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THE INORGANIC GEOCHEMISTRY OF COAL: A SCANNING ELECTRON MICROSCOPY VIEW

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Abstract

The scanning electron microscope (SEM), equipped with an energy dispersive X-ray analyzer (EDX), has been widely used to study the inorganic geochemistry of coal. This system was instrumental in establishing that the bulk of most trace elements in bituminous coals are associated with fine-grained accessory minerals. Textural evidence, as observed in the SEM, indicates that many of these minerals are embedded in relatively large organic particles. As a consequence of this association, these minerals, and the elements they contain, can be rafted up into the lighter specific gravity fractions during sink-float separation of the coal. Textural evidence also indicates the presence of two distinct mineral suites. The first suite includes kaolinite, sulfides, carbonates, and crandallite-group minerals. They occur predominantly in the pores of the inertinite macerals. These minerals commonly exhibit crystal faces and are intimately intergrown with one another. An authigenic origin is indicated for these minerals. The second suite occurs in bands of intermixed maceral fragments and angular to subrounded mineral grains that are probably of detrital origin. This suite includes quartz (some rutilated), illite, mixed-layer clays, rutile, and zircon.

The perfection of ancillary techniques, such as cathodoluminescence and automated image analyses, will enhance the future value of the SEM in the study of coal geochemistry.

**KEY WORDS:** coal, geochemistry, macerals, minerals, scanning electron microscopy, energy dispersive x-ray analyzer, trace elements

Introduction

Over the past 10-15 years the scanning electron microscope (SEM) has become a standard analytical tool in most coal science laboratories. The SEM, generally equipped with an energy dispersive X-ray analyzer (EDX), has been used in a wide variety of coal related problems. However, the SEM has had its greatest impact on coal research in the area of inorganic geochemistry. It is this topic that forms the basis of this review.

Recent evidence has shown that the bulk of most trace elements in bituminous coals is associated with minerals dispersed throughout the organic matrix (Finkelman, 1981). In general, these minerals are exceedingly fine-grained. Sarofim et al. (1977) report a mean grain size of about 2 microns for the minerals in the two coals they studied. Strehlow et al. (1978) found mineral grains in coal down to the limits of resolution of a transmission electron microscope ( $\leq 4$  nm). Even with imposing an arbitrary 2 micron lower limit, Finkelman (1978) found the mean grain size of the accessory minerals to be about 5 microns. Thus, most of the minerals in coal are near or below the practical limits of resolution of the optical microscope. Moreover, these minerals are intimately intermixed with the organic constituents of the coal, the macerals.<sup>+</sup> An understanding of the mineral and maceral associations may be extremely important for coal utilization, especially for coal cleaning, combustion, and conversion. Therefore, it is desirable to observe the mineral in situ so that these textural relationships may be preserved.

Application of the SEM

The SEM-EDX system is a nearly ideal tool for studying the minerals in coal, thus elucidating the inorganic geochemistry of this complex rock. The secondary electron imaging mode has the spatial resolution to allow observation of most minerals in coal. The EDX system can provide major and minor element data

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<sup>+</sup>The Appendix contains definitions of the coal petrographic terms used in this paper.

to aid in mineral identification and in determining the mode of occurrence of many trace elements. All of this can be done on minerals in situ, thus preserving the important textural relationships between the various minerals and between the minerals and the macerals. In addition, the sensitivity of the back-scattered electron image to variations in mean atomic number greatly facilitates the search for mineral grains containing heavy elements. By adjusting the contrast on the back-scattered electron image, a mineral whose atomic number is only slightly higher than that of quartz and clays, can be made to appear relatively bright. In this manner, a single, micron-sized accessory mineral grain can easily be recognized among thousands of clay and quartz particles.

The SEM-EDX system also offers a great deal of flexibility in the type of sample preparation. Among the sample types used in SEM studies of coal are: polished pellets prepared from a slurry of coal particles (generally -20 mesh) and epoxy resin; oriented polished blocks; petrographic thin sections; fracture surfaces; and both polished and unpolished concentrates of minerals. These minerals can be obtained from coal by physical separation methods or by high temperature (>550°C) or low temperature (<200°C) ashing. Stanton and Finkelman (1979) discuss the relative merits of each of these preparation procedures.

