

A Chemist Looks at Coal Petrology

P. H. Given

Department of Fuel Technology
Pennsylvania State University
University Park, Pa.

Petrology is in general defined as the study of rocks, and is considered a branch of geology. In the study of inorganic rocks the petrologist relies heavily for identification of mineral species on such optical properties as refractive index and birefringence, and on characteristic crystal form or morphology. The coal petrologist also relies on optical properties to distinguish "macerals" in the organic rock, coal, but has to use reflectance or color in transmitted light rather than refractive index, and cannot derive help from crystal form. Instead he has to study the palaeobotany of the sample and make what use he can of differences in botanical structure or of types of association of differently shaped bodies in a sample; it is this difference from inorganic petrography that gives the study of coal its peculiar difficulty.

The nomenclature and classification of the entities discerned in coals by petrologists is a complicated matter which has been productive of much controversy, and there is still no universally accepted system. Consequently it is not easy for other workers in coal science to grasp the nature and significance of the petrologist's work, and they may be tempted to dismiss the work as still too ill-defined and controversial to be worth basing their own researches on, or even to be worth finding out about.

Such a dismissal would be a grave mistake. It is true that there is still lack of agreement about the significance of some of the entities claimed to be present in coal samples, and about their classification and origin. Nevertheless, there is a body of solidly established fact which should be taken account of by any chemist or physicist studying coal, and which is of demonstrable importance even in practical operations for the use of coal. It is regrettable that papers are still being published in which often excellent experimental work is marred by inadequate choice and description of samples. Furthermore, it is often forgotten that describing a coal solely in terms of one of the various national technological classification systems, such as the A.S.T.M., has little scientific value even to a worker familiar with the system, and none at all to workers elsewhere. The systems were devised to define whole coals for technological purposes.

It is the purpose of this paper to review briefly how "macerals" come to be present in coals, and to discuss the relation between those aspects of contemporary classification systems that seem of most importance to the chemist and physicist. It is hoped that this will facilitate the use of petrological concepts by non-petrologists.

Most major coal measures were laid down in elongated depressions in the earth's surface known as geosynclines. For substantial deposition of any kind of sediment in a geosyncline, it is necessary that the rate of accumulation of sediment is approximately balanced by the rate of subsidence of the floor of the depression due to the increasing load on it. Vegetation can only thrive and its products of decay be preserved while the physical conditions, particularly the level of the water table, remain within fairly narrow limits. Since the two rates referred to above do not remain in balance indefinitely, a core of the material accumulated in a geosyncline

reveals a fairly regular variation in type of sediment with depth. Thus the coal seams are separated by a regular and repeating sequence of inorganic sediments, with fossils indicating the varying depth of the water in which the sediment was transported from neighboring high land and then deposited.

Even during the formation of one coal seam, conditions vary. Varying water level and movement changes the degree of aeration and hence the activity of aerobic bacteria in bringing about decay. The different types of chemical substance present in plants - cellulose, lignin, resins, waxes, tannins, etc. - are present in different relative proportions in living woody tissue, in dead cortical tissue, in seed and leaf coatings, and so on; and also these substances show differing degrees of resistance to decay. It can therefore be seen that as conditions fluctuate during the accumulation of plant debris, the botanical nature and chemical composition of the material surviving complete breakdown will fluctuate also. This fluctuation is the origin of the familiar banded structure of coal seams, which is visible to the naked eye, and it provides a prima facie case for supposing that the banded constituents will differ chemically and physically.

There is another deduction to be made from the mode of origin of the banded constituents. The average nitrogen content of coals is appreciably more than that of plants, and it is commonly supposed that the extra nitrogen originates from the protein content of the bacteria that brought about decay in the peat swamp, the bacterial remains having been included in the coal structure. Varying nitrogen contents in coals therefore reflect varying amounts of metamorphosed protein mixed in with the plant debris.

The character of the biochemical system and of the physical conditions was never such as to preserve only one kind of plant debris to the exclusion of others. Consequently the banded constituents are merely concentrates of some more fundamental components. The European classification of these components into material derived from woody tissue (vitrinite), from spores, seed coatings, cuticles, etc. (exinite), from woody tissue carbonized or changed in some other way to "natural charcoal" (fusinite), and from an unknown source, possibly humic mud (micrinite), is too well known to need discussion here (see, for example, Van Krevelen¹, Brown²). The significance of this basic classification has been confirmed by chemical, carbonization, and other studies (see Given³ and references therein).

