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Articles



Diagenesis 8. Chemistry and Evolution of Organic Matter

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Introduction

Organic matter occurs in almost all sedimentary rocks. In some rocks, such as coal and oil shale, organic matter is a major component, but in most sedimentary rocks it occurs in minor or trace amounts (Fig. 1). The economic importance of organic matter, however, far outweighs its relative abundance. Organic matter, in one form or another, comprises the fossil fuel resources. The diagenesis of organic matter is thus of particular importance in understanding the generation and migration of oil and gas, in evaluating source rocks and in estimating levels of maturation of oil shales and coals. Organic matter plays an important role in transport of metal complexes (Barker, 1982), the formation of strata-bound and stratiform ore deposits (Anderson and Macqueen, 1982; Macqueen and Powell, 1983), and has a significant influence on the diagenesis of other minerals (Powell *et al.*, 1978; Schmidt and McDonald, 1979; Foscolos and Powell, 1980). While the diagenesis of organic matter is less understood and more com-

plicated than that of the common minerals, significant progress has been made. It is now possible to predict the diagenetic state of organic matter if the burial and thermal history of the strata are known. The degree of diagenesis of organic matter has also become an accepted geothermometer to which other diagenetic reactions can be compared (Bostick, 1979).

In this paper we describe organic diagenesis from both petrographic and geochemical perspectives. The petrographic study of organic matter evolved from coal petrology, which has strongly influenced the terminology used. In a similar way, petroleum geochemistry has provided much of the terminology and techniques of organic geochemistry. The nomenclature of these fields is complex, sometimes inconsistent and, to most geologists, unfamiliar. We have attempted to simplify the terminology without, it is hoped, a major loss of information. In this paper we provide the background to the geochemistry and petrography of organic matter and trace its progressive diagenesis, which generally accompanies increasing depth of burial. A second paper will delineate some of the

methods of quantifying diagenesis and will evaluate predictive models. Because of the breadth of organic diagenesis, we can only present an overview of the subject here, and thus have avoided both controversial topics and those we consider less important; other workers in the field would make different choices. The reference list is essential for those readers who wish to pursue the subject in greater depth.

General Considerations. Diagenesis of organic matter begins early and proceeds rapidly under surficial conditions. As a result, the terminology of diagenesis, which was largely developed for more slowly changing inorganic materials, requires some modification. Some of the changes take place even during sedimentation, and are thus "pre-diagenetic" by traditional definitions. For example, it is commonly estimated that no more than one percent of the phytoplanktic organic matter produced in the marine euphotic zone survives microbial decomposition and zooplankton grazing to reach the sea floor unaltered (Wakeham *et al.*, 1980; Knauer and Martin, 1981). Diagenetic changes that take place in

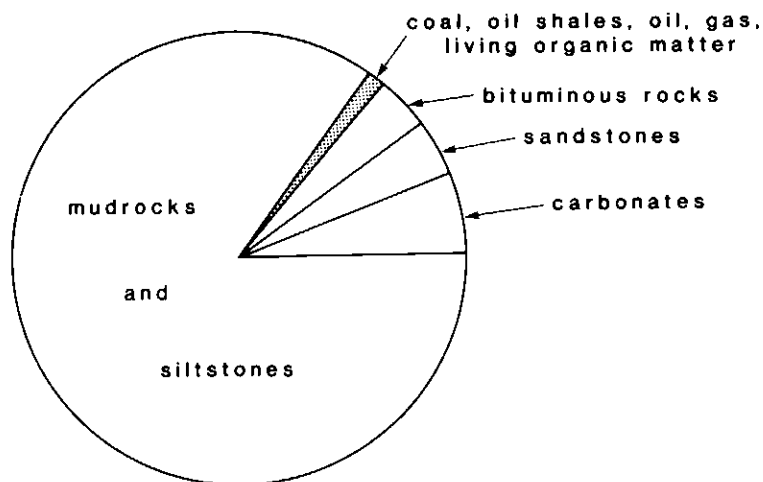


Figure 1 Occurrence of organic matter in sediments as percentage of mass of organic carbon. Hydrocarbons dissolved in water are not in-

cluded. (Modified from Vassoyevich, 1973 and Vassoyevich *et al.*, 1976 in Bostick, 1979)

organic matter at shallow depths below the sediment-water interface are largely biochemical, and occur as a result of the metabolism of fungi, bacteria and other micro-organisms. At greater sediment depths, microbial activity is much slower, and geochemical parameters more familiar to geologists (time, temperature, pressure) become dominant.

The diagenesis of organic material is progressive and irreversible with few exceptions. The progressive diagenesis of organic matter has been considered in terms of different stages. Tissot and Welte (1978) and many others (see Durand, 1980) refer to three stages of organic diagenesis: diagenesis, catagenesis and metagenesis.

For the purpose of this paper *eogenesis* (Choquette and Pray, 1970) is used to refer to those biological, physical and chemical changes in organic matter that occur at temperatures less than those required for significant cracking of hydrocarbons (Fig. 2). As such, our *eogenetic* stage is equivalent to the *diagenetic* stage of Tissot *et al.* (1974) and we introduce the term solely to prevent confusion between *diagenesis* as a stage of diagenesis and diagenesis as the term is conventionally used by geologists. Diagenetic changes occurring at greater depths (and thus higher temperatures) in the lithosphere are referred to sequentially as catagenesis and metagenesis (Fig. 2). Diagenetic reactions resulting from the organic material coming in contact with meteoric water or atmospheric oxygen following burial are referred to as telogenesis (Choquette and

Pray, 1970). The different diagenetic stages do not have well defined boundaries, but rather are gradational, which to some extent results from the heterogeneous composition of organic matter. Eogenetic, catagenetic and metagenetic stages are summarized in Figure 3. The processes and products of the diagenesis of organic matter can be described in kinetic terms. Because the compounds formed are metastable, and because the system is open, enabling migration of generated hydrocarbons, equilibrium, if ever established, is continually displaced (Durand, 1980). If diagenesis proceeds into what is generally considered the metamorphic realm, the organic residue ultimately will be transformed into graphite (Wedeking and Hayes, 1983).

The results of diagenetic studies of organic matter are significantly affected by the methods of sample preparation, analytical procedures and equipment used. As a result, data must be interpreted in terms of what fraction of the total organic matter present in the sample was "seen" by the method selected. Organic matter in rocks occurs as gases, liquids and solid particles; they differ in their physical and chemical properties and in their accessibility to extraction by organic solvents or, in the case of gases, to stripping by mechanical processes. Extractable organics are analyzed by a broad array of chemical and spectrometric methods. The analytical data obtained are used (1) in modern environments to monitor the fate of organic matter from natural biogenic sources and industrial pollutants; (2) to "fingerprint" oils and

source rocks for oil-source rock correlations; (3) to assess maturation in coals; and (4) to assess the effects of maturation, migration and biodegradation which occur during the diagenetic conversion of biological lipids to petroleum. Solid organic matter tends to be finely disseminated as discrete sedimented organics or precipitates. Although it is a minor component of the rock, it forms the major part of the organic matter present. With the exception of coals, it requires concentration before petrographic analysis by treatment with acids, bases and organic solvents to remove silicates and carbonates, or, in the case of pollen preparations, to remove extractable organics (Karr, 1978a, b; 1979).

Sources of Organic Matter.

Precursor organic material varies considerably in its chemistry, depending on its source and depositional environment. Unlike simple minerals or even solid solution series, organic matter consists of a complex array of compounds. These compounds mainly fall into four or five general classes that react differently, particularly during eogenesis (Fig. 4).

