



Readings and Notes

An Introduction to Earth Science

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Coal Genesis

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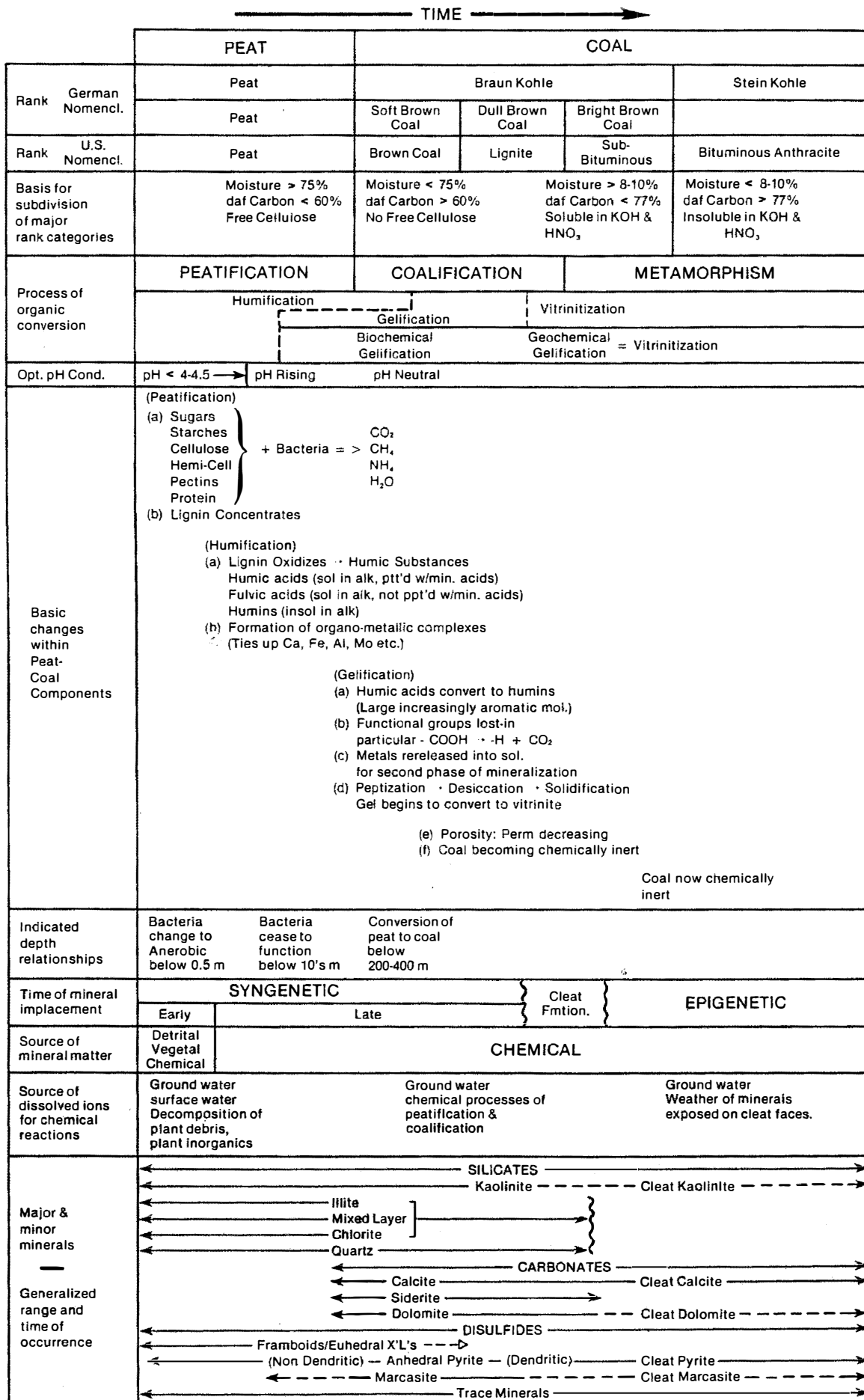
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FIGURE 1. Coal Genesis



COAL GEOLOGY - A SYNOPSIS

INTRODUCTION: Most textbooks classify coal as a sedimentary rock even though it does not fit the definition of a sedimentary rock. While a sedimentary rock is a "rock formed from the products of weathering and erosion", coal forms from the remains of land plants. In fact, coal doesn't even fit the definition of a rock. A rock is defined as "mixture of minerals" and minerals are defined as "natural occurring, solid, *inorganic* substances..."

Coal is composed largely (~90+%) of *organic* substances (macerals) which, by definition, are not minerals. If coal must be classified as a rock, because it forms from a "previously existing rock by the application of heat, pressure, and chemically active fluids", it would best fit the definition of a metamorphic rock. All of this points up the shortcomings of classification systems. Rather than forcing coal to fit a classification scheme in which it does not belong, a better definition is that coal is "a natural-occurring, carbon-rich, combustible solid found in association with terrestrial sedimentary rocks."

Plant Sources: Coal forms from the tissues of land plants with the major contributor being wood that accumulates and is preserved in wetland environments. Land plants first evolved in the Devonian and by the end of the period had adapted to most terrestrial environments. Beginning in the Pennsylvanian, vast portions of the super-ontinent of Pangea were covered by coal-forming swamps and bogs, environments that were to be repeated throughout the remainder of the Paleozoic Era and again in the Jurassic, Cretaceous, and Tertiary. It was during these times that the combination of climatic conditions and wetland environments developed that were conducive to the growth and preservation of large volumes of wood-rich plants, largely as the result of tectonic events that placed continental masses in the proper climatic settings while at the same time producing the topographic settings under which vast peat-forming environments could be maintained for long periods of time. Some coals, such as many of those in the western United States, formed from peat that accumulated in land-locked basins created by extensional tectonics while others formed from peat that accumulated in areas of low topographic relief along the margins of continents where they were near but, as will be seen later, not chemically influenced by the chemistry of ocean waters.

The rates at which plant debris accumulates varies greatly depending on the particular type of plant. From the standpoint of the accumulation of dry plant matter, for example, the most prolific plants are cat-tails (*Typha*)₂ that provide plant debris at rates from 5 to as much as 15 kg/m²/yr. The remains of cat-tails are converted into peat that adds to the surface of the peat mat at a rate of about 0.5-1.0 mm/yr. In comparison, swamp forests in Florida generate plant debris at a rate of about 2-3 kg/m²/yr with subsequent peat accumulation of about 1-2 mm/yr;

the higher rate of peat accumulation reflecting the higher concentration of woody tissue in the mangrove trees that inhabit the Florida swamp forests. In temperate and cooler boreal regions (tundra and taiga), on the otherhand, plant accumulation rates rarely exceed $1 \text{ kg/m}^2/\text{yr}$ due to the lack of large wood-rich trees but because the cooler climates inhibit the activity of the microbes responsible for plant decay, peat deposits are widespread.

From these few data, it can be seen that the rate of peat accumulation depends on factors other than plant productivity. A simple, and speculative, model relates peat accumulation rates to mean temperature and annual precipitation. Under temperate conditions where cooler temperatures and limited rainfall inhibit microbial activity that would decompose the plant debris, the rate of accumulation of plant litter increases with increased precipitation, reaching a maximum of about $1.3 \text{ kg/m}^2/\text{yr}$ at a precipitation level of 2.2 m/yr after which the accumulation rate decreases with increasing levels of precipitation. Under such conditions, peat may form, even on non-wetland sloping surfaces with annual precipitation rates of only 1.5 m/yr . Under tropical conditions, the rate of litter accumulation increases to a maximum of about $4 \text{ kg/m}^2/\text{yr}$ at an annual precipitation of 2.8 m . Again, increased precipitation results in decreased accumulation. It is important to note that in tropical regions, except for basins where water may accumulate, very high rates of precipitation are required for the accumulation of peat. Studies have shown that even under suitable wetland conditions, the increased rate of microbial degradation of the plant litter in tropical areas requires a minimum of 2 m of annual precipitation just to maintain a peat mat.

