Geochemistry, Organic

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GLOSSARY

Biodegradation Alteration of organic matter in near-surface sedimentary rocks or of crude oil in the reservoir by microorganisms.

Biological markers Chemical compounds in sediments, crude oils, or coal with an unambiguous link to specific precursor molecules in living organisms (molecular fossils, geochemical fossils, biomarkers); among the most common biological markers are isoprenoids, steroids, triterpenoids, and porphyrins.

Bitumen Fraction of organic matter in sediments which is extractable with organic solvents.

Catagenesis Thermocatalytic transformation of organic matter in sedimentary rocks at greater burial depths (usually more than 2 km) and higher temperatures ($>50°$C) into smaller molecules, particularly liquid and gaseous hydrocarbons which become part of the bitumen fraction.

Diagenesis Transformation of sedimentary organic matter under mild conditions (usually $<50°$C) involving both low-temperature chemical reactions and microbial activity.

Hydrocarbon (petroleum) potential Ability of a sediment that is rich in organic matter to generate hydrocarbons (petroleum) under the influence of geological time and temperature, expressed quantitatively in terms of milligrams of hydrocarbons per gram organic carbon (or kilograms per metric ton).

Kerogen Macromolecular organic matter in sediments that is insoluble in organic solvents and consists of structural remnants of dead organisms as well as diagenetic transformation products of various biopolymers and biomonomers.

Macerals Organic particle types specifically in coal but more generally also in dispersed sedimentary organic matter which can be recognized under the microscope and are characterized by their different structural (shape) and optical (color, reflectance, fluorescence) properties; the most common macerals are liptinite, vitrinite, and inertinite.

Maturation Thermal evolution of organic matter (kerogen and bitumen) in the subsurface; maturity is measured by various physical and chemical maturation parameters (e.g., vitrinite reflectance, carbon preference index of *n*-alkanes, biological marker compound ratios).

Migration Movement of hydrocarbons in the subsurface from a source rock into a carrier bed (primary migration, mainly pressure controlled) and along a carrier bed into a reservoir rock (secondary migration, mainly buoyancy driven) to form a hydrocarbon accumulation.

Organic facies A mappable unit of sediment or sedimentary rock with (largely) uniform properties of its organic matter content.

Petroleum General term for fossil fuels, comprising both crude oil and natural gas.

Reservoir rock Porous rock unit (e.g., sandstone, limestone, or dolomite) suitable to contain a hydrocarbon accumulation (crude oil, gas) if structurally closed and sealed by an impermeable cap rock.

Source rock Organic matter-rich rock unit which under the influence of geological time and temperature has generated and expelled hydrocarbons (effective source rock) which may eventually have migrated into a reservoir to form a petroleum accumulation; a potential source rock (e.g., an oil shale) has not yet reached a sufficiently high maturation level for hydrocarbon generation.

ORGANIC GEOCHEMISTRY studies the distribution, composition, and fate of organic matter in the geosphere on both bulk and molecular levels, combining aspects of geology, chemistry, and biology. The biomass of decayed organisms is incorporated into sediments in the aquatic and terrestrial environment and is eventually buried to greater depth depending on the subsidence and depositional history of a sedimentary basin. Under the influence of temperature, catalysis, and (in shallow sediment layers) microbial activity, the organic matter undergoes a succession of complex chemical reactions which may ultimately lead to the formation of fossil fuels such as crude oil, natural gas, or coal.

I. ACCUMULATION OF ORGANIC MATTER IN THE GEOSPHERE

A. Bioproductivity and the Global Organic Carbon Cycle

The development of life on earth has a history of more than 3 billion years. Procaryotic organisms started biosynthesis in the Precambrian, and remnants of their biomass still are present in ancient sedimentary rocks of that time. Mass production of organic matter did not occur, however, before oxygenic photosynthesis was established worldwide in the oceans by cyanobacteria about 2 billion years ago. At the same time, the initially reducing atmosphere gradually became enriched in free oxygen, which was the basis for the evolution of higher forms of life.

Cyanobacteria and unicellular algae prevailed until the early Paleozoic, about 550 million years (m.y.) ago. During the Cambrian, Ordovician, and Silurian, a variety of phytoplanktonic organisms evolved, and these contributed significantly to the organic carbon production on earth. At the end of the Silurian (400 m.y.), land plants started to settle the continents and spread out in the Devonian. During the Late Carboniferous (300 m.y.), the first massive woods occurred, which are documented today by a first maximum of extensive coal seams. Evolution of the terrestrial higher plant kingdom then continued in the Permian with the gymnosperms and finally during the Early Cretaceous (125 m.y.) with the angiosperms, which are the dominant species of the modern flora.

The production and decay of biomass is a cyclic process of a complex food chain in connection with the carbon dioxide (CO_2) in the atmosphere and the oceans (Fig. 1). This part of the global carbon cycle is the smaller one and has a relatively rapid turnover. It is connected via a small "leak" to the massive carbon reservoir of the lithosphere. Estimates of the mass of carbon stored in the different sections of the global carbon cycle are shown in Table I. It is evident that the world's oceans contain the bulk of the carbon in the productivity cycle, although only about 2.5% of these 40,000 billion metric tons of carbon are organic. Carbon in the atmosphere is of the same order of magnitude as the biomass on the continents. Most of the organic carbon in the lithosphere is finely disseminated in sediments. In the most optimistic estimates, less than one-thousandth of it occurs as fossil fuels in various forms.

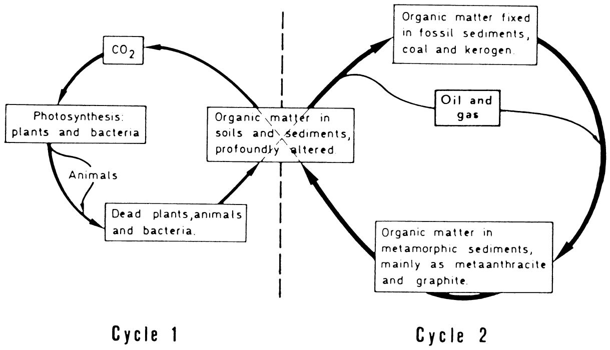


FIGURE 1 The two major organic carbon cycles on earth. Organic carbon is mainly recycled in cycle 1. The crossover from cycle 1 to cycle 2 is a tiny leak through which passes less than 0.1% of the primary organic biomass. [Reprinted with permission from Tissot, B. P., and Welte, D. H. (1984). "Petroleum Formation and Occurrence," 2nd ed., p. 10, Springer-Verlag, Berlin and New York. Copyright 1984 Springer-Verlag.]

TABLE I Estimates of Carbon in Different Compartments of the Global Carbon Cycle[a]

Compartment	Mass of carbon ($\times 10^9$ tons)
Atmosphere	700
Oceans	
Inorganic	39,000
Organic	1,000
Continents	
Biomass	600
Humic matter in soils	2,000
Lithosphere	
Inorganic	50,000,000
Organic	20,000,000
Including fossil fuels (upper limits)	
Oil, gas, tar sands	800
Coal	6,300
Oil shales	9,500

[a] After Grassl, H., Maier-Reimer, E., Degens, E. T., *et al.* (1984). *Naturwissenschaften* **71,** 129–136.

Compared to the figures in Table I, the amount of carbon involved in the annual turnover is relatively small. The gross exchange rate between atmosphere and oceans is of the order of 80 billion metric tons/yr, whereas the annual production of biomass just exceeds 100 billion metric tons. Less than 250 million metric tons of carbon reach the marine sediments every year. The anthropogenic influence by fossil fuel consumption and cement production amounts to about 5 billion metric tons/yr.

B. Chemical Composition of the Biomass

Despite the diversity of living organisms in the biosphere, their chemical composition can be confined to a limited number of principal compound classes. Many of them are also represented in fossil organic matter, although not in the same proportions as they occur in the biosphere because of their different stabilities toward degradation during sedimentation and diagenetic transformation.

1. Nucleic Acids and Proteins

Nucleic acids, such as ribonucleic acids (RNA) or desoxyribonucleic acids (DNA), are biological macromolecules that carry genetic information. They consist of a regular sequence of phosphate, sugar (pentose), and a small variety of base units, i.e., nitrogen-bearing heterocyclic compounds of the purine or pyrimidine type. During biosynthesis, the genetic information is transcribed into sequences of amino acids which occur as peptides, proteins, or enzymes in the living cell. These macromolecules vary widely in the number of amino acids and thus in molecular weight. They account for most of the nitrogen compounds in the cell and serve in such different functions as the catalysis of biochemical reactions and the formation of skeletal structures (e.g., shells, fibers, muscles).

During sedimentation of decayed organisms, nucleic acids and proteins are readily hydrolysed chemically or enzymatically into smaller, water-soluble units. Amino acids occur in rapidly decreasing concentrations in Recent and subrecent sediments, but may also survive in small concentrations in older sediments. A certain proportion of the nucleic acids and proteins reaching the sediment surface may be bound into the macromolecular kerogen network of the sediments and there become protected against further rapid hydrolysis.

2. Saccharides, Lignin, Cutin, and Suberin

Sugars are polyhydroxylated hydrocarbons which together with their polymeric forms (oligosaccharides, polysaccharides) constitute an abundant proportion of the biological material, particularly in the plant kingdom. Polysaccharides occur as supporting units in skeletal tissues (cellulose, pectin, chitin) or serve as an energy depot, for example, in seeds (starch). Although polysaccharides are largely water insoluble, they are easily converted by hydrolysis to C_5 (pentoses) and C_6 sugars (hexoses) and thus in the sedimentary environment will have a fate similar to that of the proteins.

Lignin is very common in supporting plant tissues, where it occurs as a three-dimensional network together with cellulose. Lignin essentially is a macromolecular condensation product of three different propenyl (C_3) phenols. It is fairly well preserved during sedimentation and is abundant in humic fossil organic matter.

Cutin and suberin are lipid biopolymers of variable composition which are part of the protective coatings on the outer surfaces of all higher plants. Chemically, cutin and suberin are closely related polyesters composed of various fatty and hydroxy fatty acid monomers. Both types of biopolymers are sensitive to hydrolysis and, thus, after sedimentation have only a moderate preservation potential.

3. Insoluble, Nonhydrolyzable Highly Aliphatic Biopolymers

Insoluble, nonhydrolyzable aliphatic biopolymers were discovered in higher plants and in algal cell walls as well as in their fossil remnants in sediments. These substances are called algaenan, cutan, and suberan according to their origin from algae or co-occurrence with cutin and suberin in extant higher plants. They consist of long-chain aliphatic hydroxy esters crosslinked via ether bonds. Pyrolysis and rigorous chemical degradation methods are the only way of decomposing these highly aliphatic biopolymers. This explains why they are preferentially preserved in sediments.

4. Lipids (Monomers)

Biogenic compounds that are insoluble in water but soluble in organic solvents such as chloroform, ether, or acetone are called lipids. They are common in naturally occurring fats, waxes, resins, and essential oils but in a wider sense also include membrane components or certain pigments. The low water solubility of the lipids is responsible for their higher survival rate during sedimentation compared to other biogenic compound classes such as amino acids or sugars. The analysis of lipids and their conversion products in geological samples is a major objective of molecular organic geochemistry.

Various saturated and unsaturated fatty acids are the lipid components of fats, where they are bound to glycerol to form triglyceride esters (see Fig. 2 for examples of chemical structures of lipid molecules). In waxes, fatty acids are esterified with long-chain alcohols instead of glycerol. In addition, waxes contain unbranched, long-chain saturated hydrocarbons (*n*-alkanes) with a predominance of odd carbon numbers (e.g., C_{27}, C_{29}, or C_{31}), in contrast to the acids and alcohols which show an even-carbon-number predominance.

Isoprene, a branched diunsaturated C_5 hydrocarbon, is the building block of a large family of open-chain and cyclic isoprenoids or terpenoids (Fig. 2). Monoterpenes (C_{10}) with two isoprene units are enriched in essential oils of higher plants. Farnesol, an unsaturated C_{15} alcohol, is an example of a sesquiterpene with three isoprene units. Diterpenes (C_{20}) are common constituents of higher plant resins, where they occur mostly as bi- to tetracyclic components (e.g., abietic acid; Fig. 2). The acyclic diterpene phytol is esterified to chlorophyll *a* and, thus is widely distributed in the green pigments of plants. Sesterterpenes (C_{25}) are of comparatively lower importance.