European and other petrologists have believed for some time that the four main categories are themselves not fundamental, and research on proper sub-division and classification continues actively. No doubt in time purified samples of the sub-components will become available for further study by other techniques. So far no attempt has been made to substantiate physically and chemically the petrological distinction between tellinite and collinite (forms of vitrinite with and without cellular structure respectively). Of the various members of the exinite group, only sporinite (from megasporae) has received any extensive chemical study.

In the chemical and physical study of coals it is customary to correlate, for a series of samples, the property being measured with some other property presumed to measure rank. Even with pure vitrinites there is appreciable scatter in any plot; there is much scatter with spore-rich exinites; while with fusinites the concept of rank seems to break down altogether since no rank parameter gives any correlation. The scatter may be due to the incorrect choice of rank parameter (on this, see below) or to the random operation of nature in the metamorphic process. However, the scatter may also be taken to indicate that the materials are still heterogeneous, and that the petrologists are correct in insisting on further sub-division of the classification referred to.

The European maceral concept has been criticized by American petrologists on the grounds that it takes no account of rank. In the author's view this criticism

is based on a misconception. Clearly the fundamental point is that to define a pure sample completely, at least two statements are necessary: one showing the maceral group to which the specimen must be assigned, and the other locating the point in the sequence of changes from plant material to graphite (or graphitic carbon) reached by metamorphosis. This point can be indicated in a number of ways, of which the commonest are the use of carbon content, yield in the standard volatile matter test, and maximum reflectance under oil immersion.

European workers (and chemists elsewhere) most commonly define rank by means of the carbon content (d.a.f. or d.m.m.f.) of the sample or in the case of fusinite by the carbon content of the associated vitrinite. Since metamorphosis is essentially a chemical process, and its trend is towards pure carbon, the carbon content appears to the author to be the best available and most nearly direct measure of rank. However, it must be admitted that if reflectance is used as a measure of rank, the same set of microscopic observations can be used both to identify the maceral group and assign a specimen to its place in the group; use of the carbon content requires a separate observation.

In recent years, a number of new ideas have been introduced into coal petrology by American workers, which involve a considerable amount of re-definition of concepts. Groups of workers at Pennsylvania State University, the U. S. Steel Corporation, the Illinois Geological Survey and other centres have been active in formulating these ideas, which however have not yet been made widely available to chemists.

Spackman, Berry and their co-workers⁴ have made extensive microscopic studies of coals by transmission of light through thin sections. They observed that the material derived from woody tissue (vitrinite) commonly contained fairly well-defined regions of different color, some of which showed remains of cellular structure and some did not. In a suite of samples covering a wide range of rank they observed regions of color ranging from bright yellow through orange, red and deep red to an almost opaque red-brown. In any one sample there were not more than two or three predominating colors, and in general the color shifted across the spectrum towards red as the rank of the sample increased. They felt that in a series of samples nine different shades of color could be reproducibly distinguished, and termed the components of different color vitrinoids. The vitrinite from a low-rank bituminous coal might therefore be composed on their hypothesis predominantly of vitrinoids 2 and 3, a medium-rank of vitrinoids 4 and 5, and so on. Two vitrinitic coals of similar rank might differ chiefly in the relative proportions of the same vitrinoids. By specifying the vitrinoid analysis of a sample, therefore, they were defining both the maceral group and the rank from the same set of observations. However, there is one reservation: in certain cases it is difficult to distinguish a high-rank vitrinoid from a semi-fusinite; this point is discussed below.

Some confirmation that the vitrinoids differ in some significant manner was obtained from color cinematography of samples mounted on the hot-stage of a microscope; in this way differing behavior - melting, swelling, change of color, etc. - of the various components could be observed directly. Further evidence of the significance of this vitrinoid concept was obtained as a result of the preparation of pure vitrinoids by careful micro-manipulative techniques applied to selected samples. In a series of experiments, the pure vitrinoids were carbonized in mixture with various proportions of inert filler (fused alumina), and the hardness of the coke was then measured. It was found that the curve obtained by plotting coke hardness against proportion of inert had a characteristic shape for each vitrinoid, the shape of the curve being reproducible with samples of the same vitrinoid separated from different coals.

