

## Chapter 4

# Composition of Coal

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### INTRODUCTION

As in any other sedimentary rock, the composition of coal is extremely heterogeneous. Coal is largely a macromolecular organic rock, derived from the burial and compaction of peat deposited under various wetland conditions (Stach et al., 1982; Hatcher et al., 1983; Schobert, 1989; Teichmüller, 1989). The nature of a *peat mire* is largely controlled by the nature of the water source (ground water versus rainfall) and supply of nutrients. The formation of peat is controlled by several complex parameters as depicted in Figure 1A. A peat mire can be classified as *rheotrophic* (recharge both from ground water and rainfall) or *ombrotrophic* (recharge solely from rainfall) (Moore, 1987; Calder et al., 1991). A *minerotrophic* peat is derived through recharge from mineral-rich ground water. The relative influence of ground water and rainfall (precipitation versus evaporation ratio) determines the various type of peat mire (swamp, fen, or bog) (Figure 1B).

Coal is composed mainly of organic material with inorganic material as a minor constituent. An inorganic (mineral matter) content of 30% in a coal is considered to be the boundary between coal and impure coal, otherwise known as coaly middlings (intermediate between shale and coal; Alpern, 1981). The major organic constituents of peat are floral components of vascular (forested or marsh vegetation) and nonvascular (aquatic vegetation) plants such as bark, wood, stems, roots, spores, pollen, cuticles, and grasses as well as algae which are associated with fungal, bacterial, and animal remains. The inorganic constituents include minerals or mineral-maceral associations and trace elements (either within the mineral or organic parts).

The formation of peat requires the preservation of plant remains. In an oxygenated environment, the plant remains ultimately decay to CO<sub>2</sub> and H<sub>2</sub>O by fungal and bacterial action. However, in an anaerobic environment, plant remains are also degraded by bacteria, but decay is different and less efficient. Under prolonged anaerobic conditions, some plant biopolymers are selectively degraded and may escape complete destruction; they are thereby preserved and peat accumulates.

Peat undergoes chemical and physical transformation during diagenesis. With prolonged burial, an increase in temperature and pressure results in additional physico-

chemical transformation of the peat. These transformations or *coalification* convert peat to lignite, bituminous coal, and eventually to anthracite coal. The process of coalification occurs in several stages: *diagenesis*, *catagenesis*, and *metagenesis* (Tissot and Welte, 1984). Coals formed within the diagenetic stage include *peat*, *lignite* (A and B), and *sub-bituminous C and B* which are formed from the compaction, loading, and chemical transformation due to bacterial activity and temperature. The coals formed within the catagenetic stage are called *subbituminous A* and *high-, medium-, low-volatile bituminous*, which are formed through the effect of heat, pressure, and time; coals formed at the metagenetic stage are termed *semi-anthracite* and *anthracite* and are formed by the prolonged action of temperature and pressure. Coal formed within the metamorphic stage are termed *metanthracite* and *graphite*, which are formed by mega-tectonic or micro-tectonic oriented pressure (Stach et al., 1982; Teichmüller, 1989; Oh et al., 1991), rather than multiaxial pressure.

The composition of coal is determined by physical, physico-chemical, and chemical analytical methods. These methods characterize the diversity and heterogeneities of coal at various coalification stages. Coal can be examined by macroscopic (physical), microscopic (physical and physico-chemical), and chemical methods. This chapter will review the genesis of macerals and maceral-mineral networks and discuss the chemical characterization of the organic and inorganic constituents of coal.

### PHYSICAL AND PHYSICO-CHEMICAL COMPOSITION OF COAL

#### Compaction and Coal Rank

The degree of compaction from peat to lignite to bituminous coal is a matter of controversy. Ting (1977) suggested a compaction ratio of 4:1 when peat is transformed to lignite. Ryer and Langer (1980), Law et al. (1983), Elliot (1985), and Calder (1991) reviewed the work of various authors concerning the thicknesses involved during the transformation of coal from peat to semi-anthracite stage, and they concluded that compaction ratios vary between 4 and 20; compaction is mainly caused by loss of moisture content in

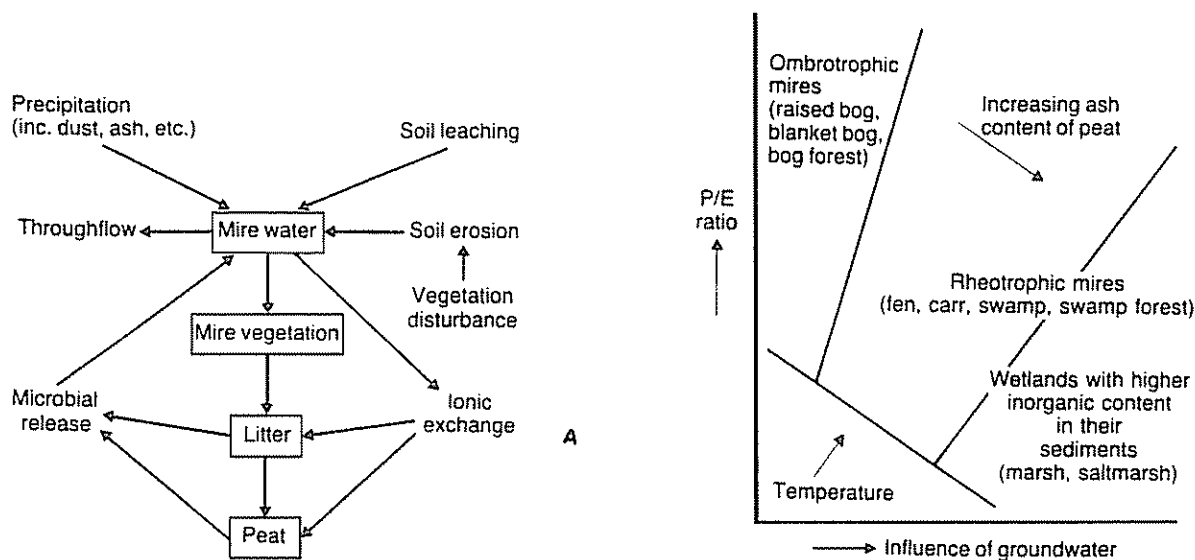


Figure 1. (A) Nutrient flow pattern in a mire ecosystem (after Moore, 1987). (B) Relationship between the relative influence of ground water and rainfall for mire development (after Moore, 1987). P denotes precipitation and E denotes evaporation.

coal (peat to HVB can change moisture content from 93 to 7%). As an approximate estimate, 6 m of peat are required to form 1 m of bituminous coal.

## Lithotypes and Macerals

### Historical Review

The characterization of recognizable plant material in coal was first undertaken using transmitted white light microscopy (Thiessen, 1912; Thiessen and White, 1913), and subsequently elaborated upon by megascopic (Stopes, 1919) and microscopic (using both incident and transmitted light) techniques including both coal petrography and palynology (Thiessen, 1925, 1926; Potonie, 1925; Stach, 1927; Seyler, 1929, 1935; Stopes, 1935; Cady, 1942; Dahme and Mackowsky, 1950; Selvig et al., 1950; Abramski et al., 1951; Teichmüller, 1940, 1950; Schopf, 1960; ICCP, 1963, 1971; Ammosov, 1956).

The megascopic (macroscopic) components of coal are termed *ingredients* (Stopes, 1919) or *lithotypes* (Stach et al., 1982). The microscopic components are termed *macerals* which are comparable to the mineral grains in other rocks, although organic components do not show any crystalline structure (Stopes, 1935). The natural association of various bituminous macerals or macerals and minerals under reflected light microscopy is called a *microlithotype* (ICCP, 1963). Since 1936, the understanding of the composition of coal has been greatly enhanced by the application of incident light fluorescence microscopy (Schohardt, 1936; Jacob, 1952; van Gijzel, 1967; Ottenjann et al., 1974; Teichmüller, 1974a; Davis, 1984; Lin and Davis, 1988; Stout and Bensley, 1987; Ottenjann, 1988; Mukhopadhyay, 1992). For a review of the historical development of the Stopes-Heerlen Classification System and earlier research on lithotype, maceral, and microlithotypes, the reader is referred to Stach et al. (1982), Noel (1987), and Teichmüller (1989) and to Lin and Davis (1986), Teichmüller (1982, 1986), and Mukhopadhyay (1992) for a review of the various aspects of fluorescence microscopy.

### Lithotype

According to its megascopically recognizable components (termed its lithotype), coal is classified into two types: humic and sapropelic (Stach et al., 1982). Humic coal is generally banded whereas sapropelic coal is unbanded. The banded bituminous coal lithotypes, classified as vitrain, clarain, durain, and fusain, were defined from the early works of Stopes (1919). Vitrain is bright black, glassy, shiny, and brittle. Clarain is semibright, silky, and slightly duller than vitrain. Durain is dull, greasy, and blocky. Fusain is a fossil charcoal and is dull, flaky or fibrous, and powdery. The term *clarodurain* or *duroclarain* was added to the lithotype terminology later to better characterize coal by megascopic methods (Cady, 1942). Vitrain and clarain usually comprise the bright coal lithotypes and durain and fusain comprise dull coal lithotypes; duroclarain and clarodurain are an intermediate form of these two lithotypes (Stach et al., 1982). ASTM (1991) classified lithotypes according to banded, nonbanded, and impure coal. Vitrain, attrital coal, and fusain are considered within the banded coal; cannel or boghead or transition between these varieties lies within nonbanded coal; bone coal and mineralized coal lie within impure coal. Hower et al. (1990) further modified the lithotype terminology by adding bright clarain and dull clarain (replacing clarodurain and duroclarain) according to the degree of preservation of the matrix versus wood comparing both peat and bituminous coal (Table 1). Bone coal, a term usually used by American miners to describe impure high ash coal, was also included in the lithotype classification (Table 1). Hower et al. (1990) also pointed out the relationship between lithotype, microlithotype, and percentages of macerals (Figure 2).

In lignite, the diversities of plant components related to megascopic observation are more complex due to the lack of homogenization. Hagemann and Hollerbach (1980) classified lignite lithotypes into four major classes based on the presence or absence of plant structure (xylite) or minerals, banding type, color and hue, evidences of gelification, inclusion, and surface texture. Mukhopadhyay (1986) modified their lithotype classification by introducing two major

Table 1. Classification of lithotypes in bituminous coal (after Hower, 1990).

| Lithotypes     | Proportion of Bright and Dull Bands |
|----------------|-------------------------------------|
| Vitrain        | <10% dull bands                     |
| Bright clarain | 65–90% bright (vitrain) bands       |
| Clarain        | 35–65% bright bands                 |
| Dull clarain   | 10–35% bright bands                 |
| Durain         | <10% bright bands                   |
| Fusain         | Fibrous; silky luster               |
| Bone           | High ash                            |

| LITHOTYPE <sup>1</sup> | MICROLITHOTYPE    | GROUP MACERALS <sup>2</sup>                 |
|------------------------|-------------------|---|
| Vitrain                | vitrinite         | V > 95%                                     |
| Bright clarain         | clarite           | V + L > 95%                                 |
|                        | vitrinertite      | V + I > 95%                                 |
|                        | duroclarite       | V > I,L; each > 5%                          |
|                        | clarodurite       | I > V,L; each > 5%                          |
|                        | vitrinertoliptite | L > V,I; each > 5%                          |
| Dull clarain           | durite            | L + I > 95%                                 |
|                        | carbominerite     | 20–60% vol. minerals<br>5–20% vol. sulfides |
| Durain                 |                   |   |
| Bone                   |                   |   |
| Fusain                 | inertite          | I > 95%                                     |

<sup>1</sup>Groupings are generalized but do show expected range of composition.

<sup>2</sup>V - vitrinite; L - liptinite; I - inertinite

Figure 2. Generalized microlithotype and group maceral composition of lithotypes (after Hower, 1990).

lithotype classes (pure and impure detrital) based on the study of Texas lignites. A similar classification was later adopted by Hagemann and Wolf (1987).

In peat, the lithotype classification is even more complex, because most plant components are preserved nearly in their original condition with little modification. Peat is usually classified as fibric, coarse hemic, hemic, fine hemic, sapric, and clayey according to lithotype (Esterle, 1990). Cohen and Spackman (1980), Cohen et al., (1987), Moore and Ferm (1988), and Esterle (1990) provide further details of the lithotype terminology for peat.

## Macerals

### Preview

Macerals are the microscopically recognizable constituents of coals that originate from the different organs or tissues of plants (e.g., spores, algae, bark, etc.). The physical, chemical, and technological properties of the macerals vary continuously with increasing rank, but in different proportions (ICCP, 1971). All macerals contain the suffix "inite" (Stopes-Heerlen System, ICCP, 1963, 1971). Some of the macerals contain various submacerals.

Until 1950, study of the banded components of bituminous coal in the United States was usually undertaken by transmitted light microscopy and using the component

terms such as anthraxylon, attritus, and fusain (Theissen, 1925, 1926). The modern maceral classification system is based on incident light microscopy and is called the "Stopes-Heerlen System" (ICCP, 1963; Stach et al., 1982). Macerals, termed *components* by Thiessen (1926), were introduced by Stopes (1935). According to the Stopes-Heerlen System of classification, three maceral groups are usually identified by their relative reflectance in incident light (Table 2) (ICCP, 1971; Stach et al., 1982). The three maceral groups are *huminite/vitrinite*, *liptinite (exinite)*, and *inertinite*. Liptinite macerals have the lowest reflectance, vitrinite macerals are of intermediate reflectance, and inertinite macerals show the highest reflectance under oil immersion. The name *vitrinite* is derived from their glassy appearance, *liptinite* is derived from lipid components of the plant and other substances, and *inertinite* is derived from the inertness of their components to chemical reaction. Vitrinites originate from the ligno-cellulosic parts of plants; liptinites come from the exine and lipid substances of plants; and inertinites represent the oxidized components of plant lignin, cellulose, exine, fungi, lipid, and faunal remnants.

The maceral and maceral types from the huminite/vitrinite group are evolved through several physical and chemical processes of homogenization known as *humification*, *gelification*, and *bituminization* (Stach et al., 1982; Stout and Spackman, 1987; Teichmüller, 1989; ASTM, 1991).

### Procedures for Maceral and Microlithotype Analysis

According to the efforts of the International Committee for Coal Petrologists (ICCP, 1963, 1971) and Stach et al. (1982), procedures have been standardized for maceral and microlithotype compositional analysis of bituminous coal by the International Standards Organization (ASTM, 1991). For petrographic analysis, the coal sample is ground and polished by making a pellet using either whole coal (oriented sample) or crushed (-20 mesh) coal impregnated in cold-set epoxy resin. Pellets are observed under oil-immersion objectives (>25× to <63×).

For microlithotype analysis, the maceral assemblage must have a minimum band width of 50 μm to be considered a microlithotype. It is usually measured with a graticule on the specimen covering an area of 50 × 50 microns.

### Homogenization of Macerals

The process of homogenization has a profound influence on the change in rank, porosity, and permeability in coal. The homogenization processes involved in the formation of humic and sapropelic coal are different. This is because humic coal contains mainly vascular plant material with a dominance of lignin, cellulose (carbohydrate) and tannins, and some lipids, whereas sapropelic coal contains mainly marsh and aquatic plants whose essential chemical ingredients are cellulose, lipids, and protein. The process of homogenization, involving the breakdown of xylem and other plant parts (such as tracheids), is usually controlled by two overlapping phases called *humification* and *gelification* (Stach et al., 1982; Teichmüller, 1989). Stout and Spackman (1987), however, advocated that three processes are involved: *alteration*, *degradation*, and *gelification*.

*Humification*, according to Stach et al. (1982) and Teichmüller (1989), is a combination of biological and chemical processes active during the formation of peat and strongest at the peat surface. This process involves hydrolysis and oxidation by fungi and bacteria and partial (50–75%) or total (more than 90%) loss of cellulose and concomitant selective preservation of lignin-derived components. During this period, formation of humic acid and fulvic acid is common. Under the microscope, the relative loss of cellu-

Table 2. Classification of maceral groups and macerals with their characteristic features (modified after Teichmüller, 1989).

| Group Macerals                 | Macerals   | Morphology   | Characteristics  |
|--------------------------------|--|--|--|
| <i>Primary</i>                 |  |  |  |
| Vitrinite                      | Telinite   | Cell structures visible  | Cell walls   |
|                                | Collinite  | Telo-<br>Eu-<br>Detro-<br>Cell structures faintly visible<br>Amorphous appearance<br>Fine-grained matrix | Tissue<br>Amorphous (gel or gelified)<br>Detritus                            |
|                                | Corpocollinite<br>Vitrodetrinite   | Rounded or oval amorphous bodies<br>Fine to small angular grains   | Cell fillings<br>Detritus  |
| Liptinite                      | Sporinite  | Well-preserved structures  | Spores, pollen   |
|                                | Cutininite   | Well-preserved structures  | Cuticles   |
|                                | Suberininite   | Well-preserved cell structures   | Suberitized cork cell walls  |
|                                | Fluorinite   | Oval or rounded oily substance   | Plant essential oils   |
|                                | Resinite   | Rounded or oval bodies within<br>or without cell structures  | Resins, waxes and latex  |
|                                | Alginite   | Tel-<br>Large colonial or unicellular algae  | Algae  |
| Chlorophyllinite<br>Bituminite | Lam-<br>Lamellar algal bodies<br>Oval or rounded bodies within cells<br>Amorphous lenses, streaks or bands | Algae<br>Chlorophyll<br>Amorphous (bacterial, algal or faunal)   |  |
| Liptodetrinite                 | Fine grained matrix  | Detritus   |  |
| Inertinite                     | Fusinite<br>Semifusinite   | Well-preserved or broken cells<br>Incipient cell structures  | Cell walls (charred, oxydized)<br>Cell walls (partially charred or oxydized) |
|                                | Sclerotinite<br>Macrinite  | Well-preserved structures<br>Amorphous appearance  | Fungal cell walls<br>Amorphous gel (oxydized, metabolic)                     |
|                                | Micrinite<br>Faunal Relics   | Amorphous grainy<br>Shreds of faunal fragments   | Oxydized amorphous gel<br>Fish or other animal fragments                     |
|                                | <i>Secondary</i>   |  |  |
| Liptinite                      | Exsudatinite   | Amorphous maceral within fractures   | Exudates   |
| Inertinite                     | Micrinite  | Amorphous and grainy   | Relics of oil generation   |
| Inertinite                     | Rank-inertinite  | Inertinized spore, cuticle etc.  | High rank liptinites   |

lose can be identified by the loss of green to yellow fluorescence (derived mainly from the cellulose), which changes either to brown fluorescence or nonfluorescent cell structures (xylem tissue).

Biochemical *gelification* (after Stach et al., 1982; Teichmüller, 1989) of humic substances (mainly occurs at the lignite stage) includes partial or total loss of cell structures, peptization, softening or plasticity, and compaction. Chemically, the lignin phenols (guaiacyl and syringyl) yield an aromatic network of phenols and alkylbenzenes through an intermediate product (catechol) via demethylation (Hatcher et al., 1989a). Microscopically, the appearance of biochemical gelification involves the formation of fine-grained or massive amorphous gel.

Geochemical *gelification* (of Stach et al., 1982; Teichmüller, 1989) or *vitrinitization* begins at the boundary between lignite and subbituminous coal where huminite macerals are homogenized and compressed (due to loss of

water) forming vitrinite macerals. Microscopically, more homogenized vitrinite macerals are formed as a result.

Compared to the *humification* and *gelification* described by Stach et al. (1982) and Teichmüller (1989), the homogenization processes (alteration, degradation, gelification) described by Stout and Spackman (1987) are early phenomena and occur within the peat stage. *Alteration* involves only chemical changes (possibly by oxidation) whereby fluorescence of xylem tissues changes from green or yellow to blue. *Degradation* involves the selective hydrolyzation by oxidation (possibly bacterial) of cellulose-rich middle cell walls and partially lignified cell walls and the accumulation of degraded material within the cell lumens. The fluorescence of the cell lumens is greatly reduced. During *gelification*, fine-grained isotropic gel-like material is formed and is associated with swelling of the secondary cell wall. Chemically, the main processes involved in early peatification or homogenization, according to Stout et al. (1988), are:

(1) relatively rapid removal of pentosans (hemicellulose) by microbial hydrolysis, (2) introduction of fungal carbohydrate remains into the residual wood material in surface litter, (3) biochemical depolymerization of the cellulose, and (4) the gradual biotransformation of the lignin macromolecule by depolymerization, demethylation, demethoxylation, and further defunctionalization. Timewise, all four of these processes of Stout and Spackman (1987) are completed within the time period of *humification* of Stach et al. (1982) and Teichmüller (1989). At the lignite stage the processes are: (1) apparent gradual removal of all carbohydrate by anaerobic microbial and/or geochemical processes and (2) geochemical transformation of the residual lignin leading eventually to a predominantly aromatic hydrocarbon network.

Teichmüller (in Stach et al., 1982, and Teichmüller, 1989) suggested another process of homogenization called *bituminization*. In this process, petroleum-like hydrocarbons are generated and expelled from perhydrous vitrinite and liptinite macerals, in turn causing aromatization and condensation of the remaining coal macerals. The process of bituminization, which is possibly initiated at the boundary of subbituminous A and high-volatile bituminous coal (Teichmüller, 1989; Ottenjann et al., 1974; Ottenjann, 1988), results in major changes in fluorescence alteration (a process of increase or decrease of fluorescence intensity under ultraviolet excitation).

The homogenization process in sapropelic coal involves the formation of gyttja and subsequent changes due to putrefaction (fermentation) by mild oxidation and anaerobic decomposition. Sapropelic coal contains mainly phytoplankton, fine detritus of marsh or subaquatic plants in contrast to woody tissue from bark, stem, wood, etc. The components of sapropelic coal are rich in cellulose, wax, fatty acids, and lipids and are hydrogen-rich compared to the humic coals. In general, three types of sapropelic coals are present: one rich in spore exine (cannel), another rich in phytoplankton (boghead), and the third rich in completely biodegraded humic and lipid organic matter (can be termed *sapropelitic*; Stach et al., 1982). The first two types of coal (cannel and boghead) are formed under mild oxidizing conditions leaving finely detrital gyttjae (shreds of huminitic and liptinitic detritus), well-preserved spores or algae, colloidal humic substances (phlobaphinite or corpohuminite), and detritus of oxidized organic matter (inertodetrinite). However, in a true anaerobic environment, attrital remains of herbaceous plants and humic and lipid remains of aquatic plants are mostly destroyed and mixed with bacterial lipids that form amorphous lipid-rich huminite (saprohuminite and densinite—the low-rank counterpart of desmocollinite and saprocollinite) and liptinite (bituminite) macerals.

### Characterization of Macerals

All macerals present within vitrinite, liptinite, and inertinite groups are categorized either as *primary* or *secondary* (Table 2). *Primary* macerals are those that are either derived or formed from various plant, bacteria, fungi, and animal remains at the time of deposition or during early diagenetic stage (Teichmüller, 1974; Mukhopadhyay et al., 1985). *Secondary* macerals are those that are formed at the expense of some primary macerals due to coalification during late diagenesis or catagenesis (Teichmüller, 1974; Stach et al., 1982; Mukhopadhyay et al., 1985).