Prior to the Devonian, photosynthetic marine phytoplankton and bacteria were the principal sources of organic matter. At present, marine organisms contribute approximately 60 percent of the total organic productivity, with terrestrial plants making up most of the rest. Aquatic organisms contribute mainly proteins, lipids and, in the phytoplankton, carbohydrates; in addition, higher plants contribute resins,

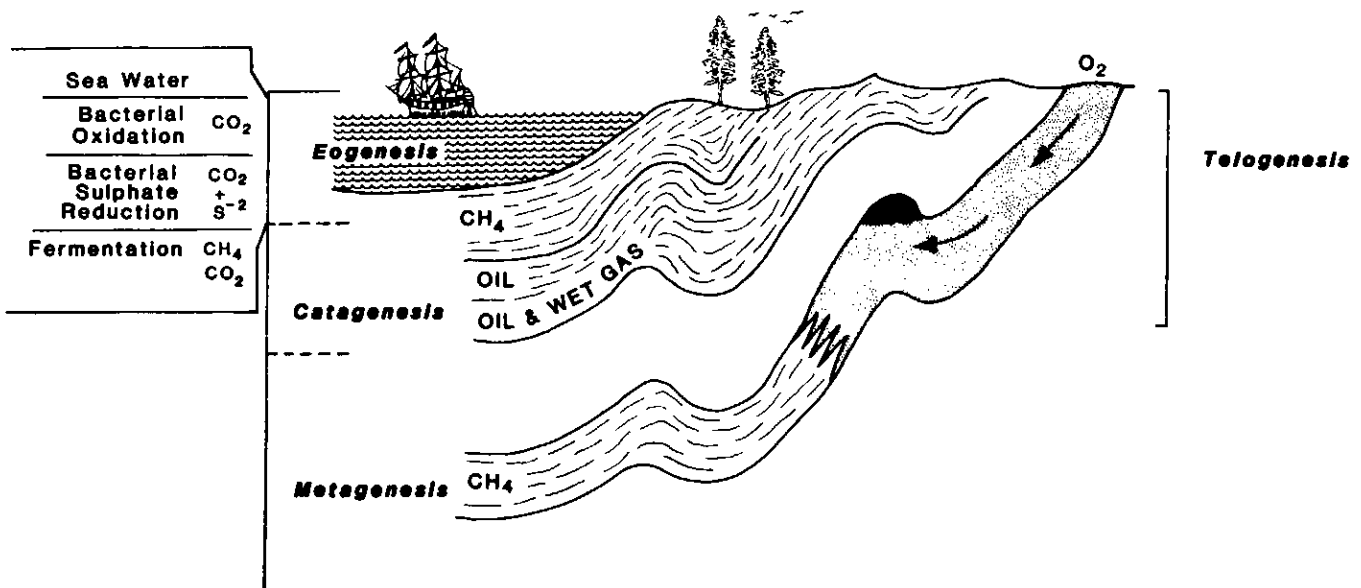


Figure 2 Schematic representation of the terminology commonly used in describing the stages of diagenesis of organic matter (Tissot and Welte, 1978, and others). The terms "eogenetic", "mesogenetic" and "telogenetic" were originally

used by Choquette and Pray (1970) to refer to the stages of diagenesis of carbonate rocks. The eogenetic zone includes reactions that are partly, or even mainly, biochemical. The eogenetic stages shown are modified from Curtis

(1977). Catagenetic and metagenetic reactions are chemical, in response to the thermal history of the strata. Telogenesis results from contact with meteoric water or atmospheric oxygen

waxes, lignins and carbohydrates in the form of cellulose (Fig. 4). Lipids, which are major contributors to petroleum, contain fewer heteroatoms (nitrogen, sulphur and oxygen) than do proteins and carbohydrates. Thus, petroleum tends to be rich in carbon and hydrogen, and poor in heteroatoms. Rates of primary productivity in aquatic environments are affected by the amounts of light and nutrients present. Most photosynthesis takes place in the upper 60 to 80 m of the water column, with rates being highest where abundant nutrients are present, such as in areas of upwelling and near river mouths. Open marine waters have estimated organic productivities that average $50 \text{ g C m}^{-2} \text{ a}^{-1}$ (grams carbon per square metre per year); coastal waters average about twice that value, except on the western margins of continents, where values as great as $300 \text{ g C m}^{-2} \text{ a}^{-1}$ occur (Krey, 1970). Preservation is more important than productivity, however, in determining the organic content of sediments.

Eogenesis

The term eogenesis covers all low temperature diagenesis of organic matter; eogenetic reactions are partly biochemical, arising from metabolic processes occurring within organisms, and partly abiotic chemical reactions which incorporate metabolic products released to the sediments. The effects of temperature and pressure are subordinate and eogenetic reactions cannot be simulated by simple pyrolysis (Tissot and Welte, 1978, p. 88).

Preservation of organic matter is a function of the oxygen content of the environment. Estimates of the preservation of primary organic matter in the surficial sediments of marine environments average about 0.1% (Menzel and Ryther, 1970). Preservation in subaerial environments is even less, as chemical oxidation and aerobic microbial decomposition are favoured by the high oxygen content of air as compared to only a few ml l^{-1} dissolved in water. Regions of rapid terrestrial sediment deposition, such as deltas and continental slopes and rises, have low organic contents because of dilution by inorganic sediments; however, the preservation of this organic matter is relatively high because of limited diffusion of oxygen into the sediments. Terrigenous organic components are better preserved than those from aquatic sources (Meyers *et al.*, 1984). The maximum preservation of primary organic matter, about 4 percent, occurs in anoxic environments such as the Black Sea (Deuser, 1971), as anaerobic microbial processes result in less complete decomposition of the initial organic compounds. The products are protected from chemical oxidation by dissolved oxygen,

but are subject to oxidation during bacterial sulphate reduction.

Rapid sedimentation limits exposure to oxygen, and thus favours the preservation of organic matter. Areas where organic matter tends to be preserved and concentrated include continental marginal environments, such as shelves, slopes and rises, marine landlocked basins and lakes. Peats accumulate in regions of slow continuous subsidence with water tables at or near the surface, low pH (3 to 5) and negative Eh. Most paralic coals were formed in swamps developed on deltas, interdeltaic plains, coastal plains and in back barrier regions.

Proteins, carbohydrates (sugars, cellulose and chitin), lipids (fats, waxes and steryl esters) and lignins are the principal biopolymers contributed by organisms to sediments (Fig. 4). However, these origi-

nal biopolymers are rapidly depolymerized to their monomers by microbial processes occurring during and shortly after sedimentation. As a result, the dominant organic compounds found in sediments are geopolymers (humic compounds and kerogen) which arise from the random chemical recombination of monomers released by these micro-organisms. During biosynthesis of the original biopolymers by organisms, their monomers were linked together in bonds through the elimination of water; the resulting biopolymers are sensitive to hydrolytic cleavage with the reincorporation of water by either chemical or microbial processes (Fig. 4).

