COAL STRUCTURE AND COAL SCIENCE: OVERVIEW AND RECOMMENDATIONS

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Coal is a sedimentary rock accumulated as peat and composed principally of macerals, subordinately of minerals, and containing water and gases in submicroscopic pores. Macerals (mas' er - als) are organic substances derived from plant tissues and exudates that have been variably subjected to decay, incorporated into sedimentary strata, and then compacted, hardened, and chemically altered by natural (geological) processes.

Coal is not a uniform mixture of carbon, hydrogen, oxygen, sulfur, and minor proportions of other elements; nor is it, as is often implied, simply a uniform, polyaromatic, "polymeric" substance. Rather, it is an aggregate of microscopically distinguishable, physically distinctive, and chemically different macerals and minerals.

Coal is analogous to a fruitcake, formed initially as a mixture of diverse ingredients, then "baked" to a product that is visibly heterogeneous. The heterogeneous nature of coal is evident in Figure 1, a photomicrograph of a polished surface of a piece of typical coal. The different macerals reflect different proportions of incident light and are therefore distinguished as discrete areas exhibiting different shades of gray. It should be evident that any attempt to characterize the chemical structure of this coal without recognizing the organization of the elements and molecules into discrete substances would be like trying to describe the essence of a fruitcake by grinding it up and analyzing its elemental composition.

The heterogeneity of coal, exemplified by Figure 1, is inherited from the diversity of source materials which accumulated in a peat swamp. Coals may be compared, contrasted and classified on the basis of variations in the proportions of these microscopically identifiable components. Such a classification is referred to as a classification according to type. Coals may also be classified according to how severely geological alteration processes, referred to collectively as metamorphism, have affected their properties. This is classification according to rank. These two classification methods are independent and orthogonal; therefore, within certain limits, any type of coal can be found at any rank.

Classification according to type involves the relative proportions of both the inorganic substances and the different organic substances. Because only the organic material is altered by metamorphic processes, rank classification is independent of inorganic content. Inorganic material is significant in commercial uses of coal, and its presence must be accounted for in scientific studies. The present discussion, however, concentrates on the properties of the organic substances, because only the organic macerals make coal the valuable material that it is.

In Figure 1, selected areas are identified as vitrinite, liptinite, and inertinite. These terms refer to the three major classes of macerals recognizable in all ranks of coal except those of the highest ranks. A few of the more significant features of these major classes of macerals and of their more important subclasses are summarized in Figure 2. It can be seen from Figure 2 that the differentiation of coals according to type, viz. according to the content of materials assignable to each of the maceral classes, is really a differentiation according to the ingredients which initially accumulated as peat to form that coal. Although the rank scale according to ASTM has been arbitrarily divided, and specific segments have been identified by an epithet (i.e., lignitic, bituminous, anthracitic coals), there are no such well-recognized classes of coal types.

In this sense, there is essentially a continuous series of coals of different types, defined by microscopic quantification of their maceral (and mineral) contents. Particles of crushed coal, when cemented together as a solid block with a catalytically solidified resin or plastic, can be polished and examined microscopically. Individual particles derived from different layers of a coal seam, may differ significantly in maceral and mineral contents. Recognition of this feature has led to the concept of the microlithotype, wherein each particle can be classified according to its maceral content. In this procedure, arbitrary classes of particles are recognized according to specific maceral proportions as shown in Table 1. It is important that the scientist or technologist recognize that particles of the different microlithotypes are likely to perform quite dissimilarly when analyzed or processed; therefore, coals must be sampled carefully to prevent the selection of non-representative particles.

Each of the materials recognized as belonging to a specific maceral class (according to the criteria shown in Figure 2) has physical and chemical properties that depend upon its composition in the peat-swamp and the effects of subsequent metamorphic alteration. Thus, for instance, in all coals there is material derived from the structural tissues ("wood") of plants. These "woody" substances (lignin, cellulose) are the dominant components of plants, and hence their derivatives dominate in typical coals. In the peat swamp, some of the woody tissues may have been pyrolyzed by fire, forming a carbon rich char recognized as fusinite in the coal. In some coal layers, this may be the dominant maceral, and such layers would be referred to as fusinite-rich types of coal.