Below the rank of subbituminous C, vitrinite macerals are termed *huminite*. The name *huminite* implies the presence of humic and fulvic acids, which can be extracted by alkali. The huminite/vitrinite group shows different maceral

assemblages in the peat or lignite stage compared to the bituminous stage, because they are more susceptible to physical and chemical degradation during coalification. The liptinite and inertinite maceral groups show similar maceral assemblages (with some exceptions) throughout their entire rank range. The exceptions are chlorophyllinite, exsudatinitite, micrinite, and rank-inertinite (meta-liptinite). Chlorophyllinite (a primary maceral within the liptinite group), which is derived from plant chlorophyll, is only present in peat and lignite (Teichmüller, 1989). On the other hand, exsudatinitite, micrinite (mostly), and rank-inertinite are secondary macerals; exsudatinitite started forming at the lignite stage and is recognizable until medium-volatile bituminous coal stage, micrinite forms at the boundary of subbituminous B and A and remains visible until the anthracite stage, whereas rank-inertinite forms at the low-volatile bituminous stage and is recognizable until the anthracite stage. According to reflectance, exsudatinitite is included within the liptinite group and micrinite and rank-inertinite are included within the inertinite group.

All three maceral groups (vitrinite, liptinite, and inertinite) include three forms of macerals (Table 2). They show either remnant plant structures (e.g., telinite, sporinite, fusinite, etc.) or occur as either detrital (e.g., vitro-, inerto-, or liptodetrinite) and amorphous (e.g., gelocollinite, bituminite, or macrinite, etc.) forms.

*Huminite/vitrinite Group*: These macerals are the main component (in terms of volume %) of most humic coals (of peat to anthracite in rank) of Recent (Esterle, 1990) to Devonian (Goodarzi and Goodbody, 1990) age (except in some lower Gondwana coals of the southern hemisphere).

Vitrinite in coal or in dispersed organic matter is believed to be formed from vascular land plants (Stach et al., 1982) and is considered to be nonexistent in pre-Silurian rocks. However, a few researchers reported the occurrence of vitrinite-like macerals in Cambrian, Ordovician, and even in pre-Cambrian rocks (VLM as referred by Buchardt and Lewan, 1990 and references therein; Mukhopadhyay, 1992). According to Buchardt and Lewan (1990), these vitrinite-like macerals (VLM) are derived from cellulose and polysaccharides.

The huminite/vitrinite group macerals (*telinite*, *collinite*, [*gelinite*], *corpocollinite* [*huminite*], and *vitro* [*or humo*] *detrinite*) and maceral types are presented in Table 3 and Figures 3 to 8 (Figure 3 shows the macerals during various stages of coalification).

*Telinite* macerals or submacerals show well-preserved plant cell structures, which are either void or filled with amorphous humic matter or resin/essential oils or minerals. At the peat, lignite, and subbituminous A ranks, *telinite* macerals are called *textinite* (means tissue or structure). *Telinite* (in bituminous rank) is rare in bituminous coal possibly because homogenization processes change it to telocollinite. Under incident white light, the huminite/vitrinite macerals in all ranks show various shades of gray color (Figure 4). In low rank coal, textinite often shows strong yellow (for cellulose-rich components; Figure 6A or with free cellulose; Figure 4A) to blue fluorescence (for lignin) (Stout and Bensley, 1987; Teichmüller, 1989; Esterle, 1990) or is nonfluorescent and often filled with resin bodies (Figure 11G of Mukhopadhyay, 1989). Macerals such as *ulminite*, on the other hand, are partially gelified huminite macerals. In *texto-ulminite* (Figure 4B) most of the original cell structures can be seen, whereas in *eu-ulminite* most of the cell structures are gelified (Figure 4C). Some of these macerals in the bituminous stage are referred to as *telocollinite*.

Within the *collinite* (*gelinite*) subgroup, two maceral types are common in the low rank coals (*porigelinite* and

Table 3. Classification of macerals and maceral types within huminite/vitrinite group (after Teichmüller, 1989).

| Lignite       |                  |               |                      | Bituminous             |                |                |               |                |
|---------------|------------------|---------------|----------------------|------------------------|----------------|----------------|---------------|----------------|
| Maceral Group | Maceral Subgroup | Maceral       | Maceral Type         | Maceral Variety        | Maceral Type   | Maceral        | Maceral Group |                |
| Huminite      | Humotelinite     | Textinite     |                      | A (dark)<br>B (bright) | Telinite 1     | Telinite       | Vitrinite     |                |
|               |                  | Ulminite      | Texto-Ulminite       | A<br>B                 |                |                |               |                |
|               |                  |               | Eu-Ulminite          | A<br>B                 | Telinite 2     |                |               |                |
|               | Humodetrinite    | Attrinite     |                      |                        |                |                |               | Vitrodetrinite |
|               |                  | Densinite     |                      |                        | Desmocollinite |                |               |                |
|               | Humocollinite    | Gelinite      | Levigelinite         | Detrogelinite          |                | Telocollinite  |               | Collinite      |
|               |                  |               |                      | Telogelinite           |                | Gelocollinite  |               |                |
|               |                  |               |                      | Eugelinite             |                |                |               |                |
|               |                  | Porogelinite  |                      |                        |                |                |               |                |
|               | Corpohuminite    | Phlobaphinite | Pseudo-Phlobaphinite |                        |                | Corpocollinite |               |                |
|               |                  |               |                      |                        |                |                |               |                |

*levigelinite*). Porogelinite is a fine-grained colloidal gel that has discrete internal reflection under white light (Figures 3B and 4A, C, and D), whereas levigelinite is completely structureless and homogeneous (Figures 3B and 4D and E). Levigelinite maceral types have three varieties: *detrogelinite* (humic detritus), *telogelinite* (homogenized cell structures), and *eugelinite* (completely homogenized). Both porogelinite and levigelinite are precursors of *gelocollinite* (bituminous coal) which show shrinkage cracks and cleats (Figure 3E). Telogelinite represents *telocollinite* (Figure 3F), and detrogelinite partially corresponds to *desmocollinite* and partially represents *vitrodetrinite* in the bituminous rank. According to the ICCP (1971), gelocollinite denotes gel of desmocollinite. However, Calder et al. (1991), Stanton and Moore (1991), and Mukhopadhyay (1992) have suggested that gelocollinite can occur both as fracture-filling or as large homogenized bands instead of only as fracture-filling gel.

*Corpohuminite* generally occurs as plant cell fillings (Figures 4F and 5D and E). They are formed as cell excretions from the original plants (*phlobaphinite*) (Figure 4G) or colloidal cell infillings (*pseudophlobaphinite*), sometimes via porogelinite (Figure 4H). In bituminous coal both are termed *corpocollinite*. Stanton and Moore (1991), by using etching techniques on polished coals of bituminous rank, showed the presence of three types of corpocollinite that are derived either from telocollinite and desmocollinite or directly as corpocollinite. They introduced the term *gelinite* in the bituminous coal nomenclature which is possibly derived from secondary (?) humic gel.

The *humo/vitrodetrinite* subgroup shows an intimate mixture of humic detritus and humic gel and contains two macerals at the peat and lignite rank: *attrinite* (more detritus than gel; Figures 3A and 5A and B) and *densinite* (more gel

than detritus; Figure 5B). In the bituminous rank, detritus is subdivided into *desmocollinite* (more gel than detritus; Figure 3D) and *vitrodetrinite* (more fragmented vitritinic maceral than gelified macerals; Figure 9G) (ICCP, 1971; Stach et al., 1982). Mukhopadhyay (1989) suggested that the abundance of liptinitic detritus within this type of maceral can be termed *mixinite* or *liptinite-rich desmocollinite*. In the subbituminous and bituminous rank, this maceral can be termed *saprocollinite* (Figure 5D) (Mukhopadhyay, 1992).

Petrographically, *pseudovitrinite* (*pv*) is usually gray in appearance with white patches (under incident white light); it shows narrow oriented slits or small fractures (Figure 3C). *Pv* has an intermediate reflectance between the vitrinite and inertinite group of macerals. It is generally considered to be formed due to external oxidation of coal in any rank (Benedict et al., 1968; Mukhopadhyay, 1992).

Taylor (1991), using a transmission electron microscope (TEM), suggested that most of the vitrinite maceral types are heterogeneous and can be separated into two kinds of heterogeneity, some of which contain an abundance of fine liptinitic shreds (suberin or remains of microorganisms).

*Liptinite Group*: In contrast to the vitrinite group, hydrogen-rich liptinitic macerals represent a diverse assemblage of plant and animal remains (Table 3); they are chemically heterogeneous. Liptinites are derived from phytoplankton (alginate), bacteria, and higher plant sources (such as cuticle, spore/pollen, suberin, resin, etc.).

Macerals of the liptinite group are darker (in white light) or brighter (in transmitted white or incident blue-light) than the vitrinite group of macerals. These macerals are generally characterized by their fluorescent color and intensity, because these macerals show autofluorescence under UV or blue-light excitation (Stach et al., 1982; Mukhopadhyay,

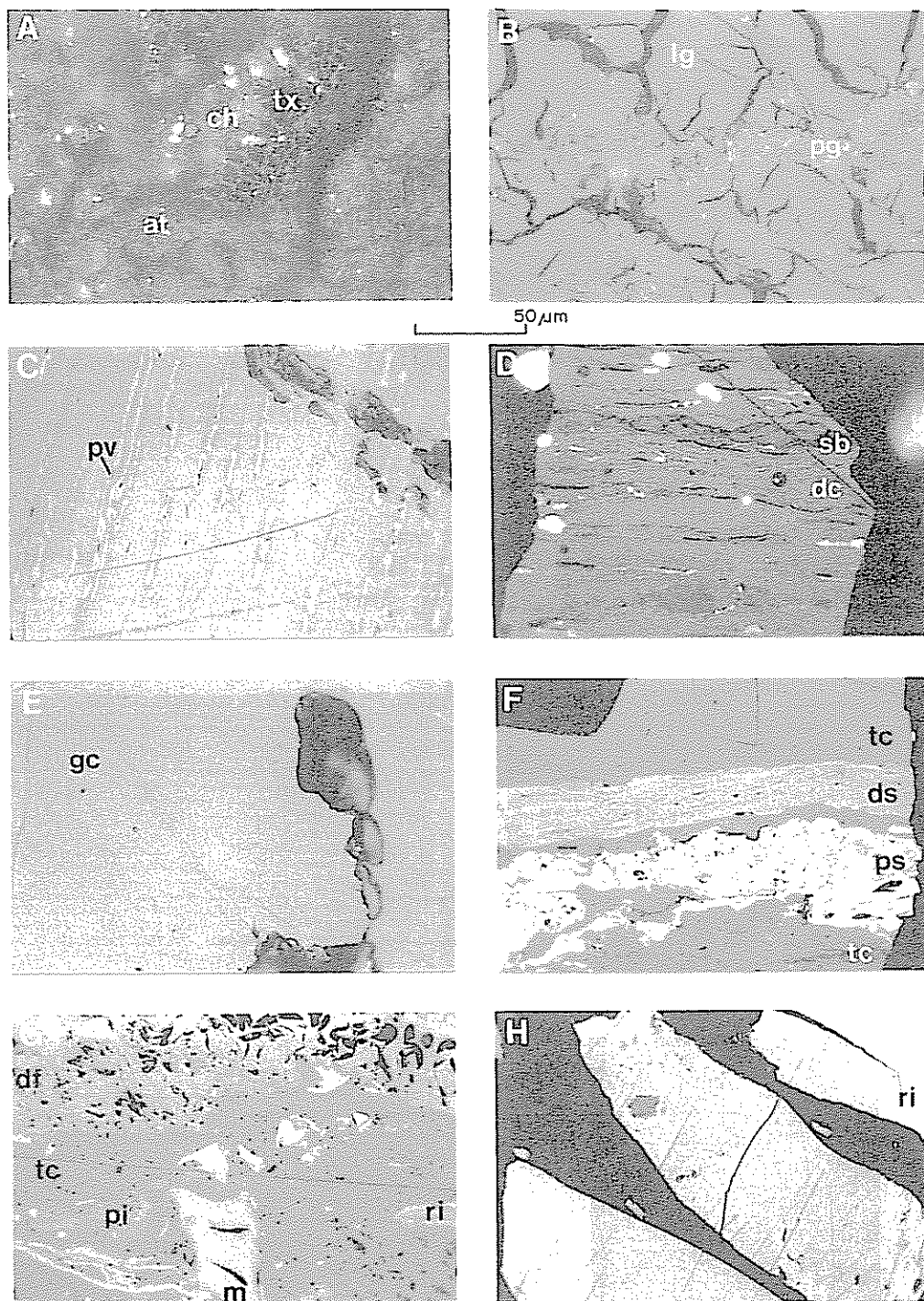


Figure 3. Photomicrograph under incident white light.  $R_o$  = mean huminite/vitrinite reflectance. (A) Textinite (tx), attrinite (at), corpohuminite (ch). Recent Peat, Sumatra, Indonesia.  $R_o = 0.15\%$ . (B) Desiccation crack within levigelinite (lg) and porigelinite (pg). Lignite, Eocene, Wilcox Group, Texas,  $R_o = 0.32\%$ . (C) Formation of pseudovitrinite (pv). subbituminous coal, Eocene, Japan.  $R_o = 0.65\%$ . (D) Desmocollinite (dc) with subberinite (sb). High-vol. bituminous coal. Carboniferous, Nova Scotia, Canada.  $R_o = 0.88\%$ . (E) Gelocollinite (gc). High-vol. bituminous coal. Carboniferous, Nova Scotia.  $R_o = 0.85\%$ . (F) Semifusinite (both pyro-, ps, and degrado-, ds), telocollinite (tc), and corpocollinite. High-vol. bituminous coal. Carboniferous, Nova Scotia, Canada.  $R_o = 0.86\%$ . (G) Degradofusinite (df), telocollinite (tc), macrinite (m), inertodetrinite, and rank-inertinite (ri). Semi-anthracite coal. Permian, Allan, Antarctica.  $R_o = 2.15\%$ . (H) Collinite and rank-inertinite (ri). Anthracite coal. Carboniferous, England.  $R_o = 3.5\%$ .

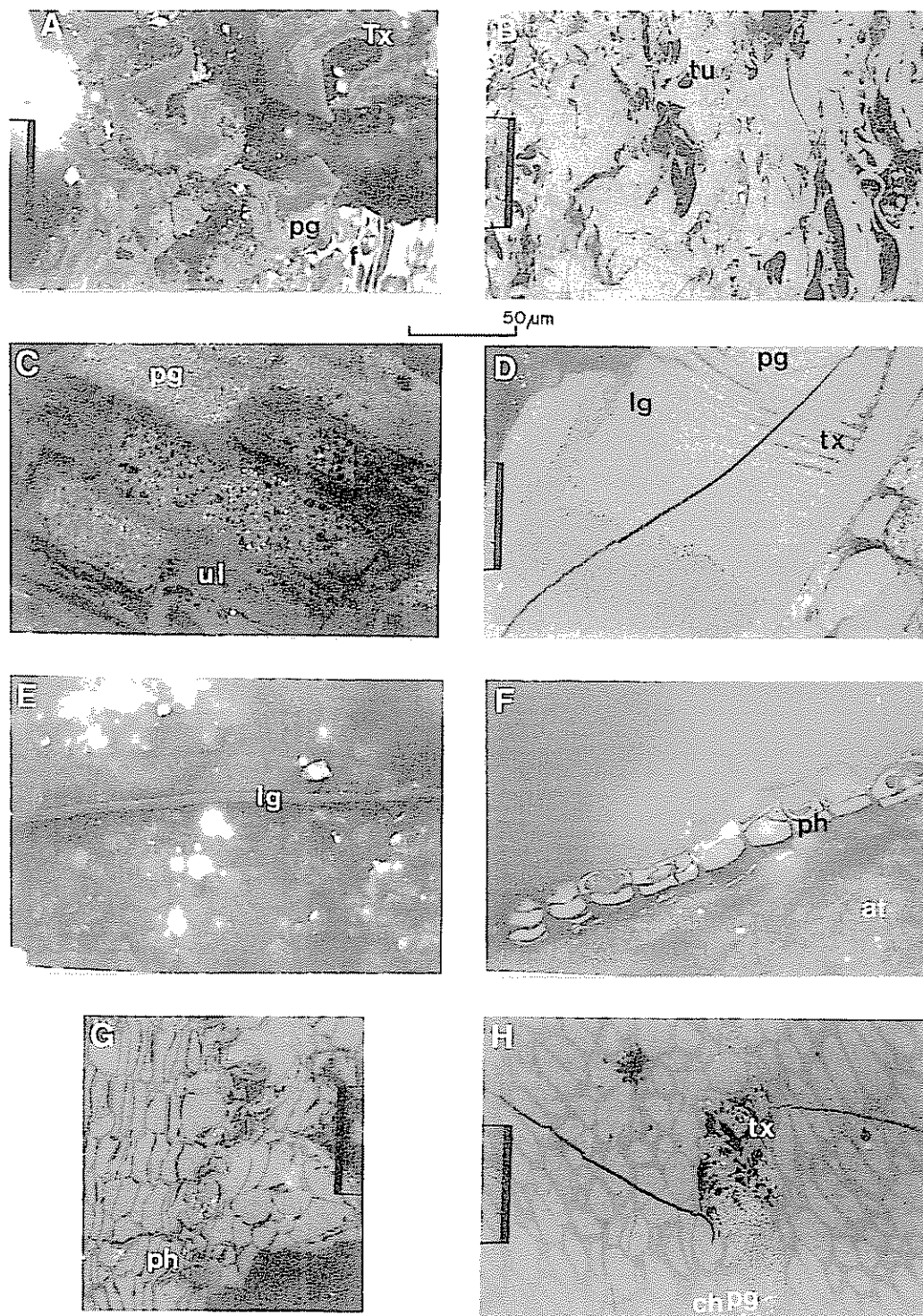


Figure 4. Photomicrographs under incident white light. (A) Cellulose-rich textinite A (tx), porigelinite (pg), and fusinite (f). Lignite, Eocene, Jackson Group, Texas.  $R_o = 0.24\%$ . (B) Textoulminite (tu) with porigelinite. Lignite, Eocene, Wilcox Group, Texas.  $R_o = 0.35\%$ . (C) Ulminite A (ul) and porigelinite (pg). Lignite, Eocene, Jackson Group, Texas.  $R_o = 0.28\%$ . (D) Levigelinite (lg) and porigelinite (pg) are formed from the gelification of textinite (tx). Dark granular substances are porigelinite mixed with minerals. Lignite, Eocene, Wilcox Group, Texas.  $R_o = 0.32\%$ . (E) Levigelinite (lg) band within textinite. Recent Peat, Atchafalaya Basin, Louisiana.  $R_o = 0.14\%$ . (F) Partially oxidized phlobaphinite (ph) and attrinite (at) with nongelified textinite. Recent Peat, Sumatra;  $R_o = 0.16\%$ . (G) Phlobaphinite (ph) and suberinite. Lignite, Eocene, Jackson Group, Texas.  $R_o = 0.28\%$ . (H) The transition from textinite (tx) to porigelinite (pg) to corpohuminites (ch). Lignite, Eocene, Jackson Group, Texas.  $R_o = 0.28\%$ .



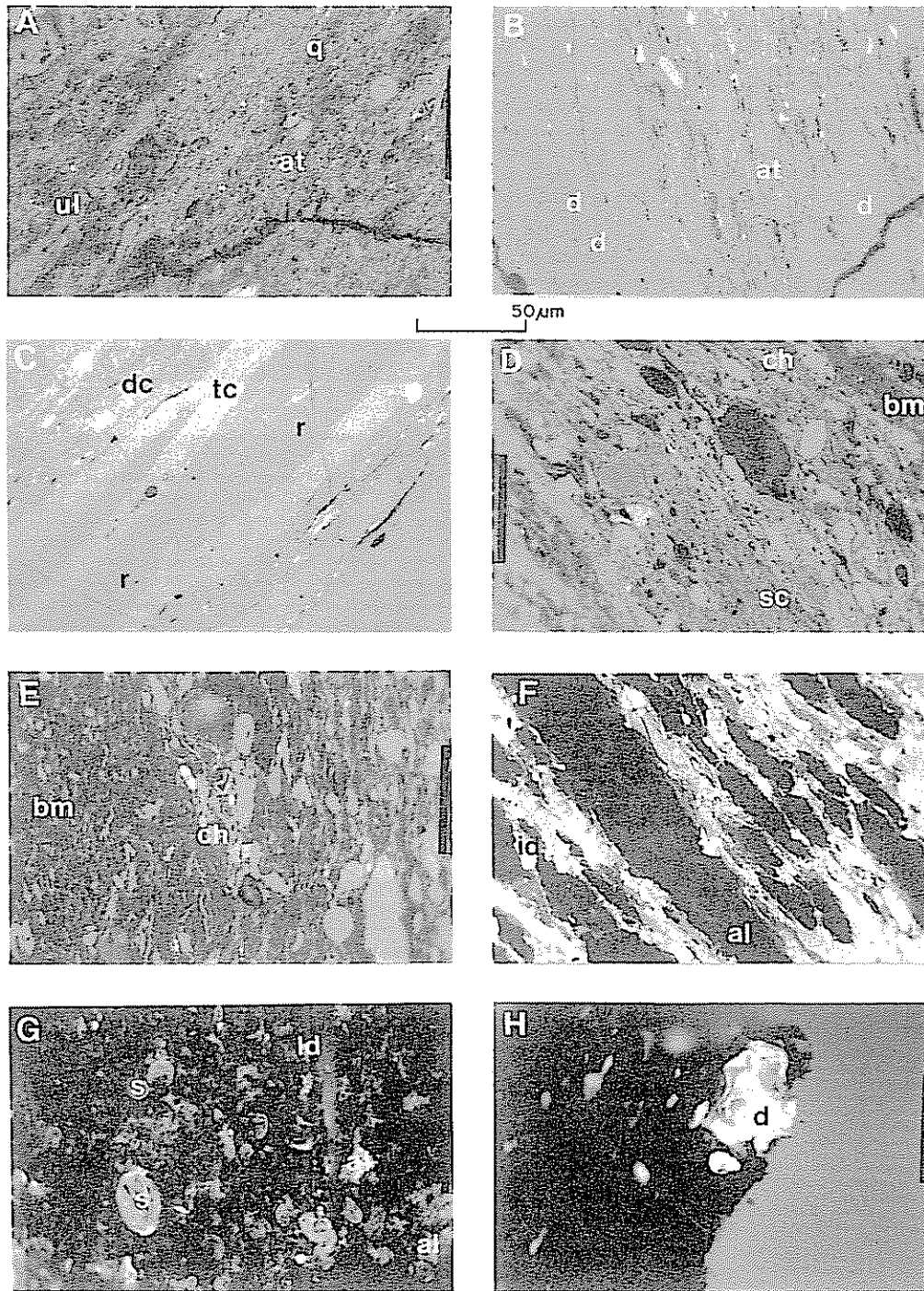


Figure 5. Photomicrographs under incident white light (Nos. A, B, C, D, E, and F) and blue light excitation (Nos. G and H). (A) Attrinite (at), ulminite (ul) with quartz (q), and fine-grained liptinite. Lignite, Eocene, Wilcox Group, Texas.  $R_o = 0.30\%$ . (B) Attrinite (at) and densinite (d) changing to desmocollinite. Subbituminous coal, Eocene, Wilcox Group, Texas.  $R_o = 0.50\%$ . (C) Telocollinite (tc) with resinite (r) impregnation and desmocollinite (dc). High-vol. bituminous coal. Carboniferous, Nova Scotia, Canada.  $R_o = 0.85\%$ . (D) Saprocollinite (sc), corpohuminite (ch), bituminite (bm). Subbituminous coal. Eocene, Claiborne Group, Texas.  $R_o = 0.50\%$ . (E) Bituminite (bm), corpohuminite (ch), quartz, sclerotinite, and inertodetrinite. Subbituminous coal. Eocene, Claiborne Group, Texas.  $R_o = 0.50\%$ . (F) Alginite (al), inertodetrinite (id), corpocollinite. High-vol. bituminous coal. Permian. South Africa.  $R_o = 0.70\%$ . (G) Sporinite (pollen and spore - s), alginite (al), and lipodetrinite (ld). Lignite, Eocene, Wilcox Group, Texas.  $R_o = 0.30\%$ . (H) Dinoflagellate (d). Lignite, Eocene, Jackson Group, Texas.  $R_o = 0.28\%$ .

