

Influence of Environments of Deposition on the Inorganic Composition of Coals

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Introduction

The mineral composition of coal is the result of physical, chemical and biological processes acting on the system from the time of peat accumulation, through burial and subsequent increase in rank, to the present. With respect to origin, inorganic constituents may be classified as: inherent (being derived from inorganic components within the peat-forming plants) or adventitious (being derived from outside the peat swamp and forming either during or after peat accumulation); and detrital (those transported into the peat swamp) or authigenic (those formed within the environment). Mackowsky (1) further differentiates between syngenetic minerals, formed during the accumulation of peat, and epigenetic minerals, which formed later.

In recent years considerable controversy has surrounded the origin of minerals in coal: the question is whether most of these materials are derived from inorganic substances originally contained within peat-forming plants (inherent), or from sources outside the peat swamp (detrital).

Studies of modern peat-forming environments have emphasized the importance of detrital influx (2,3), syngenetic formation of pyrite (4) and biogenic silica (2,5), and in-situ mixing with underlying sediments (2,6) to account for mineral constituents in coal. Within the peat environment certain unstable detrital clays may undergo alteration or dissolution (3,7); other clays, such as kaolinite, may form authigenically; and biogenic silica dissolves, possibly contributing to later authigenic mineralization (3,5). In coals, authigenic kaolinite formation along cleats is common (8,9). Clays may also form by alteration of volcanically-derived material (10). Opposing the concept of a major detrital input, Cecil and his co-workers (11,12) consider the major source of ash components to be the inorganic fraction of peat-forming plants, and total mineral content to be a function of the degree of peat degradation.

While this controversy still lingers, it appears that several origins are possible for minerals in peat and coal, including detrital influx, biogenic input, and precipitation either during or after peat accumulation, including some contribution from inorganic substances derived from plants. Various studies have attempted to relate inorganic composition to conditions existing at the time of peat accumulation. Pyrite has frequently been associated with marine and brackish peats (4,13), and the pyrite content of coal has been related to roof lithology (14,15). Clay assemblages of coals and underclays also have been related to depositional environment (9,16).

The purpose of this paper is to describe variability in the inorganic content of a single coal and attempt to explain the distribution of minerals in a framework of depositional environments. In western Pennsylvania, the Lower Kittanning seam provides an opportunity to study coal that was influenced by freshwater, brackish and marine conditions, as indicated by a previous study of the overlying shale (17). Several geologic controls are thought to have influenced deposition during this time: differential subsidence resulted in a thickening of sediments (and coal) towards the center of the basin; a basement high to the north of the field area may have supplied clastic material, adding

to a predominantly eastern sediment source; and active folds and variations in paleogeography may have also influenced sedimentation patterns (18).

Sampling and Methods

Forty-three channel samples of the Pennsylvanian-aged Lower Kittanning coal (Kittanning Formation, Allegheny Group) were collected in western Pennsylvania. Samples are representative of all three suggested depositional environments (Figure 1) and also of the increase in rank from high volatile bituminous in the west to low volatile bituminous in the southeast. Analyses included major and minor elements, total sulfur and sulfur forms, and low-temperature ashing. LTA's were obtained according to standard procedures (19). X-ray diffraction analysis of LTA's provided qualitative, quantitative (for quartz and pyrite), and semi-quantitative (for clays in the $< 2 \mu\text{m}$ fraction) data using procedures modified from Russell and Rimmer (20). Kaolinite was quantified using infra-red spectroscopy. Mineral composition was also calculated by normative techniques modified from Pollack (21) and Given *et al.*, (22).

Results and Discussion

The major mineral components of this coal include quartz, pyrite (and marcasite), and clays (predominantly kaolinite and illite/mica, with lesser amounts of expandable clays). Total mineral content (percent LTA) varies considerably across the basin, with very high ash contents occurring in the center of the basin and along sections of the Allegheny Front. To further understand these variations, individual mineral distributions were examined.

Pyrite distribution shows a definite basinal trend, with high pyrite contents occurring across the center of the basin (Figure 2). Whereas much of this area underlies marine and brackish roof rocks, the relationship is not perfect. Highest pyrite content appears to be most closely related to the eastern brackish zone. Factors influencing the distribution of sulfur in peat and coals include availability of iron and sulfate, and pH. Sulfate is thought to be introduced by marine and brackish waters (4). Recent work on pyrite distribution in the Florida Everglades (23) indicates highest pyrite content is associated with brackish environments rather than marine, and this has been related to the availability of iron. In freshwater, iron is transported in organic colloids which flocculate quickly upon entering brackish water, resulting in a higher availability of iron in brackish environments (24). pH is also a factor, as much of the pyrite appears to form as a by-product of sulfate-reducing bacteria (4). Compared to the more acidic freshwater environments, higher levels of microbial activity would occur in the neutral to basic pH conditions existing in marine or brackish waters. Pyrite content is therefore highest in areas that were influenced at least by brackish conditions.

The central part of the basin was experiencing more rapid subsidence than the margins, thus any marine influence would be greater in this area. Apparent discrepancies in the relationship between pyrite content and roof lithology may be explained on the basis of iron availability. (Data to be discussed later suggest a detrital influence towards the eastern margin of the basin, providing clay-rich sediments which may have contributed to the supply of iron). Other workers have also commented on this lack of correlation and suggest epigenetic pyrite formation along cleats and joints may be responsible (25). A third alternative is that the zone of maximum brackish and marine influence shifted during the history of the peat swamp.

Quartz content is highest in the north-central part of the basin, with isolated quartz-rich pods along the Allegheny Front. The origin of quartz in coal has been debated at length. Detrital quartz has been distinguished by many

authors (1,3) while other workers (11,12) believe much of this quartz is derived from silica originally contained within the plants. Petrographic observations of quartz in this coal revealed an association with attrital bands, suggesting a detrital origin. The distribution may be related to the basement high that existed to the north during this time (18). Transportation within the swamp of quartz-rich sediments derived from this high was possibly restricted by the baffling effect of vegetation, a phenomenon noted in modern swamps (2). In addition, lesser amounts of quartz may have been carried in from the east. Sediment derived from this latter source appears to have been predominantly clay. Comparable quartz distributions were noted in the underclay (26), thus the influence of in-situ mixing also exists.

Kaolinite is the major clay constituent of the coal and occurs in highest concentrations along the basin margins, with illite increasing towards the central part of the basin. Once again a similar distribution was noted in the underclays (26). Differential flocculation within the basin, together with chemical regrading of clays, could be used to explain this distribution. Holbrook (26) argues against this mechanism for the underclays on the basis of flocculation studies in modern environments, and suggests differential leaching related to variations in paleotopography may have been important. Another control could be the effect of peat chemistry on the clay assemblage. Kaolinite appears to be highest in freshwater environments where, under lower pH conditions, it would be the most stable clay mineral. Thus, in these areas not only could kaolinite be detrital, but also the product of clay alteration and authigenesis. The presence of high-temperature polytypes suggest a detrital origin for illite/mica in the Lower Kittanning coal and underclay, as discussed by Davis et al. (3) and Holbrook (26). Detrital illite/mica would be better preserved in more basinward areas.

One additional control on the clay mineral assemblage could be rank. With the increase in rank exhibited by this coal, certain diagenetic changes might be expected. No consistent trends in mineralogy were observed, however a general lack of smectite and highly-expandable clays (which can be seen in lower rank coals) was noted. This could be related to rank, or be a function of provenance.

Summary

The distribution of minerals within the Lower Kittanning coal can be related to depositional environments. Total mineral content varies considerably across the basin, and variations can be explained by examining the distributions of individual minerals.

Pyrite content is controlled by availability of sulfate and iron, and pH. Highest concentrations are seen towards the center of the basin where subsidence was more rapid and marine and brackish influences (affecting sulfate availability and pH) were felt during and after peat accumulation. Iron availability may have been associated with the transport of organic colloids or clay into the basin.

Quartz appears to be limited to the northern part of the field area and isolated areas along the Allegheny Front. It is suggested that quartz-rich sediments were derived from a positive area to the north. Much of the sediment brought in from the east appears to have been clay-rich.

The chemistry of the peat may have had a strong influence on clay mineral assemblage. Kaolinite may have been both detrital and authigenic, whereas illite/mica appears to be detrital. Rank has had little effect on the overall clay assemblage.

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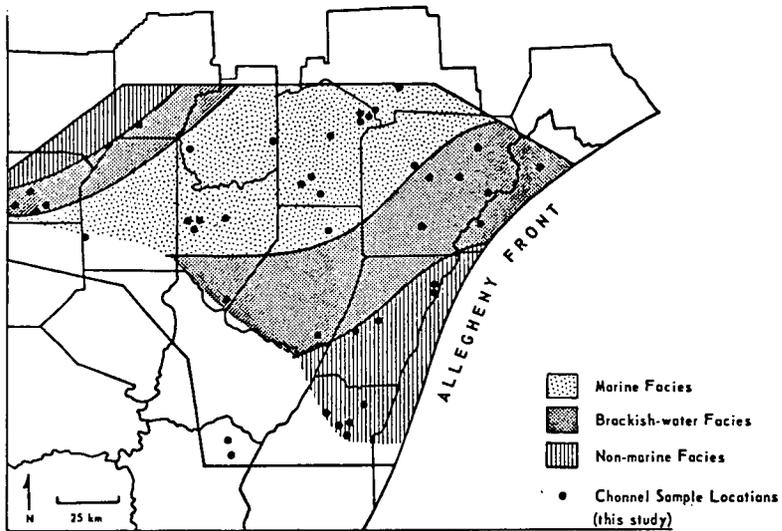


FIGURE 1. DISTRIBUTION OF SAMPLES IN WESTERN PENNSYLVANIA IN RELATION TO SUGGESTED ENVIRONMENTS OF DEPOSITION FOR THE OVERLYING SHALE

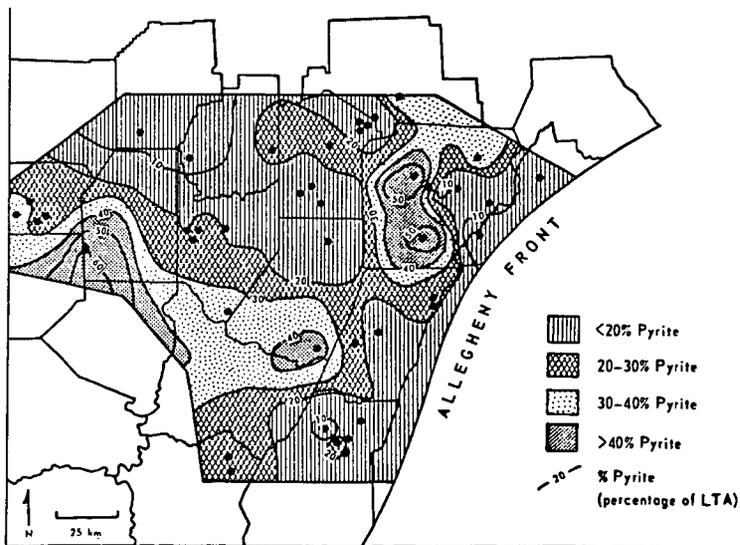


FIGURE 2. LATERAL VARIABILITY IN PYRITE CONTENT (LTA BASIS), AS DETERMINED BY X-RAY DIFFRACTION ANALYSIS

The Origin of Quartz In Coal

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Introduction

Mineral matter in coal can originate as (1) inorganic elements from plants that were incorporated during peat formation, (2) wind- or water-borne detritus that settled in the peat-forming environment, and (3) epigenetic minerals that formed during or after burial of the peat (Stach and others, 1982). The latter two processes generally are considered to be the principal contributors to the amount and variety of minerals in coal of commercial quality. Certain physical properties, such as the shape of quartz grains, have led some workers to postulate that quartz in coal is primarily of detrital origin (Finkelman, 1981a, 1982b; Davis and others, 1981); however, evidence for such a hypothesis may be highly subjective and inconclusive. In contrast, Cecil and others (1982) suggested that mineral matter in the Upper Freeport coal bed is dominantly authigenic, on the basis of statistical relationships among major-, minor-, and trace-element, maceral, and mineral data. Mineral matter in coal, exclusive of pyrite and calcite, was probably derived from plants that contributed to peat formation (Stevenson, 1913; Cecil and others, 1982).

Cathodoluminescence (CL) petrography was used in the present investigation to obtain quantitative data on the amounts of authigenic and detrital quartz in the Upper Freeport coal bed. CL is the emission of visible light during electron bombardment. It is used widely as a tool in sandstone petrology to distinguish between detrital and authigenic quartz grains. CL in quartz results from molecular or other lattice imperfections; molecular imperfections which include the addition of "activator" ions (Al^{+3} or Ti^{+3} that substitute for Si^{+4}), and other lattice imperfections are related to temperature (Zinkernagel, 1978). Zinkernagel observed three distinct types of luminescence in quartz grains that included (1) "violet" luminescing quartz (spectral peaks at 450 and 610-630 nm), (2) "brown" or orange luminescing quartz (spectral peaks at 610-630 nm), and (3) non-luminescing quartz. He examined quartz from 46 localities and ranging in age from Precambrian to Tertiary, and in all cases the CL color was dependent on the temperature of crystallization. "Violet" or blue luminescing quartz was characteristic of fast-cooled volcanic, plutonic, and high-grade metamorphic rocks that were formed at temperatures greater than 573°C. "Brown" or orange luminescing quartz was characteristic of high-grade slow-cooled metamorphic rocks formed at temperatures ranging from 573°C to 300°C. Quartz that was formed at temperatures below 300°C and that was not heat tempered did not luminesce in the visible range. The origin of quartz can be inferred from CL data because detrital quartz, which has a high-temperature origin (>300°C), luminesces in the visible range whereas authigenic quartz, formed at low temperatures (<300°C) does not luminesce.

Methodology

Both a scanning electron microscope (SEM) and an electron microprobe (EMP) were used in this study to analyze the CL properties of quartz grains in samples of the Upper Freeport coal bed because quartz grains in coal are small (silt sized) and below the resolution capabilities of a standard luminescope. Quartz grains were identified by the detection of silicon alone with energy dispersive X-ray units attached to both the SEM and the EMP.

The SEM was used to observe and photograph the quartz grains. The EMP which was equipped with both a photomultiplier tube (spectral response 185-930 nm) and a monochromator, was used to measure wave length and intensity of CL. The EMP, instrument conditions were calibrated using a reference sample of the upper part of the Raleigh Sandstone Member of the New River Formation (Pennsylvanian age), which contained both orange and blue luminescent detrital quartz grains and non-luminescent authigenic overgrowths of low-temperature origin (fig. 1).

Quartz grains from the Upper Freeport coal bed were analyzed in (1) ash samples that were prepared by low-temperature plasma ashing (LTA) of facies channel samples, (2) pulverized coal samples of size-gravity separates, and (3) oriented blocks of mineral-rich bands, vitrain, fusain, clay-rich parting material, and roof-shale that were each cut from a coal core. All samples were mounted in epoxy and polished prior to analysis.

