurs as linnaeite group minerals. Perhaps some cobalt also occurs associated with the clay.

<u>Copper</u>: The mean value for copper in coal is 19 ppm (Swanson et al., 1976).

There is no question that substantial amounts of copper in coal occurs in the mineral chalcopyrite ($CuFeS_2$). Its presence in coals has been reported in numerous studies (Bethell, 1962; see Appendix II). Furthermore, chalcopyrite had the highest frequency of occurrence of all the accessory sulfides observed in this study (Table 10), occurring in more than one third of all the coals examined (Table 8). In the attempt to quantify the mode of occurrence of the trace elements in the Waynesburg coal (Section 2.173), about 75 percent of the copper was accounted for by chalcopyrite particles. This was in spite of the fact that the lithotype used in this sample (carbominerite) was deficient in macerals with which chalcopyrite is commonly associated.

Ion probe analysis of Waynesburg coal pyrites indicates that they contain less than 100 ppm Cu. If this amount of Cu were uniformly distributed throughout all the pyrite, it would account for only a few percent of the copper in this coal. EMP analysis of pyrites from the Upper Freeport coal (J. Minkin, personal communication, 1979) indicates Cu values generally below the limits of detection (∿100 ppm). Brown and Swaine (1964) found Cu in Australian pyrites to be at the ppm level or below the limits of detection. Cambel and Jarkovsky (1968) found up to 50 ppm Cu in the pyrite extracted from Czechoslovakian coals. It does not appear that solid solution of copper in pyrite is a major mode of occurrence for this element.

Several other copper-bearing phases have been reported (bornite, malachite; see Appendix II), but they appear to be of minor or of only local importance.

In this study, the only copper-bearing phases detected, other than chalcopyrite, were copper sulfides in the Washington coal and the coal from Brazil, and a copper oxide in the Spitzbergen coal.

It has been suggested that copper in coal is, in part, organically bound. Reynolds (1948) has demonstrated the association of copper with specific macerals. Otte (1953) and Leutwein and Rosler (1956) indicate that copper is associated with the "organic substance." In the sink-float experiments of Gluskoter et al. (1977) copper exhibited some organic affinity in several samples and inorganic leanings in other samples. Bogdanov (1965) found Cu to have an intermediate affinity. In the studies of Schultz et al. (1975), Zubovic (1961) and Horton and Aubrey (1950), copper showed a tendency towards an inorganic association. Nicholls (1968) suggests that copper is in part organic and in part inorganic, most of the copper being located in the sulfides.

Miller and Given (1978) found that in addition to traces of copper in pyrite, most of the copper in their low rank coals was in the acid-soluble lighter specific gravity fractions. They suggest that copper is either in ion exchangeable complexes or in chelate complexes.

In the sink-float experiment on the Waynesburg LT ash, copper showed a mild concentration in the float fraction (Appendix IIIB). This could indicate that some of the fine-grained chalcopyrite may have been trapped in the clay fraction, or copper may have been absorbed onto the clays. An unknown factor in these considerations is the behavior of any organically bound copper. It is not clear what form the organically bound copper would be in upon ashing and how it would behave in the subsequent sink-float separations.

In the sink-float separation of the Waynesburg coal, copper was concentrated in the lighter fractions. This is attributed to the rafting effect of the light organic particles buoying up the finely divided chalcopyrite grains.

The evidence seems to indicate that significant amounts of copper occur as chalcopyrite in most coals, but organically bound copper may be important in low rank coals.

Fluorine: The mean value for fluorine in U. S. coals is 74 ppm (Swanson et al., 1976).

The correspondence of fluorine and phosphorus contents in some coal samples have led many people to assume that fluorine is to be found in fluorapatites (Crossley, 1944; Francis, 1961; Swaine, 1975). Wandless (1957) questioned this assumption. Durie and Schafer (1964) found that fluorine and phosphorus are not always associated in a single mineral. They conclude that in some coals almost all the fluorine occurs as fluorapatite; in other samples it may occur in fluorapatite and in other (unspecified) fluoride minerals. Lessing (1934) found F in British coals to be concentrated in the fusain compared to the vitrain, clarain and durain. He found the greater proportion of F to be extractable by dilute NaOH and concluded that most of the F was present as fluorite (CaF_2).

Fluorine could also substitute for OH^- in clays and micas. Wedepohl (1972) cites several studies that report percent concentrations of fluorine in these minerals. Bethell (1962) suggests the possibility that some fluorine may be ionically bound in the coal.

No detailed sink-float data on F appear in the literature. Miller (1974) feels that the apparent organic association of F (and P) in the samples he studied may be caused by finely disseminated particles of fluorapatite that cannot be separated from the coal by washing. Unpublished data on F in the Upper Freeport coal (B. Cecil, personal communication, 1979) show no systematic variation of F with Sp. G. fraction in most splits (in one sample F was concentrated in the sink 1.8 Sp. G. fraction).

Apatites have been found in many coals (Appendix II), but the abundance of apatite in the 79 coals examined for this study appears to be negligible. In no more than one or two coals did there appear to be sufficient apatites (assuming them to be fluorapatites) to account for the fluorine. It appears that F associated with apatite may be of only local significance.

The only other F-bearing minerals encountered were the authigenic (?) amphiboles in the Waynesburg LT ash. Finkelman and Stanton (1978) state that in the Waynesburg coal far more fluorine is associated with the amphibole (∿0.2 weight percent F) than with the rare apatite. As similar F-bearing amphiboles were not found in any other samples, it would seem that this mode of occurrence of F is also of only local significance.

The problem of the mode of occurrence of F remains unresolved. It is possible that this element has a very complex mode, occurring in apatites, fluorites, amphiboles, clays and micas. In individual coals one form may dominate over the others.

Gallium: The mean value for gallium in coals is 7 ppm (Swanson et al., 1976).

The geochemical behavior of gallium is dictated by the similarity in size of the trivalent gallium cation with that of aluminum. Because of this similarity, most of the gallium in the lithosphere is found in aluminum minerals (Goldschmidt, 1954). However, the sink-float data of Zubovic (1961), Otte (1953), Horton and Aubrey (1950), indicate that gallium has a strong organic affinity. The data of Gluskoter et al. (1977) show a range of affinities from organic to inorganic. Leutwein and Rosler (1956) found Ga to have inorganic tendencies. Ratynskiy and Glushnev (1967) suggest that gallium occurs in both the organic fraction of the coal and the inorganic fraction, particularly the clays. They indicate that there is a good correlation between Ga content and clay concentration in their samples. Nicholls (1968) also suggests organic and inorganic associations for Ga. He states (p. 277) that "a certain amount of gallium may be associated with the inorganic fraction of the coals, but in gallium-rich coals this element is also associated with the organic fraction." Roberman (1973) found a negative correlation between Ga and ash content. He suggests that this indicates Ga was introduced during periods of weak tectonic activity.

Dalton and Pringle (1962) were able to extract Ga from coal only with HF. They concluded that most of the Ga was associated with the dispersed alumino-silicates, but between 9 and 46 percent may be organically associated or in the fixed adventitious inorganic matter. Bethell (1962) cites a study in which the gallium content of a coal did not increase with purification from the ash, which suggests an inorganic association. Zubovic (1966 B) notes that gallium exhibits near-source enrichment in the Illinois Basin, indicative of strong chelating properties. Gallium, however, showed somewhat more variation than other elements (Be, B, Ge) which are also considered by Zubovic to be organically bound.

The SEM offered little evidence as to the occurrence of gallium in coal. Gallium was detected in a lead selenide, a lead sulfide, and in the montroesite from the Venezuelan asphaltite.

Wedepohl (1972) indicates that the $\frac{Ga \times 10^3}{Al}$ ratio of sedimentary rocks is fairly consistent at about 0.2. The coal samples examined in this study were analyzed by a semiquantitative emission spectroscopic technique (Appendix IIIC), so individual ratios are subject to large errors. However, there is a clear trend of increasing Ga/Al ratio with increasing specific gravity fractions in both the Waynesburg LT ash and the coal. In contrast, there is a small but steady decrease in gallium content in these samples. One explanation for this observation is that there is a non-aluminum-bearing heavy mineral component that contains gallium.

Goldschmidt (1954) notes that a subordinate amount of gallium is not associated with aluminum but enters into certain sulphide minerals, which indicates that the metal has some chalcophile character. Wedepohl (1972) cites analysis of sphalerites with up to 1000 ppm Ga. He notes that high Ga concentrations are characteristic of low temperatures of formation. Chernevskii (1975) found Ga in sphalerites from Russian coals. It is therefore not unreasonable to expect some gallium in the sulfide fraction of the Waynesburg coal. Although the influence of this sulfide-associated gallium is detectable in the heavy Sp. G. fractions, no more than a few percent of the gallium in the sample can have this mode of occurrence.

It is interesting to note that the low-ash Indiana Block coal has one of the lowest Ga/Al ratios. If this ratio is valid, it would argue against substantial organic accumulation of gallium.

It would appear from the foregoing discussion that there is little consensus on the way gallium is incorporated in coal. Nevertheless, the evidence for substantial inorganic association of gallium is far more compelling than the largely circumstantial evidence indicating organic association. Dalton and Pringle (1962) acknowledge that substantial amounts of clay cannot be physically separated from even the finest and lightest fractions of coal. It seems reasonable that the gallium in these intimately held clays is being interpreted as organically bound gallium. If so, it would seem that the bulk of the gallium in most coals is associated with the clays; a few percent is associated with the sulfides; and perhaps some, but no more than a few percent, may be organically bound.

Germanium: The mean value for germanium in Eastern coals is 6.5 ppm (Zubovic et al., 1979). Gluskoter et al. (1977) report a mean value of 1.6 ppm Ge for Eastern U. S. coals, 6.9 ppm for Illinois Basin coals, and 0.91 ppm for Western U.S. coals.

Germanium in coal has received a great deal of attention because of the extraordinarily high concentrations of this rare element in the ashes of some coals and lignitized wood. Goldschmidt (1954) reports on a British coal with 1.6 percent GeO_2 in the ash, and Stadnichenko et al. (1953) report 7.5 percent Ge (10.9 GeO_2) in the ash of wood coal from the University of Maryland, College Park campus. These are, admittedly, exceptionally high values, but concentrations of Ge in excess of 1000 ppm are not uncommon (see Table 32-L-1, Wedepohl, 1970; Bethell 1962). Consideration has been given to coal as an economic source of germanium. Weber (1973) states that coal may constitute the largest germanium reserves available in the future.

The literature on germanium in coal is voluminous. Reviews on the subject can be found in Breger, 1958; Bethell, 1962; Wedepohl, 1970; Abernethy and Gibson, 1963; and Swaine, 1975.

There appears to be agreement that most of the germanium in coal is of secondary origin, perhaps absorbed from percolating solutions (Swaine, 1975); this has led to the near universal concentrations of Ge at the tops and bottoms of coal beds.

Numerous studies have indicated an association of Ge with the organic fraction of coal (see Wedepohl, 1970; Swaine, 1975; Bethell, 1962; Ratynskiy et al., 1966). Equally numerous studies have discussed how Ge may be bound to the organic matter in coal (see Wedepohl, 1970; Manskaya and Drozdova, 1968; Sofiyev et al., 1964). With the possible exception of bromine, germanium appears to have the highest organic affinity of any element as determined by sink-float testing (Gluskoter et al., 1977; Ratynskiy and Glushnev, 1967; Bogdanov, 1965; Zubovic et al., 1960; Leutwein and Rosler, 1956; Otte, 1953; Horton and Aubrey, 1950).

Gordon et al. (1958) found 83.3 to 97.3 percent of the germanium in the humic acid extracts of coal. This appears to be consistent with the study of Sofiyev et al. (1964), where 70-90 percent of the germanium in coals were extracted by electrodialysis. Both authors conclude that this extractable germanium was organically bound.

Hawley (1955) noted an association between high Ge contents and high sulphide values in a Nova Scotia coal. However, he found no Ge in the heavy fraction of the coal. Nicholls (1968) suggests that Ge may have been incorporated in primary sulfides, expelled upon recrystallization and subsequently sorbed by organic matter or clay.

Despite the overwhelming evidence that germanium is organically bound in coal, there are indications that some Ge is inorganically bound.

In one sample studied by Gluskoter et al. (1977), Ge decidedly demonstrated an inorganic affinity. Nicholls (1968) reports that germanium may be associated with both fractions in coal, but only in high germanium coals is it largely associated with the organic fraction. He reports one sample in which Ge appears to be largely associated with the inorganic fraction. Breger et al. (1955) noted with surprise that germanium was concentrated in the mineral separate of a uraniferous lignite. Gordon et al. (1958) favor germanium-bearing silicates or germanates for the non-organically bound germanium (up to 44.8 percent of the germanium in a durain studied by Gordon et al.).

Although Ge readily substitutes for silicon in silicates, it also exhibits chalcophile behavior, preferentially entering sphalerites at low temperatures (Goldschmidt, 1954). Wedepohl (1970) cites substantial amounts of Ge (>1000 ppm) in sphalerites. Germanium in sphalerites extracted from Russian coals has been reported by Chernevskii (1975). Swaine (1975) reports that little Ge is found in pyrites associated with coal. During weathering Ge is firmly fixed to clays (Wedepohl, 1970). It is unlikely that detrital clays contribute much Ge to coal, but adsorption on clays of Ge from percolating solutions should not be discounted.

The only Ge detected by the SEM-EDX system was in a kaolinitic pore filling in a Sewell coal inertinite. This is clearly an authigenic development and would be consistent with coprecipitation of Si and Ge from percolating solutions.

Germanium was concentrated in the lighter Sp. G. fractions of both the Waynesburg coal and LT ash. The highest concentration of germanium (100 ppm in the ash) in the coals studied for this report was detected in the low-ash Indiana Block coal.

In summary, it would appear that the bulk of the Ge in most coals is organically bound. Inorganically bound Ge, which can be a substantial part of the total Ge in some coals, most likely is present in association with sphalerite or with the clays.

Gold: No information could be found on the abundance of gold in coal, other than the data of Goldschmidt and Peters (1933), giving Au values of 0.5-1 ppm in the ashes of 10 low-ash coals, and the data of Block and Dams (1975) showing a range of 10-40 ppb for Belgian coals.

Bodganov (1965) found Au to have a distinct inorganic association. But Manskaya and Drozdova (1968) suggest that the solubility of gold in humic acids may account for its concentration in coals. Bethell (1962) states that the most probable mode for gold in coal is as auriferous pyrite. Cambel and Jarkovsky (1967), however, found only traces of Au in several of the pyrite particles extracted from Czechoslovakian coals. Furthermore, there seems to be little disagreement that most, if not all, the sulfides in coal are authigenic. Wedepohl (1974) states that the amounts of gold in sulfides appear to depend largely on environment. Thus, pyrites forming in the coal environment should not be expected to contain much gold.

Gold (11 ppm in the ash) was detected in only one of the chemically analyzed samples, a sink 1.7 Sp. G. split of the Waynesburg coal (Appendix IIIB). This sample also had relatively high silver concentration (0.7 ppm in the ash).

In the course of this study, several flecks of elemental gold and one gold telluride particle were encountered in polished sections. The largest gold particle, about 10μm on edge, was found in a heavy mineral concentrate of the Upper Freeport coal. The Ferron coal from Utah had the highest frequency of occurrence of elemental gold particles. There were three such grains (one containing Ag) in a polished block. One small gold particle (∿0.5μm) was included in a quartz grain in a carbominerite band of the Waynesburg coal (Figure 5). In all probability, these gold flecks are of detrital origin.

Stone (1912) offers an interesting report on a gold-bearing coal from near the Black Hills. Coke made from the coal assayed at $2.46 per ton in gold when gold was valued at $20 per ounce. Stone (p. 64) noted that "there is more gold in the splint and bony coal than in the best bituminous." He suggests that the gold may be associated with pyrite. Stone observed that there were no known gold-bearing dikes or veins in the vicinity. He regards the idea that gold was introduced into the swamp either in solution or as very fine particles in suspension as not impossible, yet not readily conceivable. Stone suggests that the roof rock is derived in part from old gold-bearing alluvium. While the sand was being deposited, the fine gold particles may have worked their way down into the underlying bog and are now found in the coal.

This explanation seems a bit farfetched. It seems reasonable that water flow during periodic inundations of the swamp would have been vigorous enough to carry in finely divided gold from the gold-bearing alluvium. The additional detritus brought in along with gold would have diluted the organic material and generated the high ash splint and bone coals that now contain the gold.

Obviously, more analytical data on gold in coal is necessary before a definitive statement can be made on its mode of occurrence. Nevertheless, it seems likely that detrital particles of elemental gold and gold alloys are a major mode of gold in most coals.

Hafnium: The mean value for hafnium in Eastern U. S. coals is 0.81 ppm (Zubovic et al., 1979). Gluskoter et al. (1977) report the following mean values for Hf: 1.2 ppm for Eastern U.S. coals, 0.54 ppm for Illinois Basin coals, and 0.78 ppm for Western U.S. coals.

The chemical properties of hafnium are virtually identical with those of zirconium, and they are invariably associated in minerals (Goldschmidt, 1954). There is no discussion in the literature of the mode of occurrence of hafnium in coals. In the sink-float data of Gluskoter et al. (1977), hafnium exhibits a distinct inorganic association very similar to that of zirconium.

In the sink-float experiment on the Waynesburg LT ash, hafnium (and zirconium) were concentrated in the lighter fractions (Appendix IIIC). In the experiment on the whole coal, hafnium tended to be concentrated in the 1.5 - 1.7 Sp. G. fractions; the trend for Zr could not be detected in the semiquantitative emission spectroscopic data (Appendix IIIA).

Small quantities (<1 percent) of hafnium were detected by EDX analysis of zircons from several coals. It was demonstrated earlier that in the Waynesburg coal, zirconium occurred quantitatively as zircon (Table 9). As zircons are one of the most common accessory phases in all coals (Table 8), it seems reasonable to expect that the bulk of the hafnium in coals is associated with this mineral.

Indium: Shaw (1952) reports a value of 7 ppb for a shungite (Precambrian coal). Kuhn et al. (1978) report In values of 20 ppb for both coals studied. Gluskoter et al. (1977) give the following means for In: 160 ppb for Illinois Basin coals; 230 ppb for Eastern U.S. coals, and 110 ppb for Eastern U.S. coals; and 110 ppb for Western U.S. coals. Goldschmidt (1937) reports 2 ppm In in a coal ash. This probably corresponds to several hundred ppb on a whole coal basis. Block and Dams (1975) found 30-60 ppb In in Belgian coals.

Geochemically, indium displays chalcophile behavior although it can replace Fe in silicates, hydroxides, and carbonates

(Goldschmidt, 1954; Wedepohl, 1972). Wedepohl (1972) reports In concentrations in sphalerites of up to 5000 ppm and up to 1500 ppm in chalcopyrites. Chernevskii (1975) detected In in sphalerites from a Russian Jurassic coal. Indium is also a common constituent of iron-bearing carbonates. Wedepohl (1972) reports a mean value of 4 ppm in siderites and concentrations of almost 2000 ppb in calcite and aragonite.

The data of Kuhn et al. (1978) show an interesting correlation between In and the alkali earth elements. In the Pittsburgh No. 8 coal, In had a strong positive correlation with Mg and a negative correlation with virtually all the other components. In the Rosebud coal, indium displayed a very strong positive correlation with Sr; it was positively correlated with Mg, Ca, B and Co and negatively correlated with all other components. This may indicate that most of the indium in these samples is in epigenetic carbonates.

No indium-bearing minerals were observed, and In was below the limits of detection (6.8 ppm by OES) in all the samples analyzed for this study.

It seems safe to suggest that the bulk of the indium in coals will be found in the sulfides and/or the carbonates.

Iodine: Gluskoter et al. (1976) reports the following mean values for iodine: 1.7 ppm in Illinois Basin coals; 2.0 ppm for Eastern U.S. coals; and 0.42 ppm for Western U.S. coals. Kuhn et al. (1978) report iodine values of 0.3 ppm for both of their samples. Block and Dams (1975) found a range of 1.3 - 4.1 ppm I in Belgian coals. These values seem considerably lower than those reported in other studies. Gulyayeva and Itkina (1962) found 13.7 ppm I in coals of continental facies and 9.5 ppm in coals from near-shore marine facies. Wilke-Dörfurt and Romersperger (1930) found 0.85 - 11.17 ppm I (ave. 8 ppm) in German coals, and Cosgrove (1970) found 72 ppm in a coaly zone of the Kimmeridge shale.

Gulyayeva and Itkina (1962) found that I (and Br) values in the ash correlated well with the percent organic matter. Cosgrove (1970) also found a strong positive correlation between I (and Br) on a whole-coal basis and organic matter. Both authors conclude that biological activity was responsible for the accumulation of this element. Goldschmidt (1954) assumes that I, a biophile element, is concentrated in peats and coals by chemical fixation to organic compounds.

Iodine was volatilized in the LT ashing experiment of Lutz et al. (1978). This behavior is suggestive of an organic association.

In the sink-float results from Kuhn et al. (1978), iodine has organic tendencies in the Pittsburgh No. 8 coal, whereas in the Rosebud seam iodine has the lowest organic affinity of any element! It is also interesting to note that Kuhn et al. (1978) report iodine to correlate with the ash component and to have strong negative correlations with other halogens. At first this may seem to contradict the data of Gulyayeva and Itkina (1962) and of Cosgrove (1970). However, a closer examination of the relationship of I to organic matter in Gulyayeva and Itkina (Figure 37) reveals that I (and Br) values change only slightly over the range of 60-95 percent organic matter (5-40 percent ash). At higher values of organic matter, there is a marked increase in iodine content. This trend is suggestive of some inorganically bound I (and Br) at low concentrations (<100 ppm in the ash, 11.7 ppm whole coal). The I values in the samples of Kuhn et al. clearly fall well below this value.

Iodine was not analyzed for in the coals studied for this report, nor were any iodine bearing minerals observed.

It would seem to be a safe bet that the bulk of the iodine in most high iodine ($\gtrsim 10$ ppm) coals is organically bound. It seems probable that some, perhaps a substantial amount, of the iodine in low iodine coals is inorganically bound, perhaps fixed to the clays.

Lead: The mean value for lead in coal is 16 ppm (Swanson et al., 1976).

Brown and Swaine (1964) state that lead commonly occurs either as or associated with sulfides. They found concentrations of up to one weight percent lead in some pyrite concentrates of Australian coals. Cambel and Jarkovsky (1967) found rare traces of Pb in

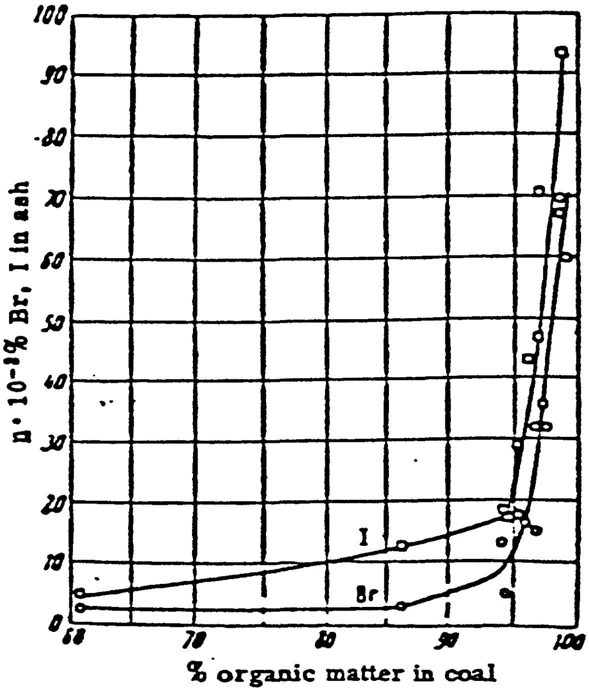

Figure 37. Concentration of iodine and bromine in coal ash as a function of the content of the organic matter in coal. (From Gulyayeva and Itkina, 1962).

the pyrites they extracted from Czechoslovakian coals. Pyrite will not normally accommodate that much lead in its structure, but it may be present in impurities in the pyrite such as galena (Deer et al., 1962). Galena, the lead sulfide, has been reported from a number of coals (Bethell, 1962; Appendix II).

Nicholls (1968) found lead to behave as if it were associated with the inorganic fraction. In most of the samples studied by sink-float procedure, Gluskoter et al. (1977) found that lead displayed behavior characteristic of inorganic associations. Ratynskiy and Glushnev (1967) found lead to have the lowest organic affinity of the elements for which they analyzed. Breger et al. (1955) found lead to be associated with the minerals in a uraniferous lignite. In the studies of Leutwein and Rosler (1956) and Otte (1953), Pb displayed intermediate behavior. In the study of Bogdanov (1965), Pb appeared to be associated with the "organic substance."

In the size-density separation of the Waynesburg coal, there was a small relative concentration of lead in the 1.5 - 1.7 Sp. G. fraction of all three size splits. On an absolute basis, however, 70-94.5 percent of the lead remained in the lighter two specific gravity fractions (Table 15). In the density separation of the Waynesburg LT ash lead was strongly concentrated in the heavy fraction.

In this study a new and possibly significant mode of occurrence of lead was observed. As noted earlier (Section 2.182), grains of PbSe (clausthalite?) were found in over 50 percent of the coals in the Appalachian Basin and in about 10 percent of the coals outside the Basin. Selenium-lead ratios indicate that no more than 50 percent of the Pb in the Waynesburg coal can be complexed in this form. In the Upper Freeport coal only 3.5 to 25 percent of the Pb could occur as PbSe. As it is unlikely that all of the Se occurs as PbSe (see comments on Se), lead must also occur in other forms. As noted earlier, Pb in the form of galena seems to be the dominant mode outside the Appalachian basin. Numerous crystals of galena were found in the coal from Nova Scotia which had a very high value of lead in the ash (790 ppm; Appendix IIIE).

Analysis of pyrite (EMP, IMP, EDX) indicates that even traces of lead are rare. J. Minkin (personal communication, 1978) found up to one percent Pb in sphalerites from the Upper Freeport coal. In the Waynesburg coal a lead tungstate, a lead-barium aluminum silicate, and a lead-bearing epidote(?) were found. None of these is likely to be a major mode of occurrence for lead.

The similarity in charge and size allows lead to substitute readily for barium. Perhaps small amounts of lead can be found in the barites which are very common in coal (Table 8). Certainly, lead could be in the crandallite minerals. Plumbogummite $\{PbAl_3(PO_4)_2(OH)_5 \cdot H_2O\}$ is a member of that mineral group. A rare-earth, lead-bearing crandallite grain was detected in the Ohio peat sample. Substitution of Pb in barium carbonates is also possible.

It would appear that the sink-float behavior of Pb would be very sensitive to the mode of occurrence of this element. That portion of the Pb that occurs as micron-size crystals of PbSe would tend to be rafted up into the lighter Sp. G. fractions by the organic matrix. That portion of the Pb that occurs as PbS would probably sink.

In summary, there seems to be little question that the lead in coal is inorganically associated. The specific mode of occurrence, however, seems to vary with geographic location. Substantial amounts of Pb in the Appalachian Basin occurs as PbSe. Outside the Appalachian Basin most Pb occurs as PbS. It is probable that Pb substitutes for Ba in authigenic sulfates, carbonates, phosphates, and silicates. Indeed, in sulfide poor coals this may be a major mode of occurrence.

Lithium: The mean value for lithium in coal is 20 ppm (Swanson et al., 1976).

No discussion of the mode of occurrence of lithium was encountered other than the suggestion of Bethell (1962) that if lithium had an extrinsic association in coal, it would most likely be found associated with the mica minerals. None of the sink-float studies reported on the behavior of lithium.

The low atomic number (No. 3) of lithium precludes its detection by the EMP and EDX systems. Lithium was below the limits of detection in the sink-float study of the Waynesburg coal and LT ash. IMP analysis of the Waynesburg coal detected low concentrations of Li in one vitrinite grain and in a pyrite framboid (in the intersticies?); analysis of Upper Freeport clays indicated Li contents of about 50 ppm.

The only lithium-bearing mineral (aside from clays and micas) detected in the coals was tourmaline, which usually contains less than 2 weight percent Li_2O (Deer et al., 1962).

Nicholls and Loring (1962) suggest that most of the Li in the shales they studied is incorporated in illite. The mean value for Li in shales is about 70 ppm (Wedepohl, 1970). Thus, compared to shales, coal ash would be relatively enriched in this element. Nicholls (1968) suggests that Li in coal is most probably sorbed by clay minerals, but some may be associated with organic matter. Razdorozhniy and Petrus (1975) note that Li in Russian coals is associated with the minerals.

The lack of data precludes any definitive statements on the mode of occurrence of lithium in coal. It is likely that much of the lithium is associated with the clays; certainly, some is to be found with the detrital micas and tourmalines. Whether this is sufficient to account for all the Li in the coal is problematical.

Manganese: The mean value for manganese in coal is .01 percent (Swanson et al., 1976).

Brown and Swaine (1964) state that the association of manganese and ankerite is known; however, they find the correlation is not exact. They suggest that other carbonate minerals may contain manganese and cite calcite and siderite concentrates with 1 percent Mn.

Manganese was the only element that Otte (1953) found solely attributable to the extraneous ash. Gluskoter et al. (1977) found manganese to exhibit a strong inorganic affinity in all samples. O'Gorman and Walker (1971) found that the coal sample with the highest manganese content also had the highest concentration of siderite. Leutwein and Rosler (1956) and Schultz et al. (1975) found Mn to have an inorganic affinity, but Bogdanov (1965) found it to behave in an intermediate fashion.

The possibility of organic association was considered by Brown and Swaine (1964), who suggest that in carbonate poor coals, manganese may be bound to carboxyl groups. Miller and Given (1978) say that one might expect that high concentrations of Mn in coal are related to exchange with organic functional groups. They note, however, that most of the manganese in the samples they studied appears to be associated with minerals; 72 percent was extracted by HCl, 3 percent was in the heavy fraction (they found 37 ppm Mn in a hand-picked pyrite crystal), and 25 percent in the ammonium acetate extrast, which they attribute to ion exchangeable site on clays.

Relatively little in the way of carbonate minerals was found in the Waynesburg coal, although some Mn-bearing siderite crystals were detected in the LT ash. In the float-sink separation of the LT ash, Mn was concentrated in the lighter fractions. In the float-sink separation of the Waynesburg coal, Mn was concentrated in the sink 1.7 Sp. G. fraction of the coarsest coal and in the sink 1.5 Sp. G. fractions of the two finer splits (Appendix IIIB). These data seem to indicate that in the absence of sufficient carbonates, manganese may be associated with the clays.

In this study manganese was detected in carbonates (predominantly iron-rich carbonates) in several samples, and it was a major component in a manganese-aluminum silicate in the Upper Freeport coal.

In the carbonate rich Upper Freeport coal, the sample richest in manganese (0.17 percent in the ash, 0.03 on a whole coal basis) had large pockets of illite in which there were numerous Mn-bearing anthigenic siderite crystals (Figure 38). The analysis for Mn in these crystals was qualitative. However, the EDX peak height indicated that there were several percent Mn in these crystals, probably sufficient to account for all the Mn in this sample.

Small amounts of Mn may be associated with pyrite. Fleischer (1955) found Mn values of up to 1 percent reported from pyrite analysis. Cambel and Jarkovsky (1967) found 20-50 ppm Mn in pyrites from Czechoslovakian coals. IMP analysis of pyrite from the Upper Freeport coal found several hundred ppm Mn.