#### Early SEM Work on the Inorganic Chemistry of Coal

Despite the current widespread use of the SEM in coal research, few papers on the subject appeared prior to 1976. Among the first to use the SEM for coal research were Nandi et al. (1970). Using an SEM, they established that macerals are recognizable in both the secondary- and back-scattered electron modes. Their back-scattered electron images indicated the presence of minerals in the various macerals. Hughes (1971) used an SEM to study the minerals in underclays and in cleats. Vassamillet (1972), using an SEM with an EDX, concluded that a large fraction of the iron not associated with sulfur is widely distributed throughout the coal matrix in sub 10-micron grains of a high density mineral. Dutcher et al. (1973) were the first to propose the systematic use of the SEM to determine the distribution of minerals, their sizes, shapes, and orientations, and the partitioning of elements between the organic and inorganic phases. Gluskoter and co-workers (Gluskoter and Lindahl, 1973; Rao and Gluskoter, 1973; Ruch et al., 1974; Gluskoter, 1975) used SEM photomicrographs to illustrate minerals in cleats and minerals from the low-temperature ash (LTA) of coal. Augustyn (1976) compared SEM and petrographic characteristics of brown coals.

By the late 1970's a number of researchers were carrying out systematic studies of coal geochemistry using the SEM. Huggins, Lee and co-workers (Lee et al., 1978; Huggins et al., 1980) developed automatic image analysis procedures.

Greer (1977, 1978, 1980) used the SEM to study the size, morphology and distribution of pyrite. Finkelman and co-workers (see below) documented the distribution of minerals and the modes of occurrence of trace elements in coal. Other papers using the SEM to study minerals in coal include Sheihing et al. (1978), Harris et al. (1980), Senkayi et al. (1982), and Zhou et al. (1983).

#### Minerals and Trace Elements in Coal

SEM-EDX studies have made substantial contributions to our knowledge of the variety of minerals that occur in coal. In a detailed study of mineral-rich bands (carbominerite; Fig. 1) from an Appalachian bituminous coal, 27 accessory minerals were found (Finkelman and Stanton, 1978; Finkelman et al., 1979). Rutile, zircon, and the rare-earth phosphates, monazite and xenotime, were the most abundant; lead selenide and native gold, the rarest. Twenty-two accessory phases were extracted from the LTA of the same coal sample including a euhedral magnetite crystal (Fig. 2) and an ablation product from a meteorite (Fig. 3).

The study of minerals in coal was expanded to include over 100 coals with worldwide distribution (Finkelman, 1981). Special attention was paid to the textural relationships between the various minerals and between the minerals and the macerals. Over 100 different accessory minerals were documented, approximately 15 of which had not previously been reported in coal. In the two coals most intensively studied, both Appalachian bituminous coals, each contained approximately 50 different minerals. Despite the impressive variety of accessory minerals in these and several other coals, these minerals apparently constitute no more than about one percent of the total mineral grains in each coal. Due to their small size and relative rarity, the accessory minerals may be inconspicuous; however, SEM-EDX study has shown that they certainly are not insignificant.

From SEM images of a carbominerite band in the Waynesburg coal, Finkelman and Stanton (1978), calculated the volume percent that each accessory mineral grain would present. Then, from the number of accessory minerals, their densities, and the weight % of elements they contain, calculations were made of the concentrations of these elements. This calculated value represents the amount of the element occurring in the accessory mineral phases in the carbominerite band. The results of this study are reproduced in Table 1. It is evident that, for many of the trace elements, the calculated values were in good agreement with the analytical values obtained from the same carbominerite band. Finkelman and Stanton (1978) concluded that these elements quantitatively occur in the Waynesburg coal in the specific accessory mineral phases indicated. It was suggested that the discrepancy for Ti was attributable, in part to Ti associated with illite and mixed-layer clays, and in part to organically bound Ti. The presence of

