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ADVANCED SEM TECHNIQUES TO CHARACTERIZE COAL MINERALS

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Abstract

Research at the University of North Dakota Energy and Environmental Research Center (EERC) has focused on methods to characterize the inorganic components in coals. Because the scanning electron microscope and electron probe microanalysis system (SEM/EPMA) provide both morphologic and chemical information, the SEM/EPMA system is well-suited to the characterization of discrete minerals in coal. Computer-controlled scanning electron microscopy (CCSEM), along with simultaneous automated digital image collection, is one means of gaining more detailed insight into coal mineralogy. Computer-stored images of coal surfaces already analyzed for minerals using CCSEM can be reanalyzed to discern mineral morphologies and coal-to-mineral associations. Limitations may exist when using just CCSEM to characterize chemically and physically complex clay minerals without complimentary data on the association of the minerals to the coal organic matrix. Mineralogic investigations of San Miguel and Beulah lignites and Upper Freeport bituminous coal using CCSEM and automated digital image collection are given with a particular reference to the clay minerals present. Total mineral quantities generated for the three coals were in good agreement with total ash content, provided that organically bound constituents were taken into account for the lignites. Classification of the more complex aluminosilicate minerals was aided by the use of distribution plots of Si/Al ratios and concentrations of ion exchangeable cations derived from the CCSEM analysis. Morphologic analysis of stored SEM images proved to be helpful in characterizing kaolinite group minerals.

KEY WORDS: Coal, Minerals, Computer-Controlled Scanning Electron Microscopy, Image Analysis, Morphology, Clays

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Introduction

Increased public and governmental concern for a clean environment, plus the ever increasing need for electric power will no doubt facilitate a growing interest in understanding the inorganic composition of coals for the purpose of controlling pollution and predicting combustion behavior. Advanced analytical techniques have been developed to meet the growing need for comprehensive coal inorganics characterization. Research at the University of North Dakota Energy and Environmental Research Center (EERC) has focused on methods to characterize the inorganic components in coals, specifically discrete minerals and organically bound inorganic constituents. This paper will focus on the techniques used at EERC to characterize coal minerals using computer-controlled scanning electron microscopy (CCSEM) and electron probe microanalysis (EPMA).

Coal contains a mixture of different minerals and inorganic constituents of various sizes and associations with the organic matrix. Low-rank coals (lignite and subbituminous) contain finely dispersed organically associated elements such as Na, Mg, Ca, K, and Sr in addition to discrete mineral grains. Organically associated elements are primarily present as salts of organic acid groups [2]. In contrast to low-rank coals, the inorganic components in bituminous coals consist mainly of discrete mineral grains with very minor amounts of organically associated materials. Major types of minerals observed in coal include quartz, kaolinite, illite, montmorillonite, pyrite, and calcite. These minerals can be associated with the coal as individual particles within mineral-rich partings, as secondarily deposited infillings of pores within deposited plant remains, as fracture or cleat infillings, and as finely dispersed individual grains. Because the scanning electron microscope and electron probe microanalysis (SEM/EPMA) system provides both morphologic and chemical information, it is well-suited to the study of coal minerals.

Various analytical techniques have been used to identify and characterize mineral matter in coal. One commonly used and widely accepted technique for analyzing coal minerals [17,19] is x-ray diffraction (XRD). One advantage of XRD is that it positively identifies the minerals based on their crystalline structures, provided the mineral has a large enough concentration to create a discernable diffraction pattern. However, there are limitations when using XRD to quantify minerals in coal, especially minerals not producing a strong diffraction pattern. The most significant limitation is that the minerals must be physically separated from the coal due to the dilution effects of the coal organic matrix. Low-temperature ashing (LTA) is one technique used to separate the minerals from the organic matrix, but the LTA may alter the original mineralogy and does not permit observation of the minerals relation to the organic matrix. The SEM/EPMA system does not identify mineral phases based on crystalline structure, as does the XRD procedure; rather, the relative concentrations of the elemental constituents are used to categorize distinct mineral types.

A great advantage of the SEM/EPMA system over XRD is that the chemistry of very fine-grained individual minerals can be observed, while preserving the original relationships of the minerals to the organic matrix [6,10,18,19]. Other applications of the SEM/EPMA system to the study of coal inorganics include the elemental composition of macerals, determination of the morphology of the organic constituents, identification of minerals, and description of the mineral morphology [1,3,5,8,23]. Several automated SEM/EPMA and image analysis techniques have been developed to size and quantify coal particles, elements in coal particles, and coal minerals [9,10,11,14,15,16,20,21,22]. Part of the motivation behind the development of automated SEM/EPMA techniques was to be able to characterize statistically significant numbers of particles in a short period of time in order to produce quantitative data on particle size and chemistry [12,20].

Computer-controlled scanning electron microscopy (CCSEM) and image analysis are presently used for coal mineral analysis at EERC. Essentially, the CCSEM and image analysis techniques automate the scanning microscopy and electron microprobe functions. Specific applications of these methods include the determination of the size, composition, morphology, and association of minerals in coal. The limited number of major mineral phases in coal makes the CCSEM technique especially valuable because the identification process is less prone to error. We have found that coals typically contain only 3-4 phases, comprising nearly 100% of the discrete minerals. The elemental percentages of the minerals encountered in a routine CCSEM analysis are usually unique to a particular mineral. An exception to this observation is that the clay minerals commonly have variable and complex compositions. Generally, CCSEM mineral identification programs use wide compositional ranges to encompass the varied chemistries of clay minerals. These broad composition categories can lead to serious errors in the identification of clay minerals. Advanced microprobe and image analysis techniques use morphologic analysis coupled with composition analysis to identify clay minerals more accurately. For example, dickite and halloysite are commonly identified as kaolinite, using standard CCSEM techniques, because all three are nearly pure aluminosilicates with Si/Al ratios of approximately 1.0. These clays can only be distinguished by crystalline structure or morphology. Also, some of the grains identified as illite could easily be muscovite. Illite and muscovite can have similar chemical compositions, but they usually differ, even if only slightly, in Si/Al ratio, potassium concentration, and in crystalline structure. The method we are using to better identify clays using CCSEM is to incorporate morphologic data with careful determinations of Si/Al ratios and quantities of alkali-alkaline earth elements in coal aluminosilicates.