Mercury: The mean value for mercury in U.S. coal is 0.18 ppm (Swanson et al., 1976).

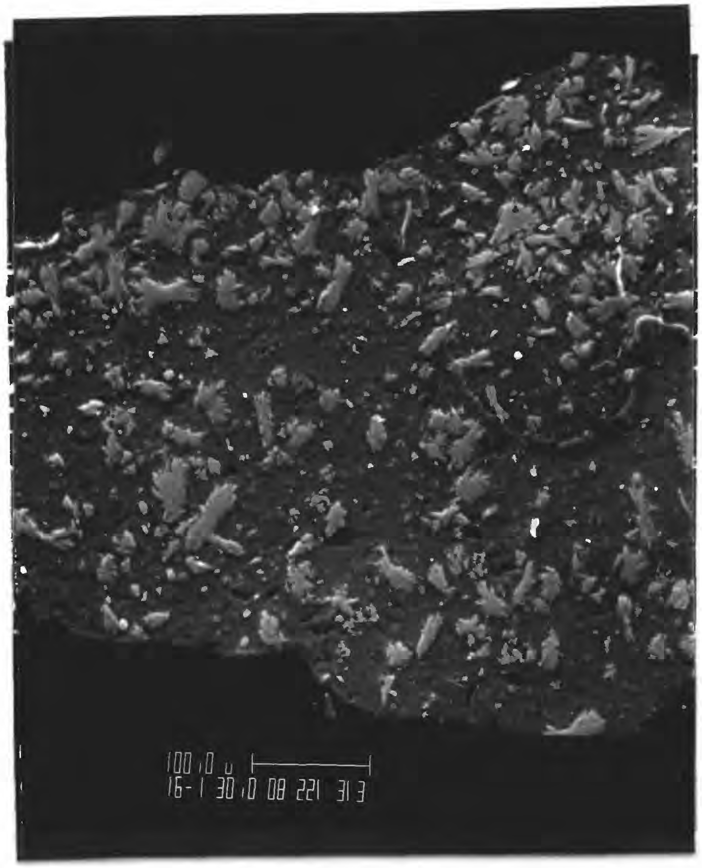

Figure 38. SEM photomicrograph of authigenic manganese-bearing "siderite" crystals in "illite".

Swaine (1975) cites two studies of Russian coals. In one study, mercury was found in pyrite, and in the other, Hg was considered to be mainly organically bound and also present in sulfide form with small amounts of metallic Hg. Porritt and Swaine (1976) found that the correlation between mercury and pyrite in Australian coals does not follow any clear pattern. They conclude that some of the Hg is associated with pyrite and some with the coaly matter. They also suggest the possibility that mercury occurs in elemental form in coal. Lutz et al. (1978) noted a loss of Hg on LT ashing. As there was no corresponding loss of other volatile chalcophile elements, this may reflect the volatilization of organically bound mercury.

The sink-float data of Gluskoter et al. (1977) and Ruch et al. (1974) indicate a clear inorganic association for Hg. Filby et al. (1977) estimated that 47 percent of the Hg in their sample was inorganically bound. In a study of the mercury content of Illinois coals, Ruch et al. (1971) examined, in detail, the distribution of Hg in Sp. G. fractions of one coal. They found a significant part of the Hg in this sample to be associated with pyrite, and the remainder (up to 50 percent) to be in the lightest fraction (less than 1.26 Sp. G.). Ruch et al. (1971) suggest that a part of the mercury in the light Sp. G. fraction may be in organic association. They also caution against making generalizations about the mode of occurrence of Hg in coal. They note that the coal sample in which they found the highest level of Hg contained only a trace of pyritic sulfur.

By physical separation of minerals Tkach (1975) found that Hg is associated only with epigenetic pyrite in coal. He suggests that the mercury is derived from hydrothermal solutions percolating through fractures in the coal. This conclusion is similar to that of Finkelman et al. (1979). They found that in the Upper Freeport coal, mercury has a strong positive statistical correlation with arsenic and pyritic sulfur. Mercury and arsenic also behaved similarly in the size-gravity separations (Table 15). In all probability the mode of occurrence of mercury is similar to that of arsenic (see section on arsenic) which was found to be associated with pyrite, probably emplaced by reaction of the pyrite with epigenetic arsenic-bearing solutions (Minkin, Finkelman et al., 1979). The association of mercury with epigenetic pyrite has also been demonstrated by Tkach (1966), Dvornikov (1965), and by Dvornikov and Tikhinenkova (1973).

Two mercury-bearing particles were detected, a mercury sulfide (cinnabar?) in the Sharon coal and a mercury copper sulfide in the Vermillion coal. If mercury were present in the pyrite, organics, or the clays, its concentration was below the limits of detection of the analytical equipment.

Although there is little direct evidence, there is strong circumstantial evidence to indicate that a significant proportion of the Hg in coal is associated with pyrite, probably by secondary enrichment. In view of the low concentration of Hg in coal, it is somewhat surprising to have found two accessory sulfides. Probably the high atomic number of mercury (80) contributes to its detection in the SEM. The occurrence of mercury sulfide may be significant in some coals. The occurrence of organically bound Hg and elemental Hg await analytical confirmation.

Molybdenum: The mean value for Molybdenum in coal is 3 ppm (Swanson et al., 1976).

Molybdenum is another of the elements for which there is no consensus in the literature on its mode of occurrence. Bethell (1962) cites a study of Hungarian coals in which molybdenum was found to be proportional to uranium concentration. The same authors (Almassy and Szalay, 1956) also report that molybdenum is bound to the organic matter in Hungarian coals. Bethell (1962) also cites Russian studies in which molybdenum concentration was found to be correlated with sulphur content. Vorskresenskaya (1968) reports that pyrite in Russian coals contain up to 30 ppm Mo, although most had less than 10 ppm.

Ratynskiy and Glushnev (1967) and Nicholls (1968) both suggest that Mo is associated with both the organic and inorganic fractions. Nicholls says that Mo appears to be associated with the inorganic fraction in low Mo coals, the organic fraction in high Mo coals.

Data from the sink-float studies are equally ambiguous. Both Horton and Aubrey (1950) and Zubovic et al. (1961) show Mo to have intermediate organic affinities, perhaps with a slight inorganic tendency. In the data of Gluskoter et al. (1977), Mo has distinct inorganic affinities in two samples and a distinct organic affinity in a third. Otte (1953), Leutwein and Rosler (1956), and Bogdanov (1965) all found Mo to have an organic affinity.

Korolev (1957) found a relationship between Mo content and Fe^{+2}/Fe^{+3} ratio in coals. He concluded that in coals in which Mo is not directly connected with organic substance, its accumulation depends on the degree of reduction; that is, the ferrous/ferric ratio. In the samples Korolev worked with, he found a correlation between Mo content and ash content. Heavy fractions of these samples, consisting almost entirely of pyrite, contained 75-90 percent of the molybdenum. In a later experiment Korolev (1958) found that 70-96 percent of the Mo in solution coprecipitated with the iron sulfides.

Cambel and Jarkovsky (1967) found up to 30 ppm Mo in pyrites from Czechoslovakian coals.

Golovko (1961) suggests that Mo was retained by organic matter during the initial stage of coal formation, but during diagenesis the Mo was released to form sulfides. This suggestion parallels that of Petrov (1961). Manskaya and Drozdova (1968) note that several authors are of the opinion that organic substances of coal play no role in the accumulation of Mo. They state (p. 230) that Mo in coals "is frequently at present not tied to the organic matter."

In the size-density separation of the Waynesburg coal, Mo was concentrated in the two finer sink 1.7 Sp. G. fractions. Smaller relative concentrations are found in the lightest fractions of all three size splits (Appendix IIIB). In absolute terms the majority of the Mo floated in this sample. In the ash the highest concentration of Mo was in the floats, the lowest in the intermediate fraction.

No Mo-bearing minerals were detected, except perhaps for one pyrite particle which may have had percent concentrations. This, however, could not be confirmed. Vorskresenkaya et al. (1962) report the occurrence in coal of jodesite (MoS_2) and ilsemannite ($Mo_3O_8 \cdot nH_2O$).

The highest concentration of Mo was found in the sulfide-rich Nova Scotia coal (110 ppm in the ash).

The data does not offer any clear insights into the mode of occurrence of Mo. Molybdenum has strong chalcophile tendencies; certainly some is associated with the sulfides, perhaps in solid solution with the pyrite. It is possible that finely divided grains of MoS_2 (molybdenite) dispersed throughout the organic constituents could account for much of the apparent organic affinity of Mo, i.e. its concentration in the lighter Sp. G. splits. However, the possibility of organically bound Mo must certainly be considered.

Nickel: The mean value for nickel in U. S. coals is 15 ppm (Swanson et al., 1976).

The substantial literature on nickel in coal has been thoroughly reviewed by Swaine (1980). In part the interest in this element is attributable to its relatively high concentrations in certain low-ash carbonaceous deposits (see Jones and Miller, 1939; Reynolds, 1948; Goldschmidt, 1954). Values up to 10.3 percent NiO in the ash have been reported (Jones and Miller, 1939). Zubovic (personal communication, 1979) suggests that some of these deposits may have acted as conduits for groundwater, affording the organic matter the opportunity to absorb unusually high concentrations of trace elements such as Ni, Ti, V and Cr.

The propensity for nickel to form organo-metallic complexes has often been cited as a reason for the enrichment of this element in carbonaceous sediments (Reynolds, 1948; Zubovic, 1966A; Swaine, 1980), although Manskaya and Drozdova (1968) acknowledge that very little is known about how Ni is retained by the organic matter.

Swaine (1980) suggests that some nickel may have been derived from nickel-rich meteoritic ablation products. Such particles have, indeed, been recognized in coal (Figure 8), initially by Finkelman and Stanton (1978) and subsequently by Alexander et al. (1980). Finkelman (1972) demonstrated that there is an inverse correlation between the abundance of meteoritic ablation products (cosmic spheres) and the rate of accumulation of the sedimentary deposit in which they are found. In consonance with this observation and the relatively rapid rate of accumulation of peat deposits, cosmic spheres appear to be extremely rare in coals, so rare that they could not have any appreciable influence on the nickel content of the coal.

In the sink-float experiments of Horton and Aubrey (1950), and Zubovic (1961), nickel exhibited intermediate organic affinities. Nickel had clear organic tendencies in most of eight samples studied by Gluskoter et al. (1977) and in both samples of Kuhn et al. (1978). However, Ruch et al. (1974) and Gluskoter (1975) state that although there is a partial organic association, Ni is more closely associated with the inorganics. Hawley (1955) found Ni to be concentrated in the sink fraction of a Nova Scotia coal, although there is a lesser concentration in the floats.

Filby et al. (1977) estimated that 100 percent of the nickel in their sample was inorganically bound.

In the sink-float study of the Waynesburg coal there was a slight relative enrichment of nickel in the sink fractions. Recalculating these data to whole coal basis, it is evident that nickel is strongly enriched in the lighter fractions (Appendix IIIB). This can be due to the rafting effect of the organic particles on nickel-bearing minerals or to organically bound nickel.

In the Waynesburg LT ash, nickel exhibited a slight enrichment in the sink fraction (Appendix IIID).

High concentrations of nickel were found in the ash of the Alaskan coal (1000 ppm). Carbonate minerals predominated in this coal; no nickel was detected by the SEM-EDX system. The low ash Indiana coal had 420 ppm Ni in the ash. This relatively high value could be due to epigenetic mineralization or to organic complexing of nickel. The ash of the Venezuelan asphaltite had >15,000 ppm Ni! The major mineral phase in the asphaltite was montroseite {VO(OH)} which contained variable but significant amounts of nickel.

Nicholls (1968) found that Ni displayed a variable relationship. In some samples it appears to be associated with the organic fraction; in others it just as clearly appears to be associated with the inorganic fraction. He suggests that in coals containing substantially more than 3 ppm Ni, the element would largely be associated with the inorganic fraction. Nicholls attributes high concentrations of Ni in the margins of coal seams to post-burial enrichment, the nickel being primarily associated with the sulfides. In low-sulfide coals Ni can be sorbed by clays or coprecipitated with iron-bearing carbonates.

Miller and Given (1978) found 16 percent of the nickel in their North Dakota lignite in the heavy fraction, presumably in inorganic association. Seventy-eight percent of the Ni was in the two lighter Sp. G. fractions; they suggest an organic association for this nickel.

Leutwin and Rosler (1956) and Otte (1953) found Ni to be associated with the "organic substance," whereas Bogdanov (1965) found it to be associated with the inorganic matter. Zubovic (1966A) believes the organically bound nickel in coal is held as chelated complexes. Filby et al. (1977) are of the opinion that nickel in coal occurs partly as porphyrin. A crystalline nickel porphyrin, abelsonite, has recently been described from the organic-rich Green River shales (Milton et al., 1978).

Swaine (1980) summarizes the conflicting interpretations on the mode of occurrence of nickel with the comment that "while there is much to link nickel with the coal substance itself, there is no direct evidence of the kind of association between nickel and organic matter in coal."

In contrast to the speculation about organically associated nickel, there is direct evidence on the form of the inorganically bound nickel. The association of millerite (NiS) with coal has been known since 1842 (Miller, 1842). Goldschmidt (1954, p. 675) states that ". . . the rather frequent occurrence of crystals of millerite, NiS in coal seams as well as the cobalt mineral linnaeite $(Co, Ni)_3S_4$ may be genetically connected with such concentrations of nickel in the mineral substance of coal." Spencer (1910) found a NiSbS (ullmannite) in veins penetrating an English coal.

In the present study nickel was detected by the SEM-EDX system in numerous minerals from many samples. Most commonly it was found in sulfides. Traces of Ni were detected in galena, sphalerite, pyrite, clausthalite, and unidentified complex sulfides. Nickel is one of the few elements that readily fits into the pyrite structure. Cambel and Jarkovsky (1967) found up to 1450 ppm nickel in pyrites from Czechoslovakian coals. One sample had a mean of 600 ppm Ni in the pyrite. Nickel was also a trace constituent in zircons, an elemental gold particle, and a clay. It was a major component in several linnaeite grains, a vanadium-titanium silicate (Beulah lignite), a tin nickel oxide (?), a copper-nickel sulfide, and in the nickel silicates from the Waynesburg coal.

The evidence on the mode of occurrence of nickel in coal seems to indicate that in certain coals and carbonaceous deposits, substantial amounts of Ni may be organically complexed. The inorganically bound Ni appears to be largely associated with the sulfides. Many of these phases appear to be either epigenetic or diagenetic. Additional detailed studies on the proportion of nickel in pyrite are necessary before more definitive statements can be made on the mode of occurrence of nickel in coal.

Niobium: The mean value for niobium in U. S. coals is 3 ppm (Swanson et al., 1976).

The only mention in the literature of the mode of occurrence of Nb in coals is by Ratynskiy and Glushnev (1967). These authors suggest that the sink-float behavior and distribution of Nb with respect to the ash indicate that Nb is associated with both the organic and inorganic fractions.

In the size-density separation of the Waynesburg coal, Nb was concentrated in the lighter fractions of all three size splits. The lowest concentrations were in the sink 1.7 Sp. G. splits. In the Waynesburg LT ash the Nb is also concentrated in the lighter fractions.

The behavior of Nb might be construed as having some organic character. However, it can be seen in Appendix IIIB that Nb and Zr behave in an identical fashion (r = 0.92). (The Nb:Zr ratio is mirrored in the Ta:Hf ratio, discussed in the section on tantalum.) Niobium is not depleted nearly as strongly as Zr in the sink 1.7 Sp. G. splits, which suggests that some Nb is in a heavy phase unrelated to zirconium.

Goldschmidt (1954) notes that some Nb can enter into certain varieties of zircon but that most is associated with titanium minerals such as rutile and ilmenite. There does not appear to be a direct correlation between Nb and Ti. This is, perhaps, due to the diverse mode of occurrence of titanium (see below). The ratio of Zr:Nb in this sample is about 10:1. Goldschmidt (1954, p. 504) remarks that "there seems to be rather a close parallelism between the percentages of zirconium and niobium in igneous rocks." He notes that the average amount of niobium in igneous rocks is about one tenth that of zirconium. "This parallelism between the concentrations of niobium and zirconium does not seem to be directly connected with the crystal structure of any of the more common minerals involved. . . ." (Goldschmidt, 1954).

It seems reasonable to assume that both the Nb and Zr (as well as Ta and Hf) were derived form the same source. As it is unlikely on crystal chemical grounds for Nb and Zr to be in the same mineral, the Nb is probably associated with the titanium minerals. It is worthwhile noting that Nb was detected by the EDX system in a rutile from the sink 2.7 Sp. G. fraction of the Waynesburg coal. The only other grains in which Nb were detected were a probable columbite group mineral in the Canadian Devonian coal and in a tungsten-bearing titanium grain in the Pewee coal. Therefore, what the Nb:Zr ratios and statistical correlation probably reflect is a similar physical behavior of the Nb-bearing titanium minerals and zircons. This, of course, is precisely the reason why these minerals are both found concentrated in the heavy suite of detrital sediments. As noted earlier (Table 13), these minerals are physically associated in the carbominerite bands. Thus the geochemical, mineralogical, and textural evidence seems to be consistent. This conclusion has important implications on the controversy surrounding the origin of the minerals in coal (see Section 3.12).

In summary, it is possible that most of the niobium in the Waynesburg coal is associated with detrital rutile. Also, some Nb may be associated with clays, but there seems to be no compelling evidence to suggest an organic association. The coherence of the Nb:Zr ratio to that of the igneous rocks (the likely ultimate source) would argue against organic complexing in light of the fact that Zr, in most coals, seems to occur quantitatively in zircons (Table 9).

It would be interesting to determine the Nb content of the titanium minerals and zircon. Deer et al. (1962) suggest that the Nb content of zircon may be used for distinguishing zircons from different sources. This may apply to the titanium minerals as well.

Phosphorus: Although generally not considered a trace element, phosphorus is discussed here because the analytical approaches used in this study shed light on the mode of occurrence of this important element.

Abernethy and Gibson (1963) give P values for 32 U. S. coals; the mean is 185 ppm, range 20 - 1430 ppm.

An X-ray fluorescence technique was developed by this author to determine the P content of whole coal. Using this technique, the mean value for 754 samples from the Appalachian Basin was found to be 182 ppm, the range from <50 to 1100 ppm (Finkelman, unpublished data).

Brown and Swaine (1964) state that in Australian coals, phosphorus mainly occurs as one of the apatite (usually fluorapatite) minerals. They note that other inorganic phosphates may also be present in some coals. Brown and Swaine could find no evidence for the occurrence of organically bound phosphorus.

Breger (1958) cites a Russian study which reported bright coals to contain 8 to 10 times less P than semidull coal (generally higher in ash), although no correlation was observed between ash content and phosphorus. Other studies confirm the concentration of P in fusite (dull coal) (Wedepohl, 1978, Table 15-L-10).

Gluskoter et al. (1977) found strong organic tendencies for P in about half of the eight samples studied and a strong inorganic tendency for P in one sample. The data of Kuhn et al. (1978) suggest an organic affinity for P, although there is a strong correlation with fluorine in the Pittsburgh No. 8 sample. Bogdanov (1965) found P to be associated with the "organic substance."

Abernethy and Gibson (1963) cite a study in which substantial amounts of phosphorus and ash were removed from two coals by coal washing methods. The P content of five other coal samples could not be appreciably reduced by washing. Two aluminum phosphate minerals, evarisite and wavellite, were found to account for 12 percent of the phosphorus in a coal parting.

Rao et al. (1951) separated several coals into eight Sp. G. ranges. In each of the Sp. G. fractions at one site they found P and F occurred in almost the exact ratio necessary for fluorapatite. In other coals, only 60-70 percent of the necessary P was present. They concluded that most of the P occurred in inorganic form but noted that in very low ash fractions the P content is much higher than warranted by the ash present. This perhaps indicates some organically bound phosphorus.

As noted earlier (Table 8), phosphate minerals, particularly RE-phosphates, appear to be relatively common in most coals. Monazite occurred in over 50 percent of the coals examined, and xenotime occurred in about 33 percent. Members of the crandallite mineral group were found in about 10 percent of the samples, as were apatites. In some samples, apatite was among the more abundant accessory phases. Apatites have been reported from many coals; other phosphate minerals have also been reported (see Appendix II).

In the experiment to quantify the accessory minerals, 35 monazite and xenotime grains were observed (Table 9). Several apatite particles were also detected. Plugging the appropriate values into the formula in Section 2.173, a value of 55 ppm is obtained for P in the inorganic phosphates. The analytical value for P in the Waynesburg coal is about 100 ppm. Some of the discrepancy between the calculated and analytical values may be due to crandallite group minerals not detected in the survey (see Section 2.173 for more complete discussion). Certainly, some of the discrepancy may be attributable to organically bound P. In view of the biological significance of P, it would not be surprising if some P in coal were to be retained in organic associations. Wedepohl (1978) states that P occurs in both the inorganic and organic fractions of the coal. He cites a study in which organophosphates, such as nucleoproteine and hexosephosphate, were extracted from coal.

Undoubtedly, substantial amounts of phosphorus in many coals occur in RE-phosphates and/or apatite. The proportion of organically bound P is still to be determined.

Platinum group (ruthenium, rhodium, palladium, osmium, iridium, platinum): There exist only a few scattered analyses in the literature of the abundance of platinum group elements in coal. Not only is the information available meager, but the situation is thoroughly confused by an incredible series of wrongly attributed data. Bethell (1962) misquotes both sources he cites. Wedepohl (1968) erroneously attributes the analysis he cites. Goldschmidt (1954) also misquotes the same source as the others, which, incredibly, is one of his earlier publications (Goldschmidt and Peters, 1933). The following table summarizes the confusion (Table 17).

Block and Dams (1975) found a range of 7-9 ppb Ir in Belgian coals, and 90-170 ppb Ir in the coal ash. No values were found for ruthenium, generally the most abundant element in this group.

No sink-float data nor organic affinity estimates were found in the literature. No minerals containing platinum group elements were observed and no platinum group elements were detected in any of the samples analyzed for this report.

Table 17. Reported Values for the Platinum Metals in Coal Ash

(Values are in ppb)

	Pt	Os	Pd	Rh	
Wedepohl (1968)	200				Attributed to Goldschmidt & Peters (1933)
Wedepohl (1968)	100-500	50-500	20		Attributed to Goldschmidt & Peters (1933)
Bethell (1962)			50	100	Attributed to Goldschmidt & Peters (1933)
Goldschmidt (1954)			50-500	100-1000	Attributed to Goldschmidt & Peters (1933)
Goldschmidt & Peters (1933)	up to 1000		50-500		
Goldschmidt (1935)	up to 700		up to 200	up to 20	

Goldschmidt (1954) suggests that solute ions or complex ions of platinum metals will be precipitated by organic matter in soils (and peats), just as in the case of gold. However, we have seen that gold apparently occurs as discrete grains of native gold or gold alloys. It is probable that the platinum group elements have a similar mode of occurrence.

Finkelman and Aruscavage (unpublished data), using an atomic absorption technique, have determined Pt, Pd, and Rh in a series of coals. They have found these values to be no more than a few ppb, on a whole coal basis, with most values below 1 ppb. These values are generally several orders of magnitude lower than the values in the literature (Table 17). These lower values are consistent with a detrital source for the platinum group elements.

Rare Earth Elements (elements 57-71 inclusive): The concentrations of the rare earth elements (REE) in coal appear in Table 18.

Tsui et al. (1979) report that the sum of the concentrations of all fourteen rare earth elements in the ashes of twelve Illinois coals ranged from 230 to 630 ppm.

In the sink-float data of Gluskoter et al. (1977), the behavior of the REE is rather curious: Ce and Sm generally have strong inorganic tendencies; Dy displayed strong organic tendencies; Eu and Tb generally had intermediate affinities; and those of La, Yb and Lu varied from organic to inorganic. In the data of Kuhn et al.

Table 18. Concentrations of the Rare Earth Elements in Coal

	1	2	3	4	5	6
lanthanum	10 ppm	4.9 ppm	3.3 ppm	6.8 ppm	15 ppm	5.2 ppm
cerium	19	12.2	10.8	14	25	11
prasecdynium	--	1.8	2.6			
neodymium	12.7	8.0	3.6			
(promethium)	--	--	--			
samarium	1.9	1.22	2.0	1.2	2.6	0.61
europium	0.37	0.52	0.81	0.26	0.52	0.20
gadolinium	--	1.22	1.9			
terbium	0.3	0.22	0.36	0.22	0.34	0.21
dysprosium	--			1.1	2.3	0.63
holmium	--	0.19	0.42			
erbium	--	0.50	0.73			
thulium	--	0.06	0.13			
ytterbium	0.89	0.37	0.57	0.56	0.83	0.38
lutetium	0.16	--	0.072	0.09	0.22	0.07

1. Zubovic et al. (1979)
2. Schofield and Haskin (1964), Western Pennsylvania
3. Schofield and Haskin (1964), Southern Illinois
4. Gluskoter et al. (1977), mean for Illinois Basin Coals
5. Gluskoter et al. (1977), mean for Eastern U.S. Coals
6. Gluskoter et al. (1977), mean for Western U.S. Coals

(1978), the REE showed clear organic tendencies. La showed inorganic tendency in the data of Zubovic et al. (1960) and Ratynskiy and Glushnev (1967). Bogdanov (1965) found Ce and La to exhibit inorganic affinities, but Miller and Given (1978) found Yb to be concentrated in the lighter Sp. G. fractions of the North Dakota lignite. Yershov (1961) found only Yb (and Y) to be concentrated in the light Sp. G. fraction of the coal he studied.

Filby et al. (1977) estimated that from 77 (Tb) to 100 (Eu, Ce, Sm) percent of the REE were inorganically bound in the coal they studied.

In the sink-float testing of both the Waynesburg coal and LT ash, the REE were concentrated in the lighter Sp. G. fractions. The sink-float data do not appear to shed much light on the mode of occurrence of the REE.

Goldschmidt and Peters (1933) found Y contents of coal ash to far exceed the Y content to be expected if the ash were composed of detrital minerals. They concluded that inorganic processes alone were not sufficient to account for the REE in coals, and some type of biologic accumulation had occurred. Yershov (1961) attributed the deviation of the REE distribution in his samples to selective capture of these elements by organic matter. He found, however, only ytterbium and yttrium to be concentrated in the light (Sp. G. <1.4) fraction of the coal. Haskin et al. (1966) acknowledged that the REE distribution indicated by Yershov could occur through the selective capture of heavy REE plus detrital material with a normal crustal RE pattern.

Biological and chemical mechanisms are also called upon by Schofield and Haskin (1964) and Kosterin et al. (1963) to account for the REE distribution in their coal samples. Haskin et al. (1966) noted that the same mechanism (reduction of Eu to the +2 state) is invoked to explain the enrichment of Eu in one coal and its absence from another. They concluded (p. 298) that "aside from the probable biogenic origin of much of the REE in these coals, little is understood about the origin of the RE patterns."

Perhaps some of the conflicting data may be due to inaccurate analyses by some of the earlier workers. Both Kosterin et al. (1963) and Yershov (1961) used spectrographic techniques to determine the RE abundances. The present author found that spectrographic data were not sufficiently precise to determine the REE trends.

More recently, Eskenazy (1978) determined the abundance and distribution of REE in thirteen coals from Bulgaria. She found (1) a relative increase of heavy lanthanides in low ash coals; (2) an increase in the absolute REE concentration with increasing ash content; (3) the REE distribution pattern approached that for shales in the high ash coals. She concluded that the REE are associated predominantly with inorganic matter and to a lesser degree with the organic matter in coal.

In contrast to the earlier studies, Tsui et al. (1979) found the average relative distribution of the REE in Illinois coals to be almost identical to that of shale. They found the concentration of each REE in the ash to be approximately equal to its concentration in shale. They concluded that much of the REE in Illinois coals is inorganically associated. Their conclusion was supported by leaching experiments which indicated that the REE were in the mineral matter.

Similar results have been obtained from the Waynesburg coal in this study and from the Upper Freeport coal (data from B. Cecil, personal communication, 1979). The summations of La, Ce, Sm, Eu, Tb, Yb, and Lu in the ashes of these coals are less than 5 percent higher than their corresponding value for North American shales as reported by (Haskin et al., 1966). The distribution of chondrite normalized RE abundances in the ash of these two coals is virtually identical to that of a composite of these shales (Figure 39). The only notable differences are the depletion of Eu and the enrichment of La in the coal ash. The depletion of Eu can be accounted for by its reduction to the +2 state and removal from the rest of the REE. No explanation can be offered for the anomalously high La values.

Bethell (1962) has speculated on the specific mode of occurrence of the REE. He has suggested that the REE in coals occur extrinsically in clays. However, in the present study, Re-bearing phosphate minerals were found in most coals. Monazite (see Section 2.13) was found in about 50 percent of the coals studied, xenotime in about 25 percent (Table 8). Scarce RE-bearing silicates were

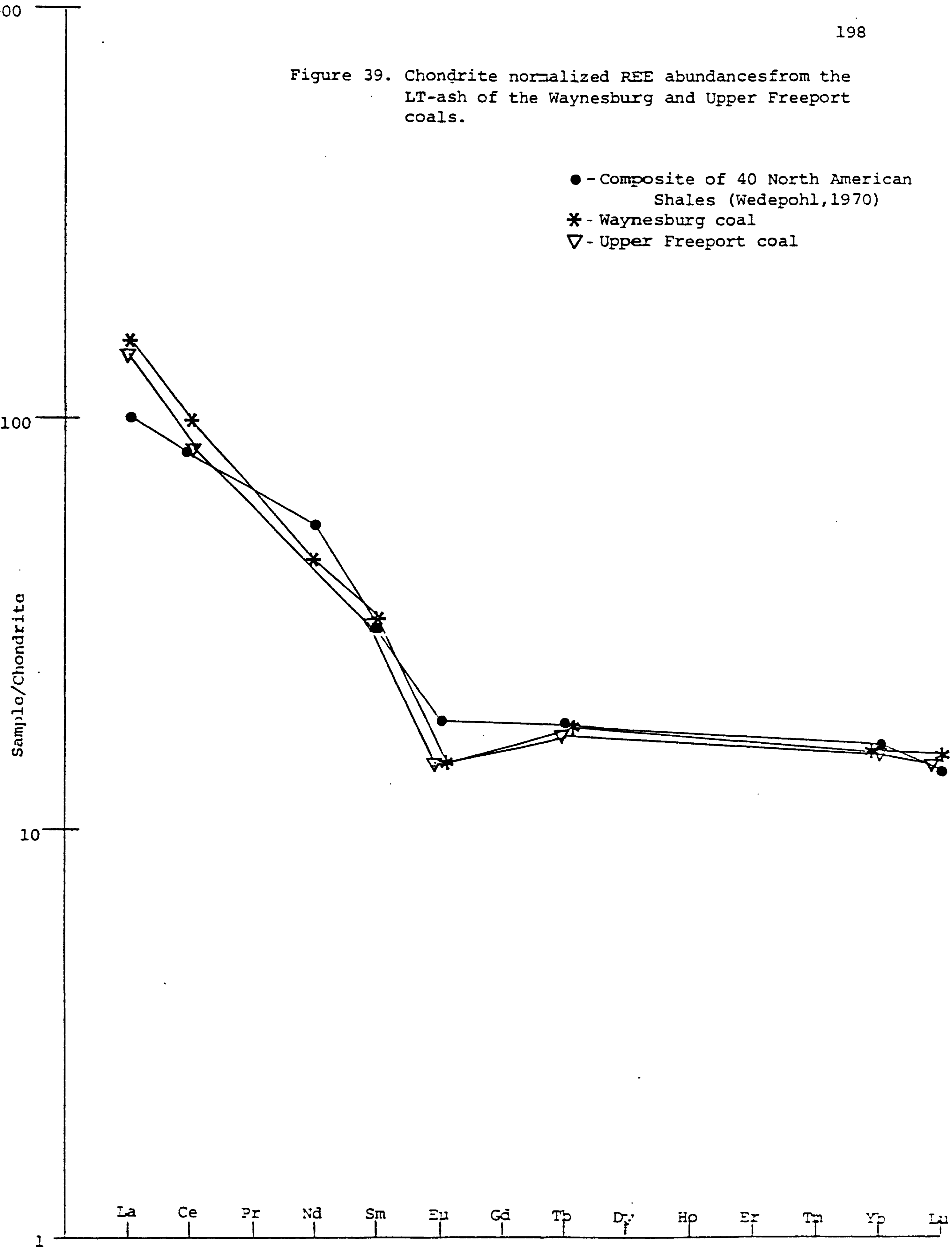

Figure 39. Chondrite normalized REE abundances from the LT-ash of the Waynesburg and Upper Freeport coals.

also observed and REE were detected in some of the crandallite group minerals and more rarely in zircons. Other RE-bearing minerals include Nd-monazites in the Upper Freeport and Canadian Devonian coals, a Pr-monazite in the Upper Freeport coal, and a Yb phase associated with pyrite in the South African coal. Quantitative results from the Waynesburg coal (Table 9) indicate that the RE-phosphates were sufficiently abundant to account for all the REE in the lithotype sample studied. These minerals appear to be similarly abundant in most of the other coals examined in the SEM.