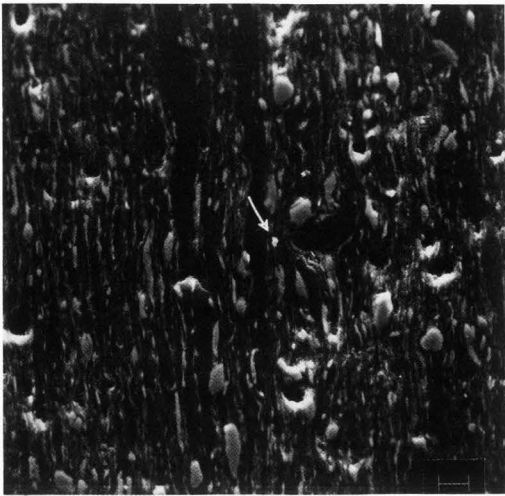


Figure 1. Mineral-rich band consisting primarily of aligned clays (illite and mixed-layer), angular to subrounded quartz grains and a xenotime particle (bright particle in center). Bar = 10  $\mu\text{m}$ .

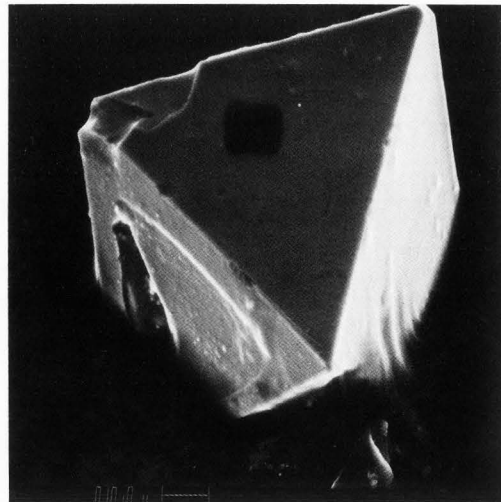


Figure 2. Euhedral magnetite octahedron extracted from LTA of Waynesburg coal. Dark patch on the surface was caused by rastering electron beam during energy-dispersive X-ray analysis. Bar = 10  $\mu\text{m}$ .

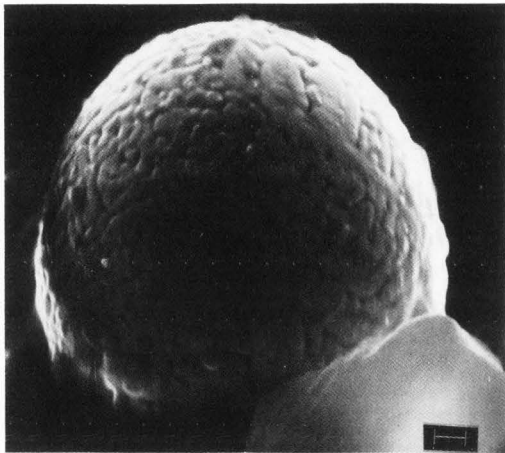


Figure 3. Probable meteorite ablation sphere extracted from heavy (Sp. G. = 3.33) magnetic split of Waynesburg LTA. Bar = 1  $\mu\text{m}$ .

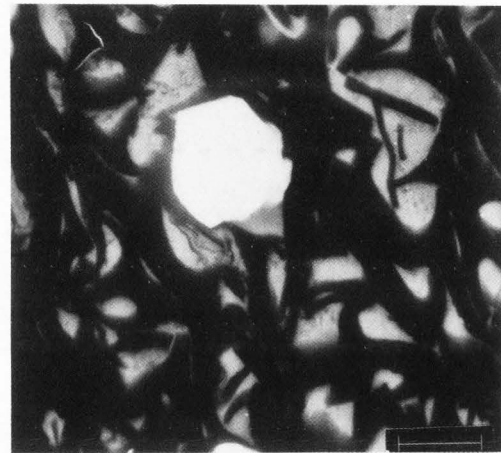


Figure 4. Sphalerite crystal in crushed inertinite particle. Light gray material is kaolinite. Bar = 10  $\mu\text{m}$ .