Cyclization of squalene (or its epoxide) is the biochemical pathway to the formation of a variety of pentacyclic triterpenes (C_{30}) consisting of six isoprene units. Triterpenoids of the oleanane, ursane, lupane, and other less common types are restricted to higher plants. The geochemically most important and widespread triterpenes are from the hopane series, such as diploptene, which occurs in ferns, cyanobacteria, and other eubacteria. The predominant source of hopanoids is bacterial cell wall membranes which contain bacteriohopanetetrol (and closely related molecules) as rigidifiers. This C_{35} compound has a sugar

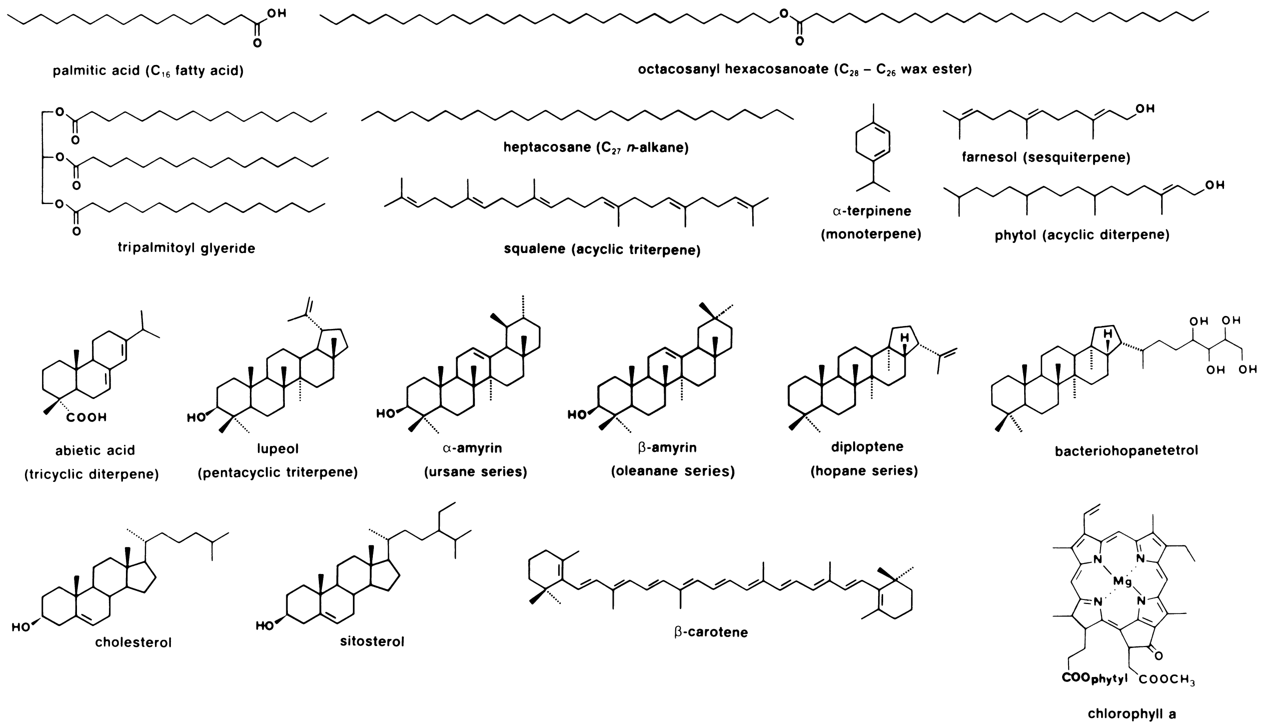


FIGURE 2 Structural formulas of representative organic lipids in living organisms and in the geosphere.

moiety attached to the triterpane skeleton (Fig. 2). The widespread distribution of bacteria on earth through time makes the hopanoids ubiquitous constituents of all fossil organic matter assemblages.

Steroids are tetracyclic compounds which are also derived biochemically from squalene epoxide cyclization, but have lost, in most cases, up to three methyl groups. Cholesterol (C_{27}) probably is the most widespread sterol in animals and many plants. Higher plants frequently contain C_{29} sterols (e.g., sitosterol) as the most abundant compound of this group. Steroids together with terpenoids are typical examples of biological markers (molecular fossils) because they contain a high degree of structural information which is retained after sedimentation. Thus, they provide an unambiguous link between the sedimentary organic matter and the biosphere. Steroids and terpenoids are among the most extensively studied classes of organic compounds in the geosphere.

Carotenoids, red and yellow pigments of algae and land plants, are the most important representatives of the tetraterpenes (C_{40}). Due to their extended chain of conjugated double bonds (e.g., β-carotene; Fig. 2), they are labile and found only in relatively small concentrations in surface sediments. Aromatization probably is one of the dominating diagenetic pathways in the alteration of the original structure in the sediment.

A second pigment type of geochemical significance are the porphyrins (tetrapyrroles) and related, not fully aromatized chlorins. Most porphyrins in sediments and crude oils are derived from the green plant pigment chlorophyll *a* and similar compounds in bacteria. It was the detection of porphyrins in crude oils and sediment extracts more in the 1930s that laid the basis for modern molecular organic geochemistry and provided the first strong molecular evidence for the biogenic origin of crude oils.

C. Factors Influencing the Preservation and Accumulation of Organic Matter in Sediments

The accumulation of sediments containing organic matter occurs primarily in the aquatic environment. The amount and composition of the organic component, i.e., the organic facies, are controlled by a number of complex, mutually dependent factors. A high primary bioproductivity alone is not a sufficient criterion for the enrichment of organic matter in the sediment. Preservation of the decayed biomass is as decisive as a balance with the geological conditions and the supply of mineral components.

In a given depositional environment, organic matter may be contributed by the biomass production in the aquatic system, the transport of terrigenous organic matter from the continent by river discharge, or, usually less important, eolian dust, and by the erosion and recycling of previously deposited sediments. The relative importance of these factors will have an influence on the bulk composition of organic matter in the sediment. In the marine environment, bioproductivity is particularly high in areas of coastal upwelling, where coast-parallel winds bring cold water from deeper layers, enriched in nutrients, to the surface. This is presently significant on the western continental margins off southern California, Peru, Namibia, and on parts of the Indian Ocean margins. The supply of terrigenous organic matter to the ocean depends on the climate on the neighboring continent. A warm, humid climate supports both terrestrial vegetation and river discharge.

Consumption in the food chain or oxidation in the presence of free oxygen leads to (partial) mineralization of the organic matter and thus limits its preservation. Both processes may occur during transport to the site of deposition, during settling through the water column, and in the upper sediment layers. It is estimated that less than 0.1% of the annually produced biomass on average reaches the sediment. Different types of organic matter have different stabilities toward degradation. Marine organic matter, consisting essentially of proteins, saccharides, and lipids, is more labile than terrestrial organic matter, which contains chemically more stable compounds and lipids protected by relatively resistant supporting tissues. In fact, *n*-alkanes from higher-plant waxes frequently survive long-distance transport to remote sites in the oxic deep ocean. In oxic environments, such selective mineralization leads to an organic facies in the sediment that is not representative of the local aquatic ecosystem.

In addition to the oxygen content of the water column, water depth and sediment accumulation rates determine the preservation of organic matter. Residence time of organic particles in the water column depends on water depth as well as particle size and shape. Well-rounded large, rapidly settling particles such as fecal pellets have a great chance to reach the sediment surface even under oxic conditions. A high sedimentation rate favors organic matter preservation due to rapid burial and protection of the labile material from the oxic regime. A very high supply of mineral matter, on the other hand, may cause dilution of organic matter and thus lead to sediments with a relatively low organic matter content despite a high accumulation (preservation) rate.

Under certain conditions, an anoxic water body may develop. High surface-water bioproductivity leads to depletion of oxygen in the underlying water, because oxygen is consumed in the organic matter degradation of decayed organisms. If there is no adequate water circulation to replenish the oxygen, the whole water column down to the

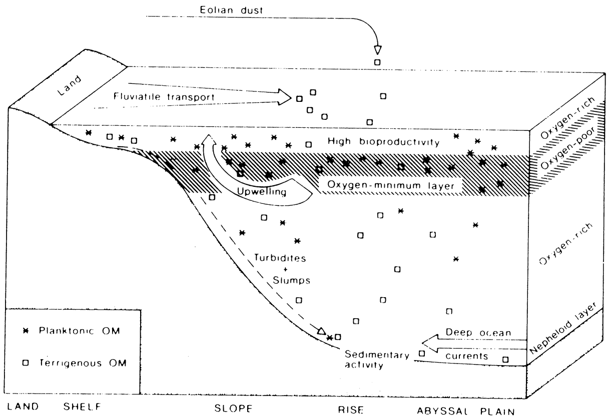


FIGURE 3 Schemalic diagram showing the factors that control organic matter accumulation of marine continental shelf, slope, and rise sediments. [Reprinted with permission from Rullkötter, J., *et al.* (1983). *In* "Coastal Upwelling—Its Sediment Record, Part B" (J. Thiede and E. Suess, eds.), pp. 467–483, Plenum Press, New York. Copyright 1983 Plenum Press.]

sediment surface may become oxygen depleted. This typically happens during eutrophication of small lakes. The Black Sea is an example of a stagnant oceanic basin with an anoxic bottom water mass. A shallow sill largely separates the Black Sea from the Mediterranean Sea and suppresses the exchange of deep-water masses. In addition, density stratification due to heavy saline bottom water and lighter fresh water from river discharge at the surface prevents vertical mixing, so that over time all oxygen below a water depth of about 150 m has been consumed, and free hydrogen sulfide (H_2S) is now present in the deep anoxic waters of the Black Sea.

In the open ocean, a different process of oxygen depletion may occur (Fig. 3). A midwater oxygen-minimum layer develops in high-productivity areas, due to coastal upwelling. Where this layer impinges on the continental shelf or slope, preservation of organic matter in the sediment is highly favored. Resedimentation processes (turbidite flow, slumping) may transport such organic matter-enriched sediments down the slope to the deep, oxygenated ocean floor. Nevertheless, rapid burial of this redeposited material may protect the organic matter in it from destruction. Deep oceanic currents resuspending sediment material into a so-called nepheloid layer have an opposite effect on organic matter preservation.

II. TRANSFORMATION OF ORGANIC MATTER IN THE SEDIMENT

A. Diagenesis, Catagenesis, and Metagenesis

Organic matter that has been incorporated into a sediment will undergo a series of geochemical alterations which are summarized schematically in Fig. 4. The microbial and chemical transformation of the original biomolecules, which started during sedimentation, is continued in the upper sediment layers. A series of still not well understood reactions, formally termed polymerization and condensation, leads to the initial "geopolymers," i.e., fulvic acids, humic acids, and humin. On a molecular level, these components are not well defined, but they are differentiated on the basis of their acid or base solubility. They are certainly not true polymers, but rather macromolecules with a variety of different building blocks which may include largely intact biopolymers. Among these, the insoluble, nonhydrolyzable, highly aliphatic biopolymers are of great importance. Kerogen is formed toward the end of the first transformation sequence, which is called diagenesis. This happens at relatively low temperatures (<50°C) and involves the activity of microorganisms inhabiting the sediment. Kerogen is a complex organic geomacromolecule which is soluble in neither organic solvents nor in acids or bases. Its chemical composition at this stage is strongly heterogeneous and varies greatly depending on the organic facies.

A certain proportion of the organic constituents inherited from the biological system are small compounds extractable from the sediment with organic solvents. This bitumen fraction contains a number of (geo)chemical fossils,

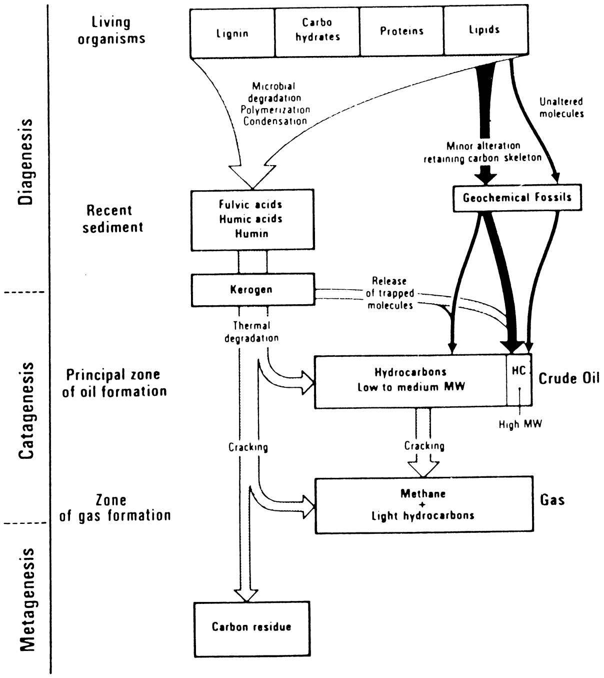


FIGURE 4 Schematic summary of geochemical transformation reactions of organic matter in the geosphere. [Reprinted with permission from Tissot, B. P., and Welte, D. H. (1984). "Petroleum Formation and Occurrence," 2nd ed., p. 94, Springer-Verlag, Berlin and New York. Copyright 1984 Springer-Verlag.]

i.e., unaltered molecules or compounds only slightly altered with essentially intact carbon skeletons compared to the precursor biomolecules. These may be hydrocarbons from higher-plant waxes or functionalized compounds such as alcohols, fatty acids, sterols, and triterpenes. The bitumen in Recent sediments accounts for only a very small portion of the total organic content.