Brown and Swaine (1964) noted a poor correlation between P and La (or Y). This lack of correspondance may be due to the presence of RE-silicates or to the presence of other phosphate minerals, such as apatites, which are common in Australian coals, as indicated by Swaine (1964).

It appears that the more recent work indicates an inorganic association for the bulk of the REE. The data from this study indicate that the REE, perhaps in most coals, occur in the RE-phosphates, monazite and xenotime. The suggestion that the bulk of the REE are currently inorganically bound in coal does not preclude some complexing of the REE earlier in the history of the coal. It was noted earlier that many RE-phosphate minerals appear to be authigenic. If organic complexing of the REE did occur, it does not seem to have had any significant effect on the REE distribution in the Waynesburg and Upper Freeport coals.

Rhenium: Wedepohl (1969) cites a Russian study reporting 0.095-0.327 ppm Re in Brown coals with high molybdenum contents. Because Re geochemically follows Mo, these values may be on the high side of the mean value of Re in coal.

In a series of leaching experiments Kuznetsova and Saukov (1961) found Re (and Mo) to be present in low-ash bright coals as organo-metallic compounds, and in high-ash, sulfide-rich dull coals as sulfide inclusions.

No Re-bearing minerals were detected in this study, and Re was below the limits of detection (10 ppm by OES) in all samples analyzed for this report.

Rare Gases (helium, neon, argon, krypton, xenon, radon): Breger (1958) cites a study of coal mine gas from the Ruhr region, which contained 4 percent helium, 0.1-0.2 percent neon, and small amounts of argon and krypton. Xenon and radon were not mentioned. Murich (1973) found that the average concentration of helium in adsorbed coal gases in the Donets Basin did not exceed 0.05 percent. In free gases it varied from 0.1 to 0.3 percent, and in dissolved gases from 0.1 to 0.25 percent. Murich details the geologic factors that influence the accummulation of helium in natural gases. The contribution of coal combustion to the radon content of the atmosphere has been discussed by Anderson et al. (1954) and Anderson and Turner (1956).

Rubidium: Gluskoter et al. (1977) give the following means for Rb: 19 ppm in Illinois Basin coals; 22 ppm in Eastern U.S. coals; and 4.6 ppm in Western U.S. coals. Block and Dams (1975) report the following data on three sets of Belgian coals:

Rb (ppm)	Ash percent
5.0	3.7
7.7	5.4
72.0	32.5

Abernethy and Gibson (1963, p. 27) state that "little information is available on the rubidium content of coal." This statement is almost as accurate today as it was 17 years ago. There is virtually no discussion in the literature on the mode of occurrence of this element, other than the comment by Bethell (1962) that if extrinsic, Rb most likely would be associated with mica.

In the sink-float data of Gluskoter et al. (1977) and Kuhn et al. (1978), Rb displayed a very strong inorganic affinity. Filby et al. (1977) calculated that in the coal sample they studied, virtually all the Rb was inorganically bound. Based on an inverse relationship between Rb and ash content of Russian coals, Razdorozhniy and Petrus (1975) concluded that Rb is associated with the organic matter.

Geochemically, Rb follows potassium (Goldschmidt, 1954). The bulk of the rubidium on the earth's crust is found in K-feldspars and K-micas. These phases are generally not common in coals. It is probable that substantial amounts of Rb in coal are in the illite and mixed-layer clays. Degens et al. (1957) found a strong correlation between Rb and the illite/kaolinite ratio of shales.

It would be desirable to have more data on the Rb content of coals. Certainly, the K/Rb ratio may be instructive in deciphering the geochemical history.

Selenium: The mean value for Se in U.S. coals is 4.1 ppm (Swanson et al., 1976). The data of Gluskoter et al. (1977) indicate that there may be some geographical variation in the concentration of Se in coals. They report the mean values for Se of 2.2 ppm for Illinois Basin coals, 4.0 ppm for Eastern coals, and 1.4 ppm for Western coals.

Selenium displayed inorganic tendencies in five sink-float samples of Gluskoter et al. (1977), organic tendencies in the other three samples. In the data of Kuhn et al. (1978), Se exhibited intermediate tendencies in one sample and a strong inorganic tendency in the other.

Wedepohl (1972) states that the main part of Se in coal is present in the sulfides and reports 10-30 ppm Se in pyrites extracted from coal. He notes that the existence of organic Se compounds cannot be excluded. Wandless (1957) reported that up to 70 ppm Se had been found in pyrite from British coal. Se exceeded 100 ppm in about 10 percent of those analyses reporting this element (Fleischer, 1955).

Porritt and Swaine (1976) found that Australian coals with the highest total and pyritic sulfur values generally had the highest Se values, although other samples did not follow any clear pattern. They feel that the data indicate that some of the Se is associated with pyrite and some with the organic matter. They suggest that small amounts of Se could also be present in other sulfide minerals and iron oxides as well as occurring in elemental form in coal.

As noted earlier (Section 2.18), a lead selenide (perhaps the mineral clausthalite) was found in over 50 percent of the Appalachian Basin coals and in less than 10 percent of the coals outside the Appalachian Basin. Perhaps this difference in frequency of occurrence of the PbSe is due to the slightly higher Se values for the Appalachian coals.

Minkin, Finkelman et al. (1979) found Se rich (0.2 weight percent) isolated points in some of the pyrite grains in the Upper Freeport coal. The selenium content of pyrite concentrates from the columnar sample studied appears to parallel the As content. Minkin, Finkelman et al. argue for an epigenetic origin for the As which they find in the pyrite. Perhaps some of the Se in this sample is also of epigenetic origin. It is interesting to note that in another column sample of this coal (collected 1200 meters apart), the concentrations of Se and As are negatively correlated.

In an experiment conducted with Blain Cecil of the U. S. Geological Survey, a sample of the Upper Freeport coal was ground, splits were LT ashed and ashed at 550°C in air. The whole coal and the resultant ash samples were sent for NAA. Of the 24 elements analyzed for, only Se and Br exhibited significant losses upon LT ashing (Table 19). Over 50 percent of the Se was driven off during the LT ashing procedure; this is strongly suggestive of organic bonding for at least that portion of the Se that was volatilized under these very mild conditions. In a similar experiment, Lutz et al. (1978) did not observe a loss of Se.

In the sink-float experiment on the Waynesburg coal, Se is relatively enriched in the sink fractions. However, when recalculating the data to a whole coal basis, it is apparent that the bulk of the Se is in the lighter fractions (Table 15). The concentration of Se in the floats is due to both organically bound Se and the rafting effect of the organic particles on the micron-size inclusions of PbSe.

In the sink-float separation of the Waynesburg LT ash, Se was strongly enriched in the sink fraction. In all probability, the organically bound Se has already been driven off, and we are looking only at the inorganically bound selenium.

In the SEM-EDX selenium was detected in the lead selenides, in several pyrite grains, in an arsenic-bearing chaleopyrite particle, in a grain of galena, and in a complex sulfide (Table 10).

It is apparent that substantial amounts of selenium can occur in organic complexes, in solid solution with pyrite and other sulfides, and in at least the Appalachian Basin, as lead selenide.

Table 19. NAA Analysis of Upper Freeport Coal, LT Ash, and HT Ash*

(recalculated to a whole coal basis; values in ppm)

	Whole Coal	LT Ash	HT Ash
Se	1.15	0.44	0.16
Br	68.0	1.25	1.3
Sb	1.4	0.95	0.99
Fe	0.96	1.01	1.08
As	39.2	45.3	47.0
Zn	11.0	11.9	9.5
Cr	5.0	6.5	6.2
Co	4.0	3.6	3.7
W	0.4	0.4	0.4
Sc	1.83	1.75	1.75
La	3	3	3
Cs	0.2	0.2	0.2
Hf	0.2	0.2	0.2
Th	0.7	0.8	0.7

---

* In cooperation with Blaine Cecil; analysis by Louis J. Schwartz.

The proportions of the various modes of occurrence vary even within a single coal bed.

Scandium: The mean value for scandium in U.S. coals is 3 ppm (Swanson et al., 1976).

In the only study devoted to Sc in coal, Swaine (1964) found this element to be concentrated in the vitrains. Based on the difference in Sc contents of coals before and after demineralization, Swaine concludes that 40-95 percent was organically bound. He also detected up to 40 ppm Sc in siderites and calcites, and up to 25 ppm in kaolinite separates from the coals. Deul (1955) found Sc to be always enriched in the organic-rich concentrates of coal compared to the original coal and to the separable minerals. In contrast, Ratynskiy and Glushnev (1967) interpret the distribution of Sc in Sp. G. fractions of ash and whole coal to indicate both organic and inorganic associations. The sink-float data of Gluskoter et al. (1977) show scandium to have organic tendencies in some samples, inorganic tendencies in others. Scandium displayed organic tendencies in both samples studied by Kuhn et al. (1978) and in the studies of Bogdanov (1965) and Miller and Given (1978).

Filby et al. (1977) estimated that 88 percent of the Sc in their sample was inorganically bound.

Borisova et al. (1977) found that of the Sc present in coal fractions of Sp. G. less than 1.6, as much as 87 weight percent was in the organic matter. In brown coal fractions with Sp. G. of greater than 1.5, up to 70 percent of the Sc was in the mineral matter. It appears that the proportion of organically bound Sc increased with coal rank in these samples.

In the sink-float separation of the Waynesburg coal and LT ash, Sc was found concentrated in the intermediate to lighter Sp. G. splits.

In the SEM-EDX approach, Sc was detected in two grains from the Upper Freeport coal, in a clay, and in a yttrium-bearing zircon. It was also detected in zircons from the Laredo coal, the Australian coal, and the English Hem Heath coal.

In the sedimentary environment, Sc is believed to be adsorbed by clays and by hydrous Al and Fe^{3+} oxides. The Sc content of argillaceous rocks rarely exceeds 20 ppm (Wedepohl, 1970). This would be insufficient to account for the Sc in coals; values for Sc in the ash reach 1000 ppm (Wedepohl, 1970). Organic complexing of Sc is certainly a possibility, but the charge to radius ratio indicates that Sc should have only a low to modest organic affinity (see Zubovic, 1966A). Another possible site for Sc would be in the aluminum phosphates. Frondel et al. (1968) found almost one weight percent Sc_2O_3 in variscite, crandallite, goyazite and other species. Small proportion of the Sc appears to be associated with zircons, but this cannot be a major mode of occurrence for this element.

The data for scandium point to both organic and inorganic associations. It is evident that more work on this element is required before firm conclusions can be drawn.

Silver: The mean value for silver in Eastern U.S. coals is 0.06 ppm (Zubovic et al., 1979). Gluskoter et al. (1977) give the following mean values for Ag: 0.02 ppm for Eastern U.S. coals; 0.03 ppm for Illinois Basin coals; and 0.03 ppm for Western U.S. coals. Kuhn et al. (1978) found 0.12 ppm in the two coals studied.

Boyle (1968), in a thorough review of the occurrence of silver in coal, has cited a number of early studies showing Ag values over 100 ppm in the ash. He summarizes his observations as follows:

1. Higher silver contents are generally recorded from coal seams low in ash and rich in trace elements such as Cu, Pb, and Zn.
2. Higher silver contents are found in sulfide enriched (pyrite) parts of the seam.
3. Higher silver contents tend to occur in the coal near the top and bottom of individual seams. (No comment was made on relation of sulfides to seam margins.)

Silver values are particularly high where coals have developed on mineralized rock (Wedepohl, 1974).

Boyle (1968) suggests the following modes of occurrence for silver in coal:

1. Some Ag may be found as metal-organic complexes.
2. A very small amount may be adsorbed to the coaly substances.
3. Much silver is present in or associated with pyrite. Some Ag is generally present in the other sulfides

present in coal.

4. Very small amounts may occur in calcite, siderite, barite, and hematite. In rare instances silver minerals such as argentite (Ag_2S) and freibergite $\{(Ag, Cu)_{12}(Sb, As)_4S_{13}\}$ may be present.
5. He notes that native silver and chlorargyrite (AgCl) have been observed in coal fragments in sandstone.
6. In weathered coal silver may occur in jarosites and iron oxides.

Bethell (1962) assumes that most of the Ag is in argentiferous pyrite; however, some may be associated with the coal substance. Swaine (1964) could not detect silver in sulfide or carbonate concentrates of Australian coal. Using a laser microprobe, Carruccio (1972) found silver present (no values given) in "reactive" pyrite (i.e. readily oxidized), but he found no silver in the "inert" pyrite. Cambel and Jarkovsky (1967) found no detectable silver in pyrite from Czechoslovakian coals. Fleischer (1955) found Ag to exceed 100 ppm in only two of 73 pyrite analyses.

Kuhn et al. (1978) found silver to concentrate in the heavy Sp. G. fractions of both of the coals they studied. Leutwein and Rosler (1956) found Ag to have organic tendencies. Bogdanov (1965) found Ag to display a strong inorganic association.

If we consider the relative scarcity of Ag in coal, a surprisingly large number of silver-bearing particles have been observed in the present study with the SEM-EDX. Silver was detected in gold particles from the Canadian Devonian coal and the Ferron coal; silver sulfides (argentite?) were observed in the Upper Freeport coal and in the coal from South Africa; and a fleck of native silver was observed in the Waynesburg coal. A silver sulfide was also detected with the SEM by Lee et al. (1978).

In the sink-float tests of the Waynesburg coal and LT ash, the highest values of Ag were found in all of the sink fractions, although substantial amounts remained in the lighter Sp. G. fractions of the coal.

Silver was detected in most of the coals analyzed for this report, generally in concentrations less than 1 ppm in the ash. Exceptionally high values were found in the sulfide-rich Nova Scotia coal (7.2 ppm in the ash) and in the Beulah coal (7.4 ppm in the ash).

Boyle's (1968) comprehensive list probably contains all of the possible modes of occurrence of silver in coal. From the micromineralogical observations, it seems that the proportion of Ag occurring as silver sulfides (probably argentite) may be more significant than Boyle allows.

Strontium: The mean value for strontium is 100 ppm (Swanson et al., 1976).

In the sink-float experiments of Gluskoter et al. (1977), Sr exhibited the highest organic affinity in one sample and one of the lowest organic affinities in another. In the remaining three samples and in the samples of Kuhn et al. (1978), strontium displayed a strong organic affinity. Both Hawley (1955) and Bogdanov (1965) found Sr to display intermediate behavior.

Brown and Swaine (1964) found 0.5 percent Sr in Australian calcites; no Sr was detected in siderite. Because the Sr content of some Australian coals is fairly high, Brown and Swaine reason that there must be other sources of Sr in addition to the small amounts associated with barium and calcium minerals. As no strontium minerals were detected, they suggest that in low-rank coals, Sr may be organically bound to carboxyl groups, as is calcium. Miller and Given (1978) found the majority of the Sr in a North Dakota lignite is attached to carboxyl groups, whereas barium appeared to be inorganically bound. Similar results were obtained from two lignites from Alabama and a Texas lignite. However, in the Wall seam, a subbituminous coal from Wyoming, an appreciable proportion of the Sr was found in the acid extracts and in the acid insoluble fractions.

Working with a high rank coal, Filby et al. (1977) calculated 71 percent of the Sr was inorganically bound. Strontium is one of only three elements (Mn and Ba are the others) that Leutwein and Rosler (1956) attribute almost exclusively to foreign ash. Nicholls (1968) concluded that Sr is generally associated with the inorganic fraction of the coal, probably with the carbonates, but some Sr may have been sorbed into clays.

In the sink-float experiment on the Waynesburg coal, Sr was strongly concentrated in the lightest fraction of all size splits. It was also concentrated in the lighter fractions of the LT ash. Barium was not as strongly fractionated in the sink-float separations.

In the IMP analysis of the Waynesburg coal, Sr (at the several hundred ppm level) was detected in all the vitrinite samples and in a resin body. It was not observed in a microspore. The microspore was the only organic sample in which the K/Ca ratio was greater than unity. This may indicate that Sr is complexed in a manner similar to Ca in the organic matter.

In this study numerous strontium bearing minerals were encountered in many coals. These include the crandallite group minerals; in at least one grain the Sr concentration appeared to be high enough for it to be classified as the Sr end-member, goyazite; barites, with varying amounts of Sr; celestite (strontium sulfate) in the Beulah coal; Sr-bearing rare-earth phosphates; Sr-bearing carbonates; strontianite (strontium carbonate) in the Sewell coal; and Sr-bearing clays (O'Gorman, 1971, suggests that Sr may be absorbed by illite).

In the samples chemically analyzed for this report, the highest concentration of Sr was found in the Beulah lignite (13,000 ppm in the ash). This sample contained numerous Sr-bearing barite grains and the celestite particle. High values of Sr were also observed in the Alaska coals (up to 2900 ppm in the ash). These samples had an abundance of calcium-barium carbonates, but strontium appeared to be present in very low concentrations in these carbonates.

It is apparent that Sr can occur in both organic and inorganic association in coal. It would seem that a greater proportion of the Sr in low-rank coals is organically bound, but the IMP analysis of the Waynesburg coal indicates that even in bituminous coals, substantial amounts of Sr may be organically bound. Inorganically bound Sr can occur in a number of different mineralogical forms, as indicated above.

Tantalum: Rankama (1944) found tantalum values of 60 and 80 ppb in two European coals. Kuhn et al. (1978) report Ta values of 170 ppb for an Appalachian bituminous coal and 130 ppb for a subbituminous Montana coal. Gluskoter et al. (1977) report the following mean values for Ta: 150 ppb for Illinois Basin coals; 330 ppb for Eastern U.S. coals; and 150 ppb for Western U.S. coals.

Geochemically, tantalum closely follows niobium. The Nb/Ta ratio on the earth's crust is about 10 (Wedepohl, 1978). If the mean value for Nb in coals is 3 ppm (Swanson et al., 1976), then the mean value for Ta should be close to 300 ppb.

Rankama (1944) suggested the possibility of organometallic complexing of Ta in coal. The sink-float data of Kuhn et al. (1978) show Ta to be relatively enriched in the sink fractions of both coals studied. They attribute an intermediate organic affinity to Ta. In the sink-float experiments of Gluskoter at al. (1977), Ta displays a strong inorganic affinity. Solodov et al. (1975) found Ta to increase with ash content; this is indicative of an inorganic association.

In the Waynesburg coal, Ta was detected in three intermediate splits. In the LT ash, Ta was found in the two lighter fractions. It was pointed out earlier (see niobium) that the Zr/Nb ratios of these sink-float splits were uniform, and it was speculated that this ratio reflects the physical association of detrital Nb-bearing titanium minerals with zircons. The Hf/Ta ratio is equally uniform, ranging from 2.6 - 4.6 with a mean of 3.7. The Hf/Ta ratios from the data of Gluskoter et al. (1977) are 3.6 for Illinois Basin coals, 3.6 for the Eastern U.S. coals, and 5.2 for Western U.S. coals. This favorably compares to a ratio of 3 that would be expected from a granitic source (D. Gottfried, personal communication, 1979). In the data of Kuhn et al. (1978), Ta exhibits a very strong positive correlation with both Ti and Hf.

Tantalum was detected in the Devonian coal by the SEM-EDX system in one particle which is probably a member of the columbite-tantalite group.

Not surprisingly, it appears that Ta, like Nb, is primarily associated with the detrital inorganic matter in coal.

Tellurium: No values could be found for tellurium in coal. Goldschmidt (1954) notes that tellurium has been reported in small amounts in coals; however, he gives no further data. Wedepohl (1972) states that Te has not yet been detected in coal or lignite ashes. Kuhn et al. (1978) found Te to be less than 1 ppm in both samples studied.

The Se:Te ratio in common igneous rocks is about 70:1 (data from Wedepohl, 1972). The concentration of Te in coal would, therefore, not be expected to be much more than about 60 ppb. However, the geochemistry of Te does not parallel that of Se very closely. Te displays strong chalcophile tendencies but does not readily replace S in sulfides as does Se. A reflection of the differences in the geochemistry is the large number (about 40) of independent minerals of this rare element (Wedepohl, 1972).

Tellurium was not detected in any of the samples chemically analyzed in this study. In the SEM-EDX, a micron-sized gold-tellurium particle was observed in the Upper Freeport coal, probably one of the half-dozen known gold tellurides.

Thallium: From the data of Voskresenskaya et al. (1962) and Voskresenskaya (1968), it appears that there is slightly less than 1 ppm thallium in coal. Gluskoter et al. (1977) report a mean of 0.66 ppm Tl for Illinois Basin coals. Kuhn et al. (1978) found 0.54 ppm Tl in the Appalachian coal and 0.46 ppm in the Western coal.

Voskresenskaya (1968) claims that the concentration of Tl in coal varies with the source rocks. High Tl values are derived from erosion of granitic terrains, low Tl values from carbonate sources. Voskresenskaya (1968) found pyrite from coal could have as much as 200 ppm Tl and in some areas average over 30 ppm. Wedepohl (1972) cites several studies of marcasite that contain over 1000 ppm Tl. Wewerka et al. (1978) detected Tl by EMP analyses of pyrite from Illinois Basin coal. But Cambel and Jarkovsky (1967) could not find any Tl by spectrochemical analysis of pyrites extracted from Czechoslovakian coals.

Bodganov (1965) found Tl to have a strong organic affinity (as do most chalcophile elements in his study).

Voskresenskaya (1968, p. 158) states that "It has been established that thallium in coals of a series of coal basins accumulates in sulfide inclusions, chiefly in pyrite, and is lacking in the organic coal mass." No other discussion of the mode of occurrence of Tl in coal was found.

Although the association of Tl with the sulfides is certainly a major mode of occurrence of this element in coal, it is probably not the only one. Goldschmidt (1954) points out the similarity of geochemical behavior of Tl and the alkali metals (K, Rb, and Cs). On the earth's crust the behavior of Tl is dominated by this resemblance. Surely some thallium is in the micas and clays. The possibility of Tl being adsorbed in clay minerals has been pointed out by Shaw (1957). Furthermore, thallium precipitates with manganese in strong oxidizing environments (Wedepohl, 1972). This mechanism should not be discounted as inappropriate for coals. Thallium was detected in only one sample analyzed in this study (Brazil coal: 7.8 ppm in the ash). This sample, with modest sulfide content, had the highest Mn concentration encountered (1800 ppm in the ash). It is, of course, conceivable that the Tl coprecipitated with the Mn and was subsequently incorporated into the sulfides.

In this study, a trace amount of Tl was believed to have been detected by the SEM-EDX system in a chalcopyrite grain from the Fruitland coal. About 850 ppm Tl was detected by IMP analysis of an iron sulfide particle from the Upper Freeport coal.

In the Upper Freeport coals, Cecil et al. (1979A) found that thallium statistically correlated with CaO (calcite), Fe_2O_3, As, and total sulfur, a rather diverse assemblage of components.

The epigenetic origin of the As has already been discussed, and it is likely that substantial amounts of iron (reported as Fe_2O_3) and sulfur also have an epigenetic origin. The obvious implication of the statistical correlation is that significant amounts of Tl are associated with the epigenetic sulfides. The curious correlation with CaO, most of which is present as calcite, may reflect the similar geologic controls on all epigenetic mineralization. The abundance of both calcite and epigenetic sulfides (with As and Tl) may have been controlled by the amount of fracturing or the permeability of the coal.

Thorium: The mean value for thorium in U.S. coals is 4.7 ppm (Swanson et al., 1976).

Bethell's (1962, p. 415) comment that "nothing appears to be known of the occurrence of thorium in coal" reflects the state of the knowledge at that time.

The sink-float data of Gluskoter et al. (1977) shows thorium to have generally strong inorganic affinities. In contrast, Kuhn et al. (1978) suggest that Th has organic tendencies, despite the fact that Th was relatively enriched in the heavier Sp. G. fractions.

Filby et al. (1977) estimated that 97 percent of the Th in their sample was inorganically bound.

In the sink-float tests of the Waynesburg coal and LT ash, Th was concentrated in the intermediate Sp. G. fractions (Appendices III B and D).

In the present study, thorium was detected in many of the monazite grains analyzed in the SEM-EDX system. The most common varieties of monazite contain from 4 to 12 percent ThO_2 (Deer et al., 1962). The median, 8 percent ThO_2, corresponds to about 7 percent thorium. This seems somewhat high for the monazites found in coal. The SEM-EDX analysis, while essentially qualitative, nevertheless allows order of magnitude differences to be distinguished. The Th contents of the monazites in coal appeared consistently closer to 1 or 2 percent than to 10 percent. A mean of 3-4 percent Th seems reasonable. Plugging 3½ percent Th into the formula used in Section 2.173 to calculate elemental abundances in the ash, we obtain a value of 13 ppm Th. This compares favorably to the 11.6 ppm found by OES in the Waynesburg coal LT ash.

The Th/Zr ratio of the Waynesburg coal is identical to that of the crustal average (Taylor, 1964); this implies a predominant detrital source for Th (see discussion of Zr).

Monazite is one of the few minerals that occurred as both authigenic and as detrital grains in roughly equal abundance. It would be interesting to know the Th concentrations of the monazites with these two distinct origins. It may be possible that the apparent low mean value of Th in coal monazites is due to low Th values in the authigenic particles. If this is true, the seemingly contradictory results of Gluskoter et al. (1977) and Kuhn et al. (1978) may simply reflect different behavior of authigenic and detrital monazites. The detrital Th-rich grains would be concentrated in the ash-rich zones, readily sinking to the heavier Sp. G. fractions, whereas the authigenic Th-poor monazites, enmeshed in the organic constituents, would tend to float.

In this study, small amounts of Th were also detected in a few zircons and in some xenotime grains. Thorium was a major component in one RE phosphate.

Baranov and Titayeva (1961), in a study or organic rich sediments, concluded that thorium entered the sediments with the detrital and colloidal materials.

It is apparent that most of the thorium in coals is inorganically bound, probably in monazite particles that are present in most coals (Table 8). Smaller amounts are found associated with xenotime, zircon, and perhaps with the clays.

Tin: Gluskoter et al. (1977) give the following mean values for tin in U.S. coals: 2 ppm in Eastern coals; 3.8 ppm in Illinois Basin coals; and 1.9 ppm in Western U.S. coals.

In a rare display of unanimity, Horton and Aubrey (1950, Zubovic (1961), Gluskoter et al. (1977), and Kuhn et al. (1978) all indicate that tin exhibits a strong inorganic tendency in all sink-float experiments.

Brown and Swaine (1964) found no evidence of the form in which Sn occurs in coal. They did not detect it in the sulfides or carbonates from Australian coals. Cambel and Jarkovsky (1967) found essentially no tin in pyrite from Czechoslovakian coals.

Leutwein and Rosler (1956) found tin to be bound to the organic residues in coal. An organic association is supported by the data of Terbenina and Angelova (1962) who found tin enriched in the benzene and ethanol extracts of coal. Otte (1953) concluded that tin is associated with both the "coal substances" and the minerals. Bogdanov (1965) found tin to be associated with the inorganic matter. According to Wedepohl (1969), the tin content of coals generally increases with increasing ash content, an indication of an inorganic association.

Miller and Given (1978) ascribe organic affinities for many of the trace elements in the North Dakota lignite; however, they note that in contrast to these other elements, tin was detected only in the heavy fraction of this coal.

O'Gorman (1971) found high values of tin (4250 ppm) in the ash of a Pennsylvania anthracite. The tin was found to concentrate in the sink fraction. X-ray diffraction data of 600^{o}C ash suggested the presence of cassiterite (SnO_2).

In the sink-float separation of the Waynesburg LT ash there was no clear differentiation of tin.

A number of tin-bearing minerals were encountered in the SEM-EDX scans. These included five tin oxides, two tin sulfides, a tin nickel oxide, and a tin-iron-copper sulfide. Several other minerals (silicates, carbonates) had trace to minor amounts of tin. Some of these minerals occurred as micron-size grains in the organic matrix. In the LT ash of the Waynesburg coal, several green tin-copper-lead oxides were observed. No X-ray powder pattern could be obtained from these particles, which are assumed to be contamination.

The evidence in the literature and the results of the present study point to a decided inorganic affinity for tin. It is possible that much of the tin occurs as finely disseminated oxides (cassiterite?) and sulfides.

Titanium: The mean value for titanium in U.S. coals is 0.08 percent (Swanson et al., 1976). Although Ti is not a trace element, the information obtained in this study was helpful in understanding the modes of occurrence of this technologically important element.

In the sink-float data of Gluskoter et al. (1977), titanium generally exhibited an inorganic association. Bodganov (1965) also found Ti to be associated with the inorganic matter. In the study of Kuhn et al. (1978) Ti had an organic tendency in one sample and an inorganic tendency in the other. In the studies of Otte (1953), Zubovic (1961), and Horton and Aubrey (1950), Ti exhibited organic tendencies.

Brown and Swaine (1964) suggest that some titanium may occur in organic combination in coals as well as in mineral form. In support of their suggestion they cite the titanium rich vitrains. Reynolds (1948) described a vitrain with 15 percent TiO_2 in the ash, and Jones and Miller (1939) report 24 percent TiO_2 in a "cauldron vitrain." These unusual structures are believed to be fossilized tree trunks. Zubovic (personal communication, 1979) believes they may have acted as conduits for the gorundwater, allowing the organic matter to adsorb unusually high concentrations of Ti, Ni, V and Cr. Sherbina (1956, cited in Manskaya and Drozdova, 1967) concluded that only the formation of humate complexes could explain the concentration of titanium in these coals.

In the sink-float study of the Waynesburg coal and LT ash, Ti was concentrated in the lighter fractions.