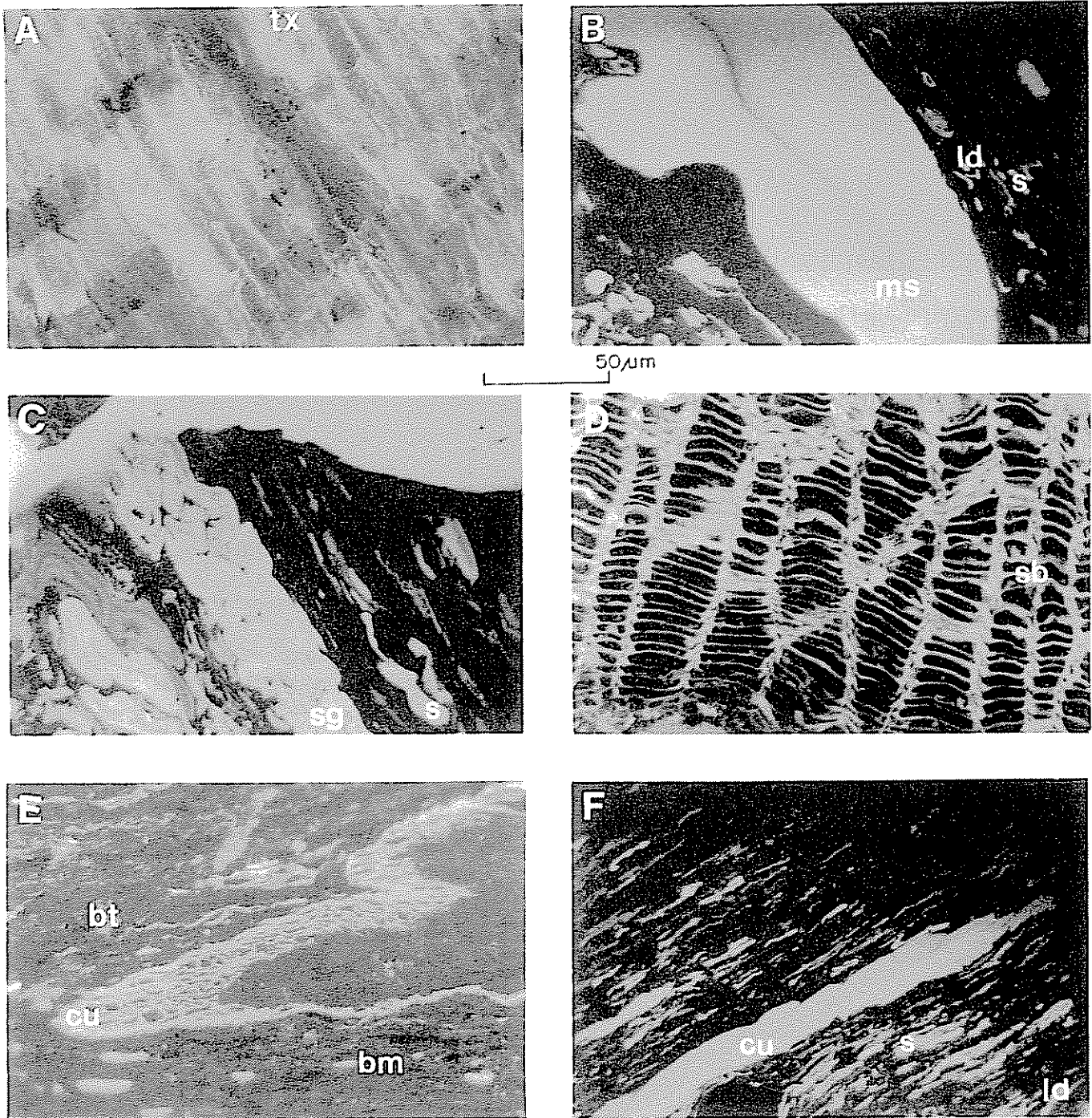


Figure 6. Photomicrographs under incident blue light excitation (fluorescence mode). (A) Textinite (Tx) (gray textinite of Esterle, 1989) with well-formed cell structure. Recent Peat, Sumatra, Indonesia.  $R_o = 0.15\%$ . (B) Sporinite (megaspore, ms, and microspore, s) and liptodetrinite (ld). High-vol. bituminous coal, Carboniferous, Nova Scotia, Canada.  $R_o = 0.85\%$ . (C) Sporinite (Sporangium, sg, and microspore, s). High-vol. bituminous cannell coal, Carboniferous, Nova Scotia, Canada.  $R_o = 0.85\%$ . (D) Suberinite (sb), with phlobaphinite (dark). Lignite, Miocene, Germany.  $R_o = 0.28\%$ . (E) Cutinite (cu), bituminite (bm), bitumen (bt), and liptodetrinite. Subbituminous coal, Tertiary, Indonesia.  $R_o = 0.50\%$ . (F) Cutinite (cu), sporinite (s), and liptodetrinite (ld). High-vol. bituminous coal, Nova Scotia, Canada.  $R_o = 0.88\%$ .

1992). Landis et al. (1987) characterized various liptinitic macerals by fluorescence decay times (in nano- and sub-nano-second range) and the percentage contributions of the individual fluorophores.

*Sporinite* is the most common liptinitic maceral in humic and cannell (sapropelic) coal and in clarain or durain lithotypes. It is derived from the outer cell walls of spores and pollen of plants. The typical appearance of a sporinite is a flattened elongated body with a central cavity (spore; Figures 6B,

C, and F, and 7C) or oval flattened bodies with a central cavity (pollen; Figure 5G). Sporinite shows a greenish yellow (peat to lignite) to orange or red (bituminous) fluorescence. At the medium volatile bituminous rank, it loses its fluorescence.

*Cutinite* is derived from the cutin or cuticular layers in leaves, shoots, stalks and stems, and other epidermal tissues, which have waxy coatings; cutinite is the main maceral in paper or leaf coal. Cutinite is also derived from conifer needles having octagonal shape (Figure 5D of Mukhopadhyay, 1989;

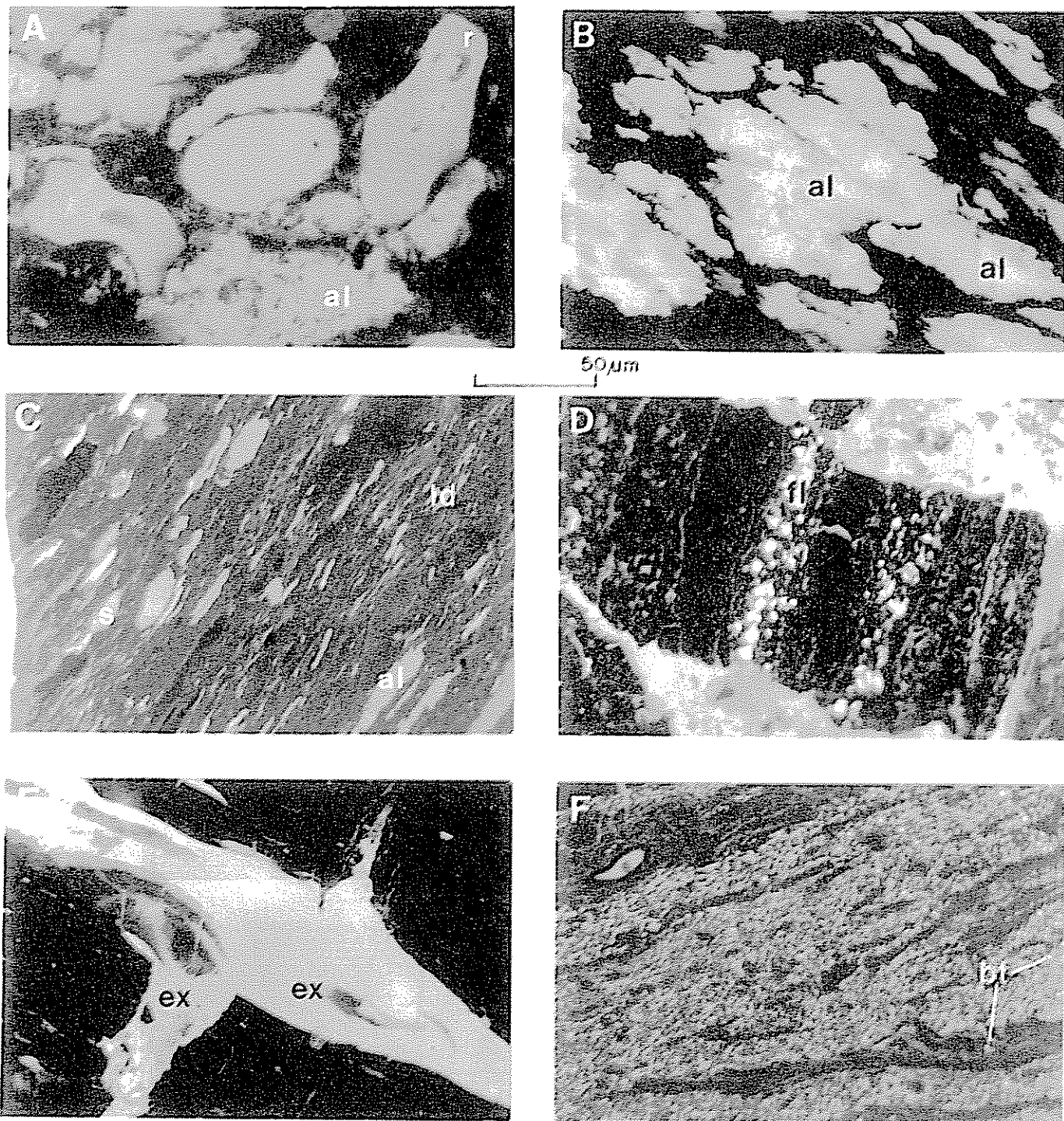


Figure 7. Photomicrographs under incident blue light excitation (fluorescence mode). (A) Resinite (r) and partially biodegraded alginite (possibly botryococcus, al). Lignite, Eocene, Jackson Group, Texas.  $R_o = 0.28\%$ . (B) Alginite (*Botryococcus*, al). High-vol. bituminous coal, Permian, South Africa.  $R_o = 0.70\%$ . (C) Alginite, sporinite, liptodetrinite (ld), bituminite. High-vol. bituminous coal, Eocene, Wilcox Group, Texas.  $R_o = 0.75\%$ . (D) Fluorinite (fl). Lignite, Eocene, Jackson Group, Texas.  $R_o = 0.30$ . (E) Exsudatinites (ex). Subbituminous coal, Tertiary, Utah.  $R_o = 0.52\%$ . (F) Bitumen (bt, both solid and liquid) within clay minerals. High-vol. bituminous coal, Eocene, Wilcox Group, Texas.

Teichmüller, 1989). Cutinite is characterized by its serrated or tooth-like margin with (thick) or without (thin) broad stromata (under incident white light) and characteristic yellow to red fluorescence with well-preserved structures (Figure 6E). Cutinite, which contains mainly cutin (insoluble polymer) and wax, is highly resistant to chemical weathering and protects the delicate soft parts of the plants from desiccation. However, under subaquatic and anaerobic conditions, cutinite can be

degraded to form bituminite (Mukhopadhyay et al., 1985).

*Suberinite* originates from the suberin-rich layer of cork cell tissues such as barks. Suberinite shows a characteristic cell structure whose outer dark layers (under incident white light) are derived from suberin (green to red fluorescence under blue light excitation; Figure 6D) and the inner lighter layer is either derived from plant cell secretion (phlobaphenite—nonfluorescent) or wax (Mukhopadhyay, 1989).

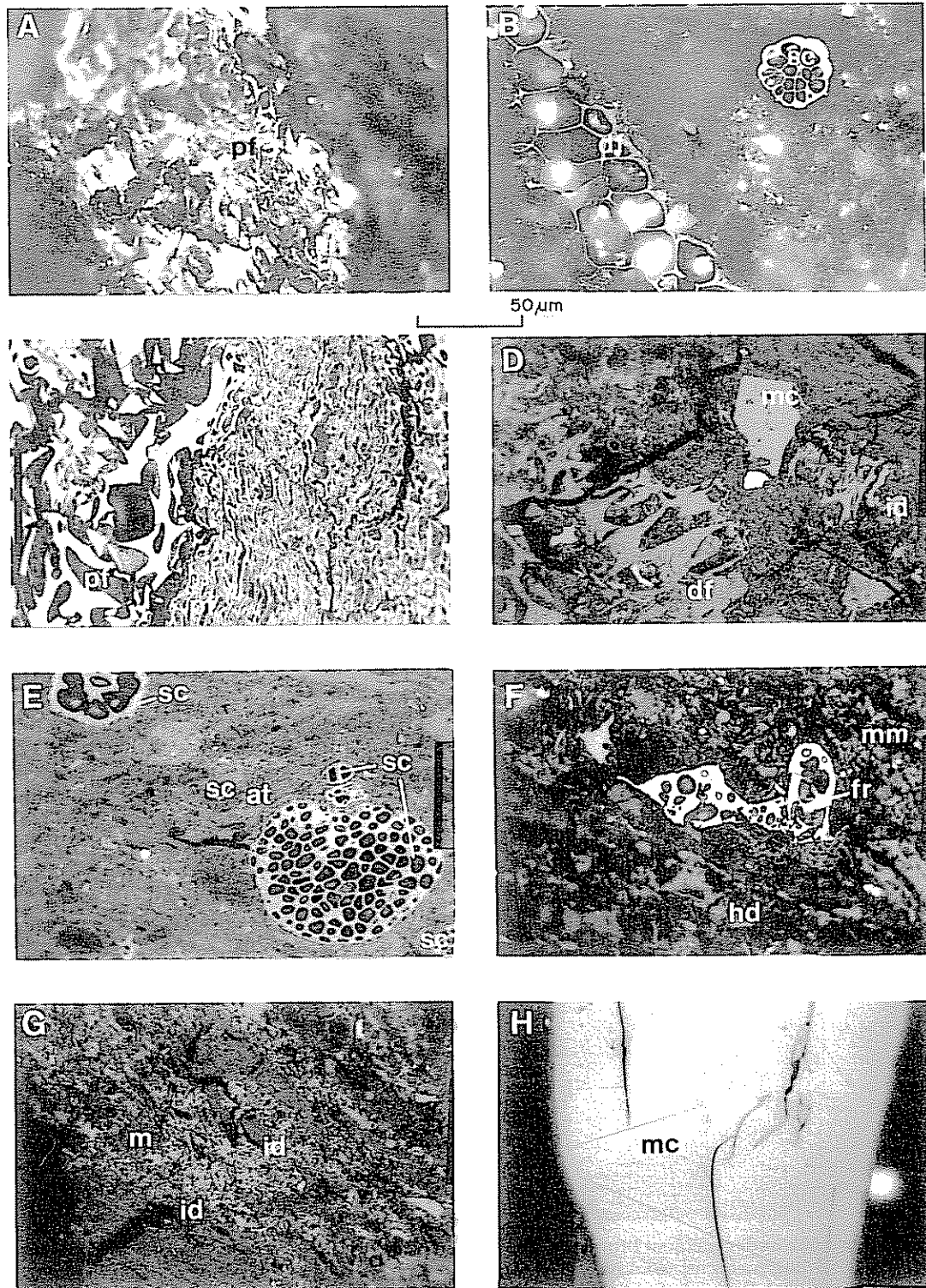


Figure 8. Photomicrographs under incident white light. (A) Pyrofusinite (pf). Recent Peat. Sumatra, Indonesia.  $R_o = 0.15\%$ . (B) Degradofusinite (df) and sclerotinite (sc). Recent Peat. Atchafalaya Basin, Louisiana.  $R_o = 0.14\%$ . (C) Pyrofusinite (pf). Lignite, Eocene, Wilcox Group, Texas.  $R_o = 0.30\%$ . (D) Degradofusinite (df), macrinite (mc), and inertodetrinite (id). Lignite. Eocene, Wilcox Group, Texas. (E) Various types of fungal sclerotia (sclerotinite, sc), atrinite (at), and fine-grained liptodetrinite. (F) Inertinitized faunal relics (fr), humodetrinite (hd), minerals (mm), and liptodetrinite. Lignite, Eocene, Wilcox Group, Texas. (G) Inertodetrinite (id) and micrinite (m), ulminite. Lignite, Eocene, Wilcox Group, Texas.  $R_o \approx 0.28\%$ . (H) Macrinite (mc) with desiccation cracks. High-vol. bituminous coal. Carboniferous, Nova Scotia, Canada.  $R_o = 0.95\%$ .

Similar to cutinite, suberinite prevents desiccation of the soft parts of the plants and is resistant to weathering. Suberinite is abundant in Tertiary and Mesozoic coals of forested swamp (telmatic) origin. Contrary to an earlier report (Teichmüller in Stach et al., 1982, and Teichmüller, 1989), suberinite is also recorded in the Paleozoic coals from Nova Scotia (Figure 3D) (Calder et al., 1991). Suberinite usually loses its fluorescence as a result of the generation and expulsion of liquid hydrocarbons (Khorasani, 1989) starting from subbituminous rank. After the loss of liquid hydrocarbons from suberinite-rich coals, suberinite displays a characteristic feature similar to that of telinite or telocollinite in the bituminous rank.

*Resinite* and *cerinite* are the metabolic products of fossil resins, waxes, balsams, copals, and essential oil (see fluorinite). According to Stach et al. (1982) and Teichmüller (1989), resinates occur in three forms: (1) terpene resinite (derived from resins and copals), (2) lipid resinite or *cerinite* (derived mainly from wax and fat; Hunt, 1991), and (3) fluid secondary resinite (derived from secondary exudates). Resinite (as oval or convolute bodies) occurs (1) within the telinite or telocollinite, (2) mixed with telocollinite (sometimes called collo-resinite; Figure 5C), and (3) as separate discrete bodies within the coal matrix (Figure 7A). The color of resinite in both incident white or blue light varies widely even within a single coal sample because of varying oxidation levels. The color varies from light gray to dark gray with strong internal reflection (white light) or greenish yellow to reddish brown (blue light) (Figure 7A).

Based on pyrolysis-gas chromatography (py-gc) and spectral fluorescence studies, Senftle and Larter (1988) differentiated angiosperm and gymnosperm resinates using recent and ancient samples. Crelling et al. (1982), Mukhopadhyay and Gormly (1984), and Teerman et al. (1987) have further differentiated various types of resinates based on fluorescence colors and spectral fluorescence parameters.

*Fluorinite* consists of essential oils of various plants which generally occur within the cell structures of telinite. It is dark gray (incident white light) with a characteristic rounded or oval shape, and under blue light excitation, it shows the highest fluorescence (green to yellow) (Figure 7D) compared to other liptinite macerals.

*Alginite* represents the coalified remains of phytoplanktons that occur either as unicellular bodies or in colonial form. It has the characteristic oval crenulated structure and dark gray color (Figure 5F) and displays internal reflection. Under blue light excitation, it shows a golden yellow to red fluorescence with its characteristic structure (Figure 7B). Alginite is often attacked by bacteria and is biodegraded (showing orange to red fluorescence at lower rank; Figure 7A) because it contains mainly cellulose and protein. Under severe biodegradation, alginite is altered to bituminite. Alginite occurs in both humic and sapropelic coal whenever it is deposited under subaquatic conditions. Within various oil shales, alginite is classified as telalginite (large colonial or unicellular bodies) or lamalginite (lamellar structures) based on the size and shape of the maceral (Hutton, 1987). *Botryococcus* (with two varieties, *Pila* and *Reinchia*) is the common telalginite in coal (Figure 7B). However, coals of lower delta plain and strandplain environments contain other varieties of both telalginite (*Pediastrum*; Mukhopadhyay, 1989) and lamalginite (dinoflagellate; Figure 5H).

*Bituminite*, which is formed by the bacterial degradation of other plant lipids (such as algae, spores, cuticles, and suberins) at the sediment-water interface (Teichmüller,

1974; Mukhopadhyay et al., 1985), is a primary amorphous liptinite. Bituminites are generally irregularly shaped and occur either as dispersed lenses and streaks or as ground-mass. In incident white light, they are dark gray (Figure 5E) and show yellow to reddish brown fluorescence (Figure 6E). Bituminite, which is generally associated with sapropelic coal (Teichmüller, 1974, 1989), is also known in humic coal (Mukhopadhyay et al., 1979; Hagemann and Wolf, 1989).

*Chlorophyllinite* is mainly formed as small rounded particles of approximately 1–5 microns in diameter (ICCP, 1971). Under blue light excitation, it has a striking blood-red fluorescence. Chlorophyllinite is rare in most coals and cannot be distinguished beyond the lignite stage.

*Liptodetrinite* consists of the mechanically degraded fragments of various liptinite macerals. Under incident white light, it has a dark gray appearance (Figure 5E), whereas under blue-light excitation, it has a green to red fluorescence (Figures 5G, 6B, and 7C).

*Exsudatinitite* (or *migrabitumen* of Jacob, 1989) is a secondary maceral formed during the coalification process (starting from the lignite stage). It shows yellow to red fluorescence and occurs as fracture-filling or cell-filling within telinite, telocollinite, gelocollinite, fusinite, and sclerotinitite (Figure 7E) or as a matrix (Figure 7F). Exsudatinitite indicates primary migration of hydrocarbons within the coal network (Mukhopadhyay et al., 1991).

*Inertinite Group*: As discussed earlier, the inertinite group of macerals comprises the oxidized form of various vitrinite and liptinite macerals. They are carbon-rich, hydrogen-poor, and are formed as a result of forest fire (pyrofusinite) or bacterial/surface oxidation (degradofusinite or semifusinite and macrinite). They are, in general, chemically inert (except for some semifusinite and micrinite) and offer no source potential for the generation of major liquid or gaseous hydrocarbons. Fusinite, semifusinite, and most sclerotinitite macerals show well-preserved structures whereas macrinite and micrinite are amorphous. Inertinite macerals are, in general, nonfluorescent and show higher reflectance than the vitrinite macerals. Some inertinite macerals such as sclerotinitite or fusinite often show some yellow to dark brown fluorescence because of impregnation with other liptinite macerals. Diessel (1985) considered this fluorescence to be primary. Some of the secretions of medullosan seed ferns are termed by Lyons et al. (1986) as *secretinitite*, which are mainly inertinitized secretions.

Inertinite macerals can be primary or secondary (Teichmüller, 1989). Secondary fusinite is termed rank-fusinite and is derived from the coalification of bituminous-rich cell walls (such as cellulose or resins). Fragments of faunal relics (e.g., from fish, scelecodonts, and other animals) are often preserved as inertinite, which are termed *faunal relics*.

A detailed description of the inertinite macerals is not included in this manuscript, because inertinite macerals do not contribute much to the generation of liquid or gaseous hydrocarbons in coal. For descriptions of fusinite (both pyro- and degrado-), semifusinite, macrinite, sclerotinitite, inertodetrinite, and micrinite, see ICPC (1971) and Stach et al. (1982). Photomicrographs of various inertinite macerals were illustrated in the following figures: degrado- and pyrofusinite and semifusinite are illustrated at various stages of coalification in Figures 3G (anthracite), 3F (bituminous), 4A and 8C (lignite), and 8A and 8B (peat); sclerotinitite in Figures 8B and 8E; macrinite in Figures 3G and 8H; micrinite in Figure 8G; inertodetrinite in Figures 3G and 8C; rank-inertinite in Figures 3G and 3H; and inertinitized faunal relics in Figure 8F.

