

Chemistry and Characterization of Coal Macerals

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FOREWORD

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PREFACE

COAL IS AN EXTREMELY COMPLEX, heterogeneous material that is difficult to characterize. It is a rock formed by geological processes and composed of a number of distinct organic substances called macerals and of lesser amounts of inorganic entities called minerals. Each coal maceral and mineral has a unique set of physical and chemical properties that contributes to the overall behavior of coal. Although much is known about the mineral properties of coal, surprisingly little is known about the properties of the individual macerals.

This volume covers a wide range of fundamental topics in coal maceral science that varies from the biological origin of macerals to their chemical reactivity. Several chapters report novel applications of instrumental techniques for maceral characterization. These new approaches include solid ^{13}C NMR, electron spin resonance, IR spectroscopy, fluorescence microscopy, and mass spectrometry. A recently developed method for maceral separation is also presented; many of the new instrumental approaches have been applied to macerals separated by this new method. The contributions in this volume present a sampling of the new directions being taken in the study of coal macerals to further our knowledge of coal petrology and coal chemistry.

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Chemistry and Characterization of Coal Macerals: Overview

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The Maceral Concept

All of the papers in this book deal with the chemistry and characterization of coal macerals and, as such, recognize the heterogeneous nature of coal. Coal is, in fact, a rock derived from a variety of plant materials which have undergone a variety of physical and chemical transformations. While a number of chemical studies of coal have found the concept of a single "coal molecule" useful, the papers in this book are aimed at characterizing in some way the various macromolecules that comprise the many kinds of coal macerals.

Although the heterogeneous nature of coal has long been recognized in microscopical studies, for example by White and Thiessen in 1913 (1) and in 1920 (2), the term "maceral" was introduced only in 1935 by Marie C. Stopes (3). In this paper (page 11) she says:

"I now propose the new word "Maceral" (from the Latin macerare, to macerate) as a distinctive and comprehensive word tallying with the word "mineral". Its derivation from the Latin word to "macerate" appears to make it peculiarly applicable to coal, for whatever the original nature of the coals, they now all consist of the macerated fragments of vegetation, accumulated under water."

The concept behind the word "macerals" is that the complex of biological units represented by a forest tree which crashed into a watery swamp and there partly decomposed and was macerated in the process of coal formation, did not in that process become uniform throughout but still retains delimited regions optically differing under the

microscope, which may or may not have different chemical formulae and properties. These organic units, composing the coal mass I proposed to call macerals, and they are the descriptive equivalent of the inorganic units composing rock masses and universally called minerals, and to which petrologists are well accustomed to give distinctive names."

The concept was well received and the term maceral is now recognized around the world. Today, many coal scientists, especially those outside of North America, regard coal macerals as the smallest microscopically recognizable unit present in a sample. However, in 1958 Spackman (4) presented a concept of macerals that is significantly different and more useful in the chemical aspects of coal science:

" . . . macerals are organic substances, or optically homogeneous aggregates of organic substances, possessing distinctive physical and chemical properties, and occurring naturally in the sedimentary, metamorphic, and igneous materials of the earth."

The essence of this concept is that macerals are distinguished by their physical and chemical properties and not necessarily by their petrographic form; thus, even though two substances may be derived from the same kind of plant tissue, for example, cell wall material, and have a similar petrographic appearance, they would be different macerals if they had different chemical or physical properties.

Maceral Characterization

Two serious problems confront the coal scientist trying to characterize coal macerals. First, the macerals are very difficult to separate from the coal matrix and it is, therefore, rare to have a pure maceral concentrate to study. For this reason much of the maceral characterization has been done in situ with petrographic methods including reflectance and fluorescence analysis. The second problem is that coal is, in truth, a metamorphic rock; any given coal sample is part of a metamorphic (rank) series ranging from peat through lignite, sub-bituminous coal, bituminous coal, to anthracite. As the rank of coal increases, the physical and chemical properties of the coal change, and therefore, the various macerals change also. The nature of this change is poorly understood; for example, it may be a continuous change analogous to solid solution in minerals, or it may be discontinuous in some way. The inescapable constraint of the rank property of coal macerals is that in any

study of maceral properties, the coal rank must always be determined and included in maceral characterization. Even in studies of similar macerals in the same coal seam, variation in coal rank can occur and, therefore, cause differences in maceral properties.