Results

All the Upper Freeport coal bed samples examined contained both luminescent and non-luminescent quartz grains (table 1, fig. 2). More than 200 grains were visually examined, and 76 measured spectra were obtained.

In the LTA samples, 95 percent of the quartz particles examined were non-luminescent and 5 percent were luminescent. Most grains luminesced in the orange range.

Twenty-nine measured spectra of quartz grains were obtained from the lightest (1.275 float) and the heaviest (1.800 sink) size-gravity separates. Only nine grains were analyzed in the lightest gravity separates because of the paucity of mineral matter. All nine grains were non-luminescent and were associated with vitrain. In the heaviest gravity separates, 60 percent of the quartz was non-luminescent; this quartz is petrographically associated with both vitrain, mineral-rich bands, and shale partings. The remaining 40 percent of the quartz grains in the heavy gravity separates were luminescent and are associated with mineral-rich bands and shale parting material.

Data from CL analyses of the blocks of coal from the core revealed that luminescing quartz was relatively rare and is associated only with mineral-rich bands. Of the 29 quartz grains analyzed, only 17 percent luminesced. The non-luminescent grains are petrographically associated with both vitrain and mineral-rich bands.

Roof-shale samples from the core were also examined. Ninety-three percent of the quartz analyzed was luminescent and only 7 percent was non-luminescent. The quartz grains analyzed were similar in size to the quartz grains in coal.

Conclusions

Seventy-six percent of the quartz grains examined in the Upper Freeport coal samples are non-luminescent; therefore the quartz is interpreted to be dominantly authigenic. The authigenic quartz is petrographically associated with both vitrain and mineral-rich bands. The remaining 23 percent of the quartz analyzed luminesced in the visible range and is therefore interpreted to be detrital in origin. Detrital quartz was petrographically associated with mineral-rich bands and clay-parting material.

In contrast, quartz grains in the samples of shale directly overlying the Upper Freeport coal bed are interpreted to be predominantly detrital in origin. The quartz grains are in the same size range as quartz grains in the coal samples.

Data from CL petrography support the interpretation of Cecil and others (1982) that quartz in Upper Freeport coal bed is primarily authigenic and derived from plant ash. Although it is impossible to ascertain the ash content of Pennsylvanian plants that grew in the Upper Freeport paleo-peat forming environment, it seems reasonable that the plants did contain silica, as do most modern plants. Biogenic silica can be preserved as phytoliths (Smithson, 1956; Baker, 1960; and Jones, 1964; Andrejko and others, 1983) and quartz grains in coal are similar in size to plant phytoliths (Wilding and Drees, 1974).

Most quartz grains in the commercial-quality Upper Freeport coal bed samples are authigenic in origin, but this interpretation does not rule out a detrital source for areas of the bed containing higher amounts of ash (approximately 20 percent) or for other high ash bituminous coal beds. The percentage of detrital quartz would be expected to increase approaching stream channels and the margins of the paleoswamp environment, but vegetal matter is probably the dominant source for quartz in interior portions of the paleoswamp.

Table 1. CATHODOLUMINESCENT AND PETROGRAPHIC CHARACTERISTICS OF QUARTZ GRAINS IN COAL AND SHALE

[Determined by using an electron microprobe (EMP). TNA, Total number of grains analyzed; Nonlum, nonluminescent grains; Lum, Luminescent grains; *, data was not obtained because coal was crushed; N/A, not applicable.]

	LOW-TEMPERATURE ASH		SIZE-GRAVITY SEPARATES			
	(Facies channel samples)		Float 1.275 (TNA = 9)		Sink 1.800 (TNA = 20)	
	Nonlum	Lum	Nonlum	Lum	Nonlum	Lum
Number of grains	39	2	9	0	12	8
Grain size range (in μm)	*	*	6-22	N/A	5-14	9-32
Mean grain size (in μm)	*	*	9.9	N/A	8.4	18.9
Percent of total	95	5	100	N/A	60	40
Association	*	*	Vitrain	N/A	Vitrain Mineral-rich band Shale parting	Mineral-rich band Shale parting

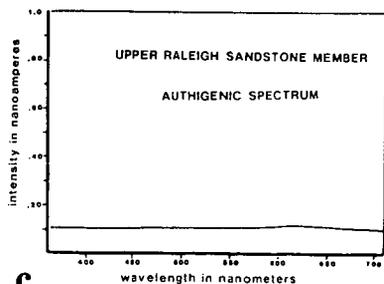
	COAL BLOCKS (TNA = 9)		ROOF-SHALE BLOCKS (TNA = 15)	
	Nonlum	Lum	Nonlum	Lum
Number of grains	24	5	1	14
Grain size range (in μm)	8-20	7-22	N/A	6-32
Mean grain size (in μm)	12	14.8	7	13.5
Percent of total	83	17	7	93
Association	Vitrain	Mineral-rich	Shale	Shale



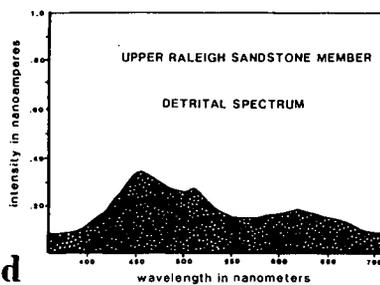
a



b



c



d

Figure 1 - Reference sample for EMP. (a) SEM backscatter electron photomicrograph, (b) CL SEM photomicrograph. Note luminescing detrital quartz grains, (c) EMP CL spectrum of non-luminescing authigenic overgrowth, (d) EMP CL spectrum of blue luminescing detrital quartz grain.

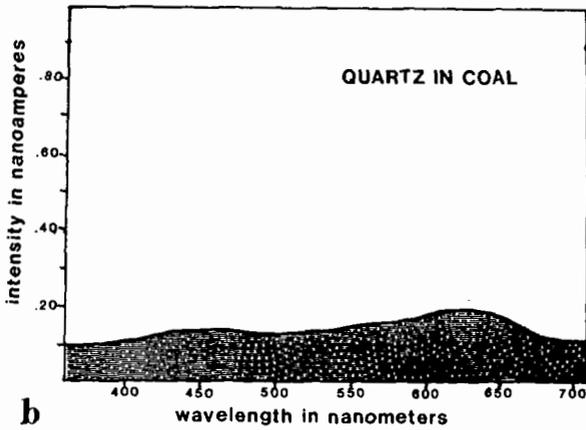
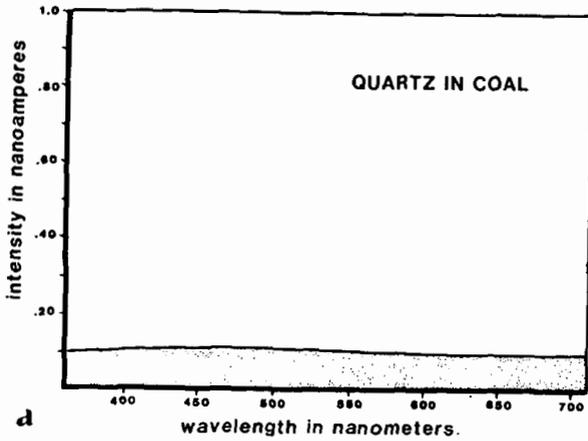


Figure 2 - EMP CL spectra of quartz in the Upper Freeport coal bed. (A) Non-luminescing authigenic spectrum, (B) Luminescing detrital spectrum.

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SEMI QUANTITATIVE DETERMINATION OF COAL MINERALS BY X-RAY DIFFRACTOMETRY

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INTRODUCTION

The purpose of this paper is to present and support the argument that abundance estimates of the minerals in coal based upon x-ray diffraction data can only be considered semi-quantitative with expected errors of determination of 10 percent or more of the reported values. The compositional and physical characteristics of the low temperature ash components of coal relative to the preparation and mounting of ash for XRD analysis must also be considered.

MINERALS IN COAL

The minerals commonly found in coal are listed in Table 1. In the average coal, clay minerals may constitute up to 60 weight percent of the mineral matter (1,2). Quartz is usually the second most abundant mineral, with up to 20 weight percent being common. The carbonate minerals (calcite, siderite and to a lesser extent, dolomite and ankerite) and the iron disulphide minerals (pyrite and marcasite) make up, on the average, about 10 weight percent each group. Sulphate minerals of calcium and iron and the feldspar minerals are commonly present but rarely in concentrations of more than a few weight percent. Except for unusual cases such as the sulphide rich coals of the northern Illinois Basin, the occurrence of the other minerals in concentrations exceeding a few percent is rare. It must, however, be kept in mind that the mineralogy of the inorganic portion of coal shows systematic variation both geographically and locally reflecting the geochemistry of the original peat forming environment (3). As a result, "average" values of concentration may have little practical meaning.

Most coals considered for conversion processes such as liquification, and thereby those of prime interest to chemists, are generally high in ash (>10 weight percent) and sulfur (>1 weight percent). In such coals, illite would invariably be the dominant clay material, constituting, in some coals, up to half or more of the mineral content. Most of the sulfur contained in these coals will be in the form of pyrite although marcasite may be locally dominant (4).

QUANTIFICATION BY X-RAY DIFFRACTION

The most commonly employed quantitative XRD procedure used to evaluate the concentration of mineral components in a multicomponent mixture of minerals compares the Bragg intensity data of unknowns to those generated from a suite of known standard samples. Mineral specimens are acquired to represent each of the minerals expected in the unknowns. The specimens are ground to a uniformly small size (less than 44 microns) and mixed together in concentrations which represent the range of concentrations expected for each mineral. An internal standard such as calcium fluoride, aluminum oxide or powdered aluminum is usually added in order to monitor and correct for variations in sample absorption and instrumental variables. Working curves are then prepared by plotting the ratio of intensity (preferably integrated intensity) of the Bragg reflection chosen to quantify the mineral to that chosen for the standard versus the weight percent of the mineral in the standard samples.

This procedure will provide analyses of high precision provided certain basic assumptions are met: (1) the high composition and crystallinity (degree of ordering) of the individual minerals in the unknowns are both reasonably constant from sample to sample and (2) the composition and crystallinity of the standard minerals chosen for the preparation of the standard samples reasonably duplicate the composition and crystallinity of the respective minerals in the unknowns. The purpose of the following discussion is to demonstrate that, in the case of coal minerals, neither of the above assumptions is valid and as a result, any such quantitative procedure will reflect the inherent degree of departure from these basic assumptions and will therefore be semi-quantitative. Other procedures using data normalized to the total integrated intensity and quantification procedures utilizing weighting factors based upon standard chemical formulae for the minerals can be used but with no improvement in quantitative errors (5,6).

Illite and pyrite were specifically cited in the above discussion to make a point relative to the precision and accuracy with which coal minerals can be quantified by XRD. First, illite is NOT a mineral. Illite is "...a general term for the clay mineral constituents of argillaceous sediments belonging to the mica group (7). To a clay mineralogist, the term illite is synonymous with variability in both composition and crystallinity (8). The situation is even further complicated by the fact that much of the material in coal referred to a "illite" is actually an illite dominated mixed layered clay wherein the illite lattices are randomly interstratified with 14A clay lattices; usually chlorite. This mixing of clay mineral lattices further adds to the inherent variability in both composition and crystallinity of the illite material. The constitution of "illite" can therefore be expected to vary significantly from sample to sample. It should be quite apparent from the above discussion that no "standard" illite exists that could be used to represent illite in standard samples.

The iron disulphides may represent 10 weight percent or more of high ash-sulphur coal ashes. Usually, pyrite is the major disulphide. Pyrite occurs in coal in a number of morphological forms and sizes (9). Not only does the pyrite in coal vary in morphology and size but also in stoichiometry and crystallinity. Studies have been conducted in the author's laboratory on cut and polished surfaces of coal blocks wherein the blocks have been exposed to the atmosphere and the pyrites observed over a period of time. Some pyrite grains, the

euohedral forms, remain bright and show little tendency to react. The massive forms of pyrite, on the other hand, show a wide variation in apparent reactivity with crystals of iron sulfates being observed to form on some pyrite surfaces within a matter of hours and in some cases, within minutes.

Another study involved in quantification of pyrite in different coal lithotypes. Coals are described megascopically based upon the degree of bright and dull banding. Zones are delineated within the coal and designated as a "lithotype" based on the relative percentage of bright and dull bands within the zone (10). Dominantly bright bands are called "VITRAIN", dull bands, DURAIN and those intermediate between the two; "CLARAIN". Although the designation as to lithotype is solely made depending upon megascopic description, the lithotypes differ in basic organic composition as illustrated by the data for the Waynesburg Coal shown in Table 2.

TABLE 2. COMPOSITION OF LITHOTYPES OF THE WAYNESBURG COAL

LITHOTYPE	%VITRINITE	%EXINITE	%INERTINITE	%MINERAL MATTER
Vitrain	93.1	1.8	2.4	2.7
Clarain	84.2	4.4	5.6	5.8
Durain	43.4	17.8	24.9	13.9

The low temperature ash of each lithotype was then submitted to XRD analysis. The integrated intensities of each of the selected analytical Bragg reflections selected for the individual minerals were summed for all minerals present in each sample to give a "total integrated intensity". This value was then divided into the integrated intensity of the pyrite analytical Bragg reflection to give the "percent of total integrated intensity". The data are summarized in Figure 1. It is apparent that there is a systematic relationship between the composition/crystallinity of the pyrite and the basic organic makeup of the coal. Most important is the observation that equal concentrations of pyrite give different intensity responses. Volume for volume, the pyrite contained within the bright coal (Vitrain) showing significantly higher Bragg intensities than the pyrite contained in the duller coals.

To compound the problem, marcasite for reasons unknown to the author, does not show the intensity response, volume for volume as pyrite. It has been the author's experience that the marcasite coals that have been shown by optical examination to be insignificant concentration show almost no indication of being present on a diffractogram generated from the low temperature ash.

It must be apparent from the above discussion that the great number of variables other than concentration affect the intensities of mineral pattern as observed on a diffractogram. Inasmuch as they cannot be monitored and compensated for mathematically, these variations must be reflected in the error of determination. This would be true regardless of the quantification procedure employed. The conclusion, therefore, is that the inherent variability in composition and/or crystallinity that exists within the major mineral components of the low temperature ashes of coal will be reflected in the statistical error of determination and that error will be of sufficient magnitude to preclude the use of the term "quantitative" to describe the procedure. Therefore, any procedure using x-ray diffraction to determine the minerals in coal must be considered semi-quantitative at best.

SAMPLE PREPARATION & MOUNTING

Any procedure for the preparation and mounting of coal low temperature ashes for XRD analysis MUST take two properties of the material into account: (1) minerals exist which react with water to produce acidic solutions (the iron disulphides) which in turn dissolve acid soluble components such as calcite and (2) the clay minerals by virtue of exceptionally well developed (001) cleavage surfaces have a dominant platy crystal form. The significance of the first attribute is that the ashes cannot be placed in water thereby precluding certain sample preparation techniques such as dispersion in water followed by vacuum mounting on filters or ceramic blocks. The second characteristic, possession of a platy crystal form, precludes the attainment of the theoretically required randomly oriented sample. Those who work with the clay minerals, realizing a random sample cannot be prepared and that the clay particles will deposit in preferred orientation, purposely prepare and mount the samples such that the preferred orientation of the individual platelets is maximized and thereby minimize any variations in diffraction intensity due to variations in particle alignment within the sample. The orientation of the clay platelets parallel to the sample surface positions the "C" crystallographic axis perpendicular to the sample surface. Because the diagnostic interplanar spacing for the clay minerals is along the "C" crystallographic direction, such an orientation is ideal for clay mineral identification. The simplest method to mount a low temperature ash for XRD analysis is to press the ash onto the surface of a pellet prepared from the coal from which the ash was derived.