### Macerals at Various Rank Stages

During the evolution from peat to anthracite, macerals follow both homogenization and bituminization processes. Primary macerals of the vitrinite and liptinite groups show major changes while primary inertinite macerals do not show much change throughout the coalification process except for compression and change in reflectance.

At the peat stage (<0.2%  $R_o$ ), huminite macerals, which are very diverse in nature, show bright to dark brown fluorescence (although some are nonfluorescent). At the lignite stage (>0.2 to <0.38%  $R_o$ ), they become nonfluorescent. At the subbituminous stage (>0.38 to <0.66%  $R_o$ ), more homogenized macerals such as densinite, ulminite, and gelinite prevail. From subbituminous A (0.48%  $R_o$ ) through to the medium-volatile bituminous stage (1.45%  $R_o$ ), vitrinite macerals such as desmocollinite, telocollinite, and gelocollinite show light to dark brown fluorescence owing to impregnation of generated liquid hydrocarbons (derived from liptinite macerals) within their microspores. These impregnated hydrocarbons are sometimes called the *mobile phase* (Given, 1984). Beyond the medium-volatile bituminous stage (1.45%  $R_o$ ), all vitrinite macerals lose their secondary fluorescence and characteristic structures and often show generation of micrinite (secondary inertinite) at the surface.

Among the liptinite macerals, the bituminization process is more rapid in resinite, suberinite, and bituminite than it is in alginite, sporinite, and cutinite (Snowdon, 1980; Teichmüller, 1982; Mukhopadhyay and Gormly, 1984; Mukhopadhyay et al., 1985; Khorasani, 1989). The stages of bituminization can be assessed by fluorescence intensity and color and generation of hydrogen-rich (exsudatinite or solid bitumen) and hydrogen-poor (micrinite and rank inertinite) macerals. Beyond the medium-volatile bituminous stage, all liptinite macerals are converted to rank-inertinite/inertodetrinite and micrinite, which shows higher reflectance than the corresponding vitrinite (Figures 8G and 8H). At this stage, the identification of high rank meta-liptinite is extremely difficult (Teichmüller and Ottenjann, 1977; Teichmüller, 1986; Mukhopadhyay et al., 1985; Mukhopadhyay and Wade, 1990).

### Coal Network: Microlithotypes, Mineral-Bituminous Groundmass, and Minerals

#### Preview

The *coal network* includes microlithotypes (macerals in natural association), mineral-bituminous groundmass, and distinct mineral phases. Gray (1991) defined the coal network as maceral and nonmaceral microstructures such as normal coal (macerals), fine coal, pseudovitrinoids, microbrecciated, oxidized (both weathered and thermal), coarse mineral matter, cenospheres (after combustion), and contamination, which are applied to combustion and coke-making technology. The coal network, as defined here, is applied toward the study of coal facies, liquid hydrocarbon generation, and coal-bed methane.

#### Mineral-Bituminous Groundmass

The term *mineral-bituminous groundmass* was introduced by Teichmüller and Ottenjann (1977) and Teichmüller (1988) for the fluorescent mineral matrix in oil shale. However, in some mineral-rich lacustrine and lower delta plain coals, mineral-bituminous groundmass is also a common constituent. It is a complete intermixture of microscopic to submicroscopic grains of minerals (clays/carbonates/

quartz) and dispersed bituminite or bitumen. It can only be identified by its characteristic strong yellow to red fluorescence under UV or blue-light excitation; this fluorescence is distinctive compared to mineral fluorescence. Mineral-bituminous groundmass can be either primary (minerals mixed with bituminite) or secondary (minerals mixed with bitumen or oil).

#### Microlithotypes and Mineral Matter

The microlithotype is the natural association of macerals or maceral-mineral network as seen under incident light microscopy whose minimum band width is not less than 50 microns; it has the suffix "ite" (ICCP, 1971). Mineral-lean maceral associations (density <1.5 g/cm<sup>3</sup>) are termed *microlithotypes*, and mineral-rich microlithotypes are referred to as *carbominerite* (density >1.5 to <2.0 g/cm<sup>3</sup>). There are three major groups of microlithotypes: (1) monomaceralic, (2) bimaceralic, and (3) trimaceralic (Table 4). Carbominerite, according to the percentages of minerals present, is divided into five groups such as carbargillite (Figure 9G), carbopyrite (Figures 9E and 9F), carboankerite, carbosilicate, and carbopolyminerite (Figure 9H) (Table 4). Hower et al. (1990) showed the relationship between lithotype, microlithotype, and range of group maceral composition (Figure 2).

In addition to organic matter, coal contains up to 30% (by volume) of inorganic constituents or *mineral matter*. The inorganic constituents occur as either distinct mineral phases or in organic combination (as chelated ions). According to Gluskoter et al. (1981), the *mineral in coal* can be classified as *detrital* (allogenic: transported from outside the peat swamp) or *authigenic* (formed within the peat swamp). The authigenic minerals can be further classified as *syngenetic* (contemporaneous with the peat formation) or *epigenetic* (formed during early to late diagenesis and catagenesis). The minerals, whether detrital or syngenetic, are generally fine-grained (commonly less than 5  $\mu$ m in diameter) and show lateral within-seam continuity. However, epigenetic minerals are neither fine-grained nor intergrown with the macerals; they generally occur within cleats or fractures commonly perpendicular to the bedding. Table 5 shows the mode of origin for various types of minerals in coal. Hydrated silicates (clay minerals), carbonates, sulfides, silicates, and sulfates (only important in weathered coal) are the major mineral species in coal (Table 6).

The elements in these minerals can be grouped into (1) *major elements* (>0.5% of whole coal), which may include aluminum, calcium, iron, sulfur, and silicon; (2) *minor elements* (>0.02 to 0.5% of whole coal), which may include potassium, sodium, titanium, and less commonly phosphorus, barium, and strontium; and (3) *trace elements* (<0.02% or 200 ppm to ppb), which include most of the other elements such as arsenic, gold, lead, cadmium, cesium, chlorine, gallium, germanium, etc. All elements in the mineral matter portion of coal (except C, H, O, N, and S) are considered to be inorganic. Coal also contains a wide variety of trace elements including the actinides and lanthanides. Finkelman and Gluskoter (1983), Finkelman (1982, 1986), Goodarzi (1987, 1988), Goodarzi and van der Flier-Keller (1988), and Finkelman et al. (1990) have presented data on the distribution of trace elements in various North American coals. For details of the analytical procedures on the determination of trace elements in coal, see Gluskoter et al. (1981) and Finkelman et al. (1990). For the genesis, distribution, and association of trace elements, see Swaine (1983, 1990) and Finkelman (in press). The majority of the trace elements are within the clays, sulfides, and accessory heavy minerals.

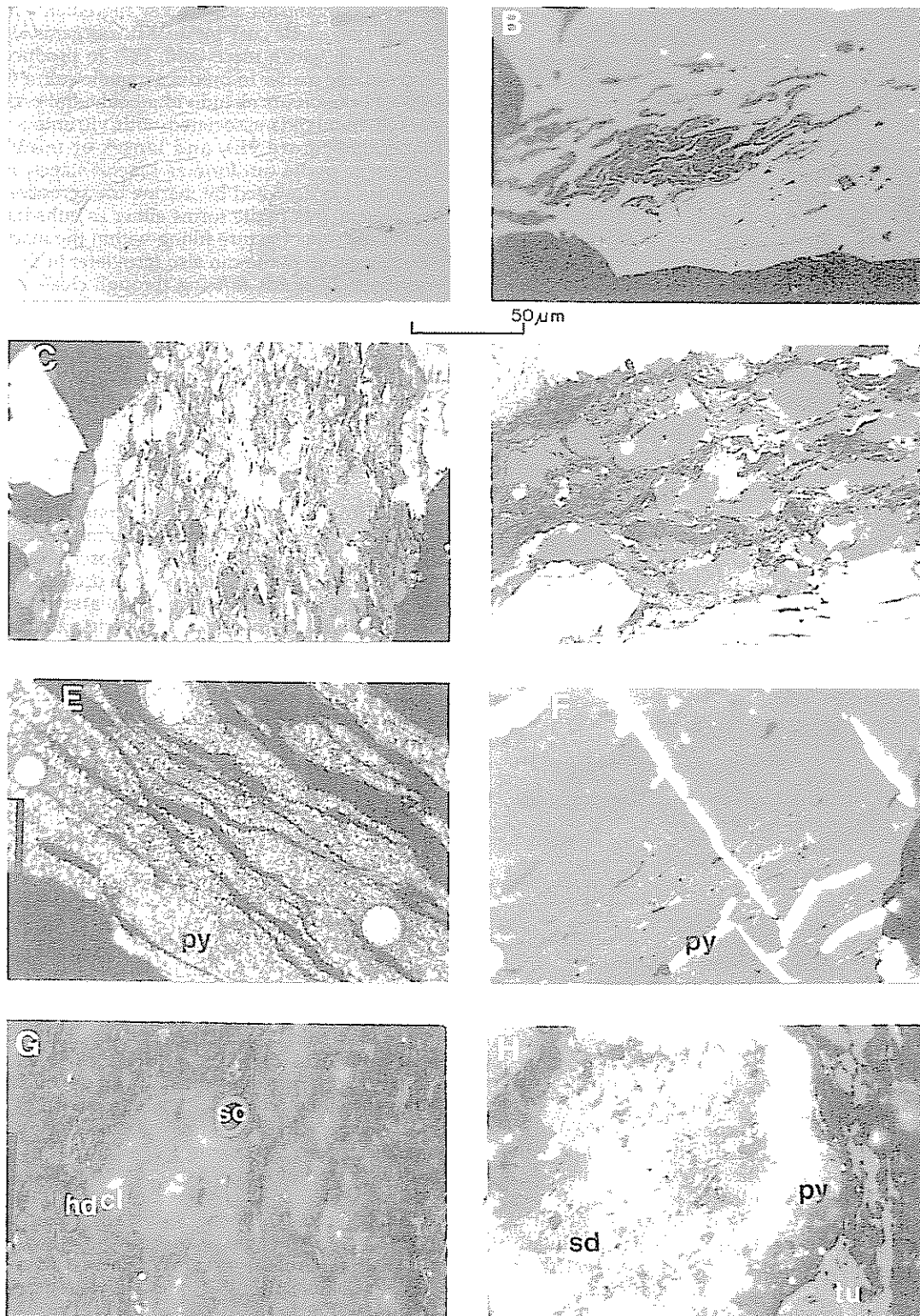


Figure 9. Photomicrographs under incident white light. (A) Vitrite. Carboniferous, Nova Scotia, Canada. (B) Clarite. Carboniferous, Nova Scotia, Canada. (C) Duroclarite, Carboniferous, Nova Scotia, Canada. (D) Duroclarite, Carboniferous, Nova Scotia, Canada. (E) Carbopyrite with framboidal pyrite (py) replacing huminite. Eocene, Wilcox Group, Texas. (F) Secondary pyrite (py) occurs along the fracture of huminite macerals. Eocene, Jackson Group, Texas. (G) Carbargillite with clay minerals (cl), humodetrinite (hd), and sclerotinite (sc). Eocene, Wilcox Group, Texas. (H) Carbopolymnerite with siderite (sd) and pyrite (py) with texto-ulminite (tu). Subbituminous coal, Eocene, Japan.

Table 4. Microlithotype classification (macerals and maceral-mineral combinations) (after Bustin et al., 1985).

|               | Microlithotype    | Maceral-Group<br>Composition<br>Mineral-Free |
|---------------|-------------------|--|
| Monomaceralic | Vitirite          | V > 95%                                      |
|               | Liptite           | L > 95%                                      |
|               | Inertite          | I > 95%                                      |
| Bimaceralic   | Clarite           | V + L > 95%                                  |
|               | Vitrinertite      | V + I > 95%                                  |
|               | Durite            | L + I > 95%                                  |
| Trimacerite*  | Duroclarite       | V > L and I                                  |
|               | Clarodurite       | I > V and L                                  |
|               | Vitrinertoliptite | E > V and I                                  |

V = vitrinite, L = liptinite, I = inertinite.  
\* in trimacerites at least 5% of each maceral must be present.

| Association of Coal<br>with a Specific<br>Mineral or Mineral<br>Group | Composition+                         | Collective Term<br>for Imprecisely<br>Designated<br>Coal-Mineral<br>Association |
|---|--------------------------------------|---|
| Carbargillite   | Coal + 20–60 vol %<br>clay minerals  |   |
| Carbopyrite   | Coal + 5–20 vol %<br>sulfides        |   |
| Carbankerite  | Coal + 20–60 vol %<br>carbonates     | Carbominerite   |
| Carbosilicite   | Coal + 20–60 vol %<br>quartz         |   |
| Carbopolyminerite   | Coal + 20–60 vol %<br>mineral matter |   |

+The lower limit can be reduced by 5% depending on the content of sulfides.

### Minerals

**Clay Minerals.** Clay minerals constitute about 60 to 80% of the total minerals in coal (Bustin et al., 1985), the most common being kaolinite and illite. Clay minerals in coal can be classified as: (1) synformed (detrital input to the swamp), (2) transformed, and (3) neofomed (for details of various mineral types, see Gluskoter et al., 1981, and Finkelman, in press). Clay minerals can occur in a finely dispersed form associated with macerals or as tonsteins, clay bands, or cleat and fracture fillings (Stach et al., 1982). Clay minerals are identified either by their XRD pattern or by their chemical composition using a SEM-EDX. Under the incident white light microscopy, clay minerals (except tonstein) are dark and grainy; they often show internal reflection (Figure 9G). Under blue light excitation, they are usually nonfluorescent but often show strong bright yellow fluorescence due to impregnation of bitumen or crude oil.

**Sulfides and Sulfates.** Iron sulfides in coal include pyrite, marcasite, and melnikovite. Sulfate solution, ferrous iron,

and microorganisms are the key ingredients in the formation of syngenetic coal pyrite. Microorganisms reduce sulfate to  $H_2S$ , which reacts with  $Fe^{2+}$  to produce pyrite and with organic matter to produce organic sulfur (Casagrande, 1987). Pyrite occurs as individual euhedral crystals, loosely packed framboids associated with vitrinite and inertinite macerals (Figure 9E), and lenses or minute crystals. Epigenetic pyrite can form as several stages. For example, when peat is drowned by marine transgression or by alkaline waters, this pyrite forms either as euhedral crystals or framboids or as fracture filling within the macerals (Figure 9F). Epigenetic pyrite can also form later in the coalification process from fluids flowing through cleats and fractures. Under incident white light, pyrite is yellowish white and shows very high reflectance (>>inertinite) or shows blue fluorescence (possibly due to effect of high reflectance, and therefore can be termed as pseudo-fluorescence) under UV excitation. Other forms of pyrite including marcasite, chalcocopyrite, sphalerite, galena, etc., occur as minor to trace components. They are formed epigenetically from the mineral-rich solutions pervasive in coal fractures (Finkelman, 1982).

Sulfate minerals such as gypsum and barite, and hydrous iron sulfates, such as coquimbite and jarosite, are reported in coal (Stach et al., 1982; Spackman, 1989) and are mostly alteration products. Gypsum occurs as veins formed by the precipitation of ground water in an arid area. Coquimbite and jarosite owe their origin to the oxidation of pyrite and usually occur as crystalline deposits of cleat infillings. A few, such as barite, are indigenous to the coal.

**Carbonates.** Siderite, the major carbonate in coal, generally occurs as cell infillings or as individual grains (Figure 9H) and is considered to be syngenetic. Calcite occurs both syngenetically or epigenetically as fracture filling in the form of sparry calcite. Dolomite occurs as syngenetic idiomorphic crystals and like calcite can also be epigenetic. Under incident light microscopy, siderite shows a gray to colorless appearance with internal reflection (Figure 9H); occasionally characteristic crystal forms are observed. Siderite is nonfluorescent. Calcite and dolomite show greenish yellow mineral fluorescence. Dolomite crystals occasionally contain hydrocarbon inclusions.

**Oxides.** The most common oxide in coal is quartz, which occurs as detrital grains (syngenetic) and also as euhedral (authogenic) grains. Quartz is usually identified by a black shadow or void appearance with internal reflection (incident white light, dry objective) (Figures 5A and 8F). Quartz can also appear in precipitated form as finely intergrown blebs (syngenetic) or along the fractures of the maceral grain (epigenetic). Titanium oxides such as rutile, brookite, and anatase are common in coal while other oxide minerals such as hematite and goethite are rare in most coals.

**Accessory Minerals in Coal.** Through the use of the SEM and SEM-EDX (Finkelman, 1978, 1988; Russel and Rimmer, 1979) and incident light microscopy (Mackowsky in Stach et al., 1982), some of the accessory minerals in coal such as zircon, tourmaline, diopside, hornblende, mica, apatite, gypsum, microcline, and talc have been identified. Finkelman (1982) and Stach et al. (1982) indicated their probable mode of occurrence in coal (either as syngenetic or epigenetic). Finkelman (1978), from his SEM studies, showed that some of the elements such as Cr, Y, Zr, Ni, and the rare earth elements are dominantly bound in some specific accessory minerals. Further details on accessory minerals in coal may be obtained in Lindahl and Finkelman (1986), who reviewed the factors influencing the major, minor, and trace elements in major U. S. coals.



Table 5. Classification of mineral matter in coal according to their mode of origin (after Gluskoter et al., 1981).

| Mineral Group                               | First Stage of Coalification:<br>Syngenetic Formation,<br>Synsedimentary-Early Diagenetic<br>(intimately intergrown) |  | Second Stage of Coalification:<br>Epigenetic Formation  |  |
|---|--|--|---|--|
|   | Transported by<br>Water or Wind  | Newly Formed   | Deposited in<br>Fissures, Cleats,<br>and Cavities<br>(coarsely intergrown)  | Transformation of<br>Syngenetic Minerals<br>(intimately<br>intergrown)                 |
| Clay minerals                               | Kaolinite, illite,<br>sericite, clay minerals<br>with mixed-layer structure<br>Montmorillonite, tonstein             |  |   | Illite, chlorite   |
| Carbonates                                  |  | Siderite-ankerite calcite,<br>concretions, dolomite,<br>ankerite<br><br>Siderite   | Ankerite<br>Calcite<br>Dolomite<br>Ankerite in fusite   |  |
| Sulfides                                    |  | Pyrite concertions<br><br>Melnikovite-pyrite<br>Coarse pyrite (marcasite)<br>Concretions of<br>FeS <sub>2</sub> -CuFeS <sub>2</sub> -ZnS | Pyrite<br><br>Marcasite<br>Zinc sulfide (sphalerite)<br>Lead sulfide (galena)<br>Copper sulfide<br>(chalcopyrite)<br>Pyrite in fusite | Pyrite from the<br>transformation of<br>syngenetic concretions<br>of FeCO <sub>3</sub> |
| Oxides                                      |  | Hematite   | Goethite, lepidocrocite<br>("needle-iron ore")  |  |
| Quartz                                      | Quartz grains  | Chalcedony and quartz<br>from the weathering of<br>feldspar and mica   | Quartz  |  |
| Phosphates                                  | Apatite  | Phosphorite, apatite   |   |  |
| Heavy minerals<br>and accessory<br>minerals | Zircon, rutile,<br>tourmaline, orthoclase,<br>biotite  |  | Chlorides, sulfates,<br>and nitrates  |  |

### Organically Associated Elements

Certain specific groups of organic coaly matter (having elements such as C, H, N, and O), namely carboxylic (-COOH), phenolic hydroxyl (-OH), mercapto (-SH), and amino (= NH), are often associated with various other trace elements such as B, Ba, Cu, Mn, Sr, etc. (Swaine, 1990). The elements C, H, O, and S can also occur in close association with other inorganic constituents; carbon as carbonates of calcium, magnesium, and iron; hydrogen in free water and water of hydration; oxygen as oxides, water, sulfates, carbonates, silicates, and phosphates; and sulfur as sulfides and sulfates.

Organic sulfur in coal can occur as thiosulfates, ester sulfite, marcaptane, etc. (Swaine, 1990; Finkelman, personal communication, 1992). Combining optical microscopy (fluorescence mode with dry objective) and SEM-EDX, Demir and Harvey (1991) showed the distribution of organic sulfur within various macerals in a series of high- to medium-

volatile bituminous coal. They demonstrated that organic sulfur content is highest in liptinite (especially sporinite: 0.39 to 7.22 wt % in dmmf basis) and lowest in inertinite (0.16 to 3.56 wt %). Organic sulfur content in vitrinite (0.45 to 4.78 wt %) is intermediate to liptinite and inertinite.

Elements that are found associated with the macerals include B, Be, Br, Ga, Ge, I, Mo, Se, and W (Swaine, 1990). Some other elements such as F, Ti, and Cl are bounded in an organic compound; F and Ti are within vitrinite and liptinite macerals and Cl is within vitrinite (Martinez-Tarazona et al., 1988; Swaine, 1990). Elements observed in both minerals and macerals include Cl, Cu, Sn, Sr, and V (Birk and White, 1990).

### Coal Components and Genesis of Coal Facies

As discussed earlier, the composition (macerals and minerals) of coal is influenced predominantly by the depo-

Table 6. List of mineral matter identified in coal (after Gluskoter et al., 1981).

| Mineral                              | Formula  |
|--------------------------------------|--|
| <i>Clay minerals</i>                 |  |
| Montmorillonite                      | $Al_2Si_4O_{10}(OH)_2 \cdot H_2O$              |
| Illite-sericite                      | $KAl_2(AlSi_3O_{10})(OH)_2$                    |
| Kaolinite                            | $Al_2Si_2O_5(OH)_4$                            |
| Halloysite                           | $Al_4Si_4O_{10}(OH)_8$                         |
| Chlorite<br>(prochlorite, penninite) | $Mg_5Al(AlSi_3O_{10})(OH)_8$                   |
| Mixed-layer clay<br>minerals         |  |
| <i>Sulfide minerals</i>              |  |
| Pyrite                               | $FeS_2$  |
| Marcasite                            | $FeS_2$  |
| Sphalerite                           | $ZnS$  |
| Galena                               | $PbS$  |
| Chalcopyrite                         | $CuFeS_2$                                      |
| Pyrrhotite                           | $Fe_{1-x}S$                                    |
| Arsenopyrite                         | $FeAsS$  |
| Millerite                            | $NiS$  |
| <i>Carbonate minerals</i>            |  |
| Calcite                              | $CaCO_3$                                       |
| Dolomite                             | $(Ca, Mg)CO_3$                                 |
| Siderite                             | $FeCO_3$                                       |
| Ankerite<br>(Ferroan dolomite)       | $(Ca, Fe, Mg)CO_3$                             |
| Witherite                            | $BaCO_3$                                       |
| <i>Sulfate minerals</i>              |  |
| Barite                               | $BaSO_4$                                       |
| Gypsum                               | $CaSO_4 \cdot 2H_2O$                           |
| Anhydrite                            | $CaSO_4$                                       |
| Bassanite                            | $CaSO_4 \cdot 1/2H_2O$                         |
| Jarosite                             | $(Na, K)Fe_3(SO_4)_2(OH)_6$                    |
| Szomolnokite                         | $FeSO_4 \cdot H_2O$                            |
| Rozenite                             | $FeSO_4 \cdot 4H_2O$                           |
| Melanterite                          | $FeSO_4 \cdot 7H_2O$                           |
| Coquimbite                           | $Fe_2(SO_4)_3 \cdot 9H_2O$                     |
| Roemerite                            | $FeSO_4 \cdot Fe_2(SO_4)_3 \cdot 12H_2O$       |
| Mirabilite                           | $Na_2SO_4 \cdot 10H_2O$                        |
| Kieserite                            | $MgSO_4 \cdot H_2O$                            |
| Sideronatrite                        | $2Na_2O \cdot Fe_2O_3 \cdot 4SO_3 \cdot 7H_2O$ |
| <i>Chloride minerals</i>             |  |
| Halite                               | $NaCl$   |
| Sylvite                              | $KCl$  |
| Bschofite                            | $MgCl_2 \cdot 6H_2O$                           |
| <i>Silicate minerals</i>             |  |
| Quartz                               | $SiO_2$  |
| Biotite                              | $K(Mg, Fe)_3(AlSi_3O_{10})(OH)_2$              |
| Zircon                               | $ZrSiO_4$                                      |
| Tourmaline                           | $Na(Mg, Fe)_3Al_6(BO_3)_3(Si_6O_{18})(OH)_4$   |
| Garnet                               | $(Fe, Ca, Mg)_3(Al, Fe)_2(SiO_4)_3$            |
| Kyanite                              | $Al_2SiO_5$                                    |
| Staurolite                           | $Al_4FeSi_2O_{10}(OH)_2$                       |
| Epidote                              | $Ca_2(Al, Fe)_3Si_3O_{12}(OH)$                 |
| Albite                               | $NaAlSi_3O_8$                                  |
| Sanidine                             | $KAlSi_3O_8$                                   |
| Orthoclase                           | $KAlSi_3O_8$                                   |
| Augite                               | $Ca(Mg, Fe, Al)(Al, Si)_2O_6$                  |

sitional environment of the peat mire which, in turn, is determined largely by the nature of water supply: ombrotrophic (solely rain-fed), rheotrophic (flow-fed), or mesotrophic (rain- and flow-fed). Ombrotrophic mires are termed bogs, whereas rheotrophic mires are divided into fens and swamps (Calder et al., 1991). The nature of the mire can be related to nutrient supply and divided into eutrophic, mesotrophic, and oligotrophic types (Stach et al., 1982). Mires can also be classified according to their relationship to the water table: terrestrial (dry mire above water table), telmatic (wet swamp), limno-telmatic (subaquatic), and limnic (aquatic). The genetic characterization of a coal facies can be determined by observing: (1) the variation in lithotype and microlithotype composition, (2) the change in the varieties of huminite/vitrinite macerals and their association with the inertinite and liptinite group of macerals, (3) the increase and decrease in mineral matter content and change in the nature of the mineral matter (of major, minor, and trace elements), and (4) the change in the floral succession.