Much more commonly, though, the woody tissues accumulated below a water covering where imperfectly understood, largely microbiological processes converted them to humic substances of somewhat variable composition. These humic substances were subsequently altered by metamorphic processes (heat, pressure) into substances classifiable as one of the vitrinite macerals. Therefore, the physical and chemical properties of the vitrinitic materials in a specific coal were largely conditioned by the magnitude of temperature and pressure to which they were subjected after burial. Thus, one could say that the properties of the macerals in a given coal reflect the rank of the coal; or more correctly, one should say that the rank of the coal reflects the properties of macerals as conditioned by the severity of the metamorphic processes to which the coal was subjected.

One of the properties of macerals that changes progressively with metamorphic severity is the microscopically measurable reflectance of polished surfaces. Using a sensitive photomultiplier cell mounted on a microscope, it is possible to measure objectively the absolute percentage of incident light reflected from very small areas (5μm diameter) of polished coal surfaces. In Figure 3 is shown a series of reflectance distributions, each representing a sampling of the material in a coal of the rank indicated. These distributions are arbitrarily constructed to show what would happen to a given peat if it were to be subjected to increasingly more severe metamorphism. Recognize, of course, that these are "slices" through a continuum, and that no jump from rank to rank is implied. Properties such as carbon content, oxygen content, degree of aromaticity, and many others, could be substituted for the reflectance scale and a similar sort of picture would emerge. In Table 2, some typical values are shown for selected properties of vitrinite macerals in different rank coals. In Table 3, a number of the properties of non-vitrinite macerals are compared to those of vitrinite from coal of the same rank.

Typical U.S. coals are relatively vitrinite-rich, therefore analyses of whole coals, when appropriately corrected for inorganic content, reflect, to a first approximation, the composition and properties of the included vitrinite. For this reason, the parameters employed to classify coals according to rank, reflect the rank (stage of metamorphic development) of the vitrinite. Calorific values or fixed carbon yields are calculated to a so-called mineral-matter-free basis for use in the ASTM classification of coals according to rank (1). It is essentially impossible to obtain inorganic-free samples; therefore, to represent organic matter accurately in comparative studies of any of the organic properties of coal, analytical data must be converted to an inorganic-free basis. Commonly, a dry, ash-free (DAF*) basis is employed. It is preferable, however, to convert to a dry, mineral-matter-free (DMMF) basis, as discussed by Given and Yarzab (2). In fact, the most meaningful assessment of coal rank or of the properties of coals of different ranks should be done with samples of concentrated vitrinite or on samples where the vitrinite comprises more that about 80% of the organic fraction. Because reflectance is closely correlative with many rank-sensitive properties and its determination can be made on vitrinite alone, it has become a widely accepted parameter to designate the rank of a coal (see Figure 4). Unfortunately, even when a reflectance value is available, it may not be reported in scientific publications. I strongly recommend that petrographic analyses and vitrinite reflectance be reported for samples on which structural studies are conducted.

Although many properties of vitrinites appear to change in a more or less parallel fashion as a result of metamorphism, there is considerable scatter in their correlation. Figure 5 is offered as evidence of this contention. The data plotted in Figure 5 are from coals containing more than 80% vitrinite on a DMMF basis (3). It is obvious that the progression from high to low H/C and O/C values reflects the influence of more severe metamorphic alteration; in other words coals toward the lower H/C and O/C end of the band are are higher rank. However, the fact that the data do form a band, rather than a linear progression, implies that there is not a simple scale which defines the rank progression. As Given and his co-workers have so eloquently shown, the geological/geographical disposition of U.S. coals appears to exert some, as yet undefined, influence on the intercorrelations of coal properties (4).

Clearly, neither geology nor geography are coal properties and hence cannot be "measured". Different source materials, depositional conditions (including especially sulfur availability), and time/temperature/pressure conditions during metamorphism, interacted so as to provide a multitude of potential paths which different coals (or even vitrinites in different coals) followed to their present condition. In other words, the concept of a single rank progression is more fallacy than fact.