Eogenetic changes, arising from chemical and microbial processes, profoundly affect (1) the physical structure and chemical stability of organic matter, which can

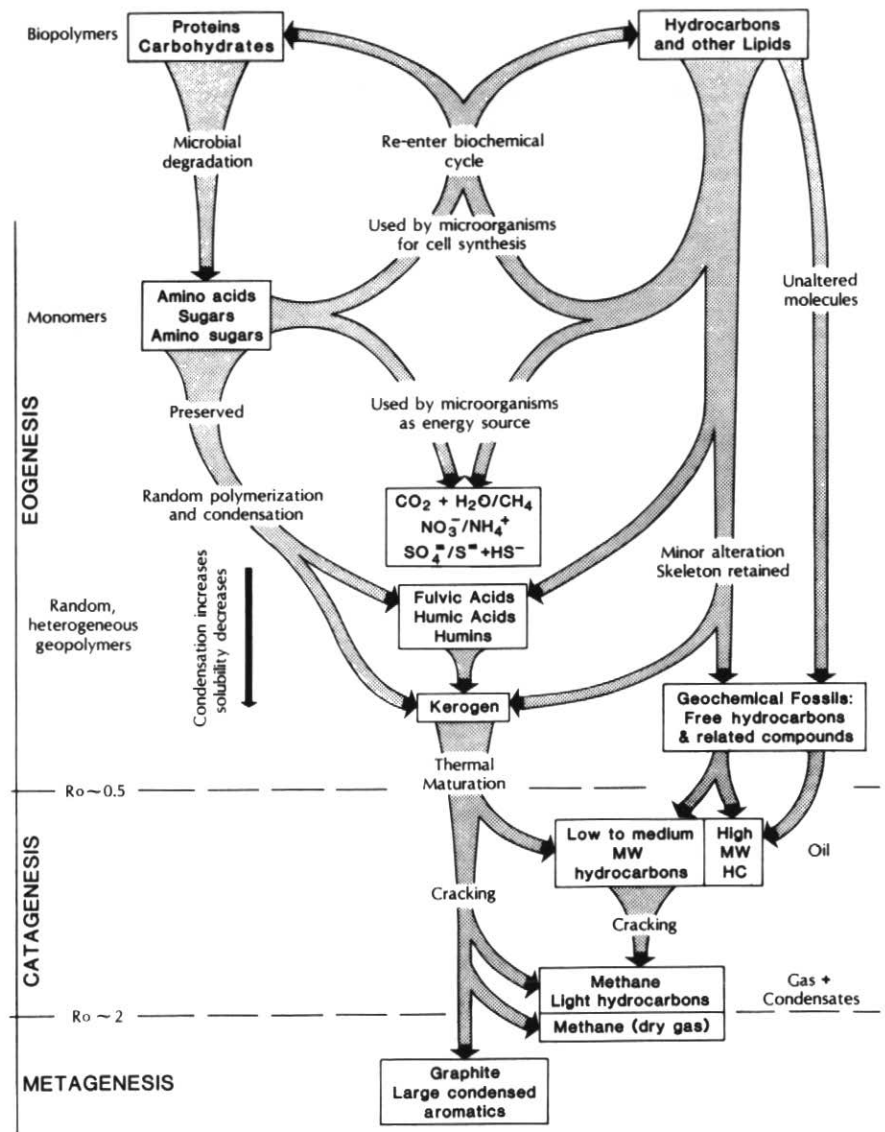


Figure 3 Diagenetic fate of organic matter in sediments (after Tissot and Welte, 1978, pp. 71, 90 and 93)

subsequently become fossil fuel after burial and catagenesis; (2) the fate of organic pollutants arising from humankind's activities; (3) the formation of humic compounds which form metal complexes and act as metal transport agents in groundwater systems; and (4) Eh, pH, the precipitation of carbonates and the formation of sulphides in sedimentary environments. Two carbon cycles affect the constitution of organic matter: a primary cycle that occurs in both the water column and the sediment, and a secondary cycle that occurs in sediments and sedimentary rocks (Fig. 3). The primary cycle, which is by far the more rapid, is the biochemical cycle operated mainly by microbial metabolism, which hydrolyzes the various polymers (Trudinger and Swaine, 1979). The primary cycle operates on a total pool estimated at 2.7 to 3.0×10^{18} g organic carbon, with a turnover half-life ranging from days to tens of years. The secondary, geochemical, cycle affects a pool of organic carbon which is about 2000 times larger, but has a turnover half-life of several million years (Wetzel, 1970).

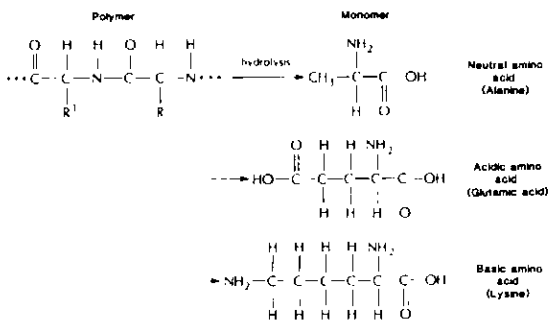
As a result of the primary cycle, the major constituents of organisms – proteins, carbohydrates, lipids and lignins – comprise less than 20 percent of the organic matter present in sediments and are much less significant in older sedimentary rocks. Primary cycle hydrolysis produces monomeric amino acids and sugars that (1) provide energy for bacteria, leading to the formation of CO_2 , H_2O , CH_4 , NH_3 and other simple inorganic products; (2) are incorporated into new biopolymers in microbial cell walls; and (3) are chemically condensed and randomly recombined to form the irregularly organized geopolymers known as humic compounds (Fig. 3). The term humic compounds includes the humic and fulvic acids, the humins and kerogen, all of which are defined simply on the basis of their solubility and molecular weight. Because they form by random recombination, their structures are variable, depending on the monomers available and the diagenetic conditions at the time of their formation. Humic compounds increase in molecular weight and decrease in solu-

bility in progressing from fulvic acids through humic acids and humins to kerogen.

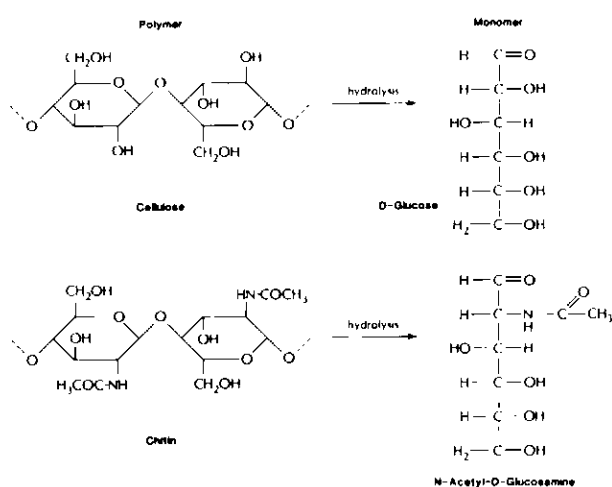
The humic and fulvic acids are defined on the basis of their solubility in bases and acids (Schnitzer, 1975; Schnitzer and Khan, 1972). Fulvic acids are soluble in both acids and bases and range in molecular weight from 700 to 10,000 (Rashid and King, 1969). Humic acids are base soluble polymers which range in molecular weight from 10,000 to 100,000 and can be up to 10 nm in size. They are soluble in acids above pH 2; at pH 2 or less, they are insoluble and precipitate.