In the past, two types of organic associations have been used to determine the facies of a mire from peat through to the bituminous rank stage. One association is mainly maceral-based whereas the other is microlithotype-based. Both maceral-based and microlithotype-based coal facies often use vegetation type and megascopic characteristics of coal (lithotype). Teichmüller (1989) gave a detailed account of the genesis of a peat mire related to maceral-based and microlithotype-based interpretations of earlier researchers (between 1933 and 1988). Some of the classical earlier work was done between 1950 and 1970 (Teichmüller, 1950; Smith, 1962; Hacquebard and Donaldson, 1969; and other references within Teichmüller, 1989). Some of these interpretations will be employed in the ensuing discussion of the genetic implications of macerals, lithotype, and microlithotype of coal.

It is generally accepted that: (1) sapropelic coals with dark clarain and unbanded lithotype were formed under limno-telmatic to limnic conditions, (2) abundant vitrite-rich microlithotypes, when associated with clay partings and syngenetic pyrite, are considered to have been deposited under telmatic (wet swamp) conditions, and (3) coal rich in inertinite (with fusinite, semifusinite, and macrinite) is considered to have formed under dry conditions (terrestrial). Inertinite can also be associated with clastic-rich facies, probably representing extrabasinal material (from forest fires or other sources) washed into low-lying areas once the cover of vegetation has been stripped off by fire (Calder, personal communication, 1992).

Smith (1962) described combined microlithotype and miospore-based assemblages of Carboniferous coal from England. He showed a succession of eutrophic (lycospore phase with vitrite + clarite) to oligotrophic raised bog (densospore phase with durite) as well as transitional and incur-sion facies.

Hacquebard and Donaldson (1969), using a microlithotype-based four-component facies diagram and employing the northern European terminology of "moors," demonstrated the presence of various coal facies within the Harbour and other seams from the Carboniferous coals (Sydney Basin) of Nova Scotia, Canada; the coal facies interpretation on dull bands of Hacquebard and Donaldson (1969) is different from that of Smith (1962).

From the study of various Australian Gondwana (Permian) coals, Smyth (1984) used microlithotype analysis to define various coal facies in terms of depositional environments such as fluvial, lacustrine, upper and lower delta-

ic, and lagoon. Accordingly, a durite and inertite microlithotype association is considered to have formed mainly in lakes and on lower delta plains, whereas vitrite and clarite-rich microlithotypes occurred in upper deltaic (wet), fluvial (wet swamp), or lagoonal (wet) environments.

Teichmüller (1950, and in Stach et al., 1982) demonstrated a horizontal sequence of environments from open water (wet) through reed marsh, *Nyssa-Taxodium* swamp (slightly wet), and dry bush moor (*Myricaceae-Cyrillaceae*), to driest *Sequoia* moor on the basis of maceral and palynological assemblages. Mukhopadhyay (1986, 1989) showed a similar sequence of depositional environments for Eocene lignites (Wilcox, Claiborne, and Jackson groups) using a maceral-based lithotype and palynological association (Figure 10). Mukhopadhyay (1989) also considered that the association of humotelinite and humodetrinite with alginite, cutinite, and low inertinite (mixture of detrital and xylitic lithotype) with *Nyssa-Betulaceae-Myricaceae* pollen is derived from the floatant vegetation in the region of the swamp-marsh complex.

From the study of peat deposits of the Frazer River Delta, Styan and Bustin (1983) showed a horizontal sequence of various peat types with their characteristic maceral and microlithotype assemblages. They showed that

under freshwater conditions (both as ombrotrophic or rheotrophic), telocollinite, telinite, terpene resinite, and fusinite are abundant, whereas under marine or brackish water conditions, desmocollinite with alginite, sporinite, and cerinite (wax-rich resinite) is more common.

Harvey and Dillon (1985) suggested that the ratio of vitrinite/inertinite is inverse to the degree of oxidation in a swamp. However, Rimmer and Davis (1988), based on maceral associations of the lower Kittanning coal (western Pennsylvania), suggested that the variation of telocollinite and desmocollinite is dependent on the rate of subsidence and vegetation type. Diessel (1986) defined various Australian coal facies on the basis of two ratios of maceral association. He termed these ratios *Gelification Index* (GI) and *Tissue Preservation Index* (TPI), which are dependent on the Eh of the paleomire. The *Gelification Index* of Diessel (1986) is the ratio of vitrinite + macrinite/semifusinite + fusinite + inertodetrinite; the *Tissue Preservation Index* is the ratio of telinite + telocollinite + semifusinite + fusinite/desmocollinite + macrinite + inertodetrinite. As an example, he considered high GI and high TPI values to indicate dry terrestrial conditions whereas low GI and TPI indicated wet conditions for the telmatic or limnotelmatic zone of the paleomire.

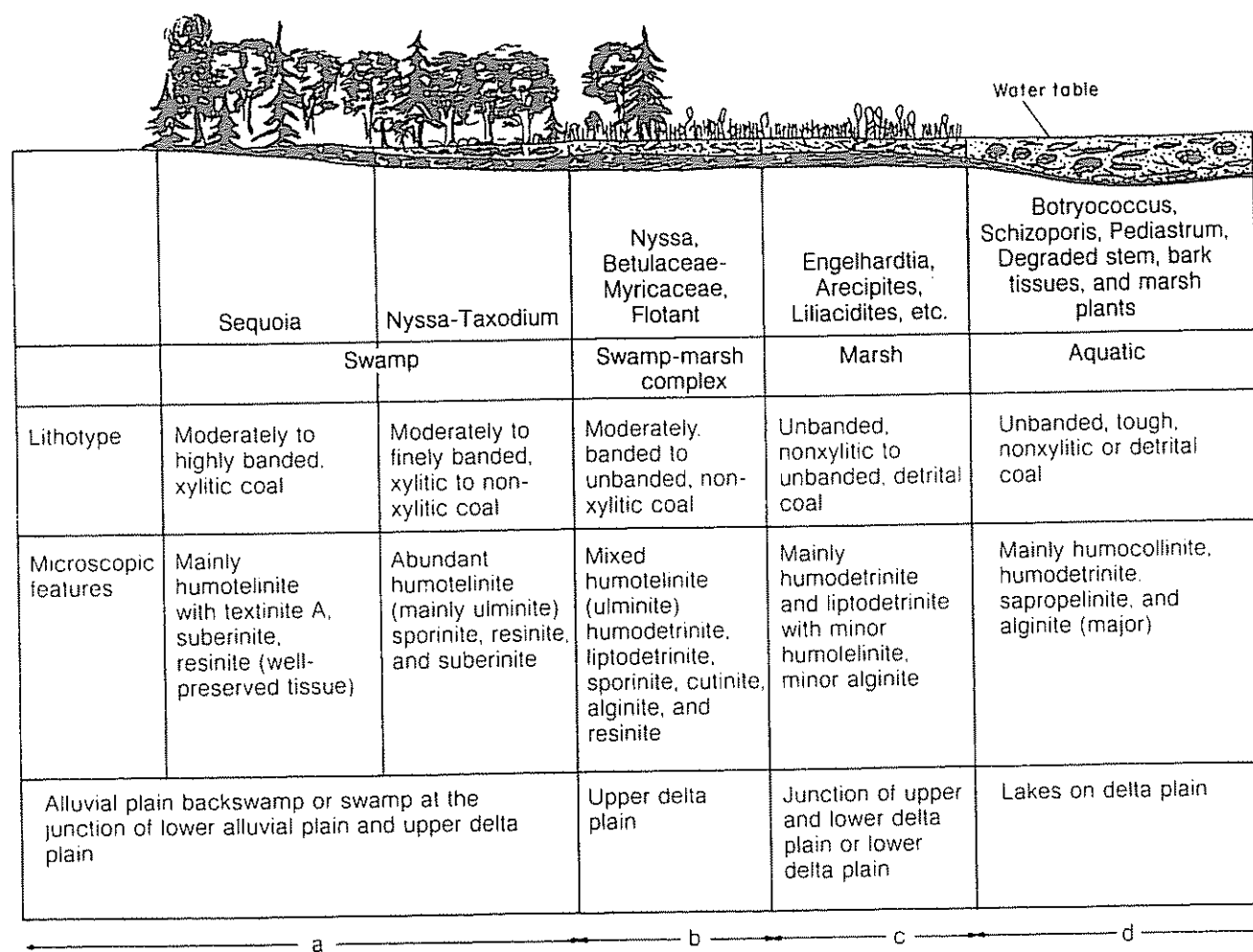


Figure 10. Schematic profile and lithotype/maceral and floral characteristics of peat-forming environments of the alluvial and delta plain based on the study of Texas lignite (after Mukhopadhyay, 1989).

Calder et al. (1991) considered a new approach to define coal facies. They proposed that maceral assemblages are dependent on the influence of ground water (clastic input and pH) and vegetation. They emphasized the importance of lignin-rich arboraceous versus cellulose-rich, herbaceous derivatives and progressive gelification of huminite/vitri- nite as an indicator of increasing rheotrophic conditions within the paleomire. They also defined two different maceral association ratios, termed: (1) *Groundwater Influence Index* (GWI), the ratio of gelocollinite + corpocollinite + mineral matter/telinite + telocollinite + desmocol- linitite; and (2) *Vegetation Index* (VI), the ratio of the macerals derived from presumably lignin-rich forested plants (telinite + telocollinite + fusinite + semifusinite + suberinite + resinite) and macerals inferred to be of herbaceous, cellulose-rich affinity together with those that accumulated preferentially in the limno-telmatic zone (desmocol- linitite + inertodetrinite + alginite + liptodetrinite + sporinite + cutinite) (Figure 11). Using this diagram, Calder et al. (1991) differentiated the hydrologic evolution of the paleomire in a piedmont, inner mire, and riverine zone of a single seam (the No. 3 seam) from the Cumberland Basin, Nova Scotia (Figure 11).

Pierce et al. (1991), based on a concept similar to that of Calder et al. (emphasis more on pH than Eh) of maceral and miospore association but employing etching, suggested a sequence of mire development (lower Freeport coal) from eutrophic or mesotrophic to oligotrophic domed peat.

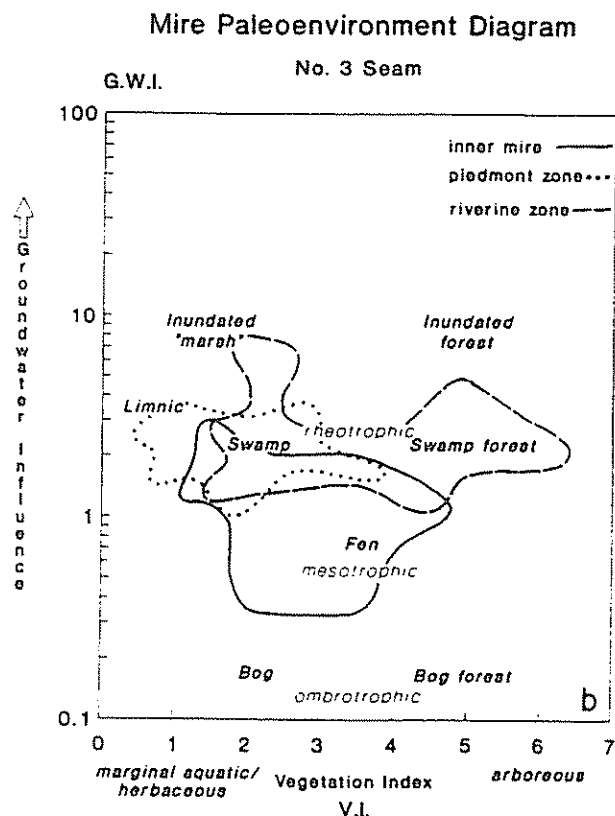


Figure 11. Mire paleoenvironmental diagram of No. 3 seam from the Cumberland Basin in terms of Groundwater Influence (GWI) and Vegetation Index (VI), which are based on maceral ratios (after Calder et al., 1991).

Lateral trends in mineral composition have also been related to depositional environment. Syngenetic pyrite and sulfur in coal indicate the presence of alkaline ions, which most authors attribute to brackish water overlying the peat (Casagrande, 1987; Rimmer and Davis, 1988). Increased quartz content has been inferred to indicate nearness to a basement high (Rimmer and Davis, 1988). Boron concentration (in ppm) in coal has been used as a measure of marine influences in coal (Swaine, 1990); freshwater coals show less than 40 ppm, paralic coals have 50–90 ppm, and brackish or marine coals have >125 ppm of boron (Swaine, 1971; Gluskoter et al., 1977; Goodarzi, 1988). Banerjee and Goodarzi (1990) showed the variation of both sulfur and boron concentration in sediments of different depositional environments.

## CHEMICAL COMPOSITION

According to chemical characterization, whole coal comprises two fractions: (1) *volatile* and (2) *nonvolatile*. Volatile fractions are usually determined by heating to temperatures less than 150°C or by mild Soxhlet extraction (using nonpolar organic solvent), whereas nonvolatile fractions can be determined by combustion or Soxhlet extraction (using both polar and nonpolar solvent). Volatile fractions can either be *organic* such as methane and other low molecular weight compounds or *inorganic* such as moisture. Nonvolatile compounds can also be organic (high molecular weight compounds of the macerals) or inorganic (most of the mineral matter).

Usually, the bulk chemical composition of coal is determined by *proximate analysis* or *ultimate analysis* (ASTM, 1991). Proximate analysis employs destructive distillation and shows an approximate estimation of moisture, volatile matter, fixed carbon, and ash. As discussed earlier, the organic fraction of coal comprises five elements (carbon, hydrogen, oxygen, nitrogen, and sulfur). The determination of these elements (as wt %) by combustion and chemical processes is termed *ultimate analysis*. Two other indices (calorific value and Hardgrove Grindability Index) are often used to determine the physical properties of coal. For details of these analytical techniques, see ASTM (1991). Analytical techniques that generate information about the intricate structural configuration of coal are Fourier Transformation Infrared Spectroscopy (FTIR), nuclear magnetic resonance (NMR), and gas chromatography-mass spectrometry (GC-MS) (part of which will be discussed later).

## Proximate Analysis

### Introduction

The terms *fixed carbon* (FC), *volatile matter* (VM), and *ash* are related to the experimental conditions, formulated after ASTM (1991) for the residue (ash) or liberated material (VM) during combustion. *Fixed carbon* represents the residue (other than ash) after the moisture and volatile matter are liberated from the coal. Mineral matter is the major contributor to ash yield. The proximate analysis is often referred to as *as received*, *air-dried*, *dry/moisture-free*, *moist-ash-free*, *dry-ash-free*, and *dry-mineral matter-free* (Figure 12A), which were calculated according to different laboratory and normalization processes (ASTM D3180, ASTM, 1991).

The mineral matter in coal is usually calculated by a formula that takes the difference of the ash and sulfur content of the coal (Stach et al., 1982; Given, 1984). Volatile matter (VM) on a dmmf basis also requires the volatile matter to be

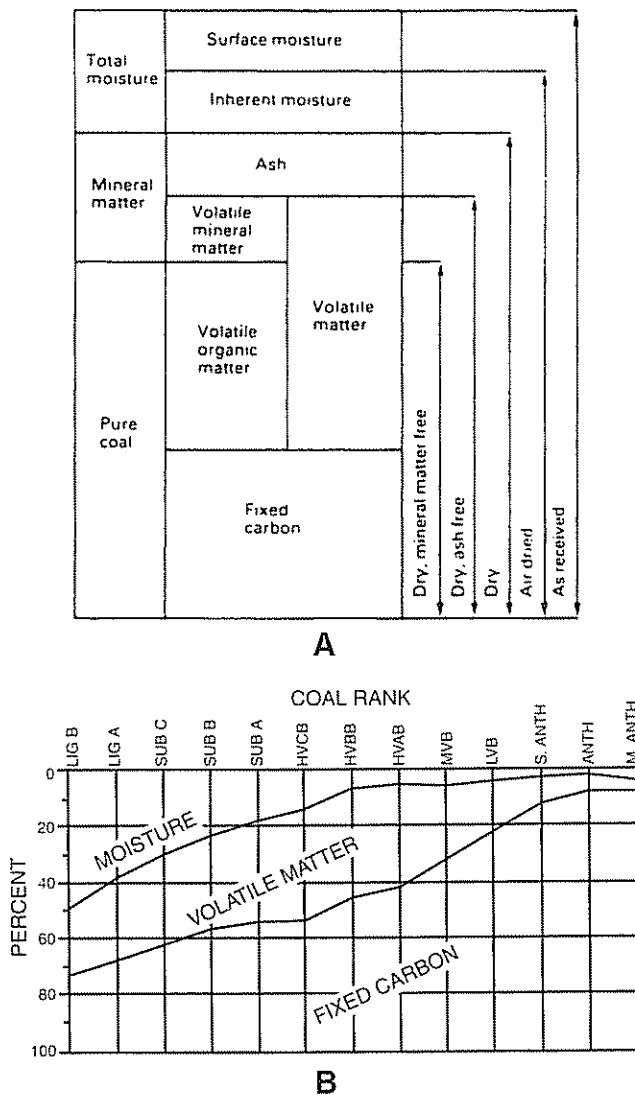


Figure 12. (A) Different basis of proximate analysis (after Ward, 1984). (B) Relation between moisture, volatile matter, and fixed carbon content and rank of coal (after Averitt, 1975).

adjusted substituting the VM contributed from the mineral matter (Given, 1984).

### Moisture in Coal and Its Significance to Composition and Porosity of Coal

Four types of moisture in coal are usually considered. These are (Levine, 1991):

1. *Adherent or free moisture*—retained in coal in a free state on the surface, cracks or cavities. It is not connected to the structure of coal and has normal vapor pressure.
2. *Inherent or bed moisture*—physically adsorbed in the micropores and capillaries of the coal structure and has subnormal pressure (Levine, 1991).
3. *Chemically bound moisture or water of decomposition*—organically associated within the molecular structure of the coal. During artificial or natural coalification, this moisture is released.

4. *Water of hydration*—associated with the inorganic (mineral matter) constituents of coal such as clay minerals (especially kaolinite and illite-montmorillonite) and gypsum. During artificial or natural coalification, kaolinite, illite-montmorillonite, and gypsum release 14 (wt %), 8 (wt %), and 23 (wt %) water of hydration, respectively. For detailed analytical procedures for determination of the moisture content in coal, see ASTM (1991).

The moisture content of coal is dependent on its rank and composition; it decreases progressively with rank (Figure 12B) from over 75 to 90% in peat, to 30–50% in lignite, to 10–7% in high-volatile bituminous, to 1–5% in low-volatile bituminous coal. The water of decomposition, which is bound on the oxygen-functional group (such as hydroxyl, carboxyl, carbonyl), is generally released at <120°C (Allardice and Evans, 1978; Tissot and Welte, 1984). The presence or release of water (moisture content) from coal has a profound effect on coal-bed methane studies. In particular, the presence of water as (1) *adherent free water* suppresses the permeability of the gas flow (generated from the coal matrix), and (2) *inherent moisture* suppresses the methane sorption capacity especially in low rank coal.

The moisture content of coal is reduced drastically according to depth and rank. In the Tertiary lignites of Germany, the moisture content is reduced from 65 to 48% within a depth of 400 m. In the Carboniferous bituminous to semi-anthracite coals of the Saar Region, the moisture content decreases from 6 to 0.5% within a depth of 1500 m within the same sequence. The drastic release of water (moisture content) from the coal matrix by dehydration or decarboxylation possibly results in the formation of *cleats* (fractures in conjugate pairs) within the coal matrix (Ting, 1977; Levine, 1991). The formation of cleats is most abundant near the boundary of subbituminous and high-volatile bituminous rank. One of the possible origins of cleats is related to the drastic reduction of moisture content (from 30 to 7%) and subsequent volumetric change of coal. The formation of cleats is also related to coal lithotype; vitrain-rich coal (bright—microlithotype mainly vitrite) more commonly has cleats than does durain-rich coal (dull—microlithotype mainly inertite) (Ting, 1977). This is probably because vitrain-rich coals (less porous) have more oxygen functional groups (water of decomposition) in their structure than does durain-rich coal.

Law et al. (1983) have shown, from the coal-dewatering model, that the amount of water released from lignite through anthracite is closely related to the corresponding reduction of porosity in the associated sandstone. They have suggested that coal-derived freshwater pore fluid can cause abnormally high pressure in an associated sandstone reservoir due to the dissolution and precipitation of cements. They also pointed out that the sources which contribute to the total water in coal are uncertain, because of continuous release of fresh water.

The water of hydration is released mainly when kaolinite is transformed to sericite and finally to illite at the low-volatile to semi-anthracite stage of coalification (Teichmüller, 1987).