Morphologic analysis not only aids in the identification of clays, but it is also an important parameter when attempting to acquire accurate mineral sizes. In a typical CCSEM analysis of coal minerals, large particles of clay minerals and pyrite are often identified as one grain, when closer examination of the morphology reveals that these particles are actually an aggregate of many smaller grains. The use of image analysis to determine particle sizes from measured particle areas is one technique being developed at the EERC which may more accurately define the size of mineral particles in aggregates.

This paper describes how the advanced SEM techniques of CCSEM and image analysis, along with more standard analytical techniques, were used to characterize the abundance of minerals in Beulah and San Miguel lignites and Upper Freeport bituminous coal. Special reference is made to the characterization of the clay minerals in these coals.

Methodology

Sample Preparation

The coal samples were ground to 80% -200 mesh, mixed 1:1 with a quick-hardening epoxy mounting media, pressed into a 1-inch diameter cylindrical mold suitable for SEM analysis, and rotated while hardening to lessen the effects of settling. The coal-epoxy plug was then sliced perpendicular to its length using a low deformation diamond saw, and the exposed surface was ground and polished, with the final polishing compound being a 1-μm diamond paste. A carnauba wax mounting media was used for the bituminous Upper Freeport coal because it gave a better contrast between the coal and mounting media. Lower- rank coals have substantial quantities of organically bound constituents such as calcium, that give the coal matrix a brighter appearance compared to the epoxy in the backscattered mode during SEM analysis.

CCSEM Analysis

The CCSEM technique is used to determine the size, shape, quantity, and semiquantitative composition of mineral grains in coal. Shape is determined by measurement of the aspect ratio of the mineral grains. The semiquantitative chemical composition data obtained are used to classify particles into mineral or chemical categories.

The SEM/EPMA system at EERC (see Figure 1) consists of a JEOL 35U scanning electron microscope/microprobe, a GW Electronics backscattered electron detector, an ultrathin window energy dispersive x-ray detector, a wavelength dispersive x-ray detector, a digital beam controller, a Tracor Northern model TN 5600 EDS analyzer, and a Tracor Northern model TN 8500CX image analyzer. This system is interfaced with a MicroVax II and a personal computer (PC) for data manipulation. The Tracor Northern 5600 can be programmed for stage, column, and wavelength dispersive spectrometer (WDS) automation.

The key components of the SEM/EPMA system that make it possible to image, size, and analyze inorganic particles are the backscattered electron detector, the digital beam controller, and the ultrathin window energy dispersive x-ray detector.

Backscattered electron imaging (BEI) is used for CCSEM because the intensity of the backscattered electrons is a function of the average atomic number of the features on or near the specimen surface. Thus the image produced by the detector will be an image for which the varying gray scales reflect different chemical compositions. Areas rich in high atomic number elements will appear brighter than areas relatively rich in low atomic number elements. For coals, where the average atomic number of the carbonaceous matrix is about 6, the mineral phases will be clearly observed, as their average atomic number is greater than 6.

Because the mineral or ash particles appear brighter relative to the lower atomic number matrix, a distinction can be made among coal, mounting media, and mineral grains. The electron beam is programmed to scan over the field of view to locate the bright particles that correspond to mineral or ash species. On finding a bright inclusion, the CCSEM program finds the center of the inclusion, performs eight diameter measurements of the inclusion, and collects an energy dispersive spectrum (EDS) at that point for 2 seconds. Our system is set to analyze for 12 elements: Na, Mg, Al, Si, P, S, Cl, K, Ca, Fe, Ba, and Ti.

The size, area, perimeter, and chemical composition (based on EDS count percentages for each element considered) of each mineral grain are then determined, and this data is transferred simultaneously to a PC or the MicroVax II for storage on tape or disk. Software developed at the EERC classifies mineral grains based on elemental composition and size. The chemical parameters used to identify the minerals are based on published compositions of minerals [4,10] and on an extensive data base of mineral chemistries determined by microprobe analysis at the EERC. Table 1 lists the various minerals and mineral associations that CCSEM identifies. A mineral association, such as aluminosilicate/gypsum, is a discrete particle that contains at least two adjacent or intimately associated minerals. The EDS spectra will reveal a combination of the proper elemental ratios for these associated minerals. Such associations cannot be determined as accurately for minerals that share common elements such as siderite ($FeCO_3$) and pyrite (FeS_2).

The list of compositional types allows for a nearly complete classification of all major minerals observed in coal. This is made possible by the limited number of major mineral species associated with coal and its combustion products. No attempt is made to force all of the phases into mineralogical categories, as this can be misleading. Aluminosilicate species such as the clay minerals are particularly difficult to categorize using elemental compositions derived from EDS analysis because of the complexity of the clays. An "unknown" category contains those phases which cannot be otherwise classified.

After the minerals are classified, the CCSEM program groups the minerals by average diameter into six separate user-defined size bins so that the size distribution of individual minerals can be ascertained. The number of mineral grains and their areas are tallied in each size bin for each mineral type, and several summary tables are configured and then output as one large summary file. An additional file containing all of the raw data is also output at this time.

The summary output file contains the following information: 1) a table of total areas of minerals in their respective size categories, 2) a series of tables listing quantities of minerals in their respective size categories in terms of number, area, and weight percents on a coal and mineral basis, 3) bulk mineral quantities based on area and weight percent, and 4) total area and weight percentages of all the minerals in each size bin (which corresponds to a bulk particle-size distribution). The weight percents are calculated using published mineral density data. An example of CCSEM summary output for weight percent mineral content in Beulah lignite is given in Table 2.

A second very large output file contains all of the raw data on a particle-by-particle basis. The information included for each particle consists of the following: 1) the identification number of the mineral which corresponds to a particular mineral name or type, 2) the total number of x-ray counts, 3) the percent counts for each of the 12 elements analyzed, 4) X and Y coordinates of the mineral grain, 5) the area of the grain, 6) the average diameter, 7) the shape factor, and 8) the frame number.