Peat-Accumulating Environments: Over the years, much confusion has been introduced into the literature because of the terminology applied to peat-forming environments, especially the over-use of the term *swamp*. In recent years, the term *mire* has been adopted for all freshwater peat-forming environments with the particular kind of mire being primarily based on the relative dominance of the two sources of water, **rainwater** and **groundwater**. The importance of the water source lies in the totally different chemistries of rainwater and groundwater. Rainwater is almost always acidic because of reactions between atmospheric moisture and gases such as CO_2 and invariably is characterized by very low ion content. Groundwater, on the other hand, because of the influx of dissolved solids generated by the chemical weathering of the surrounding bedrock is typically neutral to alkaline with relatively high ionic content.

Mires that are totally fed by rainwater are only found in **everwet** regions that receive precipitation during 10-11 months of the year. Such mires are termed **ombrotrophic** and are referred to as **bogs**. Bogs where the vegetation is dominated by trees are referred to as **bog forests**. Because of the everwet conditions that characterize ombrotrophic mires, precipitation always dominates over evaporation, resulting in high rates of vegetal growth. The combination of high rates of litter accumulation and

reduced microbial activity due to the presence of the acidic waters, the peat surfaces in ombrotrophic swamps become elevated above the influence of the groundwater, forming **domed peats**. Because the domed peat within ombrotrophic bogs is totally subjected to percolating, acidic rain water, much of the inorganic constituents originally present within the plant litter and subsequently formed peat are removed by dissolution. As a result, domed peats are the precursors to low-ash, low-sulfur coals. Many of the raised mires in eastern Europe and in the temperate regions of North America are of this type with the vegetation consisting of an upper story of coniferous trees below which grows a dwarf shrub layer and a ground cover of Spagnum moss. In the tropics, such forests are dominated by angiosperm trees. Modern analogs of the peat-forming bog forests that provided the peat for the Carboniferous coals are those of Indonesia.

In areas with more seasonal rainfall, i.e., with periods of wet and dry throughout the year, mires are subjected to a combination of rainwater and ground water. Such mires are termed **rheotrophic**. Because of the increased microbial activity in the more neutral waters, doming of the peat does not take place and the peat mat develops dominantly in a *lateral* direction to form **planar peats** with the upper surface of the peat essentially located at the watertable. Examples of rheotrophic mires are estuarian and maritime wetlands such as saltwater marshes and coastal mangrove swamps. In such settings, the high rates of microbial degradation often precludes the accumulate of peat, certainly peats that would be precursors to coal. At best, such environments would give rise to carbonaceous shales. As we will see, the fundamental difference in the chemistries of neutral to alkaline groundwater and acidic rain water is responsible for many of the compositional differences seen in coal, in particular the **quality** of coal, i.e. the relative abundance of ash and sulfur that characterizes the coal and associated rocks.

The term **swamp** is restricted to rheotrophic wetlands in which the dry season water table is almost always above the surface of the underlying sediment. The term **swamp forest** usually refers to a tropical or sub-tropical swamp, such as the mangrove swamps of southern Florida, where trees make up a major portion of the vegetation. Rheotrophic wetlands located in temperate areas are usually referred to by the Scandinavian term, **carr**. It is important to note that the modern analogs to the "coal-forming swamps" of the past are in fact not rheotrophic swamp forests but rather ombrotrophic bog forests.

BASIC PLANT COMPOSITION

As is the case with most living things, water makes up most plant mass. Typically, the dry weight of combined plant materials is only about 10% of the original bulk weight with ash (mineral matter) making up about 10% of the dried plant materials. Although coal contains the entire suite of plant parts from roots to leaves, the greatest volume of the coal is composed of the

remains of woody tissues. Compared to other plant parts, wood contains less water with the dry weight of wood being about 50%.

The organic portion of plant debris is composed of a number of different organic materials including: 1) protoplasm, 2) chlorophyll, 3) oils, 4) carbohydrates which in turn include a) starches and b) cellulose, 5) proteins, 6) lignin, 7) epidermis, 8) seed coats, 9) cuticles, 10) spore and pollen exines, 11) waxes, and 12) resins. The first three materials decompose rapidly and quickly disappear while the last six are very resistant and are commonly found in coal in recognizable forms. From the standpoint of peat formation, the principle peat-forming components are *carbohydrates* (10-55%), 2) *protein* (0.2-18%), and 3) *lignin* (10-35%).

Carbohydrates are long-chained organic compounds that include the monosaccharides (simple sugars such as glucose, $C_6H_{12}O_6$), and monosaccharide polymers such as starch (the form in which glucose is stored in plants) and **cellulose**. Cellulose, $(C_6H_{10}O_5)_n$, forms the basic framework of plant cell walls and is the most abundant glucose polymer, containing approximately half of all the organic carbon in the biosphere. From the standpoint of coal formation, cellulose is the most important carbohydrate.

Proteins are complex chain structures consisting of at least 50 amino acids. An amino acid is a carboxylic acid with an amino group (NH_2) on the carbon chain. A carboxylic acid is a carbon chain ending with a carboxyl group, ($-COOH$).

Lignin consists of an aromatic nucleus (one made from benzene rings), a side chain with three carbon atoms, hydroxyl groups ($-OH$), and methoxyl groups ($-OCH_3$). The lignin content of the wood ranges from 25 wt% to 30 wt%. Lignin and cellulose are the primary plant components from which the great volume of coal forms.

MICROBIAL DEGRADATION

Introduction: The process of coalification begins with microbial attack on the accumulating plant debris. Aerobic conditions at the very surface of the mire support the life processes of microbes including **fungi**, **actinomycetes** (microorganisms resembling both fungi and bacteria), and **bacteria**, all of which take part in the biochemical reactions that initiate the transformation of the cellulose and lignin contained within plant debris into peat. In order for peat to accumulate, the rate of plant growth must obviously exceed the rate at which the microorganisms decompose the plant debris. In order for this to occur, the decaying plant materials must be transferred into an environment where microbial activity progressively decreases. The most effective environment for this to occur is a waterlogged site (a wetland) with living plants at the surface, dead plants undergoing decomposition immediately below the surface the serve

as a major source of nutrients for the living plants, all underlain by a mass of decayed plant debris encountering decreasing rates of biochemical decomposition.

Controls on Microbial Activity: Under most (non-wetland) surface conditions, plant debris is totally decomposed by a combination of microbial activity and chemical oxidation and is recycled. In order for a coal-forming peat to accumulate, processes of plant decay must be inhibited to the point that the rate of litter accumulation exceeds the rate of litter decay. The major process that must be affected is microbial degradation.

Microbial activity is largely controlled by: 1) availability of moisture, 2) temperature, 3) supply of nutrients, and 4) the acidity/alkalinity of the water. Of the four, moisture is the main factor. Excessive moisture, such as is present in waterlogged mires, reduces the overall activity of bacteria to a minimum by excluding air from the aerobic bacteria while at the same time allowing the continued growth of plants at the surface of the mire. As long as the mire is kept wet by either high levels of precipitation or poor drainage or both, the rate of decomposition will be depressed relative to the rate of plant growth and peat will accumulate. Note also that under typical wetland conditions, chemical oxidation is severely inhibited as dissolved oxygen reacts with the abundantly available carbon to form CO₂.

Assuming the availability of adequate moisture, the rates of both plant growth and bacterial activity increase with increasing temperature, reaching a maximum in warm, humid climes. Plants, however, are less affected by variations in temperature than are bacteria with bacterial activity decreasing at a faster rate than plant growth with decreasing temperature. As a result, while plant growth will be maintained in cool, temperate climates, bacterial activity will be reduced to the point that allow the preservation of increased amounts of plant debris and the subsequent formation of peat; explaining why modern peat development is most extensive at latitudes greater than 45°. Another example of peat accumulation in cool, moist climates is the fact that the most extensive peat accumulations in Europe are located along the Atlantic coast where the combined effect of high rainfall, dense clouds, and cool summers prevail. In comparison, although plant growth will be maximized in tropical climates, the accumulation of peat in tropical regions requires bacterial activity to be reduced to such a level that the rate of growth greatly exceeds that of decay, a scenario that requires either the presence of acidic water such as is found in the domed swamps or the presence of toxic materials generated during the decomposition process.