With increasing cross linkage and loss of acidic functional groups (carboxyl and phenolic groups), the humic and fulvic acids lose their base solubility and form an insoluble humin/kerogen fraction. The term humin is used for the base insoluble fraction of soils and young sediments. Humins are partly hydrolyzable; they can reincorporate water and release 15 percent to 40 percent of their weight as monomers or lower molecular weight polymers during

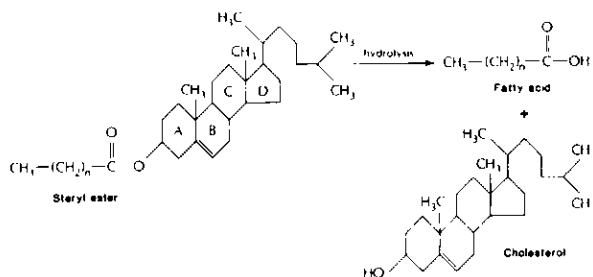
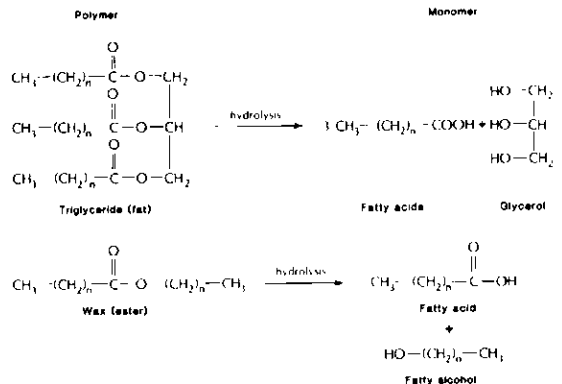
PROTEINS



CARBOHYDRATES



LIPIDS



LIGNIN

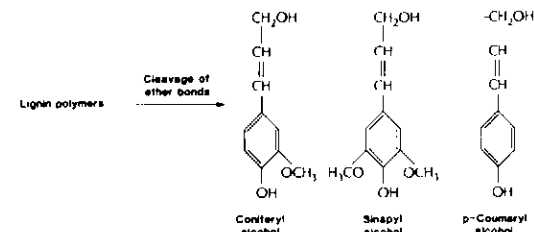


Figure 4 Chemical structure of proteins, carbohydrates, lipids and lignins

demineralization with hydrofluoric acid, the standard method used in sample preparation to remove silicates. In contrast to the humin fraction, kerogens are high molecular weight geopolymers which are stable to hydrolysis with HF and are insoluble in organic solvents, acids and bases. While some kerogen formation occurs through loss of functional groups and cross linkage early in the diagenetic history of organic matter (Philp and Calvin, 1976), most forms later, reaching a peak during thermal maturation at the catagenetic stage. Kerogen also can arise directly from monomers without an intervening humic stage, especially under anoxic conditions (Huc and Durand, 1977; Debysier *et al.*, 1977).

Microbial metabolism in the water column and the upper few centimetres of the sediment is commonly aerobic and produces carbon dioxide and water as end products (Sundby *et al.*, 1983). In areas of high productivity, aerobic processes can deplete the oxygen content of the water, leading to the development of anoxic conditions. Anaerobic metabolism, on the other hand, allows more of the initial biological compounds to survive; it also leads to the reduction of sulphate to sulphide, the reduction of ferric iron, and the production of methane and ammonia. These processes are favoured by restricted water circulation arising from salinity or temperature stratification. Anaerobic processes are themselves limited by a lack of nutrients and the toxicity of their end products. Relative to the very labile proteins and carbohydrates, lipids and lignins are more resistant to primary cycle metabolism. Depolymerization of lignins requires cleavage of chemically stable ether bonds. Many of the lipids are preserved in stable cell wall residues of micro-organisms or are associated with water-insoluble waxes and cutin from higher plants. As a result, lignins and lipids tend to survive and are concentrated along with spores, pollen, cutin, chitin and plant resins in the humin/kerogen fraction. This is especially true in anoxic environments, which lack oxygen-requiring lignolytic fungi (Debysier *et al.*, 1978). In peat bogs the concentration of humic acids also tends to decrease the activity of decomposers. This is partly the result of the low pH (3 to 5) and partly because the humic compounds are themselves relatively immune to decomposition because of the presence of phenolic groups, which inhibit microbial activity. The irregularity of the linking bonds in humic compounds and their bulky three dimensional structures make them a poor fit for templating by the microbial enzymes which catalyze their hydrolysis and decomposition.

These diagenetic processes not only produce energy for the microbial populations, but also release large quantities of new compounds which significantly alter the Eh, pH and ionic composition of pore waters in the sediments. The Eh decreases abruptly from the oxic to the anoxic zone. The pH increases slightly, with the production of ammonia and sulphide and the loss of carbon dioxide, leading to the precipitation of carbonates and to the dissolution of amorphous silica and, to a lesser extent, quartz. Iron (and copper, lead and zinc, if they are present) may be precipitated as sulphides. The complex role organic matter plays in the sulphur cycle and the formation of sulphide minerals is reviewed by Krouse and McCreedy (1979).

Those amino acids and sugars which were released by hydrolysis of proteins and carbohydrates, but not utilized in the energy cycles of micro-organisms, can recombine through abiotic chemical processes to form the geopolymers found in sediments and sedimentary rocks.

The boundary between eogenesis and catagenesis is gradational, although it is generally considered to be coincident with the boundary between sub-bituminous and high volatile bituminous coals, which corresponds to a vitrinite reflectance of about 0.5% (Fig. 5). Base soluble humic compounds are usually negligible, although they are found in some sub-bituminous coals. Thermal history, a combination of time and temperature, plays a significant role in the formation of high-volatile bituminous coals. Otherwise coal would remain

at a peat or lignite level of diagenesis, as is the case for the Lower Carboniferous lignites of the Moscow Basin (Teichmüller and Teichmüller, 1982, p. 58). Similar processes control the eogenesis of organic matter, whether it is disseminated in sediments or concentrated in peats, which can become coals, or in algal muds, which can become oil shales.

Hydrocarbon generation during eogenesis is restricted to *biogenic* gas which originates from anaerobic decay of organic matter (Oremland, 1981). Relative to gas generated by catagenesis, biogenic gas is primarily methane (up to 99 percent) and carbon dioxide (0-8 percent), with minor amounts of heavier gases (Claypool and Kvenvolden, 1983). Locally, biogenic gas may form significant accumulations as gas hydrates (Bily and Dick, 1974; Hitchon, 1974; Kvenvolden and McMenamin, 1980; Kvenvolden *et al.*, 1983). Other hydrocarbons present at the eogenetic stage of diagenesis are inherited from the organic matter. Those changes in organic matter occurring during eogenesis which are evident in optical microscopy are most noticeable in the huminite fraction (Fig. 6). This fraction originates from humic acids and forms vitrinite during catagenesis. The huminite passes through a stage referred to as gelification (Teichmüller, *in* Stach *et al.*, 1982, p. 228) in which it swells and its reflectivity increases (from 0.15 to 0.50%, oil immersion); it becomes slightly darker and increasingly opaque in transmitted light. The lipid-rich fraction (liptinite) shows little or no change in incident light