The CCSEM technique described is used for the standard analysis of coal. However, more detailed analysis of the coal minerals may be necessary to determine how minerals are associated with the coal organic matrix. This type of analysis becomes more important when coal minerals are studied with a view to combustion products. During pulverization of the coal, some coal minerals are liberated from the coal matrix and will experience different combustion conditions and undergo different transformations and reactions than the minerals present within the coal matrix. Therefore, whether a mineral is contained within the coal matrix (included) or is separated from the coal matrix (excluded) is an important parameter to define, especially when considering coal combustion. Another parameter to consider is mineral-to-mineral relationships,

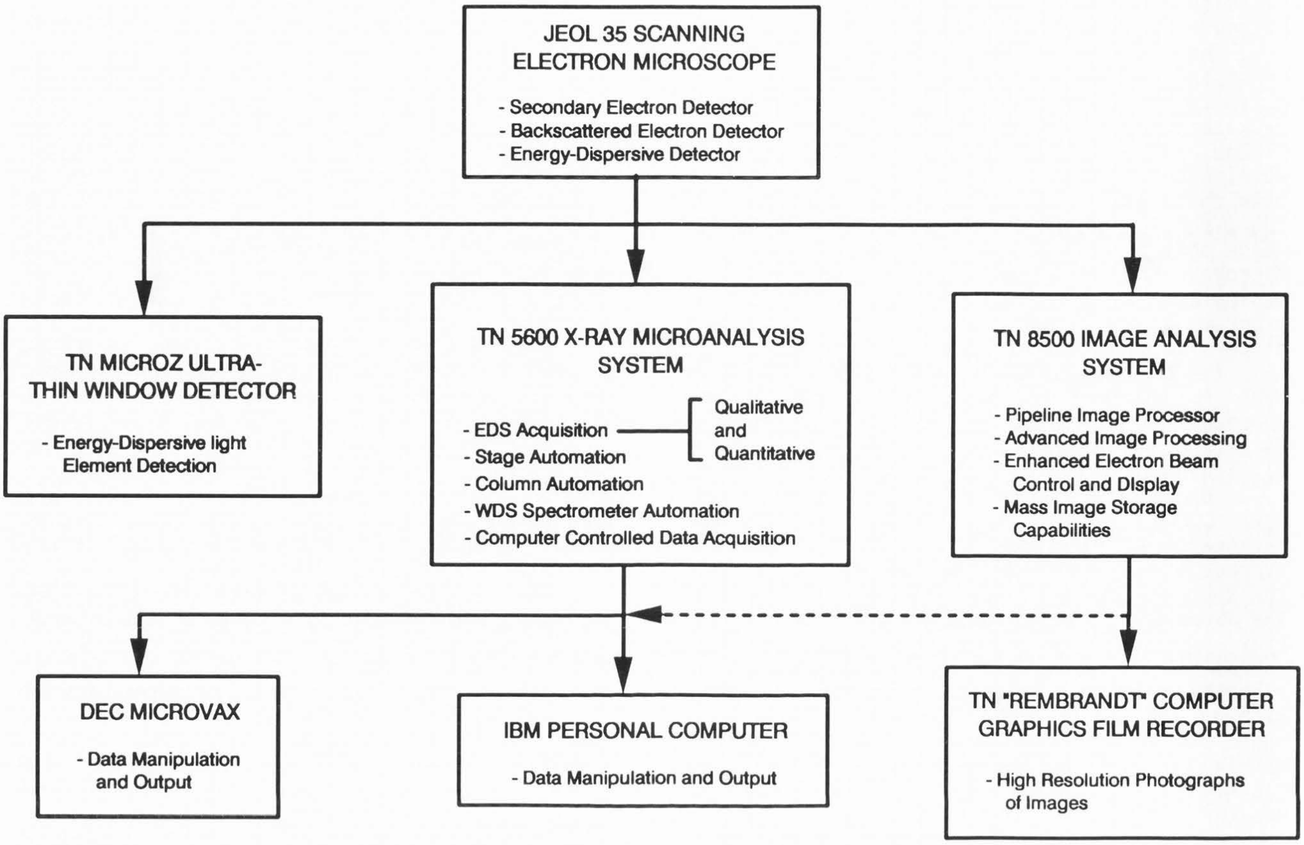

Figure 1. Schematic of SEM/microprobe system and its operation

referred to here as juxtaposition. For example, it is not uncommon to have quartz and calcite or pyrite and kaolinite intimately associated in a single recognizable particle. The analysis of this particle by CCSEM will show correct elemental ratios for both minerals. The present method used to determine the juxtaposition of coal minerals uses the chemical analysis of minerals from the standard CCSEM analysis of the coal, along with a digital backscattered image of the frame of area containing those minerals, to decide if a particle is actually a combination of two minerals. The standard CCSEM output data can then be modified to include juxtapositional relationships.

The Beulah, San Miguel, and Upper Freeport coals were analyzed using CCSEM and image analysis according to the techniques described.

Chemical Fractionation and X-ray Diffraction Analysis

The San Miguel and Beulah lignites were analyzed for organically bound inorganic constituents using a wet chemistry technique called chemical fractionation. Basically, chemical fractionation allows for quantifying coal inorganic constituents which are beyond the detectability of the SEM imaging system. For example, low-rank coals can contain substantial amounts of sodium and calcium that are bound in the organic matrix of the coal as cations of carboxylic acid groups. Details of this technique are discussed elsewhere [2]. X-ray diffraction (XRD) analysis was used to verify the minerals identified in the coals using CCSEM. Beulah lignite and the Upper Freeport coal were first low-temperature ashed to concentrate the inorganic constituents. The San Miguel lignite, with its high ash content, was not subjected to the lower-temper ashing procedure; however, it was ground to less than 100 μm in size. A Philips APD 3600 powder x-ray diffractometer was used in conjunction with the Joint Committee on Powder Diffraction Standards data base for identifying the minerals. Operating parameters included: copper radiation, 45 kV, 40 mA, and a goniometer scan range of 5-70° at steps of 0.02°.