Miller and Given (1978) found significant proportions of acid-insoluble titanium in all Sp. G. fractions of the North Dakota lignite. They note that the more common Ti-bearing minerals are all acid insoluble. However, the concentration of acid-insoluble Ti increased somewhat in the lighter Sp. G. fraction. Furthermore, they noted that no titanium minerals were identified during extensive hand-picking studies and that there is a somewhat larger proportion of acid-insoluble Ti in the lighter fractions than would be expected if Ti were wholly present in the scarce clay minerals. They concluded that a portion of this Ti was associated with clay minerals, but some of the acid-insoluble titanium may also be organically held.

It is possible that the distribution of the acid-insoluble Ti observed by Miller and Given (1978) may be due to the rafting effect of the organic constituents on the included titanium minerals. As noted above, Ti in the Waynesburg coal was also concentrated in the lighter Sp. G. fractions. Yet, at least 50 percent of the titanium on the Waynesburg coal appears to be inorganically bound.

Miller and Given (1978) also found significant proportions (30-51 percent) of the Ti in the lighter Sp. G. fraction was acid soluble. They conclude that this Ti is present in organic complexes.

In the other low-rank coal seams they examined, they found that a significant proportion of the Ti at most levels is acid soluble. In all seams the proportion of acid-soluble Ti was always much higher in the coal than in the adjacent inorganic sediments. They conclude that much of the acid-soluble Ti in marginal zones of the coal and in the associated inorganic sediments is due to detrital minerals, whereas the acid-soluble Ti is present as an organic complex (perhaps derived from a breakdown of detrital Ti-bearing minerals).

It was noted in Section 2.173 that only one third of the titanium in the Waynesburg lithotype could be accounted for as titanium dioxide. Taking into account the Ti in clays and other accessory minerals, it still appears that not much more than 50 percent of the Ti can be accounted for by inorganic association. It was suggested (Section 2.173) that the unaccounted for Ti may be organically bound.

Microprobe analysis by Minkin, Chao et al. (1979) indicated 200-500 ppm Ti uniformly dispersed in the vitrinite of the Upper Freeport coal. This may be organically bound Ti or it may be attributable to submicron Ti-bearing minerals dispersed throughout the vitrinite (Harris et al., 1977).

Titanium oxide minerals were present in ∿33 percent of the coals examined. In some coals they appeared to be quite abundant. X-ray diffraction patterns of rutile were obtained from particles extracted from the LT ash of the Waynesburg coal. Diffractometer tracings of LT ash of the Upper Freeport coal indicated the presence of anatase (Finkelman, Dulong et al., 1979). Miller and Given (1978) report appreciable amounts of anatase in an Alabama lignite. An X-ray diffraction pattern of brookite was obtained from fusinite cell fillings extracted from the LT ash of the Ollerton coal. Alekseev (1960) reports finding leucoxene as well as anatase and brookite in Russian coals.

Other Ti-bearing minerals detected in coal samples include ilmenites, sphenes, a titanium-tungsten grain, and a vanadium titanium silicate (Beulah lignite). Many of these titanium bearing minerals appear to be authigenic. Titanium was also detected in a pyroxene (augite), and in low levels in many clays, predominantly illites and mixed-layer clays. Minkin, Chao et al. (1979) report up to 0.49 percent TiO_2 in Upper Freeport illites.

Apparently Ti can also be incorporated into the pyrite structure. Cambel and Jarkovsky (1967) report that pyrite extracted from Czechoslovakian coals average 30-390 ppm Ti, with a maximum of 870 ppm. Caruccio (1972) also reports Ti was found in "stable" pyrite from Appalachian coals. In this study Ti was observed by the SEM-EDX system in pyrite from the Pittsburgh coal.

The highest values of titanium were found in the Wanamie anthracite (0.69 percent in the ash) and in the Spitzbergen coal (0.80 percent in the ash). Numerous titanium and titanium iron oxides were found in the Spitzbergen coal; many appeared to be authigenic. No titanium minerals were found in the Wanamie anthracite.

The mode of occurrence of titanium in a specific coal may be quite complex. It is clear that some Ti may be organically bound, particularly in the low-rank coals. In most coals, substantial amounts of Ti occur as titanium oxides (rutile, anatase, brookite, etc.). Equally substantial amounts of Ti may be associated with the clays. Some Ti may be found in other accessory Ti-bearing minerals (ilmenite, sphene, pyroxene, etc.). Small amounts of Ti may also be associated with pyrite.

Tungsten: Gluskoter et al. (1977) give the following mean values for W: 0.69 ppm in Eastern U. S. coals; 0.82 ppm for Illinois Basin coals; and 0.75 ppm for Western U.S. coals. Block and Dams (1975) found 0.4 to 1.2 ppm W in four groups of Belgian coals.

The sink-float data of Gluskoter et al. (1977) show W to have strong organic tendencies in two samples and an intermediate organic affinity in a third sample. In the experiment of Kuhn et al. (1978), W exhibited organic affinities in both samples. Ratynskiy and Glushnev (1967) concluded that W was probably organically bound. Bogdanov (1965) found W to be associated with the inorganic fraction.

Adsorption and desorption studies led Eskenazy (1977) to conclude that W probably formed covalent organometallic complexes in coal. The ionic potential of W (5.5) is consistent with a high organic affinity (see Zubovic, 1976).

There was no observable concentration of W in the Sp. G. splits of the Waynesburg coal, but W was concentrated in the lighter fractions of the LT ash.

Tungsten was detected in two particles: in one it was associated with lead (perhaps as lead tungstate) in the Waynesburg coal; in the Pewee coal it was associated with titanium and minor niobium. It is perhaps significant that Goldschmidt (1954) remarks on the "rather frequent occurrence of stoltzite ($PbWO_4$) as a secondary mineral . . ."

Tungsten and Mo have similar geochemical behavior except for the stronger chalcophyllic tendency of Mo. Because the mode of occurrence of Mo in coal is currently unclear, this relationship offers us no assistance.

The data at hand suggest a substantial amount of W may be organically bound. Clearly, more detailed studies on this element are desirable.

Uranium: Gluskoter reports the following mean values for uranium in U.S. coals: 1.5 ppm in Eastern coals; 1.5 ppm in Illinois Basin coals; and 1.2 ppm in Western coals. Values much higher than these have been reported. For example, Vine (1956) described a Northern Great Plains lignite that averaged 80 ppm U with concentrations up to 10 weight percent!

There is an extensive literature on the occurrence of U in coals. Abernethy and Gibson (1963) have cited 82 papers on this subject. Akers et al. (1978) have referenced 43 papers on uranium minerals in coal. Other comprehensive discussions include those of Page et al. (1956), Kehn (1957), Breger (1958), U.S. Geological Survey (1959), and Bethell (1962).

Manskaya and Drozdova (1968) offer an extensive discussion on the occurrence of uranium in coal and the types of organic bonding that might exist.

Detailed studies on the mode of occurrence of uranium have been carried out by Breger et al. (1955A) and by Breger et al. (1955B), who found that 98 percent of the U in a subbituminous coal to be associated with the organic components.

Breger (1974) outlined the mechanism by which uranium is concentrated in coal. When solutions carrying complex alkali uranyl carbonates come into contact with coal, the uranium is readily absorbed. Initial retention may be in the form of complex or insoluble uranyl compounds which may be reduced to form uraninite or coffinite.

In the sink-float study of Gluskoter et al. (1977), uranium exhibited organic affinities in three samples and inorganic affinities in two others. Uranium had a generally organic affinity in the two samples studied by Kuhn et al. (1978). Uranium was not determined in any of the samples chemically analyzed for this report.

Cecil et al. (1979D) found the U content of a column of the Upper Freeport coal to vary inversely with the ash content, which is an indication of organic association.

Although there is strong evidence to indicate that the bulk of the uranium in coal is oragnically bound, inorganically bound uranium may be significant in certain coals.

Numerous uranium minerals have been reported from the detailed studies of low-rank Western U.S. coals. Ackers et al. (1978) list about 15 such minerals (see Appendix II). The occurrence of substantial amounts of U in secondary uranium minerals is probably only of significance in mineralized areas such as in the Western U.S. Vine (1956) questions whether these visible uranium minerals are sufficiently abundant to account for all the uranium present in the coals. Nevertheless, this mode of occurrence is of little importance in the far more abundant non-uraniferous coals.

In order to determine the mode of occurrence of uranium in non-uraniferous coals, the "Lexan" technique (described in Section 1.27) was applied to the LT ash of several coals and to a sample of the Chattanooga shale.

In the Waynesburg and Upper Freeport coals, which have about 1-2 ppm U (Swanson et al., 1976), most of the damage in the "Lexan," caused by fissioning of uranium, occurred as single, scattered tracks (Figure 40). This is suggestive of small amounts of dispersed uranium, probably having an organic association in the coal. Up to 20 percent of these tracks occurred in coherent clusters (Figure 40) which were generated by uranium-bearing zircons. Calculations (see Appendix IV) indicate that the zircons contained from 0.06 to 0.5 weight percent uranium. This seems to be consistent with the observations of Hurley and Fairbain (1957) on the U contents of zircons.

In the Laredo coal from Missouri (50-60 ppm U) the bulk of the uranium occurs as micron-sized grains of uraninite (Figure 41). Identification was based on the chemistry of several particles and

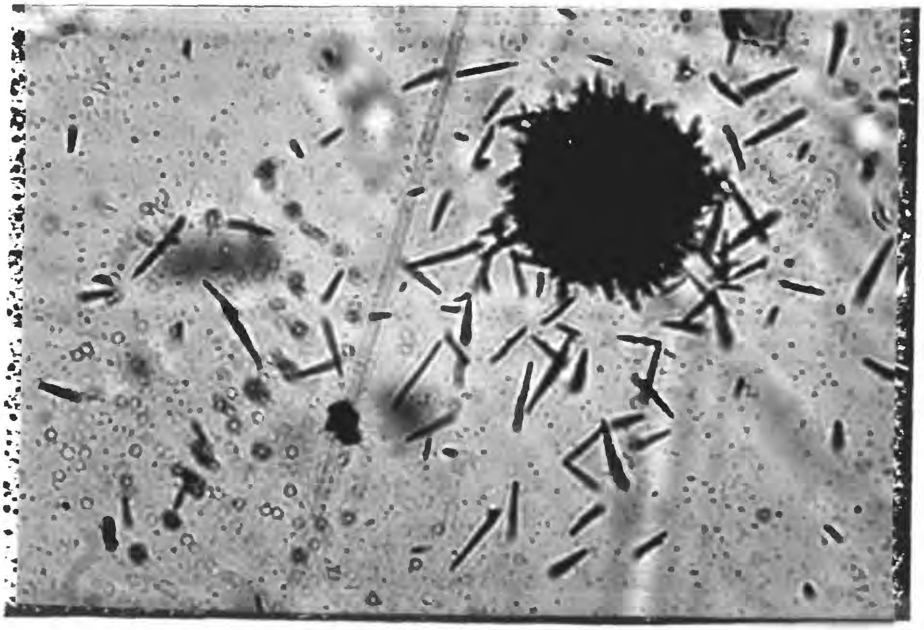

Figure 40. Optical photomicrograph of fisson tracks in "Lexan". Single tracks and a point source "star" are illustrated.

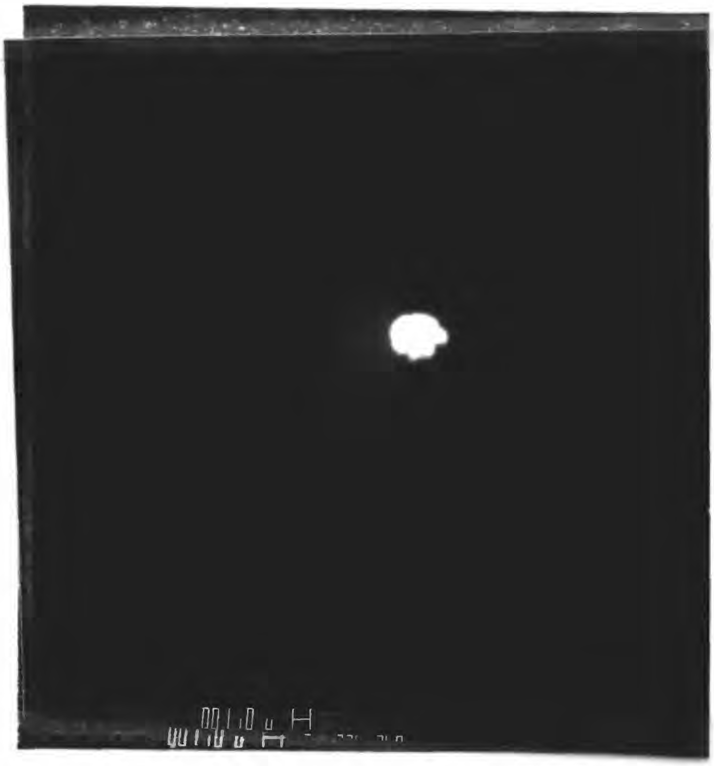

Figure 41. SEM photomicrograph of a urannite crystal from the Laredo coal. Backscattered-electron image.

from an X-ray powder pattern obtained from a single grain. This observation supports the suggestion (Breger, 1974) that uranium is reduced from U^{+4} to U^{+2} in coal.

Preliminary data from several other Missouri coals (U contents of 13-19 ppm) indicate that the uranium is associated with a variety of minerals such as apatite, monazite, uraninite, zircon, calcite, rutile and a lead-bismuth phase. The last phase is of interest. Particles were detected in two different samples. Both Pb and Bi are radiogenic daughter products of U-235, U-238, and Th-232. If indeed the Pb and Bi in the coal mineral are radiogenic daughter products, this particle would have had to have been derived from an earlier generation of uranium mineralization than the coexistent uraninite.

The uranium in the Vermillian coal from Wyoming appears to be virtually all in organic association. Perhaps one percent of the uranium is in accessory phases, primarily zircons.

About one third of the uranium in the carbonaceous Chattanooga shale is found in zircons. The rest may be organically bound. A recent report (Judzis and Judzis, 1978) claims to have detected uraninite, uraniferous apatite and titanium oxides in the Chattanooga shale.

In the SEM-EDX system small amounts of uranium were detected in zircons, but larger amounts (perhaps several tenths of a percent) were observed in a number of RE-phosphates.

In summary, much of the uranium in coal appears to be organically bound. However, substantial proportion may be associated with accessory minerals such as zircons and RE-phosphates. In low-rank Western coals, secondary mineralization may create a diverse suite of uranium minerals.

Vanadium: The mean value for vanadium in U.S. coals is 20 ppm (Swanson et al., 1976).

Vanadium, like nickel and titanium, is often found in unusually high concentrations in certain carbonaceous deposits. Reynolds (1948) reports 14.1 percent V_2O_5 in the ash of an English vitrain. (See the discussion for either of these other elements for comments on the enrichment process.)

Bethell (1962) summarized the extensive work on the distribution of V in coals, and Swaine (1975) discussed the biological significance of this element. Numerous authors have commented on the mode of occurrence of vanadium in coal.

The sink-float studies of Horton and Aubrey (1950), Zubovic (1961), Gluskoter et al. (1977), and Kuhn et al. (1978) all show vanadium to have a generally organic association. Szilagyi (1971) interprets the distribution of V in Hungarian coals and coal ash as indicative of both organic and inorganic associations. This conclusion is shared by Leutwein and Rosler (1956) and by Bogdanov (1965). Nazarenko (1937) and Razdorzhnyy (1967) both found that V contents of Russian coals increased with ash content, a relationship indicative of an inorganic association.

Otte (1953) found V to be associated with the "organic substance," as did Almassey and Szalay (1956). However, Manskaya and Drozdova (1968) have noted that there are no experimental data on the type of organic bonding of V in coals.

Based on sink-float data, Gindy et al. (1978) suggested that V has a high organic affinity on a whole coal basis. However, they report that V was depleted in vitrain separates. These data appear to be consistent with V being associated with the clays.

Miller and Given (1978) found 72 percent of the vanadium in the two lighter Sp. G. fractions of their North Dakota lignite. They interpret this to indicate that the vanadium is organically bound by chelation or by ion exchange. The remaining V, they suggest, could be accounted for as present in clay minerals.

Zubovic (1966 A) believes that V replaces other metals in existing organic complexes in degraded woody material. However, when he (Zubovic, 1966B) examined an Illinois Basin coal in which V was concentrated in the upper part of the bed, he found the V to show a large degree of inorganic association in the enriched part and a completely organic association in the unenriched part.

Miller (1974) found V to be highly correlated with clays, especially mixed-layer clays.

Nicholls (1968) found V to be predominantly associated with the inorganic fraction of the two coals in which he looked at the variation of the element with ash content. Nicholls suggests that the bulk of the V in coals is adsorbed on clays. He suggests that the possibility of some V being associated with the sulfides should not be eliminated. But Brown and Swaine (1964) could find virtually no V in pyrites from Australian coals. Cambel and Jarkovsky (1967) found less than 50 ppm V in pyrites from Czechoslovakian coals. In a literature survey on minor elements in sulfides, Fleischer (1955) found that pyrite can contain up to 1000 ppm V. However, only one study reported finding more than 200 ppm V.

In the sink-float study of both the Waynesburg coal and LT ash, vanadium was concentrated in the lighter Sp. G. fractions.

Relatively few vanadium-bearing minerals were detected in this study. A vanadium titanium silicate intimately intergrown with a vanadium-bearing iron silicate (Figure 42) was observed in the Beulah lignite. Curiously, the lignite had only 61 ppm V in the ash. Vanadium was observed in only one other mineral, a V-Ti-bearing potassium aluminum silicate in the coal from China.

Bethell (1962, p. 417) indicates that for V, "the most favored mode of extrinsic combination proposed is carnotite ($K_2O \cdot 2UO_3 \cdot V_2O_5 \cdot 3H_2O$)." This suggestion may have significance in areas of uranium mineralization, but it has no relevancy for the V in most coals. The available data point to a possible organic association for some vanadium and a probable association of inorganically bound V with clays. If all the vanadium were in the clays, they would, on the average, contain about 400 ppm V. This appears to be somewhat high (Wedepohl, 1974). It is perhaps possible that montroseite {VO(OH)} occurs in coal.

Figure 42. SEM photomicrograph of an intergrowth of an iron silicate (dark) and a vanadium silicate (light) from the Beulah coal.

Figure 43. SEM photomicrograph of montroseite crystals in a Venezuelan asphaltite. Backscattered-electron image.

Asphalts, bitumen and some crude oils have long been known to contain extraordinary amounts of vanadium in the ash. Goldschmidt (1954) reports values of 50-75 percent V_2O_3. A Venezuelan asphaltite having more than 1000 ppm V in the ash was examined in the SEM. The only inorganic phase observed was a myriad of small (∿5 μm) randomly oriented crystals (Figure 43) containing major vanadium, with minor iron and nickel. An X-ray powder pattern of the LT ash (2.5 weight percent) indicated that the vanadium-bearing phase was montroseite. Two Venezuelan coals (one with 260 ppm V in the ash) were also examined, but no vanadium-bearing minerals were noted.

Ion microprobe analyses of the Upper Freeport coal indicated that V was below the limits of detection (a few ppm) in the vitrinite and the inertinite. About 40 ppm was found in kaolinite. Values of 140 and 250 ppm V were detected in two analyses of illites. An average of 200 ppm V in the illites would probably be sufficient to account for all the vanadium in this particular sample.

Yttrium: The mean value for yttrium in U.S. coals is 10 ppm (Swanson et al., 1976).

Geochemically Y is closely related to the Rare-Earth elements, particularly the heavier Rare-Earths, Gd → Lu, with which Y forms the phosphate mineral xenotime.

Brown and Swaine (1964) noted that there was poor correlation between phosphorus and yttrium and the rare-earths. This is not surprising in view of the relatively high abundance of apatites in Australian coals (Kemezys and Taylor, 1964). Also, see the comments on the significance of correlation coefficients in Section 3.214.

Bodganov (1965) found Y to behave as if it were associated with the organic matter. Zubovic et al. (1960) found Y to have an intermediate affinity. Miller and Given (1978) found Y to be concentrated in the lighter Sp. G. fractions of the North Dakota lignite. Because of this, they attribute a high degree of organic association to this element.

Goldschmidt and Peters (1933) and Ratynskiy and Glushnev (1967) both suggested that yttrium (and the rare-earths) has both organic and inorganic associations in coal.

In the sink-float testing of the Waynesburg coal and LT ash, Y follows the rare earths and is concentrated in the lighter Sp. G. fractions.

There is a good correlation ($r = 0.84$) between Y and Yb in the various coal splits, although Yb seems to be preferentially enriched in all the sink 1.7 fractions.

Xenotime was observed in at least 25 percent of the coal sample studied (Table 8). In the Waynesburg coal there was a sufficient number of xenotime particles to account for all the yttrium in the ash (Table 9).

Clearly, substantial amounts of Y in many coals occur in the abundant xenotime particles. The sink-float data is consistent with finely dispersed minerals in an organic matrix which is the usual occurrence of xenotime. For further discussion of possible alternative modes of occurrence, see the section on the rare earths.

Zinc: The mean value for zinc in U.S. coals is 39 ppm (Swanson et al., 1976).

Bethell (1962) reviewed the literature on zinc and concluded that amounts up to about 50 ppm can be associated with the "coal substance," while higher concentrations are attributable to sphalerite. Presumably, cleat sphalerite is implied here.

The occurrence of sphalerite (ZnS) in cleats and fractures in coal has been discussed by numerous authors (see for example: Sprunk and O'Donnell, 1942; Gallagher, 1940; Kemezys and Taylor, 1964; Hatch et al., 1976 A and B). Here as elsewhere in this study, the primary concern is not with the mode of occurrence of the elements in cleats but with their occurrence in the "coal substance."

Gluskoter et al. (1977) and Kuhn et al. (1978) found zinc to have a generally inorganic association. Zubovic et al. (1960) found zinc to have the lowest organic affinity of the elements studied. Horton and Aubrey (1950) attributed an intermediate association to zinc. Ratynskiy and Glushnev (1967) found zinc to have a very low organic affinity. The minor increase in zinc content of the lightest fractions of the coal and ash were attributed to concentrations of zinc by constituents of the exain group. Nicholls (1968) believes Zn to be associated with the inorganic fraction, probably as a sulfide. Both Leutwein and Rosler (1956) and Bogdanov (1965) have cited zinc as being associated with the "organic substance." Miller and Given (1978) found the zinc in their North Dakota lignite (1 ppm level) to be in the acid (HCl)-soluble fraction. They suggest that the zinc was held as ion-exchangeable complexes or as chelate complexes.

In the sink-float study of the Waynesburg coal, zinc displayed a relative enrichment in the higher Sp. G. fractions of all three size splits. Recalculating these data to a whole coal basis shows zinc to be enriched in the lighter fractions (Table 15). This behavior is attributed to the rafting effect of the macerals in which the micron-size sphalerite particles are enmeshed. Zinc was enriched in the sink fraction in the Waynesburg LT ash sink-float experiment.

The highest value for zinc was found in the sulfide-rich Nova Scotia coal (540 ppm in the ash).

In the quantitative determination of trace elements in the Waynesburg ash (Table 9), all of the zinc in the ash was accounted for by the sphalerite particles. Sphalerite had the second highest frequency of occurrence of the accessory sulfides, occurring in almost half of the samples studied (Table 8). Zinc was detected in only a few other minerals; all were sulfides (a trace of zinc was noted in a carbonate from a Florida peat). Two of these sulfides had major calcium (in the Denver lignite and in the coal from mainland China). Zinc was detected in only a few pyrite particles and generally at very low concentrations. One cluster of pyrite grains in the Upper Freeport coal appeared to have percent levels of zinc. IMP analysis of Waynesburg coal pyrites indicated zinc to be generally less than 100 ppm.

The ability of zinc to enter the pyrite structure appears to be limited. In a study of trace elements in pyrites from Czechoslovakian coals, Cambel and Jarkovsky (1967) found zinc to be generally below 10 ppm, although in one coal province, the pyrite had an average of 110 ppm zinc.

It seems that the bulk of the zinc in most coals occurs in sphalerite. Small amounts occur in other sulfides including pyrite. Some zinc in low rank coals (low zinc concentrations?) may be organically bound.

Zirconium: The mean value for zirconium in U.S. coals is 30 ppm (Swanson et al., 1976).

Zirconium exhibited strong inorganic tendencies in all the samples of Gluskoter et al. (1977) and Kuhn et al. (1978). Bogdanov (1965) found Zr to be associated with inorganics, but Leutwein and Rosler (1956) and Otte (1953) found Zr to be associated with the "organic substance."

In the Waynesburg coal, Zr was concentrated in the lighter fractions and was strongly depleted in the heaviest fraction (perhaps due to dilution by pyrite). In the LT ash there was a slight enrichment of Zr in the two lighter Sp. G. splits.

The occurrence of zircon in coal is well established (see Appendix II). Hoehne (1957) conducted a detailed petrographic study of zircons in coal. It was shown (Table 9) that there were sufficient zircons in a Waynesburg coal lithotype to account for all the Zr in the ash. In this report the coal with the highest Zr content (Brazil: 2400 ppm in the ash) had numerous zircons in the clay, in the organic material, and in the detritus (Figure 44).

From the SEM-EDX study there is textural evidence, such as crystals in inertinite pores, that suggests that some zircons in coal are authigenic.

Butler (1953) found a positive correlation between Zr values and ash. He suggested that the association was due to detrital zircons. However, he noted high (0.1 percent) concentrations of Zr in the ash of clarains. He interpreted this as indicating that Zr is not entirely of detrital origin. No suggestion was offered as to the mode of occurrence of the non-detrital zirconium.

Miller and Given (1978) found Zr to be concentrated in the lighter Sp. G. fractions of a North Dakota lignite. They suggest that an organic complex of Zr could exist in lignite. A mineralogical (SEM) study of the North Dakota lignite would be highly desirable, because zircons were detected in only one of the four lignites studied.

Another possible mode of occurrence of Zr in coal would be in isomorphic substitution in clays (Degenhardt, 1957).

The data for Zr clearly point to a predominant inorganic association. Probably the bulk of the Zr in most high rank coals occurs as zircon. The mode of occurrence of Zr in lignites should be investigated further.

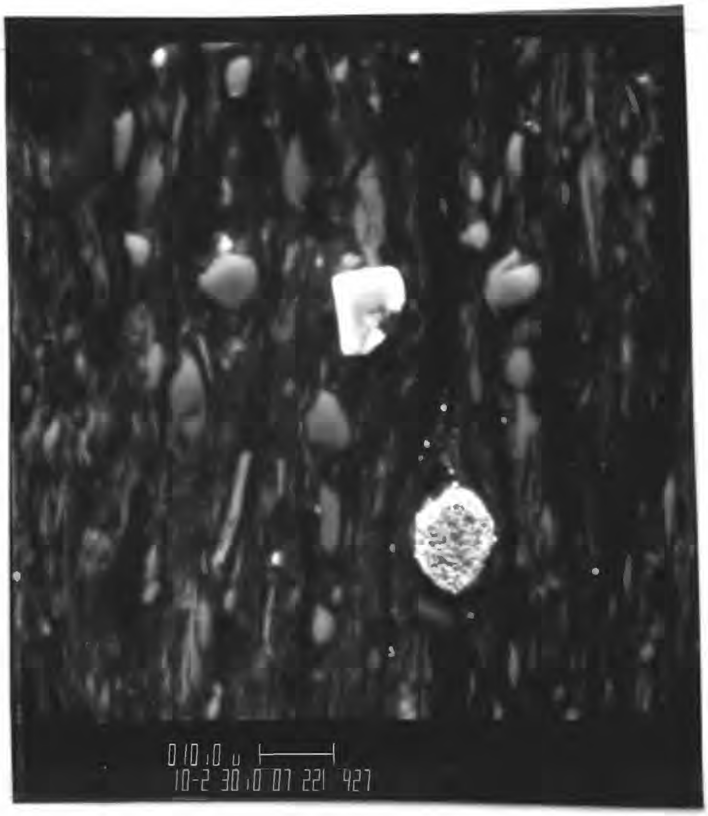

Figure 44. SEM photomicrograph of a "zircon" crystal. Note the pyrite framboid to the lower left.

Other Elements (polonium, astatine, francium, radium, actinium, protoactinium): Few comments could be found concerning the occurrence in coal of these rare, radioactive elements.

Anderson and Taylor (1956) found 0.5 - 3.3 x 10^{-7} ppm Ra in several British coals. Lloyd and Cunningham (1913) found an average of 2 x 10^{-6} ppm Ra in the ash of Alabama coals. Similar values were found in studies cited by Anderson and Taylor (1956) and by Bethell (1962). Sherbina (1957) found radium to exhibit a strong tendency to be absorbed by clays and sulfates (especially barite) and by some organic matter. White (1958) has reported radioactive Ra-bearing barite from Dakota lignites.

Gentry et al. (1976) has suggested that some of the radiohalos in coalified wood from the Colorado Plateau may be due to ^{210} Po accumulation in Pb-Se inclusions.

McBride et al. (1978) and U. S. Environmental Protection Agency (1979) have estimated the annual airborne radioactive materials released from model coal fired power plants. Values for various isotopes of Po, Ra, Ac, Rn, and Pa are given.

No other comments were found concerning the occurrence of astatine, francium, actinium or protoactinium in coal.

Trans-Uranium elements: Bethell (1962, p. 415) says that "nothing appears to be known of the occurrence of . . . the transuranic elements in coal."

3.23 Concluding Remarks

It is evident that most trace elements appear to have an inorganic association in most high-rank coals. It should not be inferred from this observation that organic complexing of trace elements in coal is of minor importance. Indeed, the author believes that many of the trace elements that appear as authigenic phases in coal may have passed through a phase involving organic complexing, either in the living plant or in the decaying organic matter.

It is freely acknowledged that in any one coal, the mode of occurrence of a single trace element or even most of the trace elements may be different than the forms that have been suggested. Nevertheless, it is only by offering suggestions to use as a standard that we are able to evaluate the significance of the differences.

It is hoped that these suggestions will stimulate thought which will ultimately lead to decisive experiments designed to test their merits.

3.3 Mode of Occurrence - Geochemical and Technological Considerations

The major thrust of the current study has been to provide a broad foundation of basic information dealing with (1) the distribution of accessory minerals in coal; (2) the relationships between the accessory minerals and trace elements; and (3) the likely modes of occurrence of trace elements in coal.

Time constraints precluded pursuing any of the interesting applied or practical aspects of these problems. Several of these aspects are briefly treated in the following Sections. They are offered here as suggested areas for future research, research that would require the existence of a data base, such as the one generated by this study.

3.31 Geochemical Considerations

Just as a detailed study of the detrital components of a sedimentary rock can shed light on the type of rocks supplying the detritus, so, too, can a detailed study of the authigenic minerals in coal shed light on the geochemical history of the coal basin.

Intergrowths of authigenic minerals can provide clues as to the conditions prevailing at the time of their formation. For example, an intergrowth of sphalerite and crandallite was observed in the Upper Freeport coal. Sphalerite is stable in acidic, reducing conditions (Garrels and Christ, 1965). Crandallite can form by intense lateritic alteration (Altschuler, 1973). Thus, despite the probable reducing conditions, the groundwater was not stagnant.

The absence of minerals may be just as revealing as their presence. Cecil et al (1979 A) have speculated on the role of pH (as indicated by the occurrence, or absence, of $CaCO_3$) in controlling the trace elements, pyrite content, and total ash in the Upper Freeport coal.