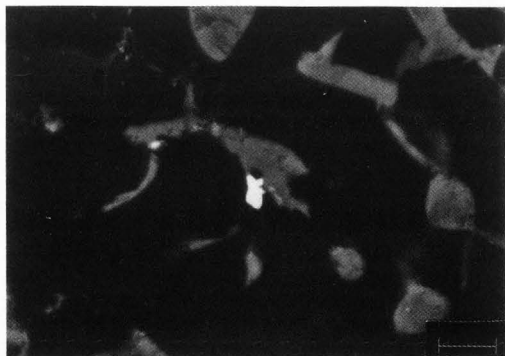


Figure 5. Chalcopyrite replacing kaolinite in pore of inertinite particle. Bar = 10  $\mu\text{m}$ .

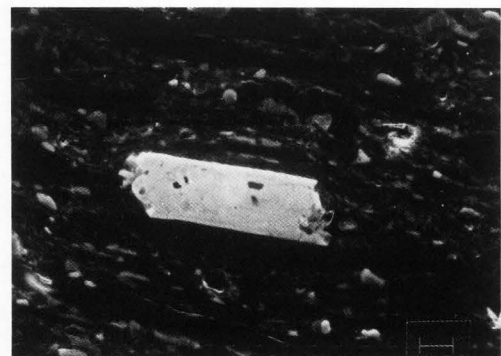


Figure 6. Relatively large subhedral zircon crystal, probably of volcanogenic origin. Zircon contains several silica inclusions (dark areas). Bar = 10  $\mu\text{m}$ .

Table 1 Comparison of calculated and analytical concentrations for selected trace elements in the Waynesburg Coal.  
(From Finkelman and Stanton, 1978)

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

\* = optical emission spectrography; + = instrumental neutron activation.

organically bound Ti has recently been confirmed by secondary ion mass spectroscopy (McIntyre et al. 1985). The discrepancy for Ba and Sr may be attributable to the fact that minerals containing these elements occur, preferentially, in the vitrinite and inertinite maceral groups rather than in the carbominerite. Strontium may also have an organic association, even in bituminous coals.

These and other studies (Huggins et al., 1983; Palmer and Filby, 1983; Benson et al., 1984; Minkin et al., 1984; Birk and O'Neil, 1985; Timmer and van der Burgh, 1985; Finkelman, 1985) have provided insight into the modes of occurrence of the trace elements in coal. Table 2 contains a list of the suggested modes of occurrence of selected trace elements. It is likely that not all of a particular element in a coal will be in the mode or modes suggested, nor will the element even occur in the suggested mode in every coal. Nevertheless, there appears to be sufficient evidence to indicate that substantial amounts of the element will be found in most coals in the modes indicated.

#### Mineral-maceral relationships

SEM-EDX results indicate a clear preference for certain of the minerals to be associated with specific macerals. The more commonly observed mineral-maceral associations are listed in Table 3.

The accessory sulfides (those other than pyrite and marcasite) offer an excellent example of the significance of the mineral-maceral relationships. Most of the accessory sulfides dispersed in coal occur in the pores of the inertinites (Figs. 4 and 5), less commonly in the vitrinite, and rarely in the carbominerite bands (Finkelman, 1981). As a consequence of this intimate association with the macerals, the accessory sulfides are rafted up into the lower specific gravity (Sp.G.) fractions during sink-float separation of the coal. Finkelman et al. (1979) found that about 70 weight percent of Cd, Pb, Zn, and Cu in the Upper Freeport coal, reported to the 1.4 and lighter Sp.G. fractions, and about 90 weight percent of Cu, Pb, and Zn reported to the 1.5 and lighter Sp.G. fractions of the Waynesburg coal. In contrast to the behavior of Cd, Pb, Zn, and Cu, much lower concentrations (about 33 weight percent) of As and Hg reported to the lighter Sp.G. fractions.

The difference in behavior is attributable to the different modes of occurrence. Arsenic and Hg, in these coals, are physically associated with the pyrite (Minkin et al., 1984) whereas, the Cd, Pb, Zn, and Cu occur in accessory sulfides (Cecil et al., 1979). It is apparent that in the sink-float procedure, pyrite is much more effectively separated from the coal than are the accessory sulfides.