FUTURE PROSPECTS

A few years ago, an ad hoc group of workers interested in coal minerals, The Mineral Matter in Coal Group, prepared and distributed a round-robin low temperature ash to ten laboratories. Each laboratory was to prepare, mount and quantify the mineral components in the ash by their respective XRD techniques. The data were then compared. Even though a wide variety of techniques was used for each phase of the analysis, with the exception of the clay mineral estimates made by one laboratory (significantly lower than the others) and the pyrite estimate made by another (too high), the data compared reasonably well. The averages of all the submitted estimates are summarized in Table 3.

TABLE 3. RESULTS OF ROUND ROBIN L.T.A. ANALYSIS

MINERAL	AVE. CONC. WT%	S.DEV.	C.V.
Illite+Mix L	30	7.07	0.24
Kaolinite	18	4.85	0.27
Quartz	21	6.31	0.30
Calcite	10	3.59	0.36
Pyrite	18	4.93	0.27

Another objective of the exercise was to discuss the results and procedures used and come to some agreement on a "standard" procedure for sample preparation, mounting and quantification that would be acceptable to all the workers. The agreement that was reached was that no agreement would be forthcoming on any of the phases of the analysis. With no one procedure demonstrably better than the other, each laboratory was expected to maintain their own procedure. As long as a procedure is scientifically and analytically sound and reflects a thorough understanding of the characteristics of minerals contained in coal and the requirements and limitations of x-ray diffraction, one procedure will probably be as good as another but none will be better than semi-quantitative. With all its shortcomings, x-ray diffraction is still the best and most practical method for the estimation of the abundance of the individual minerals in coal.

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TABLE 1
COMMON COAL MINERALS

Major	Silicates	Clay Minerals	Kaolinite	$Al_2Si_2O_5(OH)_4$
			Illite	a
			Mixed Layer	b
			Chlorite	
			(Mg ₂ FeAl) ₆ (SiAl) ₄ O ₁₀ (OH) ₈	
			Quartz	SiO ₂
Minor		Carbonates	Calcite	CaCO ₃
			Dolomite	(Ca,Mg)(CO ₃) ₂
			Ankerite	Ca(Fe,Mg)CO ₃
			Siderite	FeCO ₃
		Disulfides	Pyrite	FeS ₂ (cubic)
			Marcasite	FeS ₂ (orthorhombic)
		Sulfates	Coquimbite	Fe ₂ (SO ₄) ₃ · 9H ₂ O
			Szmolnokite	FeSO ₄ · H ₂ O
			Gypsum	CaSO ₄ · 2H ₂ O
			Bassanite	CaSO ₄ · 1/2H ₂ O
Anhydrite	CaSO ₄			
Jarosite	KFe ₃ (SO ₄) ₂ (OH) ₆			
Feldspars	Plagioclase	(NaCa)Al(AlSi)Si ₂ O ₈		
	Orthoclase	KAlSi ₃ O ₈		

^aIllite has a composition similar to muscovite-
KAl₂(Si₃Al)O₁₀(OH)₂, except for less K⁺ and more SiO₂ and H₂O

^bMixed layered clays are usually randomly interstratified mixtures of illitic lattices with montmorillonitic and/or chloritic lattices.

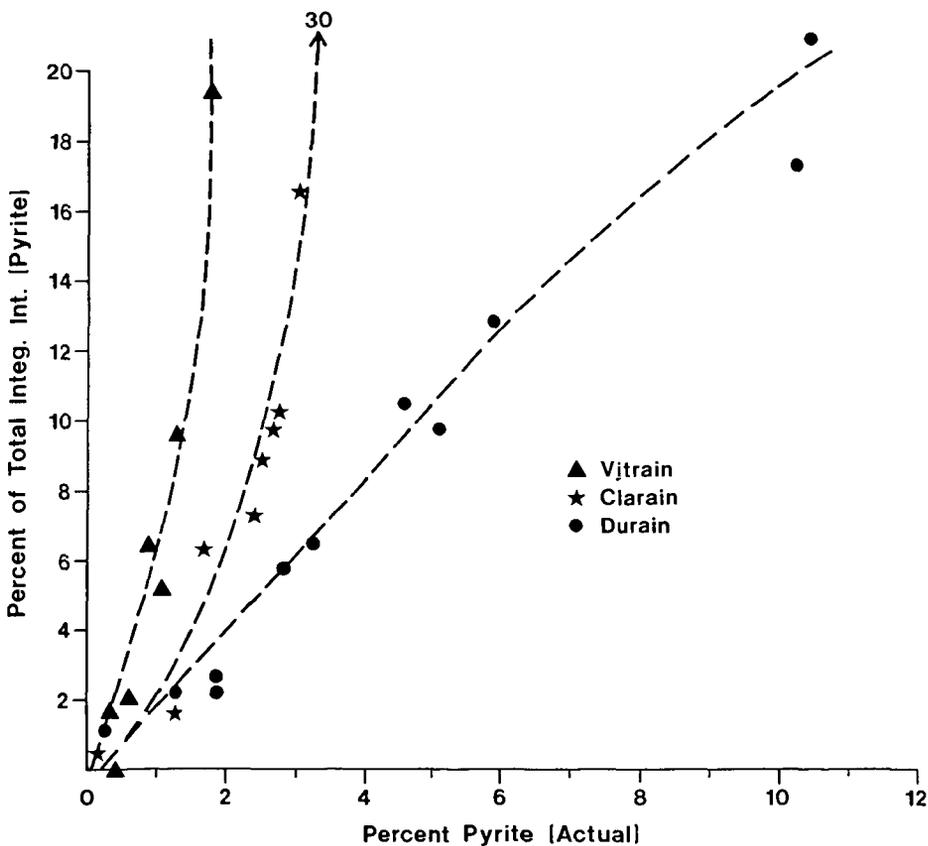


Figure 1. Relationship between actual pyrite composition and relative percent total integrated intensity of pyrite in low temperature ashes of Waynesburg coal lithotypes.

FACTORS INFLUENCING TRACE ELEMENT
VARIATIONS IN U.S. COALS

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INTRODUCTION

Although trace element data exist for thousands of coal samples, more will be required to better elucidate trace element trends within coal basins and to help decipher the geological and geochemical controls on trace element distribution and mode of occurrence. However, increased numbers of analyses will not necessarily provide all the answers. We run the risk of ending up information rich but knowledge poor.

The purpose of this paper is to give our analysis of coal trace element data in the literature. Several valuable compilations of trace element data exist for U.S. coal (1-4). We have borrowed freely from these compilations to illustrate their value in elucidating just one aspect of coal geochemistry: the factors influencing trace element variations.

Trace elements are generally defined as those elements with concentrations below 0.1 wt. % (1000 ppm). Despite concentrations in the parts-per-million range, certain trace elements can have a significant impact on coal utilization. For example, the chalcophile elements As, Cd, Hg, Pb, and Se, which are released during coal combustion or leached from coal waste products, can present significant environmental hazards; halogens such as Cl and F can cause severe boiler corrosion, and volatilized Ni or V can cause corrosion and pitting of metal surfaces. Moreover, although not strictly a trace element, sodium, even in small concentrations, can contribute to boiler fouling or to agglomeration of fluidized-bed reactors. On the positive side, some trace elements (e.g., Ge, Zn, U, Au) may eventually prove to be economic by-products, and others may be useful in helping to understand depositional environments (e.g., B) and to correlate coal seams (5,6).

In early studies of trace elements in coal (7-11), coal ash was analyzed using emission spectroscopy. Recent studies (3,4,12,13) have employed quantitative multi-element instrumental methods. Because a particular analytical technique is better suited for certain elements than for others, a combination of methods is usually necessary to determine all elements of interest. Methods for determining trace elements in coal must be accurate and precise. In addition, if possible, they should determine a large number of elements of interest simultaneously, require relatively little sample preparation, be capable of automation, produce an output compatible with computerized data processing, and be rapid.

Trace element concentrations in coal show variations from a microscopic to a worldwide scale. From a resource evaluation perspective, the most significant variations occur within and between coal basins. The rest of the paper will discuss factors that cause these variations.

DISCUSSION

Ash Related Variations

The amount of ash in a coal is a major factor influencing trace element content. In general, trace element concentrations increase as ash content increases. This relationship reflects the fact that most inorganic elements in coal are associated with minerals (5). Figures 1 and 2 illustrate this relationship for K in eastern Kentucky coals and for Ti in coals from the Uinta Region.

The above relationship also holds when comparing trace element concentrations among coal basins. Table I compares trace element data for coals from the Black Mesa Field, the Powder River Region, and the San Juan Region. As shown in Table I, the concentrations of the following elements increase as the ash contents of the coals increase: Si, Al, Na, K, Cu, Th, V, Li, Pb, and Se. The reason for the variation of these elements with ash content is that most are, or were, associated with the silicate (detrital) minerals brought into the depositional basins during the formation of the coals. Chemical alteration of minerals within the coal basin can remobilize some elements, which then precipitate as authigenic nonsilicate minerals, e.g., Cu and Pb, as sulfides or selenides (14). The good correlation between element concentration and ash content indicates that most elements have remained within the coal basin despite remobilization (15).

Table I. Concentrations of Selected Elements in Coal Samples from Black Mesa, Powder River, and San Juan Regions¹

	<u>Black Mesa</u>	<u>Powder River</u>	<u>San Juan</u>
Ash, %	8.0	9.9	21.1
Si, %	1.1	1.5	5.4
Al, %	0.69	0.78	2.7
Ca, %	0.78	1.1	0.67
Mg, %	0.1	0.2	0.1
Na, %	0.09	0.1	0.2
K, %	0.04	0.05	0.16
Fe, %	0.31	0.54	0.54
Ti, %	0.05	0.04	0.11
Cu, ppm	5.5	11.2	13.3
Th, ppm	2.2	4.3	5.9
Zn, ppm	5.6	20	15.1
Cr, ppm	3	7	5
Ni, ppm	2	5	3
V, ppm	7	15	20
Mn, ppm	9.7	51	29
Li, ppm	3.9	5.9	19.7
Pb, ppm	2.7	5.6	13.1
Se, ppm	1.6	1.7	2
Ba, ppm	300	300	300
Sr, ppm	150	200	100
Nb, ppm	1.5	1.5	3
Zr, ppm	15	15	50

¹Data from Reference 4; results are calculated on a moisture-free coal basis (mf coal).

Elements not increasing in concentration with ash content are generally those with (a) organic affinities (Ca, Mg, Sr, Ba); (b) sulfide affinities (Fe, Zn); (c) carbonate affinities (Ca, Mn, Mg); or (d) sulfate affinities (Ba, Sr, Ca). Sulfides, carbonates, and sulfates are generally epigenetic phases. Presence of these phases affects element concentration more than ash content. The concentrations of Zr and Nb would be expected to increase with ash content. The reason that this

behavior is not apparent in Table I may be the poor resolution of the technique (semiquantitative spectrographic analysis) used to obtain the data.

Rank-Related Variations

Several elements exhibit a distinct variation in concentration with coal rank. Table II illustrates the general decrease in concentration of alkaline-earth elements (Mg, Ca, Sr, Ba), Na, and B with increasing coal rank. It is generally accepted that these elements are associated with organic functional groups (e.g., carboxylic acids) in low-rank coals. With increasing coal rank, these groups are destroyed, thus displacing organically associated inorganic trace elements.

Table II. Rank-Related Variations¹

	<u>Anthracite</u>	<u>Bituminous</u>	<u>Subbituminous</u>	<u>Lignite</u>
Ca, %	0.07	0.33	0.78	1.2
Mg, %	0.06	0.08	0.18	0.31
Na, %	0.05	0.04	0.10	0.21
B, ppm	10	50	70	100
Ba, ppm	100	100	300	300
Sr, ppm	100	100	100	300

¹Data from Reference 1; mf coal.

Organic association has been proposed for other trace elements, such as Be, Sb, Ge, U, and some halogens (3,16). Finkelman (15) suggests that organic association of these elements is significant mainly for low-rank, low-ash coals.

Concentrations of organically bound elements in coal can decrease with increasing amount of detritus (Figure 3). Also, note that the concentrations of boron decrease with increasing ash contents (Table I).

Variations Due to Geochemical Factors

Geochemical factors, such as Eh and pH during and subsequent to coal formation, can have dramatic effects on trace element contents. The effect of these geochemical factors can be seen in Table III, in which selected data for Appalachian and Interior Province coals are compared. Coals from both areas are similar in rank and ash content, but the Interior Province coals have significantly higher contents of all six trace elements. The higher content of Ca is perhaps due to carbonate mineralization (high pH), whereas that of Fe, Cd, Pb, and Zn is attributable to sulfide mineralization (low Eh). The higher content of B is perhaps attributable to greater marine influence (high salinity).

Table III. Concentrations of Selected Elements in Coal Samples from Appalachian and Interior Coal Basins

	<u>Appalachian</u> ¹	<u>Interior</u> ²
Ash, %	13.3	15.7
Ca, %	0.12	1.2
Fe, %	1.9	3.3
Cd, ppm	0.7	7.1
Pb, ppm	15.3	55
Zn, ppm	20	373
B, ppm	30	100

¹Data from Reference 2; mf coal.

²Data from Reference 4; mf coal.

The occurrence of cleat-filling sphalerite and galena in the Interior Province coals is a classic example of how epigenetic mineralization can affect trace element content (17). Dramatic intra- and interseam variations are common. Cobb (18) reports that zinc content from benches of the Herrin (No. 6) coal varied from 20 to 14,900 ppm.

Variations Due to Geologic Factors

Ash chemistry is another important factor affecting trace element variations. Its influence is, however, generally more subtle than the other factors. In Table IV the trace element contents are compared for Appalachian Province coals and Wasatch Plateau coals. Both are bituminous coals with similar ash contents and rank. However, with a few exceptions, the trace element contents of the Wasatch coals are lower than those of Appalachian coals. The lower content of chalcophile elements in Wasatch coals may be due to a lower pyrite content. The lower concentration of lithophile elements (e.g., Li, Zr, Nb, Th, Sc, Y) but higher Si content may reflect a higher quartz content in the detrital component of Wasatch coals; this, in turn, may be a reflection of differences in the mineralogy of the source rocks.