Development of Petrographic Characterization

The development of the petrographic characterization of coal macerals closely followed the development of petrographic techniques. Some of the earliest petrographic characterization of coal macerals used mainly transmitted light techniques and examples can be found in the papers of Cady (5), Marshall (6), and Parks and O'Donnell (7). Although the technique of reflected light microscopy was also used elsewhere, it was developed and used extensively in Germany (8-10). Also, during the late 1940's Hoffmann and Jenkner (11) developed the use of optical reflectance measurements to characterize some coal macerals.

In the late 1950's and early 1960's the reflectance characterization of coal macerals was used with great success in carbonization studies. For example, it was shown by Spackman *et al.* (12) that the properties of the various coal macerals controlled the carbonization behavior of coal. Based on this work and that of Ammosov *et al.* (13) methods were developed to predict the carbonization properties of single coals and coal blends (14-17). These methods use a maceral point count analysis to give the maceral distribution and a reflectance analysis to characterize the thermal properties of the macerals.

The most recent petrographic method used to characterize coal macerals is quantitative fluorescence analysis. In this method the macerals are excited by incident ultraviolet light and the spectrum of the resulting fluorescent light is used to characterize the macerals. This technique has led to the discovery of new macerals (18), the quantitative discrimination between certain macerals in a given coal (19), and the correlation of the fluorescence properties of macerals to the rank, and technological properties of coal (20-22).

Previous Petrographic Characterization

As Stopes seems to have anticipated, a large number of macerals have been identified and named. All macerals, however, can be conveniently grouped into three major subdivisions - vitrinite, liptinite, and inertinite. The vitrinite group of macerals are derived from plant cell wall material (woody tissue) and usually make up 50-90% of most North American coals. Although there are a large number of named varieties of

vitritine macerals, it is interesting to note that most researchers studying the vitritine macerals divide them into two general groups. The terms telecollinite and desmocollinite are used in many cases to distinguish these two groups. Brown et al. (23) used the term vitritine A to separate a homogeneous higher reflectance variety from a duller, finely laminated, matrix variety (vitritine B). Taylor (24) used transmission electron microscopy (TEM) to show that at high magnification vitritine A was homogeneous while vitritine B contained inclusions of other macerals. Alpern (25) distinguished homocollinite and heterocollinite along the same lines. In carbonization studies Benedict et al. (26) found a less reactive variety, pseudovitritine, characterized by a higher reflectance and a more homogeneous nature than normal vitritine. Although the terms are not strictly synonymous, pseudovitritine, homocollinite, vitritine A, and telecollinite, have the coincident properties of higher reflectance, greater homogeneity, and lower carbonization reactivity than normal vitritine, heterocollinite, vitritine B, and desmocollinite. The appearance of pseudovitritine under reflected white light is shown in Figure 1A. It also should be noted that it is pseudovitritine that tends to occur in homogeneous vitreous layers in coal seams and, therefore, the material collected in the hand picking of these layers tends to be pseudovitritine and not, in fact, the more abundant normal vitritine.

The liptinite group of macerals is derived from the resinous and waxy parts of plants such as resin, spores, and pollen. This group makes up 5-15% of most North American coals and is the most aliphatic and hydrogen rich group of macerals. The most common varieties of liptinite macerals are sporinite, cutinite, and resinite. Sporinite is usually the most abundant variety and the study of sporinite in coal and other rocks is the essence of the science of palynology in which the various sporinite morphologies are examined to discern both age and botanical relationships. A good collection of papers on sporinite is found in Sporopollenin (27). Cutinite is derived from cuticle, the waxy coating on leaves, roots, and stems. Cutinite is quite resistant to weathering and is sometimes concentrated as "paper coal" or "leaf coal" where it can be easily extracted and characterized. One such occurrence in Indiana has been studied by Neavel et al. (28-30).