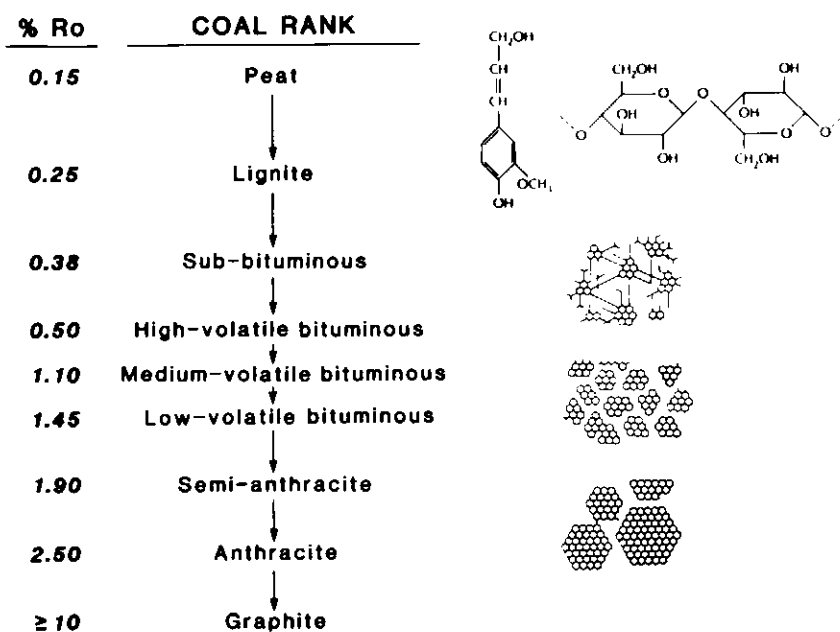


Figure 5 Variation in huminite-vitrinite reflectance in oil (Ro%), level of diagenesis (coal rank) and typical molecular structures at different diagenetic levels. The aromatic clusters are

shown in plan view and show increases in ordering and cluster size with increases in coal rank (modified in part from Teichmüller and Teichmüller, 1982)

and becomes progressively darker in transmitted light, changing from nearly colourless to light brown. Under ultraviolet irradiation the peak fluorescence intensity shifts from 500 nm wavelength (at deposition) to between 560 and 580 nm. Carbon-rich components, such as semi-inertinite and inertinite which originate from fires (charcoal) or fungal attack, show no visible change. All organic components become physically compacted with increased burial, and previously visible cells and tissues become progressively less distinct.

Catagenesis

With increased burial organic matter undergoes progressive diagenesis in response to increased temperature and time. Increased pressure has little diagenetic effect on organic matter, other than compaction; it may actually retard diagenesis (Teich-

müller and Teichmüller 1982). Kerogen makes up the great bulk of organic matter present at the catagenetic stage. Kerogen is an irregular geopolymer formed by random chemical recombination of organic compounds released by microbial decomposition of proteins, carbohydrates and lipids. As such, its structure is variable and cannot be predicted in the same way that the structures of biopolymers such as proteins or carbohydrates can be predicted from their constituents. Kerogens are commonly characterized by the use of bulk parameters, such as the H/C and O/C atomic ratios, obtained from elemental analyses and expressed as a "van Krevelen diagram" (Fig. 7). On the basis of these ratios, three types of kerogen have been defined which appear to follow distinct diagenetic pathways. This type of diagram was originally used to characterize coals

and their coalification pathways (van Krevelen, 1961), but was later applied to kerogens (McIver, 1967; Durand *et al.*, 1972). A similar plot of hydrocarbon index versus oxygen index is obtained from measurements of the volumes of hydrocarbon gases and carbon dioxide released during the pyrolysis of rock samples containing kerogen (Espitalié *et al.*, 1977). Type 1 kerogen has high initial H/C and low O/C ratios. The small amount of oxygen present occurs mainly in ester bonds (Robin *et al.*, 1977). Up to 80 per cent by weight of immature type 1 kerogens can be volatilized during pyrolysis (Tissot and Welte, 1978). The source material is mainly algal, or a combination of algal lipids and waxes from higher plants, which have been selectively concentrated by microbial reworking. It forms part of the liptinite macerals in coal. Examples of type 1 kerogens include the

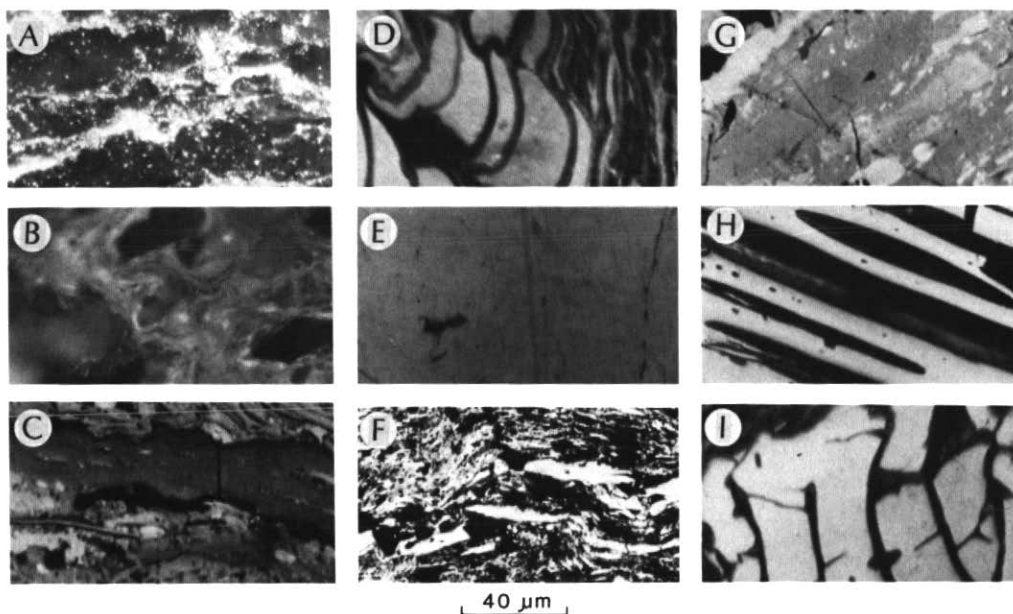
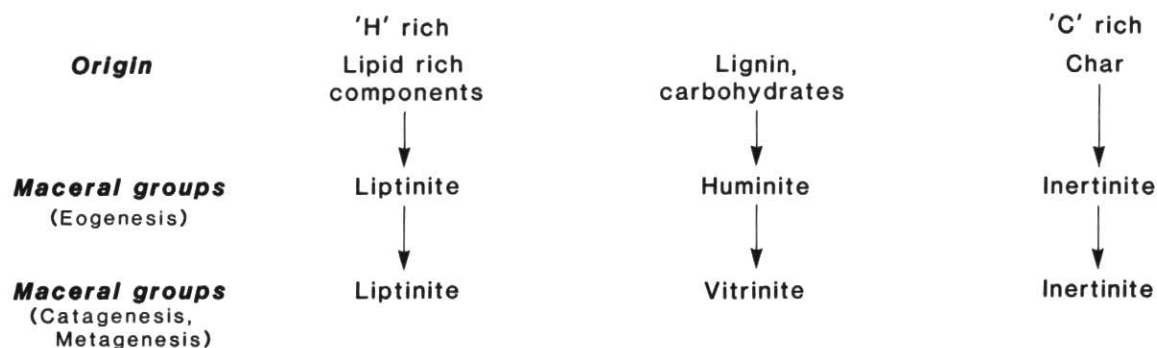


Figure 6 Terminology of organic petrography and representative photomicrographs of the main maceral groups at different diagenetic levels. Photomicrographs are oil immersion, reflected light images. Liptinite group: (a) alginite [Ro

0.3%]; (b) cutinite (blue light excitation) [Ro 0.50%]; (c) bituminitesporinite [Ro 1.0%]. Huminitite-vitrinite group: (d) huminitite [Ro 0.30%] (e) vitrinite [Ro 1.2%] (f) vitrinite [Ro 4.0%]. Inertinite group: (g) inertinite and semi-inertinite [Ro

0.60%]; (h) inertinite [Ro 1.2%]; (i) inertinite [Ro 4.0%]. The correlation between vitrinite reflectance (Ro%) and diagenetic level is shown in Figures 3 and 7

lacustrine Green River "oil shales", the Songliao basin of China, the Scottish torbanites and algal bog-head coals (Tissot and Welte, 1978; Powell and Snowdon, 1983).

