OVERVIEW OF MINERAL MATTER IN U.S. COALS

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INTRODUCTION

Minerals in coal have been a subject of much interest during the past 20 years. Early studies approached the subject somewhat indirectly by means of chemical analysis of high temperature ash and back calculation to obtain estimates of the mineral matter (1). Others supplemented chemical studies by hand picking the coarser minerals or making density separations for chemical tests and optical microscopic study (2,3). With the advent of radio frequency ashing at low temperature (<150°C) it became possible to directly investigate all the mineral constituents (4). This led to progress in quantitative analyses of the mineral composition by x-ray diffraction methods (5-8). This paper summarizes some geological aspects related to minerals, their classification and occurrences in coal, and presents a compilation of available data on the mineralogical composition in coals from some of the major coal basins in the United States.

CLASSIFICATION OF MINERAL MATTER IN COAL

Coal is a sedimentary rock composed of three categories of substances: organic carbonaceous matter, termed macerals, inorganic (mainly crystalline) minerals, and fluids. The latter occur in pores within and between the other two solid constituents. The fluids in coal prior to mining are mainly moisture and methane. Applied to coal, the term mineral matter is an inclusive term that refers to the mineralogical phases as well as to all other inorganic elements in the coal; that is, the elements that are bonded in various ways to the organic (C,H,O,N,S) components. The term mineral refers only to the discrete mineral phases.

Because coal is a type of sedimentary rock, 100 or so different minerals can occur in coals; however, only about 15 are abundant enough to have high importance. These are listed in table 1 along with the stoichiometric chemical formula of each. It must be noted that minor impurities commonly substitute for the major cations as well as some anions which account for a considerable fraction of the minor and trace elements reported in coals (9-10).

Minerals in coal occur as discrete grains or flakes in one of five physical modes: (1) disseminated, as tiny inclusions within macerals; 2) layers or partings (also lenses) wherein fine-grained minerals predominate; 3) nodules, including lenticular or spherical concretions; 4) fissures (cleat and fracture fillings and also small void fillings); 5) rock fragments, megascopic masses of rock replacements of coal as a result of faulting, slumping, or related structures.

The minerals listed in table 1 are classified by their physical modes of occurrences. Description of mineral impurities in coal deposits, based on this classification is useful in a number of ways. Thick layers and abundant nodules or rock fragments hamper mining operations, but are easily removed by standard coal preparation (cleaning) facilities. On the other hand, disseminated minerals and the thinner (microscopic) layers are not much removed by existing preparation facilities. The latter two modes are dominated by mixtures of illite, quartz, and pyrite (table 1).

Useful also is a genetic classification of minerals in coal, wherein they are classified according to Mackowsky (11) as detrital, syngenetic, or epigenetic (table 1). Detrital minerals are those that were deposited in a coal forming peat swamp from slowly moving water or wind currents. Flakes of illite clay and microscopic grains of quartz, feldspars, zircon, apatite, rutile and perhaps others were deposited as discrete grains which became interbedded with peat and ultimately with the resultant coal. Most wind deposited minerals are recognized as such by the presence of certain high temperature phases. These are therefore, dust particles derived from distant volcanoes. Layered deposits of these dusts are termed tonsteins.

Syngenetic minerals are those that formed within the peat during the early stages of its coalification - before the peat was deeply buried by other sediments, probably by not more than about 50 feet. Under these conditions disseminated pyrite is thought to have formed in sulfate bearing peat by bacterial reduction of the sulfur. Much of this type of pyrite has a spherical form and is described as framboidal pyrite. Nodules of peat mineralized with various carbonates and nodules comprised of microcrystalline quartz and/or hematite formed early in the development of coal. Ultra-small crystallites of some minerals disseminated within macerals may also be syngenetic in origin, notably micrometer sized crystals of kaolinite and possibly illite observed by Strehlow, et al. (12) and by Wert and Hsieh (13). These crystallites, as well as some of the tiny disseminated grains of quartz are thought by some to have crystallized from inorganic matter inherited from the original plant material (2,3,14).

Epigenetic minerals are mainly those found in fissures and void fillings. Much of the calcite in coals as well as part of the pyrite and kaolinite in coals are recognized as epigenetic. This class of minerals formed long after the peat was consolidated and coalified enough to allow joints to develop where in these minerals precipitated. For most coals, this precipitation probably occurred during the late lignite or early subbituminous stages of coalification.

DISTRIBUTION OF MINERALS IN COALS

Typically, different layers of a seam vary considerably in their mineral matter as well as specific mineral components (fig. 1). The thin layer labeled BB is a carbonaceous shale and it contains the highest amount of mineral matter, which is mainly comprised of clay (illite, kaolinite, and smectite minerals) and quartz. At one site in the mine studied this layer was enrichedin pyrite (see lower part of the figure). The pyrite distribution at the four sites is fairly consistent in the upper layers at each site, but this epigenetic type of mineral is enriched in the lowest layer at three of the four sites (fig. 1). At this mine, and elsewhere, the conditions under which peat accumulated are thought to have been fairly consistant over regional geographical areas, much as they are today in existing peat swamps. Therefore, comparisons of mineral matter between coals are usually made by comparing analyses of channel samples that represent all layers in the seam (10).