Trace elements appear to exhibit a wide variation of mobility in the depositional basins. As we have seen (Section 3.22), solutions containing As and Hg have flowed through the fractures in the Upper Freeport coal. In the Waynesburg coal, Cr displayed some mobility (Section 2.1211). Comparison of the concentrations of Na, Mg, and K in coal to their crustal abundances (Taylor, 1964) indicates that significant proportions of these elements have been removed from the depositional basin. In contrast, elements such as Zr, Hf, Cs, Th and Li appear to be chemically immobile. Copper, Zn, Cd, and Pb are no longer in the form in which they entered the depositional basin. But, the mobility of these elements appears to be restricted to the confines of the basin (Section 2.182).

In this context, it would indeed be interesting to know the trace element budget of a modern peat swamp (see for example, Casagrande and Erchull, 1977). What are the chemical forms of the elements as they enter (or leave) the basin? It is likely that organic complexing plays a larger role at this stage than during subsequent stages of the coalification process.

Organic complexing does not appear to have played an important role in the distribution of trace elements in the Waynesburg and Upper Freeport coals. The textural relationships of the accessory minerals, as well as the trace element ratios, appear to be typical of detrital sediments. The apparent lack of organic complexing may be due to the "swamping" of the organically complexed trace elements by the abundant detrital matter. The Indiana coal, with no observable detritus, has a relatively low La/Y ratio. This is consistent with a high degree of complexing of the small, highly charged Y ions by organic matter (Zubovic, 1966B).

Much attention has been given to those elements that are relatively enriched in coal compared to crustal abundances (see for example, Goldschmidt, 1935; Altschuler, 1978). This is understandable in view of the potential environmental, economic, and technologic significance that these concentrated elements may have. In contrast, almost no attention has been given to those elements that are significantly depleted in coal. This is somewhat surprising in view of the fact that from a geochemical standpoint, the depletion processes should be just as revealing as the enrichment processes. Butler (1953) suggested that K, whose simple compounds are nearly all soluble, is readily removed by percolation from decaying coal vegetation.

There have been relatively few attempts to use trace elements in coal to correlate coal seams (Butler, 1953; Alpern and Morel, 1968; O'Gorman, 1971). These studies have looked for relationships among elements with diverse geochemical behaviors. Among the elements considered in these studies are those that have a tendency to form organic complexes (B, Ge, Be), those that form sulfide complexes (Zn, Cu, Pb), those that form soluble compounds (Na, Mg, K, Mn, Ca), and those elements that appear to be chemically inert (Zr, Nb, Ta, Th, Cs, Sc). It is no wonder that these studies have not been successful.

This latter group of "inert" elements does not appear to take part in any chemical reactions in the depositional basin. Their ratios would, therefore, be unaffected by changes in Eh, pH, rate of detrital influx, changes in the plant or bacterial communities, availability of sulfide ions, marine incursions, etc. It would seem that they offer the best chances for success in using trace elements to correlate coal seams.

3.32 Technological Considerations

The main emphasis of this report has been on the attempt to elucidate the modes of occurrence of trace elements in coal. With the type of information generated in this study, equipment and processes could be designed to use our coal resources more efficiently. A few brief comments are in order on the possible practical applications of these data.

Perhaps the most immediate use of these data would be in the realm of coal cleaning procedures. Knowledge of the mode of occurrence of the elements and the form and maceral associations of the minerals should enable engineers to design efficient cleaning techniques. Obviously, attempts to remove physically the accessory sulfides and other finely dispersed accessory phases by present means would be ineffective, but perhaps a combined physical and chemical cleaning procedure may be effective.

Another area of immediate application involves the corrosive effects of trace elements such as Cl and F and the fouling effects of others such as Ti and P. These problems have been discussed by Watt (1968, 1969), and by Grant and Weymouth (1967). Knowing the mode of occurrence of potential feed coals should help to reduce or even to avoid these costly problems.

In recent years there has been considerable concern about the catalytic activity or poisoning effects that certain elements and minerals may have during liquefaction reactions (Coleman et al., 1978; Filby et al., 1977; Gray, 1978; Guin et al., 1979; Mukherjee and Chowdhury, 1976). The factual data generated in studies such as this one may soon be utilized in assessing the role of accessory minerals in liquefaction processes.

There has also been a great deal of concern about the fate of trace elements upon combustion of coal (Torrey, 1978). If the modes of occurrence of the elements are known, it would be a simple matter to predict their behavior during the combustion process, whether it is in coal-burning furnaces or in situ.

Mining of coal generates large quantities of waste that are generally disposed of by creating huge waste piles, commonly referred to as gob piles or culm banks. Lapham et al. (1980) have considered the environmental effects created by the natural combustion of the waste banks. Wewerka et al. (1978) have studied the leaching of trace elements from these banks. Here, too, a knowledge of the mode of occurrence of the trace elements in the raw coal should allow us to anticipate the behavior of the elements during combustion or leaching of the waste banks. This may even lead to more intelligent ways of preventing or avoiding the problems associated with the disposal of coal mine refuse.

Limited use has been made of the potentially vast trace element resources in coal ash. Approximately 100 million tons of coal ash will soon be processed annually. With the knowledge of the mode of occurrence of elements such as Zn, U, Ge, it may be economically feasible to recover them (see for example, Cobb et al., 1979).

4. Summary and Conclusions

Those who know coal best caution most against making generalizations. Nevertheless, generalizations serve a useful purpose as they provide a standard against which observations and hypotheses can be tested. It is with this in mind that the following generalized conclusions are offered.

This study has demonstrated that the SEM-EDX system is a superb tool with which to study the distribution of minerals in coal. The system is ideally suited for determining both the mineral-maceral (textural) relationships and the distribution of those minerals that contain the heavy elements ($Z > 20$).

Based on the textural relationships observed in the 79 samples studied, there appear to be two distinct suites of syngenetic minerals: a detrital suite, consisting of quartz, illite, rutile, zircon, etc., occurring in bands; and an authigenic suite, consisting of kaolinite, carbonates, and sulfides, that generally occur in pores of maceral or in vitrinite.

The accessory minerals in coal may be inconspicuous but they are certainly not insignificant. This study has shown that many trace elements in coal are associated entirely with micrometer-size accessory minerals that are intimately dispersed throughout the organic matrix. As a consequence of this distribution, many of the micrometer-size accessory minerals, and the trace elements they contain, are rafted into the lighter Sp. G. fractions during physical cleaning of the coal constituents for study or in industrial processes. Sink-float data may, therefore, not accurately portray the true chemical environment of most trace elements. Obviously then, the sink-float data must be interpreted with extreme caution when determining organic-inorganic affinities.

A consequence of this distribution and the eventual behavior of the accessory minerals during cleaning of coal is that the lighter fractions, ostensibly the cleanest coal, may contain substantial amounts of potentially toxic (Wood, 1974) trace elements. During the utilization of the coal these elements may get into the environment despite efforts to prevent that from occurring.

The abundance of authigenic accessory minerals observed in this study suggests the existence of a period, during the formation of the coal, in which many elements were quite mobile. Other elements, such as Zr, Hf, Cs, and Th appear to be chemically immobile. This immobility suggests that these latter elements may be particularly useful for correlation of coal seams.

The results obtained in this study indicate that organo-metallic complexing of trace elements may not be of significance in most coals above the rank of lignite. Such complexing may have been significant at an early stage in the coalification process, perhaps coincident with the mobility of the metals. However, the effects of organo-metallic complexing seem to have diminished with increasing rank of coal. The complexing also appears to be diluted by the influx of detritus.

Characteristically there is great variability in the distribution of accessory minerals, and trace elements within and between coal beds. Nevertheless, certain regional characteristics have begun to emerge during the course of this study. The high frequency of occurrence of PbSe grains in coals of the Appalachian Basin is the most obvious of these regional differences. In order to evaluate intra- and inter-basin differences, much more effort is needed in characterizing the

the accessory minerals.

Furthermore, this study has shown that the widespread distribution of most accessory minerals in coal indicates that their mere presence or absence may not be sufficient criteria for characterization of a sample. Rather, recognition of diagnostic mineral suites or quantitative determination of individual accessory minerals is necessary.

Despite the significant progress made in this study in understanding the inorganic aspects of the geochemistry of coal, it is evident that no single analytical tool can provide a complete solution to this complex subject. A unified approach, combining the full capability of each of the analytical tools used in this study is necessary for this purpose.

Much effort in this country is currently being devoted to generating chemical analyses of coals. The data, particularly the concentrations of the trace elements, will undoubtedly be of increasing value as we become more dependent on coal for conversion processes and combustion. But, such analyses offer only a partial picture. The full picture comes into focus only when we know the modes of occurrence of these elements. Perhaps, the single most significant observation to come from this study is that: *it is as important to know how each element occurs in coal as to know how much of the element there is*.

Certainly the modes of occurrence of many trace elements in coal can be variable and complex. However, the geochemical environments prevailing in the peat-forming swamps must have been very similar. This uniformity is evidenced by the fact that most of the mobile trace elements had similar modes of occurrences in most of the coal samples examined for this report. A brief summary of the more probable modes of occurrences of trace elements in coal is presented in the following list.

Sb - probably as an accessory sulfide in the organic matrix

As - solid solution in pyrite

Ba - in barite, crandallites, and other Ba-bearing minerals

Be - organically associated

Bi - accessory sulfide, perhaps bismuthinite

B - generally organic association, some may be in illite

Br - organic association

Cd - in sphalerite

Cs - inorganic association - feldspars, micas, or clays

Cl - organically associated

Cr - clays

Co - associated with sulfides such as pyrite and linnaeite

Cu - chalcopyrite

F - unclear, probably several inorganic associations, such as apatite, amphibole, clays, mica

Ga - clays, organic association, sulfides

Ge - organic association, rarely in silicates, sphalerite

Au - native gold, gold tellurides

Hf - in zircons

In - sulfides or carbonates

I - organic association

Pb - coprecipitated with Ba, galena, PbSe

Li - clays

Mn - in siderite

Hg - in solid solution with pyrite

Mo - unclear, probably with sulfides, or organics

Ni - unclear, may be with sulfides, organics, or clays

Nb - in oxides

P - in various phosphates, some may be organically associated
Pt - probably native Pt alloys
Rare earths - in RE phosphates
Re - sulfides or organics (?)
Rb - probably in illite
Sc - unclear, clays, phosphates or may have organic association
Se - organically associated, as PbSe in Appalachian coals, in pyrite
Ag - probably silver sulfides, but may be complex
Sr - carbonates, phosphates, organic association in low rank coals
Ta - in oxides
Te - unclear
Tl - in sulfides, probably epigenetic pyrite
Th - in RE phosphates
Sn - inorganic, tin oxides or sulfides
Ti - titanium oxides, organic association, clays
W - unclear, may be organically associated
U - organic association, zircon
V - in clays (illite)
Y - RE phosphates
Zn - sphalerite
Zr - zircon

This information on the modes of occurrence of trace elements in coal will be useful for predicting how the elements will behave during the cleaning, combustion, conversion (gasification, liquefaction), and leaching of coal and coal by-products. It may assist us in anticipating the contribution of these elements to corrosion and fouling in coal-burning power plants. Eventually these data may be used in resource recovery technology. Such knowledge should also aid us in reconstructing the geochemical history of coal and should give us some insights in other problem areas in the field of low-temperature inorganic geochemistry.

The following points are considered by the author to be the most significant contributions of this study.

- Demonstration of the usefulness of the SEM in studying accessory minerals in coal and their relationships to the organic constitutents. Perhaps the single most important aspect of the SEM-EDX system is that one can rapidly scan over areas containing thousands of mineral grains and still be able to distinguish most of the micrometer-size particles containing the elements of environmental, technologic, economic, or geochemical interest. The large number of grains that can be surveyed make it easy to accumulate statistically significant data or to rapidly scan large numbers of samples. Thus, in a reasonable time heterogeneous coals can be characterized for the purpose of evaluating their suitability for physical or chemical cleaning, combustion, liquefaction, gasification, or correlation.

- Recognition that data from sink-float experiments are subject to misinterpretation. Many trace elements in coal occur in micrometer-size minerals dispersed throughout the organic matrix. These minerals, and the elements they contain, behave as if they are organically bound. Many conclusions in the literature on the mode of occurrence of trace elements in coal are based on sink-float data and are, therefore, suspect.

- Recognition that certain trace elements are extremely mobile during and after coal formation. These labile elements ultimately formed a complex suite of minerals including sulfides, selenides, carbonates, phosphates, oxides, silicates, etc. Other elements appear to be relatively immobile in this environment and the detrital phases in which they entered the depositional basin remain unchanged throughout the coalification process.

- Finally, an observation noted above bears repeating. It is as important to know how each element occurs in coal as to know how much of the element there is.

APPENDIX I

Coal Petrographic Nomenclature Used in This Report

(Principally from ASTM, 1977)

Attrital coal - the ground mass or matrix of banded coal in which vitrain and commonly fusain bands as well are embedded or enclosed.

Banded coal - coal that is visibly heterogeneous in composition, being composed of layers of vitrain and attrital coal, and, commonly, fusain.

Boghead coal - nonbanded coal in which the exinite (the waxy component) is predominantly alginite.

Bone coal - impure coal that contains clay or other fine-grained detrital mineral matter.

Cannel coal - nonbanded coal in which the exinite is predominantly sporinite.

Carbominerite - association of coal with 20-60 volume percent of mineral matter. (International Committee for Coal Petrology, 1971).

Cleat - the joint system of coal beds, usually oriented normal or nearly normal to the bedding.

Coal - a brown to black combustible sedimentary rock (in the geological sense) composed principally of consolidated and chemically altered plant remains.

Fusain - coal layers composed of chips and other fragments in which the original form of plant tissue structure is preserved; commonly has fibrous texture with a very dull luster.

Lithotype - any of the banded constituents of coal: vitrain, fusain, clarain, durain or attrital coal, or a specific mixture of two or more of these.

Mineral parting - discrete layer of mineral or mineral-dominated sediment interbedded with coal along which, in mining, separation commonly occurs. Layers of bone coal having indefinite boundaries usually are not considered to be partings because they do not form planes of physical weakness. They may merge vertically or horizontally with layers that are bony or coaly shale and that do form planes of physical weakness.

Mineralized coal - impure coal that is heavily impregnated with mineral matter, either dispersed or discretely localized along cleat joints or other fissures. Pyritic or calcareous mineralized coal is most common.

Nonbanded coal - consistently fine-granular coal essentially devoid of megascopic bands.

Vitrain - shiny black bands, thicker than 0.5 mm, of subbituminous and higher rank banded coal.

The classification of the microscopic constituents into groups of similar properties in a given coal is as follows:

Maceral Group	Maceral
Vitrinite	vitrinite
Exinite (or liptinite)	alginite cutinite resinite sporinite
Inertinite	fusinite macrinite micrinite sclerotinite semifusinite

Alginite - a maceral derived from waxy walls (thimble cups) of *Botryococcus* or allied types of algae.

Cutinite - a maceral derived from the waxy coatings (cuticles) of leaves and other plant parts.

Exinite (or liptinite) - a group of macerals composed of alginite, cutinite, resinite, and sporinite.

Fusinite - the maceral distinguished by the well-preserved original form of plant cell wall structure, intact or broken, with open or mineral-filled cell lumens (cavities), and by having a reflectance (except in meta-anthracite) well above that of associated vitrinite.

Inertinite - a group of macerals composed of fusinite, semifusinite, micrinite, macrinite, and sclerotinite.

Maceral - a microscopically distinguishable organic component of coal, but including any mineral matter not discernable under the optical microscope.

Macrinite - the maceral that is distinguished by a reflectance higher than that of associated vitrinite, absence of recognizable plant cell structure, and by a particle size 10µm or greater on any diameter of the section under examination.

Micrinite - the maceral that is distinguished by reflectance higher than that of associated vitrinite, absence of recognizable plant cell structure, and occurring as dispersed or aggregated particles of size less than 10µm and commonly about 1µm.

Resinite - a maceral derived from the resinous secretions and exudates of plant cells, occurring as discrete homogeneous bodies or clusters, individuals of which are usually round, oval, or rod-like in cross section.

Sclerotinite - a maceral having reflectance between that of fusinite and associated vitrinite and occurring as round or oval cellular bodies of varying size (20 to 300 µm) or as interlaced tissues derived from fungal remains.

Semifusinite - the maceral that is intermediate in reflectance between fusinite and associated vitrinite, that shows plant cell wall structure with cavities generally oval or elongated in cross section, but in some specimens less well defined than in fusinite, often occurring as a transitional material between vitrinite and fusinite.

Sporinite - a maceral derived from the waxy coatings (exines) of spores and pollen.

Vitrinite - the maceral and maceral group composing all or almost all of the vitrain and like material occurring in attrital coal, as the component of reflectance intermediate between those of exinite and inertinite.

APPENDIX II

[mineral name, major cations, reference numbers (strong-line X-ray data)]

```
               MINERALS ASSOCIATED WITH COALS
               Silicates
mica 15,35,
 muscovite si,al,k, 11,17,20,22,23,28,42,49,66,67,69, (9.97 3.33 2.57 4.99 4.49)
  hydromuscovite si,al,k, 11,22,51, (3.35 2.60 1.99 10.0)
  sericite  si,al,k, 1,2,44,49,63,66, (9.96 4.47 3.32)
 glauconite si,al,k,na,mg,fe, 52, (10.1 2.59 4.53)
 biotite si,al,k,fe,mg, 1,2,11,22,23,42,43,67, (10.1 3.37 2.66)
pyrophyllite si,al, 12,20,25,48,66, (3.04 4.57 9.14 4.43)
talc si,mg, 41, (9.35 1.53 4.59)
gibbsite al, 49,66, (4.85 4.37 4.32)
clays 15,52,62,
 kaolinite si,al, 1,2,3,4,5,6,7,8,9,11,12,13,14,18,19,20,21,22,23,24,25,28,33,34,35,37,38,40,42,44,45,48,49,50,51,53,55,62,63,
 66,69,70,71, (1.48 2.33 4.34 7.13 3.56)
  dickite si,al, 13,18,49,66, (7.15 3.58 2.33)
  halloysite si,al, 2,42,45, (4.41 7.40 4.34 10.4 1.48)/
  allophane si,al, 36,
  livesite si,al, 11,
  metahalloysite si,al, 11,13 (4.42 7.50 3.63 1.49)
  nacrite si,al, 10,18 (3.58 7.17 4.41 2.43)
 montmorillonite si,al,mg,ca,na, 1,2,3,4,7,11,18,37,40,42,44,45,48,49,55,69, (11.9 4.45 2.56 15.0 5.01 3.07)
  nontronite si,al,fe,na, 65, (15.4 13.9 4.56 3.54 1.52)
  beidellite si,al, 2,13, (15.1 17.6 4.42 3.02 1.52 2.62 2.58 4.52 3.95)
 vermiculite si,al,mg,fe, 48, (14.2 1.53 4.57)
 illite si,al,k, 1,3,4,5,6,7,8,11,12,14,18,25,33,34,35,37,38,40,42,45,48,49,50,51,53,55,62,63,69,70,71, (4.46 3.36 2.57 10.0)
  brammallite na,k,si,al 71,
  hydromica si,al,k, 44,
 mixed -layer clay si,al,mg,k, 1,3,5,9,37,48,55,
  bravaisite si,al,mg, 11,
 expandables si,al,mg,k, 5,33,38,62,
chlorite si,al,mg,fe, 1,2,3,15,20,22,23,33,34,42,48,49,53,55,62,63,
 penninite si,al,mg, 11,28, (7.19 4.80 3.60 14.2 2.84 4.72)
 chamosite si,al,mg,fe, 34,51, (7.06 3.53 2.46 14.0)
 thuringite si,al,fe,mg, 34 (7.05 3.53 2.52 14.1)
 prochlorite (ripidolite) si,al,fe,mg, 1,11,28,66, (7.07 14.1 3.54)/p
staurolite si,al,fe,mg, 2,11,22,23,35,43, (3.01 2.69 2.31 1.39 1.96)
garnet si,ca,mg,fe,al,cr, 2,11,28,35,67,
 grossularite si,al,ca, 13,23, (2.65 1.58 2.96)
epidote si,al,fe,ca, 2,11,12,22,23,35,49,66, (2.90 2.40 1.64 2.68)
pyroxene 35,55,
 augite si,al,ca,mg,fe,ti, 2,11,13,22,23, (2.99 1.62 1.43)
 diopside si,mg,ca, 41, (2.99 2.53 2.89)
olivine(fayalite) 43, (2.50 2.83 1.78)
kyanite si,al, 2,11,22,23, (3.18 1.37 1.93)
andalusite al,si, 66,
lawsonite ca,al,si, 50, (2.62 1.55 2.73)
amphibole 2,35,
 hornblende 11,16,23 (2.70 3.09 3.38)
 magnesioarfvedsonite(?) si,ca,fe,mg,k,al, 41, (8.58 3.15 2.70)
```

Silicates continued

feldspar 11,35,38,48,49,62,63,66,69.
 plagioclase si,al,ca,na, 7,17,41,42,55,69.
  albite si,al,na, 16,23,44, (3.19 4.03 3.21)
  oligoclase si,al,na,ca, 44,45, (3.18 4.03 3.20)
 potash 55.
  sanidine si,al,k,na, 2 (3.26 3.22 3.76)
  microcline si,al,na,k, 23,34,43,44,69, (3.24 4.21 3.83 3.29)
  orthoclase si,al,k, 1,2,23,42,44,45, (3.31 3.78 3.28 4.22)
tourmaline si,al,ca,mg,fe,b,11, 1,2,11,14,22,23,28,35,41,45,69, (2.58 3.99 2.96 4.25 4.00)
zircon si,zr, 1,2,11,22,23,28,29,31,35,41,42,45,49,52,55,66, (3.30 4.43 2.52)
sphene si,ca,ti, 35,41, (3.23 2.99 2.60)
topaz si,al,f, 11,22,23, (2.94 3.20 3.69 1.40)
analcime si,al,na, 7,71, (3.43 5.60 2.93)
chrysotile si,mg, 12 (7.36 3.66 2.45)
laumontite si,ca,al, 32 (4.18 6.97 3.53 9.49)
allanite ? re,si,fe, 41, (2.92 2.71 3.53)

Sulfides

pyrite fe,s, 1,2,3,4,5,6,10,11,12,13,14,15,18,19,20,21,22,23,25,28,29,32,33,34,35,37,38,42,45,48,49,50,51,52,53,55,62,63,66,67,
 69,70,71,
(1.63 2.71 2.42)
marcasite fe,s, 1,2,4,11,12,22,34,42,45,49,53,55,63,67,69,70, (2.71 1.76 3.44)
melnikowite (greigite ?) fe,s, 1,2,45.
sphalerite zn,s, 1,2,4,6,7,22,26,29,31,32,41,42,46,49,55,60,70, (3.12 1.91 1.63)
galena pb,s, 1,2,4,29,31,32,42,46,49,55,72, (2.97 3.43 2.10)
chalcopyrite cu,fe,s, 1,2,29,31,32,41,42,46,55,72, (3.03 1.88 1.60)
pyrrhotite fe,s, 2,49,55,70, (2.06 2.64 2.98)
arsenopyrite as,fe,s, 16,31, (2.68 2.66 2.42)
millerite ni,s, 2,29,30,32,54,57,72, (2.78 1.86 2.51)
linnaeite co,s, 31,46,54,55,57, (1.68 2.84 1.82 2.36)
bornite fe,cu,s, 29,31, (1.92 3.30 2.74 3.18)
cinnabar hg,s, 29,46,72, (3.36 2.86 1.98)
argentite ag,s, 46,51,55.
bismuthinite bi,s, 46.
ulmannite sb,ni,s, 59.
polydymite ni,s 72.
covalite cu,s 72.
realgar as,s 67.
orpiment as,s 67.

Oxides

magnetite fe.2.11.12.28.35.41.51(?).55. (2.53 1.49 2.97 1.61)
diaspore al. 2.11.12.28.55. (3.99 2.32 2.13)
hematite fe. 1.2.3.10.11.12.28.55.69.70. (2.69 2.52 2.70)
goethite fe. 1.2.12.42.48. (4.18 2.44 2.69)
lepidocrocite fe. 1.11.12. (6.26 3.29 2.47 1.94)
quartz si. 1,2,3,4,5,6;7.8.9.10.11.12.13.14.15.18.19.20.21.22.23.24.25.28.32.33.34.35.37.38.40.42.44.45.48.49.50.51.52.53.55.62.
63,66,69,70. (3.34 4.26 1.82)
chalcedony si. 1,32,42,44,45,49,66,69.
opal si. 45,55,69.
tridymite si. 45. (4.11 4.33 3.82)
rutile ti. 1,2,3,14,22.23,25,28.41,50,51,52,55. (3.25 1.69 2.49)
anatase ti. 13,29.35.39,55,62. (3.51 1.89 2.38)
bauxite al. 13
mullite si,al. 12.13 (3.39 3.43 2.21)
andalusite si,al. 49. (5.54 4.53 2.77)
cassiterite ? sn. 17 (3.35 2.64 1.77)
limonite fe. 2,22,28,42,69.
ilmenite fe,ti. 28.35.41.55. (2.74 1.72 2.54)
leucoxene ti. 35
brookite ti. 35,43. (3.51 2.90 3.37)
corundum al. 35,55. (2.09 2.55 1.60)
spinel al,mg. 35,43.
chromite ? cr,fe. 41.51(?). (2.52 1.60 1.46)
jordesite mo. 58,68.
molybdenite mo. 68.72.
ilsemannite mo. 58.68.

Sulfates

barite ba,s. 2.10.12.14.29.31,35.41,42,55. (3.44 3.10 2.12)
gypsum ca.s. 2.3.10.11.15.19.28.33.34.35.38.42.51.53.55.62.67.69. (7.56 3.06 4.27)
kieserite mg,s. 2 (3.41 4.84 3.33)
mirabilite na,s. 2 (5.49 3.21 3.26)
melanterite fe,s. 2,4.34,60,69.71. (4,34,60,69,71,.90 3.78 3.23)
thenardite na,s. 3 (2.78 4.66 3.18)
szomolnokite fe,s. 4,5,33,34,38,62. (3.44 3.12 2.52 4.84)
rozenite fe,s. 4,34,60. (4.47 5.46 3.97)
coqumbite fe,s. 4,5,6,33,38,50,55,62. (8.58 2.77 5.53 8.26 5.45)
roemerite fe.s. 4 (4.79 4.03 5.05)
siderotil fe,s. 55. (4.89 3.73 5.57)
jarosite na,k,fe,s. 4.17.34,60.62. (3.08 3.11 5.09)
natrojarosite na,fe,s. 33,34. (5.06 3.06 3.12)/
bassanite ca,s. 6,8,38,50. (3.00 6.01 2.80)
anhydrite ca.s. 12,33,35,38,50,53,63,70. (3.50 2.85 2.33)
alunogen(keramohalite) al,s. 2 (4.48 13.3 4.39)/
celestite sr,s. 35 (2.97 3.30 2.73)
alunite k,al,s. 34.60. (1.90 1.75 3.01 2.89 2.29)
natro-alunite na,k,al.s. 49.60,66. (2.96 4.90 2.97)
halotrichite fe,al.s. 34,60. (4.77 3.48 4.29)
alum k,na,al,s. 29
epsonite mg,s. 60
pickeringite mg,al.s. 60
aluminocopiapite al,fe,s. 60
sideronatrite na,fe,s. 60.61

Carbonates

carbonates 66,
calcite ca, 1,2,3,4,5,6,7,10,11,12,14,19,21,22,23,28,32,33,34,35,37,38,41,42,45,48,49,50,51,52,53,55,62,63,69,70,71,
(3.04 2.29 2.10)
siderite fe, 1,2,3,4,5,7,11,12,19,22,28,32,33,34,35,37,41,42,48,49,51,52,53,55,62,63, (2.79 1.73 3.59)
ankerite ca,fe,mg,mn, 1,2,4,11,15,37,42,45,48,49,51,53,55,63, (2.89 2.19 1.81)
dolomite ca,mg, 1,2,4,5,6,7,11,13,21,33,45,49,50,51(?),53,55,62,63,71, (2.89 2.19 1.79)
aragonite ca, 3,13 (3.40 1.98 3.27)
witherite ba, 16,19,29,31,55, (3.72 3.68 2.15)
strontionite sr, 43, (3.54 3.45 2.05)/
magnesite (?) mg, 37, (2.74 2.10 1.70)
+dawsonite na,al, 32, (5.67 2.78 2.60)
alstonite ca,ba, 59

Halides

halite na,cl, 2,11,51,55,69, (2.82 1.99 1.63)
bischofite mg,cl, 2 (4.10 2.65 2.88 2.72)
sylvite k,cl, 2,11,41,51, (3.15 2.22 1.82)

Phosphates

apatite ca,p,cl,f, 1,2,11,13,14,22,23,31,41,42,45,48,49,51,52,53,55,62,63, (2.79 2.68 2.62 3.40)
phosphorites 1,2,45,52,
 collophane ca,p, 45,
goyazite sr,al,p, 9,62, (5.73 2.9,62,6 3.49,62, 2.20 1.89,62,)
monazite ce,re,p, 41,51,55, (3.09 2.87 3.30)
xenotime y,re,p, 41,55, (3.44 2.56 1.76)
crandallite ca,ba,sr,al,p, 55, (2.97 2.18 5.75)
messelite ca,fe,p, 47,
gorceixite ba,al,p, 55

Uranium Minerals

abernathyite 64
autonite 64
  h-autonite
  meta-autonite
  na-autonite
becquerelite 64
coffenite 64
carnotite 64
meta-torbernite 64
meta-uranocercite 64
meta-zeunerite 64
sabugalite-saleeite 64
torbernite 64
uraninite 43
uranophane 64
zeunerite 64

Others
gold au, 14,55, (2.36 2.04 1.23)
malachite cu, 13,29,31 (2.86 3.69 5.06)
clausthalite pb,se, 46,55, (3.06 2.17 3.54)
wedellite ca, 9 (6.18 2.78 4.42)
whewellite ca, 9,18, (5.93 3.65 2.97)
nitrates 1,56,
dopplerite ca. 27
sulfer s, 29
mellite al, 54, (7.99 4.23 5.80)
volcanic glass 35,44,67,
* mineral found in a parting