Table IV. Concentrations of Selected Elements in Coal Samples from Appalachian Province and Wasatch Coal Field

	<u>Appalachian</u> ¹	<u>Wasatch</u> ²
Ash, %	13.3	11.3
Ca, %	0.2	0.41
Fe, %	1.9	0.26
Cd, ppm	0.7	0.06
Li, ppm	27.6	16
Pb, ppm	15.3	5.8
U, ppm	1.4	1.2
Zn, ppm	20	11
B, ppm	30	100
Nb, ppm	5	0.3
Ni, ppm	15	5
Zr, ppm	50	30
As, ppm	27	0.8
Cu, ppm	24	9.3
F, ppm	80	67
Th, ppm	4.9	1.8
Ba, ppm	100	70
Co, ppm	7	1.5
Cr, ppm	20	10
Mo, ppm	3	0.7
Sc, ppm	5	3
V, ppm	20	15
Y, ppm	10	7

¹Data from Reference 6; mf coal.

²Data from Reference 19; mf coal.

Other Factors Affecting Trace Element Content

Other factors that could modify the ash chemistry or the availability of trace elements include the salinity of waters in contact with the coal or peat, the type of chemical weathering process (arid vs. humid), and hydrologic conditions (Br and Cl may be especially sensitive to this factor). In general, these factors are still poorly understood.

CONCLUDING COMMENTS

In this paper, we made several broad generalizations regarding factors that influence trace element variations. We urge that in interpretative work these generalizations be applied carefully.

A critical evaluation of existing trace element data would probably result in identification of anomalous values and elimination of suspect data. Several questions might be answered by such an evaluation; for example, do the two K values in the high-ash region of Figure 1 deviate significantly from the trend of the other data because of analytical errors or recording errors? Are they legitimate geochemical anomalies? We encourage analytical chemists and geologists to interact closely because this is one of the best ways to improve the quality of analytical methodology and data, and geological interpretation.

The nature of trace element variations, for whatever cause, highlights the need to more judiciously select representative samples for reliable quantitative analyses.

Statistical techniques, such as principal component analysis, should help in resolving the influence of the factors affecting trace element variations in coal.

It is hoped that this paper will encourage more detailed study of factors influencing trace element variations in coals.

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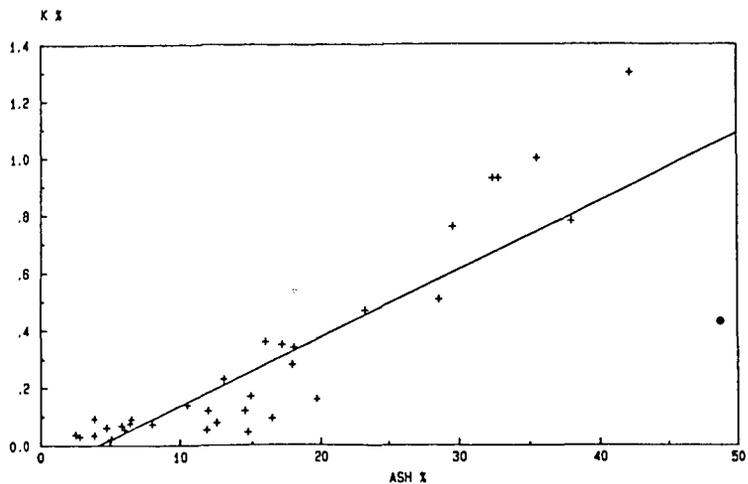


Figure 1. Relationship between K concentration in the coal and ash content for 34 coals from eastern Kentucky. $R = 0.86$. Data from Reference 1.

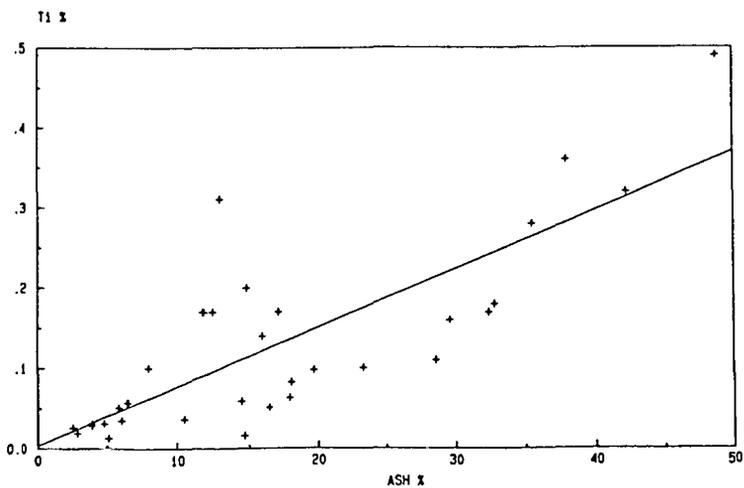


Figure 2. Relationship between Ti concentration in the coal and ash content for 26 coals from the Uinta Region. $R = 0.86$. Data from Reference 1.

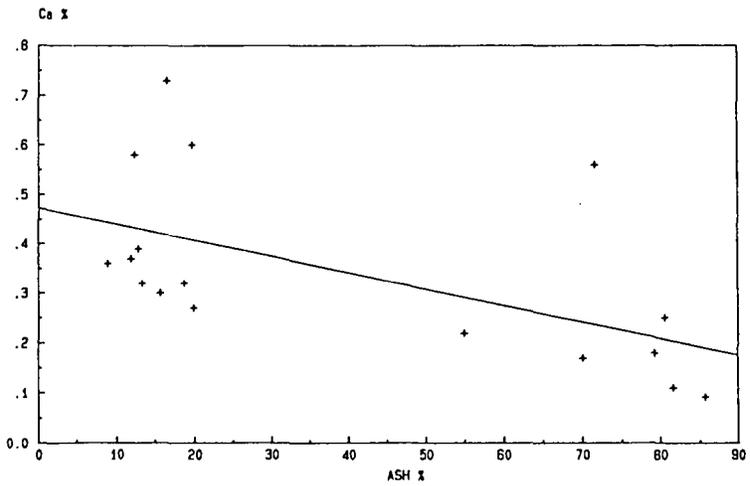


Figure 3. Relationship between Ca concentration in the coal and ash content for 17 coals and shales from the Emery Coal Field. $R = -0.57$. Data from Reference 18.

ELEMENTAL DISTRIBUTION AND ASSOCIATION WITH INORGANIC AND ORGANIC COMPONENTS IN TWO NORTH DAKOTA LIGNITES

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Introduction

The associations of major, minor, and trace elements in lignite-bearing strata of the Fort Union Region present a challenge in understanding their geochemical relationships and history. In an earlier work (1), the spatial patterns of elemental distribution within a lignite-bearing sequence were examined and were related to factors of accumulation of vast amounts of plant materials and to the depositional and post-depositional influx of inorganic matter. Lignite-bearing sediments, including the lignite, lignite overburden, and underclay, were sampled from two beds, the Kinneman Creek and the Beulah-Zap, which are part of the Sentinel Butte Formation of North Dakota. These samples were examined to determine the spatial patterns of elemental distribution within the lignite seam, modes of elemental occurrence, and organic/inorganic affinities of the inorganic constituents.

The inorganic constituents within lignites from the Fort Union Region have been classified as being very heterogeneous (2), which leads some investigators to believe that the study of geochemical relationships is futile. The modes of occurrences of the elements are generally similar from one mine to another within the Fort Union Region lignites (3). The inorganic matter in the lignites is distributed as adsorbed ions on the organic acid groups, coordinated species, detrital minerals, and authigenic minerals. The distribution of elements is determined by natural processes, and, therefore, is expected to be systematic even though complex.

The methods to qualitatively identify the interrelationships of major, minor, and trace elements include examining the spatial patterns of distribution of elements within a stratigraphic sequence (1), consideration of results of chemical fractionation procedures (4), and evaluation of organic/inorganic affinities (5,6). The spatial pattern of elemental distribution was correlated with the chemical fractionation behavior, organic/inorganic affinities, and ionic potentials of elements to infer the association or combination of associations an element may have within these coals.

Methods and Procedures

The samples were collected from freshly exposed faces within open pit mines. The lignite, lignite overburden, and underclay were collected from two pits at the Beulah Mine where lignite is mined from the Beulah-Zap seam. Samples were also collected from the Kinneman Creek seam in the Center mine. The sample collection procedures have been summarized by Karner (7) and Benson (8). Bulk channel samples were also collected and homogenized to provide large quantities for additional experiments.

The lignite samples collected at various intervals within the stratigraphic sequence were subjected to the following analyses: proximate, ultimate, heating value, ash analysis, and trace element analysis by neutron activation analysis (NAA) (9) and x-ray fluorescence (10). Minerals in the coal and the associated sediments were determined by x-ray diffraction and by scanning electron microscopy and electron microprobe analysis. A split from the bulk sample was examined by chemical

fractionation to selectively extract inorganic constituents based on how they are bound in the coal. Briefly, the chemical fractionation procedure involves extracting the coal with 1M ammonium acetate to remove soluble and ion-exchangeable inorganic components. The coal is subsequently extracted with 1M hydrochloric acid to remove elements present as carbonates, oxides, or coordinated species. The extracts and residues from the chemical fractionation procedure are analyzed by a combination of NAA, XRF, inductively coupled argon plasma (ICAP), and atomic absorption spectroscopy (AA).

Results and Discussion

The major, minor, and trace element determinations along with locations within the seams and lithology of the stratigraphic sequence are summarized in Tables I and II for the Beulah coals. The data from Center Mine stratigraphic sequence was summarized in a previous report by Karner and others (1).

In previous work (1), the spatial distribution of elemental constituents has been described as fitting into several patterns: 1) concentration at one or both margins, 2) even distribution, and 3) regular patterns. The various ways inorganic constituents accumulated in the lignite during and after deposition affect where certain elements will concentrate within the seam. The detrital constituents carried in by wind and water will most likely be enriched near the margins of the coal seam. Included in this group of inorganic constituents are clay minerals, quartz, and volcanic ash. Solutions containing ions flowing through the lignite can exchange with the coal matrix and precipitate as stable authigenic phases. Inorganic constituents are also present in the original plant material that was deposited. Even patterns of elemental distribution are characteristic of organically bound elements. Irregular distribution patterns are characteristic of concentrated occurrences of authigenic minerals.

Table I includes data from two seams within the south Beulah mine. Table II summarizes the data from a high-sodium pit (Orange Pit) of the Beulah mine. The Center mine data used in this work was reported by Karner and others (1).

In this study, the spatial patterns of enrichment and depletion of major, minor, and trace elements have been expanded to include four categories: 1) even distribution, 2) enrichment at margins (top, bottom, or both), 3) enrichment at the center of the seam, and 4) irregular. The patterns of enrichment and depletion are listed in Table III for Beulah and Center mine lignite seams.

The bulk coals were subjected to chemical fractionation analysis (3) which can be used to categorize how a particular element is associated in the coal. The elemental associations within the coal were divided into three categories: 1) ion-exchangeable, 2) acid-soluble, and 3) residual. The elements are associated in the coal in one or more of the groups described above. The categories for the elements are listed in Table III.

The organic and inorganic affinities of elemental constituents have been determined by a number of investigators (5,6). The relationship between the concentration of an element in moisture-free coal and the ash content can be used as a guide to the affinity of that element for, or incorporation in, the mineral matter or the carbonaceous material. If the concentration of an element increases with increasing ash content that element may be characterized as being associated with the inorganic species that form ash, or in other words may be said to have an inorganic affinity. If the concentration shows no correlation with ash content, that element may be said to have an organic affinity. Linear least squares correlation coefficients were calculated for the concentrations of the elements versus the ash content. For example, organic and inorganic affinities for elements from the Center mine indicate the following affinities. Seven elements - Na, Ca, Mn, Br, Sr, Y, and Ba - had correlation coefficients below 0.200 and thus show organic affinity in this suite of samples. An additional seven elements - Mg, K, Cu, As, Rb, Ce, and Eu - had correlation coefficients ranging from 0.201 to 0.600

and may be associated with both the carbonaceous and mineral portions of the coal. The remaining 24 elements show inorganic affinity.

The ionic potentials of all the elements, Z/r , where Z is the ionic charge and r is the ionic radius, are summarized in Table III. The ionic potentials of elements have a large effect on the association of the element in mineral-forming processes (13). Elements having low ionic potential ($Z/r < 3$), such as sodium, magnesium, and calcium, associate as hydrated cations. Insoluble hydrolysates have ionic potential of $3 < Z/r < 12$, which include, for example, the elements aluminum, silica, and titanium.

The elements displaying an even distribution within the coal seams have the following characteristics: 1) ion-exchangeable, 2) organic affinity or both organic and inorganic, and 3) ionic potential less than 3. The elements that are included in this group are Na, Mg, Ca, Mn, Sr, and Ba. Slight variations in distribution patterns and chemical fractionation behavior may be indicated; these generalizations were made on the basis of average trends. The elements showing enrichment of the margins in the lignite seams display the following characteristics: 1) chemical fractionation suggests association with the acid soluble and residue portions or, in some cases, distribution in all three groups, 2) inorganic affinity, and 3) ionic potential $3 < Z/r < 12$. The elements that have these characteristics include Al, Si, Cl, K, Sc, Ti, V, Cr, Co, Br, Zr, Ra, Cs, La, Ce, Sm, Eu, Yb, Th, and U. These elements are primarily associated with detrital constituents. The elements that have a random or irregular distribution within the coal seams, for the most part, have the following characteristics: 1) chemical fractionation behavior which suggests that the elements are insoluble and remain in the residue, 2) inorganic affinity, and 3) formation by authigenic mineralization. The elements included in this group are Fe, Ni, Zn, As, Se, Cd, and Sb. The irregular distribution of these elements is the result of syngenetic and epigenetic mineralization in the formation of sulfides. All of these elements have chalcophilic characteristics.

The possible associations of the elements included in this study are given in Table IV which summarizes distribution patterns, chemical fractionation behavior, organic and inorganic affinities, and ionic potential.