ANALYTICAL TECHNIQUES

There are numerous instrumental techniques that can be applied to the characterization of mineal matter in coal. Probably the most widely used technique is x-ray diffraction analysis because of its availability and extensive development by mineralogists (5,6,7). Infrared spectroscopy has been successfully applied toward the analyses of common minerals found in coal (15). Differential Thermal Analysis (DTA) under nitrogen atmosphere can be used for the identification of certain minerals (16) by monitoring decomposition temperatures. Scanning electron microscopy with an energy dispersive x-ray analysis accessory unit has been used to identify various minerals as hosts for specific elements in coal (17,18). The

ion microprobe has also been applied to the study of minerals in coal (19). Mössbauer Spectroscopy has recently become very important in the study of iron sulfide minerals in coal (20). Preconcentrating the mineral matter in coal by radio frequency low-temperature ashing has been well established and is extensively practiced (4,9,14,22). It effectively removes the carbonaceous matter while causing only minor changes in the remaining minerals. The advantages are higher sensitivity for most instrumental techniques used.

Extensive elemental analyses has primarily been carried out on coal samples or ashes of coals for purposes of distribution studies and has been reviewed (21). Chemical analyses of separated coal minerals are also available confirming element-mineral associations derived from float-sink studies (14,22).

MINERAL COMPOSITION IN SOME SAMPLES FROM VARIOUS COAL BASINS

Results of mineralogical analyses of low temperature ashes by x-ray diffraction were compiled from the files of the Illinois State Geological Survey (table 2). Samples representative of the two most mined coals in the Illinois Basin provide a good statistical bases for evaluating this basin; however, this is not the case for results listed for other basins. To date, there is insufficient mineralogical data on these coal basins to draw many conclusions. Nonetheless, these data were generated in one laboratory, using the same procedures, and they provide a basis for some preliminary comparisons. The results show the following increasing compositional trends of the mean values, expressed by the state abbreviations given in table 1.

Mineral matter: AZ<TN<MT,ND,WY = So.WV<No.WV<IL<AL<IA

Pyrite (FeS_2): AZ = MT,ND,WY = So.WV<TN<AL = IL<No.WV<IA

The samples from the Black Mesa Basin in Arizona indicate the seams mined there are lowest in mineral matter and pyrite contents; those in Iowa appear to be the highest in both of these constitutents. However, the range of mineral contents is generally high and dictates that the quality of each deposit be considered on its own quality parameters for possible feed stock to coal processing plants.

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Table 1. Minerals frequently occurring in coals, their stoichometric compositions, their modes of occurrences, and relative abundance (11).

Mineral	Composition	Chief occurrences		Abundance in min. matter
		Physical*	Genetic**	
Clay minerals				
illite (sericite, K-mica)	$KAL_2(AlSi_3O_{10})(OH)_2$	D,L	d,s(?)	common
smectite (mixed layered)	$Al_2Si_4O_{10}(OH)_2 \cdot H_2O$ (with Na, Mg and Others)	D,L	d,s(?)	common
kaolinite group	$Al_4Si_4O_{10}(OH)_8$	L,F	e,d,s(?)	common
Sulfides				
pyrite	FeS_2 (isometric)	D,N,F	s,e	variable
marcasite	FeS_2 (orthorhombic)	D(?)	s(?)	rare
sphalerite	ZnS	F	e	rare
others: greigite, galena, chalcopyrite and pyrrhotite are reported as very rare				
Carbonates				
calcite	$CaCO_3$	N,F	e,s	variable
dolomite, incl. ankerite (Fe)	$Ca(Mg,Fe)(CO_3)_2$	N	s,e	variable
siderite	$FeCO_3$	N	s,e	variable
Oxides				
hematite	Fe_2O_3	N	s	rare
quartz	SiO_2	D,L,N	d	common
others: magnetite and rutile are reported as very rare				
Others				
limonite-goethite	FeOOH	N	e	rare
apatite, incl.	$Ca_5(PO_4)_3(F,Cl,OH)$	D	d,s(?)	rare
sulfates, mainly gypsum, barite, and several iron-rich ones				
feldspars	$K(Na)AlSi_3O_8$	D,L	d	rare
zircon	$ZrSiO_4$	D,L	d	rare
others: many others reported as very rare (11)				

* D = disseminated; L = layers (partings); N = nodules; F = fissures (cleat). Each mineral listed may often occur in rock fragments within coal beds.