Results

Mineral compositions, percent ash, and organically bound inorganics are listed in Table 3 for the three coals: Beulah, Upper Freeport and San Miguel. Quartz and aluminosilicate are major (>10 wt.%) components of all the coals as

TABLE 1
CCSEM MINERAL AND COMPOSITIONAL CATEGORIES

- Quartz
- Aluminosilicate
- K-Aluminosilicate
- Ca-Aluminosilicate
- Fe-Aluminosilicate
- Iron Oxide/Siderite
- Spinel
- Aluminum Oxide
- Calcite/Calcium Oxide
- Dolomite
- Ankerite
- Rutile
- Calcium Silicate
- Apatite
- Pyrite
- Gypsum
- Barite
- Gypsum/Barite
- Aluminosilicate/Gypsum
- Calcium Aluminate
- Pyrrhotite/Iron Sulfate
- Calcium-Rich
- Silicon-Rich
- Periclase
- Unknown

determined by CCSEM. Pyrite is a major constituent for Beulah and Upper Freeport, and potassium aluminosilicate (K-aluminosilicate) is a major constituent in Upper Freeport and San Miguel. X-ray diffraction, which was performed on a low-temperature ash sample of the Beulah and Upper Freeport and on a raw coal sample of San Miguel, confirmed the major minerals observed using CCSEM (Table 3). Some of the minerals that XRD classified as minor components were actually major components. The quantity of organically bound inorganics was determined for the Beulah and San Miguel lignites by calculating the percentage of the coal that consisted of water or ammonium acetate soluble Na, K, Mg, Ca, Fe, Si, and Al. Chemical fractionation or leaching of the Beulah and San Miguel lignites revealed that these soluble elements constituted 1.4% and 6.9% of the coal, respectively (Table 3). Total inorganic content was then calculated by adding the organically bound fraction to the amount of discrete minerals as determined by CCSEM. The total thus derived for the inorganics compared well with the total ash content for the Beulah and San Miguel lignites.

CCSEM Analysis of Clays

Detailed SEM analysis was performed on the aluminosilicate fractions of the three coals to identify the clay minerals using Si/Al ratios and contents of the alkali-alkaline earth elements. Data from Deer et al. [4] for Si/Al ratios gave the following results for the three clay minerals observed in these coals: illite, mean 1.5, standard deviation 0.4, number of minerals 12; montmorillonite, mean 2.5, standard deviation 0.3, number of minerals 6; and kaolinite, mean 1.0, standard deviation 0.4, number of minerals 10. These values are used here as a reference for comparing values observed from the three coals. It is reiterated here that the CCSEM chemistries are not true weight percents, but are derived by normalizing the x-ray counts acquired during the 2-second energy dispersive spectroscopy (EDS) acquisition of the CCSEM program. Count percents from EDS are related to the atomic fraction of the elements, and the Si/Al ratios should compare reasonably well with values obtained by other means.

Examination of the Si/Al ratio distribution in the Beulah lignite material classified as aluminosilicate revealed a median value of 1.3 (Figure 2) which suggests that this clay mineral is either kaolinite or illite. The average composition of this material, given in Table 4 Column 2, reveals no significant potassium or other extraneous cation contents. The 1% Ca and S and 2% Cl contents are contamination from the Ca-S-rich coal organic matrix and mounting epoxy, respectively, which are included in the EDS output of small (usually <2-3 microns) particles because of beam penetration effects. XRD analysis identified this aluminosilicate mineral as kaolinite. The aluminosilicate mineral identified in the Upper Freeport by CCSEM had a median Si/Al value of about 1.75 (Figure 3) and a K average of 1.8% (Table 4 Column 3). The Si/Al ratios for this mineral may correspond to illite, but the K and Fe concentrations appear low compared to the literature [4]. Perhaps this is a form of mixed-layer clay or degraded illite [13] where the K and Fe contents have been partially removed. Potassium aluminosilicate was also identified by CCSEM in the Upper Freeport. It had Si/Al ratios from 2-3.5 (Figure 4) with K and Fe concentrations of 7-18% and 1-9%, respectively (Figures 5 and 6). These data, along with the average EDS composition given in Table 4 Column 4, are consistent with illite. Some of the iron in the average composition may be associated with pyrite microcrystals because of the presence of 3.7 percent sulfur (Table 4 Column 4).

It was determined from CCSEM that the San Miguel lignite had major aluminosilicates and K-aluminosilicates (Table 2). The aluminosilicate minerals had a median Si/Al ratio of approximately 2.0 (Figure 7) and very low quantities of extraneous cations (Table 4 Column 5). We were unable to identify the clay mineral using XRD. This clay was probably a form of montmorillonite or mixed clay. The K-aluminosilicate mineral detected by CCSEM had very high Si/Al ratios within a range of 3.0-13.0 (Figure 8). Potassium concentrations were in a narrow range of 1-5 percent (Figure 9). Although this mineral had sufficient potassium (Table 4 Column 6) for illite, the Si/Al ratios were too high. XRD was needed to identify the mineral as clinoptilolite $[(Na,K)_6(Si,Al)_{36}O_{72}\cdot 20H_2O]$ which is not a clay mineral, but a zeolite. The formula for clinoptilolite shows that the Si/Al ratio can vary over a wide range and K can be a major component. The CCSEM data is in agreement with this composition.

TABLE 2

EXAMPLE OF CCSEM PROGRAM OUTPUT FOR BEULAH LIGNITE MINERALS (Weight Percent Mineral Basis)

	Particle Size Categories (microns)						
Mineral	1-2.2	2.2-4.6	4.6-10	10-22	22-46	>46	Total Wt.%
Quartz	1.3	2.1	2.8	4.1	4.3	3.3	18.0
Iron Oxide	0.0	0.0	0.0	0.0	0.5	0.8	1.4
Aluminosil.	13.2	15.0	6.6	3.1	3.3	0.6	41.7
Ca-Aluminosil.	0.1	0.0	0.0	0.0	0.0	0.0	0.2
Fe-Aluminosil.	0.0	0.0	0.2	0.0	0.0	0.0	0.3
K-Aluminosil.	0.2	0.5	0.0	0.1	0.0	0.0	0.8
Ankerite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pyrite	0.2	0.3	1.7	3.8	13.7	5.3	25.0
Gypsum	0.1	0.2	0.8	0.6	0.4	0.0	2.1
Barite	0.4	0.3	0.8	0.0	0.0	0.0	1.6
Gypsum/Barite	0.1	0.1	0.0	0.0	0.0	0.0	0.3
Apatite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ca-Silicate	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Aluminosil./Gyp.	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ca-Aluminate	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Spinel	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Alumina	0.0	0.0	0.4	0.1	0.0	0.0	0.4
Calcite	0.0	0.0	0.0	0.0	0.0	0.0	0.1
Rutile	0.2	0.1	0.0	0.0	0.0	0.0	0.3
Dolomite	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Pyrrhotite	0.0	0.1	0.0	0.1	0.4	0.0	0.6
Ca-Rich	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Si-Rich	0.1	0.0	0.0	0.1	0.1	0.0	0.3
Periclase	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Unknown	2.7	2.0	1.2	0.7	0.3	0.0	6.8
Total	18.8	20.9	14.4	12.9	23.0	10.1	100.0