When a sediment becomes buried more deeply in the course of continuing sedimentation and basin subsidence, it may enter the catagenesis stage, i.e., the principal zone of hydrocarbon formation (Fig. 4). Under the influence of increasing temperature (>50°C) and geological time, hydrocarbons and other compounds are released from the macromolecular kerogen network, and they add to the bitumen phase. This is the process of crude oil generation. Hydrocarbons span a wide range from low to high molecular weight, and compounds containing heteroatoms (nitrogen, oxygen, and/or sulfur, i.e., other than carbon and hydrogen) can still account for a significant proportion of the total bitumen. In a later catagenesis stage, further thermal hydrocarbon generation from the kerogen as well as thermal cracking of the bitumen yields mainly gaseous hydrocarbons, at the end predominantly methane.

Finally, the organic matter in sediments may reach the metagenesis stage at great depth and very high temperatures exceeding 150°C. At this stage, only methane is stable, and the kerogen is converted to a carbon residue which may start some crystalline ordering leading ultimately to graphite.

B. Early Transformation of Kerogen and Biological Markers

1. Kerogen

The initial composition of a specific kerogen depends on the source organisms that contributed to the sediment. Because the kerogen structure is not readily accessible by conventional molecular analysis, other parameters have to be used to describe it chemically. One possibility is to measure the elemental composition in terms of carbon, hydrogen, and oxygen content. If the results are displayed in a so-called van Krevelen diagram of H/C versus O/C atomic ratios, three initial kerogen compositions (types I, II, and III) are distinguished together with three evolution pathways representing the changes in elemental composition during diagenesis and catagenesis (Fig. 5). Type I kerogen is of pure algal (and eventually bacterial) origin and rare. The very high H/C atomic ratio reflects the lipid content rich in saturated aliphatic structures. Type II kerogen is derived from other aquatic organisms such as phytoplankton and zooplankton and has an intermediate H/C atomic ratio. Terrestrial higher plant organic matter (type III) is characterized by a considerably lower H/C atomic ratio but is enriched in oxygen, as can be expected from the high cellulose and lignin contents.

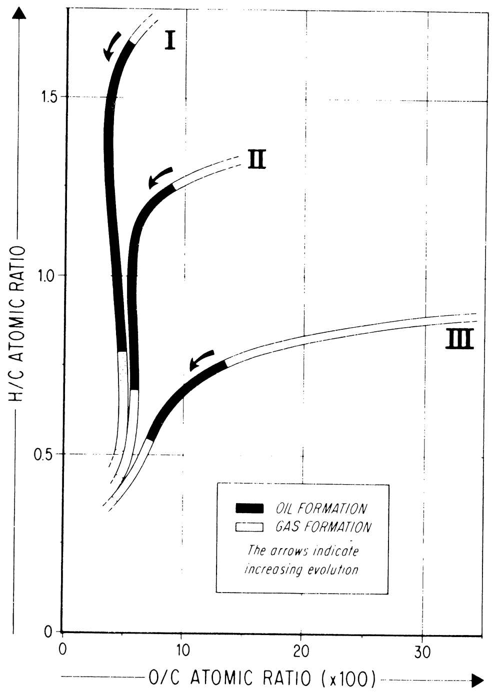


FIGURE 5 Structural evolution of various types of kerogen. [Reprinted with permission from Vandenbroucke, M. (1980). *In* "Kerogen" (B. Durand, ed.), pp. 415–443, Editions Technip, Paris. Copyright 1980 Editions Technip.]

The evolution pathways in Fig. 5, particularly for kerogen types II and III, show a decrease in the oxygen content in the first phase before the onset of oil generation. This represents the loss of small heteroatomic molecules such as carbon dioxide (CO_2) and water (H_2O) during the diagenesis stage. In addition, ammonia (NH_3) or hydrogen sulfide (H_2S) may be lost. The effect on the kerogen structure is a continuing condensation of the macromolecule with an increasing formation of carbon–carbon bonds.

2. Biological Markers

The developments in modern analytical techniques, particularly the combination of computerized capillary gas chromatography-mass spectrometry, allowed the identification of many of the compounds present in the complex mixture of organic molecules in sedimentary bitumen. This was used to follow the stepwise conversion of specific precursor compounds of biological origin into hydrocarbon products typically present in crude oils. The capillary gas chromatograph in this respect is used to separate the mixtures according to polarity and molecular weight by partitioning them between a gaseous phase, usually a stream of helium, and a stationary phase, usually a silicone gum coated to the inner wall of the fused silica capillary.

The effluent of the gas chromatograph enters a mass spectrometer, which generates spectra that provide information on the molecular weight and the chemical structure of the different compounds.

Molecules with a high degree of structural complexity are particularly informative and thus suitable to the study of geochemical reactions. They provide the chance of relating a certain geochemical product to a specific biological precursor. Such compounds, which retain a significant portion of their biogenic structural integrity throughout the geochemical reaction sequence, are called biological markers or molecular or (geo)chemical fossils.

The scheme in Fig. 6 illustrates the fate of sterols in sediments. Although it looks complex, Fig. 6 shows only a few selected structures of more than 200 biogenic steroids and geochemical conversion products presently known from sediments. The reaction sequence includes hydrogenation, dehydration, skeletal rearrangement, and aromatization. Steroids are only one example to illustrate these reactions, which likewise happen to many other compound classes.

The biological precursor in Fig. 6 is cholesterol (structure **1**, R = H), a widely distributed steroid in the biosphere. Hydrogenation of the double bond leads to the saturated cholestanol (**2**). This reaction occurs in the upper sediment layers or even in the water column by microbial action. Elimination of water gives the unsaturated hydrocarbon **3**. At the end of diagenesis, the former unsaturated steroid alcohol **1** will have been transformed to the saturated sterane hydrocarbon **4** after a further hydrogenation step. An alternative route to the saturated sterane **4** is via dehydration of cholesterol, which yields the diunsaturated compound **5**. Hydrogenation of one double bond leads to a mixture of two isomeric sterenes (**6**; double-bond isomerization indicated by dots), further hydrogenation affords the saturated hydrocarbon **4**. A sterically modified form of this molecule, e.g., **7**, is formed during catagenesis at elevated temperatures. A side reaction from sterene **6** is a skeletal rearrangement leading to diasterene **8**, where the double bond has moved to the five-membered ring and two methyl groups (represented by the bold arrows) are now at the bottom part of the ring system. This reaction is catalyzed by acidic clays. Thus, diasterenes (**8**) and the corresponding diasteranes (**9**), formed by hydrogenation during late diagenesis, are found in shales but not in carbonate rocks, which lack the catalytic activity of clays.

An alternative diagenetic transformation pathway of steroids leads to aromatic hydrocarbons. The diolefin **5** is a likely intermediate on the way to the aromatic steroid hydrocarbons **10**–**14**. Compounds **10** and **11** are those detected first in the shallowest sediment layers. They are labile and do not survive diagenesis. During late diagenesis, the aromatic steroid hydrocarbon **12** appears in the sediments, but is also stable enough to survive elevated temperatures and to be found in crude oils. As for the

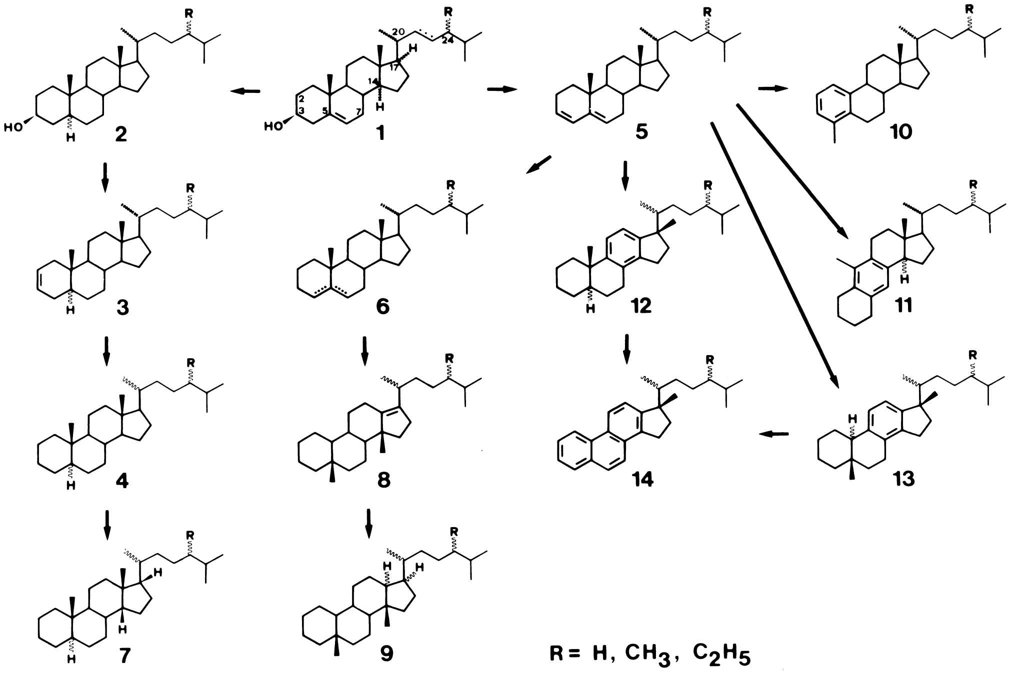


FIGURE 6 Diagenetic and catagenetic alteration of steroids.

saturated steranes, there is a corresponding rearranged monoaromatic steroid hydrocarbon **(13)**. During catagenesis, the monoaromatic steroid hydrocarbons are progressively transformed into the triaromatic steroid **14** before the steroid record is completely lost by total destruction of the carbon skeleton at even higher temperatures.

Inorganic sulfur species (hydrogen sulfide, polysulfides, or elemental sulfur) play an important role in the early diagenesis of low-molecular-weight lipids carrying double bonds or alcohol groups. Common examples of such compounds known to react with sulfur are phytol (see Fig. 2), equivalent isoprenoids with two or more double bonds occurring in bacteriochlorophylls, sterols, and hopanoids (e.g., bacteriohopanetetrol; see Fig. 2). Intramolecular sulfur addition leads to the formation of thiophenes, i.e., five-membered aromatic rings with a sulfur atom in the ring system, and related saturated thiolanes (five-membered rings) or thianes (six-membered rings). Addition of more than one sulfur atom affords di- or trithianes (two or three sulfur atoms in a saturated ring) or bi- or trithiophenes (two or three thiophene units in a single molecule). Intermolecular sulfur incorporation, on the other hand, forms high-molecular-weight organic sulfur compounds. Because the inorganic sulfur species react with only a certain portion of the sedimentary lipids, the molecular geochemical information is partitioned selectively between the low-molecular-weight lipid fraction and the macromolecular sulfur species. In order to have access to the full range of biological markers, e.g., in the paleoenvironmental assessment of a sediment, it is advisable to remove the cross-linking sulfur bridges by hydrogenation with a Raney nickel or nickel boride catalyst before analysis.

Hydrogen sulfide (H_2S) is formed by microbial reduction of sulfate in seawater under strictly anoxic conditions. In clayey sediments, H_2S is preferentially trapped as pyrite (FeS_2) by reaction with Fe^{2+} ions; thus, an excess of inorganic sulfur compounds or a low iron concentration (as in carbonates) is an additional prerequisite for the diagenetic formation of organic sulfur compounds in sediments. At a later stage of organic matter transformation in sediments, organic sulfur compounds may become constituents of crude oils.

C. Thermal Hydrocarbon Generation

In the diagenesis stage, organic matter is immature with respect to hydrocarbon generation. The hydrocarbons present in the bitumen fraction, apart from methane (CH_4) formed by methanogenic bacteria in shallow sediments, largely constitute geochemical fossils inherited from the biosphere. On a molecular level, n-alkanes, for example, can show the typical distribution pattern of higher-plant waxes with a maximum chain length above C_{25} and a predominance of the odd-carbon-number species. Similarly, cycloalkanes and aromatic hydrocarbons show a predominance of compounds with a close link to biogenic precursors.