References

1 M.-Th. Mackowsky-1968-Mineral matter in coal. in Coal and Coal-bearing Strata. D.Murchison and T.S. Westoll-Eds. Ch. 13, p309-321.
2 M.Th. Mackowsky in Stack"s textbook,1975, page 121
3 J.V.O'Gorman and P.L.Walker,Jr.- 1971-Mineral matter characteristics of some American coals-Fuel, vol.50, p135-151.
4 H.J.Gluskoter-1975-Mineral matter and trace elements in coal in Trace elements in Fuel ed. by S.Babu.Ch. 1,p1-22.
5 C.P.Rao and H.J.Gluskoter-1973-Occurrence and distibution of minerals in Illinois Coals. Illinois State Geol. Survey Circular 476.56p.
6 R.S. Mitchell and H.J. Gluskoter-1976-Mineralogy of ash of some American coals...-Fuel-v 55,no.2 p90-96
7 D.P.Rao-1977-Petrographic,mineralogical and chemical characterization of certain arctic Alaskan coals from the Cape Beaufort region. GAC program with abstracts. vol. 2, p43.
8 D.E.Pearson,M.A.Chaudhry,N.G.Colvin,and F.B.Gigliotti-1977-Mineral matter in bituminous coals of the Crownsnest Coalfield. GAC program with abstracts. vol. 2.p41.
9 C.R. Ward-Isolation of mineral matter from Australian bituminous coals using hydrogen peroxide-Fuel 1974 v53 p.220
10 L.E.Paulson,W.Beckering and W.W.Fowkes-1972-Separation and identification of minerals from Northern Great Plains Province lignite. Fuel, vol.51,2324-227.
11 J.B.Nelson-1953-Assessment of the mineral species associated with coal. BCURA Bull. vol.17,no.2,41-55.
12 A.F.Rekus and A.R. Haberkorn,III,1966.Identification of minerals in single particles of coal by the X-ray powder method. J. Institute Fuel. p474-477.
13 G.B.Mitra-1954-Identification of inorganic Impurities in coal by the x-ray method. Fuel v33,p316-330. Highly quesionable reslts
14 R.B.Finkelman,R.W.Stanton, and I.A.Breger-1976-Energy dispersive analysis of in situ minerals in coal. GSA Program with abstracts,vol.8,no.6,865-866.
15 K.Dixon,E.Skipsey and J.T.Watts-1964-The Dist. and Comp. of Inorganic Matter in bituminous coals:part1-Jour.Inst.Fuel v37 no. 286,p485-493
16 W. Francis-1961-Coal 2nd. Ed.,806p.
17 J.O'Gorman-1971-Studies on mineral matter and trace elements in North American Coals-PhD Diss.-Penn State.
18 A.J. Nalwalk,R.A.Friedel, and J.A.Queiser,1974,Peroxidation of coals-analysis of minerals. Energy Sources. Vol. 1,no.2, p179-187.
19 P.A.Estep,J.J.Kovach, and C.Karr,Jr.,1968, Quantitative infrared multicomponent determination of mineral;s occurring in coal. Analyt. Chem. v40,p358-363. P.A.Estep,J.J.Kovach,A.L.Hiser,and C.Karr,Jr.,1970 Characterization of carbonate minerals in oil shales and coals by infrared spectroscopy. Chapter 18 p.228-247.
20 W. Spackman and R.G. Moses-1961-The nature and occurrence of ash forming minerals in anthracite. Bull Mineral Industries Experiment Station.No. 75, p1-22.
21 R.S.Young and D.S.Robertson-1952-X-ray study of coal...Econ. Geol.-v47,p609-633.
22 G.C.Sprunk and H.J.O'Donnell-1942-Mineral matter in coal. U.S.B.M. Tech. Paper 648.67p.
23 C.G.Ball-1935-Mineral matter of No.6 Bed Coal at West Frankfort, Franklin County, Illinois.Illinois Geol. Survey Rept. of investigation no.33, 106p.
24 M. Lau, A.C.D. Chaklader and I.H.Warren-1977-Mineral_matter content and gross properties of Hat Creek coal. CIM Bull.,vol.9,no.784,p 139,Abst.-119
25 D.A. Augenstein and S.C.Sun,1974,Characterization of coal refuse by low temperatureashing.Trans. AIME v256,p161-166.
26 H.J.Gluskoter and P.C. Lindahl-1973-Cadmium:Mode of occurrence in Illinois coals.Science, vol.181,p264-266.
27 A. Lissner,1956 cited in W.H. Ode,1963
28 A.W.Gauger,E.P.Barrett and F.J.Williams-1934-Mineral matter in coal-A preliminary report-Trans. AIME v 108,p226-236.
29 O.Stutzer-1940-Geology of Coal. U. of Chicago Press461p.
30 L.J.Lawrence,S.St.J. Warne,and M. Booker-1960-Millerite in the Bulli Coal seam. Australian Jour. of Sci. vol. 23,p87.
31 D.J.Swaine-1967-Inorganic constituents in Australian coals. Sonderdruck etc.... -1975-Trace elements in coals. in Recent Contributions to Geochemistry and Analytical Chemistry. p539-550.
32 Cook- Australian Black Coal , 1976
33 C.R.Ward-1977-Mineral Matter in the Springfield-Harrisurg (No.5)Coal Member in the Illinois Basin. Ill.State Geol. Survey Circ. 498.
34 G.Bardossy,1964,Investigation of coals from Pecs (Mecsek Mountains) with X-ray diffractometer.
35 L.S. Alekseev-1960-Mineral impurities in coal-Doklady, Earth Sci. Section,v124,no.4,p186-188.
36 M.Deul-1959-The principal geolgical,chemical and physical factors controlling the mineral content of coal. A.C.S. Div. of Gas and Fuel Chem. Boston, Mass.
37 H.R.Brown,R.A.Durie and H.N.S.Schafer-1959-The inorganic constituents in Australian coals I-the direct determination of total mineral-matter content. Fuelvol. 38, no.3 p295-308.

References continued

38 J.J.Renton and R.V.Hidalgo-1975-Some geochemical considerations of coal.West Va. Geol. and Economic Survey, Coal-Geology Bull. 4. 38p.

39 R.N. Miller personnal communication

40 Mukherjee-1974- J.Mines Met. Fuels(Calcutta) vol.20, no.12, p363.

41 Finkelman and Stanton,1979,Identification and significance of accessory minerals from a bituminous coal

42 M. Kemezys and G.H.Taylor-1964-Occurrence and distribution of minerals in some Australian cols. Jour. Inst. Fuel vol. 37,p389-397.

43 Finkelman unpublished data.

44 I.I.Sharudo and V.I. Moskvin-1973-Mineral impurities in coals of the Bureya Basin and their origin. Lithology and Mineral Resources. vol. 8, no.1. p76-79.

45 G.Jauranek et.al.-1958-(in French).

46 Finkelman 1980

47 G.N.Vertushkov-1953 Chem Abstracts.vol.80 n018 p450-451.

48 N.A.Brown,C.B.Belcher, and T.G. Callcott-1965-Mineral matter inN.S.W. Coke-making coals:composition, determination and effects. J. Inst. Fuel,v38,no.292, p198-206.

49 C.E.Marshall and D.K.Tomkins-1964-Mineral matter in Permian coal seams. Symp. on The Inorganic Constituents of Fuel U. of Melbourne.p57-69.

50 A.F.Sarofin,J.B.Howard and A.S.Padia-1977-The physical transformation of the mineral matter in pulverized coal under simulated combustion conditions. Combustion Science and Technology. vol.16,p187-204.

51 R.J.Lee,F.E.Huggins and G.P.Huffman-1978-Correlated SEM-mossbauer studies of coal and coke. SEM/1978.

52 R.M.S.Falcon-1978-Coal in South Africa-.... Min. Sci. Engng vol.10. no. 1. p28-52.

53 R. Soong and H.J.Gluskoter -1977-Mineral Matter in some New Zealand coals. 1. Low-temperature ashing and mineralogical composition of such coal ashes. New Zealand Jour. of Sci. vol.20,p273-7.

54 Goldschmidt-1954-Geochemistry. p302 and 675.

55 Finkelman, Dulong, Stanton & Cecil, 1979, Pa. Geol.

56 Karr et al.,1968

57 Des Clauseaux 1880, Swaine 1980

58 Voskresenskaya,1968

59 Spencer, 1910

60 Cobb et al.,1979

61 Gluskoter, 1977

62 Ward, 1978

63 Plogmann and Mackowsky, 1977

64 Akers et al.,1978; King and Young,1956; White,1958.

65 Sentfle personnal communication

66 Marshall, 1959

67 Cech and Petrik,1973

68 Chernevskii,1975

69 Beising,1972

70 Korzeb and Chang,1977

71 Foster and Feicht,1946

72 Kullerud,personnal communication,1980/p

Appendix IIIA

INAA Results of Sink-float samples from the Waynesburg Coal

(Analyst: L. J. Schwarz)

Element	Bulk Sample	>10 mesh <1.3	>10 mesh 1.3-1.5	>10 mesh 1.5-1.7	>10 mesh >1.7	10-20 mesh <1.3	10-20 mesh 1.3-1.5
Fe %	0.78	0.21	1.00	7.82	28.90	0.20	0.98
Na %	0.02	0.02	0.03	0.04	0.01	0.02	0.03
As ppm	2.2	0.8	3.7	27.4	703.0	0.7	3.4
Ba ppm	140	170	180	180	<500	150	130
Br ppm	1.34	1.61	2.58	35.30	146	2.32	3.04
Co ppm	3.2	2.7	3.9	12.6	91.4	2.5	4.0
Cr ppm	7.9	8.4	11.2	17.6	<20.0	7.6	9.4
Cs ppm	<0.4	0.2	0.5	1.6	<1.0	0.3	0.5
Hf ppm	0.4	0.5	0.6	1.1	<0.9	0.3	0.6
Sb ppm	0.2	0.3	0.3	0.6	9.0	1.4	0.4
Se ppm	2.60	<3.00	2.50	19.20	31.00	<3.00	2.10
Ta ppm	<0.20	<0.30	<0.30	0.29	<0.50	<0.20	0.13
Th ppm	0.8	1.0	1.5	2.3	<2.0	0.7	1.3
W ppm	0.6	0.5	0.4	0.3	<1.0	0.5	0.4
Zn ppm	487	<7	<8	35	<30	6	9
Sc ppm	1.46	1.67	2.16	3.30	0.63	1.47	2.36
La ppm	6	6	7	10	1	5	7
Ce ppm	11	10	13	19	<7	10	12
Sm ppm	0.9	1.1	1.2	1.6	0.3	1.0	1.2
Eu ppm	0.22	0.25	0.25	0.40	<0.60	0.25	0.25
Tb ppm	0.15	0.14	<0.30	0.25	<0.70	0.12	0.20
Yb ppm	0.5	0.5	0.5	0.8	<0.8	0.4	0.6
Lu ppm	0.05	0.07	0.08	0.13	<0.20	0.06	0.08

Appendix IIIA (continued)

Element	10-20 mesh 1.5-1.7	10-20 mesh >1.7	20-80 mesh <1.3	20-80 mesh 1.3-1.5	20-80 mesh 1.5-1.7	20-80 mesh >1.7
Fe %	9.22	28.20	0.24	1.15	9.28	30.80
Na %	0.03	0.01	0.02	0.03	0.03	0.01
As ppm	32.7	490.0	0.8	3.8	27.2	343.0
Ba ppm	160	<400	150	160	<300	<400
Br ppm	48.50	75.40	2.98	19.40	147.00	78.30
Co ppm	16.9	63.5	2.5	3.9	14.6	42.8
Cr ppm	14.5	<20.0	7.4	9.5	9.2	<20.0
Cs ppm	1.0	<0.9	0.2	0.6	0.6	<0.9
Hf ppm	0.7	<0.9	0.3	0.6	0.4	<0.8
Sb ppm	1.0	5.7	0.6	0.4	0.8	3.8
Se ppm	16.60	35.30	<2.00	2.20	16.70	37.50
Ta ppm	0.17	<0.50	<0.20	<0.20	<0.30	<0.40
Th ppm	1.6	<2.0	0.8	1.3	1.2	<2.0
W ppm	0.5	<1.0	0.6	0.4	<0.9	<1.0
Zn ppm	29	<30	7	11	17	13
Sc ppm	2.81	0.74	1.54	2.31	2.04	0.64
La ppm	6	1	5	7	5	2
Ce ppm	11	<6	9	13	10	3
Sm ppm	1.2	0.3	1.0	1.3	1.0	0.3
Eu ppm	0.25	<0.60	0.21	0.24	0.21	<0.50
Tb ppm	0.34	<0.70	0.16	0.20	<0.40	<0.60
Yb ppm	0.7	<0.6	0.4	0.6	0.4	<0.5
Lu ppm	0.09	<0.20	0.06	0.08	0.07	<0.09

Appendix IIIB

OES Results of Sink-float samples from the Waynesburg Coals

(Analyst: L. Mei) H = Interference

Element	Bulk Sample	>10 mesh <1.3	>10 mesn 1.3-1.5	>10 mesh 1.5-1.7	>10 mesh >1.7
Si %	20	21	18	13	2.5
Al %	17	13	8.2	6.0	0.67
Fe %	8.3	4.5	15	>24	>24
Mg %	0.32	0.61	0.25	0.15	0.011
Ca %	1.4	1.3	0.84	0.59	0.035
Na %	0.23	0.24	0.19	0.10	<0.0046
K %	1.2	1.2	1.1	H	H
Ti %	0.64	0.70	0.54	0.49	<0.0068
P %	0.17	0.15	<0.068	<0.068	<0.068
Mn %	0.015	0.015	0.016	0.039	0.0062
Ag ppm	0.15	0.39	0.27	0.33	0.89
As ppm	<150	<150	<150	<150	1500
Au ppm	<10	<10	<10	<10	<10
B ppm	410	310	200	68	13
Ba ppm	1400	1400	960	390	200
Be ppm	17	21	15	5.7	1.3
Ce ppm	280	270	240	<43	<43
Co ppm	50	42	37	50	150
Cr ppm	150	160	130	110	7.5
Cu ppm	60	61	59	30	6.6
Dy ppm	<22	<22	<22	<22	<22
Er ppm	12	11	<10	<10	<10
Eu ppm	5.1	5.2	2.3	<1.5	<1.5
Ga ppm	73	74	54	38	31
Gd ppm	20	24	18	28	25
Ge ppm	3.4	3.6	<1.5	<1.5	<1.5
La ppm	200	160	110	59	<10
Mn ppm	150	150	160	390	62
Mo ppm	40	30	18	51	97
Nb ppm	14	25	38	23	11
Nd ppm	140	130	110	59	<46
Ni ppm	140	170	160	170	310
Pb ppm	37	66	57	100	62
Sc ppm	31	35	26	17	1.8
Sn ppm	<6.8	3.4	<1.5	H	H
Sr ppm	5900	3300	1500	270	52
Th ppm	<22	<22	<22	<22	<22
V ppm	210	220	150	84	6.4
Y ppm	120	140	100	43	15
Yb ppm	9.1	9.1	5.6	4.2	2.6
Zn ppm	69	74	79	240	230
Zr ppm	190	240	360	170	6.6

Appendix IIIB (continued)

Element	10-20 mesh <1.3	10-20 mesh 1.3-1.5	10-20 mesh 1.5-1.7	10-20 mesh >1.7
Si %	18	18	8.5	2.3
Al %	10	8.2	3.6	0.60
Fe %	12	14	>24	>24
Mg %	0.26	0.22	0.12	0.015
Ca %	1.2	0.82	0.78	0.080
Na %	0.20	0.18	0.047	<0.0046
K %	1.0	1.0	H	H
Ti %	0.50	0.56	0.19	0.019
P %	<0.068	<0.068	<0.068	<0.068
Mn %	0.015	0.016	0.020	0.0089
Ag ppm	0.21	0.37	0.49	0.70
As ppm	<150	<150	<150	990
Au ppm	<10	<10	<10	11
B ppm	350	180	H	10
Ba ppm	1100	910	310	58
Be ppm	17	14	7.1	1.7
Ce ppm	200	240	<43	<43
Co ppm	47	41	60	98
Cr ppm	150	120	65	7.9
Cu ppm	59	59	29	7.7
Dy ppm	<22	28	<22	<22
Er ppm	<10	11	<10	<10
Eu ppm	3.0	2.3	1.7	<1.5
Ga ppm	70	66	38	25
Gd ppm	18	18	<15	<15
Ge ppm	4.0	4.4	3.4	<1.5
La ppm	83	110	43	<10
Mn ppm	150	160	200	89
Mo ppm	25	20	53	74
Nb ppm	15	35	18	8.4
Nd ppm	100	100	<46	<46
Ni ppm	150	140	200	220
Pb ppm	53	54	98	66
Sc ppm	28	33	17	5.0
Sn ppm	<1.5	<1.5	H	H
Sr ppm	1800	1500	300	30
Th ppm	<22	<22	<22	<22
V ppm	180	160	64	8.8
Y ppm	86	110	44	11
Yb ppm	7.1	6.2	3.4	2.2
Zn ppm	91	87	230	200
Zr ppm	120	440	170	8.9

Appendix IIIB (continued)

Element	20-80 mesh <1.3	20-80 mesh 1.3-1.5	20-80 mesh 1.5-1.7	20-80 mesh >1.7
Si %	15	18	7.1	2.5
Al %	6.9	7.7	3.7	0.72
Fe %	20	14	>24	>24
Mg %	0.19	0.23	0.13	0.025
Ca %	0.98	0.73	0.93	0.13
Na %	0.17	0.18	0.060	<0.0046
K %	0.94	1.1	H	H
Ti %	0.42	0.40	0.14	0.016
P %	<0.068	<0.068	<0.068	<0.068
Mn %	0.013	0.017	0.043	0.016
Ag ppm	0.30	0.20	0.55	0.68
As ppm	<150	<150	<150	610
Au ppm	<10	<10	<10	<10
B ppm	360	150	60	12
Ba ppm	860	750	370	62
Be ppm	17	14	7.0	1.4
Ce ppm	280	200	<43	<43
Co ppm	53	33	61	65
Cr ppm	99	100	19	6.2
Cu ppm	73	60	41	20
Dy ppm	31	<22	<22	<22
Er ppm	<10	<10	<10	<10
Eu ppm	2.0	1.7	<1.5	<1.5
Ga ppm	68	57	37	26
Gd ppm	20	<15	<15	<15
Ge ppm	5.2	2.8	<1.5	<1.5
La ppm	130	82	28	<10
Mn ppm	130	170	430	160
Mo ppm	35	15	<6.8	<6.8
Nb ppm	41	20	13	7.8
Nd ppm	130	83	<46	<46
Ni ppm	190	130	180	170
Pb ppm	66	56	150	89
Sc ppm	22	28	12	1.9
Sn ppm	<1.5	<1.5	H	H
Sr ppm	2000	1300	380	28
Th ppm	<22	<22	<22	<22
V ppm	160	130	44	6.5
Y ppm	130	90	35	9.8
Yb ppm	5.7	5.0	3.2	2.2
Zn ppm	150	85	220	200
Zr ppm	470	310	110	12

Appendix IIIC

INAA Results of Sink-float samples from the Waynesburg LT ash

(Analyst: L. J. Schwarz)

Element	<2.5	2.5-3.3	>3.3
Fe %	2.00	3.49	41.50
Na %	0.25	0.26	0.07
As ppm	11.9	15.7	147.7
Ba ppm	1227	1275	<1119
Br ppm	217.73	217.59	98.04
Co ppm	32.5	36.0	142.1
Cr ppm	138.6	137.9	29.5
Cs ppm	4.6	4.7	<2.2
Hf ppm	4.1	4.2	2.7
Sb ppm	5.6	6.9	14.1
Se ppm	4.07	7.15	66.17
Ta ppm	1.22	1.62	<1.19
Th ppm	13.0	14.3	3.1
W ppm	5.3	6.1	<3.5
Zn ppm	132	123	66
Sc ppm	47.61	43.30	7.38
La ppm	129	69	17
Ce ppm	93	112	21
Sm ppm	11.0	11.7	2.2
Eu ppm	2.84	2.95	<1.37
Tb ppm	2.66	2.09	<3.95
Yb ppm	9.1	9.0	2.3
Lu ppm	1.29	1.26	0.34

Appendix IIID

OES Results of Sink-float samples from the Waynesburg LT ash

(Analyst: L. Mei)

Element	<2.5	2.5-33	>3.3
Si %	21	14	2.2
Al %	12	6.4	0.61
Fe %	1.6	1.4	>24
Mg %	0.24	0.20	0.015
Ca %	0.54	0.40	0.068
Na %	0.19	0.14	0.011
K %	1.0	0.67	H
Ti %	0.29	0.22	0.031
P %	0.11	0.090	<0.072
Mn %	0.080	0.045	0.025
Ag ppm	<0.10	<0.10	0.52
B ppm	280	190	<15
Ba ppm	730	600	52
Be ppm	19	18	2.5
Ce ppm	46	60	<29
Co ppm	22	24	68
Cr ppm	93	88	13
Cu ppm	63	92	120
Eu ppm	2.8	1.9	1.7
Ga ppm	89	100	22
Gd ppm	7.3	<6.8	<6.8
Ge ppm	17	12	<4.6
La ppm	77	29	<10
Mn ppm	800	450	250
Mo ppm	6.0	4.4	5.2
Nb ppm	13	12	4.3
Ni ppm	61	61	95
Pb ppm	13	<10	72
Sc ppm	30	30	3.8
Sn ppm	11	14	8.3
Sr ppm	610	560	26
V ppm	100	90	9.6
Y ppm	55	63	4.5
Yb ppm	8.0	8.9	<0.68
Zn ppm	23	45	100
Zr ppm	75	71	52

H = Interference

Appendix IIIE

OES Analyses of Ash from various coal samples

(Analysts: J. L. Harris, L. Mei, & J. Mountjoy)

Element*	Waynesburg	Burnside	Glen Burn	Wanimie	Merrimac
Si %	>34	33	25	33	29
Al %	12	26	22	28	7.6
Fe %	1.9	1.7	1.8	1.0	3.2
Mg %	0.57	0.30	0.96	0.27	1.5
Ca %	0.23	0.63	0.042	1.0	2.7
Na %	0.20	0.18	0.50	0.11	0.13
K %	2.1	0.57	4.4	0.089	0.85
Ti %	0.34	0.54	0.54	0.69	0.23
P %	0.13	0.14	0.075	0.51	<0.068
Mn %	0.017	0.0044	0.0092	0.030	0.086
Ag ppm	<0.10	0.81	0.38	0.23	<0.10
As ppm	<150	<150	<150	<150	<150
B ppm	190	120	120	26	160
Ba ppm	500	1100	1100	280	210
Be ppm	4.0	7.8	4.3	11	2.8
Ce ppm	52	<43	<43	250	47
Co ppm	8.0	68	31	63	38
Cr ppm	98	210	230	220	63
Cu ppm	47	280	290	210	100
Eu ppm	<1.5	3.0	2.5	2.9	<2.2
Ga ppm	34	49	62	33	12
Gd ppm	<6.8	<15	<15	<15	<15
Ge ppm	<4.6	<1.5	<1.5	<1.5	<1.5
La ppm	34	31	69	140	51
Li ppm	260	<68	<68	<68	<68
Mn ppm	170	44	92	300	860
Mo ppm	2.4	28	1.1	17	<1.0
Nb ppm	130	15	16	19	14
Nd ppm	<46	45	79	100	<32
Ni ppm	26	150	69	180	42
Pb ppm	31	140	69	76	93
Sc ppm	12	49	28	54	17
Sm ppm	<46	<10	<10	13	<10
Sn ppm	12	8.6	10	6.4	4.7
Sr ppm	240	730	230	780	160
Tl ppm	<10	<4.6	<4.6	<4.6	<4.6
Tm ppm	<4.6	<4.6	<4.6	<4.6	<4.6
V ppm	83	340	220	240	89
Y ppm	18	63	26	54	36
Yb ppm	5.4	8.3	6.0	5.5	3.7
Zn ppm	69	<15	45	85	350
Zr ppm	110	170	93	260	230

* Elements below limits of detection: Au, Bi, Cd, Dy, Er, Hf, Ho, In, Ir, Lu, Os, Pd, Pr, Pl, Re, Rh, Ru, Sb,

Appendix IIIE (continued)

Element*	Indiana	Lobatera	Asfalsite	Alaska	Alaska
Si %	16	17	0.40	2.9	4.9
Al %	11	12	<0.046	13	18
Fe %	2.1	15	3.0	14	5.1
Mg %	0.22	1.7	0.016	6.7	5.4
Ca %	0.45	2.5	0.091	8.7	5.1
Na %	0.88	0.23	0.17	2.3	2.5
K %	0.71	<0.068	<0.068	0.13	0.33
Ti %	0.10	0.49	0.013	0.48	0.25
P %	0.13	<0.068	1.7	<0.068	<0.068
Mn %	0.011	0.20	0.0095	0.12	0.035
Ag ppm	0.15	0.47	4.7	1.0	0.18
As ppm	<150	<150	<150	<150	270
B ppm	>1000	240	37	>680	>680
Ba ppm	210	710	26	>3200	>3200
Be ppm	120	4.3	9.9	5.4	8.3
Ce ppm	<43	110	<43	270	130
Co ppm	310	33	310	250	22
Cr ppm	100	110	93	72	50
Cu ppm	200	130	<220	68	52
Eu ppm	3.0	<2.2	3.0	2.6	<1.5
Ga ppm	33	43	110	29	22
Gd ppm	<15	<15	<15	21	17
Ge ppm	100	2.6	56	<1.5	<1.5
La ppm	27	55	<10	120	44
Li ppm	73	<68	<68	<68	<68
Mn ppm	110	2000	95	1200	350
Mo ppm	21	10	410	7.5	7.8
Nb ppm	4.1	20	<3.2	13	9.1
Nd ppm	<32	<32	<150	60	51
Ni ppm	420	89	>15000	1000	110
Pb ppm	98	63	150	89	110
Sc ppm	34	29	<1.0	43	20
Sm ppm	<10	<10	<10	<22	<22
Sn ppm	3.4	<1.5	62	5.2	4.2
Sr ppm	410	330	68	2900	1600
Tl ppm	<4.6	<4.6	<32	<3.2	<3.2
Tm ppm	<4.6	<4.6	<4.6	<4.6	<4.6
V ppm	160	260	>1000	180	77
Y ppm	200	20	<1.5	160	96
Yb ppm	13	2.4	<0.68	13	9.9
Zn ppm	390	84	410	240	120
Zr ppm	95	140	78	880	510

Appendix IIIE (continued)

Element*	Beulah	Norway	Brazil	Nova Scotia
Si %	7.2	>34	25	12
Al %	4.9	9.3	14	2.8
Fe %	2.3	0.56	2.6	>24
Mg %	6.7	0.18	0.85	0.11
Ca %	18	0.15	2.3	0.81
Na %	2.9	0.077	0.15	<0.0068
K %	0.30	1.1	2.6	H
Ti %	0.16	0.80	0.60	0.18
P %	<0.068	<0.068	<0.068	<0.068
Mn %	0.11	0.0028	0.18	0.046
Ag ppm	7.4	0.20	<0.10	7.2
As ppm	<150	<150	<150	2300
B ppm	>680	160	140	H
Ba ppm	>3200	350	320	360
Be ppm	26	10	15	26
Ce ppm	120	67	110	<43
Co ppm	8.2	10	6.1	24
Cr ppm	32	240	130	69
Cu ppm	44	42	19	480
Eu ppm	3.5	<1.5	2.7	2.5
Ga ppm	23	69	49	24
Gd ppm	<15	<15	17	26
Ge ppm	<1.5	8.0	46	60
La ppm	63	51	52	47
Li ppm	<68	68	<68	H
Mn ppm	1100	28	1800	460
Mo ppm	45	<2.2	3.1	110
Nb ppm	<2.2	38	32	14
Nd ppm	<46	59	<46	47
Ni ppm	32	77	65	130
Pb ppm	21	82	14	790
Sc ppm	62	29	48	11
Sm ppm	<22	<22	<22	<22
Sn ppm	<1.5	8.9	18	H
Sr ppm	13000	280	280	200
Tl ppm	<3.2	<3.2	7.8	<3.2
Tm ppm	<4.6	<4.6	4.8	<4.6
V ppm	61	210	280	130
Y ppm	160	41	120	120
Yb ppm	11	6.0	11	7.9
Zn ppm	<10	18	150	540
Zr ppm	130	280	2400	210

H = Interference

Appendix IIIF

INAA of ash from the Waynesburg Coal

(Analyst: L. J. Schwarz)

Element (ppm)	Waynesburg*
Na ppm	1537
Fe %	2.63
As ppm	14.5
Ba ppm	592
Br ppm	3
Co ppm	7.3
Cr ppm	78.9
Cs ppm	10.8
Hf ppm	4.9
Rb ppm	197
Sb ppm	0.67
Se ppm	3.0
Ta ppm	1.32
Th ppm	11.6
Zn ppm	66
W ppm	1.49
Sc ppm	13.03
La ppm	51
Ce ppm	84
Nd ppm	30
Sm ppm	5.7
Eu ppm	0.96
Tb ppm	0.78
Yb ppm	3.1
Lu ppm	0.52

* Average of 3 analyses

APPENDIX IV

Procedure for Calculating Uranium Concentrations

In order to calculate the concentration of uranium in individual micron-size particles, from fission track data, the following formula is used (modified from Fleischer and Price, 1964):

$$N_t = N_a C^{235} \emptyset \sigma \cos^2\theta$$

where:

N_t = Total number of tracks generated by the particle.

N_a = Total number of uranium atoms.

C^{235} = Percentage of U_{235} (= 0.007)

$\emptyset$ = Thermal flux (total flux - 10^{15} neutrons/cm).

σ = Fission cross-section of U_{235} for thermal neutrons (580×10^{-24} cm)

$\cos^2\theta$ = Critical track angle for "Lexan" ($\theta = 4^\circ$, $\cos^2\theta = .995$)

The constants equal 4.8×10^{-9}; thus:

$$N_t = N_a \cdot 4.8 \times 10^{-9}$$

The number of atoms (N_a) can be converted into a weight percent by the following procedure:

$$N_a \cdot \frac{1}{\text{Avogadros' No.}} \cdot \text{gram molecular weight U} \cdot \frac{1}{\text{particle volume} \cdot \text{density}}$$

For example, for a zircon (15µm x 10µm x 10µm) generating 50 tracks:

$$N_a \doteq 1 \times 10^{10} \text{ atoms}$$

$$1 \times 10^{10} \text{ atoms} \cdot \frac{1}{6.02 \times 10^{23} \text{ atoms}} \cdot 238 \text{ gms} \cdot \frac{1}{1.5 \times 10^{-9} \text{cm} \cdot 4.6 \text{gm/cm}}$$

$$= 0.06 \text{ percent, or } 600 \text{ ppm U}$$

Bibiliography

Abernethy, R. F., and Gibson, F. H., 1963, Rare elements in coal. U. S. Bureau of Mines, Information Circular 8163, 69 p.

Akers, D. J., McMillan, B. G., and Leonard, J. W., 1978, Coal Minerals Bibliography. U. S. Department of Energy, Fossil Energy Research, Report FE-2692-5, 222 p.

Alekseev, L. S., 1960, Mineral impurities in coal. Doklady of the Academy of Sciences Sections, v. 124, no. 4, p. 186-188.

Alexander, C. C., Thorpe, A. N. and Senftle, F., 1979, Basic magnetic properties of bituminous coal. Fuel, v. 58, no. 12, p. 857-863.

Allman, M. and Lawrence, D. F., 1972, Geological Laboratory Techniques. Arco Publishing Co. Inc. New York, 335 p.

Almassy, G. and Szaley, S., 1956, Analytical studies on vanadium and molybdenum content of Hungarian coals. Mag. Ind. Akad. Kem. Ind. Osztal. Kozl., v. 8, no. 1, p. 39-45. Cited in Swaine (1975).

Alpern, B., and Morel, P., 1968, Examen, dans le cadre du bassin houiller lorrain, des possibilites stratigraphiques de la geochimie. Annales Societe Geologique de Nord. Tome 88, no. 4, p. 185-202.

Altschuler, Z. S., 1973, The weathering of phosphate deposits--geochemical and environmental aspects, <u>in</u> Environmental Phosphorus Handbook. Griffith, E. J., Beeton, A., Spencer, J. M. and Mitchell, D. T., editors, J. Wiley and Sons, New York, p. 33.