Morphologic Analysis of Clays

Clay minerals are among the most abundant and enigmatic minerals found in coal. Their complex chemical and morphologic characteristics make the characterization of clay minerals in coal very difficult. Because the clays are commonly found in aggregates of very small particles, CCSEM particle sizing can result in misleading sizing data and errors in the abundance of the clays. For this reason, the combined CCSEM and digital image collection procedure is especially useful in the examination of clay minerals. The following examples illustrate common habits for clay minerals in coals we have examined.

Figure 10 shows a BEI of a polished section of Beulah lignite. The bright minerals dispersed in the coal matrix were identified by CCSEM analysis as relatively large grains of kaolinite. Closer inspection revealed that these materials were actually aggregates of submicron-sized kaolinite particles. The bright area in the upper left-hand corner of Figure 10 shows another common kaolinite habit in coals: very dense, massive bands of clay aggregates.

Figure 11 shows a BEI of a polished section of Beulah lignite. The two bright, mottled streaks in the center coal particle are aggregates of clay identified as kaolinite by CCSEM analysis. Figure 12 shows a highly magnified image of a portion of one of the aggregates pictured in Figure 11. The individual particles consist of spheroids or platelets that may be a form of halloysite [7], a hydrous clay mineral in the kaolin mineral group.

Clearly, CCSEM analysis without the supporting image analysis of clay minerals in coals can result in misleading particle-size data, as well as possible misclassification of clay mineral types. Depending on the clay particle size, magnification, and resolution of the backscattered electron detector, errors in the overall area attributed to clay minerals can be made as well. Dense aggregates can be measured as larger, single particles and the void space between the particles attributed as clay.

Conclusions

The SEM/EPMA system is an extremely powerful tool for the analysis of coal minerals. The chief advantages of SEM/EPMA techniques include 1) the ability to examine minerals without

TABLE 3
MINERAL COMPOSITION OF COALS
(Wt.% Mineral and Coal Basis)

	BEULAH		UPPER FREEPORT		SAN MIGUEL	
MINERAL	MIN.	COAL	MIN.	COAL	MIN.	COAL
Quartz	18.0	1.0	15.6	2.2	16.3	7.5
Iron Oxide/Siderite	1.4	0.1	1.5	0.2	0.1	0.0
Aluminosilicate	41.8	2.3	12.0	1.7	21.8	10.0
Ca-aluminosilicate	0.2	0.0	0.2	0.0	0.3	0.1
Fe-aluminosilicate	0.3	.0	2.4	0.3	0.0	0.0
K-aluminosilicate	0.8	0.0	31.8	4.5	45.8	20.0
Pyrite	25.3	1.4	29.2	4.2	0.9	0.4
Gypsum	2.1	0.1	0.7	0.1	1.0	0.5
Barite	1.6	0.1	0.0	0.0	0.1	0.0
Aluminosil./Gypsum	0.0	0.0	0.2	0.0	0.1	0.0
Calcite	0.1	0.0	3.0	0.4	0.0	0.0
Rutile	0.3	0.0	0.3	0.0	0.1	0.0
Pyrrhotite/Iron Sulfate	0.6	0.0	0.0	0.0	0.2	0.1
Si-Rich	0.3	0.0	0.2	0.0	5.8	2.8
Unknown	6.8	0.4	3.0	0.4	7.6	3.4
TOT. DISCRETE MIN.	100.0	5.6	100.0	14.3	100.0	44.9
ORG. BOUND INORG.		1.4		--[4]		6.9
TOTAL INORGANICS		.0		--		51.8
Ash Percent[2]		6.9		12.0		54.3
X-RAY DIFFRACTION[3]	Quartz (M) Calcite (m) Pyrite (m) Kaolinite (m) Bassanite (m)		Quartz (M) Kaolinite(m) Pyrite (m) Calcite (m) Illite (m)		Clinoptilolite(M) Quartz (m)	

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[1] Determined by chemical fractionation (leaching) analysis
[2] Determined by proximate analysis and reported on a dry basis
[3] M=major and m=minor (Major refers to relative XRD peak intensities that are >=50 percent of the largest peak intensity)
[4] Not determined

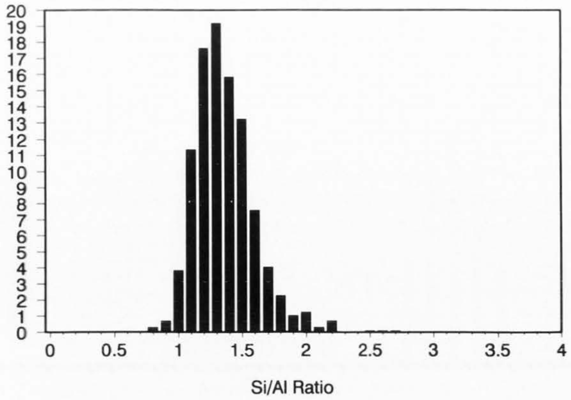

Figure 2. Si/Al distribution in Beulah aluminosilicate.