The onset of oil generation occurs at the beginning of the catagenesis stage. The total amount of hydrocarbons in the sediments increases as a consequence of thermal cracking of kerogen. Initially, the weaker heteroatomic bonds are cleaved preferentially, but with increasing temperature due to deeper burial the stronger carbon–carbon bonds are broken as well. Also, relatively large units (asphaltenes) are released from the kerogen at the early catagenetic stage.

The generation of oil-type hydrocarbons goes through a maximum (“peak of oil generation”), after which gasoline-range and gaseous hydrocarbons in the wet gas zone become the main reaction products for two reasons. First of all, the kerogen during catagenesis has become depleted in large aliphatic moieties, and only the remaining smaller units can now be released. Second, the oil-type hydrocarbons in the bitumen fraction are thermally cracked into smaller, gaseous compounds.

In the dry gas zone, almost exclusively methane (CH_4) is generated from the kerogen. At the same time, methane is also the ultimate hydrocarbon product formed by cracking of oil released from the kerogen at earlier generation stages. During the oil and gas generation phase, the H/C atomic ratio of the kerogen constantly decreases as illustrated in Fig. 5, and the kerogen becomes an inert carbon residue.

The amount of hydrocarbons generated from a specific source rock depends on the nature of the kerogen and on the extent to which the source rock has passed through the hydrocarbon generation zones under the given geological conditions, of which time and temperature are most important. The potential of a kerogen to generate hydrocarbons depends largely on its hydrogen richness as a limiting factor. Kerogen types I and II (Fig. 5) of dominantly aquatic origin are able to generate more hydrocarbons per unit carbon than the relatively hydrogen-poor kerogen type III.

The kerogen quality also influences the types of hydrocarbons generated. Aquatic organic matter and microbial biomass, both rich in aliphatic units, are the sources of abundant oil-type bitumen. On the other hand, coaly organic matter of terrigenous origin, which to a large extent is composed of aromatic ring systems with only short aliphatic chains, is more likely to yield predominantly gaseous hydrocarbons.

Because the rate of hydrocarbon generation is controlled by chemical reaction kinetics, both time and temperature are important for the transformation of kerogen. Although the geochemical reactions leading to the formation of hydrocarbons may be complicated by an influence of pressure and catalytic activity of the mineral rock matrix, the general expectation is that source rocks in relatively young sedimentary basins need higher temperatures for hydrocarbon generation than those in older basins. This is confirmed by observations in nature which showed that hydrocarbon generation in the Upper Tertiary (10 m.y.) of the Los Angeles Basin starts at about 115°C, compared to 60°C in the Lower Jurassic (180 m.y.) of the Paris Basin. Since according to chemical reaction kinetics the influence of time should be linear but that of temperature exponential, the compensation of temperature by time is limited such that very old potential source rocks, which have experienced only very low temperatures, will not generate significant amounts of hydrocarbons even over very long geological times.

D. The Chemical Composition of Crude Oils Related to Geological Factors

1. Crude Oil Classification

Crude oils can be characterized by their bulk properties as well as their chemical composition. Distillation of crude oils provides fraction profiles over a certain boiling-point range. Total oils as well as distillation fractions can be described in terms of density, viscosity, refractive index, sulfur content, or other bulk parameters. A widely used parameter in the oil industry is the API gravity, which is inversely proportional to density. Conventional crude oils range from about 20 to 45° deg API gravity. Oils with lower API gravities are called heavy oils, those with higher API gravities are condensates, although these are not rigorously defined boundaries.

In organic geochemical studies, crude oils are conventionally separated into fractions of different polarities using column or thin-layer chromatography. Usually, after removal of the low-boiling components at a certain temperature and under reduced pressure ("topping"), asphaltenes (i.e., high-molecular-weight polar components) are precipitated by the addition of a nonpolar solvent (e.g., *n*-hexane). The soluble portion is then separated into saturated hydrocarbons, aromatic hydrocarbons, and a fraction containing the polar, heteroatomic compounds (NSO compounds or resins).

Of course, the gross fractions allow further subfractionation in order to facilitate subsequent studies on a molecular level using less complex mixtures. For example, the saturated hydrocarbons can be treated with 5-Å molecular sieve or urea for the removal of *n*-alkanes, leaving behind a fraction of branched and cyclic alkanes. Aromatic hydrocarbons are often further fractionated according to the number of aromatic rings.

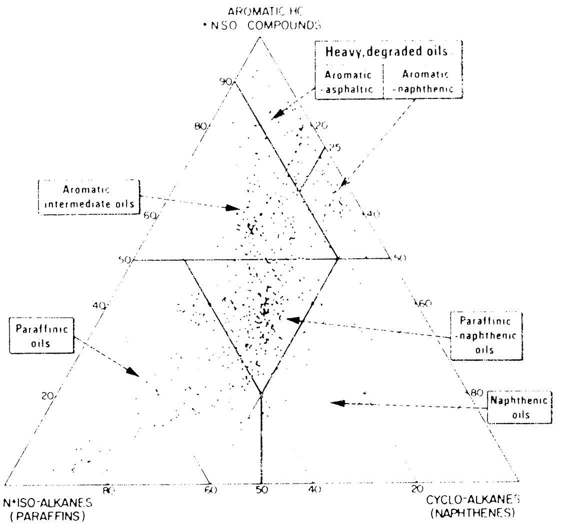


FIGURE 7 Ternary diagram showing the composition of six classes of crude oils based on the analysis of 541 oils. [Reprinted with permission from Tissot, B. P., and Welte, D. H. (1984). "Petroleum Formation and Occurrence," 2nd ed., p. 419, Springer-Verlag, Berlin and New York. Copyright 1984 Springer-Verlag.]

The ternary diagram in Fig. 7 shows the composition of six classes of crude oils based on a large number of analyses. Crude oils with more than 50% saturated hydrocarbons are called "paraffinic" or "naphthenic," depending on the relative contents of normal and branched alkanes (paraffins) and cycloalkanes (naphthenes). Paraffinic oils are light, but many have a high viscosity at room temperature due to the high content of long-chain wax alkanes. A high wax content is often an indication of a strong terrigenous contribution to the organic matter in the source rock. Such oils are commonly generated from deltaic sediments, as in Indonesia and West Africa. However, type I kerogen may also generate highly paraffinic crude oils, as is the case in the Green River Formation of the Uinta Basin, Utah. The crude oil property in the latter case is probably related to the fact that nonhydrolyzable highly aliphatic units in kerogen are derived not only from higher land plants but also from aquatic organisms (e.g., *Bottryococcus* algae; see Sect. I.A.3). The most common oil type is paraffinic naphthenic (40% of the oils in Fig. 7), whereas naphthenic oils are scarce and often the result of microbial degradation in the reservoir (see Sect. III.C). All oils rich in saturated hydrocarbons commonly have a low sulfur content (<1%).

Aromatic intermediate oils contain 40–70% aromatic hydrocarbons and a high proportion of resins and asphaltenes. They are rich in sulfur and mostly heavy. Many crude oils from the Middle East (Saudi Arabia, Kuwait, Iraq, etc.) are included in this category, which is the second most important class in Fig. 7. The aromatic naphthenic and aromatic asphaltic classes are represented mostly by altered crude oils. They are heavy, but the sulfur content may vary according to the original type of the crude oil. The Cretaceous heavy oils of Athabasca (Canada) are typical examples of these last two classes.

2. Geological Factors Influencing Crude Oil Composition

The depositional environment of the source rock, its thermal evolution, and secondary alteration processes are the most important factors determining the composition of crude oils. Among the environmental factors, those that influence the nature of the organic matter in the source rock and its mineral composition are of primary significance.

Although hydrocarbon source rocks are deposited under aquatic conditions, they may contain varying amounts of land-derived organic matter. The terrestrial contribution can be significant, particularly in intracontinental basins and in the deltas of large rivers, which may extend far into the open sea. Continental organic matter (type III kerogen) is rich in cellulose and lignin which, due to their oxygen content, are not considered to contribute much to oil formation. The subordinate lipid fraction together with the biomass of sedimentary microorganisms incorporated into the source rock yields crude oils which are rich in aliphatic units (from wax esters, fats, etc.), i.e., straight-chain and branched alkanes (paraffins). Polycyclic naphthenes, particularly steranes, are present in very low concentration. Total aromatic hydrocarbons are also significantly less abundant than in crude oil derived from marine organic matter, as is the sulfur content.

Marine organic matter (usually type II kerogen) produces oils of paraffinic naphthenic or aromatic intermediate type (Fig. 7). The amount of saturated hydrocarbons is moderate, but isoprenoid and polycyclic alkanes, such as steranes (from algal steroids) and hopanes (from membranes of eubacteria), are relatively more abundant than in oils from terrigenous organic matter. Kerogen derived from marine organic matter, particularly when it is very rich in sulfur, is particularly suited to release resin- and asphaltene-rich heavy crude oils at a very early stage of catagenesis. Type II kerogens are preferentially deposited where the environmental conditions are favorable for organic matter preservation (anoxic water column in silled basins or in areas of coastal upwelling) and where the continental runoff is limited for physiographical or climatic reasons.

The sulfur content of crude oils shows a close relationship to the type of mineral matrix in the source rocks. Organic matter in sediments consisting of calcareous (e.g., from coccolithophores or foraminifera) or siliceous shell fragments (e.g., from diatoms or radiolaria) of decayed planktonic organisms and at the same time containing abundant organic matter is enriched in sulfur. The reason for this is that under the anoxic conditions which are required to preserve organic matter, sulfate-reducing bacteria form hydrogen sulfide (H_2S). This may react with the organic matter, and the sulfur will become incorporated into the kerogen. Examples are the Monterey Formation with the related crude oils produced onshore and offshore southern California and many of the carbonate source rocks of the Middle East crude oils.

In clastic rocks containing an abundance of detrital clay minerals, the iron content usually is high enough to remove most of the H_2S generated by the sulfate-reducing bacteria through formation of iron sulfides. Because terrigenous organic matter is commonly deposited together with detrital mineral matter (e.g., in deltas), waxy crude oils derived from type III kerogen usually are depleted in sulfur.

E. Coal and Oil Shales

Most organic carbon in sediments is finely disseminated. Even in hydrocarbon source rocks responsible for oil and gas accumulations, the organic carbon contents often do not exceed 10%. Apart from the secondary accumulations such as oil or gas reservoirs and tar sands, particular enrichment of organic matter in sediments occurs in the form of coal and oil shales.

1. Coal

Coal forms by the massive accumulation of land plants under a wet climate in a slowly subsiding basin. Peat formation is the first step in the process. It is essential that the decaying plant material be rapidly covered with water to prevent its oxidative decomposition. Furthermore, peat development requires the supply of plant remains over extended periods of time and a delicate balance of organic matter supply and tectonic subsidence. In terms of geological age, coal formation is possible since the advent of terrestrial higher plants in the Devonian (380 m.y. ago).

Peat formed by chemical and microbial diagenetic reactions in the first coalification step is transformed into lignite (brown coal) in the course of increasing burial. Elevated temperatures at greater depth over geological times are required to convert lignite into bituminous coals, which ultimately reach the anthracite stage at the end of the coalification process. Table II summarizes the different coalification stages together with selected physical parameters which can be used to differentiate among the coal ranks. Mean vitrinite reflectance, R_m, is the most widely used coalification parameter. It is determined on vitrinite

TABLE II Different Stages of Coalification According to the American Society for Testing and Materials (ASTM) Classification

	Approximate		
Rank	Reflectance range, R_m, (%)	Volatile matter d.a.f. (%)[a]	Carbon content d.a.f. (%)[a]
Peat	0.20–0.25	>64	<60
Lignite	0.25–0.4	55	65
Subbituminous coal (C, B, A)	0.4–0.65	48	73
High-volatile bituminous coal (C, B, A)	0.50–1.10	40	80
Medium-volatile bituminous coal	1.1–1.5	26	87
Low-volatile bituminous coal	1.5–1.9	18	89
Semianthracite	1.9–2.5	10	90
Anthracite	2.5–ca.5	5	92
Meta-anthracite	5	<3	>92

[a] d.a.f. = dry and ash free.

particles (vide infra), which can be observed on polished coal surfaces under the microscope. Vitrinite reflectance is low in the peat and lignite stages; it increases from about 0.4% to 1.9% in the bituminous coal ranks, and to values in excess of 5% in the anthracite stage. At the same time, the content of volatile matter decreases drastically, and the carbon content of coals increases to more than 90%.