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Table I. Elemental Analysis of a Stratigraphic Sequence Containing Two Lignite Seams at the Beulah Mine, North Dakota, part per million unless otherwise indicated, dry coal basis

ID	Lithology	Height, m*	Ash, % [†]	Na	Mg	Al	Si**	P**	S**	Cl	K	Ca	Sc	Ti
3-1-A	Underclay	-0.3	--	1964	10364	84699	321178	436	2803	750	10062	3398	11.7	3574
3-2-A	Lignite	0.0	17.0	7767	722	8394	19572	679	17182	100	530	6888	11.9	829
3-3-A	Lignite	0.1	8.47	14348	678	1935	5068	332	10142	8	500	6101	2.1	207
3-4-A	Lignite	0.5	7.30	3479	642	2584	3139	286	8302	100	500	7249	4.9	100
3-5-A	Lignite	0.9	22.20	753	1598	27082	34145	387	13513	100	1908	2191	10.6	438
3-6-A	Clay	1.0	--	1821	13741	113270	298737	0	8009	750	13269	3720	15.0	4211
3-7-A	Clay	1.6	--	2159	12454	111945	307620	0	3204	750	13585	2559	16.1	4560
2-1-A	Lignite	1.7	10.80	3991	671	9428	10956	282	8823	16	500	7062	10.8	125
2-2-A	Lignite	2.1	7.20	7497	707	5192	3971	471	7698	100	500	5281	0.9	119
2-3-A	Lignite	2.6	7.60	9482	717	4542	5045	364	8522	100	713	6206	0.8	140
2-5-A	Lignite	2.9	7.10	6598	731	3431	3086	0	8046	100	500	6031	1.7	226
2-6-A	Lignite	3.3	7.40	6988	571	3886	4981	355	9720	100	500	3973	0.5	59
2-7-A	Lignite	3.4	5.60	6692	564	2664	11048	122	3453	24	500	4615	0.3	100
2-8-A	Lignite	3.6	15.28	6583	3386	7312	10072	800	20071	100	500	8261	0.8	502
2-10-A	Lignite	4.2	6.40	5907	472	4308	5475	223	6561	100	500	12635	2.4	77
2-11-A	Lignite	4.8	12.0	5631	1242	7557	12398	366	10476	100	500	8927	6.1	121
2-13-A	Top of Lignite	5.1	9.10	5561	914	5937	5360	436	10823	100	500	6423	11.5	196
2-14-A	Clay	5.2	--	3518	16012	118373	290790	436	4405	750	16692	4520	15.5	3647
2-15-A	Clay	6.3	--	4385	14031	88995	293127	0	1201	750	15654	4983	13.9	3630
2-16-A	Silt	7.3	--	3440	14605	88403	288453	0	2803	750	9177	2880	12.0	3082
2-17-A	Chert	7.5	--	464	3800	13052	56100	0	9211	1250	1000	1709	12.1	1000
2-18-A	Sandstone	7.8	--	4084	9826	49621	250117	0	2803	750	7608	27085	8.3	2426
2-19-A	Clay	8.9	--	1771	14771	81163	287518	436	4405	750	4162	6110	14.5	4017

Table I. Elemental Analysis of a Stratigraphic Sequence Containing Two Lignite Seams at the Beulah Mine, North Dakota, part per million unless otherwise indicated, dry coal basis (Continued)

ID	Lithology	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Se	Br	Ru	Cd	Sb
3-1-A	Underclay	99	66	177	24853	5.9	>25	150	66	2.51	0.20	1.10	86.00	2.50	0.65
3-2-A	Lignite	66	37	44	15358	5.5	>20	58	19	21.8	1.42	1.70	12.00	1.00	4.61
3-3-A	Lignite	4	5	42	6580	4.0	9	10	25	22.5	0.69	4.98	5.00	1.00	0.05
3-4-A	Lignite	6	6.5	40	2561	1.7	>25	11	25	2.17	0.55	1.69	5.00	1.00	0.04
3-5-A	Lignite	148	39	57	26129	13.0	90	25	9	374	4.28	3.28	16.00	1.00	5.74
3-6-A	Clay	205	91	96	15258	18.0	95	150	30	24.1	0.20	0.77	108.00	1.00	1.78
3-7-A	Clay	181	94	98	11929	2.7	>25	150	94	6.66	4.12	0.76	126.00	2.50	1.35
2-1-A	Lignite	25	16	36	3100	1.9	>25	52	33	11.5	0.43	1.73	3.26	1.20	1.33
2-2-A	Lignite	3	2.8	41	1502	1.2	>25	25	8	3.55	0.10	1.18	5.00	1.00	0.12
2-3-A	Lignite	2	2.9	46	1467	1.1	>25	25	25	5.18	0.52	1.25	5.00	1.00	1.28
2-5-A	Lignite	5	3.1	46	1489	0.7	>25	48	0	2.22	1.00	1.29	5.00	1.00	0.04
2-6-A	Lignite	3	2.5	31	6193	1.0	>25	25	30	31.5	0.39	0.45	1.42	0.65	0.01
2-7-A	Lignite	1	1.3	36	1035	1.1	>25	25	25	0.66	0.32	0.53	5.00	1.00	0.03
2-8-A	Lignite	1	4.4	58	2928	0.6	>25	25	25	4.37	0.59	0.46	5.00	1.00	0.21
2-10-A	Lignite	6	8.6	27	8711	5.2	>25	25	20	21.2	1.27	0.55	5.18	1.00	0.34
2-11-A	Lignite	5	6.5	79	2821	1.5	7	25	19	3.45	0.56	1.24	5.00	1.00	0.29
2-13-A	Top of Lignite	34	9.3	70	2405	3.0	10	10	25	7.03	0.20	1.16	5.00	1.00	0.60
2-14-A	Clay	177	81	212	22282	17.0	121	150	30	14.8	0.20	0.50	115.00	2.50	1.52
2-15-A	Clay	144	64	735	27448	12.0	15	150	30	2.63	0.20	0.50	90.00	2.50	1.04
2-16-A	Silt	136	56	1000	28123	11.0	>20	150	30	2.75	0.20	0.89	77.80	2.50	0.63
2-17-A	Chert	73	18.9	8046	273475	2.7	>25	300	200	0.50	0.20	0.89	10.00	2.50	0.49
2-18-A	Sandstone	73	55	611	15853	8.6	>20	150	52	6.09	0.54	0.25	50.64	2.50	0.19
2-19-A	Clay	134	68	738	35592	12.0	>20	150	30	2.48	3.22	1.12	87.00	2.50	0.73

Table 1. Elemental Analysis of a Stratigraphic Sequence Containing Two Lignite Seams at the Beulah Mine, North Dakota, part per million unless otherwise indicated, dry coal basis (Continued)

ID	Lithology	Cs	Ba	La	Ce	Sm	Eu	Yb	U
3-1-A	Underclay	4.96	786	32.18	48.66	2.51	1.36	1.59	1.91
3-2-A	Lignite	5.50	746	8.07	19.81	1.31	0.71	2.22	2.09
3-3-A	Lignite	0.02	756	1.29	8.46	1.42	0.36	1.37	0.50
3-4-A	Lignite	0.05	1114	2.95	9.21	1.04	0.46	1.62	0.23
3-5-A	Lignite	4.56	683	45.36	71.90	8.29	1.95	1.38	3.32
3-6-A	Clay	8.10	676	45.36	41.00	2.45	1.13	1.20	3.32
3-7-A	Clay	10.00	644	36.00	45.32	2.58	0.98	1.60	2.34
2-1-A	Lignite	1.49	1005	2.49	8.32	1.05	0.49	1.41	1.86
2-2-A	Lignite	0.05	988	9.75	14.35	0.52	0.21	0.40	0.41
2-3-A	Lignite	0.05	1158	3.75	6.98	0.35	0.12	0.38	0.36
2-5-A	Lignite	0.05	1284	11.36	16.00	0.43	0.11	0.41	0.56
2-6-A	Lignite	0.16	844	0.84	1.00	0.17	0.07	0.11	0.23
2-7-A	Lignite	0.12	1041	0.58	1.66	0.17	0.06	0.07	0.10
2-8-A	Lignite	0.05	21	2.07	4.08	0.42	0.26	0.63	0.50
2-10-A	Lignite	1.15	3045	7.47	39.27	0.63	0.55	0.42	0.24
2-11-A	Lignite	0.34	1749	4.06	9.69	0.81	0.37	1.11	0.90
2-13-A	Top of Lignite	0.02	226	3.52	6.77	0.82	0.43	1.39	2.08
2-14-A	Clay	8.50	811	36.20	52.50	2.73	1.11	1.72	2.88
2-15-A	Clay	5.31	813	35.00	45.61	3.28	1.30	1.83	1.82
2-16-A	Silt	4.35	613	28.00	39.00	2.54	1.06	1.17	2.30
2-17-A	Chert	4.00	274	11.60	10.00	1.27	0.40	1.09	0.20
2-18-A	Sandstone	3.00	725	26.70	37.00	2.65	1.18	1.26	1.54
2-19-A	Clay	5.28	851	25.60	46.70	2.63	1.43	1.81	1.75

*Height from base of first seam.

**Determined by x-ray fluorescence.

†Ash on a moisture-free basis

Table II. Elemental Analysis of a Stratigraphic Sequence Containing One Lignite Seam from the Orange Pit of the Beulah Mine, North Dakota, ppm (dry basis)

ID	Lithology	Height, m*	Ash, %	Na	Mg	Al	Si**	S**	Cl	K	Ca	Sc	Ti	V
B-1	Lignite	-0.5	7.1	7041	1041	2824	10800	65890	44.3	500	7317	2.16	132	3.02
B-2	Lignite	0.00	6.8	5178	1004	3107	12950	46240	43.9	500	9072	0.64	132	2.84
B-3	Lignite	0.50	6.7	5833	1150	3472	7940	50030	52.8	500	8891	0.57	138	2.73
B-4	Lignite	1.00	6.8	6018	1043	2675	16760	51530	41.8	500	7803	0.57	144	2.22
B-5	Lignite	1.50	13.0	5826	3526	6710	12580	65160	132.7	500	8016	0.38	326	5.84
B-6	Lignite	2.00	6.9	5313	1238	2793	39940	59750	49.2	500	7828	0.36	150	2.20
B-7	Lignite	2.50	8.5	6169	1292	4348	93000	64240	63.2	500	11998	0.43	162	2.50
B-8	Lignite	3.00	15.7	6278	1449	5869	44510	64020	70.9	500	10872	0.48	167	2.12
B-9	Lignite	3.50	10.4	5096	1483	7929	104700	56470	54.1	500	11876	1.05	226	4.85
BR-1	Overburden	3.60	--	2246	15718	91958	275900	3130	750	9724	7094	15	2390	136.00
BR-3	Overburden	4.14	--	2773	13226	89901	259700	1100	750	14994	6673	18	4256	165.00
BR-5	Overburden	4.80	--	3098	15480	97158	281400	497	100	8653	7342	16	3880	158.00
BR-6	Overburden	5.10	--	2619	15475	84833	288900	1480	100	10800	6197	5.1	3674	134.00
BR-9	Overburden	6.10	--	2389	16774	88663	294000	1350	750	14971	9553	15.8	4557	142.00
BR-11	Overburden	6.70	--	2082	9982	51610	187700	3220	750	14971	9465	18.7	2760	119.00
BR-13	Overburden	7.30	--	2842	12634	66743	277400	12710	750	6441	12042	8.97	3796	80.1
BR-13A	Overburden	7.35	--	3028	14339	78427	284900	840	150	8994	123401	12.9	4131	117.0
BR-18	Overburden	8.90	--	3028	12471	75153	286200	1070	750	8994	13916	14.0	4360	117.0
BR-19	Overburden	9.20	--	2863	12793	78030	290700	<100	750	10006	14862	14.0	3451	117.0

Table II. Elemental Analysis of a Stratigraphic Sequence Containing One Lignite Seam from the Orange Pit of the Beulah Mine, North Dakota, ppm (dry basis) (Continued)

ID	Lithology	Cr	Mn	Fe	Co	Ni	Cu**	Zn	As	Se	Br	Sr**	Y**	Zr**
B-1	Lignite	2.24	22	5147	1.68	5.75	53	12.62	10.67	0.05	1.62	360	6	8
B-2	Lignite	1.62	28	3261	0.75	10.23	33	5.48	3.90	0.40	1.40	445	6	11
B-3	Lignite	1.41	29	3462	0.70	10.71	53	6.08	3.52	0.39	1.49	480	4	13
B-4	Lignite	1.37	28	3289	0.39	13.17	58	4.78	3.34	0.50	1.04	410	2	9
B-5	Lignite	2.08	136	22202	0.37	5.00	23	25.00	27.18	0.91	0.84	320	2	<5
B-6	Lignite	1.89	37	3308	0.80	15.34	64	25.00	5.24	0.54	0.99	360	2	8
B-7	Lignite	2.30	33	1706	0.59	11.36	59	3.46	3.55	0.49	0.55	520	2	15
B-8	Lignite	2.60	48	30530	0.69	15.66	30	25.00	39.17	0.79	0.81	330	2	10
B-9	Lignite	3.51	47	2897	0.70	9.36	62	8.57	7.85	0.36	0.92	520	6	17
BR-1	Overburden	86.2	611	36878	14.02	28.88	86	30.00	12.66	1.56	0.92	262	26	112
BR-3	Overburden	93.2	2092	50756	13.57	72.84	73	30.00	2.50	0.57	1.05	223	28	94
BR-5	Overburden	92.4	467	30865	10.97	22.93	87	30.00	5.25	1.40	0.27	239	26	109
BR-6	Overburden	32.4	979	14308	3.99	95.69	81	25.00	6.23	0.42	0.55	234	31	126
BR-9	Overburden	88.0	885	39106	13.78	63.45	84	30.00	3.52	1.25	0.92	230	25	108
BR-11	Overburden	72.3	3542	147377	11.26	39.66	46	30.00	2.50	0.20	1.07	104	18	66
BR-13	Overburden	63.0	308	36902	10.14	50.09	64	30.00	27.16	1.01	1.41	255	22	169
BR-13A	Overburden	78.7	424	26437	9.95	20.00	71	30.00	5.01	0.84	1.46	274	28	165
BR-18	Overburden	90.8	670	31472	11.33	45.09	80	30.00	5.01	0.53	1.46	285	25	131
BR-19	Overburden	90.8	435	28566	11.44	36.64	73	30.00	3.34	1.08	1.08	265	27	164

Table II. Elemental Analysis of a Stratigraphic Sequence Containing One Lignite Seam from the Orange Pit of the Beulah Mine, North Dakota, ppm (dry basis) (Continued)

10	Lithology	Ru	Ag	Cd	Sb	Cs	Ba	La	Ce	Sm	Eu	Yb	Th	U
B-1	Lignite	2.00	0.15	5.00	0.01	0.01	714	7.84	8.30	0.53	0.11	0.36	0.57	0.40
B-2	Lignite	1.37	0.53	5.00	0.04	0.04	917	3.30	5.61	0.49	0.09	0.28	0.75	0.24
B-3	Lignite	2.00	0.48	5.00	0.10	0.03	943	3.62	6.39	0.43	0.06	0.24	0.81	0.23
B-4	Lignite	2.00	0.79	0.34	0.10	0.03	844	3.24	4.92	0.24	0.05	0.09	0.83	0.75
B-5	Lignite	2.00	0.05	1.10	0.07	0.01	930	12.78	13.14	0.34	0.03	0.01	0.78	0.40
B-6	Lignite	2.00	0.53	0.19	0.01	0.03	704	0.98	2.42	0.26	0.01	0.06	0.49	0.31
B-7	Lignite	2.00	0.75	5.00	0.06	0.03	1138	1.52	3.18	0.31	0.05	0.09	1.01	0.56
B-8	Lignite	2.00	0.37	1.87	0.04	0.05	1242	2.20	9.98	0.28	0.07	0.08	1.12	1.26
B-9	Lignite	2.00	0.15	5.00	0.22	0.08	720	2.38	4.97	0.55	0.12	0.38	1.75	0.99
BR-1	Overburden	114.48	0.08	2.50	0.44	6.57	1075	12.19	63.46	1.17	1.30	1.07	10.37	1.51
BR-3	Overburden	131.48	0.08	2.50	0.50	7.56	732	14.58	67.26	1.23	1.29	1.77	10.14	1.03
BR-5	Overburden	164.19	0.08	2.50	0.49	7.53	685	13.82	61.24	1.25	1.12	1.33	9.50	0.80
BR-6	Overburden	35.87	0.49	5.00	0.51	0.79	285	12.70	18.50	1.26	0.31	0.73	3.26	0.76
BR-9	Overburden	127.44	0.08	2.50	0.38	6.38	567	12.31	61.70	1.12	1.33	1.59	9.39	1.09
BR-11	Overburden	77.75	0.00	2.50	0.69	4.50	401	16.88	82.93	1.59	1.37	1.46	7.02	2.99
BR-13	Overburden	72.16	0.08	2.50	0.40	3.39	444	12.36	69.63	1.15	1.26	1.15	7.84	1.12
BR-13A	Overburden	108.76	20.08	2.50	0.38	4.53	619	14.57	63.00	1.28	1.35	1.50	9.35	0.80
BR-18	Overburden	101.83	0.08	2.50	0.38	5.10	567	14.00	63.00	1.35	1.43	1.52	9.45	1.27
BR-19	Overburden	94.82	0.08	2.50	0.30	4.69	511	13.55	64.46	1.22	1.46	1.71	10.18	1.13

*Height from base of first seam.