Altschuler. Z. S., 1978, Coal resources--a continuing assessment <u>in</u> Energy and the Environment, Proceedings of the Fifth National Conference. D. G. Nichols, E. J. Rolinski, R. A. Sevais, L. Theodore, and A. J. Buonicore, editors. American Institute of Chemical Engineers. Dayton, Ohio. p. 249-263.

American Society for Testing and Materials, 1977, Standard definitions of terms used for megascopic description of coal and coal beds and for microscopical description and analysis of coal. 1977 Annual Book of ASTM Standards. American Society for Testing and Materials, Philadelphia, Pennsylvania, Pt. 26, D2796-77, p. 346-349 and 350-354.

Anderson, W., and Turner, R. C., 1956. Radon content of the atmosphere. Nature, v. 178, no. 4526, p. 203-204.

Anderson, W., Mayneord, W. V., and Turner, R. C., 1954, The radon content of the atmosphere. Nature, v. 174, p. 424-426.

Augenstein, D. A., and Sun, S. C., 1974, Characterization of coal refuse by low temperature ashing. Transactions of the American Institute of Mining, Metallurgical, and Petroleum Engineers. v. 256, p. 161-166.

Augustyn, D., Iley, M., and Marsh, H., 1976, Optical and scanning electron microscope study of brown coals. Fuel, v. 55, no. 1, p. 25-38.

Austin, S. A., 1979, Evidence for marine origin of widespread carbonaceous shale partings in the Kentucky No. 12 coal bed (Middle Pennsylvanian) of Western Kentucky. Geological Society of America. Abstracts with Programs. v. 11, no. 7, p. 381-382.

Ball, C. G., 1935, Mineral matter of No. 6 bed coal at West Frankfort, Franklin County, Illinois, Illinois Geological Survey. Report of Investigation, no. 33, 106 p.

Baranov, V. I., Titayeva, N. A., 1961, Uranium, thorium, radium and ionium content in the Quaternary deposits of the Lena River Valley. Geochemistry, no. 2, p. 121-126.

Bardossy, Gy., 1964, Investigation of coals from Pec's (Mecsek Mountains) with X-ray diffractometer. A Maggar Allami Foldtani Intezet Evi Jelentese. 1961 (published 1964), p. 81-95 (90-94 in english).

Barnes, H. L., and Czamanske, G. K., 1967, Solubilities and transport of ore minerals, in Geochemistry of Hydrothermal Ore Deposits. H. L. Barnes, editor. Holt, Rinehart and Winston, Inc., New York. Chapter 8, p. 334-381.

Beeston, J. W., 1974, Petrographic studies and evaluation of a coal seam at Lake Elphenstone, Queensland Government Mining Journal, v. 75, no. 870, p. 126-128.

Beising, R., 1972, Die Minerale der niederrheinischen Braunkohle und ihr Verhalten bei der Verbrennung in Kraftwerken. Neues Jahrbuch fur Mineralogie, Abhandlungen. v. 117, Heft 1, p. 96-115.

Berry, L. G. and Mason, B., 1959, Mineralogy, Concepts, Descriptions, Determinations. W. H. Freeman and Co., San Francisco. 612 p.

Bethell, F. V., 1962, The distribution and origin of minor elements in coal. The British Coal Utilization Research Association, Bulletin, v. 26, no. 12, p. 401-430.

Bethke, P. M. and Barton, Jr., P. B., 1971, Distribution of some minor elements between coexisting sulfide minerals. Economic Geology, v. 66, no. 1, p. 140-163.

Block, C., and Dams. R., 1975, Inorganic composition of Belgian coals and coal ashes. Environmental Science and Technology, v. 9, no. 2, p. 146-150.

Boateng, D. A. D., and Phillips, C. R., 1976, Examination of coal surfaces by microscopy and the electron microscope, Fuel, v. 55, no. 4, p. 318-322.

Boctor, N. Z., Kullerud, G., and Sweany, J. L., 1976, Sulfide minerals in Seelyville coal III, Chinook Mine, Indiana. Mineralium Deposita, v. 11, p. 249-266.

Bogdanov, V. V., 1965, Zur genese der Mikroelemente in den Kohlefuhrenden. Sammelwerk: Materialy k 9. Ssovest. Rabotn. geol. Organ. Leningrad 7, 90-94 (In Russian). Cited in Rosler and Lange (1976).

Bohor, B. F., and Gluskoter, H. J., 1973, Boron in illite as a paleosalinity indicator of Illinois coals. Journal of Sedimentary Petrology, v. 43, no. 4, p. 945-956.

Bohor, B. F., Phillips, R. E., and Pollastro, R. M., 1979, Altered volcanic ash partings in Wasatch formation coal beds of the Northern Powder River Basin: composition and geological applications. U.S. Geological Survey Open-file Report 79-1203, 21 p.

Borisova, R. F., Guren, G. F., Komissarova, L. N. and Shatskii, 1977, Distribution of scandium in coal and brown coal. Chemical Abstracts, v. 86, no. 454116.

Boyle, R. W., 1968, The geochemistry of silver and its deposits. Geological Survey of Canada, Bulletin 160, 264 p.

Brandenstein, M., Janda, I. and Schroll, R., 1960, Seltent Elemente in Osterreich Kohlen-und Bitumengesteinen. Tschermaks Mineralogische und Petrographisahe Mittheilingen, v. 7, p. 260-285.

Breger, I. A., 1958, Geochemistry of Coal, Economic Geology, v. 53, no. 7, p. 823-841.

Breger, I. A., 1974, The role of organic matter in the accumulation of uranium, in Formation of uranium ore deposits. Symposium Proceedings, Athens, Greece. International Atomic Energy Agency, p. 99-124.

Breger, I. A., Deul, M., and Meyrowitz, R., 1955, Geochemistry and mineralogy of a uraniferous subbituminous coal. Economic Geology, v. 50, no. 6, p. 610-624.

Breger, I. A., Deul, M., and Rubinstein, 1955, Geochemistry and mineralogy of a uraniferous lignite. Economic Geology, v. 50, no. 2, p. 206-226.

Brown, H. R., Durie, R. a. and Schafer, H. N. S., 1959, The inorganic constituents in Australian coals I-the direct determination of total mineral-matter content. Fuel, v. 38, no. 3, p. 295-308.

Brown, H. R. and Swaine, D. J., 1964, Inorganic constituents of Australian coals. Part I, Nature and mode of occurrence. Journal of the Institute of Fuel, v. 37, p. 422-440.

Brown, N. A., Belcher, C. B., and Calleott, T. G., 1965, Mineral matter in N.S.W. coke-making coals: composition, determination and effects. Journal of the Institute of Fuel, v. 38, no. 292, p. 198-206.

Butler, J. R., 1953, Geochemical affinities of some coals from Svalbard. Norsk Polarinstitutt Skrifter, Nr. 96, 26 p.

Cambel, B. and Jarkovsky, J., 1967, Geochemie der pyrite einiger Lagerstatten der Tschechoslovakei. Vydavatelstvo Slovensky akedemie vied Bratislava. 493 p.

Carruccio, R. T., 1972, Trace element distribution in reactive and inert pyrite, in Proeedings Fourth Symposium on coal mine drainage research. Mellon Inst., Pittsburgh, PA p. 48-54.

Casagrande, D. J. and Erchull, L. D., 1977, Metals in plants and waters in the Okefenokee swamp and their relationships to constituents found in coal. Geochemica et Cosmochimica Acta, v. 41, p. 1391-1394.

Cavallaro, J. A., Deurbrouck, A. W., Schultz, H., Gibbon, G. A., and Hattman, E. A., 1978, A washability and analytical evaluation of potential pollution from trace elements in coal. U. S. Environmental Protection Agency Report EPA-600/7-78-038, 30p.

Cech, F., and Petrik, F., 1973, Classification and description of mineral admixtures in coal seams of the Handova-Novaky area. Chemical Abstracts, v. 79, no. 33611j, p. 99.

Cecil, C. B., Stanton, R. W., Allshouse, S. D., Finkelman, R. B., and Greenland, L. P., 1979A, Geologic controls on element concentrations in the Upper Freeport coal bed. American Chemical Society, Division of Fuel Chemistry. Preprints of papers presented at Honolulu, Hawaii, April 1979, v. 24, no. 1, p. 230-235.

Cecil, C. B., Stanton, R. W. Allshouse, S. C., and Finkelman, R. B., 1979B, Intrabed variation in and geologic controls on element concentrations in the Upper Freeport Coal. Abstract of papers, paper no. 48, Fuel Chemistry Div., American Chemical Society and Chemical Society of Japan, Chemical Congress, Honolulu, Hawaii, April 1979.

Cecil, C. B., Stanton, R. W., Allshouse, S. D., and Finkelman, R. B., 1979C, Geologic controls on mineral matter in the Upper Freeport coal bed, *in* Proceedings: Symposium on coal cleaning to Achieve Energy and Environmental goals, v. 1. S. E. Rogers and A. W. Lemmon, Jr., editors. U. S. Environmental Protection Agency Report EPA-600/7-79-098a, p. 110-125.

Cecil, C. B., Renton, J. J., Stanton, R. W., and Dulong, F. T., 1979D, Some geologic factors controlling mineral matter in coal, *in* Carboniferous Coal Short Course and Guidebook. A. C. Donaldson, M. W. Presley, and J. J. Renton, editors. Geology Department, West Virginia University, Morgantown, p. 227-238.

Chandra, D. and Taylor, G. H., 1975, Gondwana coals, *in* Stach et al., 1975, p. 139-159.

Chapman, A. C., 1901, Arsenic in coal and coke. The Analyst, v. 26, p. 253-256.

Chatterjee, P. K. and Pooley, F. D., 1977, An examination of some trace elements in South Wales coals. Proceedings of the Australasian Institute of Mining and Metallurgy, no. 263, p. 19-30.

Chernevskii, N. N., 1975, Minerals of rare elements in the Jurassic coal-bearing formation of Uzbekistan. Chemical Abstracts, v. 83, no. 100826f, p. 202.

Cobb, J. C., Masters, J. M., Treworgy, C. G., and Helfinstine, R. J., 1979, Abundance and recovery of sphalerite and fine coal from mine waste in Illinois. Illinois State Geological Survey, Illinois Mineral Note 71, 11 p.

Colby, J. W., 1975, Ion microprobe mass analysis, in Practical Scanning Electron Microscopy. J. I. Goldstein and H. Yakowitz, editors. Pleniem Press, NY, Ch. 14, p. 529-572.

Coleman, W. M., Perfetti, P., Dorn, H. C., and Taylor, L. T., 1978, Trace-element distribution in various solvent refined-coal fractions as a function of the feed coal. Fuel, v. 57, no. 10, p. 612-616.

Cook, A. C., 1976, The spatial and temporal variation of the type and rank of Australian coals, in Australian block coal-its Occurrence, Mining, Preparation, and Use. A. C. Cook, editor. Symposium proceedings held at University of Wollongong, February 1975, p. 63-84.

Cosgrove, M. E., 1970, Iodine in the bituminous Kimmeridge Shales of the Porset Coast, England. Geochimica et Cosmochimica Acta, v. 34, no. 7, p. 830-836.

Crossley, H. E., 1944, Fluorine in coal. Journal of the Society of the Chemical Industry, v. 63, p. 280-284.

Crossley, H. E., 1946, The inorganic constituents of coal. The Chemical Age, p. 629-636.

Dalton, I. M. and Pringle, W. J. S., 1962, The gallium content of some midland coals. Fuel, v. 42, no. 1, p. 41-48.

Deer, W. A., Howie, R. A., and Zussman, J., 1962, Rock-forming minerals, v. 1 Ortho-and Ring Silicates, 333 p.; v. 5, Non-Silicates, 371 p., J. Wiley and Sons Inc., New York.

Degenhardt, H., 1957, Untersuchungen zur geochemischen Verteilung des Zirkoniums in der Lithosphare, Geochimica et Cosmochimia Acta, v. 11, p. 279-309.

Degens, E. T., Williams, E. G. and Keith, M. L., 1957, Environmental studies of Carboniferous sediments. I. Geochemical criterea for differentiating marine from fresh water shales. Bulletin of the American Association of Petroleum Geologists, v. 41, p. 2427-2455.

Des Cloizeaux, M., 1880, (Report to the Society on behalf of M. Terrell on the small crystals of linnaeite which he discovered in the beds of coal in the Rhonda Valley, Glamorganshire). Bull. Societe Minerologen, v. 3, p. 170-171.

Deul, M., 1955, The origin of ash-forming ingredients in coal. Economic Geology, v. 50, p. 103.

Deul, M., 1959, The principal geological, chemical and physical factors controlling the mineral content of coal. American Chemical Society, Division of Gas and Fuel Chemistry, Boston, Mass.

Deul, M. and Annell, C. S., 1956, The occurrence of minor elements in ash of low-rank coal from Texas, Colorado, North Dakota and South Dakota. U.S. Geological Survey Bulletin 1036-H, p. 155-172.

Dixon, K., Skipsey, E., and Watts, J. T., 1964, The distribution and composition of inorganic matter in bituminous coals: part 1. Journal of the Institute of Fuel, v. 37, no. 286, p. 485-493.

Duck, N. W. and Himus, G. W., 1951, On arsenic in coal and its mode of occurrence. Fuel, v. 30, no. 12, p. 267-271.

Durie, R. A. and Schafer. H. N. S., 1964, The inorganic constituents in Australian coals. IV-phosphorus and fluorine-their probable mode of occurrence. Fuel, v. 43, no. 1, p. 31-41.

Dutcher, R. R., White, E. W. and Spackman, W., 1964, Elemental ash distribution in coal components-use of the electron probe. Proceedings of the 22nd. Ironmaking Conference, Iron and Steel Division. The metallurgical Society of the American Institute of Mining and Metallurgical Engineers. p. 463-483.

Dutcher. R. R., White, E. W., Lebiedzik, J. and Hoover, M. R., 1973, Quantitative SEM image analyses-application to coal and coke microscopy. Geological Society of America Abstracts with Program, v. 5, no. 2, p. 157-158.

Dvornikov, A. G., 1965, On the distribution of mercury, arsenic, and antimony in rocks of the Bokovo-Khrustalsk region (Donbas). Geochemistry International, v. 2, no. 3, p. 526.

Dvornikov, A. G. and Tikhinenkova, E. G., 1973, Distribution of trace elements in iron sulfides of coals from different structures of central Donbass. Geochemistry International, v. 10, no. 5, p. 1168.

Eskenazy, G., 1977, On the binding form of tungsten in coals. Chemical Geology, v. 19, p. 153-159.

Eskenazy, G., 1978, Rare-earth elements in some coal basins of Bulgaria. Geological Balcanica, v. 8, no. 2, p. 81-88.

Estep, P. A., Kovach, J. J., Hiser, A. L. and Karr, Jr., C., 1970, Characterization of carbonate minerals in oil shales and coals by infrared spectroscopy, in Spectrometry of Fuels. R. A. Friedel, editor. Plenum Press, Chapter 18, p. 228-247.

Estep, P. A., Kovach, J. J., and Karr, Jr., C., 1968, Quantitative infrared multicomponent determination of minerals occurring in coal. Analytical Chemistry, v. 40, p. 358-363.

Falcon, R. M. S., 1978, Coal in South Africa, Part II. The application of petrography to the characterization of coal. Minerals Science and Engineering, v. 10, no. 1, p. 28-52.

Fiene, F. L., Kuhn, J. K., and Gluskoter, H. J., 1979, Mineralogic affinities of trace elements in coal, in Proceedings: Symposium on Coal Cleaning to Achieve Energy and Environmetal Goals. v. 1, S.E. Rogers and A. W. Lemmon, Jr., editors. U.S. Environmental Protection Agency Report EPA-600/7-79-098a, p. 29-58.

Filby, R. H., Shah, K. R., and Sautter, C. A., 1977, A study of trace element distribution in the solvent refined coal (SRC) process using neutron activation analysis. Journal of Radioanalytical Chemistry, v. 37, p. 693-704.

Finkelman, R. B., 1972, Relationship between manganese nodules and cosmic spherules, Marine Technology Society Journal, v. 6, no. 4., p. 34-39.

Finkelman, R. B., 1973, Analysis of the ultrafine fraction of the Apollo 14 soil. Procedures of the Fourth Lunar Science Conference, Geochemica Cosmochimica Acta, Pergamon Press, Supplement 4, v. 1, p. 179-189.

Finkelman, R. B., Stanton, R. W., and Breger, I. A., 1976, Energy dispersive analysis of in situ minerals in coal. Geological Society of America, abstracts, v. 8, no. 6, p. 865-866.

Finkelman, R. B. and Klemic, H., 1976, Brannerite from the Penn Haven Junction uranium occurrence, Carbon County, Pennsylvania. U. S. Geological Survey Journal of Research, v. 4, no. 6, p. 715-716.

Finkelman, R. B. and Stanton, R. W., 1978, Identification and significance of accessory minerals from a bituminous coal. Fuel, v. 57, p. 763-768.

Finkelman, R. B., 1978, Determination of trace element sites in the Waynesburg coal by SEM analyses of accessory minerals. Scanning Electron Microscopy, 1978, v. 1, p. 143-148.

Finkelman, R. B., Stanton, R. W., Cecil, C. B., and Minkin, J. A., 1979, Modes of occurrence of selected trace elements in several Appalachian coals. American Chemical Society Preprints, Fuel Chemistry Division, v. 24, no. 1, p. 236-241.

Finkelman, R. B., Dulong, F. T., Stanton, R. W. and Cecil, C. B., 1979, Minerals in Pennsylvania coal. Pennsylvania Geology, v. 10, no. 5, p. 2-5.

Finkelman, R. B. and Stanton, 1979, Distribution of sphalerite, chalcopyrite, and lead selenide (clausthalite?) in Appalachian coals. Abstracts of papers for the Ninth International Congress of Carboniferous Statigraphy and Geology, p. 64.

Finkelman, R. B., 1980, Mode of occurrence of accessory sulfide and selenide minerals in coal. Submitted to IX International carboniferous Congress, Compte Rendu. (in press).

Finney, H. R., and Farnham, R. S., 1968, Mineralogy of the inorganic fraction of peat from two raised bogs in Northern Minnesota, in Proceedings of the Third International Peat Congress, Quebec, Canada, p. 102-108.

Firth, J. N. M., 1971, Hatchettite from the South Wales coalfield, in Programme and abstracts of the 5th International Meeting on Organic Geochemistry, Hanover, Germany. The Geochemical Society.

Fleischer, M., 1955, Minor elements in some sulfide minerals. Economic Geology, 50th Anniversary Volume, Part II, p. 970-1024.

Fleischer, R. L., and Price, P. B., 1964, Glass dating by fission fragment tracks. Journal of Geophysical Research, v. 69, no. 2, p. 331-339.

Ford, C. T., 1977, Coal cleaning to remove trace elements prior to utilization, *in* 4th Symposium on Coal Utilization, Louisville, Kentucky, October 1977, p. 146-191.

Foster, W. D. and Feicht, F. L., 1946, Mineralogy of concretions from Pittsburgh coal seam, with special reference to analcite. American Mineralogist, v. 31, nos. 7/8, p. 357-364.

Francis, W., 1961, Coal-its formation and composition. Edward Arnold Ltd. London, 806 p.

Francis, C. W., Bonner, W. P., and Tamura, T., 1972, An evaluation of zonal centrifugation as a research tool in soil science: I. Methodology. Soil Science Society of America Proceedings, v. 36, p. 366-376.

Ford, C. T., 1977, Coal cleaning to remove trace elements prior to utilization, *in* 4th Symposium on Coal Utilization, Louisville, Kentucky, October 1977, p. 146-191.

Foster, W. D. and Feicht, F. L., 1946, Mineralogy of concretions from Pittsburgh coal seam, with special reference to analcite. American Mineralogist, v. 31, nos. 7/8, p. 357-364.

Francis, W., 1961, Coal-its formation and composition. Edward Arnold Ltd. London, 806 p.

Francis, C. W., Bonner, W. P., and Tamura, T., 1972, An evaluation of zonal centrifugation as a research tool in soil science: I. Methodology. Soil Science Society of America Proceedings, v. 36, p. 366-376.

Frondel, C., Ito, J., and Montgomery, A., 1968, Scandium content of some aluminum phosphates. American Mineralogist, v. 53, nos. 7 & 8, p. 1223-1231.

Gallagher, R. T., 1940, Mineral content of the Bevier coal seam. The Mines Magazine, v. 30, no. 11, 0. 586-612.

Garrels, R. M. and Christ, C. L., 1965, Solutions, Minerals, and Equilibria. Harper and Row Publishers, New York, 450 p.

Gauger, A. W., Barrett, E. P., and Williams, F. J., 1934, Mineral matter in coal-a preliminary report. Transactions of the American Institute of Mining and Metallurgical Engineers, v. 108, p. 226-236.

Gentry, R. V., Christie, W. H., Smith, D. H., Emery, J. F., Reynolds, S. A., Walker, R., Cristy, S. S., and Gentry, P. A., 1976, Radiohalos in coalified wood: new evidence relating to the time of uranium introduction and coalification. Science, v. 194, no. 4262, p. 315-318.

Gindy, A. R., El-Askary, M. A., Khalil, S. O., 1978, Differential thermal and thermogranimetric studies and some trace-element contents of some coals and carbonaceous shales from west-central Sinai, Egypt. Chemical Geology, v. 22, p. 267-283.

Given, P. H. and Yarzab, 1978, Analysis of the organic substance of coals: problems posed by the presence of mineral matter, in Analytical Methods for Coal and Coal Products, Volume II. p. 3-41.

Gluskoter, H. J., 1965, Electric low-temperature ashing of bituminous coal. Fuel, v. 44, no. 4, p. 285-291.

Gluskoter, H. J., 1975, Minerl matter and trace elements in coal, in Trace elements in fuel, S. P. Babu, editor. Washington, D. C., American Chemical Society, Advances in Chemistry Series, no. 141, p. 1-22.

Gluskoter, H. J., 1977, An introduction to the occurrence of mineral matter in coal, in Ash Deposits and Corrosion due to impurities in combustion gases. R. W. Bryers, editor. Hemisphere Publishing Corp., Washington, p. 3-19.

Gluskoter, H. J. and Lindahl, P. C., 1973, Cadmium: mode of of occurrence in Illinois coals. Science, v. 181, no. 4096, p. 264-266.

Gluskoter, H. J. and Rees, O. W., 1964, Chlorine in Illinois coal. Illinois Geological Survey circular 372, 23 p.

Gluskoter, H. J. and Ruch, R. R., 1971, Chlorine and sodium in Illinois coals as determined by neutron activation analyses. Fuel, v. 50, no. 1, p. 65-76.

Gluskoter, H, J., Ruch, R. R., Miller, W. G., Cahill, R. A., Dreher, G. B., and Kuhn, J. K., 1977, Trace elements in coal: occurrence and distribution. Illinois State Geological Survey, Circ. 499, 154 p.

Godbeer, W. C. and Swaine, D. J., 1979, Cadmium in coal and fly-ash, in Trace Substances in Environmental Health-XIII. D. D. Heniphill, editor.

Goldschmidt, V. M. and Peters, C., 1932, Zur Geochemie des Berylliums. Nachr. Akad. Wiss. Goettingen, Math.-Physik-Kl 360-36. Cited in Wedepohl, 1969.

Goldschmidt, V. M. and Peters C. L., 1933, Uber die anreicherung seltener Elemente in Steinkohlen. Nachrichten von der Gesellschaft der Wissenschaften zu Gottingen. Math.-Physik. Klasse, Heft 4, p. 371-386.

Goldschmidt, V. M., 1935, Rare elements in coal ashes. Industrial and Engineering Chemistry, v. 27, no. 9, p. 1100-1102.

Goldschmidt, V. M., 1954, Geochemistry, Oxford Press, London, 730 p.

Goldstein, J. I., 1975, Electron beam-specimen interaction, in Practical Scanning Electron Microscopy. J. I. Goldstein and H. Yakowitz, editors. Plenum Press, New York, Chapter III, p. 49-94.

Golovko, V. A., 1961, The distribution of minor elements in carboniferous deposits of the central regions. Doklady of the Academy of Sciences of the U.S.S.R., Earth Sciences Sections, v. 132, nos. 1-6, p. 452-455.

Gordon, S. A., Volkov, K. Yr., and Mendovskii, M. A., 1958, On the forms of germanium in coal. Geochemistry, no. 4, p. 484-489.

Grant, K. and Weymouth, J. H., 1967, The influence of the inorganic constituents in Victorian brown coals on the fouling properties of the coals when used in gas generators and industrial boilers, in Symposium on the Inorganic Constituents of Fuel. (Origin, Influence, and Control). University of Melbourne, 1964.

Gray, D., 1978, Inherent mineral matter in coal and its effect upon hydrogenation. Fuel, v. 57, no. 4, p. 213-216.

Greer, R. T., 1977, Coal microstructure and the significance of pyrite inclusions. In Scanning Electron Microscopy, 1977, v. 1. O. Johari, editor. IIT Research Institute, Chicago, p. 79-93.

Guin, J. A., Tarrer, A. R., Lee, J. M., Lo, L., and Curtis, C., 1979, Further studies of the catalytic activity of coal minerals in coal liquefaction. 1. Verification of catalytic activity of mineral matter by Model compound studies. Industry and Engineering Chemistry Process Design and Development, v. 18, no. 3, p. 371-376.

Gulyayeva, L. A., and Itkina, E. S., 1962, The halogens and vanadium, nickel and copper in coal. Geochemistry, no. 4, p. 395-407.

Harris, L. A., Braski, D. N., and Yust, C. S., 1977, Electron microscopy of coal constituents. In Microstructural Science, J. D. Braun, H. W. Arrowsmith and J. L. McCall, editors, v. 5, p. 351-357.

Haskin, L. A., Frey, F. a., Schmitt, R. A. and Smith, R. H., 1966, Meteoritic, solar and terrestrial rare-earth distributions, in physics and chemistry of the earth. v. 7, Pergamon Press, Oxford and New York.

Hatch, J. R., and Swanson, V. E., 1976, Trace elements in Rocky Mountain coals, in Symposium on the Geology of Rocky Mountain Coal, p. 43-163.

Hatch, J. R., Avcin, M. J., Wedge, W. K., and Brady, L. L., 1976, Sphalerite in coals from southeastern Iowa, Missouri, and southeastern Kansas. U.S. Geological Survey Open-file report 76-796, 26 p.

Hatch, J. R., Gluskoter, H. J., and Lindahl, P. C., 1976, Sphalerite in coals from the Illinois Basin. Economic Geology, v. 71, no. 3, p. 613-624.

Hawley, J. E., 1955, Germanium content of some Nova Scotian coals. Economic Geology, v. 50, no. 5, p. 517-532.

Henley, K. J., 1977, Improved heavy-liquid separation at fine particle sizes. American Mineralogist, v. 62, p. 377-381.

Hildebrand, R. T. and Hatch, J. R., 1977, The distribution of sodium and alkaline-earth elements in coal of the Rocky Mountain and Northern Great Plains Provinces. Geological Society of America, Abstracts with Programs, v. 9, no. 7, p. 1015-1016.

Hills, E. S., 1963, Elements of Structural Geology. J. Wiley and Sons, New York, 483 p.

Hoehne, K., 1957, Zirconkristalle in Kohlenflozen. Chemie der Erde, v. 19, p. 38-50.

Hokr, Z., 1978, Arsenic in the coal of the North Bohemian brown coal basin. Chemical Abstracts, v. 88, p. 132, no. 25364b.

Horton, L., and Aubrey, K. V., 1950, The distribution of minor elements in vitrain: Three vitrains from the Barnsley seam. Journal of the Society of Chemical Industry. v. 69, suppl. no. 1, p. 541-548.

Huang, W. H. and Keller, W. D., 1970, Dissolution of rock-forming silicate minerals in organic acids: simulated first-stage weathering of fresh mineral surfaces. The American Mineralogist, v. 55, p. 2076-2094.

Hughes, R. E., 1971, Mineral matter associated with Illinois coal. University of Illinois at Urbana-Champaign. PhD. dissertation, 145 p.

Hurley, P. M. and Fairbain, H. W., 1957, Abundance and distribution of uranium and thorium in zircon, sphene, apatite, epidote, and monazite in granitic rocks. Transactions American Geophysical Union, v. 38, no. 6, p. 939-944.

International Committee for Coal Petrology, 1971, International handbook of coal petrology, 2nd edition, Paris, Centre National Recherche Scientifigue.

Jedwab, J., 1964, Coal as a source of beryllium. NASA Accession no. N65-21075, Report no. EVR-2106f, 51 p. Cited in Wedepohl, 1970.

Jones, J. H. and Miller, J. M., 1939, The occurrence of titanium and nickel in the ash from some special coals. Chemistry and Industry, v. 58, p. 237-245.

Judzis, A. and Judzis, Jr., A., 1978, Uranium Minerals in Chattanooga shale, in Eleventh Oil shale symposium proceedings. J. H. Gary, editor. Colorado School of Mines, p. 343-349.

Juranek, G., Kirsch, H., Nemetschek, Th., and Schliephake, R. W., 1958, Contribution a la connaissance des substances minerales et en particulier des mineraus argileux que l'on rencontre dans les charbons et dans les epontes du bassin de la Ruhr. Revue de l'industrie minerale, v. 40, no. 7, p. 41-49.

Karner, F. R., Beckering, W., Rindt, D. K. and Schobert, H. H., 1979, Inorganic constituents in lignite: overview and some effects on coal utilization. Geological Society of America, Abstracts with Programs, v. 11, no. 7, p. 454.

Karr, C., Jr., Estep, P. A., and Kovach, J. J., 1968, Spectroscopic evidence for the occurrence of nitrates in lignites. American Chemical Society, Division of Fuel Chemistry Preprints, v. 12, no. 4, p. 1-12.

Kehn, T. M., 1957, Selected annotated bibiliography of the geology of uranium-bearing coal and carbonaceous shale in the United States. U. S. Geological Survey Bulletin 1059-A, 28 p.

Kemezys, M. and Taylor, G. H., 1964, Occurrence and distribution of minerals in some Australian coals. Journal of the Institute of Fuels, v. 37, p. 389-397.

King, J. W. and Young, H. B., 1956, High-grade uraniferous lignites in Harding County, South Dakota, in Page et al., 1956, p. 419-431.

Kirsch, H., Pollmann, S., and Ottemann, J., 1968, Kristallchemische aspekte zum verhalten von Arsen bei der Steinkohlenfenerung in Kraftwerken. Neues Johrbuch fur Mineralogie Monatshefte, Heft 5, p. 129-140.

Korolev, D. F., 1957, Some peculiarities of molybdenum distribution in rocks of the Bylymsk coal deposits. Geochemistry, no. 5, p. 493-499.

Korolev, D. F., 1958, The role of iron sulfides in the accumulation of molybedenum in sedimentary rocks of the reduced zone. Geochemistry, no. 4, p. 452-463.

Korzeb, S. L., and Chang, L. L. Y., 1977, Distribution and occurrence of minerals in Ohio coals from Licking, Perry and Hocking Counties. Geological Society of America, Abstracts with Programs, v. 9, no. 5, p. 616-617.

Kosterin, A. V., Korolev, D. F., and Kizyura, V. E., 1963, Rare earths in the Chekhez lignite deposit. Geochemistry, no. 7, p. 721-723.