Coal, particularly at low ranks, is not homogeneous. This is conceivable from heterogeneity of the contributing plant materials and the variability of the chemical and microbial reactions after deposition due to changes in water coverage, acidity (pH value) or redox (Eh) potential in the depositional environment. Coal is composed of a number of organic particle types (macerals) distinguishable either macroscopically or, more importantly, microscopically.

Coal petrography, as this study is called, differentiates among three main maceral groups, each containing several macerals (Table III). The microscopic investigations are performed on polished coal surfaces in the reflected-light mode, and macerals are distinguished by their reflectance, shape, and structure. Occasionally, fluorescent light observations after ultraviolet irradiation are used to enhance the signal of low-reflecting liptinites. The same techniques are applied by organic petrographers to characterize dispersed organic particles in sediments.

Vitrinite is the most abundant maceral group in humic coals. Vitrinites are coalification products of humic substances which essentially originate from the lignocellulose components of cell walls; they appear gray in reflected light under the microscope. Telinite shows cell structures of wood or bark, whereas collinite is structureless. Vitrinite in hard coals corresponds to huminite in lignite or peat, where a different terminology for the macerals and a stronger subclassification of the maceral group is used (examples are given in Table III). Small detrital particles of vitrinitic material, intimately mixed into a structureless groundmass and difficult to identify, are called vitrodetrinite.

Liptinites, less abundant in coals but major constituents of petroleum source rocks, are derived from hydrogen-rich, lipid-bearing plant materials. Among these are spores and pollen (sporinite), cuticles and cuticular layers within the outer walls of leaves or stems (cutinite), resins and waxes (resinite), and corkified cell walls of barks, roots, or fruits containing suberin as a protecting agent against dessication (suberinite). Alginite is rare in coals, with the exception of the occasionally occurring sapropelic coals, which were not deposited as peats but under more anoxic conditions as subaquatic muds rich in plankton and water plants.

Inertinites have the same biological precursors as vitrinites but when occurring in the same coal have a higher reflectivity. Fusinite and semifusinite show distinct cellular structures of wood. Many of these particles appear to be fossil equivalents of charcoal, and ancient forest fires may have contributed to their formation. Sclerotinites are mostly fungal remains, although other sources have been invoked for part of the sclerotinites, particularly in older (Carboniferous and Permian) coals. Macrinite is an amorphous substance which formed by oxidation of gelified plant material. All inertinites are highly carbonized and have no potential for hydrocarbon generation.

2. Oil Shales

Oil shales are organic matter-rich sediments which have never been buried to greater depth. They contain little extractable bitumen but generate oil when heated to

TABLE III Maceral Classification of Coals Showing Main Maceral Groups and Selected Macerals[a]

Maceral group	Maceral
Vitrinite (huminite)	Telinite (ulminite), vitrodetrinite, collinite (gelinite)
Liptinite	Sporinite, cutinite, resinite, suberinite, alginite, liplodetrinite, bituminite
Inertinite	Fusinite, semifusinite, macrinite, sclerotinite, inertodetrinite

[a] Special terms used for brown coals (lignite) only are given in parentheses.

temperatures of about 500°C. Oil shales may be true shales with clay minerals as the dominant inorganic component, but commonly include carbonate as well as siliceous rocks. The organic carbon content in most cases exceeds 20%, and the H/C atomic ratio is very high (close to or above 1.5).

The organic matter often consists entirely of freshwater (*Bottryococcus*) or marine (*Tasmanites*) algae and bacterial biomass (type I organic matter; cf. Fig. 5). Because oil shales have not entered the catagenetic stage, the shale oil produced by heating contains considerable amounts of sulfur- and nitrogen-bearing compounds in addition to pyrolytically formed unsaturated hydrocarbons (olefins), which are not normally present in crude oils. There is no basic geochemical difference between oil shales and petroleum source rocks. The former just have not been buried deeply enough for thermal hydrocarbon generation under natural conditions.

Oil shales were deposited in large lake basins such as the Eocene Green River shales in Utah and Wyoming, which are several hundred meters thick, in shallow seas on stable platforms such as the Permian Irati oil shale in Brazil, or in small lakes, bogs, and lagoons, where they are often associated with coal beds. Oil shales range in age from the Lower Paleozoic (Cambrian) to the Tertiary. The world's largest oil shale reserves are in the United States, Brazil, and Russia.

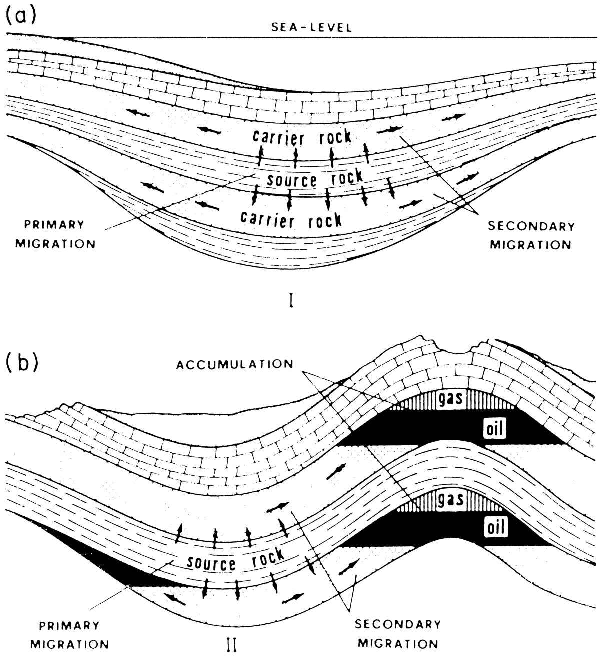


FIGURE 8 Schematic representation of primary and secondary migration leading to oil and gas accumulation: (a) initial phase and (b) advanced stage. [Reprinted with permission from Tissot, B. P., and Welte, D. H. (1984). "Petroleum Formation and Occurrence," 2nd ed., p. 294, Springer-Verlag, Berlin and New York. Copyright 1984 Springer-Verlag.]

III. MIGRATION AND ACCUMULATION OF OIL AND GAS

A. Primary and Secondary Migration

The formation of oil and gas from kerogen occurs in relatively tight hydrocarbon source rocks. The liquid and gaseous low-molecular-weight compounds generated in this process occupy a larger volume than the solid macromolecular precursor material. Because of the generally low porosity of the source rocks, the amount of hydrocarbons that can be contained in them is limited. The generation of hydrocarbons leads to an increase in pressure that eventually causes expulsion of the hydrocarbons into more porous sediments overlying or underlying the source rock. This movement of hydrocarbons is called primary migration (Fig. 8).

The oil expelled continues its movement through the wider pores of the more permeable carrier rock. Driving forces are water flow in the subsurface and buoyancy of the hydrocarbons that have a lower density than the saline waters (brines) saturating the pores of sedimentary rocks. During this secondary migration, petroleum may ultimately reach a reservoir rock that has porosity and permeability characteristics similar to those of the carrier bed but is sealed by an impermeable barrier, the cap rock (Fig. 8). In this way hydrocarbon accumulations are formed.

The most important mechanism for primary migration is transport of petroleum compounds in a continuous hydrocarbon phase with pressure as the driving force. The formation of a separate oil or gas phase in deeply buried, highly compacted sediments is favored by the fact that the amount of pore water present is low and that all or most of it is tightly bound to the mineral surface. This immobility of the pore water facilitates hydrocarbon movement. Furthermore, mineral surfaces may be covered with organic matter (kerogen network) or even be "oil wet," which further enhances transport of the apolar petroleum components. If very high pressures develop in a source rock, microfracturing may occur, which will periodically increase the migration flow toward more porous media, such as larger fractures within the source rock, or an adjacent carrier rock. Diffusion is considered an effective primary migration mechanism only in exceptional cases and mainly for gaseous hydrocarbons over short distances. Transport of hydrocarbons in aqueous solution is no longer considered a mechanism for primary migration.

Primary (and probably also secondary) migration leads to fractionation of the bitumen initially generated in the source rocks. Polar compounds tend to be preferentially retained by adsorption on mineral surfaces, and very large polar compounds such as asphaltenes may have a low chance for migration at all. Thus, crude oil in a reservoir will be depleted in polar heteroatomic compounds but enriched in hydrocarbons relative to the source rock, bitumen. The extent to which this occurs depends on the pore sizes of the migration pathway, the adsorption activity of the mineral surfaces, and the distance of migration. Fractionation among the hydrocarbons is relatively minor, as shown by numerous examples of successful oil/source rock correlation based on hydrocarbon compound ratios.

The efficiency and timing of primary migration has been a matter of debate for many years. It is now known that more than 80% of the hydrocarbons generated may be expelled during the main phase of oil formation. This contrasts sharply with the range of 10% to (exceptionally) 30% estimated in the earlier literature. Expulsion is more effective in thin source layers of a few centimeters or decimeters than in thick layers extending over several meters. In thick shales, part of the hydrocarbons retained may have to be cracked to lighter (gaseous) hydrocarbons before they get a chance to migrate out. The same occurs in rocks lean in organic matter, where the pressure buildup by liquid hydrocarbons is insufficient and not enough kerogen is present to form a continuous network supporting hydrocarbon drainage. For this reason, source rocks containing predominantly terrigenous organic matter with a low proportion of liptinite mainly generate gas, because the small amounts of liquid hydrocarbons initially formed cannot be expelled, but are later transformed into gas at higher thermal stress. Similarly, coals produce mainly gas (methane) because their microporosity and adsorption activity impede expulsion of initially formed liquid hydrocarbons. The high storage capacity of coals even for gas is well known from coal mining (pit gas).

Secondary migration of hydrocarbons through porous and permeable carrier beds and reservoir rocks is driven mainly by buoyancy due to the low densities of oil and gas. Secondary migration terminates when the retarding capillary pressures are stronger than the driving forces. If a barrier is encountered in the subsurface, then hydrocarbon accumulations will form. Otherwise, the hydrocarbons will seep out at the surface.

Oil and gas are trapped in the structurally highest position of a reservoir rock which is sealed with an essentially impermeable cap rock. Two general types of traps are commonly distinguished (Fig. 9). The sand anticline in Fig. 9a is an example of a structural trap. Other types of structural traps formed by tectonic events are associated, e.g., with salt domes, carbonate reefs, or basement highs. By far the largest amount of crude oil on earth is accumulated in anticline reservoirs, which are also the easiest to detect by geological and geophysical prospecting and are usually drilled first. The formation of stratigraphic traps is controlled by sedimentation processes. This type of trap may be associated with erosional surfaces (unconformities) as in Fig. 9b or with a change in the sediment facies (lithology). For example, when a coastal sand deposit grades into fine-grained shale farther offshore, the shale may act as a barrier to the hydrocarbons moving through the sand.

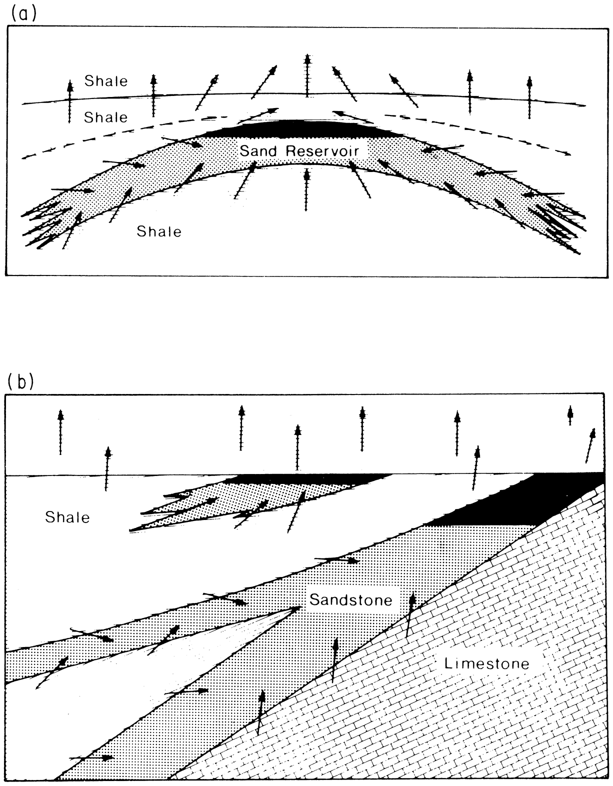


FIGURE 9 Schematic representation of two different types of hydrocarbon traps: (a) anticline as an example of a structural trap and (b) stratigraphic trap at an unconformity. [Reprinted with permission from Hunt, J. M. (1979). "Petroleum Geochemistry and Geology," pp. 223–224, Freeman, San Francisco. Copyright © 1979 W. H. Freeman and Company.]