**Determined by x-ray fluorescence.

† Ash on a moisture-free basis

Table III. Qualitative Geochemical Relationships Between Geochemical Properties and Elemental Distribution Within Seams

	Distribution Within Lignite Seams at the Beulah Mine				Distribution Within Lignite Seam at the Center Mine				
	Beulah Orange Pit	Upper Seam	Lower Seam	Chemical Fractionation Behavior	Affinity	Center	Chemical Fractionation Behavior*	Affinity	Ionic Potential Z/r
Na	E	E	CE	IE	Organic	E	IE	Organic	1.0
Mg	E	E	E	IE	NC	E	IE>>AS	NC	3.0
Al	T-MA	MA	B-MA	AS, RS	Inorganic	MA	AS, RS	Inorganic	5.9
Si	T-MA	IR	E	RS	Inorganic	MA	RS	Inorganic	9.5
P	ND	IR	B-MA	ND	Inorganic	IR	ND	Inorganic	14.3
S	IR	IR	MA	RS, IE	Organic	MA	RS, IE	Organic	17.1
Cl	E	E	E	ND	NC	B-MA	ND	Inorganic	
K	E	E	E	RS, AS	Inorganic	B-MA	IE, AS, RS	Inorganic	0.13
Ca	E	CE	E	IE, AS	NC	E	IE, AS	NC	2.0
Sc	MA	MA	MA	RS, AS	NC	MA	AS, RS	Inorganic	3.7
Ti	T-MA	IR	B-MA	RS	Inorganic	B-MA	RS	Inorganic	5.9
V	E	MA	B-MA	AS	NC	B-MA	AS, RS	Inorganic	4.0
Cr	MA	MA	B-MA	RS	Inorganic	B-MA	RS	Inorganic	4.8
Mn	E	T-MA	T-MA	AS, IE	NC	E	AS, IE	NC	2.5/6.7
Fe	IR	IR	B-MA	RS, AS	Inorganic	MA	AS	Inorganic	2.7/4.7
Co	B-MA	ND	ND	AS, RS	Inorganic	MA	AS, RS	Inorganic	2.8
Ni	IR	E	MA	RS	Inorganic	MA	RS	Inorganic	3.0
Cu	IR	E	B-MA	ND	Inorganic	B-MA	RS	Inorganic	1.0/2.8
Zn	IR	ND	ND	RS	Inorganic	MA	ND	Inorganic	.88/2.7
Ge	ND	ND	ND	ND	ND	B-MA	ND	ND	2.7/7.5
As	IR	IR	IR	RS	Inorganic	B-MA	RS	NC	10.8
Se	CE	IR	B-MA	RS	Inorganic	B-MA	RS, IE	Inorganic	14.3
Br	B-MA	MA	CE	ND	NC	ND	ND	Organic	
Rb	ND	ND	ND	ND	ND	IR	RS, AS	ND	0.68
Sr	E	ND	ND	IE	Organic	E	IE	Organic	1.8
Y	MA	ND	ND	ND	ND	IR	ND	ND	3.4
Zr	T-MA	ND	ND	RS	ND	MA	ND	Inorganic	5.1
Ru	E	E	B-MA	ND	Inorganic	B-MA	ND	Inorganic	6.0
Ag	IR	ND	ND	ND	ND	MA	ND	Inorganic	2.2
Cd	ND	E	E	RS	NC	IR	ND	Inorganic	.87/2.1
Sb	IR	B-MA	B-MA	RS	Inorganic	B-MA	AS, RS	Inorganic	4.0
Cs	T-MA	B-MA	B-MA	RS	Inorganic	B-MA	RS	Inorganic	0.6
Ba	E	T-MA	T-MA	IE, AS	NC	MA	IE, AS	NC	1.5
La	B-MA	IR	MA	AS, RS	Inorganic	B-MA	AS, RS	Inorganic	2.6
Ce	B-MA	IR	B-MA	AS, RS	Inorganic	MA	AS, RS	NC	2.9
Sm	MA	MA	E	AS, RS	Inorganic	MA	AS	Inorganic	3.1
Eu	MA	MA	MA	AS, RS	Inorganic	MA	AS	NC	3.2
Yb	MA	MA	MA	AS, RS	NC	MA	MA	Inorganic	
Th	T-MA	MA	B-MA	RS	Inorganic	MA	RS	Inorganic	3.9
U	T-MA	MA	B-MA	AS, RS	Inorganic	MA	AS, RS	Inorganic	4.2

Patterns of Distribution

- E - Even Distribution
- MA - Enrichment at both margin
- T-MA - Enrichment at top margin
- B-MA - Enrichment at bottom margin
- CE - Enrichment at the center of the seam
- IR - Irregular

*Chemical Fractionation Behavior

- IE - Ion-exchangeable
- AS - Acid soluble
- RS - Remains in the residue
- NC - No Correlation
- ND - Not Determined

Table IV. Association of Elements in North Dakota Lignites

<u>Element</u>	<u>Possible Association</u>
Na	- Organically bound
Mg	- Organically bound, carbonates
Al	- Clay minerals, possibly hydroxide or coordinated
Si	- Clay minerals, quartz
P	- Organically bound, phosphates*, associated with rare earth elements
S	- Sulfides, sulfates, organically bound
Cl	- Inorganic association
K	- Associated with illite and other k-bearing minerals, organically bound
Ca	- Organically bound, carbonates
Sc	- Inorganic association, clay minerals
Ti	- Rutile, associated with quartz
V	- Possibly has both an organic and inorganic association
Cr	- Totally an inorganic association
Mn	- Organically bound, carbonate minerals
Fe	- Oxides, hydroxides, sulfides
Co	- Inorganic association, possibly sulfides
Ni	- Inorganic association, possibly sulfides
Zn	- Inorganic association, possible sulfides
As	- Inorganic association, possible sulfides
Se	- Inorganic association, possibly sulfides
Br	- May have an organic association
Rb	- Organically bound
Sr	- Organically bound
Y	- Inorganic association, possibly carbonates
Zr	- Zircon
Ru	- Inorganic
Ag	- Inorganic, possibly sulfides
Cd	- Inorganic, possibly sulfides
Ba	- Organic, sulfates
La	- Detrital inorganic, phosphates*
Ce	- Detrital inorganic, phosphates*
Sm	- Detrital inorganic
Eu	- Detrital inorganic
Yb	- Detrital inorganic
Th	- Detrital inorganic
U	- Detrital inorganic

*Monazite has been found in Beulah lignite samples (12).

VOLCANIC ASH LAYERS IN COAL: ORIGIN, DISTRIBUTION, COMPOSITION AND SIGNIFICANCE

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INTRODUCTION

The main purpose of this paper is to call attention to volcanic eruptions as a source of mineral matter in coal. Volcanic material is apt to have mineral and chemical compositions as well as patterns of distribution different from the more usual types of mineral matter in coal. Recognition of volcanic material requires some understanding of the process of origin, an awareness of the considerable variety of materials involved, and an appreciation of the tendency of volcanic materials to undergo substantial alteration so that their genesis is obscured.

Some comments on terminology are necessary. "Volcanic ash partings" here refers to sedimentary units bounded by organic-rich material (coal, lignite, or organic shale) and which were deposited as air-fall volcanic ash with essentially no subsequent transport or mixing with terrigenous detrital silicates (clay, mud and sand). No specific grain size or composition is implied. The term "tephra" is now commonly used for modern, unaltered, uncompacted material, while the term "tuff" is used for the compacted (rock) equivalent.

A volcanic origin is obvious where there is glass, volcanic phenocrysts, characteristic mineralogy, or absence of terrigenous detritus and lack of sedimentary structures formed by moving water. With increasing age, however, there is progressive alteration and loss of recognizable volcanic features; the product is generally some kind of clay unit. As a general term they might be called altered tuffs. In marine shales they are known as bentonites; these are usually montmorillonitic (smectitic), light-colored, and sticky when wet. In coals, particularly Carboniferous coals, they are usually kaolinitic, light-colored and firm. We prefer the general term "altered volcanic ash" because there is considerable range in physical appearance, original and secondary mineralogy, as well as in the type of enclosing sediment.

ORIGIN

Volcanic ash partings in coals should not be surprising. The recent eruption of Mt. St. Helens spread volcanic ash across several western states and traces of the dust traveled around the world. Consider, however, where a recognizable layer of this ash is likely to be preserved. On land, almost all of it will be eroded by wind and water, mixed with terrigenous sand and clay, and ultimately dispersed into lakes or the ocean. An important exception is to be found in marshes or swamps, the general setting in which plant material accumulates to eventually become coal. Once deposited in a coal swamp, an ash fall has a good chance of

remaining undisturbed because the shallow water, low stream gradients, lack of relief, and sediment baffling effects of vegetation minimize processes that could cause reworking. Portions of such swamps may be so distant from major streams that they receive little or no mud from over-bank floods. Thus it is likely that some ash falls would be buried in organic debris (coal) and remain free of non-volcanic material from fluvial sources.

It follows then that there is a genetic relationship between volcanic ash partings and the coals that contain them: environments of coal deposition provide one of the best places for preservation of air-fall volcanic materials.

Not all kinds of volcanic ash have the same chance of such preservation, however. Many volcanoes, such as those in Hawaii, are characterized by relatively quiet eruptions of mostly fluid lava. Though spectacular on a human scale, these involve only minor injection of fine-grained material into the upper atmosphere where it can be carried long distances by prevailing winds. Only volcanoes characterized by particularly violent eruptive styles are likely to be important in producing the thin, widespread units of ash most commonly preserved in the geologic record. The explosiveness of eruptions is related to several factors, including gas content and geometry of the vent. Of most importance here, however, is silica content: silica increases the viscosity of magma and the tendency toward explosive eruptions rather than quiet flows. Thus volcanic ash partings in coals are primarily the product of such silica-rich eruptions; this has important consequences in terms of the composition of the ash, as will be discussed later.

FIELD APPEARANCE OF VOLCANIC ASH PARTINGS IN COALS

Most volcanic ash partings are thin, ranging from 1 mm to a few cm. A few, however, attain thicknesses of more than 1 m. Some are uniform in thickness and have either sharp or gradational boundaries with the enclosing coal. Many, however, pinch and swell rapidly and may consist of a series of lenses rather than continuous beds, a feature they share with Carboniferous tonsteins (Williamson, 1970). Light shades of gray, brown, or yellow are most common, reflecting a lower organic content than the adjacent coal. Black and dark brown partings also occur, and sometimes these become obvious only after weathering; the oxidation of organic matter then results in a light-colored surface layer of siliceous material. Figure 1 shows the most common field appearance; in this case for a Cretaceous example from southern Alaska.

To a large extent the grain size and degree of induration of these partings depends upon the amount of post-depositional alteration; this in turn is largely a function of age and depth of burial. For example, lignites almost 4-5 m.y. old in southern Alaska contain partings that are loose and sandy; in fact they are clearly recognizable volcanic ash consisting mostly of glass shards. In contrast, 300 m.y. old partings in Kentucky bituminous coal are hard and very fine grained. The latter probably was similar to the Alaskan example at first, but has completely altered to a compact variety of kaolin known as flint clay.

COMPOSITION

Composition of the partings is a function of both the original materials and conditions, and the kind and extent of post-depositional modification. Therefore it is necessary to consider the primary composition (original) separately from the secondary composition (altered).

Primary Composition

The solid products of explosive volcanism include individual glass fragments, individual crystals (phenocrysts), and aggregates of these known as rock fragments. Glass is perhaps the most common component but there is a great variety among modern volcanics. A given volcano may eject different material over its eruptive lifespan. Even a single eruption, lasting perhaps only a few days, may involve changes in ash composition.

Volcanic ashes are characterized by a limited suite of mineral components. By far the most abundant are quartz, sanidine and plagioclase feldspars, certain pyroxenes and amphiboles, magnetite, apatite, biotite, and zircon. The presence of these minerals and the absence of others constitute evidence of a volcanic origin. Certain crystal forms, such as the beta form of quartz and hexagonal prisms of biotite, are particularly useful indicators of origin. Similarly, the presence of sanidine, the high-temperature form of potassium feldspar, suggests a volcanic origin. On the other hand, the presence of non-volcanic minerals such as muscovite and garnet indicates a non-volcanic origin or at least some admixture of non-volcanic (probably fluvial) material.

The specific minerals present reflect the original compositions of the magma. As noted earlier, explosive behavior, the kind most likely to produce ash partings in coals, is characteristic of silica-rich magmas. Thus the minerals cited above, and those to be expected in volcanic ash partings, are those associated with silica-rich magmas. The glass phase will, of course, also reflect this silica-rich tendency.

Original grain size of an ash parting reflects the texture of the material produced by a given volcano plus the progressive loss of coarser and denser components as an ash cloud moves downwind. In other words, texture is in part a function of distance from the source volcano. By far the most common ash partings in coal are thin, uniform and widespread. These probably were derived from distant volcanoes and consisted originally of silt- and clay-sized particles carried by high-altitude winds. Conversely, where ash partings are coarse-grained, thick, and abundant, the volcanic source is assumed to have been relatively close.

Secondary Composition

The primary composition discussed above is important here in that it determines in part the final products of alteration. It should be noted, however, that the factors controlling the degree and direction of alteration have not been thoroughly studied. In our opinion, chemical alteration in the environment of deposition and the length of time involved are probably more important than original composition in determining the final product.

The main secondary products are clay minerals, either smectite or kaolinite. These clay minerals are derived mainly and most readily from glass, but feldspars, amphiboles, pyroxenes, and biotite also alter in part to clay minerals. The alteration to kaolinite involves essentially complete removal of soluble components such as Na, Ca, Mg, K and Fe as well as considerable silica. Pure kaolinite consists of equal parts of silica and alumina and virtually nothing else--this is thus the product of very intensive leaching. Smectite on the other hand requires some Mg and more silica; it is thus the product of less intensive leaching than that which produces kaolinite.