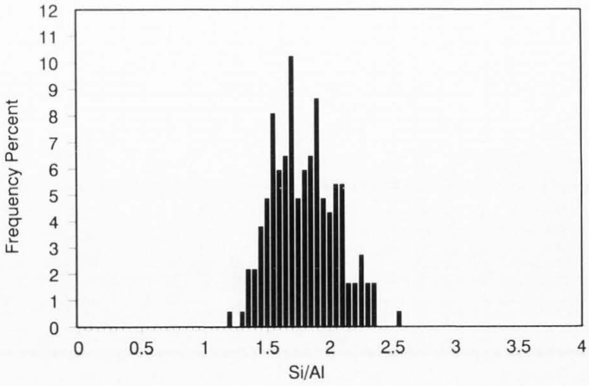

Figure 3. Si/Al distribution in Upper Freeport aluminosilicate.

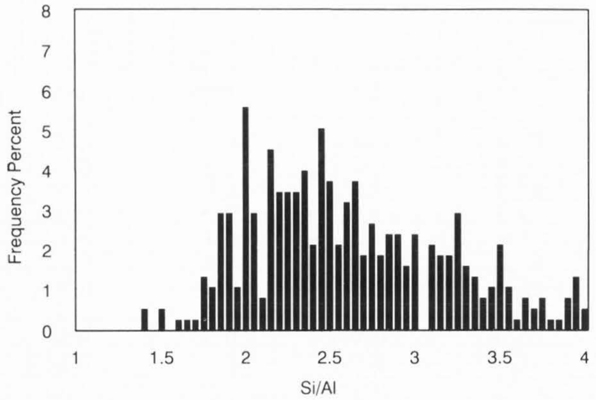

Figure 4. Si/Al distribution in Upper Freeport K-aluminosilicate.

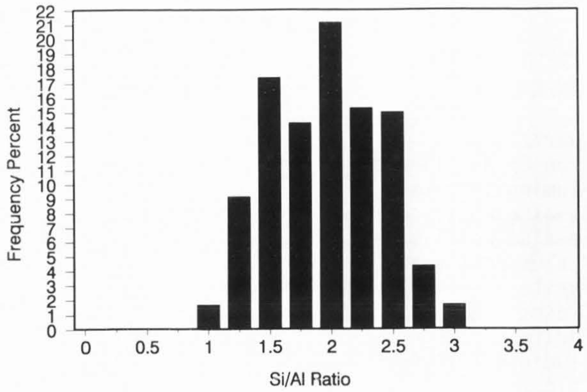

Figure 7. Si/Al distribution in San Miguel aluminosilicate

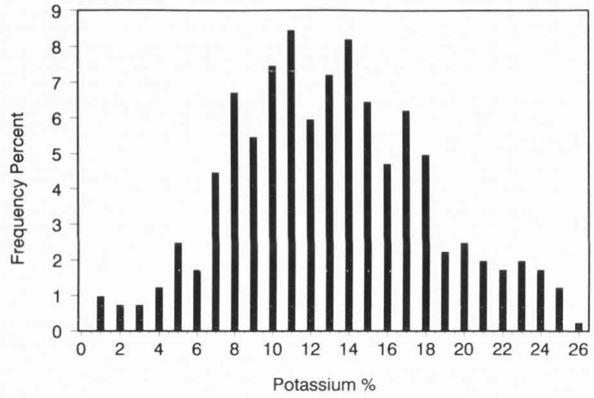

Figure 5. Potassium distribution in Upper Freeport K-Aluminosilicate.

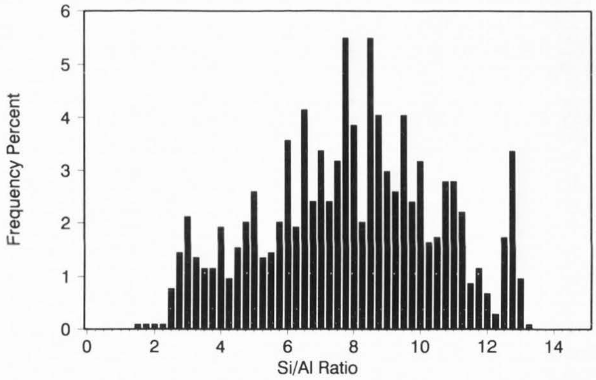

Figure 8. Si/Al distribution in San Miguel K-aluminosilicate.

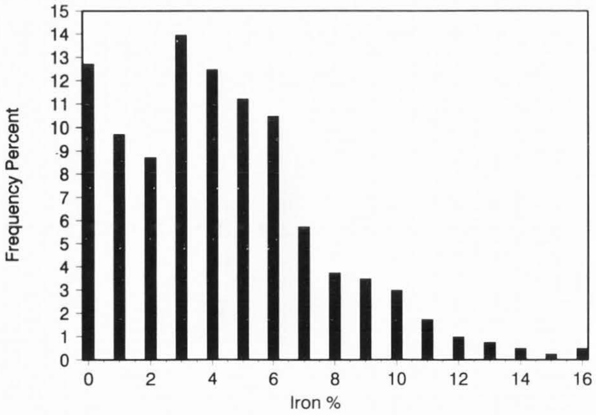

Figure 6. Iron distribution in Upper Freeport K-aluminosilicate.

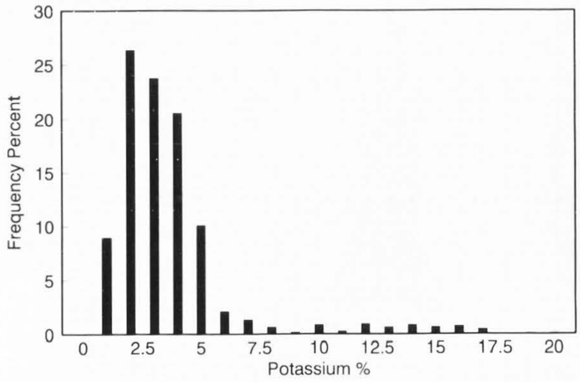

Figure 9. Potassium distribution San Miguel K-aluminosilicate.