In addition to allowing us to predict the behavior of minerals during sink-float separation of coal, the mineral-maceral associations also



Table 2. Suggested modes of occurrence  
(from Finkelman, 1982)

Sb	- probably as an accessory sulfide in the organic matrix
As	- solid solution in pyrite
Ba	- barite, crandallite, and other Ba-bearing minerals
Be	- organic association, clay
Bi	- accessory sulfide, perhaps bismuthinite
B	- generally organic association, illite
Br	- organic association
Cd	- sphalerite
Cs	- inorganic association: clays, feldspars, or micas
Cl	- organic association, NaCl
Cr	- clays
Co	- associated with sulfides, such as pyrite and linnaeite
Cu	- chalcopyrite
F	- unclear; probably several associations, such as apatite, amphibole, clays, mica, and organics
Ga	- clays, organic association, sulfides
Ge	- organic association, rarely in silicates, sphalerite
Au	- native gold, gold tellurides
Hf	- zircon
In	- sulfides or carbonates
I	- organic association
Pb	- pyrite, galena, PbSe, coprecipitated with Ba
Li	- clays: illite, mixed-layer illite/smectite
Mn	- siderite, calcite
Hg	- solid solution with pyrite
Mo	- unclear; probably with sulfides or organic constituents
Ni	- unclear; may be with sulfides, organic constituents, or clays
Nb	- oxides
P	- various phosphates; some may be organically associated
Pt	- perhaps native Pt alloys
REE	- rare-earth element (REE)-bearing phosphates
Re	- sulfides or organic constituents
Rb	- probably illite
Sc	- unclear; clays, phosphates or organic association
Se	- organic association, as PbSe, pyrite
Ag	- probably silver sulfides, but may occur in several modes
Sr	- carbonates, phosphates, organic association in low rank coals
Ta	- oxides
Te	- unclear
Tl	- sulfides; probably epigenetic pyrite
Th	- REE phosphates
Sn	- inorganic: tin oxides or tin sulfides
Ti	- titanium oxides, organic association, clays
W	- unclear; may have organic association
U	- organic association, zircon
V	- clays (illite)
Y	- REE phosphates
Zn	- sphalerite
Zr	- zircon

help to elucidate the origin of many of these minerals. Two distinct suites of dispersed 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, are intimately intergrown with one another, and occur exclusively within organic components, an authigenic origin is indicated. The second suite of accessory minerals occurs exclusively in quartz-illite rich bands (carbo-minerite) composed of intermixed minerals and macerals. The minerals in these bands are sub-angular to sub-rounded and are oriented parallel to the bedding. Most of the minerals in these bands are probably of detrital origin. This suite includes quartz, rutile, zircon, and the rare-earth bearing phases (in part). These observations are summarized in Table 4. Authigenic minerals dominate most low ash (8-10 wt %) coals; the proportion of detrital minerals increases with increasing ash content.

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. For example, the rare-earth phosphates appear to occur with equal abundance in either suite, and both authigenic and detrital rare-earth phosphates may be present in the same sample.

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). Microscopically, these deposits are characterized by relatively large, angular to euhedral crystals, and by their distinct mineralogy. A characteristic feature of ash falls is the abundance of accessory minerals such as zircon, apatite, sphene, anatase, magnetite, sanidine, goyazite, and ilmenite. Volcanic glass has also been reported (Sharudo and Moskvina, 1973). Figure 6 is an SEM photomicrograph of a volcanogenic zircon found in a western U.S. coal. The SEM has proven to be a valuable tool in studies of volcanic ash associated with coal deposits (Bohor et al., 1979; Tripelhorn and Bohor, 1981).

In some coals, diagenesis has obscured the textural relationships between mineral grains. In these instances, it is difficult to determine the source of the original minerals, even with an SEM.

Other recent applications of the SEM to the inorganic geochemistry of coal include work by Ames Laboratory using automated image analysis to characterize the minerals (Straszheim et al., 1987) and UND's Energy Research Center where the SEM is being used to characterize low rank coals (Karner et al., 1987).