The inorganic nutrients required by bacteria and fungi (potassium, phosphate, and lime) are similar in kind but not in abundance to those needed by green plants. In general, the abundance of nutrients in the mire waters is dependent on the acidity/alkalinity of the water. Acidic water will contain relatively few nutrients while nutrients are more abundant in neutral to alkaline waters because of their higher ionic

strength. While more extensive plant growth will occur on rich soils or in water with high mineral contents with the subsequent generation of increased masses of plant litter, the debris will be subjected to higher bacterial populations and subsequently higher rates of bacterial decay than plants debris derived from plants growing in poor or impoverished soils or in water low in dissolved solids. As a result, the rate of peat accumulation in the latter case will be higher.

In mires, the major factor affecting **acidity/alkalinity** is the lime content of the water. Where calcium carbonate content is high, such as where the mire is underlain by carbonate rocks or where it is influenced by ocean waters, acidity will be neutralized and the waters will be neutral to alkaline. Examples are the wetlands of the Everglades underlain by carbonate rocks and the tidal-influenced mangrove swamps of south Florida. Peat bogs fed largely by rainwater, on the otherhand, will be acid because of the low ionic strength and inherent acidity of rainwater. The microorganisms responsible for the decomposition of plant debris are highly affected by extremes in both acidity and alkalinity. Bacteria, for example, are more active near pH7 explaining the high rates of bacterial degradation of plant debris in tidal-influenced coastal swamps. Fungi, although most active in mildly acidic conditions, are not very active in strongly acidic conditions such as those that prevail in areas of high rainfall. The effect of either high acidity or lime deficiency is therefore to suppress the rate at which plant debris is decomposed relative to the rate of both plant growth and debris accumulation. The result will be an increase in the rate of peat accumulation.

Changes in Bacterial Acitivity with Depth: During the initial stages of coalification, the biological-bacterial processes take place at atmospheric temperature and pressure. Within the peat layer, the availability of dissolved oxygen decreases with depth as do the number of aerobic microorganisms until eventually the biochemical processes affecting the peat are totally driven by anaerobic bacteria. Because of the ease with which they can be utilized by the microorganisms, cellulose and its decomposition products remain the most important sources of carbon for microorganisms under both aerobic and anaerobic conditions. Only with the onset of the more severe conditions that develop at depth within the peat layer does lignin begin to decompose.

Once the peat layer is buried by sedimentation, usually fluvial, a major change takes place in the coalification process. Temperatures begin to rise within the buried peat, largely due to the geothermal gradient. Eventually, the temperature reaches 100°C. Because temperatures in excess of 100°C (the boiling point of water) for the most part preclude any type of microbial activity, burial brings the microbiological phase of coal formation to an end and physical-chemical processes take over as the driving forces of coalification.

PHYSICAL-CHEMICAL COALIFICATION PROCESSES

Introduction: Once microbial activity ceases, continued coalification becomes the result of the interaction of three physical parameters, **time, pressure, and temperature**. Notwithstanding the important aspect of time, temperature is the most important with pressure actually inhibiting the coalification process.

Temperature: After burial, most coalification processes take place at temperatures between 100°C to 200°C, the process commonly being compared to baking in a "slow oven". Although the temperatures are relatively low, they are able to support reactions that modify the composition and structure of the organic components of the peat including decarboxylation, condensation, desiccation, and the various structural rearrangements that occur during continued coalification.

Once coalification proceeds beyond the lignite stage of coal rank (we will discuss rank shortly), the chemical and physical conditions are of such severity that the process must be considered metamorphic in character. Because organic materials are far less resistant to heat than are inorganic materials, the coal materials will undergo major metamorphic changes even though the rocks that surround them will show no alteration. As coalification proceeds, the initial base-soluble organic materials such as humic acids are converted into increasingly insoluble materials with concurrent structural rearrangements within the coal mass resulting in an increase in the aromaticity of the coal molecule. By the time coalification attains the anthracite stage, the coal molecule is composed entirely of condensed benzene rings.

PROCESSES OF COALIFICATION

Three processes are involved in the transformation of plant during the peat-brown-coal stages: 1) *peatification*, 2) *humification*, and 3) *gelification*.

Peatification: The first step in coalification begins when bacteria and fungi attack the newly accumulated plant debris by decomposing the easily hydrolyzable plant components such as the sugars, starches, cellulose, and proteins. A goodly portion of these materials decompose under aerobic conditions to carbon dioxide (CO₂), ammonia (NH₃), methane (CH₄), and water (H₂O) which are either removed in solution or escape into the atmosphere. The major result of these early coalification processes is the concentration of the relatively stable lignins and mineral matter in the peat.

Humification: Of all the processes taking place during the peatification process, **humification** is probably the most important. Humification is a slow oxidation process, although it may be accelerated by the introduction of additional oxygen into the peat such as during periods of drought when the watertable is depressed or at sites where oxygenated water is introduced into the swamp. The process of humification is most severe on and

immediately below the peat surface in what is referred to as the *peatigenic layer*.

The two major plant tissues that are precursors to coal are cellulose and lignin. During the rotting of plant tissues, the linear macro-molecular (aliphatic) structure of cellulose is rapidly attacked by microorganisms to form glucose which is in turn used by them as an energy source and to make their bodily parts. Experiments have shown that in the presence of the nitrogen provided by the NH_4 generated during mineralization, cellulose will decompose fifteen times faster than lignin. The reason why lignin decomposes more slowly than cellulose is because the combined 3-D aliphatic-aromatic structural units of lignin are far more resistant to the microbial bond-breaking processes that easily break the long-chain structures of cellulose. Once the cellulose fibrils are removed from the cell walls, the lignin within the cell becomes accessible to oxidative degradation. Because lignin decomposes much more slowly than cellulose, with time, it becomes an increasingly more important material for the formation of the humic substances from which coal forms.

Oxygen is necessary for the humification of lignin. In the presence of oxygen and following the removal of the cellulose-rich cell walls, the first attack on lignin is by wood-destroying fungi followed by aerobic bacteria, converting the lignin into **humic acids**. By definition, humic acids are those organic materials that are insoluble in acids and organic solvents but soluble in alkalis. The microbial attack on lignin first removes the aliphatic side chains from the aromatic ring structures that serve as its core and then attacks the ring structures themselves. The smaller molecular units that are subsequently formed then become the basis for the formation of the humic acids. As the process continues and the -OH and -COOH groups are removed from the humic acids, they lose their acidic character and are converted into **humins**, the precursors to the vitrinite macerals (to be discussed shortly).

Gelification: The process of **gelification** follows humification and leads to the formation of vitrinite by the sub-bituminous stage of evolution. Studies indicate that the gelification process entails bringing the humins into colloidal solution with the formation of a **gel** which is subsequently desiccated. Two types of gelification are recognized, **biochemical** and **geochemical**. Biochemical gelification initiates the process during the peat and soft brown-coal stages (pre-lignite); the process being governed by the original materials, the kinds and abundance of ions available in the interstitial water, the acidity-alkalinity of the water, and the redox potential of the system. Geochemical gelification affects the humins once the materials have attained the boundary between dull and bright hard brown coal (lignite and sub-bituminous coal). Unlike biochemical gelification that goes on at atmospheric temperature, geochemical gelification requires elevated rock temperatures that are attained only after the peat has undergone a certain amount of burial. The major change brought about by geochemical

gelification is the conversion of the humins into the vitrinite coal macerals. By the time coalification has progressed to the bituminous stage, the vitrinites consist of humins that are totally insoluble in alkalis.

THE COAL MACERALS

Introduction: Macerals are to coal what minerals are to rocks; they are the microscopic entities of which the organic portion of coal is made. There are three maceral groups, **vitrinite**, **exinite (liptinite)**, and **inertinite**. Because most modern coal petrography is performed using reflected light and oil immersion lenses rather than thin sections and transmitted light, the maceral types are identified primarily on their relative colors and degree to which they reflect incident light (brightness). Vitrinite, for example is usually light to dark gray in appearance while the exinites are much darker. The inertinites are the most reflective of light and are therefore the brightest macerals when viewed under the microscope. In addition to being very bright, the inertinites are also the hardest of the maceral types and therefore commonly stand out in relief above the polished surface of the coal mount. Within the same rank, vitrinite contains relatively more oxygen, exinite more hydrogen, and inertinite more carbon. Of the three, exinite contains the highest concentration of volatile-matter (67 wt%), vitrinite is intermediate in volatile content (35 wt%), and inertinite has the lowest volatile content (23 wt%).