As unifying, underlying concepts, type and rank certainly can be validly employed to envision why coals have the properties that they do. However, it is time for a re-evaluation of coal classification concepts. How can we measure rank when we analyze coals of different types and when there is no simple rank progression even when vitrinite or vitrinite-rich coals are compared? And how can we assess type when maceral identification criteria are highly subjective, except for reflectance measurements that routinely are not even applied to the liptinite and highly variable inertinite macerals? And, finally, how can coals be classified scientifically when empirical and derived properties like calorific value and fixed carbon yield are employed as classifying parameters?

A scientific classification should be based first on the fundamental properties of the vitrinite in coals. This means, at the very least that element concentrations and molecular structure configuations must be assessed. The structural properties of most importance to classification and process responses

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*Not 'MAF', which is often unfortunately used as an abbreviation for moisture-and-ash-free.

appear to be: (1) the nature of hydrogen bonding and physical entanglement that cohere molecular moieties, (2) the nature of cyclical structures (e.g., ring condensation index, aromaticity, heteroatoms), (3) amount and distribution of hydroaromatic hydrogen, (4) scissle bridging structure (e.g., ether, sulfides, polymethylenes), (5) functional group characteristics (esp. oxygen - and sulfur-containing), and (6) organic/inorganic interactions. To develop the basis of a scientific classification, these determinations need to be made on a large number of vitrinite-rich coal samples spanning a wide range of rank. Because coals are sensitive to oxidation and moisture changes during handling, these samples must be carefully collected, prepared and preserved.

It is fairly evident that because of the complex interactions of depositionally-influenced and metamorphically-influenced properties, the fundamental chemical/structural properties will need to be related to each other in a complex statistical fashion. A multivariate correlation matrix such as that pioneered by Waddell (5) appears to be an absolute requirement. However, characterization parameters far more sophisticated than those employed by Waddell are required. One can hope that, as correlations between parameters become evident, certain key properties will be discovered which will allow coal scientists and technologists to identify and to classify vitrinites uniquely. Certain optical properties might prove valuable in this respect. It would then not be necessary for every laboratory to have super-sophisticated analytical equipment at its disposal in order to classify a coal properly. By properly identifying/classifying the vitrinite in a coal, one could then estimate accurately the many other vitrinite properties available in the multivariate correlation matrix.

Of course, elucidation of vitrinite properties and establishment of unique vitrinite class identifiers would not solve all of the problems of coal classification. Further work needs to be done to characterize the inorganic materials in coals, especially developing simple tests for quantification of inorganic species.

Once vitrinites could be properly identified and classified, then it would be necessary to characterize and to identify uniquely the members of the other maceral classes. It is probable that liptinite properties change in some fashion correlative with the changes wrought by metamorphism on vitrinite. Therefore, classification of vitrinite would automatically classify liptinite. Whether inertinite changes with rank is uncertain; but it is certain that far better differentiation of fusinites needs to be employed for it is evident that fusinite reflectance values span wide ranges in a given coal.

A multivariate vitrinite classification, supplemented by information about the inorganic matter and the proportions and properties of associated macerals, would be of little value if it could not be used to predict the response of a given coal in a processing system and thereby provide an estimate of the value of that coal. Consequently, it will be necessary to relate the scientific classification to the responses of coals in such processes as pyrolysis, liquefaction, gasification, combustion, and coke-making. This can only be done by relating the fundamental, classifying properties to empirically determined processing responses on a substantial number of samples. Again, they should be vitrinite-rich and cover a broad range of ranks.

Only through the conduct of an integrated program more or less along the lines that I have outlined is Coal Science ever going to move out of the era of the 1950's where it is now mired. The scattered probes of coal structural properties on a bewildering range of poorly selected, poorly collected, poorly prepared, poorly preserved and poorly characterized coal samples will lead us only into further confusion. Progress in Coal Science can only be made when scientific and technological investigations on coal result in a comprehensive integration and synthesis of data and information. The essence of science is "the reduction of the bewildering diversity of unique events to manageable uniformity within one of a number of symbol systems" (6). Present investigations of coal structure hardly conform to that definition today, and therefore hardly deserve the epithet of Coal Science.