TABLE 4 AVERAGE COMPOSITION OF CLAY MINERALS IN COAL (Normalized EDS Percents from CCSEM)

1	2	3	4	5	6
COAL	Beulah	Upper Fr.	Upper Fr.	San Miguel	San Miguel
CCSEM ID	Aluminosil.	Aluminosil.	K-Alumino.	Aluminosil.	K-Alumino.
CLAY ID	Kaolinite	Mixed Clays	Illite	Montmor.	Clinoptil.
No. Analyses	957	186	401	427	1649
ELEMENT					
Na	0.6	0.1	0.1	0.4	0.4
Mg	0.1	0.1	0.1	0.3	0.2
Al	40.3	31.9	19.7	33.6	11.7
Si	52.2	55.9	52.6	59.4	81.0
P	0.1	0.2	0.3	0.1	0.0
S	1.1	3.8	3.7	1.5	0.8
Cl	2.1	1.1	1.2	1.4	0.5
K	0.6	1.8	13.9	0.7	3.8
Ca	1.1	1.1	1.1	0.8	0.7
Fe	0.6	1.8	4.5	0.5	0.2
Ba	0.5	1.1	1.3	0.7	0.3
Ti	0.6	1.1	1.5	0.8	0.4

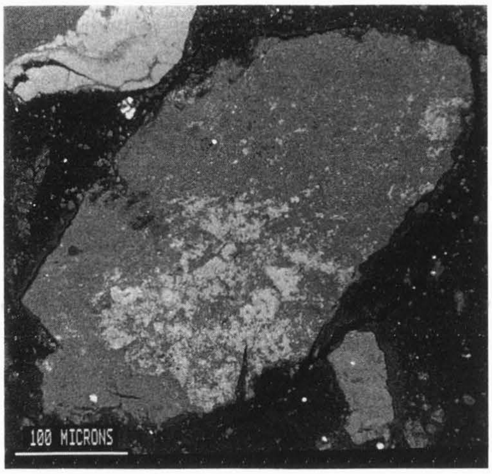

Figure 10. BEI of Beulah coal cross section showing clay mineral inclusions.

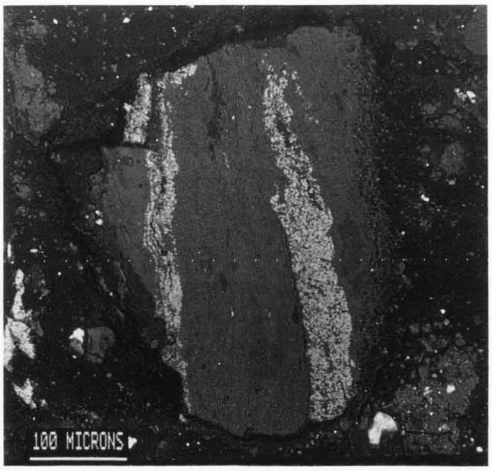

Figure 11. BEI image of Beulah coal showing bands of clay minerals.

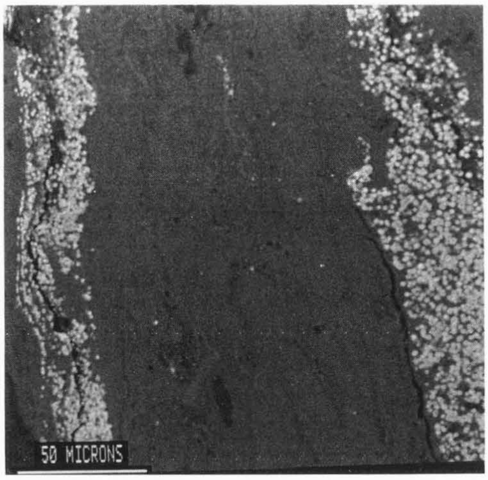

Figure 12. High magnification BEI of spheroids from band shown in Figure 11.

destroying the morphologic and chemical content present in the coal, and 2) the ability to collect highly magnified images which allow extremely detailed inspection of the nature of the materials. The CCSEM analysis provides quantitative mineralogic typing and particle-size information for coal minerals. Concurrent image analysis provides detailed information concerning the relation of minerals to the coal matrix, mineral associations, and mineral habit. Care must be taken when using automated techniques in the analysis of complex minerals like clays, where complex chemistries and morphologies are the rule.

Detailed examination of clay minerals was accomplished using Si/Al ratios and contents of the alkali-alkaline earth elements. Minerals identified as aluminosilicates by CCSEM in the Beulah, Upper Freeport, and San Miguel coals contained very small quantities of alkali-

alkaline earth elements, but had different Si/Al ratios. The Beulah aluminosilicate was kaolinite or possibly halloysite; the Upper Freeport aluminosilicate with 1.8 percent potassium was more characteristic of degraded illite or mixed clay; and the San Miguel aluminosilicate may be montmorillonite or mixed clay. Potassium aluminosilicate in the Upper Freeport could be positively identified as illite using Si/Al ratios and the quantity of K. The fairly high Si/Al ratio distribution and moderate K contents in the San Miguel potassium aluminosilicates were characteristic of a K-rich zeolite confirmed by XRD to be clinoptilolite. By collecting high-resolution images along with the CCSEM analysis, details about the physical relation of the minerals to the organic matrix of the coals can be ascertained. While the SEM/EPMA techniques generate valuable data, these techniques are still in developmental stages. The image analyzer is now fully integrated into our CCSEM system, and digital images are collected for each frame analyzed. Each particle in a given frame of area can then be sequentially marked with a circle on the image to allow for data concerning mineral-to-mineral associations (juxtaposition). A further step in the development of this program will be the automation of the assignments into juxtapositional categories. Eventually, a program which provides better chemical data (such as ZAF corrections) for each particle analyzed will be written. When combined with automated digital image collection, this program will produce data detailing the chemistry, morphology, and juxtapositional nature of coal minerals. These advanced techniques will provide more accurate and detailed information concerning coal minerals.

Acknowledgements

This work was performed in part under contract with the Advanced Combustion Engineering Research Center, Brigham Young University (L. Douglas Smoot, Director). Funds for this Center are received from the National Science Foundation, the State of Utah, 25 industrial participants, and the U.S. Department of Energy. The authors would like to extend their thanks to Dr. Smoot for his support. Part of the funding for this work was also secured through a contract with the Department of Energy under Cooperative Agreement No. DE-FC21-86MC10637. The authors thank the Contracting Officers Representative, Mr. Philip M. Goldberg, for permission to publish the results.