Thomas and Damberger (1976) have studied the relationship between the surface area ( $m^2/g$ ) of various coal lithotypes and inherent moisture content (wt % of whole coal) from various Illinois coals. The internal surface area ( $m^2/g$ ) represents the sum of the total exposed surfaces both on particle boundaries as well as internal pore walls (Mahajan, 1989). Accordingly, Thomas and Damberger

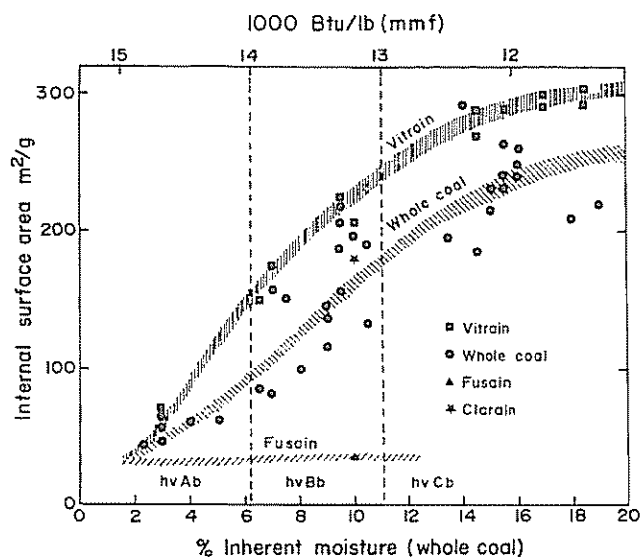
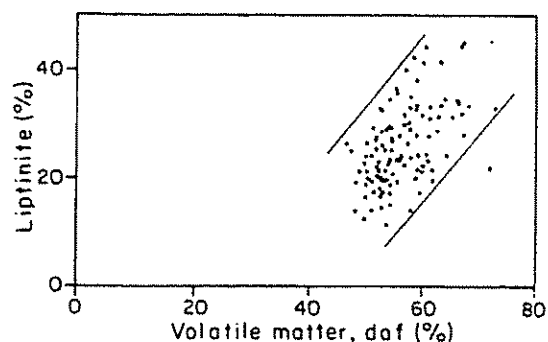


Figure 13. Relation between percent inherent moisture content (whole coal) and internal surface areas showing trends of various lithotypes (after Thomas and Damberger, 1976).

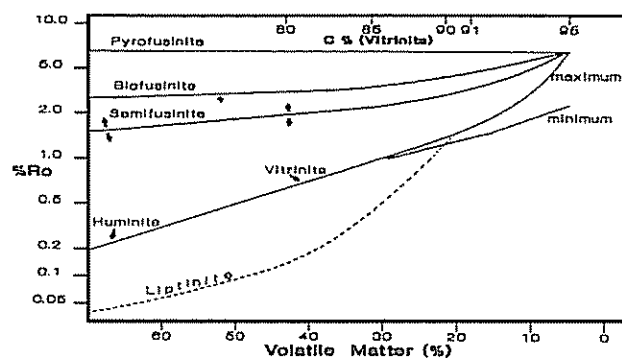
(1976) showed that vitrain has the highest surface area (50 to 300  $m^2/g$ ) compared to whole coal (50 to 250  $m^2/g$ ), clarain (179  $m^2/g$ ), and fusain (36  $m^2/g$ ) when moisture content changes from 2 to 14% (Figure 13). Thomas and Damberger (1976) also showed that a linear relationship exists between volume percent porosity and weight percent inherent moisture content of coals; porosity decreases from 25% (at 25% moisture content) to 5% (at 5% moisture content). Inherent moisture content is also related to true and apparent average pore diameter ( $\text{\AA}$ ) in coal. The difference between the mean "true" and "apparent" pore diameter is the degree of plugging of pores due to the removal of low molecular weight hydrocarbons less than  $C_{15}$  (Thomas and Damberger, 1976).

### Volatile Matter

Volatile matter includes all volatile components released from dried coal during combustion (at 950°C) under an inert atmosphere (ASTM, 1991). The total volatile matter content is the total of the hydrocarbons already generated or present plus the hydrocarbons generated during pyrolysis of the kerogen portion of the remaining coal. Hydrogen-rich macerals (liptinites and some vitrinite macerals) usually contain the major fraction of the volatile matter content and often show good correlation with volatile matter content (Figure 14A). Volatile matter content (dry-ash-free) is most useful in determining the nature of the coal (sapropelic or humic). Volatile matter content (dry-ash-free) often shows a good correlation with mean vitrinite, liptinite, and inertinite reflectance; liptinite reflectance coincides with vitrinite at about 1.0%  $R_o$  (Figure 14B). It is one of the major rank parameters between medium volatile bituminous and semi-anthracite coal. Scott et al. (1991) showed a good correlation between volatile matter content (dry-ash-free) and mean vitrinite reflectance (%  $R_o$ ) from a series of coal (lignite to low-volatile bituminous rank) of the Fruitland Formation, San Juan basin. They showed a break in the trend between 0.5 and 0.8%  $R_o$  which is interpreted as a



A



B

Figure 14. (A) Relation between volatile matter and liptinite content (vol %) from Texas lignite (after Mukhopadhyay, 1989). (B) Relation between percent volatile matter (in daf) in whole coal, percent carbon (in vitrinite), and percent vitrinite reflectance (after Alpern and Lemos de Sousa, 1970).

*coalification jump* due to the generation of major hydrocarbons in coal and which coincides with earlier results of Mukhopadhyay et al. (1979) and Stach et al. (1982).

### Ultimate Analysis or Elemental Composition of Coal

#### Methods

As discussed earlier, the organic fraction of coal comprises mainly five elements (carbon, hydrogen, oxygen, nitrogen, and sulfur). The analytical procedure for determination of these elements is termed as *ultimate analysis*, which is usually reported as wt % basis of each element. C, H, N, and S are measured by combustion (ASTM, 1991), whereas oxygen is measured either by difference or by direct combustion (Howarth, 1977) removing the liberated  $CO_2$  from the mineral matter.

#### Elemental Composition Related to Coal Type and Rank

The elemental composition of coal is dependent on both rank and coal type; C and O show close relationship with rank. Carbon content increases and oxygen content decreases with an increase in rank. Hydrogen and sulfur are mainly controlled by petrographic composition; hydrogen content, however, also decreases with an increase in rank

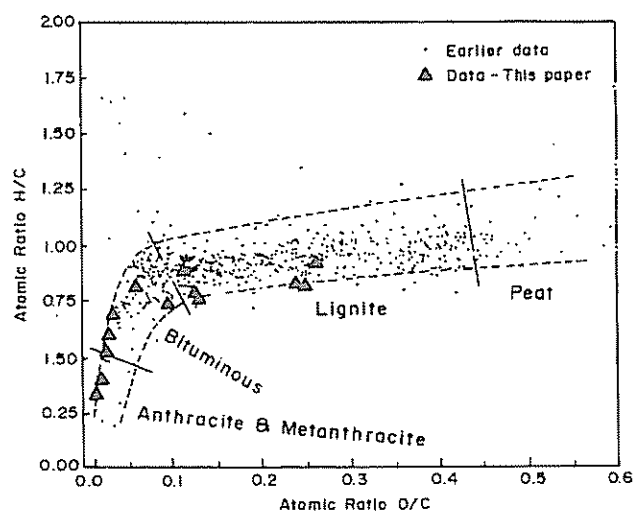


Figure 15. Van Krevelen diagram (H/C versus O/C) showing broad trend of the coalification path of coal from peat to anthracite stage (modified after Tissot and Welte, 1984); dot indicates data from Tissot and Welte (1984) and triangle denotes data collected from Sharkey and McCartney (1981) and other sources.

for the same type of coal. To better understand the variability in rank and maceral composition, the atomic ratios of H/C and O/C are commonly cross-plotted to create a Van Krevelen diagram (Van Krevelen, 1961; Tissot and Welte, 1984). During the coalification of peat to anthracite, coal first loses oxygen and finally hydrogen related to carbon content. This coalification pathway of peat through anthracite shows a smooth trend (Figure 15).

The atomic ratio of carbon and hydrogen or carbon and oxygen varies considerably between humic and sapropelic (cannel and boghead) coals within the same rank. These values are, however, different compared to source rock kerogen (type I, II, and III) and crude oil solid bitumens (Table 7). A plot of the atomic H/C and O/C ratios of three coal types (humic, cannel, and boghead) show that type I kerogen is similar to boghead coal, type II kerogen is similar to cannel coal, and type III kerogen is similar to humic coal (Figure 16). However, the elemental composition of both coal and source rock kerogens is higher in oxygen content than crude oil solid bitumens (Table 7; Figure 16).

The coalification pathway of various macerals using the Van Krevelen diagram shows that liptinite macerals lose more hydrogen compared to vitrinite and inertinite (Figure 17). Within the liptinite group, wax or cerinite and alginite are the most hydrogen-rich macerals followed by sporinite and cutinites. The huminite/vitrinite group of macerals, such as collinite and telinite, are oxygen-rich and hydrogen-lean. Vitrinite macerals are hydrogen-rich compared to the inertinite group of macerals such as macrinite and fusinite. Most of the inertinite macerals (except micrinite) are hydrogen-deficient.

A Van Krevelen diagram is also used to define the pathways for the generation of  $\text{CH}_4$  (demethanation) and elimination of  $\text{H}_2\text{O}$  (dehydration), and elimination of  $\text{CO}_2$  (decarboxylation). The generation/elimination pathways for methane, water, and carbon dioxide are different from each other. The loss of oxygen in the early diagenetic stage and concurrent enrichment of carbon and hydrogen is usually achieved by the loss of highly oxygenated humic acids that are mobilized and removed from coal during com-

paction and dewatering. Coal becomes enriched in methane compared to carbon dioxide because  $\text{CO}_2$  is more readily soluble in water compared to methane;  $\text{CO}_2$  is thereby lost during dehydration.

### Physical Parameters Related to Petrographic and Chemical Composition

Two other physical parameters (vitrinite reflectance and Hardgrove Grindability Index) are often used to correlate with petrographic (lithotype, liptinite content) and chemical parameters (volatile matter or carbon content).

### Calorific Value

Calorific value is the heat generated during combustion of coal, which is measured in a bomb calorimeter (ASTM, 1981). It is usually presented along with the proximate analysis of coal. Similar to volatile matter, it is a major rank parameter for coal and is presented on moist, mineral-matter-free (mmf) basis. Moist, mineral-matter-free calorific value (BTU/lb or KCal/g) is the official ASTM rank parameter up to a fixed carbon content of 69% (dry, mineral-matter-free basis or dmmf). Moreover, it is considered a good rank parameter for coal up to medium-volatile bituminous rank (Stach et al., 1982). Thomas and Damberger (1976) showed that, within the high-volatile bituminous coal rank, there exists a close relationship between moist, mineral-matter-free calorific value (11,000 BTU/lb or 6.0 KCal/g to 16,000 Btu/lb or 9.0 KCal/g) and percent of mineral-matter-free inherent moisture content (22 to 5%).

### Hardgrove Grindability Index (HGI)

HGI is a measurement of the relative grindability or ease of pulverization of coals relative to coals chosen as standards (ASTM, 1981). HGI is the weight of crushed coal using the formula ( $\text{HGI} = \text{wt in } -200 \text{ mesh} \times 6.93 + 13.6$ ). Within various Kentucky coal lithotypes, HGI is highest in bright clarain (61) compared to clarain (45), dull clarain (21), and durain (33) (Hower and Wild, 1988). HGI has an inverse relationship with liptinite content; HGI 70: liptinite 5%; HGI 35: liptinite 27%. Berkowitz (1979) showed the relationship between HGI and volatile matter content (% in dry-ash-free basis). He showed that both lignite (50% VM) and anthracite (5 to 10% VM) can have similar HGI values (30 to 40), whereas bituminous coal (VM 35 to 20%) has a HGI value of 90 to 110.

### Correlation of Chemical Parameters and Vitrinite Reflectance

A correlation of some of the chemical analytical parameters (percent volatile matter, daf; percent carbon in dry-ash-free basis; percent H in dry-ash-free basis; H/C ratio) with vitrinite reflectance shows a uniform increase or decrease with the increase in vitrinite reflectance (Figure 18). Figure 19 illustrates the relationship between various maturation parameters related to coalification stages, hydrocarbon generation boundaries, and the limiting condition for various rank parameters.

### Coal Classification Related to Coal Composition

Two major classification systems are being followed in various countries; these are the ASTM Classification and the Universal Classification from Alpern (1981). The ASTM classification (1981) is a rank classification based on chemical parameters of calorific value and volatile matter or fixed carbon, which were calculated on a mineral-matter-free

Table 7. Ultimate analysis (wt % in daf) data and H/C and O/C ratios of various coals (different rank), source rock kerogens and solid bitumens.

| Sample  | C    | H    | O    | N   | S   | H/C  | O/C  |
|---|------|------|------|-----|-----|------|------|
| <i>Coal</i>   |      |      |      |     |     |      |      |
| Humic Coal<br>(Lignite)<br>Milan Co, Texas**                | 70.5 | 5.1  | 20.6 | 1.5 | 2.3 | 0.87 | 0.22 |
| Sapropelic Coal<br>Subbituminous A<br>Webb Co, Texas**      | 79.9 | 6.9  | 11.0 | 1.2 | 1.0 | 1.04 | 0.10 |
| Humic Coal<br>Subbituminous A<br>South Africa               | 78.8 | 5.6  | 11.4 | 2.1 | 1.0 | 1.04 | 0.10 |
| Sapropelic Coal<br>Subbituminous A<br>South Africa          | 78.5 | 7.4  | 11.6 | 1.7 | 0.8 | 1.13 | 0.11 |
| Coal Sporinite<br>(Hand-picked) +                           | 78.9 | 7.2  | 11.6 | 1.0 | 1.3 | 1.10 | 0.11 |
| Coal Resinite<br>(Hand-picked) +                            | 85.6 | 10.4 | 3.2  | 0.4 | 0.4 | 1.46 | 0.03 |
| <i>Dispersed Organic Matter</i>                             |      |      |      |     |     |      |      |
| Type I Kerogen<br>Green River Shale<br>Piceance Basin, Co.* | 76.5 | 10.0 | 10.3 | 0.6 | 2.5 | 1.57 | 0.10 |
| Type II Kerogen<br>Paris Basin, France*                     | 72.6 | 7.9  | 12.4 | 2.1 | 4.9 | 1.30 | 0.13 |
| Type III Kerogen<br>Douala Basin, Cameroon *                | 72.7 | 6.0  | 19.0 | 2.3 | 0.0 | 0.99 | 0.20 |
| <i>Solid Bitumen</i>  |      |      |      |     |     |      |      |
| Asphaltene +  | 83.0 | 10.8 | 2.3  | 3.1 | 0.8 | 1.56 | 0.02 |
| Gilsonite +   | 85.5 | 10.3 | 1.1  | 2.9 | 0.2 | 1.44 | 0.01 |
| Grahamite +<br>Peru   | 81.8 | 7.7  | 2.9  | 1.5 | 6.1 | 1.13 | 0.03 |
| Grahamite +<br>Pennsylvania                                 | 87.6 | 7.9  | 1.7  | 1.2 | 1.6 | 1.08 | 0.01 |
| Impsonite +   | 89.2 | 5.4  | 1.6  | 2.0 | 1.8 | 0.73 | 0.01 |

\* Data from Tissot and Welte (1984).

+ Data from Sharkey and McCartney (1981).

\*\* Data from Mukhopadhyay (1989).

basis (Table 8). Accordingly, coals from lignite through high-volatile bituminous in rank are classified on the basis of calorific value (moist, mineral-matter-free basis). Medium-volatile, low-volatile, and anthracite are classified based on fixed carbon or volatile matter calculated on a dry, mineral-matter-free basis. Agglutinating character marks the difference between subbituminous A and high-volatile bituminous C or low-volatile bituminous and semi-anthracite rank coals.

In contrast to the ASTM classification, Alpern's Universal Classification System (1981) is based on both the physical and chemical rank and compositional parameters. It utilizes vitrinite reflectance as a major rank parameter because other chemical parameters are dependent on coal type. Alpern's Universal Classification also defines coal facies on the basis of percentages of mineral matter content and maceral content. Alpern's System abandons the noncoherent terms of semi- for hypo-, meso-, and meta- for each



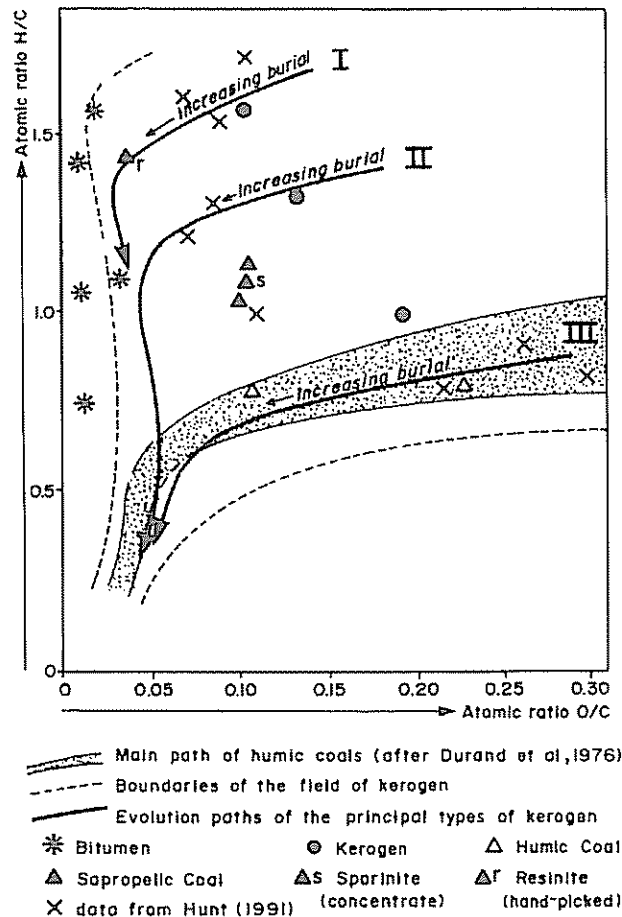


Figure 16. Principal types and evolution paths of coal, kerogen, and crude oil solid bitumen (modified after Tissot and Welte, 1984). Data are from Sharkey and McCartney (1981), Tissot and Welte (1984), and Hunt (1991).

rank stage which were termed lignitinous, bituminous, and anthracitous.

## GEOCHEMICAL ANALYSIS: HYDRO-CARBON GENERATION RELATED TO COAL COMPOSITION AND RANK

### Rock-Eval Pyrolysis

Rock-Eval pyrolysis is an effective scanning method to evaluate the hydrocarbon potential from a source rock including coal. During pyrolysis, Rock-Eval pyrolysis generates three types of peaks whose areas are used to calculate the amount of hydrocarbons already generated before pyrolyzing the kerogen ( $S_1$ ), the potential hydrocarbons to be generated after pyrolysis of kerogen ( $S_2$ ), and the amount of  $CO_2$  generated during pyrolysis ( $S_3$ ), respectively (Tissot and Welte, 1984; Espitalié et al., 1985). The parameters used to define the maturity of organic matter are the hydrogen index ( $S_2/\text{Total Organic Carbon} \times 100$ ), the oxygen index ( $S_3/\text{TOC} \times 100$ ), the production index ( $S_1/S_1 + S_2$ ), and the  $T_{\max}$  ( $^{\circ}C$ ) (the temperature at the peak of  $S_2$ ) (Espitalié et al., 1985). Hydrogen index (HI) and oxygen index (OI) are used to define the organic matter type and

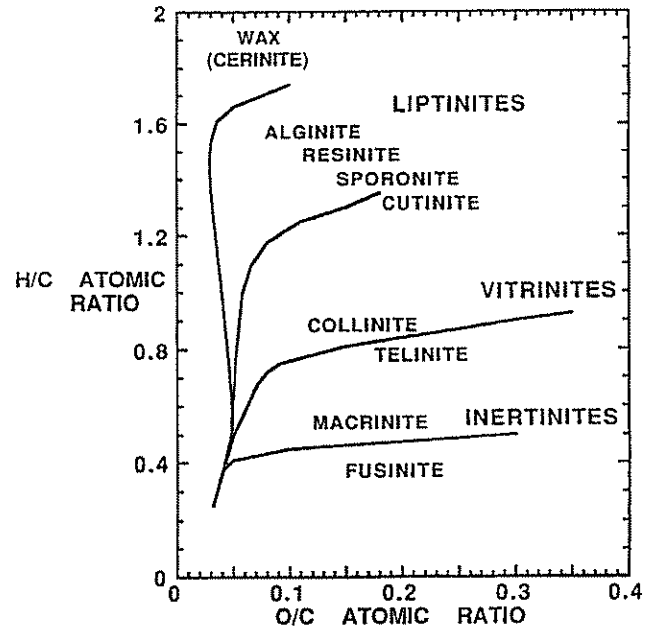


Figure 17. Van Krevelen diagram of coal macerals (after Hunt, 1991).

their evolutionary pathway similar to the Van Krevelen diagram using H/C and O/C atomic ratios. Production index (PI) defines the migration characteristics. Table 9 shows the data on HI, OI, PI, and  $T_{\max}$  from a series of coal from peat to anthracite in rank. This shows the gradual decrease in oxygen index (from 367 to 6) due to decarboxylation and increase in  $T_{\max}$  (maturation parameters) values (from 385 to  $550^{\circ}C$ ).

Teichmüller and Durand (1983) and Bertrand (1984) showed from a modified Van Krevelen diagram of hydrogen index and  $T_{\max}$  that the hydrocarbon generation from humic coal has a broad band of progressive coalification. Teichmüller and Durand (1983) also suggested that suberinite and resinite exhaust most of their liquid hydrocarbons at a much lower maturation than do sporinite and cutinite. Bertrand et al. (1986) suggested that exinite (liptinite) content is not considered as a measure of oil potential from coal. Mukhopadhyay et al. (1985), however, showed that the hydrogen index is closely related to liptinite content in coal, which was also confirmed by later researchers (Fowler et al., 1991; Hunt, 1991; Mukhopadhyay et al., 1991). Figure 20 shows the relationship between liptinite content and hydrogen index (mg HC/g TOC). Desmocollinite and saprocollinite are submacerals of collinite (vitrinite group) and contain abundant liptinitic matrix; they are more hydrogen-rich than telocollinite- or gelocollinite-rich coals (for maceral definition see ICCP, 1971, and Mukhopadhyay, 1992). Accordingly, Mukhopadhyay (1989) classified humic coal into two types: (1) humic and (2) mixinitic or mixed. Based on HI vs. OI (related to maceral associations), as plotted on a modified Van Krevelen diagram, Mukhopadhyay et al. (1991) classified coal into five types: *algal* (or *boghead*), *exinitic* (or *sapropelitic*), *mixinitic* (or *mixed*), *vitrinitic* (or *humic*), and *inertinitic* (Figure 21). These coal types can possibly be correlated to kerogen type I, IIA, IIB, III, and IV. Figure 21 shows that suberinite, cutinite, sporinite, and bituminite-rich coals have a similar hydrocarbon potential and they are grouped within exinitic-sapropelitic types.

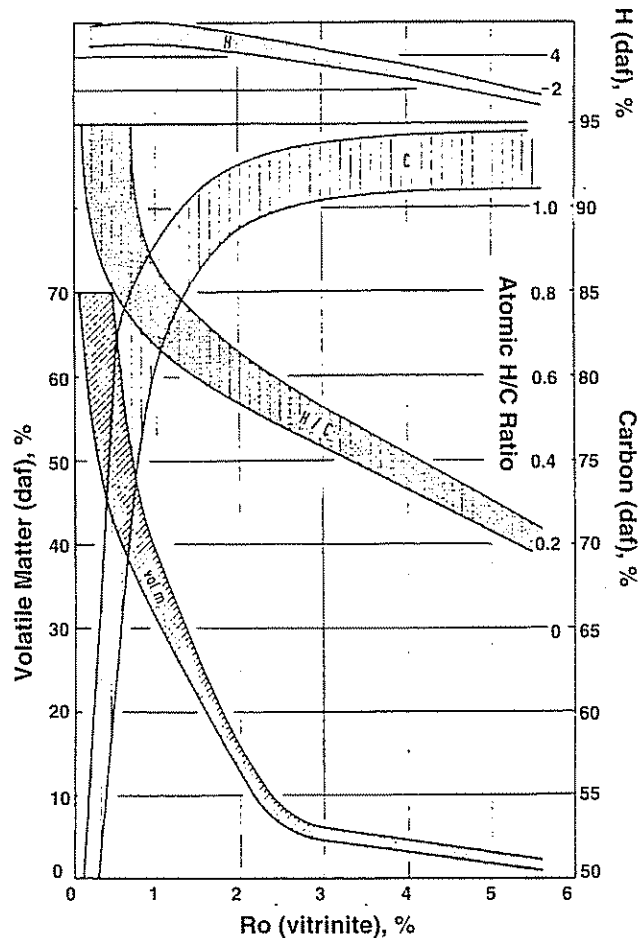


Figure 18. Relation between percent mean vitrinite reflectance and various other chemical rank parameters (percentages of volatile matter, carbon, and hydrogen in dry mineral-matter-free basis) (modified after Stach et al., 1982).