In contrast to primary migration, secondary migration may occur laterally over long distances of several tens of kilometers or even more. On the other hand, secondary migration can also be very short, e.g., from a shale source rock into an embedded sand lense. Over geological times, hydrocarbon accumulations are unstable. Tectonic events such as folding, faulting, or uplift associated with erosion can destroy hydrocarbon reservoirs completely or cause a redistribution of hydrocarbons into other reservoirs. In addition, cap rocks are not absolutely impermeable, and over

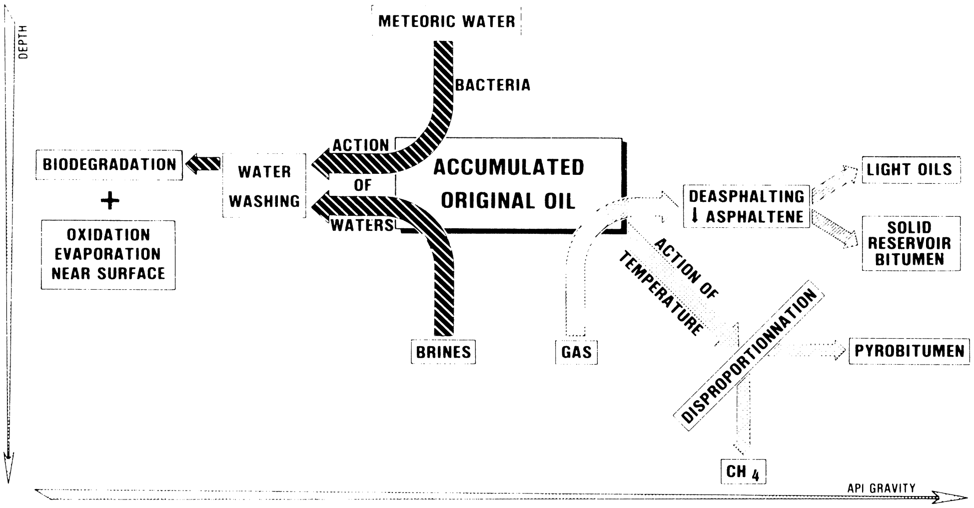


FIGURE 10 Crude oil alteration in the reservoir. [Reprinted with permission from Connan, J. (1984). *In* "Advances in Petroleum Geochemistry," Vol. 1. (J. Brooks and D. H. Welte, eds.), pp. 299–335, Academic Press, Orlando, FL. Copyright 1984 Academic Press.]

many millions of years the leakage rate may be sufficient to empty a reservoir.

B. Alteration of Hydrocarbons in the Reservoir

Even if reservoir conditions are tectonically stable, pooled hydrocarbons are susceptible to secondary alteration. The most important factors that can influence the chemical composition of petroleum in a reservoir are summarized in Fig. 10. Physical and chemical transformation processes will lead to either an increase or a decrease of the API gravity (or, conversely, the density). Alteration of hydrocarbons in the reservoir is quite common and is observed in many oil fields around the world. Petroleum can be altered to such an extent that the character of the source material is lost and the economic value decreases drastically.

Basin subsidence can bring a reservoir together with its accumulated hydrocarbons into a regime of higher temperature. Cracking reactions may then lead to the formation of lighter hydrocarbons (ultimately methane) and a residual pyrobitumen. Alternatively, long-term exposure of reservoired hydrocarbons to higher temperatures even without basin subsidence may cause cracking into smaller components. Within a basin this effect will be proportional to the reservoir depth.

Major amounts of gas entering a petroleum reservoir reduce the solubility of large polar compounds, and asphaltenes are precipitated in a process called desasphalting. The resulting oil is lighter than that originally present in the reservoir. The precipitated material forms a solid bitumen and may have a negative effect on the production properties of the reservoir by reducing the permeability.

Hydrodynamic flow of brines and the invasion of meteoric surface water can alter a crude oil by water washing, which removes the more water-soluble compounds from the reservoir. Meteoric water usually carries oxygen and in most cases microorganisms into the reservoir. This leads to microbial degradation of the crude oil, with a preferential removal of the readily metabolizable components. *n*-Alkanes are removed first, followed by simple branched and isoprenoid alkanes. Polycyclic saturated hydrocarbons are biodegraded less easily and at a much later stage. The biological alteration of the aromatic hydrocarbons is less well understood because the associated water washing coupled with the higher water solubility of the aromatic hydrocarbons often obscures the net effect of biodegradation. Biodegradation of crude oils in the reservoir is limited by the supply of oxygen and nutrients to the microorganisms and the maximum temperatures they can tolerate. Thus, biodegradation is rarely found at reservoir temperatures exceeding 70°C. In very shallow reservoirs, evaporation of volatile hydrocarbons to the surface strengthens the effect of biodegradation. As a result, heavy oils or tar sands may be formed, of which a famous example are the Athabasca tar sands in Alberta, Canada.

IV. ORGANIC GEOCHEMISTRY IN PETROLEUM EXPLORATION

The search for crude oil and natural gas is a costly and risky enterprise. After finding most of the easily detectable reservoirs in readily accessible areas, hydrocarbon exploration is now proceeding into new frontier areas including the deeper ocean and higher latitudes with their harsh climate and is looking for hitherto undetected smaller traps in previously explored basins. In order to keep the economic risk of drilling within reasonable limits, as many modern techniques as possible are used by the explorationists to help them in decision making. Sophisticated geophysical measurements (seismics) and satellite imaging are almost routine. Application of the principles of organic geochemistry in this respect has become a widely used tool in petroleum exploration.

A. The Hydrocarbon Potential of Sedimentary Rocks

The initial amount and the type of organic matter in a sedimentary rock determine its hydrocarbon potential. It is a question of the thermal evolution of such a sediment, if the potential is ever used actually to generate hydrocarbons. It is not easy to define a minimum organic carbon content for a sediment to be a source rock, but commonly accepted values are 0.5% for clastic rocks (claystones) and 0.3% for carbonates. This is based on a statistical overview of a great number of suspected or proven source rock samples worldwide, which shows that carbonates on average are leaner in organic matter than clastic rocks. Carbonates, on the other hand, often contain layers of organic matter-rich material derived from algal or bacterial mats. The restrictions imposed by the mechanisms of primary migration (expulsion; see Sect. III.A), however, may require higher minimum organic carbon values, probably on the order of 1.0–1.5%. Good to excellent hydrocarbon source rocks will have more than 2% organic carbon.

It can be roughly generalized that the quality of organic matter (hydrogen richness) in sediments increases with the total organic carbon content, because once favorable conditions for organic matter accumulation have been established, the preservation of the most labile lipid-rich material is enhanced. Examples are known, however, in which an organic carbon-rich sediment has little hydrocarbon potential because the kerogen it contains is woody or highly oxidized.

While the total organic carbon content is usually measured by combustion after removal of the carbonate carbon by acid treatment, several methods are available to assess the type of organic matter in a sediment. One way is by microscopic maceral analysis in which a specific hydrocarbon potential is ascribed to different macerals. Liptinites are believed to have a high potential for oil generation, whereas vitrinites may generate some oil but mainly gaseous hydrocarbons.

A standard pyrolysis method in petroleum geochemistry allows a quick assessment of the bulk hydrocarbon generation potential of a sediment. This so-called Rock-Eval pyrolysis uses a small amount of ground rock sample which is progressively heated to 550°C in a stream of helium. The hydrocarbon products released are monitored by combustion in a flame ionization detector. The first signal (S_1), observed at low temperature, corresponds to the volatile bitumen in the rock, whereas the second peak (S_2) in the pyrogram represents the compounds produced by thermal cleavage of the kerogen (Fig. 11, left). Separately, the carbon dioxide evolved from the kerogen during heating is also registered (not shown in Fig. 11). If S_2 and the carbon dioxide signal are normalized to the total organic carbon content of the sample, a hydrogen index and an oxygen index are obtained which are independent of the amount of organic matter in the sample and closely related to the elemental composition of the kerogen. They can be plotted in a van Krevelen-type diagram (Fig. 12). Like the H/C and O/C atomic ratios (cf. Fig. 5), which are more tedious to determine, the hydrogen and oxygen indices show the evolution pathways of different kerogen types. The quality of organic matter, i.e., the hydrocarbon potential of a source rock, is related directly to the value of the hydrogen index.

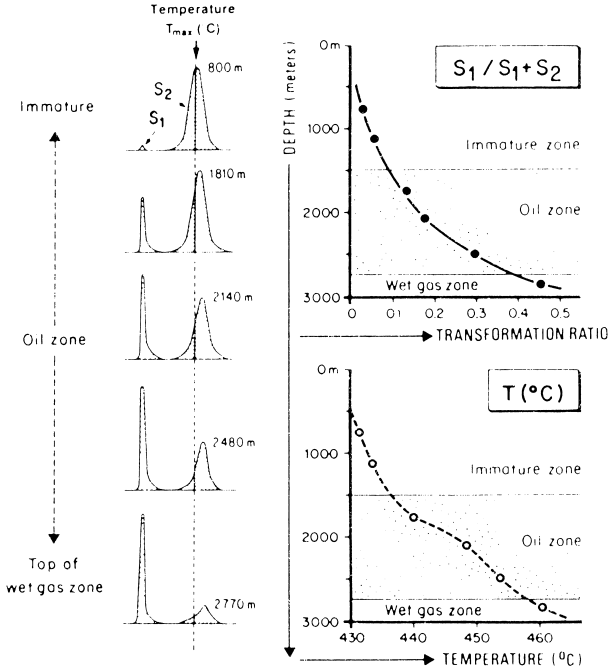


FIGURE 11 Characterization of source rocks by Rock-Eval pyrolysis. [Reprinted with permission from Tissot, B. P., and Welte, D. H. (1984). "Petroleum Formation and Occurrence," 2nd ed., p. 521, Springer-Verlag, Berlin and New York. Copyright 1984 Springer-Verlag.]

B. Maturity of Organic Matter

The thermal evolution of organic matter, a process called maturation, continuously changes the chemical

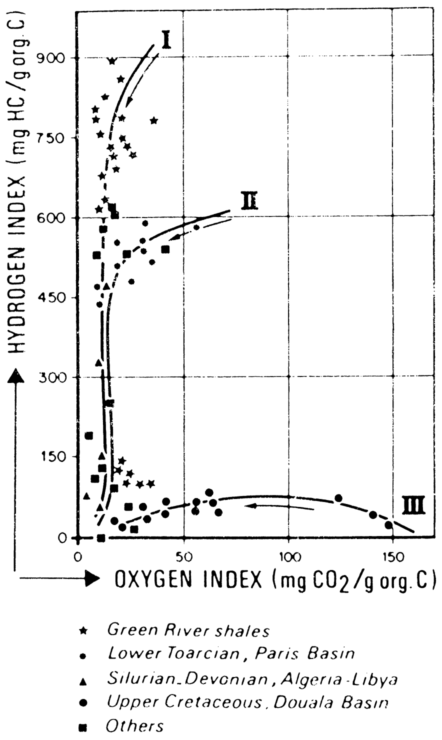


FIGURE 12 Classification of kerogen types by using hydrogen and oxygen indices from Rock-Eval pyrolysis. [Reprinted with permission from Tissot, B. P., and Welte, D. H. (1984). "Petroleum Formation and Occurrence," 2nd ed., p. 512, Springer-Verlag, Berlin and New York. Copyright 1984 Springer-Verlag.]

composition and the related physical properties. In petroleum exploration, it is important to know if a source rock has already entered the hydrocarbon generation zone or if it is above or below this zone. An immature sediment when analyzed for the quality of its organic matter will show the full hydrocarbon potential. A source rock within the generation zone will show only that potential which remained after the earlier release of hydrocarbons now present as bitumen or migrated out of the source rock. A sediment below the hydrocarbon generation zone will have a negligible residual hydrocarbon potential. To determine the thermal evolution stage of organic matter in sediments, a number of bulk and molecular parameters are available and are often used in combination with each other to account for the complexity of geochemical reactions and the time–temperature interrelationship.

1. Bulk Maturity Parameters

Rock-Eval pyrolysis in addition to information about the type of organic matter and its hydrocarbon potential also provides a sensitive measurement of the thermal history of a sediment. With increasing maturation the maximum of the pyrolysis peak (S_2) is shifted to higher temperature values (T_{max}) as shown in Fig. 11. At the same time, the relative proportion of the volatile material in the rock, represented by the S_1 peak, increases (Fig. 11). In most sediments there is a good correlation between the S_1 yield and the amount of extractable bitumen. The production index or transformation ratio [$S_1/(S_1 + S_2)$] is, however, affected by any hydrocarbons that have migrated out of or into the sediment, and it is recommended to study downhole trends (Fig. 11) rather than using single measurements. The sum of S_1 and S_2 represents the total genetic potential of a rock minus the amount of hydrocarbons which have left the rock during primary migration.