The hypothesis of Spackman and Berry and their supporting evidence at least establish a case for the heterogeneity of vitrinites which is worthy of further investigation. The hypothesis is easily comprehended in chemical terms, and it should not be difficult to devise experiments for testing it provided sufficiently

sensitive physical and chemical methods are available. On the other hand, it is not easy to see how any probable combination of biochemical and geological conditions could have produced such a strictly limited number of fundamental constituents of which all vitrinitic coals are to be presumed to be composed. Moreover, since the absorption of light by coals is unselective, that is, not in well-defined bands, division into materials of color shade distinguishable by eye has an element of arbitrariness.

Because of the necessary lack of objectivity in separating materials according to their color in transmitted light, current petrological research is placing more emphasis on the use of reflectance measurements. A detailed system of classification of coal components based on reflectance has now won general acceptance among petrologists in this country (see Schapiro and Gray⁵). In this system, the observed range of reflectance values of vitrinitic materials in oil is divided up arbitrarily into smaller ranges or steps of 0.1% reflectance, experimental values being significant to about 0.01%. A component of vitrinite having a reflectance of 0.83%, for example, is designated vitrinoid no. 8 or V8, and one of reflectance 1.37% is V13. (Note that the same word vitrinoid is used as in Berry's system, though the significance is different; note also that the numbering in the two systems does not correspond at all.) Other macerals are designated similarly. Thus the system includes both maceral type and an indication of rank. The reflectance of the technically important medium to low volatile vitrinites is a good index of rank, and varies rapidly with carbon content. The reflectance of low to medium rank vitrinites, however, is low and varies only slowly with carbon content. The system has practical advantages in specifying coking blends and predicting carbonization behavior, but no fundamental significance is claimed for the reflectance ranges used to define the maceral type number.

No correlation has yet been established between the two "vitrinoid concepts". According to the Fresnel equation, the reflectance of a substance is a function of the refractive index and the absorption index. In the case of medium to low rank coals, the absorption index makes a relatively small contribution to the reflectance of visible light, and the latter property is therefore determined mainly by the refractive index, which in turn is related to the density and electron polarizability of the substance. (With high rank coals absorption becomes more important.) Hence reflectance and absorption measurements often relate to different fundamental properties. However, if the vitrinoids distinguished by color by Spackman and Berry have fundamental significance one might expect the reflectance values of a large number of points on the polished surface of a single block of vitrinite to fall into a bi- or tri-modal distribution curve. In fact a range of reflectance values are found for a series of points on a vitrinite surface, but they are distributed fairly evenly over the range, no sign of two or more peaks being observed as a rule. Reflectance measurements, in that a range of values is found for one sample, do therefore support to some extent the idea that vitrinites are still heterogeneous, but not that they are heterogeneous in the sense suggested by Spackman and Berry. Some histograms illustrating the spread of reflectance values found in vitrinites are shown in Fig. 1.

There is one major difficulty common to all systems of detailed classification; this arises from the fact that there appears to be a completely continuous gradation in both color in thin section and in reflectance from high-rank vitrinites through semi-fusinites to fusinites. Thus Berry and Spackman frequently observed regions of very dark-colored material in predominantly light-colored (low-rank) vitrinite; one can either suppose this material to result in the peat swamp from the same kind of biochemical process that led to the formation of vitrinites but more severe, or that it is a product of the same process that produced fusinite, again at the peat stage. At any rate the differentiation of this material from the rest must have occurred at an early stage of coalification and not during geological metamorphism. Similar observations to the above are made in reflectance studies at all levels of rank. Carbonization data are of no help in making distinctions, since vitrinitic materials

of very dark color or of reflectance in oil above about 2.5% are inert, in the sense that they do not swell or fuse on heating; in this respect they have the same behavior as semi-fusinites and fusinites. Matters are made more difficult by the fact that the nature of the fusinization process is not known.

It is clear therefore that in any attempt to identify and group correctly pure components in coals there is at present an ambiguity about some small part of the whole sample; it could be either chemically akin to the rest of the vitrinite family but highly altered, or it could be the remains of woody tissue that has undergone some fusinization, whatever that may be, and belong chemically with the fusinite group. In any case the distinction becomes both harder to make and less important in high rank coals.