The resinite macerals are in some ways the most varied group. They are derived from both the wound resins (terpenes) of plants and various other plant fats and waxes making up the lipid resins. The terpene-derived resinites are the most abundant type and they are found in most North American coals as ovoid masses. However, in some coals, especially in the western USA the resinite occurs mainly as a secondary form showing

evidence of having been mobilized (see Figure 1B). This form is of considerable interest because it can be commercially exploited and marketed as a chemical raw material (31,32). The occurrence and infrared spectral properties of various resinites have been well studied by Murchison and Jones (33-36). Teichmüller has reported on the origin and fluorescence properties of secondary resinites (20).

The inertinite group of macerals is derived from degraded woody tissue and usually makes up 5-40% of most North American coals, although in some western Canadian, and all southern hemisphere coals, it can make up a greater percentage. The inertinite macerals have the highest reflectance, as seen in Figure 1A and C, and carbon content in any given coal and are usually divided into five general types. Fusinite and semi-fusinite are characterized by well-defined cell texture with fusinite having the highest reflectance (see Figure 1D). Semi-fusinite is the most abundant inertinite maceral type and has the largest range of reflectance - between vitrinite and fusinite. Macrinite and semi-macrinite are similar in reflectance to fusinite and semi-fusinite, respectively, but without the presence of cell texture. The processes of both forest-fire charring and biochemical degradation (composting) have both been thought to be involved in the origin of all of these maceral types (37-39). The fifth inertinite variety, micrinite, is a granular high-reflectance material that may be both highly reactive and of secondary origin (18,40,41).

In the first half of this introductory chapter the maceral concept has been discussed and the main maceral groups and their important maceral types described. Emphasis has been placed on in situ characterization techniques which rely mostly on microscopy. The rest of this chapter will examine other techniques used for chemical characterization and examine the reactivity of coal macerals in thermal processes. The availability of separated maceral concentrates was a necessary component of the studies which will be described.

Separations

The preparation of maceral concentrates for study has been achieved by one of two approaches, either by hand picking or by a variety of techniques which exploit the variation in density between the various maceral groups. The first level of hand picking is the judicious sampling of lithotypes. This term is used to identify the various layers found in a coal seam. For humic coals there are four main designations of lithotypes: vitrain, clarain, durain, and fusain (42). Vitrain bands are sources of fairly pure vitrinite group macerals while fusinite and semi-fusinite can be obtained from fusain. These are the