References

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TABLE 1. CLASSIFICATION OF MICROLITHOTYPES

	Microlithotype	Maceral	Volume Percent
Monomaceralic	Vitrite	Vitrinite (V)	> 95%
	Liptite	Liptinite (L)	> 95%
	Inertite	Inertinite (I)	> 95%
Bimaceralic	Clarite	V + L	> 95%
	Vitrinertite	V + I	> 95%
	Durite	I + L	> 95%
Trimaceralic	Duroclarite	V + I + L	V > (I + L)
	Clarodurite	V + I + L	I > (L + V)
	Vitrinertoliptite	V + I + L	L > (I + V)
	Carbominerite	V, L, I and Mineral Matter (MM)	MM > 20%, < 60%

TABLE 2. SELECTED PROPERTIES OF VITRINITES IN COALS OF DIFFERENT RANKS

	Lig.	Sub-Bit.	Bit.	Anth.
Moisture Capacity, Wt.%	40	25	10	< 5
Carbon, Wt.% DMMF	69	74.6	83	94
Hydrogen, Wt.% DMMF	5.0	5.1	5.5	3.0
Oxygen, Wt.% DMMF	24	18.5	10	2.5
Vol. Mat., Wt.% DMMF	53	48	38	6
Aromatic C/Total C	0.7	0.78	0.84	1.0
Density (He, g/cc)	1.43	1.39	1.30	1.5
Grindability (Hardgrove)	48	51	61	40
Btu/lb, DMMF	11,600	12,700	14,700	15,200

DMMF = Dry, Mineral-matter-free basis. These are typical values for rank classification. Sulfur and nitrogen are rank-independent and not shown.

TABLE 3. PROPERTIES OF MACERALS COMPARED TO VITRINITE IN SAME COAL (Subbituminous and High-Volatile Bituminous Only) Magnitude of property greater than (>), less than (<), or equal to (=) that of associated vitrinite.

	Inertinite			
Optical Properties	Semi-Fusinite	Fusinite	Micrinite	Exinite
Reflectance	>	> >	>	<
Fluorescence				>
Chemical Structure				
Basic carbon structure				=
Molecular weight				>
H/C ratio	<	< <	=	>
H aliphatic/H total;-CH_2; hydroaromaticity				>
Fraction aromatic C; rings/unit		>	>	<
$Oxygen_{OH}/Oxygen_{Total}$		<		<
Unpaired spins by ESR		>		<
Unpaired spins of fusinite with same carbon as vitrinite		>		
Reactivity				
Methane sorption		>		
Decomposition temperature				<
Oxidizability				<
Reduction with Li in EtDA		<	=	<

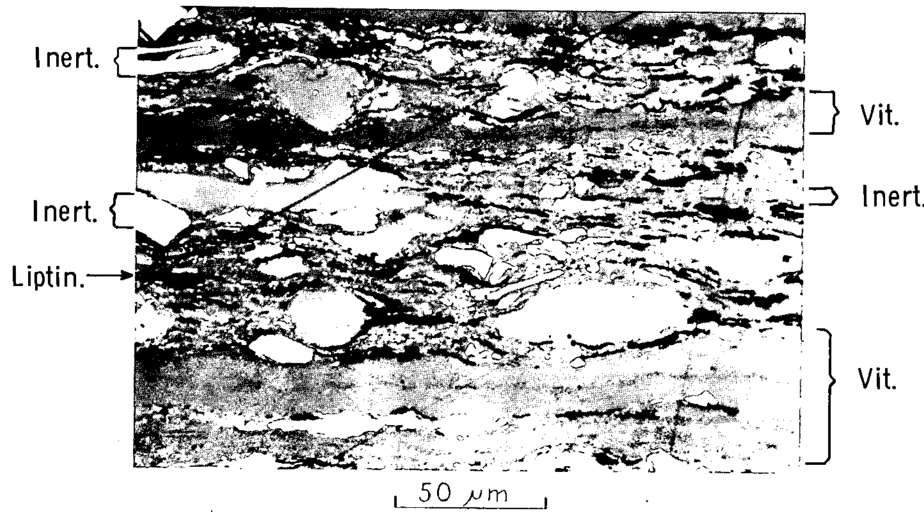
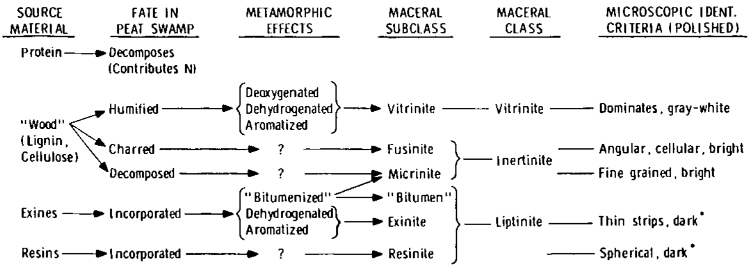