This group cannot be termed canneloid coal, because it does not represent only spore-rich coals. For the generation of major liquid hydrocarbons, exinitic or sapropelitic and mixinitic or mixed coals are considered source rocks (Mukhopadhyay et al., 1991), because boghead or algal coal is rare in nature. Humic coals that generate less than 200 mg HC/g TOC (hydrogen index) are not considered as potential source rock for liquid hydrocarbons. Pure resinite has a hydrocarbon potential similar to alginite while resinite-rich coal has potential similar to other humic, mixed, and exinitic or sapropelitic coals depending on resinite content. Quantitatively, the amount and type of liquid hydrocarbons generated from various coals are evaluated by short-term and long-term anhydrous and hydrous pyrolysis coupled with gas chromatography. For source rock characteristics and quantitative estimation for liquid hydrocarbon generation from various coal types, see Saxby et al. (1986), Bertrand (1984), Bertrand et al. (1986), Murchison (1987), Mukhopadhyay (1989), Hunt (1991), Khorasani and Michelson (1991), Mukhopadhyay et al. (1991), Fowler et al. (1991), Teerman and Hwang (1991), and Boreham and Powell (this volume).

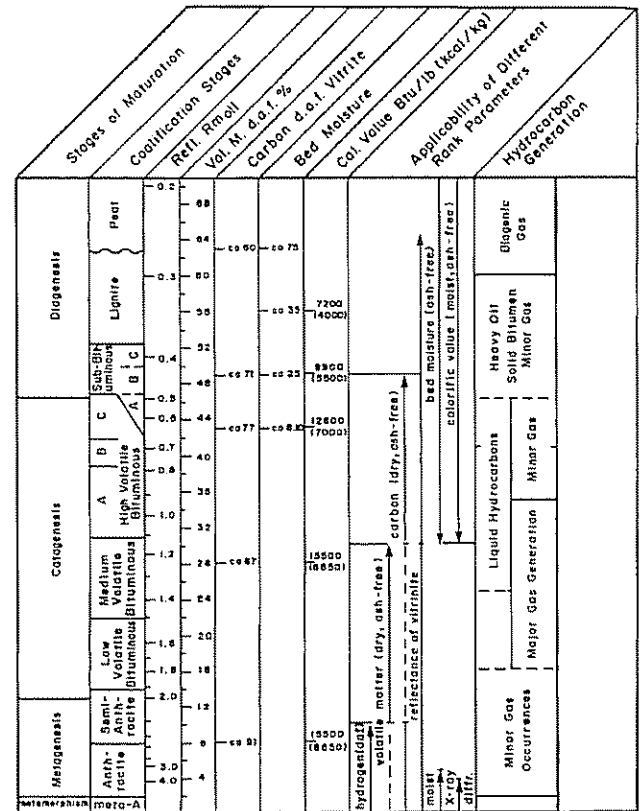


Figure 19. Correlation of various rank parameters related to coalification stages and hydrocarbon generation (modified after Stach et al., 1982).

### Bitumen Extraction and Liquid Chromatography

The nature and percentages of  $C_{12+}$  hydrocarbons (saturate and aromatic fractions), resin, and asphaltene from various coals are usually determined by Soxhlet extraction (with both polar and nonpolar organic solvents) and liquid chromatography (Hunt, 1979; Sharkey and McCartney, 1981; Tissot and Welte, 1984). Even using an extremely polar solvent, it is difficult to recover the major portion of the bitumen from coal because it is retained within the molecular sieve-like pore structure. The variation of bitumen extract (in mg HC/g TOC) and the percentages of saturate, aromatics, resin (NSO) + asphaltenes from coals varies according to rank and maceral composition. The highest extract yield (125 mg HC/g TOC) was observed in suberinite-, cutinite-, alginite-, and bituminite-rich coals (Khorasani and Michelson, 1991; Mukhopadhyay et al., 1991). Humic coals are generally lean in extract yield; desmocollinite-rich humic coals showed higher extract than telocollinite + gelocollinite-rich coals (Boudou, 1984; Bertrand et al., 1986; Mukhopadhyay, 1989). In general, the saturate fraction of the extract is less than 10% of the total extract. Only bituminite and suberinite-rich coals beyond a maturity of 0.5%  $R_o$  show more than 20% saturate fraction of the extract; those extracts are comparable to other source rock bitumens (Tissot and Welte, 1984; p. 381). Suberinite-, bituminite-, and liptodetrinite-rich coals contain more than 20% aromatics which are comparable to bitumens from

Table 8. Parameters used for ASTM Coal Classification<sup>a</sup> (after ASTM, 1991).

| Class              | Group                              | Fixed Carbon Limits, % (Dry, Mineral-Matter-Free Basis) |           | Volatile Matter Limits, % (Dry, Mineral-Matter-Free Basis) |                    | Gross Calorific Value Limits, Btu/lb (Moist, <sup>b</sup> Mineral-Matter-Free Basis) |                  | Agglomerating Character             |
|--------------------|------------------------------------|---|-----------|--|--------------------|--|------------------|-------------------------------------|
|                    |                                    | Equal or Greater Than                                   | Less Than | Greater Than   | Equal or Less Than | Equal or Greater Than  | Less Than        |                                     |
| I. Anthracitic     | 1. Meta-anthracite                 | 98  | —         | —  | 2                  | —  | —                | nonagglomerating                    |
|                    | 2. Anthracite                      | 92  | 98        | 2  | 8                  | —  | —                |                                     |
|                    | 3. Semianthracite <sup>c</sup>     | 86  | 92        | 8  | 14                 | —  | —                |                                     |
| II. Bituminous     | 1. Low volatile bituminous coal    | 78  | 86        | 14   | 22                 | —  | —                | commonly agglomerating <sup>e</sup> |
|                    | 2. Medium volatile bituminous coal | 69  | 78        | 22   | 31                 | —  | —                |                                     |
|                    | 3. High volatile A bituminous coal | —   | 69        | 31   | —                  | 14 000 <sup>d</sup>  | —                |                                     |
|                    | 4. High volatile B bituminous coal | —   | —         | —  | —                  | 13 000 <sup>d</sup>  | 14 000           |                                     |
|                    | 5. High volatile C bituminous coal | —   | —         | —  | —                  | 11 500<br>10 500   | 13 000<br>11 500 |                                     |
| III. Subbituminous | 1. Subbituminous A coal            | —   | —         | —  | —                  | 10 500   | 11 500           | agglomerating                       |
|                    | 2. Subbituminous B coal            | —   | —         | —  | —                  | 9 500  | 10 500           |                                     |
|                    | 3. Subbituminous C coal            | —   | —         | —  | —                  | 8 300  | 9 500            |                                     |
| IV. Lignite        | 1. Lignite A                       | —   | —         | —  | —                  | 6 300  | 8 300            | nonagglomerating                    |
|                    | 2. Lignite B                       | —   | —         | —  | —                  | —  | 6 300            |                                     |

<sup>a</sup> This classification does not apply to certain coals.

<sup>b</sup> Moist refers to coal containing its natural inherent moisture but not including visible water on the surface of the coal.

<sup>c</sup> If agglomerating, classify in low-volatile group of the bituminous class.

<sup>d</sup> Coals having 69% or more fixed carbon on the dry, mineral-matter-free basis shall be classified according to fixed carbon, regardless of gross calorific value.

<sup>e</sup> It is recognized that there may be nonagglomerating varieties in these groups of the bituminous class, and that there are notable exceptions in high volatile C bituminous group.

Table 9. Rock-Eval pyrolysis data from a series of coal from peat to semi-anthracite in rank (modified after Teichmüller and Durand, 1983 and Mukhopadhyay, 1989).

| Sample type / age             | Location    | Hydrogen Index | Oxygen Index | Production Index | T <sub>max</sub> (°C) | R <sub>o</sub> |
|-------------------------------|-------------|----------------|--------------|------------------|-----------------------|----------------|
| Peat (Pleistocene)            | Germany     | 326            | 367          | 0.26             | 385                   | 0.10           |
| Lignite (Pliocene)            | Rumania     | 192            | 233          | 0.0              | 398                   | 0.28           |
| Lignite (Eocene)              | Texas       | 111            | 52           | 0.03             | 411                   | 0.34           |
| Subbituminous (Cretaceous)    | Pakistan    | 246            | 34           | 0.01             | 423                   | 0.47           |
| Subbituminous (Eocene)        | Texas       | 369            | 10           | 0.03             | 432                   | 0.49           |
| High-Vol. Bit. Carboniferous  | Nova Scotia | 262            | 5            | 0.05             | 427                   | 0.67           |
| High-Vol. Bit. (Oligocene)    | Japan       | 294            | 11           | 0.02             | 436                   | 0.74           |
| High-Vol. Bit. (Oligocene)    | Japan       | 259            | 8            | 0.02             | 439                   | 0.84           |
| High-Vol. Bit. (Tertiary)     | Japan       | 254            | 6            | 0.01             | 452                   | 1.05           |
| Low-Vol. Bit. (Carboniferous) | USA         | 50             | 4            | 0.08             | 525                   | 1.35           |
| Semi-anthracite               | Antarctica  | 7              | 8            | 0.09             | 549                   | 2.15           |

High-Vol. Bit. = High-volatile bituminous coal; Low-Vol. Bit. = Low-volatile bituminous coal

type I and II source rocks (Tissot and Welte, 1984, p. 381). Except for suberinite- and bituminite-rich coals, the peak of hydrocarbon generation in coal lies within 0.7 and 1.0% R<sub>o</sub> (Leythaeuser and Welte, 1969; Mukhopadhyay et al., 1979; Tissot and Welte, 1984). For details on hydrocarbon generation from coal, see Boreham and Powell (this volume) and Leythaeuser (this volume).

The generation of methane and other volatiles including H<sub>2</sub>O and CO<sub>2</sub> is generally related to coal composition. Hunt (1979) estimated that the relative yield of CH<sub>4</sub> and H<sub>2</sub>S is much higher from sapropelic coal than from humic coal; humic coal generates more CO<sub>2</sub> than sapropelic coal. Jüntgen and Karweil (1966) and Jüntgen and Klein (1975) estimated the amount of methane generation from coal related to volatile matter content. Levine (1987) estimated the amount of cumulative gas production (cm<sup>3</sup>/g of solid product) from various coal macerals (Figure 22). For the calculation, Levine (1987) used mole fractions of CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub>O at various points on the slope of the maceral coalification trends (on a Van Krevelen diagram). According to Levine's (1987) estimate, alginite (boghead coal) generates more than twice the amount of gas compared to sporinite (exinitic or sapropelitic), whereas sporinite generates twice the amount of gas compared to vitrinite (humic). For elabo-

rate quantitative estimation of methane generation from coal, see Levine (this volume).

## STRUCTURE, GENESIS, AND SOURCE ROCK POTENTIAL OF COAL MACERALS

### Introduction

The chemical composition of coal is presently viewed as a complex assemblage of mostly macromolecular structures despite recent attempts to describe it as a two-component system composed of mobile and rigid phases (Given, 1984). Many recent studies suggest that coal macromolecules exist as a three-dimensional macromolecular network held together by covalent cross-links and hydrogen bonds (Larsen, 1981; Lucht and Peppas, 1981; Green et al., 1982). It may well be that smaller molecules are trapped within this three-dimensional network and are detected as a "mobile phase" that was described as a major (40%) component of coal based on measurements of molecular mobility using <sup>1</sup>H-NMR methods (Jurkiewicz et al., 1982). Support for the presence of this mobile phase was provided by Youtcheff et

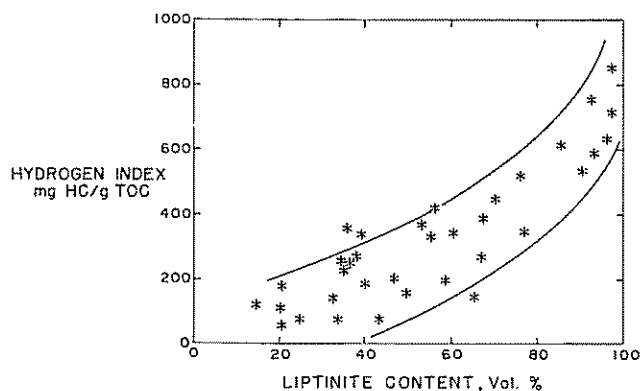


Figure 20. Correlation between liptinite content (vol %) and hydrogen index (mg HC/g TOC) (modified after Mukhopadhyay et al., 1985, and Hunt, 1991).

al. (1983) who argued that extractable organic matter does not entirely represent this mobile phase because many small molecules are trapped and not extractable under ordinary conditions. It has become clear that a differentiation between molecular "mobility" and small molecules trapped in a network must be made before the issue is completely resolved (Given et al., 1988). The mobile components detected by NMR are likely to include both trapped small molecules and mobile flexible parts of the macromolecular network.

Coal is formed from a complex assemblage of plant remains in peat swamps in which the biomolecules are altered through coalification processes to produce the complex macromolecules that exist in coal. It was once thought that the plant remains were degraded to small molecules which recombined via a condensation-polymerization process to form the macromolecular coal components. Such a process would be difficult to maintain while explaining the occurrence of macerals having physical morphologies resembling plant structures. A more plausible mechanism for coalification, one that is completely in accord with petrographic observations, is one which describes coalification as a biological and thermal alteration of the most resistant plant-derived biopolymers (such as lignin and long-chain hydrocarbons derived from wax and cutin) which would be transformed to varying degrees to form the backbone structures in coal macromolecules. Under such a scenario, coal structures would have chemical characteristics inherited from their biological precursors. In as much as petrographic integrity could be preserved and later recognized as coal macerals under such a plan, it is realistic to view coal structure as an assemblage of macromolecules whose collective properties are closely tied to maceral composition. Therefore, chemical compositions of individual macerals can best clue us as to the ultimate composition of most coals. This will eventually lead us to predict the amount of liquid and gaseous hydrocarbons to be generated from a particular coal.

It is difficult to uniquely characterize individual macerals by a single composition because maceral chemistries will be modified by the course of coalification in a manner that is dependent on their initial compositions. To date, only a few studies have been made of the gradational changes in chemical composition of individual macerals as a function of rank or degree of coalification. Coalified xylem and resin are the two macerals, reflecting vitrinite

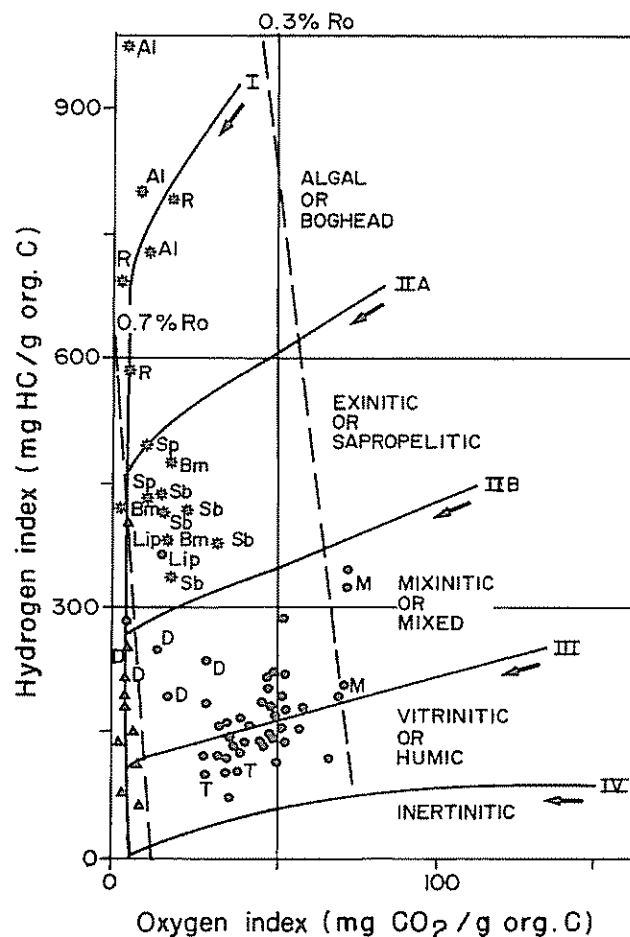


Figure 21. Classification of different types of coal based on hydrogen index (mg HC/g TOC) and oxygen index (mg CO<sub>2</sub>/g TOC) (modified after Mukhopadhyay, 1989, and Mukhopadhyay et al., 1991); abbreviations in the figures indicate coal rich in particular liptinite or vitrinite macerals such as Al = alginite, R = resinite, Sp = sporinite, Bm = bituminite, Lip = liptodetrinite, Sb = suberinite, D = desmocollinite, and M = mixinite. The different symbols indicate data from various sources.

and resinite, respectively, whose chemistries as function of increasing rank have allowed for a better understanding of the chemical composition of coal containing these two macerals. In other cases, we can only make comparison of the chemistries of isolated macerals in coal with those of maceral precursors in modern plants.

### Chemistry of Vitrinite

Although there are at least four types of vitrinite macerals, the most easily recognizable derives from woody tissue of vascular plants (telinite). In a continuing study of coalified xylem from gymnosperms (Hatcher et al., 1989a) and angiosperms (Hatcher et al., 1989b) wood, data clearly demonstrate the rank-dependent chemical structural characteristics of vitrinite (textinite or telinite). Figure 23 shows a series of solid-state <sup>13</sup>C-NMR spectra of coalified gymnospermous xylem (after Hatcher et al., 1983) showing

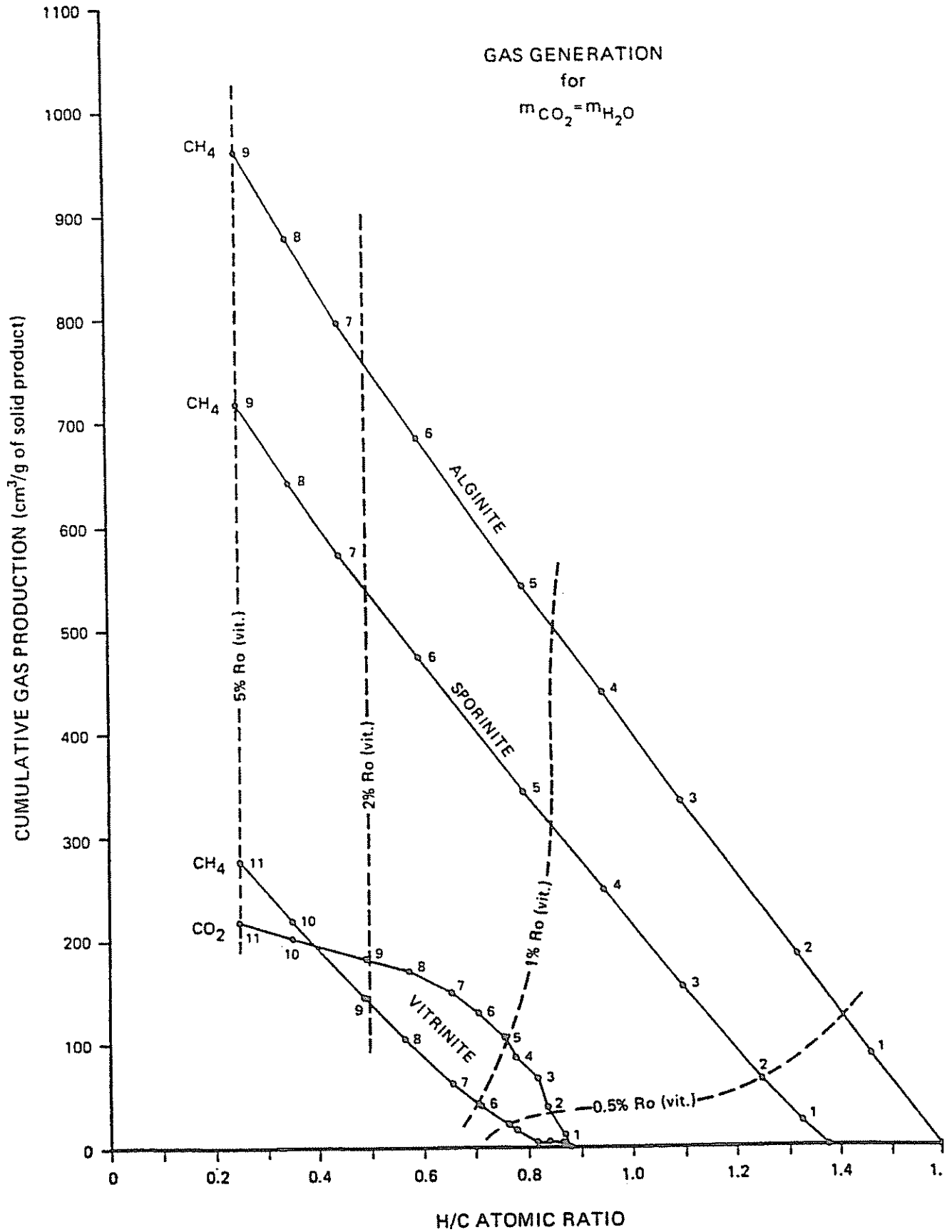


Figure 22. Relation between atomic H/C ratio and cumulative gas production (cm³/g of solid product) (after Levine, 1987).