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Discussion with Reviewers

W.E. Straszheim: It may be that the authors should limit their discussion to the chemistry of the clays with only a very brief discussion of the distribution of the clays in the organic matrix. Please comment.
Authors: Although the paper addresses advanced techniques for characterizing coal minerals in general, it is clear that the main emphasis is the identification of clay minerals. The bulk of the identification procedure is based on EDS analysis of the minerals. However, experience has shown us that the morphology of the clay minerals may also aid in their positive identification and should be at least considered at this stage as a valid tool to aid in clay identification.

W.E. Straszheim: Would the authors please comment on the general nature of the San Miguel lignite in view of its inordinately high ash content? What commercial use is made of such a lignite?
Authors: At the time of the coal sample collection, the San Miguel lignite was being used to fuel a mine-mouth, 400-megawatt electric power generating station in South Texas. The lignite seam is part of the Lower Jackson Group of South Texas and averaged 28 percent moisture, 30 percent ash, 2.0 percent sulfur, and 5179 Btu/lb as received. It is not unusual for samples of this coal to contain 50 percent ash on a dry basis (Ayers WB Jr (1987) Geology of the San Miguel lignite mine, Jackson Group, South Texas. In: The Fourteenth Biennial Lignite Symposium on the Technology and Utilization of Low-Rank Coals, Finkelman RB, Casagrande DJ, Benson SA, (eds), Environmental and Coal Associates, Reston, VA 22090, 69-82).

W.E. Straszheim: Is the CCSEM/image analysis system used here by the authors analagous to automated image analysis (AIA)? Many investigators use the terms AIA and CCSEM interchangeably. It appears that the analysis is divided among two analysis systems, either of which might be described as CCSEM or AIA.
Authors: The differentiation between our CCSEM and image analysis systems admittedly is not very distinct. The basis for our differentiation pertains to the definition of "image analysis." From our standpoint, "image analysis" refers to gaining information from stored scanning electron microscope digital images using the TN 8500 image analyzer. Types of information gained are particle sizes and areas, which are determined by analyzing digital images on a pixel-by-pixel area basis, differentiating minerals by gray scale, marking chemical or morphological features with different colors, etc. For all practical purposes, the CCSEM program is a particle recognition and characterization routine where information on particles is collected and stored simultaneously with the running of the program. The CCSEM program is controlled by the TN 5600 computer to locate, size, and type classify particles. Using a series of eight diameters through the center of a particle, the average diameter and area of a particle are calculated.

R.B. Finkelman: You imply that image analysis can be used to differentiate between kaolinite, dickite, and halloysite and between illite and muscovite. Can you describe the criteria you will use? If you are using grain mounts having random orientations, how is the mineral orientation taken into account?
Authors: The idea we are conveying is that chemical information from CCSEM analysis on clay minerals such as the kaolinite group minerals, illite and muscovite, is often not diagnostic for their positive identification. Morphology of minerals, however, as observed using image analysis, can aid in identifying those minerals. The type of image analysis we propose is not a stand-alone technique for mineral identification and, from a practical standpoint, can only be done for selected representative minerals and not every mineral encountered. Orientation would not be a real factor as every mineral is not being analyzed. For example, we have observed through microprobe and SEM image analysis that muscovite generally has less silica and more potassium than illite, and it also has a more platy habit or structure.

R.B. Finkelman: In comparing the CCSEM data to that of XRD, it appears that pyrite is overestimated by the CCSEM technique. Straszheim has recently addressed this problem. Do you have any comments?
Authors: The XRD data we presented is essentially semiquantitative. Minerals are designated as major or minor simply by comparing XRD peak intensities. Therefore, we generally use XRD to verify the presence of minerals identified using CCSEM. In addition, recent work performed, to develop the CCSEM technique, compared known quantities of chalcopyrite and quartz in a mixture to measured quantities using CCSEM. The results showed no overestimation of the chalcopyrite (Zygarlicke CJ, Benson SA, Hurley JP, Steadman EN, Brekke DA (1989) Combustion Inorganic Transformations. Univ. North Dakota Energy Research Center Fourteenth Technical Progress Report for the period July

through September 1989, Prepared for U.S. Dept. Energy, Pittsburgh Energy Technology Center, DE-FC21-86MC10637).

D.W. Strickler: It would be useful to discuss the origins of the clays in the various coal seams. Are they primarily formed in situ or carried in a detrital material during the deposition of the coal?
Authors: The type of image analysis system described in this paper would function quite well for studying the origins of the clays; however, this was not the focus of the paper. To study the origins of the clay minerals would require changes in the sample preparation and SEM analysis. We would prepare the samples using a larger average coal size to preserve the original form of the minerals and their association with the organic matrix. We also would acquire many more stored SEM images of the various types of clay minerals in each coal, because the origin of the minerals is deduced primarily on the basis of mineral morphology and association with the coal organic matrix.

Reviewer IV: Please discuss the uncertainties in the identification of the particular sulfates, clays, or zeolites that you specify as being present.
Authors: The major minerals that were identified by CCSEM, excluding montmorillonite, mixed clay, and zeolite, corresponded to known compositions and were verified, at least semiquantitatively, by XRD. One sulfate mineral which may be identified erroneously using our CCSEM program is iron sulfate ($FeSO_4 \cdot H_2O$), which could be confused with pyrite (FeS_2). The criteria for distinguishing pyrite from sulfates or pyrrhotite (FeS) in the CCSEM program are fairly rigid, however, and the errors are marginal. The calcium and barium sulfates have diagnostic chemistries that are easily identified by CCSEM. We feel there is a large uncertainty at this stage with identifying the clay minerals and zeolites except for kaolinite and illite. Zeolites, at this stage in the development of CCSEM, would require confirmation by XRD.

Reviewer IV: How might the LTA process affect the phase identification decisions?
Authors: The LTA process may actually oxidize some of the pyrite to hematite (Fe_2O_3) and iron sulfate and, for the lignites, transform organically bound calcium and sulfur to bassanite ($CaSO_4 \cdot 0.5H_2O$)(Miller RN, Yarzab RF, Given PH (1979) Determination of the mineral-matter contents of coals by low-temperature ashing. Fuel 58, 4-10). Clay structures may be altered also, especially hydrous clays such as halloysite which may lose water during the ashing procedure.