** d = detrital; e = epigenetic, second state of coalification (mainly along joints (cleat) in coal beds); s = syngenetic, first stage of coalification (disseminated, intimately intergrown with macerals). The first listed occurrence is the more common one in U.S. coals; others are reported in some coal fields.

Table 2. Mineral composition of channel samples in various US coals*

Minerals	Great Plains Basins MT,ND,WY %	(range)	Western Interior Basin IA %	(range)	Illinois Basin IL,IN,W-KY %	(range)	Central Appalachian Basin Southern WV %	(range)	Central Appalachian Basin Northern WV+PA %	(range)
No. Samples	23		3		107		3		6	
LTA**	13	(7-27)	28	(23-34)	16	(9-28)	13	(13-14)	14	(10-15)
Pyrite	<1	(0-2)	8	(7-9)	2	(<1-12)	<1	(<1-1)	4	(2-5)
Quartz	2	(<1-6)	4	(1-7)	2	(<1-5)	1	(<1-3)	2	(1-2)
Calcite	<1	(0-3)	4	(1-7)	1	(<1-5)	<1	(0-<1)	1	(<1-3)
Clays†	11	(4-25)	13	(9-16)	9	(3-19)	11	(10-12)	8	(6-9)
Others (traces)	sulfates &/or nitrates feldspar aragonite chlorite		none det.		sulfates marcasite sphalerite feldspar hematite		siderite ankerite		siderite feldspar	

	Black Mesa Basin AZ %	(range)	Southern Appalachian Basin AL %	(range)	Southern Appalachian Basin TN %	(range)
No. Samples	3		5		4	
LTA	9	(5-12)	18	(13-28)	12	(10-16)
Pyrite	<1	(<1)	2	(0-6)	1	(<1-1)
Quartz	2	(2-3)	2	(<1-4)	1	(<1-2)
Calcite	<1	(0-1)	<1	(0-1)	none det.	
Clay†	6	(2-9)	18	(12-21)	11	(9-14)
Others (traces)	none det.		siderite apatite sericite		none det.	

* Mean weight percent and range on a whole coal basis.
** Total mineral matter by low temperature ashing methods.
† By difference.

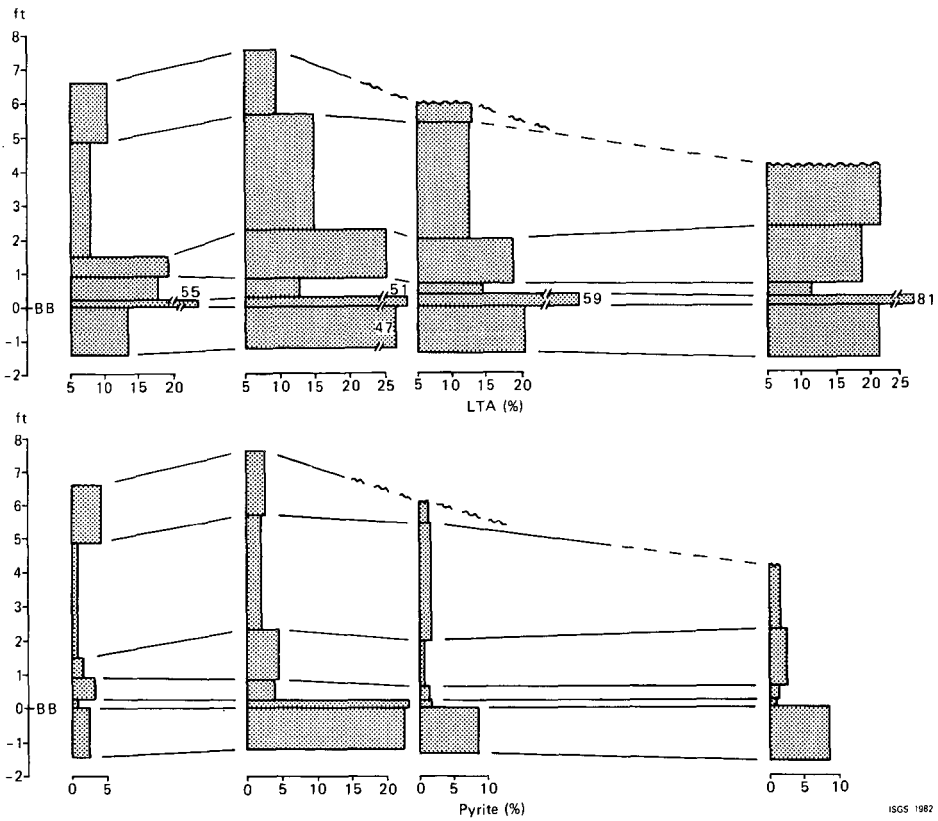

Figure 1. Vertical variation of mineral matter within a seam at four sites in a large mine: the total mineral matter content is shown in the upper diagram and the pyrite (FeS_2) fraction below. Geological analysis of the layers indicated that the upper most layer at three sites was not present at the fourth, shown on the right.