Vitrinite

Of the three maceral types, vitrinite is volumetrically the most abundant and is responsible for the brilliant, black bands seen in coal. Vitrinite forms primarily from trunks, branches, stems, leaves, and roots. There are three types of vitrinite: 1) **telinite** which forms from the remains of cell walls and in which the cell structures are visible within the vitrinite, 2) **collinite** which is the structureless constituent of vitrinite formed from preserved cell fillings, and 3) **vitrodetrinite** which consists of aggregates of small, irregular-shaped fragments of vitrinite that cannot be assigned with any assurance to either of the other two types. Many observations of vitrodetrinite indicates that the vitrinite components actually formed early in the degradational history of the peat materials and do not simply represent fragments of vitrinite that have been formed by the pressure-crushing of existing vitrinite.

Often the telinite (cell walls) is filled with collinite. Collinite is considered to be a preserved gel, explaining its structureless appearance. The name is derived from the Greek word "kolla" meaning glue; collinite does in fact commonly serve as the binder or *glue* with which the other coal components are held together. In cases where cell structures are difficult to see, the maceral is simply recorded as vitrinite. Pure telinite is relatively rare.

Compositionally, vitrinite consists of aromatic nuclei surrounded by aliphatic groups such as -OH, -COOH, and -CH₃. With increasing rank, the peripheral aliphatic groups are lost and the aromatic nuclei increase in size.

Exinite

Exinite, also called **liptinite**, is derived from the remains of the most chemically resistant plant components, namely, spores, cuticles, resins, and algae giving rise to the four kinds of exinite macerals, **sporinite**, **cutinite**, **resinite**, **alginite**. A fifth exinite maceral, **liptodetrinite** is to the exinite maceral group what vitrodetrinite is to the vitrinite maceral group. As a result of compositional changes that take place within the exinite materials during metamorphism, exinite cannot be microscopically distinguished from vitrinite beyond the upper end of the low-volatile bituminous rank.

Sporinite consists of the skins of spores and pollen. In most Paleozoic bituminous coals, sporinite is overwhelmingly the major maceral of the exinite group. It is estimated that, on the average, a gram of Carboniferous coal contains 5 million spores. Spores are easily recognized under reflected light because of their dark colors. Because spores are invariably compressed by burial, they are identified by their cross-sectional shape.

Spores are classified based on size as **megaspores** (>200 microns) and **microspores** and on the thickness of the cell wall as either **tenuispores** (thin-walled) or **crassispores** (thick-walled). Megaspores have been identified with diameters as large as 3 mm. The composition of sporinite is thought to be similar to that of vitrinite (aromatic ring structures with aliphatic side chains) but with fewer condensed rings. When heated, sporinite yields more gas than the total coal sample and typically generates exceptionally high tar yields.

Cutinite is made up of the highly resistant skin, or *cutin*, that covers and protects the surfaces of leaves, needles, shoots, stalks, and thin stems of plants. It should be noted that some plants that grow under water do not possess cutin. The widespread occurrence of cutinite in coal is due to several factors including the high resistance of cutin to chemical reactions, its resistance to heat, and the fact that it is not accepted as a food supply by bacteria and fungi. In Paleozoic bituminous coals, cutinite is less abundant than sporinite. The characteristic compositional feature of cutinite is its high hydrogen content (> 50 atomic%).

Resinite includes all the resinous components in coal. Resins, such as sap, are the products of plant metabolism. With increased metamorphism, much of the resinite present in lower-rank coals is converted into vitrinite. Typical of exinites, resinite is enriched in hydrogen, in fact, studies have shown that resinite

contains more hydrogen than sporinites of the same carbon content.

Preserved algae, or **alginite**, has the lowest reflectivity and therefore appears as the darkest bodies under reflected light. Alginite is not usually found in humic (layered) coals but in boghead coals where it represents the preserved remains of the algae *Pila* and *Reinschia*.

Liptodetrinite is the catch-all classification for finely divided particles of exinite that cannot be assigned with reasonable certainty to any other member of the exinite group.

From the standpoint of coal-utilization, especially the conversion of coal into gaseous and liquid fuels, the exinite macerals are the most important. Because exinite is enriched in hydrogen, it produces the greatest volume of tars upon heating. The tar yield from spores and cuticles ranges from 20% to 40% while waxes and resins produce as much as 80% to 90% tar.

Inertinite

The name derives from the fact that while the vitrinite and exinite macerals soften during the coking process, the inertinite macerals are little affected. Compared to exinite, inertinite is poor in hydrogen and rich in carbon. The inertinite maceral group consists of **fusinite**, **semi-fusinite**, **macrinite**, **micrinite**, **sclerotinite**, and **inertodetrinite**.

Fusinite and vitrinite forms from the same plant materials. Although particularly common in bituminous coals, fusinite rarely exceeds a few percent by volume. Based on the mode of origin, fusinite is subdivided into **pyrofusinite** and **degradofusinite**. Pyrofusinite is the charred remains of woody tissue that forms by rapid oxidation during swamp fires while degradofusinite is the result of slow, chemical oxidation.

Studies of the woody tissues found in modern peat that has been subjected to swamp fires have shown continuous transitions from totally carbonized wood (pyrofusinite) to partially charred wood (semi-fusinite) to unoxidized wood. Comparable transitions are commonly observed on preserved wood sections within coal with a wood fragment being converted to fusinite (completely burned wood) on one end while the other end has been converted to vitrinite (unburned wood).

Most of the fusinite found in Carboniferous and Permian coals is degradofusinite that forms during the moldering of peat by bacteria and fungi at the surface of the peat mat where the supply of oxygen is at a maximum. Reports have also been made of wood having been converted to fusinite in karst areas by the subsurface percolation of oxygen-rich groundwater. Because of the periodic wetting and desiccation of the peat, little if any of the original wood structure is preserved.

Fusinite is characterized by high carbon and low hydrogen contents with both chemical and physical properties showing little change with increasing rank. It might also be pointed out that fusinite is the coal component that makes it "dirty".

Semifusinite represents an intermediate stage between fusinite (total carbonization) and telinite (no charring). Most of the semifusinite in Carboniferous and Permian coals is of the degrado-semifusinite type.

Macrinite is a more or less amorphous, non-granular groundmass exhibiting high reflectance. As a maceral, it is relatively rare and appears mostly in durites and clarodurites (coal lithotypes that will be discussed below).

Micrinite is characterized by its rounded shape and small size (≈ 1 micron in diameter). Micrinite can occur in all lithotypes but is especially abundant in durites.

Sclerotinite forms from the sclerotia of fungi (masses of branched structures within which food is stored). Compared to Tertiary coals, sclerotinite is relatively rare in Carboniferous and Permian coals.

COAL TYPES

Coals are classified on their structure and source of origin as being either **humic** or **sapropelic**. Humic coals are layered or banded coals form from peat that accumulate in swamps with the peat forming from plant debris by the process of peatification. Sapropelic coals, on the other hand, are non-stratified coals that form from a combination of finely divided plant debris, spores, and algae accumulated in stagnant or standing bodies of water and are initially converted by the process of *putrefaction*. Sapropelic coals include **channel coal** and **boghead coal**, both of which are relatively high in volatiles and typically dull in appearance. Humic coals are, by far, the more dominant of the two; sapropelic coals are, in fact, quite rare.

COAL LITHOTYPES

Humic Coals: Humic coals are characterized by macroscopic layers or bands called **lithotypes** that are identified based on their degree of brightness and differ compositionally in the relative abundance of the various maceral. The humic coal lithotypes are **vitrain** (bright bands), **clarain** (semi-bright bands), **durain** (dull bands) and **fusain** (mineral charcoal). **Duroclarain** and **clarodurain** represent the transition between clarain and durain. The coal lithotypes and their characteristic maceral groups and individual maceral types are summarized in the following table.