Type 2 kerogen has intermediate initial H/C and O/C ratios, and larger contributions by aromatic and carboxylic acid groups than the type 1 kerogens. Ester bonds are abundant, as are medium length aliphatic hydrocarbon chains and naphthenic rings. Both algal and higher plant sources appear to contribute to type 2 kerogens (liptinite coal macerals). Organic sulphur is present in heterocyclic groups and in sulphide bonds. Up to 60 per cent of immature kerogen can be volatilized during pyrolysis (Tissot and Welte, 1978, p. 144). Most type 2 kerogens are found in reduced marine strata and have been the source for major oil and gas deposits. Examples of type 2 kerogens formed in moderately reducing clastic sediments are found in the Sverdrup Basin, in Upper Devonian, Mississippian and Upper Cretaceous strata of Alberta, and in the Jeanne d'Arc sub-basin east of Newfoundland (Powell and Snowdon, 1983). Examples of type 2 kerogens formed in highly reducing marine evaporites or carbonates are found in the Permian Phosphoria Formation of the northern United States and in Middle Devonian reefs of northern Alberta and north-eastern British Columbia. Mixed kerogen types are common. For example, marine sourced organic matter with some contribution by terrestrial higher plants produces a kerogen that falls between types 1 and 2 because of the increased O/C ratio, as in the shales of the Viking Formation (McIver, 1967).

Type 3 kerogen has an initial H/C ratio less than 1, an initial O/C ratio of 0.2 to 0.3, and is derived dominantly from terrestrial plants. It consists mainly of aromatic groups formed from lignins and humic compounds, and represents the huminite/vitrinite fractions of coal petrography. Aerobically oxidized semi-inertinite and inertinite macerals also may be present. Oxygen is present as carboxylic acids, ketones and ethers rather than in ester bonds (Robin *et al.*, 1977). Lesser amounts of aliphatic groups may be present in liptinite and resinite macerals, depending on the preservation of resins and lipids from higher plant and algal sources. Deposition is mainly in deltaic and other thick, rapidly accumulating continental margin sediments; as a result, relatively unaltered higher plant compounds also can accumulate, as they are protected by rapid sedimentation from aerobic degradation. Type 3 kerogens have conventionally been considered as sources of gas rather than oil. The proportions of resinite, liptinite and vitrinite in terrestrially derived kerogen,

however, strongly control both the level of thermal alteration necessary for petroleum generation and the relative proportions of oil, wet gas and dry gas produced (Snowdon and Powell, 1982; Powell and Snowdon, 1983). Liptinite- and resinite-rich kerogens can be sources of both oil and gas, whereas vitrinite-rich kerogens are mainly gas sources. Examples of type 3 kerogens include those of the Lower Mannville shales of Alberta and of the Mahakam delta of Indonesia (Durand and Oudin, 1980). Resinite-rich type 3 kerogens are found in the Beaufort-Mackenzie Basin; liptinite-rich but resinite-poor type 3 kerogens occur on the Labrador Shelf (Powell and Snowdon, 1983).

Catagenesis takes place at moderate temperatures (50°C to 150°C) and pressures (30 to 100 or 150 MPa), corresponding to the zone of bituminous and anthracite coal, and of oil and wet gas generation. At the end of catagenesis, aliphatic chains have been cleaved from kerogens, and the size of aromatic units has increased through chemical condensation, with the development of significant ordering (Fig. 5). Coals progressively increase in rank from sub-bituminous to anthracite during catagenesis.

Changes in chemical structure of hydrocarbons and the quantities generated with increasing burial depth are summarized in Figure 8. Hydrocarbons contributed to the sediment by precursor organisms are called biogenic; geochemical fossils, on the other hand, are compounds, unknown in

living organisms, which are generated during diagenesis but which still retain a "fingerprint" characteristic of biogenic sources. Biogenic hydrocarbons can include methane and small amounts of ethane and ethylene from bacteria (Orem-land, 1981), C₁₆-C₁₈ alkanes from plankton, and long chain hydrocarbons (C₁₂-C₃₅) from higher plant waxes. Biogenic hydrocarbons in the immature zone are characterized by normal alkanes with a significant odd-carbon preference, by acyclic (open chain) branched hydrocarbons, by cycloalkanes with 2 to 5 rings, and by terpenes, some of which are partly to fully aromatized during early eogenesis and form geochemical fossils (Wakeham *et al.*, 1980; Barnes and Barnes, 1983). The characteristic fingerprints for biogenic hydrocarbons and those generated during eogenesis are shown in Figure 8 (upper profile).

As burial increases, hydrocarbons generated by catagenetic processes dilute precursor compounds, and there is a gradual loss of the biogenic fingerprint as oil generation progresses (Fig. 8, middle profile). The level of catagenesis and its relation to hydrocarbon generation is of particular importance in defining petroleum potential. The levels of catagenesis corresponding to the *oil birth line* and the *oil death line* have been used to define an "oil window" (Fig. 8). The oil birth line is the level of catagenesis which initiates generation of medium to low molecular weight (liquid) hydrocarbons from kerogen and corresponds to a vitrinite reflectance of approxi-

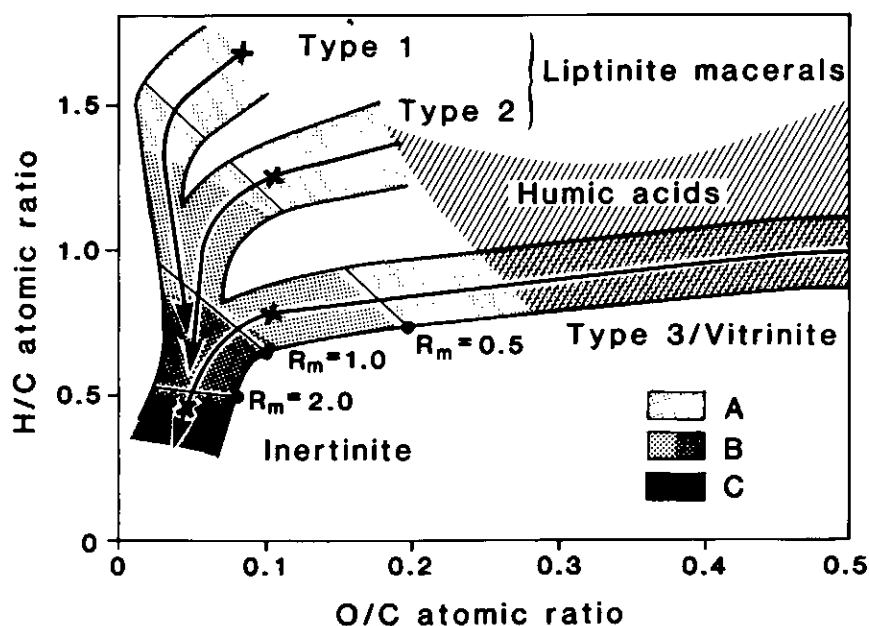


Figure 7 "van Krevelen plot" of diagenesis of kerogen types and coal macerals. A = immature, field of humic acid occurrence overlaps region of immature Types 1 and 2 kerogens; B = mature, boundary represents region of maximum oil generation; C = overmature; R_m = iso-evolution

as measured by vitrinite reflectance; * site where coal macerals coincide with kerogen types; as diagenesis increases in the mature kerogen, coal macerals plot at slightly lower O/C values (after Durand, 1980; van Krevelen, 1961; Tissot and Welte 1978)

mately 0.5% (Dow, 1977). The amounts of polyaromatic compounds formed during eogenesis are relatively small, and are extensively diluted in petroleum by those aromatic compounds generated during catagenesis.