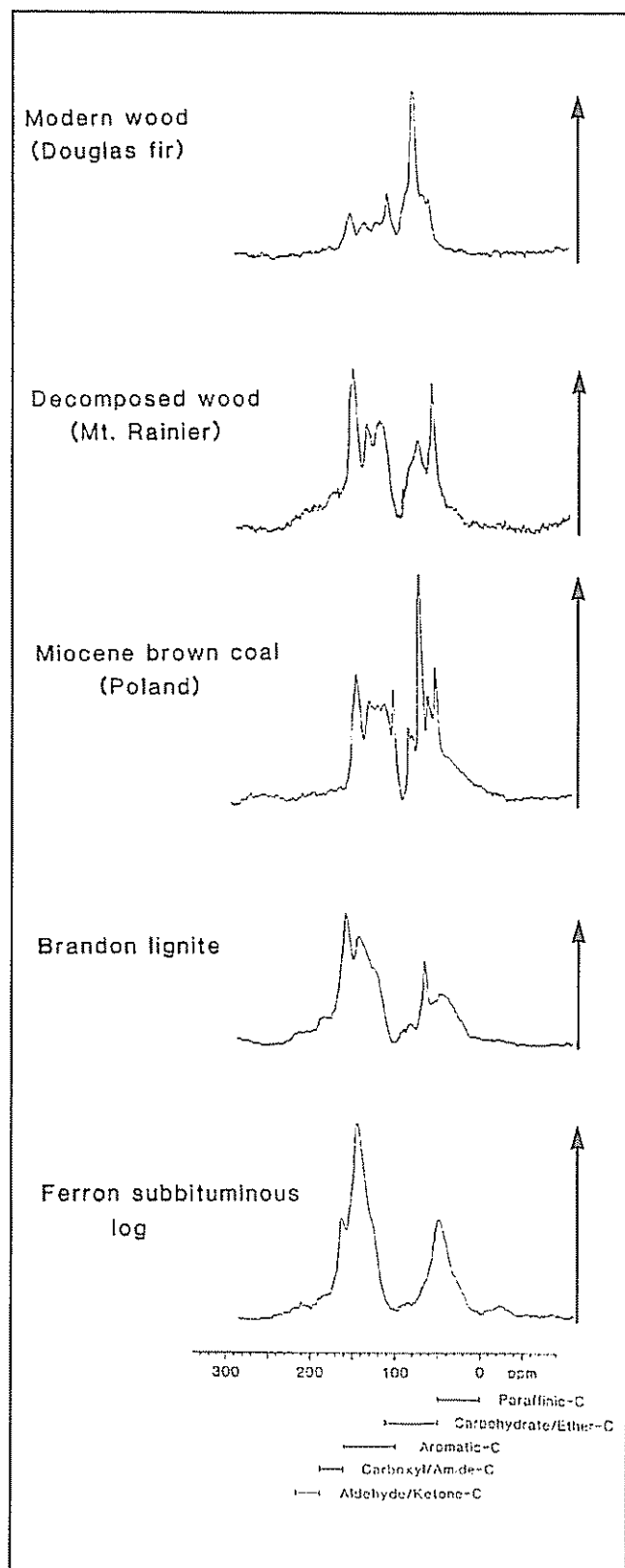


Figure 23. Solid-state  $^{13}\text{C}$ -NMR spectra of a series of coalified wood showing changes in the structure resulting from coalification to the rank of subbituminous coal (after Hatcher et al., 1983). Information about the specific changes in peaks can be found in Hatcher et al. (1983).

changes in the structure resulting from coalification to the rank of subbituminous coal. Information about the specific changes in peaks can be found in Hatcher et al. (1983). The NMR studies, backed up by flash pyrolysis studies (Hatcher et al., 1988; Stout et al., 1988) and other chemical analysis, have clearly shown that vitrinitic coal structure evolves from lignin biopolymers. The cellulose in wood is biologically labile and is completely degraded early during coalification. This can be seen by the loss of cellulosic carbons in NMR spectra (peaks at 72 and 106 ppm in Figure 23). As the rank of lignin increases to bituminous coal, a sequential series of transformations depicted by structural changes in Figure 24 occurs. Demethylation of methoxyphenols to form catechols, cleavage of aryl-ether linkages, reduction of the three-carbon side chain, and cross-linking of aromatic rings characterize the processes that transform lignin to peat/lignite xylite and lignitic textinite. Increased coalification leads to the loss of phenolic groups from aromatic rings and increased reduction of the three-carbon side chain. Variation in bituminous coals is predominantly composed of aromatic rings with short alkyl chains, probably derived from the original three-carbon side chain. Increasing rank leads to dealkylation and aromatic ring condensation to the point where the vitrinite is predominantly composed of only multiring aromatic structures. NMR studies have shown that initially the dealkylation occurs in concert with increased hydrogenation of the aromatic rings, but condensation reactions among aromatic rings eventually reduces the average number of hydrogens per ring (Figure 24).

While the above studies focused on vitrinite derived from xylem, the data are similar to the many published NMR spectra and other characteristics of vitrinite isolated from whole coal by physical methods (Pugmire et al., 1982; Zilm et al., 1981; Maciel et al., 1982).

### Chemistry of Resinite

As discussed earlier, resinite derives from resin exudates from plants who secrete this material as "sealant" to wounds. Studies of freshly exuded resin from trees and fossil resinite and amber show chemical structural details that allow us to progressively map the coalification of resin. Fresh resin is largely composed of diterpenoid and/or sesquiterpenoid acids that polymerize at the side chain sites to produce progressively more insoluble polymers that become more brittle with increasing rank (Thomas, 1969; Simoneit et al., 1986). For resinite produced from gymnosperms, diterpenoid acids polymerize and lose their acidic functional groups, probably via decarboxylation. In studies of resinates from Australian lignite by NMR and pyrolysis/mass spectrometry (Wilson et al., 1984; Anderson et al., 1990; Anderson and Winans, 1991) and analytical pyrolysis (Van Aarsen and de Leeuw, 1991) the polymerization of a precursor, *trans* communic acid occurs by processes shown in Figure 25. Although the chemical shifts are indicated in the figure, many of these chemical shifts remain unassigned to specific structures related to the alicyclic diterpenoid structures of the resin. The NMR spectrum is consistent with a structure proposed by Anderson et al. (1990) for coalified resin. The diagram in the upper left portion of the figure depicts the proposed transformation from labdatriene monomers present in fresh resins.

Coalification does not appear to have a significant effect on the aliphatic structures up to ranks of bituminous coal. However, few resinates from coals of higher ranks have

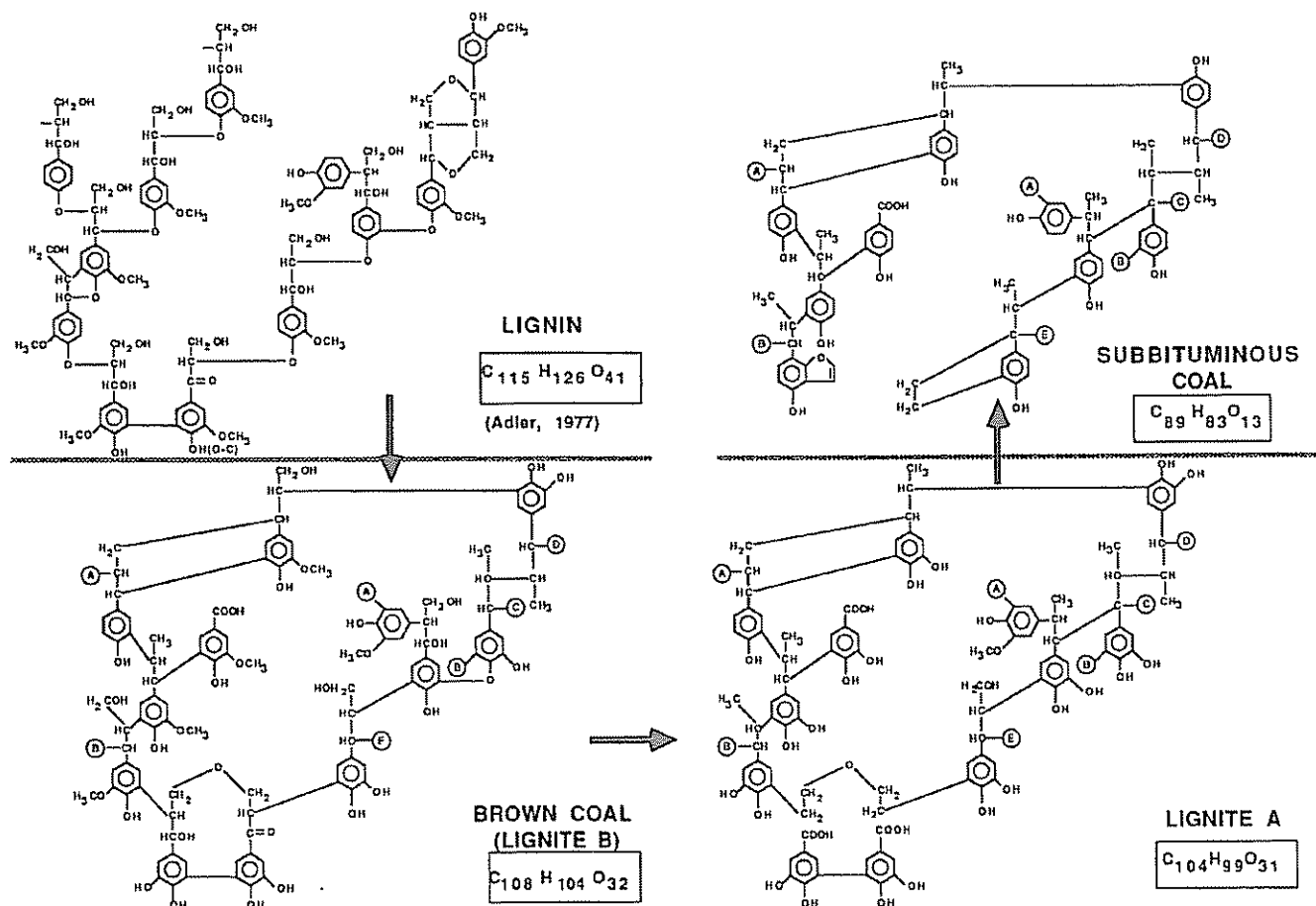


Figure 24. Proposed chemical structures for coalified wood at different stages of coalification (lignin to subbituminous coal). The structures are constructed from the lignin model of Adler (1977), which is used as a template.

been recognized and studied. Murchison and Jones (1964) examined resinites from bituminous and higher rank coals and observed that increasing coalification tended to decrease the hydrogen contents. They suggested that this is because the polyalicyclic ring systems become aromatized.

Snowdon (1980), Mukhopadhyay and Gormly (1984), and Teerman et al. (1987), based on pyrolysis-gas chromatography of hand-picked resinite and liquid chromatography-gas chromatography of bitumen from resinite-rich coals, showed that resinite generates mainly terpenoid hydrocarbons.

### Chemistry of Cutinite

Studies of modern cuticles by analytical pyrolysis, NMR, and other techniques have demonstrated that certain cuticles contain a resistant biopolymer that appears to be aliphatic, producing a homologous series of long-chain n-alkanes upon pyrolysis (Nip et al., 1986). Figure 26 represents <sup>13</sup>C-NMR spectra of cutinane (upper spectrum) isolated from cuticles of *Agave americana* and described by Nip et al. (1986, 1988). The peak at 15 ppm is that of methyl groups, and the doublets at 30 and 33 ppm are assigned to methylene carbons in long-chain polymethylene structures. The peaks in the aliphatic region (0–50 ppm) in the lower spectrum (sample of a cutinite-rich Eocene lignite from Texas), especially the doublet at 30 and 33 ppm, are similar to those of cutinane (upper spectrum, Figure 26). The solid-

state <sup>13</sup>C-NMR of this polymer resembles that of polyethylene. Only minor peaks can be observed in other regions of the NMR spectrum, indicating that this polymer is composed of polymethylene structures. Studies of fossil leaves (cutinite) in coal by NMR (Wilson et al., 1987) and analytical pyrolysis reveal that the aliphatic biopolymers persist and become the major structural components. The presence of the cuticular long-chain aliphatic structures can be readily recognized in coal from their pyrolysis fingerprints (Nip et al., 1986, 1989) but also from their solid-state <sup>13</sup>C-NMR spectra. Figure 26 is indicative of the presence of the aliphatic biopolymers from cutinite in coal. It is difficult at this time to speculate on the macromolecular structure of cutinite; however, it is clear that the major component units are long-chain polymethylenes.

### Chemistry of Alginite

Algae or alginite in coal is recorded as spore forming and non-spore forming. It is likely that both types contain biopolymers which contribute to coal structure. Recent studies (Largeau et al., 1990) have shown that microlaminae in ancient shales and algal deposits can be physically traced to similar structures in modern algae. It is believed that the resistant biopolymers of algae are concentrated in these microlaminae and these biopolymers are selectively preserved over geologic time as aliphatic macromolecules with characteristics similar to those of cutinite polymer (Tegelaar



## COALIFICATION OF RESIN

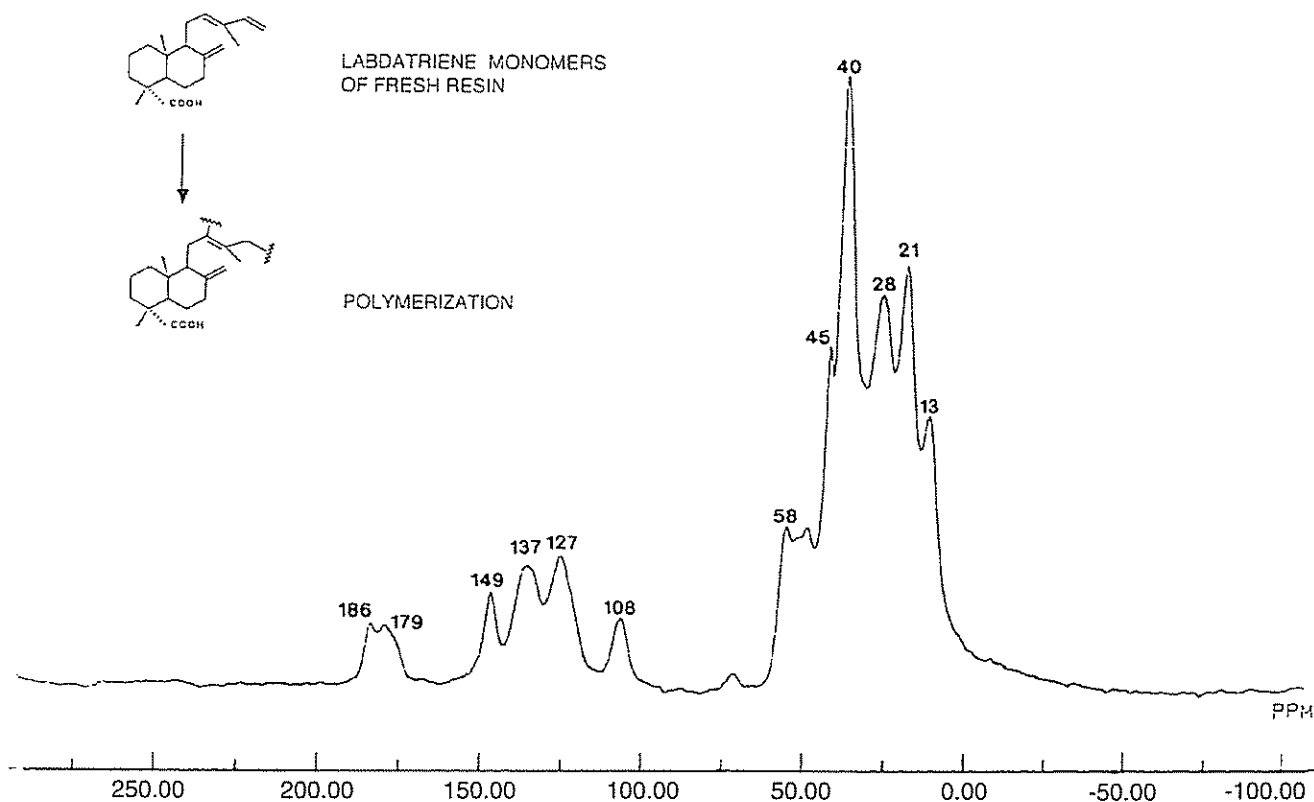


Figure 25. Solid-state  $^{13}\text{C}$ -NMR spectra of a pure resin collected from Yallourbe Open Pit of Victorian brown coal of Australia. Peaks: 0–50 ppm = unsubstituted aliphatic carbons (diterpenoids); 179 and 186 = carboxyl; 100–150 ppm = olefinic carbons (diterpenoids).

et al., 1989). Figure 27 shows the solid-state  $^{13}\text{C}$ -NMR of two torbanites or algal coals compared to a spectrum of *algaenan* (resistant biopolymer) isolated from *Botryococcus braunii* (NMR spectrum is from Zeliber et al., 1988). The one distinguishing feature of all the spectra is the presence of a sharp and intense signal centered at 30 ppm which differs from cutinite in that it is not a doublet. It is apparent that the aliphatic structures of alginite are also composed of long-chain paraffinic macromolecules, but they differ in the type of the hydrocarbons from those of cutinite, which is also revealed by analytical pyrolysis (Goth et al., 1988; Mukhopadhyay et al., 1991). Again, no specific macromolecular structures can be drawn at this time, but it is clear that long-chain paraffins or polymethylenic structures are extremely important constituents of alginite.

### Chemistry of Sporinite

Sporinite is a maceral derived from spore and pollen of vascular plants or algae. Algal spores of *Tasmanites* (bright yellow fluorescence), described in certain boghead coals from Tasmania, have been recognized as having resistant components not unlike the resistant exines of vascular plant pollen (Brooks et al., 1971). However, recent studies (Derenne et al., 1988) argue that the resistant components of algae should not be likened to those from sporinite because they are mostly composed of macromolecules having a lin-

ear polymethylene structure rather than the branched-poly-methylene structures described for resistant residues from pollen. The algal-derived sporinite, therefore, is not included within sporinite but within alginite as described above. The resistant exine of vascular plant spores and pollen, which is most likely to be incorporated into coal, is thought to be primarily composed of a biopolymer called sporopollenin, whose chemical composition is thought to be derived from an oxidative co-polymer of  $\beta$ -carotene (Brooks and Shaw, 1978; Shaw, 1971). The structural composition for sporopollenin was disputed by Schenck et al. (1981) and more recently by Hayatsu et al. (1989). The recent studies of sporopollenin suggest that carotenoids are not the precursors but that complex macromolecular paraffinic structures unlikely to be of a carotenoid nature and formed by polymerization of unsaturated fatty acids or alcohols are the principal component (Hayatsu et al. 1989). Solid-state  $^{13}\text{C}$ -NMR spectra of sporinite show a predominantly aliphatic character, like modern sporopollenin. The resistance of sporopollenin (with its highly aliphatic structure) to bacterial and fungal decay concentrate sporinite in highly degraded coal.

### Chemistry of Fusinite

Inertinitic maceral fusinite originated from charred or oxidized plant material and is expected to resemble char-

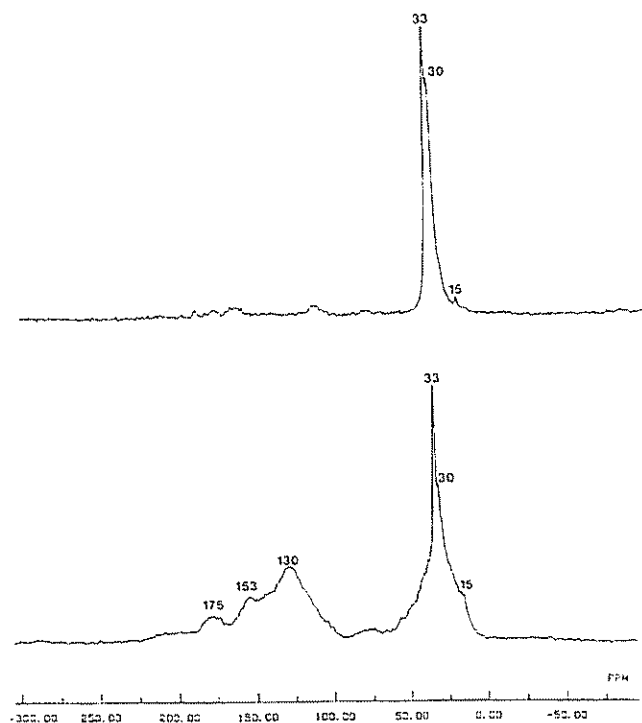


Figure 26. Solid-state  $^{13}\text{C}$ -NMR spectra of : Upper Spectrum—cutinane isolated from cuticles of *Agave americana* (after Nip et al., 1986); Lower Spectrum = cutinite-rich lignite (Jackson Group; Eocene, Texas). Peaks: 0–50 ppm = aliphatic carbon; 100–160 = aromatic carbons; 153 = phenolic carbon; 30 and 33 ppm = methylene carbons.

coal. Numerous reports on the chemistry of fusinite confirmed this fact (Given, 1984). Highly condensed aromatic structures are the primary constituents. NMR spectra are simply composed of aromatic resonances with few aliphatic structures discernible, and carbon aromaticities of greater than 85% are characteristic (Pugmire et al., 1982).

#### Relation between Maceral Association and Hydrocarbon Potential

The NMR and pyrolysis data revealed that hydrogen richness of a coal is dependent on the amount and nature of liptinite and some vitrinite (desmocollinite and saprocollinite) macerals. The preservation of some of these macerals are, in turn, solely dependent on the input of plant types and oxidation level of the peat mire.

As discussed earlier, the abundance of liptinite macerals in coal is the major criterion to consider coal as potential source rock for liquid hydrocarbons. A minimum of 15–20% liptinite content in a coal is considered as important for source rock (Hunt, 1991; Fowler et al., 1991; Mukhopadhyay et al., 1991).

The macerals, such as alginite, bituminite, cutinite, and liptodetrinite, which are mainly derived from aquatic or marsh plants and are subjected to periodic anaerobic decomposition, show higher potential to generate liquid hydrocarbons of waxy nature than resinite- or sporinite-rich coals. Coals rich in alginite, cutinite, and bituminite generate more than 10–15% (or >225 mg HC/g TOC) of liquid hydrocarbons (on whole coal basis) during natural or artificial pyrolysis. Alginite- and cutinite-rich coals have the

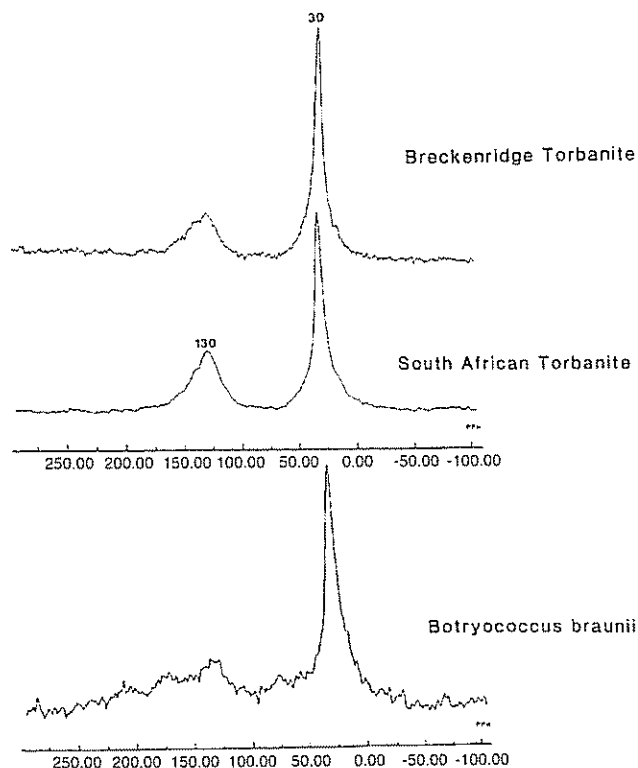


Figure 27. Solid-state  $^{13}\text{C}$ -NMR spectra of alginite-rich (coalified algae—upper two spectra) torbanites and modern algae (*Botryococcus braunii*—lower spectra).

highest potential for liquid hydrocarbons (of waxy nature), because these macerals contain abundance of long-chain methylene group in their structure. The coals that are rich in suberinite (derived mainly from the vascular plants) also generate abundant waxy crude oil. However, suberinite-rich coals are rare in nature. Bituminite-rich sapropelic coals are also important as potential source rock for liquid hydrocarbon. However, the nature of the crude oil (waxy, naphthenic, or aromatic) generated from a bituminite-rich coal depends on the precursor maceral from which bituminite is formed. Resinite and sporinite-rich (sporopollenin) coals that have the lowest potential for liquid hydrocarbons of waxy nature have potential for naphthenic crude oil and condensates. The schematic diagram (Figure 28), which is based on various published literature, relates the processes leading to the formation of various coal and coaly shale types that have distinctive potential for crude oil, condensate, and gas. Algal, exinitic (sapropelitic), and mixed (mixinitic) coals are perhydrous and are considered to be potential source rock for major liquid and gaseous hydrocarbon reservoir.

## SUMMARY AND CONCLUSIONS

This chapter has presented a composite review of the present status of our existing knowledge of coal composition in relation to depositional environment and early diagenesis, characteristics of various physical and chemical changes during coalification, implications for the elimination of water and volatiles from coal, and the criteria for



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