LITHOTYPE	MACERAL GROUP	INDIVIDUAL MACERAL TYPES
VITRAIN	Vitrinite(Vt)	collinite(cell fillings) telinite(cell walls)

FUSAIN	Inertinite(I)	micrinite massive(inertinite detritus) fine(microspore protoplasm) semifusinite fusinite sclerotinite(fungal remains)

	Exinite(E)	cutinite(skins of leaves) resinite(resin bodies, cell fillings) sporinite(spore remains) alginite (algae, Pila, Reinschia)

CLARAIN	Vt + E	
DUROCLARAIN	Vt + E + I	
CLARODURAIN	I + E + Vt	
DURAIN	I + E	

Sapropelic Coals: Sapropelic coals are subdivided into two lithotypes, **cannel coals** and **boghead coals** with transitions in between. As previously indicated, a major difference between humic and sapropelic coals is that humic coals are stratified (layered) while sapropelic coals are not. Because of their composition and lack of internal structure, sapropelic coals are dull, very dense, and very strong. From prehistoric times, for example, sapropelic coals have been carved into statuary and jewelry. Even today, cannel coals are used in the production of "coal art".

Macroscopically, cannel coals and boghead coals are difficult to distinguish; both being black, dull, exhibiting a greasy luster and conchoidal fracture. Microscopically, however, they differ in that cannel coals show micro-stratification, contain little or no alginite, and are commonly rich in spores. Boghead coals, on the other hand, are non-stratified and are composed primarily of alginite.

COAL RANK

Introduction: Rank refers to the degree of coalification or metamorphism to which the plant material has been subjected and takes into account all of the chemical and physical changes that take place within the material. The rank series begins with peat as the lowest rank coal and ends with meta-anthracite as the highest rank (see Table below). Metamorphism of coal beyond the meta-anthracite stage results in the formation of graphite. The numbers in the table represent estimated averages for the mid-

range rank. Note that sub-bituminous A and high-vol bituminous C ranks are the same. The higher designation was initiated for sales purposes.

RANK	VIT. REFL. %Ro	d.a.f. VOL. MAT.	d.a.f. CARBON	CAL. BTU/lb
Peat	0.25	67%	55%	4500
Lignite	0.32	58%	65%	7000
C	0.40	51%	69%	9000
Sub-B	0.45	48%	72%	9900
Bit. A	0.60	45%	75%	12000
Hi- C	0.60	45%	75%	12000
Vol. B	0.72	41%	78%	13000
Bit. A	0.82	35%	82%	14100
Med. Vol. Bit.	1.3	29%	87%	15500
Low Vol. Bit.	1.7	18%	89%	15500
Semi- Anth.	2.1	11%	90%	15500
-----	2.5	8%	92%	-----
Anth.	3.2	5%	95%	15500
Meta. Anth.	>4	<2	>95%	15500

During the first stages of coalification, the biological-bacterial processes dominate and convert plant debris into the lowest rank coal, peat. By the time the rank has risen to the lignite stage, conditions of temperature and pressure preclude the survival of microorganisms and the processes become purely chemical or physical in nature with most of the energy used to drive the coalification process being provided by heat. Beyond the lignite stage, the changes that take place within the coal are sufficiently severe that the coalification process can realistically be considered metamorphic in character.

Affect of Depth of Burial: In most cases, the primary factor driving the metamorphic process is the heat provided via the geothermal gradient. Studies have shown that in a few isolated cases, the heat was provided by magmatic sources located below the basin of accumulation. Overburden pressure, although responsibly for physical changes such as compaction that take

place within the coal, is **not** responsible for **any** of the chemical changes that take place with increasing rank. Recent experiments conducted under the same temperatures and for the same lengths of time but under different pressures showed that the degree of carbonization as measured by reflectance decreased with increasing pressure. It is very important, however, to note that carbonization is accelerated by **tectonic pressure**. Recent work has definitely shown that coalification from the meta-anthracite to graphite range requires the conditions brought about by tectonic deformation where the important agent was the involvement of **tectonic shear**.

It is also important to repeat the fact that, except for the change of anthracite to graphite where temperatures in the range of 300-350°C (and higher) are involved, the temperatures involved in the coalification process rarely exceed 200°C. In the discussions that follow, keep in mind the factor of time. *Shallow* burial of peat over *long* periods of time can produce the same result as *deep* burial over *short* periods of time. It is also important to note that the entire coalification process from peat to the beginnings of anthracite has taken place before any changes in the surrounding sedimentary materials (diagenesis) has begun.

One of the first studies to document the effect of depth of burial on coalification was reported in 1963 based on samples removed from the German Munsterland I borehole in the Saar region of western Germany, at the time the deepest borehole in Europe. The maximum temperature measured in the borehole was 209°C at a depth of 5956 m. The borehole encountered about 100 coal beds and thin coal bands with the uppermost Carboniferous beds encountered at 1844 m and the deepest coal being encountered at 3445 m. Data from the study showed that with increasing depth: a) the d.a.f. (dry ash free) volatile matter decreased almost linearly from 35% to about 5%, b) moisture decreased from 4% to 0.8%, c) vitrinite reflectance increased from slightly more than 1%Ro to almost 4%Ro, d) d.a.f. carbon increased from 80.5% to 90%, and e) a.f. (ash free) calorific content increased from 7600 kcal/kg to 8700 kcal/kg. Another important discovery from this and other studies is that the increase in rank with depth of burial is *totally* independent of the composition of the coal.

Determination of Rank: Because of the systematic changes in the various coal parameters with rank, any one of the discussed parameters could be used to determine rank. The parameter(s) used depend primarily on the coal rank itself. For coals lower in rank than medium-volatile bituminous, changes in d.a.f. carbon, d.a.f. volatile matter, and vitrinite reflectance are not only irregular but the changes with any incremental change in rank is very small. As a result, they are not the best rank indicators for coals below the rank of medium-volatile bituminous. On the other hand, the a.f. moisture and calorific values for these coals show marked changes with rank and, as a result, are the best indicators of rank.

As the rank increases beyond high-volatile bituminous, moisture and moisture-dependent calorific content change little with increasing rank. Between 30% and 8% volatile matter (from medium-volatile bituminous to semi-anthracite coal), volatile matter and vitrinite reflectance are the best determiners of rank.

The most common parameter used to determine the rank of bituminous and anthracite coals is vitrinite reflectance (%Ro), a measure of the percent of incident light reflected from a polished coal surface. Once rank has attained the anthracite and meta-anthracite level, hydrogen content is the best rank indicator.

Compositional/Physical Changes with Increasing Rank: In the hard brown-coal stage (lignite to sub-bituminous coal), vitrinite undergoes profound physical changes. Below the rank of lignite, cell walls and cell contents are readily visible in the stems of plants. As the coal enters the lignite rank stage, the process of gelification has resulted in the compaction and homogenization of the cell tissues leading to the formation of a gel from which the homogenous vitrinite of bituminous coal forms. As a result of these combined chemical-physical modifications, the coal changes from soft, brown, and dull to black, hard, and bright. Water is expelled as the change takes place, explaining the marked decrease in moisture content during early coalification. Because the calorific content of ash-free coal is highly dependent on the moisture content, the decrease in moisture is accompanied by a parallel increase in calorific content. During this stage of coalification, the humic substances lose increasing numbers of -COOH, -C=O, -OCH₃, and -OH groups from their aromatic cores resulting in the concurrent increase in the aromaticity of the coal and decrease in the oxygen content.

At approximately 87% carbon and 29% volatile matter (medium-volatile bituminous), an important change referred to as the **coalification break** takes place. By this time, desiccation of the humic gel formed by the gelification process is near complete. With increasing rank, the hydrogen-rich methyl (-CH₃) groups associated with the aromatic core are reduced and methane, CH₄, begins to evolve. With the loss of the methyl groups, the aromatic clusters begin to condense into larger groupings, further concentrating the aromatic carbon and subsequently resulting in an increase in the vitrinite reflectance.