Coal ranks are most satisfactorily determined by the measurement of vitrinite reflectance. This method, developed in coal petrography, has been extended to kerogen particles disseminated in sedimentary rocks in order to assess the maturity level of organic matter. From the correlation of vitrinite reflectance with hydrocarbon yields from the extraction of source rocks, but also with other maturity parameters, it has become common to define zones of hydrocarbon generation in terms of vitrinite reflectance (Table IV). The boundaries are approximate and vary with kerogen type, due to variations in the chemical composition of the respective organic matter. Another influence comes from the heating rate which the organic matter has experienced. This is due to the fact that the chemical reactions responsible for hydrocarbon generation from kerogen and for vitrinite reflectance increase have different kinetics and, thus, respond differently to temperature increase and time.

Excellent hydrocarbon source rocks often lack vitrinite particles because all their organic material consists of the remains of aquatic organisms. Also, early bitumen generation in these rocks may impregnate the few eventually present vitrinite particles, which leads to a vitrinite reflectance lower than corresponding to the actual maturation stage. In these cases, maturity assessment is made by measuring vitrinite reflectance in adjacent, less prolific rocks which contain more terrigenous organic matter or by chemical maturation parameters.

TABLE IV Approximate Boundaries for Hydrocarbon Generation Zones in Terms of Vitrinite Reflectance

	Vitrinite reflectance for different kerogen types (%)		
Generation zone	I	II	III
Onset of oil generation	0.7	0.5	0.7
Peak of oil generation	1.1	0.8	0.9
Beginning of gas zone	1.3	1.3	1.3
Dry gas zone	>2.0	>2.0	>2.0

2. Chemical Maturity Parameters

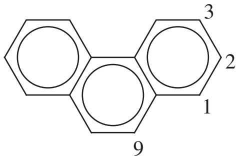
The chemical composition of bitumen is progressively changed by diagenetic and catagenetic reactions. A number of compound ratios, particularly in the hydrocarbon fractions, were found to vary systematically with increasing depth in a basin, and so these ratios can be used to measure the maturity of organic matter in a sediment. Only a few of them will be introduced here.

Because *n*-alkanes are usually the most abundant class of hydrocarbons in a sediment extract or a crude oil, much emphasis has been placed on the study of their relative compositional changes. The changes are most obvious when the sediment contains a certain amount of terrestrial higher plant material which contributes *n*-alkanes with a significant predominance of the odd carbon-number molecules that gradually disappears with increasing maturation. Several slightly differing mathematical expressions are being used to measure the maturity-dependent alteration of the *n*-alkane distribution. The most prominent among them is the carbon preference index (CPI), which uses a range of long-chain *n*-alkanes from C_{24} to C_{32}:

$$\mathrm{CPI} = \tfrac{1}{2}[(\mathrm{C}_{25} + \mathrm{C}_{27} + \cdots + \mathrm{C}_{31})/(\mathrm{C}_{26} + \mathrm{C}_{28} + \cdots + \mathrm{C}_{32}) + (\mathrm{C}_{27} + \mathrm{C}_{29} + \cdots + \mathrm{C}_{33})/(\mathrm{C}_{26} + \mathrm{C}_{28} + \cdots + \mathrm{C}_{32})] \qquad (1)$$

The heights or the areas of the corresponding *n*-alkane peaks in the gas chromatograms of the saturated hydrocarbon fractions are taken to measure the ratio. The nature of the organic matter in a sediment will influence the carbon number preference, e.g., by the fact that many aquatic organisms do not synthesize long-chain *n*-alkanes, and if they do there is no predominance of either even or odd carbon numbers. Thus, in a sedimentary basin with varying organic matter supply the *n*-alkane patterns may change unsystematically and independent of the thermal evolution in closely spaced sediment layers. As a qualitative measure, however, the decrease of the carbon number predominance of *n*-alkanes has been applied successfully for maturity assessment in many cases.

More sophisticated analytical techniques are required to monitor the maturity-dependent changes of less abundant components among the hydrocarbons in the bitumen, but the specificity of the compounds and reactions studied justify these efforts. A group of compounds found to change their relative composition in a manner closely related to the increase of vitrinite reflectance through the oil generation zone and beyond are phenanthrene and the four isomeric methylphenanthrenes commonly found in sediments (**13**; numbers indicate the positions of methyl substitution).



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With increasing depth, the relative abundances of 1- and 9-methylphenanthrene decrease and those of 2- and 3-methylphenanthrene increase due to the higher thermodynamic stability of the latter two isomers. A methylphenanthrene index (MPI) was introduced [Eq. (2); MP = methylphenanthrene, P = phenanthrene] and found to correlate positively with vitrinite reflectance at least in sediments which contain a major proportion of terrigenous organic matter:

$$\mathrm{MPI} = 1.5[(2-\mathrm{MP}+3-\mathrm{MP})/(\mathrm{P}+1-\mathrm{MP}+9-\mathrm{MP})] \qquad (2)$$

This is shown for a well in the Elmworth gas field in Western Canada in Fig. 13, where the measured vitrinite reflectance R_m was used to calibrate the vitrinite reflectance equivalent R_c calculated from the methylphenanthrene index:

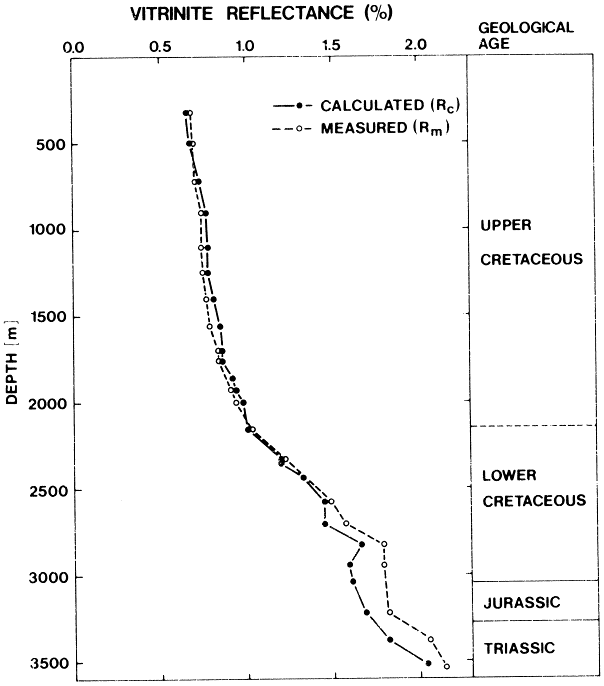


FIGURE 13 Calculated R_c and measured vitrinite reflectance R_m for selected rock samples from a well in the Elmworth gas field. [Reprinted with permission from Welte, D. H., Schaefer, R. G., Stoessinger, W., and Radke, M. (1984). *Mitteilungen des Geologisch-Paläontologischen Instituts der Universität Hamburg* **56,** 263–285. Copyright 1984 Universität Hamburg.]

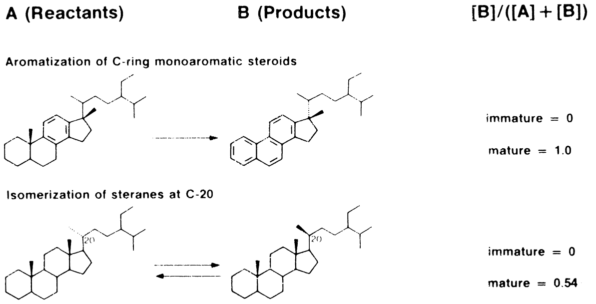


FIGURE 14 Examples of biological marker reactions used for maturity assessment of organic matter in sediments.

$$R_c = 0.60\,\mathrm{MPI} + 0.40 \qquad (3)$$

Biological marker compound ratios based on the product/reactant relationship in apparent diagenetic and catagenetic reactions (like those illustrated in Fig. 6) are molecular maturation parameters widely applied today in petroleum geochemistry. Two of the most common examples are shown in Fig. 14. They monitor the extent of isomerization and aromatization of steroid hydrocarbons by measuring the relative concentrations of the reactants A and products B. In both cases, the initial concentration of the products is zero in immature sediments. The transformation of C-ring monoaromatic into triaromatic steroid hydrocarbons is irreversible and reaches completion within the hydrocarbon-generation zone. The isomerization of C_{29} steranes at C-20 in the side chain is an equilibrium reaction where the natural 20R configuration inherited from the biosynthesized precursor steroids is converted to the 20S configuration. The equilibrium which is reached close to the peak of oil generation is slightly shifted to the right-hand side of the equation in Fig. 14. Both parameters are measured using peak areas (or heights) of characteristic mass spectral fragments in a combined gas chromatographic/mass spectrometric analysis.

More recently it was found, however, that the representation of biological marker reactions as in Fig. 14 is oversimplified. Although aromatization of monoaromatic steroid hydrocarhons to the triaromatic species may indeed occur as shown, the product/reactant ratio at the same time is influenced by the thermal destruction of both the reactant and the product. In fact, at high thermal stress, destruction of the triaromatic steroids is faster than that of the monoaromatic steroids, which leads to a reversal of the compound ratio trend at high maturities after having approached the predicted end value. Isomerization of steranes at C-20 appears not to happen at all in the way shown in Fig. 14. The empirically observed change in the ratio of the 20R and 20S sterane isomers with increasing thermal stress in sediments rather is the combined effect of the neoformation of mixtures of 20R and 20S steranes in the course of thermal hydrocarbon generation from kerogen, which add to the (comparatively small amount of) 20R steranes formed diagenetically in the bitumen fraction as shown for compound **4** in Fig. 6, and the thermal destruction of both isomers at higher temperatures. The isomer ratio of the 20R and 20S sterane mixture newly formed from kerogen follows a temperature-dependent trend with a progressively increasing proportion of the 20S isomer up to the assumed equilibrium ratio also theoretically predicted by molecular mechanics calculation. The reaction rate of thermal destruction is, however, slightly faster for the 20S isomer, so again a reversal of the compound ratio trend is observed at higher maturities. If this behavior is kept in mind, biological marker compound ratios can still be applied successfully in petroleum geochemistry, although some ambiguity may occasionally arise.

C. Oil/Source Rock Correlation

The main objective of oil/oil and oil/source rock correlation is to find out the genetic origin of reservoired hydrocarbons. In a first step, usually a correlation analysis among the various oils (or condensates, gases) from different reservoirs in a producing basin is performed to see if all the oils are uniform in their composition or if they belong to several families of different genetic origin. For each type or family of oils it has to be established if they are derived from a single source rock or if a multiple origin must be considered. The composition of the crude oils will provide some basic information on the characteristics of the organic matter and on the lithology in the source rock(s) as well as on the maturity of the organic matter in the source rock(s) at the time of hydrocarbon generation. Compositional variations due to different maturities must be distinguished from those due to different sources. In a second step, a source must be identified for each oil family by comparison with samples of all possible source rocks. If the conclusion is reached that more than one source characteristic can be attributed to different oil families accumulated in a basin, organofacies variations within a single source rock layer may be the explanation, as well as two or more source rock layers of different age.

If the source(s) of crude oil in a basin are known, this can have important implications for exploration and production strategies. The information will help to define exploration targets and will influence the development of a concept for the stepwise exploration of a sedimentary basin. A mass balance calculation based on volume and thermal maturity of the known hydrocarbon source rocks and a comparison with the already-detected oil in place will help to determine if further exploration is promising. In crude oil production, oil/oil correlations can provide information about the possible communication between different productive zones.

Oil/source rock correlation is based on the concept that oil (condensate or gas) found in a reservoir was generated from kerogen disseminated in a source rock. During expulsion, only a certain proportion of the generated petroleum compounds was released and a significant proportion stayed behind. A correlation thus should be possible between the kerogen in the source rock, the bitumen extractable from the source rock, and the hydrocarbons in the reservoirs. In order to account for the complex chemical and physical processes involved in the generation, migration, and accumulation of hydrocarbons in the subsurface, as many correlation parameters as possible should be used in any correlation study, and both bulk and compositional (molecular) correlation parameters should be considered.

A number of useful correlation parameters for different types of geochemical correlation studies are compiled in Table V. The only bulk parameters included are carbon, hydrogen, and sulfur isotope measurements on whole samples or fractions thereof. Other bulk parameters, such as the API gravity and the distribution of distillation fractions (both for oil/oil correlation), are susceptible to severe alteration during migration and to secondary processes in the reservoir. They should nevertheless not be neglected completely, and any differences observed should be explicable in terms of the geological context of the study area.