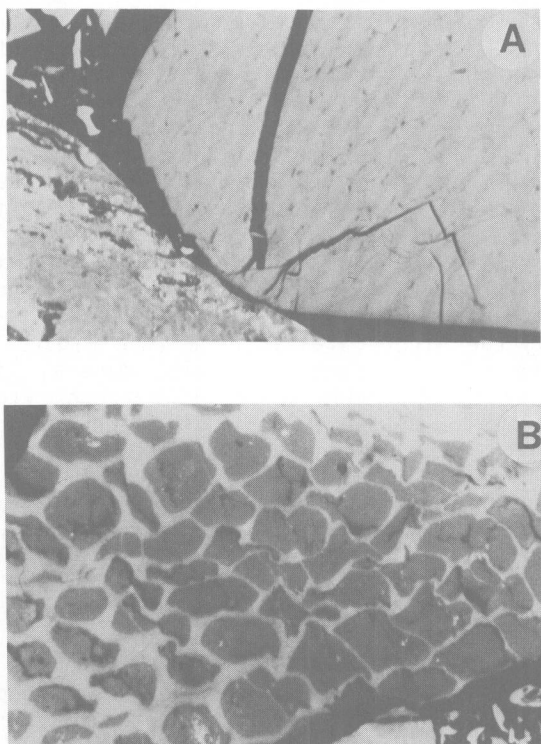
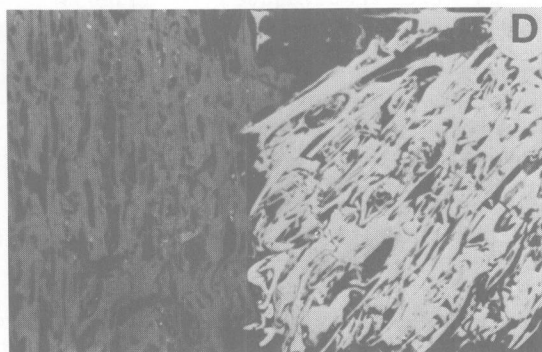
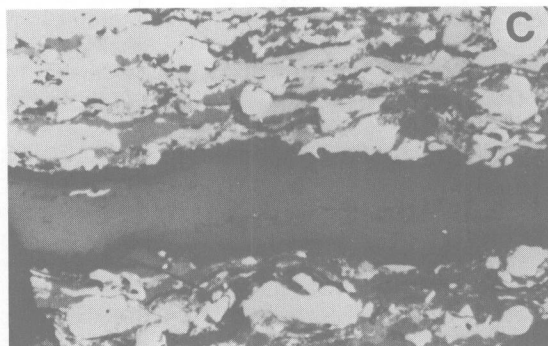


Figure 1. Photomicrographs of coal macerals from the Elkhorn No. 3 seam Eastern Kentucky - hvA bituminous rank. Reflected light in oil, diameter of field, 300 microns, crushed particle pellets.

- A. Large particle of pseudovitrinite at right showing serrated edges and well-developed cell texture. Particle at left is normal vitrinite with inclusions of sporinite (dark gray) and inertinite (white).
- B. Particles of vitrinite with cell-fillings of dark resinite.



- C. Particle made up of inertinite fragments in a vitrinite matrix with a zone of vitrinite running from left to right in the middle of the particle. Dark zones at boundaries of vitrinite are cutinite.
- D. Inertinite macerals, semi-fusinite at left and fusinite at right.

typical macerals which are concentrated by hand picking in addition to, in some cases, resinites (43). The other liptinites and the inertinite, micrinite, tend to be well dispersed among the other macerals which makes hand picking very difficult.

Due to the variation in chemical make up of coal macerals, their densities are different and this property has been exploited to produce maceral concentrates. Early studies in this area have been reviewed by Golouskin (44). Typically the macerals are fractionated by the float-sink technique using heavy liquids ranging in density from 1.2-1.5 g/cc. Kröger and coworkers (45) used mixtures of CCl_4 -toluene to fractionate each of four Ruhr coals into three groups. They found that liptinites fell in the range $\rho=1.20$ -1.25, vitrinites $\rho=1.30$ -1.35 and inertinites which they claimed were mostly micrinite $\rho=1.40$ -1.45. A problem with using CCl_4 is that it cannot be completely removed from the maceral fractions after separation (46). Also, a portion of the coal can be solubilized in these solvent mixtures. Others have used aqueous salt solutions. An example is the technique used by van Krevelen and coworkers where coals crushed to $\sim 10 \mu\text{m}$ were fractionated in aqueous ZnCl_2 (47). A problem with aqueous solutions is the tendency for coal particles to agglomerate, a tendency that increases as the size of the particles decreases. Polar solvents have been added to the aqueous solutions to disperse the coal particles. Normally, the float-sink method is accelerated by centrifuging the solutions. Kröger developed a continuous flow centrifugation method for maceral group separation (45). Flotation methods for maceral separation have up to now yielded limited results, however, in one study it has been found that exinites could be concentrated (48).