The rank stages and a summary of the basic coal characteristics are listed below:

Rank Stage	%d.a.f. carbon	volatile matter %d.a.f.	vitrinite reflect. %	moisture %	BTU/lb
Meta-anthr.					
Anthracite					

-----	91	-----	8	-----	2.5	-----	15500	--
Semi-anthr								
low-vol BC								
med-vol BC	----	87	-----	29	-----	1.1	-----	15500
high-vol BC								
-----	77	-----	42	-----	0.5	-----	8-10	--- 12600
sub-bitum								
-----	71	-----	49	-----		-----	25	---- 9900
lignite								
-----		-----	53	-----	0.3	-----	35	---- 7200
Brown Coal								
-----	60	-----		-----		-----	75	-----
Peat								

COAL QUALITY

Coal quality is determined by the ash and sulfur content of the coal and is subdivided into high-, medium-, and low-quality. In general, ash and sulfur contents increase or decrease together. We will discuss the conditions responsible for the incorporation of ash and sulfur into coal later. The subdivision of coal into high-, medium- or low-quality is purely an arbitrary decision. High-quality coal is any coal whose sulfur content is less than 1 wt% and whose ash content is less than 10 wt%. Experience has shown that coals with sulfur and ash contents below these limits can be mined and utilized with little or no environmental impact. As the ash and sulfur contents increase above these limits, however, problems involving the generation of acid mine drainage during mining and of air pollution when the coal is burned become increasingly troublesome.

Unlike the standards set for high-quality coal, the specifications separating medium- and low-quality coal is not so definite but rather depends more on the potential environmental impact. Generally, medium-quality coals would be those whose sulfur and ash contents could be reduced by various cleaning operations to produce an acceptable fuel for a coal-burning power plant. This would include coals with sulfur contents between 1 wt% and about 3 wt% and ash contents from 10 wt% to about 25-30 wt%. Coals with higher levels of sulfur and ash would be low-quality and would certainly result in unacceptable environmental problems both during mining and utilization. It should be noted, however, that state-of-the-art fluidized bed combustor technology (to be discussed) allows the burning of fuels of unlimited sulfur content. In that sense, once fluidized bed combustor facilities replace all of the older coal burning power plants, there would no longer be coal quality requirements for coal-fired power plants.

COAL UTILIZATION

Introduction: Historically, coal has been used for two purposes: 1) coking and 2) the generation of steam. Since the Industrial Revolution in the mid-1700s, the major use of coal has been the

production of steam, first to drive the steam engine, then the steam turbine. Today, most coal is used to produce electrical energy via the use of steam turbines.

Coking Coal: Whether a coal qualifies as a *coking coal* or *steam coal* is primarily a function of coal quality. Coke is produced by roasting the coal and driving off the volatile components leaving behind a residue composed primarily of carbon. The major use for coke is the reduction of iron ore (Fe_2O_3) in blast furnaces. The requirements for a coking coal are very stringent, less than 0.5% sulfur and 6% ash. Any impurities in a coal used to make coke could potentially be transferred to the molten iron which, in turn, would affect the quality of any steel produced from the iron. As a result, only the highest quality coals can be used. Although there is no rank requirement for coking coal, bituminous coal is preferred.

Steam Coal: Until the Environmental Protection Act of 1962, any coal that did not qualify as a coking coal was considered a steam coal. The major environmental problem associated with the use of coal as a fuel for power plants is that during the combustion of the coal, all of the sulfur is converted into sulfurous gases, usually indicated as SO_x . When released into the atmosphere, the SO_x gases react with water to produce the strong acids, H_2SO_x , which are, in turn, partly responsible for much of the acid rain that affects most of the industrialized countries of the world. It must be pointed out that a second major source of atmospheric acids are the HNO_x acids produced when NO_x gases generated by internal combustion engines react with moisture in the atmosphere.

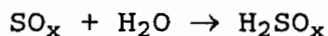
Because of the air pollution problems that arose due to the widespread burning of coal, especially during the past century, laws were enacted to limit the amount of SO_x gases that could be produced from coal-fired power plants. Today, US law requires that coals burned in coal-fired power plants cannot produce more than 1.2# of sulfur per million BTU of heat generated, essentially limiting coal burned in power plants, so-called "compliance coals", to those containing less than 1.2 wt% sulfur.

For reasons that will be discussed, significant variability in quality exists amongst coal. All coals west of the Mississippi River, for example, are in compliance with the EPA sulfur limit, as are coals in the southern Appalachian Coal Basin. The problem that arises for today's coal industry, however, is that the sulfur content of many of the coals in the northern Appalachian, Illinois, and Mid-Continent coal basins are in excess of 1.2 wt% sulfur. For example, the coal that represents about 25% of the total coal production in the northern Appalachian Coal Basin, the Pittsburgh coal, averages about 2.1 wt% sulfur. Before such coals can be utilized as steam coals, they must be subjected to one or more procedures designed to reduce the problems related to their high sulfur contents. To this end, all non-compliance coals are submitted to **coal-cleaning** processes. During coal cleaning, the coal and any associated coal-associated rock is subjected to a series of gravity-separation processes which are designed to

remove coal and rock fragments enriched in the iron disulfide minerals. The disposal of the reject material, called coal refuse, unfortunately is one source of another major environmental problem associated with the coal industry, acid mine drainage. We will discuss acid mine drainage later.

Another process designed to bring high-sulfur coal into compliance is **blending**. Blending is simply the mixing of high-quality coals with non-compliance coals such that the sulfur content of the mixture is less than 1.2 wt% sulfur.

Since 1985, all new coal-fired power plants have been required to incorporate **scrubbers**. Scrubbers are literally washing machines within which the gases emerging from the combustion chamber are washed with water that removes the SO_x gases by dissolution:



Note that the chemical reaction that goes on within the scrubber is the same as that which is responsible for the generation of acid rain in the atmosphere; scrubbers simply allow the reaction to go on within the power facility where the acid can be removed rather than being produced in the atmosphere where it can contribute to the acid rain problem.

A relatively recent development to mitigate the sulfur problem in coal-fired power plants is the use of **getters**. A getter is a chemical added to the combustion chamber along with the coal that reacts with, or "gets", the SO_x gases as they form and removes them as an inert compound. The most common material used as a getter is limestone. The reaction within the combustion chamber is quite simple. The limestone is thermally decomposed to CaO and CO₂. The CaO, in turn, reacts with the SO_x gases to produce CaSO₄ which is removed with the ash.

The most recent development, and perhaps the technology that will eventually eliminate coal-fired power plants as sources of environmental problems, is the **fluidized bed combustor** combined with the use of limestone getters and the downstream use of scrubbers. The fluidized bed combustor allows total combustion of the fuel and getter within the combustion chamber and provides ample time for the getter to react with any SO_x gases produced. This state-of-the-art system is so efficient that there is no longer any limit on the sulfur content of the fuel burned. In fact, most fluidized-bed power plants are so-called **co-generation** power plants which refers to the fact that they burn a mixture of coal and refuse. The plant at Morgantown, for example, burns a mixture of 40% coal and 60% refuse. Some plants use all refuse as fuel. Within such facilities, the SO_x being generated is constantly monitored with the amount of limestone getter introduced into the combustion chamber being computer controlled to that which all but eliminates the arrival of SO_x gases at the exhaust stack.

An additional plus for fluidized power plants is that if the amount of limestone added to the combustion chamber is in excess of that needed to react with any generated SO_x gases, the ash,

referred to as **FBC ash**, contains a combination of CaO , Ca(OH)_2 , and unused CaCO_3 . The FBC ash has been used with great success as an AMD ameliorant (to be discussed later). The CaO and Ca(OH)_2 reacting readily with water to immediately form a strong alkaline solution while the CaCO_3 dissolves slowly over time to provide a sustained alkaline production. The initial high levels of alkalinity can actually inhibit the bacterial production of AMD until the toxic material can be disposed of in such fashion to minimize further oxidation. Once buried, the CaCO_3 content can provide the lower levels of alkaline generation needed to maintain the abiotic conditions that would preclude the future generation of acid within the reclamation structure.