It is uncertain whether the path of alteration can lead directly to kaolinite or must pass through a smectite intermediate stage. Certainly the thickness of the original ash can play a role: thin partings may be altered completely to kaolinite while adjacent thicker partings contain substantial smectite (Triplehorn and Bohor, 1981; Reinink-Smith, 1982). Given more time and further leaching, these smectitic partings presumably would eventually be altered to kaolinite. On the other hand, individual minerals such as feldspars and biotite can be observed altering directly to kaolinite without any smectite involvement.

A variety of other secondary minerals may occur in altered volcanic ash partings. Some of these may be related to modification of the primary constituents but others are more likely introduced by ground water taking advantage of the higher permeabilities of volcanic ash layers relative to the adjacent organic material (now coal). Carbonate minerals in quantities too large to have been derived entirely from the primary volcanic material are not uncommon. Siderite is most abundant although dolomite sometimes is present. Such cementation may obscure the volcanic origin of the original layer because well cemented partings are similar in appearance to the purely sedimentary carbonate layers that are very commonly associated with coals.

Recently occurrences of unusual aluminum phosphate minerals have been found with ash partings in coals (Triplehorn and Bohor, 1983). Since that report we have found a number of occurrences in Alaska and one in the Appalachian area. These minerals were grouped by Palache et al. (1951) as the plumbogummite series, with the general formula $X \text{ Al}_2(\text{PO}_4)_2(\text{OH})_5 \cdot \text{H}_2\text{O}$. End members of interest here include qoyazite (where $X = \text{Sr}$), gorcunite (Ba), crandallite (Ca), and florencite (Ce, U, and other rare earths). Some layers in Alaska are sufficiently radioactive to give a distinct reading on hand-held radiation detectors in the field.

DISTRIBUTION

Because many geologists are not aware that volcanic ash partings occur in coals it is difficult to interpret the absence of published reports regarding their occurrences. The abundance of such partings is probably much greater than presently recognized. The following generalities regarding their distribution are mainly limited to North America and are based primarily on our own observations, discussions with others, and interpretation of published reports. Specific references to recognized volcanic ash partings in coals are relatively few and restricted mostly to the past few years.

In simple terms ash partings are relatively abundant in Cretaceous and Tertiary coals of the West and rare in Carboniferous coals of the East. We are less certain of the Gulf Coast Tertiary lignites but they appear to have at least a moderate abundance of such partings. To a degree this apparent distribution is related to the fact that the volcanic origin of the younger ash beds is more apparent, while older partings commonly appear as kaolinitic clay beds with little evidence of their volcanic heritage (see Bohor and Triplehorn, 1981). Even so, there is no question that the absolute frequency is higher in the West.

Locally the abundance can be highly variable. Where many coals are present ash partings may be distributed sparsely but uniformly or concentrated in just a few coals. Figure 2 shows an example in Southwestern Washington, in this case including both kaolinitic and smectitic partings (Reinink-Smith, 1982). In the West, where most of our work has been, volcanic ash partings are known from numerous coals in Utah, New Mexico, Colorado, Wyoming, Montana and Washington (Bohor, *et al.* 1978; Triplehorn and Bohor, 1981). Again, the frequency is highly variable. Individual coals in Montana and Colorado contain up to twenty or more ash partings, while the unusually thick coals of the Powder River Basin contain almost none. In Alaska, volcanic ash partings are present in all of the Cretaceous and Tertiary coals we have examined, but appear to be particularly abundant in the Cook Inlet area.

In the Appalachian coal basin and the Eastern Interior Basin, where we have had less experience, ash partings appear to be rare (Bohor and Triplehorn, 1982). The lack of ash partings in Carboniferous coals of eastern North America contrasts with their abundance in European coals of the same age. These have been studied for over a century although their volcanic origin was not generally accepted until the last few decades. Bouroz, *et al.* (1983) provides a good recent summary of some of this work in English.

SIGNIFICANCE

The geologic importance of volcanic ash partings in coals has been summarized previously by Triplehorn (1976). Of greatest importance is their use in correlation, the process of determining the time relationships among rocks exposed at different localities. The simplest use is as marker beds, where individual ash falls can be recognized and distinguished from others on the basis of some textural or compositional aspect. Beds containing the same ash layer (whether in coal or any other rock type) are the same age, although the absolute age (in years) is not indicated. Happily, the absolute age can sometimes be determined by radiometric age dating of certain minerals in the ashes. Potassium-argon dating is used for such minerals as feldspar and hornblende, while fission-track dating may be used for zircon and apatite.

It may be of interest here to note that Williamson (1970) mentioned the high radioactivity of certain ash partings (he called them tonsteins) that made them useful in bore-hole studies because they appeared as sharp maxima on gamma-ray logs of coal beds. Such maxima are conspicuous because coals are generally known for their absence of radioactivity.

He ascribed the high radioactivity of these partings to an unusual abundance of zircons. We have no specific knowledge of these occurrences, but suggest that the high radioactivity might instead be related to uranium-bearing phosphate minerals.

Thus far geologists have paid little attention to the significance of ash partings as indicators of processes and conditions in the coal-forming environment. For example, thin widespread partings without penetrating plant material suggest that these originated as ashes that fell into shallow standing water. Thick ashes should have affected the kind and amount of vegetation, and indirectly the nature of the coal immediately overlying thick ash beds. As yet there is little data in these aspects because geologists have not recognized the potential value of such studies.

For those interested in mineral matter in coal an awareness that some partings may be of volcanic origin may be useful in explaining the distribution of some of these layers and the occurrences of some unusual components, such as strontium, phosphate, or uranium. Volcanic ash partings are likely to be more widespread and uniform in texture, composition and thickness than the more common partings of fluvial origin. They are also more likely to show marked differences from layer to layer, and more likely to contain exotic mineral or chemical components.

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Figure 1. Light weathering kaolinite volcanic ash in coal, southern Alaska.



Figure 2. Multiple smectitic and kaolinitic ash partings in the Big Seam, southeastern Washington.

REACTIONS AND TRANSFORMATIONS OF COAL MINERAL
MATTER AT ELEVATED TEMPERATURES

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Introduction

Coal contains a variety of inorganic constituents that exhibit deleterious behavior in most processes that attempt to convert the energy in coal to a useful form. As coal is heated, the inorganic phases undergo transformations and reactions that yield a complex mixture of solid, molten, and volatile species. These species give rise to slagging and fouling deposits, corrosion, pollution, and other problems. Although such problems are usually associated with the combustion of coal to produce electrical power, they are also common in coal gasification and liquefaction, cokemaking, and iron production.

The current paper will briefly review research on this topic.

Nature of the Inorganic Constituents of Coal

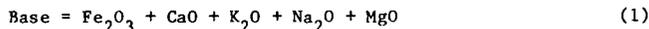
It is common practice to make a distinction between the inorganic constituents of so-called "Eastern" and "Western" coals. By definition, Western coals are those for which the CaO+MgO content exceeds the Fe₂O₃ content of the ash, while the reverse is true for Eastern coals. The inorganic constituents in Eastern coals, which are principally bituminous in rank, are predominantly in the form of discrete mineral particles. Clay minerals (kaolinite, illite) are usually dominant, followed by quartz and pyrite. The range and typical values of the mineral distribution and ash chemistry of Eastern coals are shown in Table I. These data were determined from computer-controlled scanning electron microscopy (CCSEM), Mössbauer spectroscopy, and other measurements on over a hundred coals.

Western coals are usually lignites or subbituminous coals. The range and typical values of the inorganic phase distribution and ash chemistry of approximately 20 Western coals examined in this laboratory are shown in Table II. In a recent paper, we discussed the differences between the inorganic constituents of low-rank coals and those of bituminous coals. These differences occur in the calcium-, iron-, and alkali-containing phases. In bituminous coals, the calcium content is typically low (CaO <5% of ash) and all calcium is contained in the mineral, calcite. The calcium content of lignites is high (CaO ~10 to 30% of ash) and the calcium is molecularly dispersed throughout the coal macerals as salts of carboxylic acids. The latter point has been directly confirmed by EXAFS (extended X-ray absorption fine structure) spectroscopy. Similar differences occur for the alkali elements. Minerals such as illite, which accounts for most of the potassium in bituminous coal, are usually low in lignite and subbituminous coal (see Tables I and II). In lignites, sodium and potassium are believed to occur as salts of humic or carboxylic acids. Montmorillonite and halite (NaCl) are the dominant Na-containing minerals, and they occur in both bituminous and lower rank coal. The iron-bearing minerals in unoxidized bituminous coals include pyrite, ferrous-bearing clays (illite, chlorite), and carbonates (siderite, ankerite). In lignites, only pyrite and its weathering products (iron sulfates and oxyhydroxides) are normally observed.

The diversity of transformations and reactions that such complex assemblages of inorganic matter can undergo when coal is combusted or otherwise converted to a more useful form of energy is too complex to be discussed in any detail in a short article. Our intention, therefore, is simply to outline some of the major phenomena and to provide the reader with useful references. Most of the article will deal with reactions and transformations related to coal combustion, with a short section devoted to other conversion processes.

Slagging Behavior; Ash Melting

During pulverized-coal combustion, atmospheric conditions within the coal flame are considered to be reducing in the sense that the stable ionic form of iron is ferrous. After ash particles have left the flame region, they encounter a more oxidizing environment, yielding deposits and fly ash in which the iron may be predominantly ferric or a mixture of ferrous and ferric, dependent on the air-to-fuel ratio. Consequently, it is important to understand the high temperature reactions of ash constituents in both types of environment. This point is recognized in the ASTM ash-fusion test⁵⁾ which specifies measurement of the fusion temperatures of ash cones in both a reducing (60% CO, 40% CO₂) and an oxidizing (air) atmosphere. Numerous empirical formulae have been developed to predict ash-fusion temperatures (AFTs) and the viscosities of molten coal-ash slags at higher temperatures from ash composition. Detailed discussions of these formulae and their physical basis have been given by Winegartner and his associates,^{1,6,7)} by Watt and Fereday,^{8,9)} and in a recent review article by Reid.¹⁰⁾ The dominant parameter in these relationships is usually the base-to-acid ratio, where "base" and "acid" are simply the sums of the weight percentages of the basic and acidic oxides:



Recently, we examined the behavior of ash fusion temperatures in the context of ternary phase diagrams.¹¹⁾ Significant similarities were observed between the dependence of AFTs on chemical composition and the liquidus curves in appropriate regions of the FeO-SiO₂-Al₂O₃, CaO-SiO₂-Al₂O₃, and K₂O-SiO₂-Al₂O₃ phase diagrams. The development of the Base-SiO₂-Al₂O₃ phase diagrams for the prediction of ash behavior appears to be a fruitful area for future research. An example of such a phase diagram is shown in Figure 1 where ash-softening temperatures (ST, reducing) are plotted in what is effectively the "mullite" region of a Base-SiO₂-Al₂O₃ phase diagram. The curves of equal ST exhibit great similarity to the liquidus curves in true ternary diagrams.

The arrow in Figure 1 illustrates the use of the phase diagram to predict STs. In this instance, a bituminous coal with a low ST was blended with two other coals to yield a product with a much higher ST. The blend was chosen with the aim of moving the composition of ash in a direction approximately normal to the equal ST curves. The predicted and observed STs of the original coal and the blend are shown in the inset of Figure 1. The predicted values are probably not as accurate as could be obtained with existing empirical formulae,⁶⁾ but they are nevertheless quite reasonable.

Ternary and more complex phase diagrams can also contribute to interpretation of the reactions that lead to ash melting. In a reducing environment

(60%CO-40%CO₂), the important reactions for Eastern coals occur primarily within the FeO-SiO₂-Al₂O₃ phase diagram.^{13,14} Using a variety of techniques [Mossbauer spectroscopy, computer-controlled scanning electron microscopy (CCSEM), X-ray diffraction (XRD)] to investigate quenched ash samples heat treated under conditions similar to the ASTM ash-fusion test, it was established that most Eastern coal ashes exhibit behavior similar to that shown in the schematic diagram of Figure 2. Here, phases that are molten at elevated temperatures appear as glass phases in the quenched specimens. The potassium-containing clay mineral, illite, appears to be the first phase converted to a partially molten form; presumably this is because of the numerous low-temperature eutectic points in the K₂O-SiO₂-Al₂O₃ phase diagram.¹² At approximately 900°C, wustite, derived from pyrite and other iron-rich minerals, begins to react with quartz and aluminosilicates derived from clay minerals to produce a mixture of wustite, fayalite (Fe₂SiO₄), and ferrous-containing melt phase. At somewhat higher temperatures (~1050°C), fayalite has been largely incorporated into the melt phase, and ferrous iron may react with aluminosilicates to form hercynite (FeAl₂O₄). This reaction retards melting somewhat and its importance is related to the Al₂O₃ content of the ash. Essentially all of the iron is contained in the melt phase for samples quenched from above 1200°C, as shown in Figure 3. Above 1200°C, reducing, most Eastern ashes (%Base <30%) are a mixture of molten aluminosilicates, mullite, quartz, and minor constituents such as iron sulfide, which is also molten, but is immiscible with the viscous silicate melt.

Similar, but less extensive experiments have also been performed on ash samples quenched from high temperatures in air.¹³ Below approximately 1200°C, essentially all of the glass observed in the samples is derived from the potassium-bearing clay mineral illite. Melting accelerates above approximately 1300°C and approaches completion for most Eastern ashes at temperatures of the order of 1500°C. In an oxidizing environment, calcium appears to be a more effective flux than ferric iron.

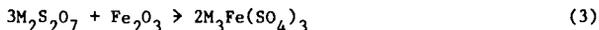
In both reducing and oxidizing atmospheres, significant partial melting of ash occurs at temperatures well below the initial deformation temperature (IDT). It is not uncommon to observe up to 50 percent of the ash in the form of glass at quenching temperatures as low as 200 to 400°C below the IDT. Such partial melting is important in deposit formation. Not surprisingly, the amount of glass observed at a given temperature in an oxidizing atmosphere is significantly less than that in a reducing atmosphere.^{13,14}

Fouling; Volatile Species

Fouling generally refers to the formation of deposits on convective heat-transfer surfaces at relatively low temperatures (600 to 1000°C). Excellent discussions of this problem have recently been given by Wibberly and Wall¹⁵ and in the general review article by Reid.¹⁰ Alkali elements (Na, K) are the principal culprits in the formation of such deposits. Within the flame, these elements become volatilized. The ease of volatilization is related to the form in which the alkalis are present in the coal. Organically bound alkalies would be expected to be easily volatilized at typical flame temperatures (1400-1500°C), as would NaCl, the most common form of sodium in bituminous coal. Potassium contained in illite would not be expected to volatilize as readily; illite should rapidly convert to a molten slag at these temperatures. For this reason, the water-soluble alkali content of coal is considered to be a more reliable indicator of fouling than the total alkali content, at least for Eastern coals. Wibberly and Wall¹⁵ list Na, NaOH, and NaCl as likely gaseous species, dependent on chlorine content of

the coal, flame temperature, and oxygen potential. Nonchloride species are probably rapidly converted to oxides (Na_2O , K_2O) on leaving the flame front. The volatile alkalis may condense on the surfaces of fly-ash particles carried by the flue gas or on cooler boiler surfaces. Wibberly and Wall¹⁵⁾ performed drop-tube experiments in which silica particles were exposed to synthetic combustion gases containing sodium at temperatures of 1200 to 1600°C. Sodium silicate layers ranging in thickness from 0.03 to 0.3 μm were observed on the particle surfaces, and sintered deposits formed rapidly on stainless steel probes inserted into the lower part of the furnace. Such alkali-silicate layers are molten at the temperatures of interest. The thickness of the sodium silicate layers was decreased by a factor of three when the sodium was introduced in the form of NaCl , rather than in chlorine-free forms.