The oil death line is the level of diagenesis at which both kerogen and previously formed liquid hydrocarbons are cracked to create low molecular weight hydrocarbons (Fig. 8, lower profile). It corresponds to a vitrinite reflectance of about 1.35% (Dow, 1977). Significant amounts of gas are generated from kerogen throughout the oil window and continue to be produced to much higher levels of diagenesis. At low levels of catagenesis wet gas is generated; as the level of catagenesis increases the proportion of methane increases, through further cracking. By the onset of meta-genesis, only methane (dry gas) remains.

The amount, timing and composition of hydrocarbons generated depend on the kerogen type as well as on the level of diagenesis (Rogers, 1980; Monnier *et al.*, 1983). The hydrocarbon generation model shown in Figure 8 applies mainly to type 2 kerogens formed in moderately reducing sediments. Different sub-types of kerogen may generate hydrocarbons at slightly

different levels of diagenesis (Snowdon and Powell, 1982). The oil birth line occurs at a somewhat lower level of maturation ($R_o = 0.4\%$) for resinite-rich type 3 kerogen and type 2 kerogen formed in highly reducing carbonate or evaporite environments; nonmarine oils generated from liptinite-rich type 1 and type 3 kerogens, however, are formed at somewhat higher levels of thermal maturation ($R_o = 0.6$ to 0.7%). The maximum gas generation for type 2 kerogen occurs with the cracking of liquid hydrocarbons at levels of thermal maturation greater than $R_o = 1.35\%$. Significant amounts of gas are generated, however, at lower levels of maturation in liptinite- and resinite-rich type 3 kerogen ($R_o > 0.55\%$) (Monnier *et al.*, 1983).

Throughout catagenesis, kerogen undergoes noticeable changes in petrographic appearance (Fig. 6). With increasing levels of catagenesis, the vitrinite component (huminites of the eogenetic stage) changes relatively uniformly (Fig. 6d, e, f). In incident light, reflectance increases (from 0.5% to about 2.0%, oil immersion); in transmitted light vitrinite becomes darker and increasingly opaque. Cell structure and plant tissues which are readily visible in the early stages of eogenesis (Fig. 6d) become

progressively more difficult to recognize without etching with acids. Liptinite undergoes a rapid change in appearance (Fig. 6a, b, c) and physical properties. The trend of these changes is discontinuous. A discrete "jump" marks the transition from eogenesis to catagenesis. Bitumen, which includes both hydrocarbons and compounds with functional groups containing N, S and O, is generated. The kerogen residue which remains after bitumen generation shows an abrupt, noticeable decrease in volatiles and a corresponding relative increase in carbon content. A second "jump" occurs with the formation of low volatile bituminous coal. In sediments with the potential for oil generation, this level of catagenesis corresponds to the oil death line; at this second jump, liptinite macerals undergo another abrupt reduction in hydrogen and volatiles. In reflected light the liptinite becomes progressively "lighter" grey; by the second "jump" it is indistinguishable in reflected light from vitrinite without etching. With ultraviolet light excitation the liptinites show a progressive increase in maximum spectral fluorescence wavelength with increasing diagenetic level, and total fluorescence intensity progressively declines. In trans-

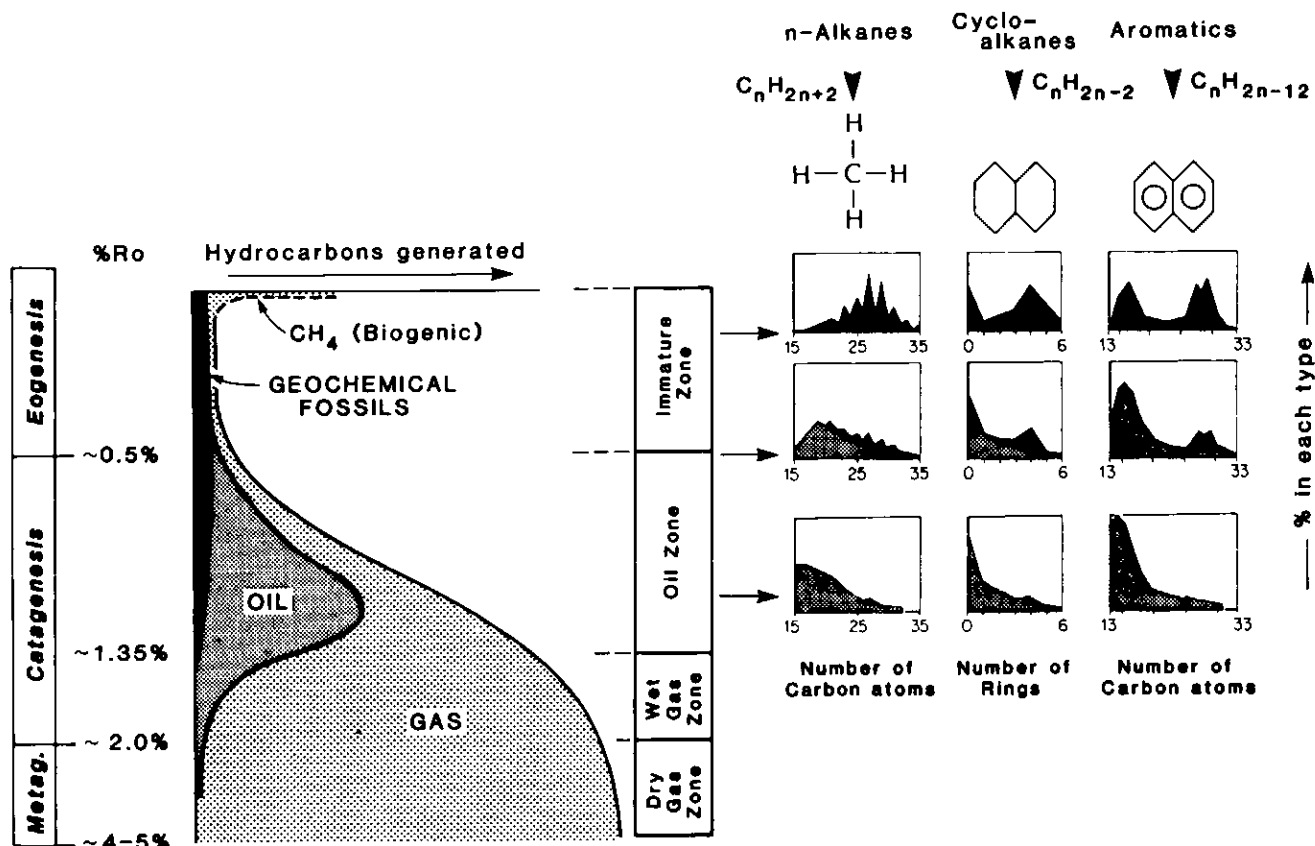


Figure 8 Hydrocarbon generation: changes in chemical structure and quantity with increased burial depth (after Tissot and Welte, 1978, p. 185). $R_o\%$ = reflectance of vitrinite in oil. Upper profile: biogenic fingerprint (eogenesis); middle

profile: dilution of biogenic fingerprint by hydrocarbons generated in the oil zone; lower profile: loss of biogenic fingerprint and chain shortening of hydrocarbons with cracking of oil to form wet gas at lower end of oil zone

mitted light the liptinite, initially pale yellow, becomes progressively darker and eventually black and opaque. The semi-inertinite and inertinite components are initially rich in carbon and strongly aromatized (Teichmüller, *in* Stach *et al.*, 1982) at the time of deposition and thus undergo little additional alteration. The degree of later alteration depends on the initial degree of charring. The reflectivity of semi-inertinite and inertinite in incident light is initially high; only at advanced levels of diagenesis does any increase in reflectivity occur (Fig. 6g, h, i). In transmitted light semi-inertinite and inertinite are opaque throughout diagenesis.