Figure 1. Photomicrograph of polished surface of a high-volatile bituminous coal.
Vit. = Vitrinite; Inert. = Inertinite; Liptin. = Liptinite

FIGURE 2. PRINCIPAL MACERAL CLASSES



* In Low-Vol Bituminous and Anthracites, Liptinite Indistinguishable from Vitrinite

FIGURE 3. REFLECTANCE DISTRIBUTION OF MACERALS IN TYPICAL COALS

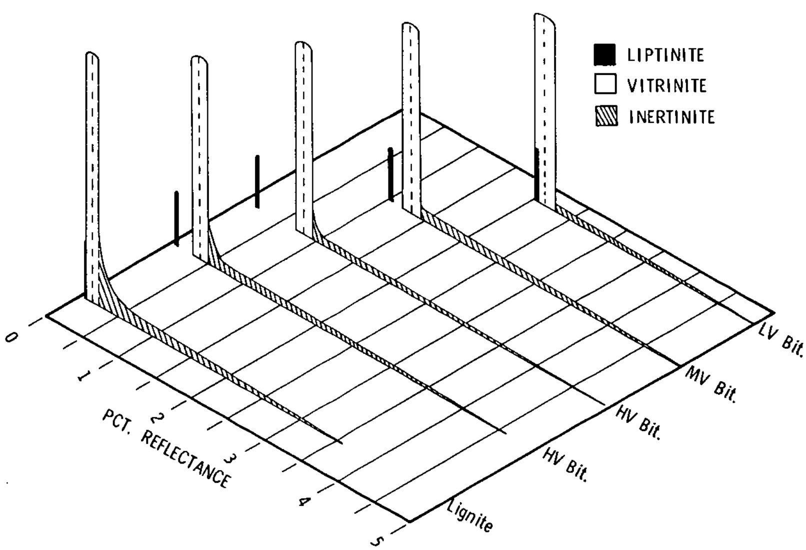


FIGURE 4. CORRELATION OF REFLECTANCE OF VITRINITE AND CARBON CONTENT OF COALS. DATA FROM REF. 3

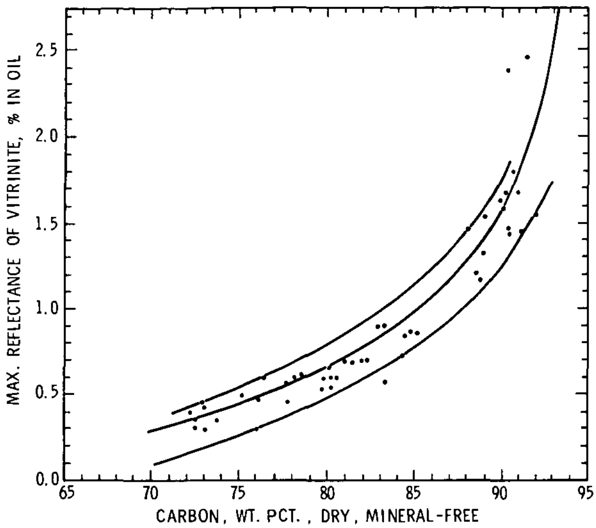


FIGURE 5. CORRELATION OF ATOMIC H/C AND O/C FOR COALS OF DIFFERENT RANKS. DATA FROM REF. 3