MINERALS IN COAL (~~with illite~~ to p 25)

Coal quality is largely determined by the abundance of minerals contained within the coal. The primary coal minerals are the silicate minerals clay minerals, including mixed layered clays, kaolinite and illite, and quartz. As a group, the silicates comprise 80-90 wt% of all the minerals found in coal. Of the clay minerals, kaolinite and illite predominate with their relative abundance reflecting the geochemical conditions that existed within the original peat-forming swamp. Coals that formed from peat that accumulated in swamps dominated by acidic water ($\text{pH} < 3$) will be dominated by kaolinite due to the fact that the ions such as potassium and iron needed to generate illite would have been removed in solution by the acidic water. With increasing pH, elements such as the alkali and alkaline earths became more abundant and consequently, illite becomes the favored clay mineral. You will remember from previous discussions that acid conditions prevail in domed swamps where the peat is influenced by percolating, acidic rain water while planar swamps, because the peat is more affected by groundwater are more alkaline.

The carbonates and disulfide minerals are second in abundance with calcite and siderite being the major carbonates and pyrite dominating over marcasite. Once again, the relative abundance of the carbonate and disulfide minerals reflects the geochemistry of the original swamp waters. Coals that formed in acidic water conditions show a relative dominance of carbonates, particular siderite. With sulfur removed by the acidic interstitial waters, any available iron reacts with the bicarbonate ion to form siderite. Coals that formed from peat that accumulated under more neutral conditions show carbonates and disulfides in more equal abundance. Siderite is conspicuous by its absence in such coals, the iron preferring to react with the available S^{2-} ion. Most important from the environmental standpoint is the increased abundance of iron disulfides in coal forming under more neutral conditions of swamp geochemistry. Once the sulfur content of Appalachian coals exceeds 1 wt%, the increased sulfur content is due to the formation of the iron disulfide minerals, mostly pyrite (FeS_2). Once pyrite begins to precipitate, it forms at the exclusion of siderite.

Depending on the coal, a variety of other minerals such as feldspars, gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), bassanite ($\text{CaSO}_4 \cdot 1/2\text{H}_2\text{O}$), anhydrite (CaSO_4), jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$), and ankerite ($\text{Ca}(\text{Fe}, \text{Mg}, \text{Mn})(\text{CO}_3)_2$) may be present, almost always in relatively low abundance.

Most of the mineral matter in coal is fine-grained with particles measuring less than 20 μm in large dimension. With the exception of massive occurrences of iron disulfides within the coal or found as part of cleat mineralization, few mineral occurrences will exceed 100 μm in large dimension. Although coal balls, concretions, and nodules of pyrite, calcite, or siderite can be locally abundant and distributed along persistent layers within the coal, most such occurrences are relatively rare. Most of the mineral matter in autochthonous coals is concentrated in layers, a fact that allows much of the mineral matter to be removed by coal-cleaning operations.

CLASSIFICATION OF COAL MINERALS

Introduction: Coal minerals can be classified as to: a) origin, b) time of emplacement, and c) relative abundance.

Origin of Coal Minerals: Based on origin, coal minerals can be classified as either *detrital*, *vegetal*, or *chemical*. A **detrital** origin implies that the mineral was derived from a source external to the peat-forming swamp and was transported as particulate matter into the swamp by water or wind. For many years it was a common misconception that most coal minerals, in particular the clay minerals and quartz, were detrital in origin having been introduced into the swamp as stream over-bank deposits during times of flood. Certainly, some such introduction of detrital sediments takes place as streams break through the levee and expunge into the adjacent swamp as a crevasse splay or as tributary streams go overbank during flood events. Studies have shown, however, that even during *major* flood events, little detritus is carried beyond the levee into the swamp. Most quartz stays within the stream channel and the clay minerals flocculate from suspension immediately upon encountering the acidic swamp waters. One need only remember that during the preparation of clay minerals for x-ray analysis, clay suspensions are flocculated onto the sample mount surface by the addition of a mere *drop* of acetic acid. Studies have definitely shown that the detrital introduction of minerals into a coal-forming swamp is at best minimal. Although some portion of the minerals in coal could be of airborne origin, it would be very small in abundance. In summary, the great volume of minerals in coal are **not** detrital in origin but, rather, are of vegetal and authogenic origin.

Vegetal Origin: Most of the minerals in coal are, in fact, of **vegetal** origin. Think of the ash remaining after the burning of a log. All plants contain inorganic material with the kinds and amounts of mineral matter depending on the type of plant, the particular plant part, the climate, and the bed rock geology of

the site upon which the plant grew. Plants draw water throughout their body structures and use whatever dissolved ions are needed for their metabolism and continued growth. Upon reaching the plant extremities, the water is transpired through the leaves into the atmosphere. Any dissolved ions remaining at the time of transpiration are disposed of by storage in unused cells, typically, the dead wood cells that are responsible for the great volume of most coals.

X-ray diffraction analysis of plant ash generated by the low-temperature ashing of various types of plant materials have shown that most of the inorganic material in plants is amorphous with elemental analyses showing that alumina (Al_2O_3) and silica (SiO_2) are the most abundant ingredients. A suite of wood samples collected by the author from the Snuggedy Swamp along the South Carolina coast, the Okefenokee Swamp on the Georgia-Florida border, and the Mississippi Delta showed an average alumina and silica content of 1.4 and 1.7 wt% (on a dry weight basis) respectively. These amorphous materials are the source materials for the subsequent formation of the silicate minerals found in coal, the clay minerals and quartz. The same x-ray diffraction study showed that the only crystalline material found in the plant ashes was calcium oxalate ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$). Calcium oxalate is a common mineral found in the tissues of sub-tropical and tropical plants..

Of the various types of plant parts, wood generally contains the least amount of ash (< 1-2 wt% on a dry weight basis). By contrast, bark and leaves contain relatively high amounts of ash with concentrations of 15-20 wt% (on a dry weight basis) not being unusual. In addition, in contrast to the material found in wood, much of the material in bark and leaves was shown by x-ray diffraction to be crystalline. The most abundant crystalline material observed in ashes from all of the woody plants that were samples was calcium oxalate. Crystalline silica was commonly found in swamp grasses although most of the silica was amorphous.

Although the actual abundance of inorganic materials found in plants is relatively low, when one considers the enormous amount of plant debris that accumulates in a coal-forming swamp, the amount of accumulated inorganic material is impressive and must be taken into account in any discussion of the origin of mineral matter in coal. Rather than proposing that the mineral matter is primarily detrital and derived from sources outside the swamp, one must explain what happens to most of the mineral matter provided by the accumulated plant debris. Simple calculations, for example, indicate quite clearly that in order to arrive at the ash content of a typical low-ash coal, >90% of the plant-derived inorganic matter must be removed from the accumulating peat, let alone any introduced from outside the swamp. It is estimated that 5.1 tons of plant debris is required to produce a 1 mm-thick layer of peat over an area of 1 acre. Assuming a peat-to-coal compaction ratio of 10:1, it would require nearly 16,000 tons of plant material to produce 1 acre-foot of coal that would in turn weigh approximately 1800 tons with.

Chemical Origin: Minerals of **chemical origin** are those that formed from materials once contained in aqueous solution. The individual minerals may form by direct precipitation from solution or as the result of a chemical reaction between the solution and both the inorganic and organic materials present in the peat or the coal.

A variety of sources exist for dissolved ions. One source, external to the swamp, is the chemical weathering of rocks in the surrounding highland. Materials that are taken into solution as the result of the attack of dissolved carbon dioxide are transported into the swamp via groundwater or surface water flow. A second source of dissolved materials is the decomposition of the plant materials within the swamp itself. Some of the inorganic materials held within the plant parts, such as calcium oxalate, are water soluble. Other inorganic plant components, although insoluble, may undergo dissolution by being attacked chemically within the swamp. In addition, the decomposition of the organic plant components that were originally held as part of the organic molecules by organo-metallic bonds will be released into solution as the bonds are destroyed. Although such releases are especially important and dominant during the early humification and peatification stages of coal formation, they may actually go on later in the coalification process.

Time of Origin:

Minerals are emplaced in coal throughout its history beginning in the earliest peat-accumulation stage and continuing up to the most recent time. There appear to be, however, two major times of emplacement, *syngenetic* and *epigenetic*.