Krynine, P. D., 1946, The tourmaline group in sediments. The Journal of Geology, v. 54, no. 2, p. 65-87.

Kuhn, J. K., Fiene, F., and Harvey, R., 1978, Geochemical evaluation and characterization of a Pittsburgh No. 8 and a Rosebud seam coal. Department of Energy, Morgantown Energy Technology Center, document METC/CR-78/8, 40+Xiii p.

Kunstmann, F. H. and Bodenstein, L. B., 1961, The arsenic content of South African coals. Journal of the South African Institute of Mining and Metallurgy, v. 62, p. 234-244.

Kuznetsova, V. V. and Saukow, A. A., 1961, Possible forms of occurrence of molybdenum and rhenium in the coals of middle Asia. Geochemistry, no. 9, p. 822-829.

Lapham, D. M., Barnes, J. H., Downey, W. F., Jr., and Finkelman, R. B., 1980, Mineralogy associated with burning anthracite deposits of Eastern Pennsylvania. Pennsylvania Geological Survey Mineral Resource Report 78, (in press).

Lau, M., Chaklader, A. C. D., and Warrenk, I. H., 1977, Mineral-matter content and gross properties of Hat Creek coal. CIM Bulletin, v. 70, no. 784, paper no. 119, p. 139.

Lawrence, L. J., Warne, S. St. J., and Booker, M., 1960, Millerite in the Bulli coal seam. Australian Journal of Science, v. 23, p. 87-88.

Lee, R. J., Huggins, F. E., and Huffman, G. P., 1978, Correlated Mossbauer, SEM studies of coal mineralogy. Scanning Electron Microscopy, 1978, v. 1, p. 561-568.

Lessing, R., 1934, Fluorine in coal. Nature, v. 134, p. 699-700.

Leutwein, F. and Rosler, 1956, Geochemische untersuchungen an palaozoischen Kohlen mittel-und Ostdeulshlends. Freiberg, Forschungsh, C 19, Alrademie Verloa, Berlin, Cited in Rosler and Lange, 1976.

Leutwein, F., 1966, Geochemische Charakteristica mariner Einflusse in Torfen und anderen quarternaren Sedimenten. Geol. Rundschan, v. 55, p. 97. Cited in Wedepohl, 1971.

Lin, J. S., Hendricks, R. W., Harris, L. A., and Yust, C.S., 1978, Microporosity and micromineralogy in a bituminous coal. Acta Crystallographica, v. 11, p. 621-625.

Lissner, A., 1956, Sitz. ber. deut. Akad. Wiss. Berlin, Kl. Chem., Geol., u. Biol., no. 1, 30 p. Cited in Ode, 1963.

Lloyd, S. J. and Cunningham, J., 1913, The radium content of some Alabama coals. American Chemistry Journal, v. 50, p. 47-51.

Lyons, P. C., Finkelman, R. B., Ofendohl, O. G., and Wendolph, J. F. Jr., 1980, Resin rods and woody rodlike structures in Pennsylvanian coal beds of the Appalachian and Illinois basins. American Association of Petroleum Geologists (abstract in press).

Lutz, G. J. Stemple, J. S., and Rook, H. L., 1978, Evaluation by activation analysis of elemental retention in biological samples after low temperature ashing. Appendix B, <u>in</u> Proceedings of Joint EPA/NBS Workshop on Recommendations and Conclusions on the National Environmental Specimen Bank. H. L. Rook, editor. U. S. National Bureau of Standards, Special Publication, no. 501, p. 33-41.

Mackowsky, M.-Th., 1975, Minerals and trace elements occurring in coal, <u>in</u> Stack et al., 1975, p. 121-132.

Mackowsky, M.-Th., 1968, Mineral matter in coal, <u>in</u> coal and coal-bearing strata. Murchison, D. G., and Westall, T. S., editors, American Elsevier, New York, p. 309-321.

Manskaya, S. M. and Drozdova, T. V., 1968, Geochemistry of organic substances. Translated and edited by L. Shapiro and I. Breger. Pergamon Press, London, 347 p.

Marshall, C. E., 1959, Petrology and preparation of certain (Permian) coal seams of India. Economic Geology, v. 54, no. 1, p. 20-56.

Marshall, C. E., and Thompkins, D. K., 1967, Mineral matter in Permian coal seams, <u>in</u> Symposium on the Inorganic Constituents of Fuel (Origin, Influence and Control), University of Melbourne, 1964, p. 57-69.

McBride, J. P., Moore, R. E., Witherspoon, J. P., and Blanco, R. E., 1978, Radiological impact of airborne effluents of coal and nuclear plants. Science, v. 202, no., 4372, p. 1045-1050.

McCartney, J. T., O'Donnell, H. J., and Ergun, S., 1966, Ultrafine structures in coal components as revealed by electron microscopy, <u>in</u> Coal Science, American Chemical Society, Advances in Chemistry Series 55, Chapter 16, p. 261-273.

Miller, R. N. and Given, P. H., 1978, A geochemical study of the inorganic constituents in some low-rank coals. Technical Report 1, U. S. Department of Energy Report FE-2494-TR-1, 314 p.

Miller, W. G., 1974, Relationships between minerals and selected elements in some Pennsylvanian age coals of Northwestern Illinois. Master of Science Thesis, University of Illinois at Urbana-Champaign, 145 p.

Miller, W. H., 1842, On the specific gravity of sulphuret of nickel. The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, v. 20, p. 378-379.

Milton, C., Dwornik, E. J., Estep-Barnes, P. A., Finkelman, R. B., Pabst, A., and Palmer, S., 1978, Abelsonite, nickel porphyrin, a new mineral from the Green River Formation, Utah. American Mineralogist, v. 63, p. 930-937.

Milton, C., Ingram, B., and Breger, I., 1974, Authigenic magnesioarfvedsonite from the Green River Formation, Duchesne County, Utah, American Mineralogist, v. 59, p. 830-836.

Minkin, J. A., Chao, E. C. T., and Thompson, C. L., 1979, Distribution of elements in coal macerals and minerals: determination by electron microprobe. American Chemical Society. Division of Fuel Chemistry. Preprints of papers presented at Honolulu, April 1979, v. 24, no. 1, p. 242-249.

Minkin, J. A., Finkelmen, R. B., Thompson, C. L., Cecil, C. B., Stanton, R. W., and Chao, E. C. T., 1980, Arsenic-and selenium-bearing pyrite in Upper Freeport coal, Indiana County, Pennsylvania. Submitted to IX International Carboniferous Congress, Compte Rendu (in press).

Mitchell, R. S., and Gluskoter, H. J., 1976, Mineralogy of ash of of some American coals. Fuel, v. 55, no. 2, p. 90-96.

Mitra, G. B., 1954, Identification of inorganic impurities in coal by the X-ray method. Fuel, v. 33, p. 316-330.

Moza, A., Strickler, D. W., and Austin, L. G., 1978, A mounting medium for coal particles. In SEM/1978/I. O. Johari, editor, SEM, Inc., Chicago, Illinois, p. 289-292.

Mukherjee, B. and Ghosh, A., 1976, Distribution and behavior of trace elements in some Permian coals of India. The Indian Mineralogist, v. 17, p. 23-30.

Mukherjee, D. K., and Chowdhury, P. B., 1976, Catalytic effect of mineral matter constituents in a North Assam coal on hydrogenation. Fuel, v. 55, no. 1, p. 4-8.

Mukherjee, S. N., Nag, A. K., and Majumdar, S. K., 1972, A study on the clay minerals in coal by derivatography. Journal of Mines, Mettalurgy and Fuels (Calcutta), v. 20, no. 12, p. 363-367.

Muller, L. D., 1967, Laboratory methods of mineral separations, in Physical Methods in Determinitive Mineralogy, J. Zussman, editor. Academic Press, New York, p. 1-30.

Murich, A. T., 1973, Helium in the natural gases of the Donets Basin. Geochemistry International, v. 10, no. 6, p. 1287-1292.

Nalwalk, A. J., Friedel, R. A., and Queiser, J. A., 1974, Peroxidation of coals-analysis of minerals. Energy Sources, v. 1, no. 2, p. 179-187.

Nandi, B. N., Montgomery, D. S., and Martin, E., 1970, The study of coal by a scanning electron microscope and electron microprobe. American Chemical Society, Division of Fuel Chemistry Preprints, v. 14, no. 1, p. 81-86.

Navale, G. K. B., 1979, Origin and nature of Indian Permian coal. Ninth International Congress of Carboniferous Stratigraphy and Geology. University of Illinois at Urbana-Champaign, May 1979, p. 147-148.

Nazarenko, V. A., 1937, The occurrence of V, Be and B in the ash of some coals. Trudy Biogeokhim, Labor, Akad. Nauk SSSR. v. 4, p. 265-271. Cited in Swaine, (1975).

Nelson, J. B., 1953, Assessment of the mineral species associated with coal. The British Coal Utilization Research Association Monthly Bulletin, v. 17, no. 2, p. 41-55.

Newberry, D. E., 1975, Image formation in the scanning electron microscope, in Practical Scanning Electron Microscopy. J. I. Goldstein and H. Yakowitz, editors. Plenum Press, New York, Chapter IV, p. 95-148.

Nicholls, G. D., 1968, The geochemistry of coal-bearing strata, in Coal and Coal-Bearing Strata. D. Murchison and T. S. Westoll, editors. American Edition, American Elsevier, N. Y., p. 269-307.

Nicholls, G. D. and Loring, D. H., 1962, The geochemistry of some British Carboniferous sediments. Geochemica et Cosmochemica Acta, v. 26, p. 181-223.

Nissenbaum, A. and Swaine, D. J., 1976, Organic matter-metal interactions in recent sediments: the role of humic substances. Geochemica et Cosmochemica Acta. v. 40, p. 809-816.

Noble, E. A., 1972, Metalliferous lignite in North Dakota, University of North Dakota Guidebook no. 3. North Dakota Geological Survey Miscellaneous Series no. 50, p. 133-134.

Ode, W. H., 1963, Coal analysis and mineral matter, in Chemistry of Coal Utilization, Supplementary Volume. H. H. Lowry, editor. John Wiley and Sons, Inc., New York, p. 202-231.

O'Gorman, J. V., 1971, Studies on mineral matter and trace elements in North American coals. The Pennsylvania State University, Dept. of Material Sciences, PhD. Thesis, 184 p.

O'Gorman, J. V. and Walker, Jr., P. L., 1971, Mineral matter characteristics of some American coals. Fuel, v. 50, p. 135-151.

Otte, M. U., 1953, Spurelemente in linigen deutschen Steinkohln. Chemie der Erde, v. 16, p. 239-294.

Page, L. R., Stocking, H. E., and Smith, H. B., 1956, Contributions to the geology of uranium and thorium by the United States Geological Survey and Atomic Energy Commission for the United Nations International Conference on Peaceful Uses of Atomic Energy, Geneva, Switzerland, 1955. U. S. Geological Survey Professional Paper 300. 739 p.

Parks, B. C., 1952, Mineral matter in coal, in Second Conference on the Origin and Constitution of Coal. Nova Scotia Department of Mines, Crystal Cliffs, Nova Scotia. p. 272-292.

Paulson, L. E., Beckering, W. and Fowkes, W. W., 1972, Separation and identification of minerals from Northern Great Plains Province lignite. Fuel, v. 51, p. 2324-2327.

Pearson, D. E., Chaudhry, M. A., Colvin, N. G., and Gigliotti, 1977, Mineral matter in bituminous coals of the Crownsnest Coalfield. Geological Association of Canada, Program with Abstracts, v. 2, p. 41.

Petrov, N. P., 1961, Molybdenum in one of the lignite regions of Uzbekistan. Sov. Geologiya, no. 9, p. 148. Cited in Manskaya and Drozdova, (1968).

Plogmann, H. and Mackowsky, M.-Th., 1977, Analyses of mineral matter in coals of the Ruhr under gasification conditions, in Ash Deposits and Corrosion due to Impurities in Combustion gasses. R. W. Bryers, editor, p. 21-37.

Porrett, R. E. and Swaine, D. J., 1976, Mercury and selenium in some Australian coals and fly-ash. Institute of Fuel, Biennial Conference, p. 18.1-18.9.

Raben, J. D., 1979, Coal: chemistry, petrography, rank and stratigraphy, in Evaluation of Coal Deposits in the Narragansett Basin, Massachusetts and Rhode Island. Skehan, J. W., Murray, D. P. and Rider, T. H., editors. Weston Observatory, Boston College, Report prepared for U. S. Bureau of Mines, p. 48-64.

Rankama, K. 1944, On the geochemistry of tantalum. Bulletin de la Commission Geologique de Finlande, no. 133.

Rankama, K., and Sahama, T. G., 1950, Geochemistry, University of Chicago Press, Chicago, Illinois, 912 p.

Rao, C. P. and Gluskoter, H. J., 1973, Occurrence and distribution of minerals in Illinois coals. Illinois State Geological Survey Circular 476, 56 p.

Rao, D. P., 1977, Petrographic, mineralogical and chemical characterization of certain arctic Alaskan coals from the Cape Beaufort region. Geological Association of Canada, Program with Abstracts, v. 2, p. 43.

Rao, S. R. R., Datta, P. B., Luthra, G. B. S., and Lahai, A., 1951, Phosphorus in coking coal. Mining Geology and Metallurgical Institute of India, Transactions, v. 47, p. 113-127.

Rashid, M. A., 1974, Absorption of metals on sedimentary and peat humic acids. Chemical Geology, v. 13, p. 115-123.

Ratynskiy, V. M. and Glushnev, S. V., 1967, Relationships in the distribution of metals in coals. Poklady Akad. Nank SSSR, v. 177, p. 236-239.

Ratynskiy, V. M., Sendul'skaya, T. I., and Shpirt, M. Ya., 1966, Chief mode of entry of germanium into coal. Doklady Earth Science Sections, v. 170, p. 218-221.

Raymond, Jr., R., 1979, Relative abundances of common elements in coal macerals. 1979 Annual meeting of the Microprobe Analysis Society.

Raymond, Jr., R. and Gooley, R., 1978, A review of organic sulfur analysis in coal and a new procedure. Scanning Electron Microscopy, 1978/I, Om Johari, editor. SEM, Inc., Chicago, v. 1, p. 93-108.

Razdorozhniy, V. F., 1967, Correlation between accessory beryllium and vanadium and the inorganic fraction of coal. Geochemistry International, v. 4, no. 2, p. 403.

Razdorozhniy, V. F., and Petrus, A. G., 1975, Rare alkalies in coals of the Dnieper and Donets Basins. Chemical Abstracts, v. 82, no. 88336r.

Rekus, A. F., and Haberkorn, III, A. R., 1966, Identification of minerals in single particles of coal by the X-ray powder method. Journal of the Institute of Fuel, v. 39, p. 474-477.

Renton, J. J. and Cecil, C. B., 1979, The origin of mineral matter in coal, in Carboniferous Coal Short Course and Guidebook. A. C. Donaldson, M. W. Presley, and J. J. Renton, editors. Geology Department, West Virginia University, Morgantown. p. 208-225.

Renton, J. J. and Hidalgo, R. V., 1975, Some geochemical considerations of coal. West Virginia Geological and Economic Survey, Coal-Geology Bulletin 4, 38 p.

Reynolds, F. M., 1939, Note on the occurrence of barium in coal. Journal of the Society of the Chemical Industry, v. 58, p. 64-68.

Reynolds, F. M., 1948, The occurrence of vanadium, chromium, and other unusual elements in certain coals. Journal of the Society of Chemical Industry, v. 67, no. 9, p. 341-345.

Ribbe, P. H., 1975, Trace and minor element distributions in coals and coal minerals as determined by ion microprobe mass analysis. Geological Society of America, Abstracts with Programs, v. 7, no. 7, p. 1244.

Roberman, S. R., 1973, Gallium-aluminum-titanium relationship in the coals of Northern Donbas. Geochemistry International, v. 10, no. 6, p. 1392.

Rosler, H. J. and Lange, H., 1976, Geochemische Tabellen. Ferdinand Enke Verlag, Stuttgart, 674 p.

Ruch, R. R., Gluskoter, H. J. and Kenndey, E. J., 1971, Mercury content of Illinois coals. Illinois State Geological Survey, Environmental Geology notes, no. 43, 15 p.

Ruch, R. R., Gluskoter, H. J. and Shimp, N. F., 1974, Occurrence and distribution of potentially volatile trace elements in coal: A final report. Illinois State Geological Survey, Environmental Geology notes, no. 72, 96 p.

Sarofin, A. F., Howard, J. B., and Padia, A. S., 1977, The physical transformation of the mineral matter in pulverized coal under simulated combustion consitions. Combustion Science and Technology, v. 16, p. 187-204.

Schofield, J. A. and Haskin, L. A., 1964, Rare-Earth distribution patterns in eight terrestrial materials, Geochimica et Cosmochimica Acta, v. 28, p. 437-446.

Schultz, H., Hattman, E. A. and Booher, W. B., 1975, The fate of some trace elements during coal pretreatment and combustion, in Trace Elements in Fuel. S. P. Babu, editor. American Chemical Society, Advances in Chemistry Series 141, Chapter 11, p. 139-153.

Sharudo, I. I. and Moskvin, V. I., 1973, Mineral impurities in coals of the Bureya Basin and their origin. Lithology and Mineral Resources, v. 8, no. 1, p. 76-79.

Shaw, D. M., 1952, The geochemistry of Indium. Geochemica et Cosmochimica Acta, v. 2, p. 185-206.

Shaw, D. M., 1957, The geochemistry of gallium; indium, thallium-a review. Physics and Chemistry of the Earth, v. 2, p. 164-211.

Shcherbina, V. V., 1956, Complex ions and the transfer of elements in the supergene zone. Geochemistry, no. 5, p. 486-493.

Shcherbina, V. V., 1957, Behavior of uranium and thorium in the sulfate-carbonate and phosphate environments of the supergene zone. Geochemistry, no. 6, p. 579-597.

Smyth, M., 1966, The association of minerals with macerals and microlithotypes in some Australian coals. Commonwealth Scientific and Industrial Research Organization, Technical Communication 48, 35 p.

Sofiyev. I. S., Gorlenko, K. A., and Semasheva, I. N., 1964, The nature of bonding of germanium in coal. Geochemistry, p. 297-300.

Solodov, N. A., Kostin, Yu., P., Mertov, E. S., Bel'kov, V. I., Zyroyanov, A. P. and Pankov, E. N., 1975, Cesium and tantalum in mined coals of the U.S.S.R. Chemical Abstracts, v. 83, p. 154, no. 166700s.

Soong, R. and Gluskoter, H. J., 1977, Mineral matter in some New Zealand coals. 1. Low-temperature ashing and mineralogical composition of such coal ashes. New Zealand Journal of Science, v. 20, p. 273-277.

Spackman, W. and Moses, R. G., 1961, The nature and occurrence of ash forming minerals in anthracite. Bulletin of the Mineral Industries Experiment Station, Penn. State University, no. 75, p. 1-22.

Spears, D. A. and Rice, C. M. 1973, An Upper Carboniferous tonstein of vocanic origin. Sedimentology, v. 20, p. 281-294.

Spencer, L. J., 1910, On the occurrence of alstonite and ullmannite (a species new to Britain) in a barytes-witherite vein at the New Brancepeth colliery near Durham. Mineralogical Magazine, v. 15, p. 302-311.

Sprunk, G. C. and O'Donnell, H. J., 1942, Mineral matter in coal. U.S. Bureau of Mines, Technical Paper 648, 67 p.

Stach, E., Mackowsky, M.-Th., Teichmuller, M., Taylor, G. H., Chandra, D. and Teichmuller, R., 1975, Stach's Textbook of Coal Petrology. (Translated by D. G. Murchison, G. H. Taylor and F. Zierke). Gebruder Borntraeger, Berlin, 428 p.

Stadnichenko, T., Murata, K. J., Zubovic, P., and Hufschmidt, E. L., 1953, Concentration of germanium in the ash of American coals, a program report. U. S. Geological Survey, Circular 272, 34 p.

Stadnichenko, T., Zubovic, P., and Sheffey, N. B., 1961, Beryllium content of American coals. U.S. Geological Survey Bulletin 1084-K, p. 253-295.

Stanton, R. W., 1975, A two dimersional mineralogical and petrographic facies within a mining face of the Waynesburg coal. Dept. of Geology, University of West Virginia, M.S. thesis, 103 p.

Stanton, R. W. and Finkelman, R. B., 1979, Petrographic composition of bituminous coal: optical and SEM identification of constituents. Scanning Electron Microscopy, 1979, v. 1, p. 465-472.

Strehlow, R. A., Harris, L. A., and Yust, C. S., 1978, Submicron-sized mineral component of vitrinite. Fuel, v. 57, p. 185-186.

Stone, R. W., 1912, Coal near the Black Hills Wyoming-South Dakota. U.S. Geological Survey, Bulletin 499, 66 p.

Stutzer, O., 1940, Geology of Coal. University of Chicago Press, 461 p.

Swaine, D. J., 1961, Occurrence of nickel in coal and dirt samples from the coal cliff colliery (Bulli Seam). The Australian Journal of Science, v. 23, no. 9, p. 301-302.

Swaine. D. J., 1962, Boron in New South Wales Permian Coals. The Australian Journal of Science, v. 25, no. 6, p. 265-266.

Swaine, D. J., 1964, Scandium in Australian coals and related materials. American Chemical Society Preprints, Division of Fuel Chemistry, v. 8, no. 3, p. 172-177.

Swaine, D. J., 1967, Inorganic constituents in Australian coals. Sonderdruck aus den Mitteilungen der Naturforschenden Gesellschaft in Bern-Neue Folge, 24 Band, p.49-61.

Swaine, D. J., 1971, Boron in coals of the Bowen Basin as an environmental indicator, in Proceedings of the Second Bowen Basin Symposium. A. Davis, editor. Geological Survey of Queensland Report 62, p. 41-48.

Swaine, D. J., 1975, Trace elements in coal. in Recent contributions to geochemistry and analytical chemistry. Tugarinov, A. I., editor. Israel Program for Scientific Translantions, Jesusalem. p. 539-550.

Swaine, D. J., 1980, Nickel in coal and fly-ash. Preprint of a chapter in a book to be edited by J. Nriagu.

Swanson, V. E. and Huffman. Jr., C., 1976, Guidelines for sample collecting and analytical methods used in the U. S. Geological Survey for determing chemical composition of coal. U. S. Geological Survey circular 735, 11 p.

Swanson, V. E., Medlin, J. H., Hatch, J. R., Coleman, S. L., Wood, G. H., Jr., Woodruff, S. D., and Hildebrand, R. T., 1976, Collection, chemical analysis, and evaluation of coal samples in 1975. U. S. Geological Survey, Open-file report 76-468, 503 p.

Szilagyi, M., 1971, The role of organic material in the distribution of Mo, V and Cr in coal fileds. Economic Geology, v. 66, p. 1075-1078.

Taylor, G. H. and Warne, S. St. J., 1960, Some Australian coal petrological studies and their geological implications, in Proceedings of the International Commission on Coal Petrology, v. 3, p. 75-83.

Taylor, S. R., 1964, Abundance of chemical elements in the continental crust: a new table. Geochimica et Cosmochimica Acta, v. 28, p. 1273-1285.

Teichmuller, M., 1975, Origin of the petrographic constituents of coal, in Stach et al., 1975, p. 176-238.

Teichmuller M. and Teichmuller, R., 1979, Diagnesis of coal (coalification), in Diagenesis in Sediments and Sedimentary Rocks. G. Larsen and G. V. Chilengar, editors. Developments in Sedimentology 25A. Elsevier Scientific Publishing Co., New York, Chapter 5, p. 207-246.

Terebenna, A. and Angelova, G., 1962, Composition of the ashes of alcohol-benzene extracts of some Bulgarian coals. Compt Rend. Acad. Bulgare Sci., v. 15, p. 495, Cited in Wedephohl (1969).

Tkach, B. I., 1966, Geochemical peculiarities of mercury distribution in coal measures of the Lisichan region (Donbass). Geochemistry International, v. 3, no. 3, p. 470.

Tkach, B. I., 1975, On the role of organic matter in concentration of mercury. Geochemistry International, v. 11, no. 5, p. 973-975.

Torrey, S. (editor), 1978, Trace Contaminants from Coal. Noyes Data Corp., Park Ridge, New Jersey, 294 p.

Tsui, F. F., Cahill, R. A., and Frost, J. K., 1979, Concentrations of rare earth elements in coals of the Illinois Basin. Ninth International Congress of Carboniferous Stratigraphy and Geology. Urbana, Illinois, May 1979, p. 218.

United States Environmental Protection Agency, 1979, Radiological impact caused by emissions of radionuclides into air in the United States. Preliminary Report, U.S. Environmental Protection Agency report EPA 520/7-79-006.

U. S. Geological Survey, 1959, Uranium in coal in the Western United States. U. S. Geological Survey Bulletin 1055, 315 p.

Valiev, Yu. Ya., 1977, Geochemistry of boron in Jurassic coals of the Gissar Range. Chemical Abstracts, v. 87, no. 706896.

Vassamillet, L. F., Examination of medium rank coals by SEM, 1972, in 7th Conference on Electron Probe Analysis, Electron Probe Analyses Society of America, p. 55A-55B.

Vertushkov, G. N., 1953, Messelite from the Kustanaya region Kazakhstan S.S.R. Chemical Abstracts, v. 80, no. 18, p. 450-451.

Vine, J. D., 1956, Uranium-bearing coal in the United States, in Contributions to the Geology of uranium and thorium by the United States Geological Survey and Atomic Energy Commission for the United Nations Interantional conference on peaceful uses of atomic energy, Geneva, Switzerland, 1955. L. R. Page, H. E. Stocking, and H. B. Smith, compilers. U. S. Geological Survey Professional Paper 300, p. 405-411.

Voskresenskaya, N. T., 1968, Thallium in coal. Geochemistry International, v. 5, no. 1, p. 158-168.

Voskresenskaya, N. T., Timofeyeva, N. V., and Topkhana, M., 1962, Thallium in some minerals and ores of sedimentary origin. Geochemistry, no. 8, p. 851-857.

Wandless, A. M., 1957, British coal seams: a review of their properties with suggestions for research. Journal of the Institute of Fuel, v. 30, p. 541-552.

Wandless, A. M., 1959, The occurrence of sulphur in British coals. Journal of the Institute of Fuel, v. 32, no. 220, p. 258-266.

Ward, C. R., 1974, Isolation of mineral matter from Australian bituminous coals using hydrogen peroxide. Fuel, v. 53, p. 220-221.

Ward, C. R., 1977, Mineral matter in Springfield-Harrisburg (No. 5) coal member in the Illinois Basin. Illinois State Geological Survey Circular 498, p. 1-35.

Ward, C. R., 1978, Mineral matter in Australian bituminous coals. Australian Institute of Mining and Metallurgy, Proceedings No. 267, p. 7-25.

Watt, J. D., 1968, The physical and chemical behavior of the mineral matter in coal under the conditions met in combustion plant: a literature survey, Part I. The occurrence, origin, identity, distribution and estimation of the mineral species in British coals. British coal Utilization Research Association, Literature Survey, 121 p. Leatherhead, Surrey, England.

Watt, J. D., 1969, The physical and chemical behavior of the mineral matter in coal under the conditions met in combustion plant. Part II Thermal decomposition of the mineral species: volatization of fouling components: sintering and melting of coal ashes: ash fusibility. British, Coal Utilization Research Association, Literature Survey, Leatherhead, Surrey, England, 36 p.

Weber, J. N., 1973, Geochemistry of germanium Benchmark Papers in Geology, v. 11. J. N. Weber, Editor. Dowden Hutchinson and Ross, Inc. Publ. 466 p.

Wedepohl, K. H., editor, 1969-1978, Handbook of Geochemistry, v. II, part 1, 1969; part 2, 1970; part 3, 1973; part 4, 1974; part 5, 1978. Springer-Verlag, Berlin.

Wewerka, E. M., Williams, J. M., Vanderborgh, N. E., Harmon, A. W., Wagner, P., Wanek, P. L., and Olsen, J. D., 1978. Trace element characterization of coal wastes-second annual Progress report. DOE/EPA Interagency Energy/Environment R & D Program Report. DOE report LA-7360-PR, EPA report EPA-600/7-78-028a. 144 p.

White, E. W., 1958, Uranium mineralization in some North and South Dakota lignites. M. S. Thesis, Department of Mineralogy, The Pennsylvania State University, 79 p. Cited in Akers et al., (1978).

Wilke-Dorfurt. H., and Romersperger, H., 1930, Der Jodgehalt von Kohler. Zeitschrift zu Anorg. Chem., v. 186, p. 159. Cited in Wedepohl (1974).

Williamson, I. A., 1970, Tonsteins-their nature, origins uses. Mining Magazine, v. 122, no. 2, p. 119-125.

Woo, C. C., 1964, Heavy media column separation: a New technique for petrographic analysis. American Mineralogist, v. 49, p. 116-126.

Wood, J. M., 1974, Biological cycles for toxic elements in the environment. Science, v. 183, p. 1049-1052.

Yershov, V. M., 1961, Rare earth elements in coals of the Kizelovskii coal basin. Goechemistry, no. 3, p. 306-308.

Young, R. S. and Robertson, 1952, X-ray study of coal from Logan County, West Virginia, and a discussion of the structure of coal. Economic Geology, v. 47, p. 609-633.

Zodrow, E. L. and McCandlish, K., 1978, Hydrated sulfates in the Sydney Coalfield, Cape Breton, Nova Scotia. Canadian Mineralogist, v. 16, p. 17-22.

Zodrow, E. L., Wiltshire, J. and McCandlish, 1979, Hydrated sulfates in the Sydney coalfield of Cape Breton, Nova Scotia, II. Pyrite and its alteration products. Canadian Mineralogist, v. 17, part 1, p. 63-70.

Zubovic, P., 1966A, Physicochemical properties of certain minor elements as controlling factors in their distribution in coal, <u>in</u> Coal Science. R. F. Gould, editor. Washington, D. C., American Chemical Society Publications, Advances in Chemistry, no. 55, p. 221-246.

Zubovic, P., 1966B, Minor element distribution in coal samples of the Interior Coal Province. <u>in</u> Coal Science. R. F. Gould, editor, Washington, D. C., American Chemical Society Publications, Advances in Chemistry, no. 55, p. 232-247.

Zubovic, P., 1976, Geochemistry of trace elements in coal. <u>in</u> Symposium Proceedings: Environmental Aspects of Fuel Conversion Technology. II. F. A. Ayer, compiler. U. S. Environmental Protection Agency, Technology Series EPA-600/2-76-149, p. 47-63.

Zubovic, P., Stadnichenko, T. and Sheffey, N. B., 1960, The association of minor elements with organic and inorganic phases of coal. U. S. Geological Survey Professional Paper 400-B, p. B84-B87.

Zubovic, P., Stadnichenko T., and Sheffey, N. B., 1961, The association of minor element associations in coal and other carbonaceous sediments. U. S. Geological Survey Professional Paper 424-D, Article 411, p. D345-D348.

Zubovic, P., Oman, C., Coleman, S. L., Bragg, L., Kerr, P. T., Kozey, K. M., Simon, F. O., Rowe, J. J., Medlin, J. H., and Walker, F. E., 1979, Chemical analysis of 617 coal samples from the Eastern United States. U. S. Geological Survey Open-file Report 79-665, 452 p.