Table 3. 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			

Table 4. Characteristics of syngenetic coal minerals

	Authigenic	Detrital
Mineral	Kaolinite Sulfides Carbonates Crandallite Group	Illite Mixed-layer clays Quartz Zircon
Suite	Apatite Barite	Rutile Feldspar
Associate Maceral	Inertinites Vitrinite	Carbominerite Fragmented macerals
Textural Relationships	Dispersed Pore filling, Pods, or Isolated grains Exhibit Crystal Faces Intimately Intergrown	Banded  Concentrated, aligned Subangular to subrounded Intergrowths rare (some rutilated quartz)

Concluding Remarks

Over the past few years, use of the SEM-EDX system has made substantial contributions to our understanding of coal, particularly its physical properties and behavior in various technological processes. Further contributions will come not only from the wider application of the SEM, but from perfection of ancillary techniques, such as cathodoluminescence (Ruppert et al., 1985), automated image analysis, diffraction techniques, and quantification procedures.

Appendix

Coal petrographic nomenclature used in this report  
(from ASTM, 1981; ICCP, 1971; Stach et al., 1975)

Carbominerite - association of coal with 20-60

- Cleat - the joint system of coal beds, usually oriented normal, or nearly normal, to the bedding.
- Exinite (or liptinite) - a group of hydrogen-rich macerals derived from resins, spores, cutine, waxes and fats.
- Inertinite - a group of non-reactive, highly reflective macerals.
- Maceral - a microscopically distinguishable organic component of coal, but including any mineral matter not discernible under the optical microscope.
- Sporinite - a maceral of the exinite group derived from the waxy coatings (exines) of spores and pollen.

Vitrinite - the component of coal with reflectance intermediate between those of exinite and inertinite. Generally, the most abundant maceral, is the product of gradual alteration of plant cell substances.

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#### Discussion with Reviewers

R. Raymond: Can you be certain that Ti isn't present as submicron titanium oxide particles?  
Author: No, I am not certain of this. There is ample evidence that these particles do exist. However, there are other lines of evidence, e.g., leaching studies that indicate that at least some of the Ti is organically associated.

R. Raymond: Do the relationships noted between authigenic minerals and macerals reflect peat (coal precursor) depositional environments or later environments of coalification?

Author: My impression is that these relationships are developed during early stages of coalification (probably during the lignite stage). I am unaware of minerals in peat with similar textural relationships.

S.A. Benson: Why is pyrite more effectively separated from the coal than the accessory minerals?

Author: In addition to having significantly higher density than most accessory minerals, pyrite is present in much larger particles. Accessory minerals, especially accessory sulfides, rarely exceed 100 microns in diameter. Whereas pyrite particles mm to cm in diameter are not uncommon in coal.

S.A. Benson: What was the particle size distribution of the coal used in the float-sink procedure?

Author: Three different particle sizes were used: 8 x 100 mesh, 1/4" x 8 mesh, and 1/4". Results from each particle size were similar.

J.A. Minkin: Do your data embrace coals of various ages and ranks? If so, are there any differences in mineral groupings with age or rank?

Author: The coals that I've studied with the SEM range in age from Devonian to Holocene and in rank from lignite to meta-anthracite. No relationships between mineralogy and geologic age were observed. Some minerals appear to "favor" a particular rank. For example, barite was detected in almost all lignites studied. However, there are too few data to eliminate other factors such as depositional environment and diagenesis and conclude that these relationships are rank controlled.

S.A. Benson: What is the sensitivity of the EDX detector with regard to the trace elements of interest?

Author: No attempt was made to quantitatively determine the sensitivity of the EDX detector. Basically, we were looking at elements that were major constituents (30-60 weight %) of the mineral phase. Clearly, this was well above the sensitivity limit of the EDX detector.

S.A. Benson: What are the error limits of the data presented in Table 1?

Author: I estimate that approximately 600,000 mineral grains were visually examined in the study. Nevertheless, the number of grains observed for some of the mineral phases is very small and subject to large error. However, the purpose of Table 1 is to illustrate that the accessory minerals in coal are sufficiently abundant to account for a substantial portion of many elements found in coal. This observation has been borne out over the intervening years by numerous studies cited in the text.

J.A. Minkin: In Figure 6 there is a bright circular area in the center, and a slightly less bright area at the right-hand end of the zircon crystal. Do you think one or both of these are beam-produced artifacts, or do they indicate other mineral inclusions in the zircon?

Author: The circular area is a beam-produced artifact, whereas the squarish area at the right-hand end of the crystal is due to the inhomogeneity of the zircon.