Metagenesis

Metagenesis refers to the stage of organic diagenesis at which crystalline ordering of the organic matter begins (Tissot and Welte, 1978). Aromatic nuclei increase in size, forming clusters, and C-C bonds are broken, generating methane. Aliphatic molecules that survived catagenesis and previously generated hydrocarbons are cracked to dry gas. At the onset of metagenesis the vitrinite component of the coal has a reflectance of about 2 percent, which progressively increases with diagenesis to about 4 percent or 5 percent, where the strata are generally considered to be in the realm of metamorphism. The liptinite component of the organics (type 1 kerogen) and, at later stages, the inertinite component become visually and chemically indistinct from vitrinite.

Telogenesis

Organic compounds in rocks can be altered by late stage processes resulting from contact with meteoric waters of low salinity, or atmospheric oxygen (Fig. 2). Two distinct processes appear to be active (Bailey *et al.*, 1973b). Water washing results from the solution of hydrocarbons in ground waters, leading to a depletion of the lighter compounds, as the solubility of normal hydrocarbons in water is inversely proportional to their chain length. The second process, bacterial degradation, is more important, and can lead to the total loss of normal alkanes and isoprenoids, leaving a heavy oil residue composed of cycloalkanes and aromatics (Deroo and Powell, 1978). The heavy oil belt of Alberta is estimated to contain 142 billion m³ of oil in a 1000 km arc from the Peace River in west-central Alberta to Lloydminster in western Saskatchewan. Similarities in the distribution of cycloalkanes, aromatics and benzothiophenes were used as evidence for the relationship of oil sands and heavy oils (Lloydminster) with conventional oils (Lower Cretaceous Mannville reservoirs) (Deroo *et al.*, 1974; Deroo and Powell, 1978). Selective removal of normal

alkanes and isoprenoids on going from non-degraded oils to biodegraded heavy oils is consistent with patterns observed in incubation studies on the microbial degradation of a range of undegraded oil and oil sand samples (Rubinstein *et al.*, 1977; Rubinstein and Strausz, 1978; Crawford *et al.*, 1978). Winters *et al.* (1983) recently proposed hydrous pyrolysis as a technique for distinguishing immature from biodegraded oils. Microbial degradation of petroleum has long been recognized in the generation of sulphur in the cap rocks of salt domes (Thode *et al.*, 1954; Krouse and McCready, 1979) where sulphate from anhydrite is used by anaerobes such as *Desulfovibrio* to oxidize petroleum fractions, leading to the formation of sulphide, part of which is subsequently oxidized to elemental sulphur. Such processes have been implicated in the degradation of oils in many areas, such as the Bell Creek field, Montana (Winters and Williams, 1969) and the northern Williston Basin of Saskatchewan (Bailey *et al.*, 1973a, b; 1974). In near surface groundwaters, where sufficient dissolved oxygen may be present, aerobic bacteria can also degrade petroleum. In a study of biodegradation with aerobic cultures, Bailey *et al.* (1973a) found that isoprenoids were attacked after the removal of n-alkanes; lower ring naphthenes and low molecular weight aromatics were attacked at the same time as lighter normal paraffins and prior to removal of heavier paraffins. Similar processes affect kerogen that is exposed to the atmosphere or to oxygenated groundwater. Non-aromatic groups are preferentially removed, leading to an increase in the aromatic fraction of the kerogen (van Krevelen and Schuyer,

1957). Acidic functional groups such as carboxyl, carbonyl and phenolic hydroxyl are formed, eventually leading to the production of humic acids. Such processes are analogous to retrograde metamorphism in metamorphic rocks. If oxidation is intense, it may be distinguished petrographically by the development of darker or lighter oxidation haloes on the margins of kerogen particles (Fig. 9; Bustin *et al.*, 1983). In coals oxidation results in a marked decrease in coal quality. Coals exposed to atmospheric oxygen or meteoric water have lower than normal calorific values, poorer coking qualities, and reduced flotation properties (hydrophobicity).

Conclusion

Organic diagenesis is progressive and irreversible with few exceptions. It begins early and proceeds rapidly under surficial conditions so that, even in the most favourable environments, only a small fraction of the organic matter is incorporated into the sediment. During eogenesis, microorganisms metabolize most of the organic matter to CO₂ and H₂O in oxygenated sediments and to CH₄, CO₂, H₂ and H₂O under anoxic conditions. The remaining organic matter forms humic and fulvic acids. With increasing cross-linkage and loss of functional groups, these acids decrease in solubility and form part of the kerogen fraction. Similar processes control eogenetic reactions whether the organic matter is disseminated in sediments or concentrated in peat.

The catagenetic and metagenetic stages of diagenesis result from increased temperature and time accompanying burial of the sediment. All types of kerogen progres-



Figure 9 Photomicrograph of oxidized vitrinite in a low-volatile bituminous coal. Oxidation haloes occur on periphery of vitrinite particle

sively evolve towards pure carbon with a decrease in hydrogen and oxygen in response to the breakage of aliphatic chains and some cyclic compounds and the accompanying generation of bitumen, including hydrocarbons. By the metagenetic stage of diagenesis crystalline ordering of aromatic compounds occurs and any aliphatic molecules that survived catagenesis, as well as previously generated wet gas and oil, are cracked to dry gas. With diagenesis the petrographic constituents of the organic matter (macerals), originally distinct chemically and morphologically, become progressively similar. During eogenesis the lipid-rich components (liptinite) alter little, except during extreme oxidation. The huminite components swell with gelification and their reflectivity in incident light increases from 0.15% to about 0.5%. During the catagenetic and metagenetic stages the vitrinite (huminite of eogenesis) macerals progressively increase in reflectivity in incident light, reaching 2.0% at the end of catagenesis and about 4% or 5% at the end of metagenesis and onset of metamorphism. During catagenesis and metagenesis the liptinite component becomes progressively darker and opaque in transmitted light. Inertinite, which originates from charcoal, undergoes little change during the early stages of diagenesis and only at advanced stages of metagenesis does its reflectivity in incident light increase. Semi-inertinite macerals, which are transitional in composition between vitrinite and inertinite, increase in reflectivity with diagenesis. The increase in reflectivity depends on the amount of carbonization that occurred prior to deposition.

Hydrocarbons are generated from organic matter throughout diagenesis. During eogenesis biogenic methane forms as a result of anaerobic decay of organic matter. During catagenesis wet gas and/or oil is generated, depending on the type of kerogen, in response to increased temperature and time accompanying burial. By the metagenetic stage of diagenesis only dry gas is generated by cracking of kerogen and earlier formed hydrocarbons. Coal progressively increases in rank during diagenesis from peat through anthracite. The most noticeable changes in coal accompanying increased rank are the loss of moisture, oxygen and hydrogen and the corresponding increase in fixed carbon. Telogenesis can affect both the organic matter and generated hydrocarbons. Contact with meteoric water of low salinity results in leaching of the lighter molecules and promotes bacterial degradation of petroleum. Oxidation of kerogen may also occur, resulting in preferential removal of the non-aromatic fraction and formation of humic acids. Petrographically, oxidation is marked by the occurrence of oxidation

haloes and micro-fissures in the kerogen particles.

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