Summary and Conclusions

Vitrains may contain about 60-95% vitrinite, the balance usually being made up mostly of fusinite, spore exinite and resin inclusions. The relative proportions of the minor constituents vary from coal to coal. It is already established that such chemical properties as the proportion of phenolic hydroxyl and the distribution of hydrogen in different forms of combination differ widely between the various maceral groups.⁶ In some cases, where the purity is high or the effects of impurities tend to cancel one another out, an average property of a vitrain may differ little from that of the pure vitrinite. In other cases there will be significant differences; for example, Wyss and Given⁷ found the hydroxyl content of a series of vitrains from British coals to run consistently lower (10-20% of the total content) than the values for a similar series of pure vitrinites.⁶ Moreover the trend of values with rank was different, and only the pure vitrinite set of results was in reasonable agreement with the values found by Blom *et al.*⁸ for a series of vitrinites from continental European seams.

It is therefore submitted that in any scientific investigation the purest and most homogeneous materials available should always be used. At present these materials will be vitrinites or members of one of the other three main maceral groups. It is not difficult to obtain vitrinites at least in good purity, and the purification has the further advantage of eliminating most of the mineral matter, which greatly complicates chemical analysis if present in large amounts. If pure macerals, in the sense just defined, cannot be used, then at least a petrographic analysis should be reported.

It is not yet certain whether or how far the further sub-division of maceral groups is justified on chemical and physical grounds, and intensified research to settle this is demonstrably worthwhile and highly desirable. In the meantime, it is suggested, chemists and physicists should be aware of current thinking on the subject.

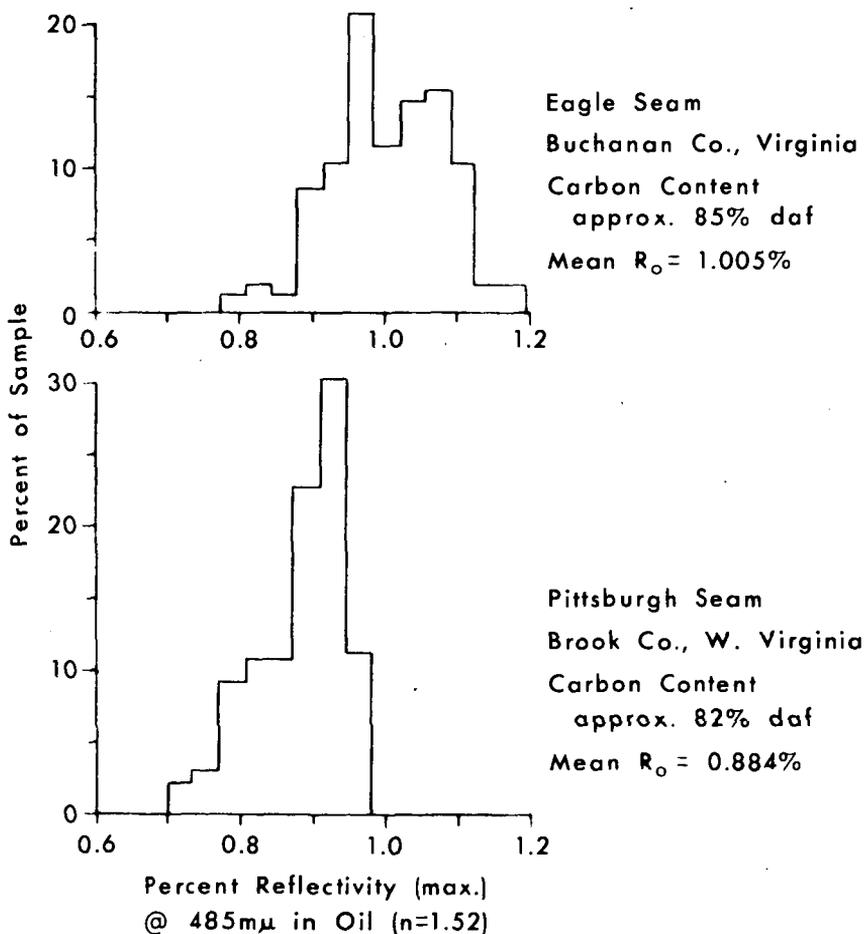
In conclusion, the author would like, with respect, to suggest to coal petrologists two urgent needs in the immediate future:

1. greater attention to the physical separation of pure components for further study.
2. research on the nature of fusinization and on the vitrinite-semi-fusinite gradation; in this, full cooperation between all disciplines will be needed.

References

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**DISTRIBUTION OF MAXIMUM REFLECTIVITY OF
VITRINITES IN SMALL ($\frac{1}{2}$ inch square)
BLOCKS OF BITUMINOUS COAL**

Figure 1