Syngenetic Minerals: The syngenetic stage of mineral formation occurs as long as solutions can move through the peat or coal mass. **Early syngenetic** mineral formation occurs during the peatification stage of coal formation up to the time of peat burial when the less-resistant plant tissues are being decomposed by microbial activity and converted into various gases, mostly CO₂ and NH₄, and water. The CO₂ subsequently reacts with water to form carbonic acid, one of the most important, and potent, agents of chemical weathering on Earth. The increase in the acidity of the water contributes to the increased mobility of many ions, especially the metals.

As the more soluble plant components undergo dissolution, cellulose and lignin survive and become concentrated in the peat. During the initial plant decomposition, the amorphous alumina and silica, commonly found in woody tissues, are released into the peat and become the precursors to the silicate minerals that dominates the mineral matter of most coals, especially the clay minerals. Although ordered clay minerals are not commonly found at this early stage, it is not unusual to find chemically precipitated, crystalline iron disulfides in the form of framboids and individual euhedral crystals. It would be at this time that any contribution of detrital materials would be made.

After burial of the peat, additional accumulation of minerals of either vegetal or detrital origin is precluded. The minerals of the **late syngenetic** stage are therefore *totally* chemical in origin. With burial, the coalification processes of humification and gelification are initiated. Upon being buried, the products of peatification, lignin and cellulose, begin to undergo oxidation and are converted to humic acids by the process of humification. As we have seen, the process of humification begins at the surface of the peat and continues at depth within the accumulating peat mass and after the peat has been completely buried by overlying sediments. The humic acids subsequently complex with cations contained in interstitial solutions such as calcium, aluminum, and iron. The late syngenetic minerals are formed in part from ions released into solution as the basic organic molecules undergo decomposition during the process of humification.

During gelification, the products of humification are further modified by fundamental structural changes within the organic material. Various functional groups are lost, carboxylic acid groups decompose with the formation of CO_2 , and the organic materials are converted into complex organic molecules called **humins**. Humins are the precursors to the vitrinite macerals. During gelification, the organic material becomes increasingly aromatic in nature as aliphatic functional groups are lost. At the same time, elements that were originally held in organo-metallic complexes are released into solution. As the materials desiccate with time, the total ionic strength of the remaining interstitial solutions increases.

With the decomposition of the organic groups, the pH of the interstitial solutions begins to rise to neutral or alkaline levels. During this phase of chemical activity, two major groups of minerals are emplaced, the **carbonates** and the **disulfides**. The decomposition of the carboxylic acid groups introduces CO_2 into solution as CO_3^{2-} while, at the same time, calcium ion, Ca^{2+} , is released into solution from disintegrating organic associations. As the pH rises, the solubility product of the calcite is exceeded and calcite begins to precipitate. Depending on the availability of magnesium, Mg^{2+} , dolomite may form although it is rarely as abundant as calcite. Siderite will form only if the activity of the sulfate ion, SO_4^{2-} , is low. Most carbonate minerals occur as pore or fracture fillings.

When the interstitial solutions contain significant concentrations of sulfate ion, the disulfide minerals form. The sulfate ion is formed by bacterial activity and is subsequently reduced by the anaerobic conditions within the buried peat to the disulfide ion, S^{2-} , which, in turn, reacts with ferrous iron, Fe^{2+} , to form pyrite, FeS_2 , and to a lesser extent, marcasite. Most of the disulfides that characterize the high-sulfur coals (>1-2 wt% S) are emplaced during this phase of mineralization and occur largely as the more massive morphological occurrences such as cavity fillings, cement within inertinites, overgrowing previously formed disulfides, and replacing coal macerals such as vitrinite and, to a lesser extent, exinite. Framboids and small

euhedral crystals continue to form during this phase of mineralization.

In addition to the carbonates and disulfides, authigenic kaolinite apparently forms during this time, filling microfractures that are beginning to develop within the coal. The microfractures are also the site of a host of trace minerals found in coal that are emplaced at this time. The late syngenetic phase of mineralization probably accounts for the greatest variety of minerals found in coal.

With continued burial, the compaction due to the increasing weight of the overlying sediments combined with the continued diagenesis of the humins to form the vitrinite macerals serves to progressively decrease both the porosity and permeability within the coal. Eventually, the dimensions of the pores remaining within the coal are reduced to that of a molecular sieve. At this point, although the coal continues to show hydraulic communication throughout, the hydrated ions from which the coal minerals form are progressively excluded from entering and moving throughout the coal mass because of their molecular dimensions. Those that do find entry find it increasingly difficult to form crystal lattices in the available space. This restriction on the entry to and movement of hydrated ions within the coal mass terminates the syngenetic phase of mineral formation.

Epigenetic Minerals: Once cleat forms, the final, or **epigenetic**, phase of mineral implement begins. The development of major fractures within the coal allows the ready movement of groundwater bearing mineral-forming ions throughout the coal bed. By this time, the organic portion of the coal has become essentially inert and no longer serves as a major Contributor of ions to groundwater nor does it react with groundwater to result in the formation of minerals. At this point in time, groundwater becomes the sole source of ions from which the epigenetic minerals forms. The most common epigenetic minerals are the carbonates, pyrite, and kaolinite. Of the carbonates, calcite is the dominant while pyrite is, by far, the dominant disulfide.

PEAT-FORMING ENVIRONMENTS

One of the most significant field trips relative to the geochemical environment of the peat-forming swamp was led by Bill Spackman, one of the world's foremost coal petrographers. The field trip was part of the GSA national meeting in Miami, Florida. The trip compared the geochemistry of the Okefenokee Swamp along the Georgia-Florida border and the Everglades of southern Florida. The Okefenokee Swamp is a fresh water swamp located behind an ancient barrier island system that completely isolates it from the Atlantic Ocean. With the exception of a small amount of limestone bedrock at its southern tip, the swamp is located entirely on non-carbonate rock materials. As a result, the swamp waters are acidic with pH values as low as 3 and with

very low concentrations of both total dissolved solids and sulfate ion.

Over most of its extent, the Everglades is a marsh rather than a swamp, the difference being that a marsh is a wetland dominated by grasses while a swamp is a wetland dominated by wood-rich plants, mostly trees. The Everglades begins as a broad overflow of Lake Okeechobee in central Florida and flows southward as a very broad, shallow "channel" to Florida Bay. Because of the underlying carbonate bedrock, the pH of the water is everywhere near neutral. In the extreme southern portion of the Everglades, the marsh changes into a swamp as mangrove trees begin to dominate over grasses. Along the coast where the swamp is influenced by marine waters via tides, the waters become alkaline.

The main objective of Spackman's trip was to compare the contribution of the plant communities to the peat and to illustrate the influence of water chemistry on organic degradation. One of the leading organic geochemists of the day, Peter Given, had installed some simple and ingenious experiments in the swamps six months prior to the trip that were designed to demonstrate the relative rates of degradation of cellulose depending on water chemistry. The experiments consisted of wrapping cellulose filters around plastic rods which were in turn driven into the peat. As the trip progressed, the experiments were removed for inspection. The results were dramatic. The experiments showed that when the water pH was below pH3, microbial activity was very low and remained low as long as the pH was below pH5. Above pH5, however, microbial activity increased markedly and reached a maximum at pH7 where the filters had been nearly completely consumed. The data clearly indicated that in order to accumulate enough peat to form a coal, the peat must accumulate in acidic (<pH3-4) conditions. Swamps within which the water pH rose above 5 would not accumulate sufficient peat to be the precursor to a mineable coal. This was directly in opposition to the reigning "truth" that coastal swamps were good models of coal-forming peat environments and that the coal was divided into marine and fresh-water facies depending on the relative influence of fresh and marine waters. At the time, the Mississippi Delta was the "premier" swamp environment with the relative influence of marine and fresh waters generating what were designated as lower-, middle-, and upper-delta plain coals. Aside from the fact that all of the data clearly indicated that the water chemistry of any swamp that had even the slightest marine influence would preclude the accumulation of sufficient peat to form a mineable coal, the areal dimensions of modern swamps located on delta surfaces were nowhere near large enough to account for the areal extent of known mineable coals such as the Pittsburgh coal.

As the result of subsequent research done in this department in conjunction with the USGS, it became apparent that all