An excellent review of the role of alkali sulfates is given by Reid.¹⁰⁾ Below 1100°C, alkali oxides and chlorides react rapidly with SO_2 and O_2 or SO_3 to form condensed sulfates on fly-ash particles and metal surfaces. Because of their low melting points, alkali sulfates are very corrosive, and form strongly bonded deposits. The melting points of the most easily formed sulfates, Na_2SO_4 and K_2SO_4 , are 882°C and 1075°C, respectively, and the minimum melting point of Na_2SO_4 - K_2SO_4 mixtures is 833°C. K_2SO_4 - CaSO_4 and Na_2SO_4 - CaSO_4 are also commonly observed mixtures, which exhibit melting points in the range from 870 to 970°C. If the SO_3 content of the atmosphere is sufficiently high, the pyrosulfates, $\text{K}_2\text{S}_2\text{O}_7$ and $\text{Na}_2\text{S}_2\text{O}_7$, may be formed from K_2SO_4 and Na_2SO_4 . These phases melt at very low temperatures: 400°C for $\text{Na}_2\text{S}_2\text{O}_7$ and 300°C for $\text{K}_2\text{S}_2\text{O}_7$. Crossley¹⁶⁾ has suggested that rapid metal wastage is caused by the reaction of the pyrosulfates with Fe_2O_3 to form low-melting point (<600°C) alkali-iron trisulfates:



where $\text{M} = \text{Na}$ or K . This point of view is supported by the work of Coats et al.¹⁷⁾ which established that liquid melts containing up to 90 percent pyrosulfate can be formed from Na_2SO_4 - K_2SO_4 mixtures in SO_3 pressures of 100 to 300 ppm at temperatures down to 335°C. Such SO_3 levels¹⁰⁾ can be readily reached via catalytic oxidation of SO_2 in the presence of Fe_2O_3 .

CCSEM analyses of fouling deposits from a boiler furnace in which a North Dakota lignite had been fired are given in Table III. Although the deposits consisted principally of calcium-enriched aluminosilicates, they also contained small but significant amounts of alkali sulfates, intermixed with calcium sulfate. Recently, we conducted potassium K-edge X-ray absorption spectroscopy (XAS) measurements on one of these samples at the Stanford Synchrotron Radiation Laboratory. The X-ray absorption near-edge structure, or XANES, shown in Figure 4, is nearly identical to that of a $\text{K}_2\text{S}_2\text{O}_7$ standard sample. It appears that XAS will be a very useful method of investigating the structure of individual elements in complex deposits.

Reactions and Transformations of Interest for Other Coal Conversion Processes

In this section, examples of the high-temperature behavior of inorganic phases in other conversion processes will be given.

Liquefaction - Montano et al.¹⁸⁾ have investigated the transformation of pyrite to pyrrhotite in coal liquefaction environments. They conducted in situ Mossbauer

spectroscopy measurements on coals maintained at 1.24 MPa nitrogen pressure and observed changes in the isomer shift at approximately 300°C that signalled the beginning of the transformation of pyrite to pyrrhotite. The transformation accelerated between 300 and 400°C, and from 20 to 80 percent of the pyrite in four different coals was transformed after one hour at 440°C. From close examination of both the in situ spectra and the spectra of cooled residues, they concluded that the pyrrhotite underwent covalent bonding to the coal molecules, causing a catalytic effect on coal liquefaction.

Carbonization - When coal is heated to temperatures ~900 to 1200°C in the absence of air, most of the volatile matter is driven off, leaving a char, or, in the case of metallurgical bituminous coal, a coke. The atmosphere in a coke oven consists principally of hydrogen and methane. Consequently, pyrite is reduced to a mixture of iron sulfide (troilite and pyrrhotite) and iron metal. The amount of iron metal formed depends on both the temperature and the composition of the coke-oven gas. The reduction of iron sulfide to iron metal is desirable since blast furnace operation is more efficient with low sulfur coke. Calcite reacts with the liberated sulfur to form calcium sulfate, thus retaining sulfur in the coke. In Figure 5, the calcium XANES spectrum of a coke produced from a Pittsburgh seam coal in which all calcium was initially present as calcite is shown. The spectrum establishes that approximately 70 percent of the calcite was converted to calcium sulfate during coking.

Gasification

Iron exhibits a great diversity of reactions at elevated temperatures when the reaction environment encompasses both reducing and oxidizing conditions at different stages of the process. For example, it is not unusual to observe five or six different iron-bearing compounds in three different oxidation states in char and ash samples obtained from coal-gasification systems. In Figure 6, the Mossbauer spectrum of a char residue from a bench-scale gasification system at the Institute of Gas Technology is shown. The input atmosphere to the gasifier was approximately 5.2% O₂, 21.2% H₂O, and the remainder N₂, and the average temperature was 1800°F. As indicated in Figure 6, six iron-bearing phases exhibiting three different oxidation states are observed: iron metal, iron sulfide (principally FeS), fayalite (Fe₂SiO₄), magnetite (Fe₃O₄), hematite (Fe₂O₃), glass, wustite, and possibly other minor phases. A more detailed discussion of this work has been given by Mason et al.

Conclusions

Even from this brief overview, it is clear that much remains to be done in the area of understanding mineral-matter behavior in coal combustion and other conversion technologies and even more in combating the sticky problems arising from this component in coal. In particular, we feel there is a great need for much more detailed investigations of full-scale technological processes, especially now that a number of relatively new and sophisticated techniques are available that can be used to characterize mineral-matter related phenomena in ways that were not possible a few years ago. Such techniques include Mossbauer and EXAFS spectroscopies, which we have highlighted in this article, that have the ability to focus on specific critical elements (Fe, K, S, etc.), and reveal very detailed information about the behavior of that element. However, the observed phenomena in full-scale processes will also need to be interpreted in terms of both kinetic (e.g., drop-tube experiments) and thermodynamic (e.g., phase diagram analysis) approaches, as

well as to take into account the form of the mineral matter and its distribution in the original coal. These areas, we feel, should be important areas for research on mineral-matter related problems in the immediate future.

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Table 1
Inorganic Constituents of Eastern Coals

Mineral Distribution			Typical Ash Chemistry	
Mineral	Range	Typical	Species	Weight %
Quartz	5-44	18	SiO ₂	54
Kaolinite	9-60	32	Al ₂ O ₃	29
Illite	2-29	14	Fe ₂ O ₃	8
Chlorite	0-15	2	CaO	2
Mixed Silicates	5-31	17	MgO	1
Pyrite	1-27	8	K ₂ O	2
Calcite	0-14	3	Na ₂ O	1
Siderite/Ankerite	0-11	2	TiO ₂	1
Other Minerals	0-12	4	P ₂ O ₅	0.2
			SO ₃	2

Table II
Inorganic Constituents of Western Coals

Mineral Distribution			Typical Ash Chemistry	
Mineral	Range	Typical	Species	Weight %
Quartz	7-22	15	SiO ₂	30
Kaolinite	13-45	30	Al ₂ O ₃	15
Illite	0-12	2	Fe ₂ O ₃	10
Mixed Silicates	0-22	8	CaO	20
Pyrite	1-26	7	MgO	8
Fe Sulfates	0-5	1	K ₂ O	0.7
Fe-rich*	0-14	2	NaO	0.6
Ca-rich**	7-49	25	TiO ₂	0.7
Other minerals***	1-10	7	P ₂ O ₅	0.4
			SO ₃	15

*Principally iron oxyhydroxide.

**Principally calcium bonded to carboxyl groups in the macerals.

***Barite, apatite, montmorillonite, and others.

Table III

CCSEM Analyses of Fouling Deposits

<u>CCSEM Category</u>	<u>Sec. Superheater, 990-1050°C</u>	<u>Preheater 750°C</u>
Ca-rich aluminosilicate*	55	63
Ca- and Fe-rich aluminosilicate**	7	6
Alkali sulfate***	2	2
Calcium sulfate + alkali sulfate	4	6
SiO ₂	3	2
Ca-rich	10	6
Hematite	2	1
Ca-Fe ferrite	2	1
Ca-Mg sulfate	3	2
Al-Si rich	5	2
Unidentified, mixed phases	7	5

*Approximate average composition (mole %) determined from CCSEM energy dispersive X-ray fluorescence spectra was 37% Ca, 8% Mg, 4% Fe, 41% Si, 10% Al.

**Average composition - 31% Ca, 7% Mg, 21% Fe, 32% Si, 9% Al.

***Average composition - Na₃₃Ca₁₆K₃S₄₈.

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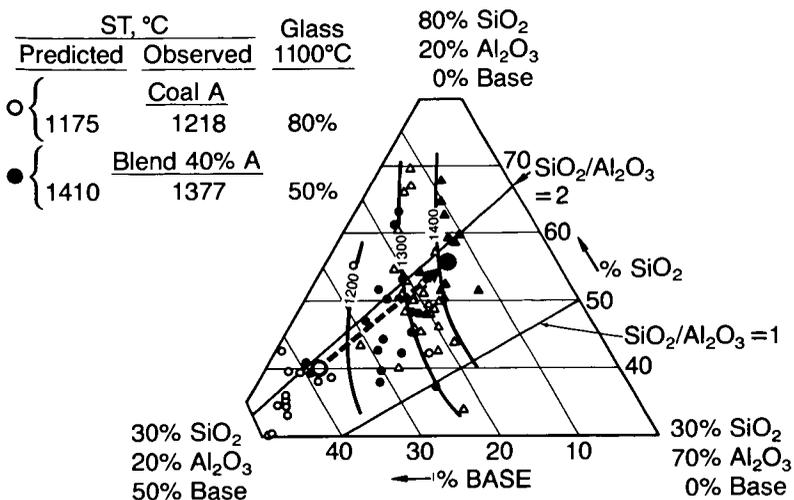


Figure 1 Pseudoternary phase diagram (Base - Al_2O_3 - SiO_2) showing spherical temperature (ST) contours. See text for discussion of points connected by arrow.

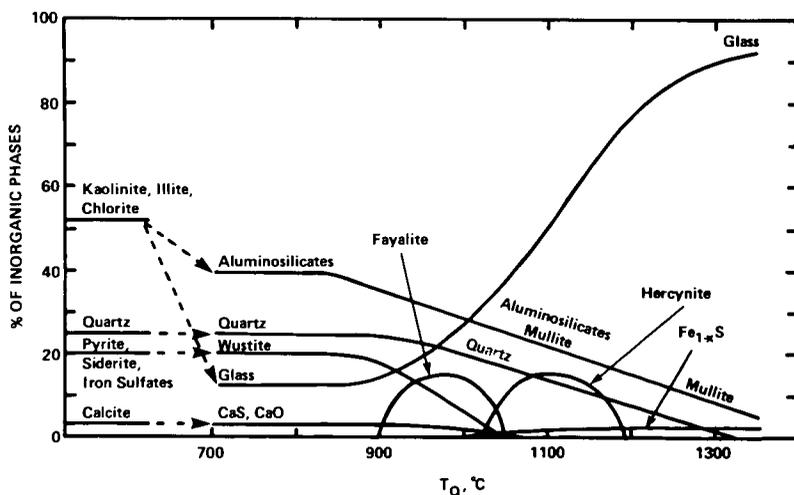


Figure 2 Schematic diagram illustrating high-temperature reactions for minerals in an Eastern-type coal under reducing conditions.

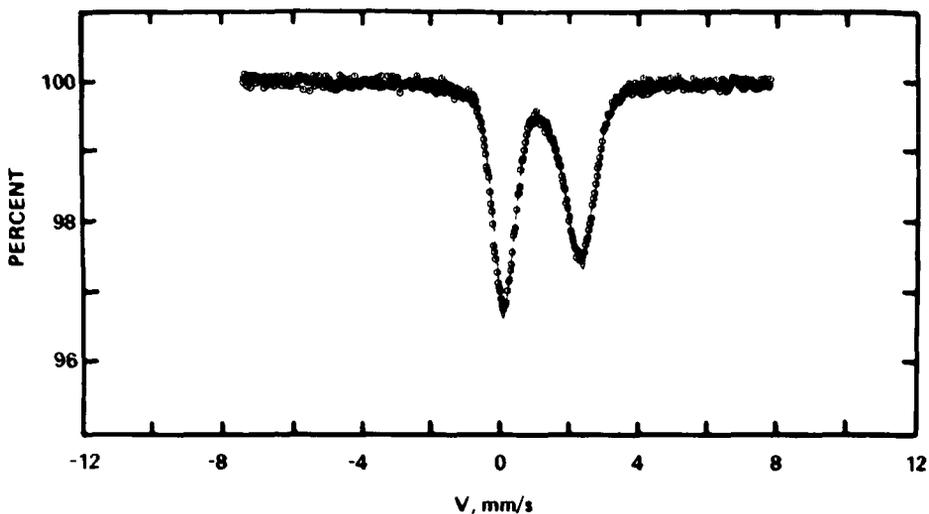


Figure 3 Mössbauer spectrum of Somerset C ash quenched from 1260°C under reducing conditions. Absorption derives entirely from Fe^{2+} in glass.

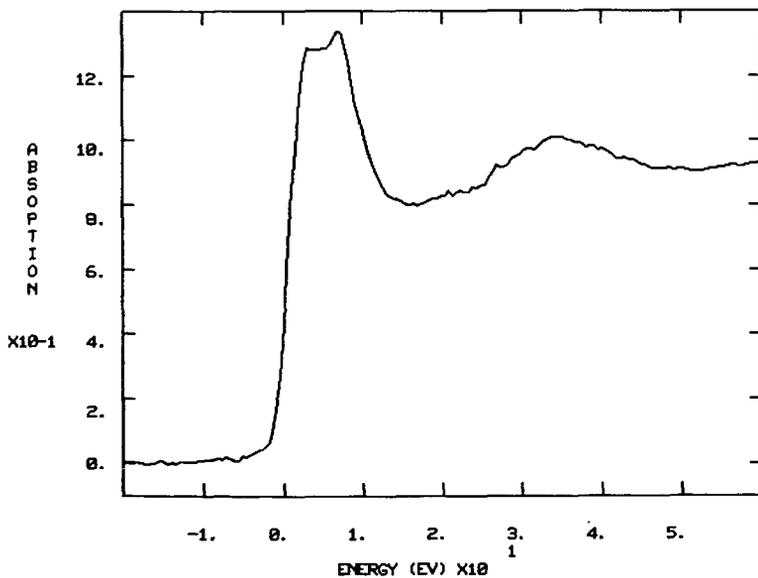


Figure 4 XANES for potassium (K edge) in the fouling deposit resulting from lignite combustion.