Recently, a new approach for exploiting the density variation in macerals to achieve separation has been developed. Dyrkacz and coworkers (49,50) have applied density gradient centrifugation (DGC) to divide coals into narrow density fractions which can yield maceral concentrates of very high purity. The multi-step technique requires a two-stage grinding procedure to produce a fairly uniform particle size distribution of 3 microns, first by ball milling and second by grinding with high-velocity nitrogen gas in a fluid-energy mill. Next, the coal is demineralized by HCl and HF under nitrogen and finally separated in an aqueous CsCl_2 gradient with a non-ionic surfactant to disperse the particles. Demineralization has been found to be necessary to achieve high-resolution separations. In the past, it was thought that 3 micron particles were too small for petrographic identification. Dyrkacz has shown that although difficult, it is possible to distinguish the three main groups especially with the use of fluorescence microscopy for the liptinites. In fact, sporinite and alginite can be separated

with the DGC technique and distinguished petrographically (50). Five of the chapters in this book describe studies of macerals concentrated by this technique.

Two other sets of separated macerals have been studied fairly extensively including the samples prepared by Fenton and Smith (51) which have been termed the "British Macerals" and more recently a set obtained by Allan (52) separated by either hand picking or by a modified van Krevelen method (47). Characterization of these samples will be described in the next section.

Characterization

Early studies on separated macerals were done by Kröger (45,48,53-58), van Krevelen (47,59), and Given (60,61). Kröger and coworkers characterized their set of macerals from composition parameters (53), heats of wetting (54), pyrolysis (55,56) x-ray diffraction (57) and by process behavior such as carbonization (53,58). In a single paper, Dormans, Huntjens, and van Krevelen presented a significant amount of information on their set of macerals which is further discussed in van Krevelen's book (59). They proposed a method of presenting elemental analysis data which is now referred to as a van Krevelen plot and used extensively by organic geochemists. An example of such a plot is shown in Figure 2 with the typical distribution for the three main maceral groups. The plot shows the differences between macerals, the variation within macerals and the changes in their composition with increasing coalification.

Given and coworkers studying the "British Macerals" took more of an organic chemist's approach to characterization. The macerals were subjected to solvent extraction, lithium reduction, hydroxyl determination, oxidation, and reaction with various reagents. N-bromosuccinimide (NBS) was used to brominate aliphatic carbons which in the case for four macerals from an Aldwarke Silkstone coal yielded per 100 carbon atoms the following distribution of hydrogen which is replaced by bromine (61): vitrinite 16, exinite 25 1/2, micrinite 12, and fusinite 6. These values were similar to those obtained by the catalytic dehydrogenation (62) of hvA bituminous coal macerals which yielded in atoms of hydrogen per 100 carbons: vitrinite 25, exinite 31, micrinite 18, and fusinite 5. Such results would suggest that vitrinites and exinites should be more reactive in thermal processes and indeed this has been found to be true and will be discussed in the section on reactivity.

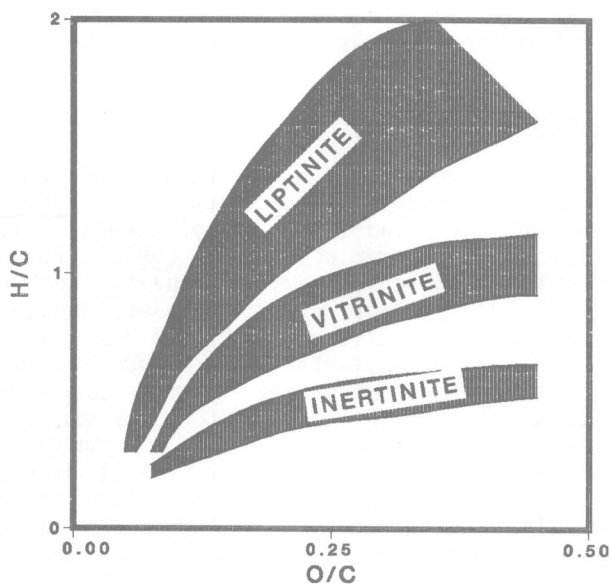


Figure 2. A van Krevelen plot showing approximate bands for the three main maceral groups.