TABLE V Correlation Parameters Useful for Different Kinds of Correlation Studies[a]

Type of correlation	Correlation parameter
Gas/gas	Carbon and hydrogen isotopes ($^{13}C/^{12}C$, $^{2}H/^{1}H$)
	Ratios of light hydrocarbons (C_2–C_8)
Gas/oil	Carbon and hydrogen isotopes of single n-alkanes
	Ratios of light hydrocarbons (C_2–C_8)
Oil/oil	Carbon, hydrogen and sulfur isotopes ($^{13}C/^{12}C$, $^{2}H/^{1}H$, ^{34}S,^{32}S)
	Ratios of specific hydrocarbons (e.g., pristane/phytane, pristane/n-C_{17})
	Homologous series (e.g., n-alkane distribution)
	Biological markers (e.g., steranes, triterpanes, aromatic steroid hydrocarbons, porphyrins)
Gas/source rock kerogen	Carbon and hydrogen isotopes
Oil/source rock bitumen	Oil/oil correlation parameters
Oil/source rock kerogen	Carbon and sulfur isotopes Oil/oil correlation parameters applied to the products of kerogen pyrolysis

[a] After Tissot, B. P., and Welte, D. H. (1984). "Petroleum Formation and Occurrence," 2nd ed., p. 548, Springer-Verlag, Berlin and New York.

Compositional correlation parameters should have characteristic compound distributions in both rocks and oils. They should be available over the proper molecular weight range (e.g., for gas/oil correlation) and possibly be present in compound classes of different polarities. They should not be too seriously affected by migration, thermal maturation, and bacterial alteration; i.e., under the given geological conditions the imprint of the source organic matter should be transferred into the hydrocarbon reservoir.

Biological markers offer one of the best correlation tools, first of all due to the high information content in their molecular structures. The characteristic distribution patterns of biological markers in crude oils often can be taken as "fingerprints" of the various organisms that contributed to the source rock. Biological markers have a narrow range of chemical and physical properties, particularly when they occur in the saturated hydrocarbon fractions. Thus, any fractionation occurring, e.g., during migration is likely to affect the whole group of biological markers and not any specific compound preferentially. In addition, biological markers are easily detected in very small concentration by the combination of computerized gas chromatography/mass spectrometry. The presence or absence of unusual biological markers in a crude oil or source rock bitumen is often highly significant, whereas other biological markers such as hopanes inherited from bacteria are ubiquitous in all geological samples and thus less specific. Many biological markers are not easily degraded in the course of microbial attack to reservoir hydrocarbons; i.e., they survive mild or even moderately severe biodegradation. The maturity effect on a great number of biological markers is known, and thus corrections and extrapolations to account for additional thermal stress are possible. There are a few disadvantages to the use of biological markers for oil/oil and oil/source rock correlation. These include the limited thermal stability of these compounds, i.e., their application is often restricted to the generation zone below the peak of oil generation. In addition, the low concentrations of the biological markers are sensitive to mixing effects in the subsurface and to contamination.

D. Experimental Simulation of Petroleum Formation

Studying the processes of petroleum formation by field observations is hampered by the fact that these processes occur in nature over periods of geological time and in an open system. Thus, many attempts were made in the past to simulate hydrocarbon generation in a well-defined confined system in the laboratory using elevated temperatures as a compensation for geological time. Hydrous pyrolysis has turned out to be the method which appears to mimic the natural processes most closely.

In this experiment, pieces of organic matter-rich rock are heated in an autoclave in the presence of water at temperatures between about 300°C and near the critical-point temperature of water (374°C) for periods of, typically, 3 days or longer. The products are an expelled oil-type phase floating on the water and a bitumen fraction retained in the rock chips. Figure 15 summarizes the variations in the amounts of kerogen, bitumen, and expelled oils for a series of experiments at different temperatures using a sample of Woodford Shale, a Devonian-Carboniferous source rock from Oklahoma, as substrate. Physically, chemically, and isotopically, the expelled oil is similar to natural crude oils. Hydrous pyrolysis experiments in this way have not only provided useful information on the bulk processes of petroleum formation, but also on their kinetics, on thermal maturity indices, and on primary migration.

E. Modelling of Geological and Geochemical Processes

The successful application of the principles of hydrocarbon generation and migration to petroleum exploration and the increasing knowledge about the chemical and physical parameters that determine the fate of organic matter in the subsurface have stimulated efforts in developing a more quantitative handling of the related geological and geochemical processes. A comprehensive quantitative approach in terms of a mathematical model would allow a more precise prediction of the quantities of hydrocarbons generated in a sedimentary basin and a better understanding of the timing of any event in the course of hydrocarbon generation, migration, and accumulation.

The first step in this direction was the calculation of the maturity of organic matter in a specific sediment based on reconstruction of the burial history and the knowledge (or assumption) of depth-dependent temperature variations in the basin. The basic concept was that generation of hydrocarbons follows simple first-order reaction kinetics, i.e., the reaction rate approximately doubles during each 10°C increase of temperature. The burial history curve, constructed using geological information, defines the time a sediment in the geological past spent within a certain depth (or temperature) interval. If the temperature factors for each 10°C temperature interval, increasing by exponentials of 2 in each step, are multiplied with the time (in millions of years) a time–temperature index (TTI) is obtained for each temperature interval. A summation of these index values provides a TTI value representing the total

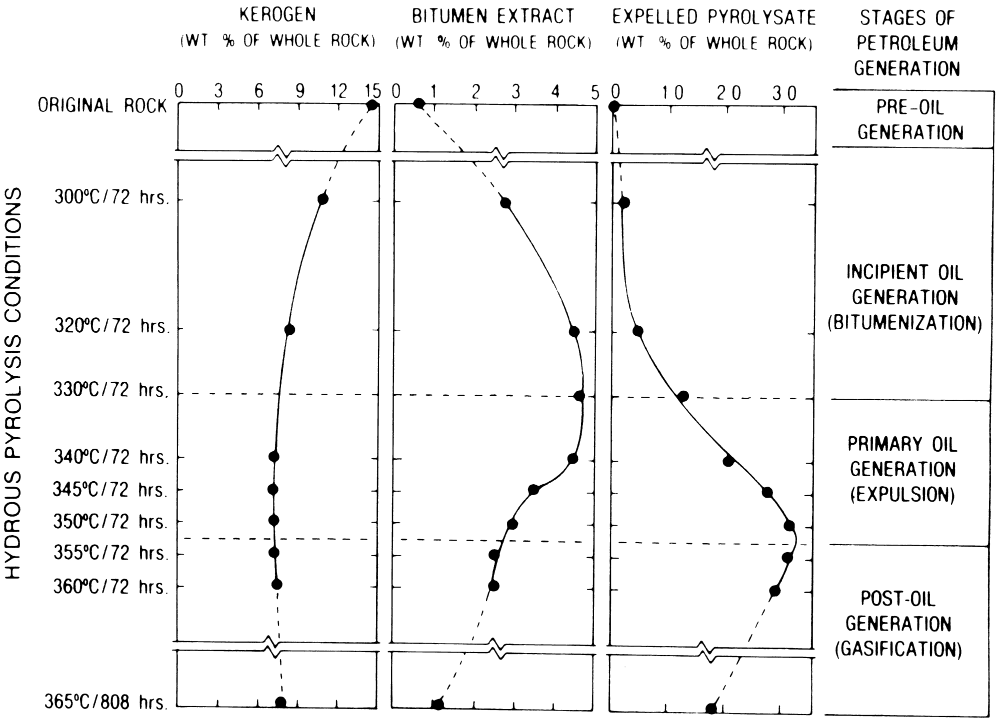


FIGURE 15 Variations in the amounts of kerogen, bitumen, and expelled oil (pyrolyzate) in series of hydrous pyrolysis experiments using Woodford Shale. [Reprinted with permission from M. D. Lewan (1983). *Geochim. Cosmochim. Acta* **47,** 1471–1479. Copyright 1983 Pergamon Press, Oxford.]

thermal evolution of the sediment. The TTI values must be calibrated against vitrinite reflectance (or hydrocarbon yields) to be a predictive, albeit simple, tool.

A considerably more sophisticated numerical treatment of hydrocarbon generation and migration starts with the three-dimensional determination of the development of a sedimentary basin using a deterministic model. Starting at a time T_0 when only the basement existed, sedimentation is followed by the model in predetermined time intervals until the present status (T_x) is reached (Fig. 16). The model continuously calculates the depth-related changes in such parameters as pressure, porosity, temperature, and thermal conductivity for each sediment layer. Mathematical equations control that a mass balance (e.g., sediment supply and water leaving the system) as well as an energy balance (e.g., heat flow from basement and energy loss to the atmosphere or as heated water) are maintained. The results of the model are compared to the real system (well and surface information), and the model approaches the real system by a series of iteration steps. As soon as the geological model is sufficiently accurate, organic matter maturity, hydrocarbon generation yields, and migration directions can be determined for each sediment layer in the basin and for each time slice in the past (Fig. 17). For this latter step a simple maturation calculation like that of the TTI values can be used. A more detailed maturation and hydrocarbon generation model will use ranges of activation energies for the different bond types in a kerogen and for different kerogen types. It will also take into account the fact that the reaction conditions will change with increasing maturation of the organic matter.

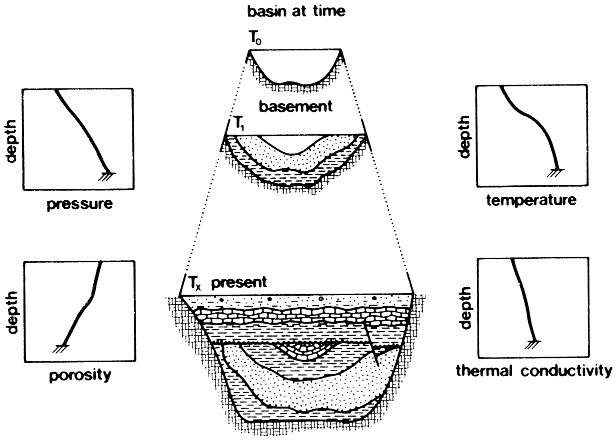


FIGURE 16 Evolution of a sedimentary basin from an initial condition at time T_0 to the present configuration at time T_x with schematic depth-related changes of physical parameters such as pressure, porosity, temperature, and thermal conductivity. [Reprinted with permission from Tissot, B. P., and Welte, D. H. (1984). "Petroleum Formation and Occurrence," 2nd ed., p. 576, Springer-Verlag, Berlin and New York. Copyright 1984 Springer-Verlag.]

V. ORGANIC GEOCHEMICAL TECHNIQUES IN PALEOENVIRONMENTAL AND PALEOCLIMATIC ASSESSMENT

While organic geochemistry in petroleum exploration focuses mainly on deeply buried sedimentary rocks, shallow sediments play an important role in understanding the global organic carbon cycle and in reconstructing past climatic and oceanographic developments. Since the mid-1970s, the international Deep Sea Drilling Project and later the Ocean Drilling Program have provided the numerous sediment cores necessary to perform such studies. In the following, a few selected approaches and techniques are outlined to illustrate how organic geochemistry contributes to these interdisciplinary objectives.

A. Marine versus Terrigenous Organic Matter

Even deep-sea sediments deposited in areas remote from continents usually contain a mixture of marine and terrigenous organic matter. For any investigation of marine paleoproductivity or marine organic matter preservation, the amount of terrigenous admixture has to be known. Furthermore, global or regional climate fluctuations have changed the pattern of continental runoff and ocean currents in the geological past. Being able to recognize variations in marine and terrigenous organic matter proportions, thus, is of great significance in paleoclimatic and paleoceanographic studies.

A variety of parameters are used to assess organic matter sources. Bulk parameters have the advantage that they are representative of the total organic matter, whereas molecular parameters address only part of the extractable organic matter, which in turn is only a small portion of total organic matter. Several successful applications of molecular parameters have shown that the small bitumen fraction may be representative of the total, but there are some examples for which this is not the case. On the other hand, oxidation of marine organic matter has the same effect on some bulk parameters as an admixture of terrigenous organic matter, because the latter is commonly enriched in oxygen through biosynthesis. It is, therefore, advisable to rely on more than one parameter, and to obtain complementary information.

1. C/N Ratio

Atomic carbon/nitrogen (C/N) ratios of living phytoplankton and zooplankton are around 6, freshly deposited marine organic matter ranges around 10, whereas terrigenous organic matter has C/N ratios of 20 and above. This difference can be ascribed to the absence of cellulose in algae and its abundance in vascular plants and to the fact that algae are rich in proteins.

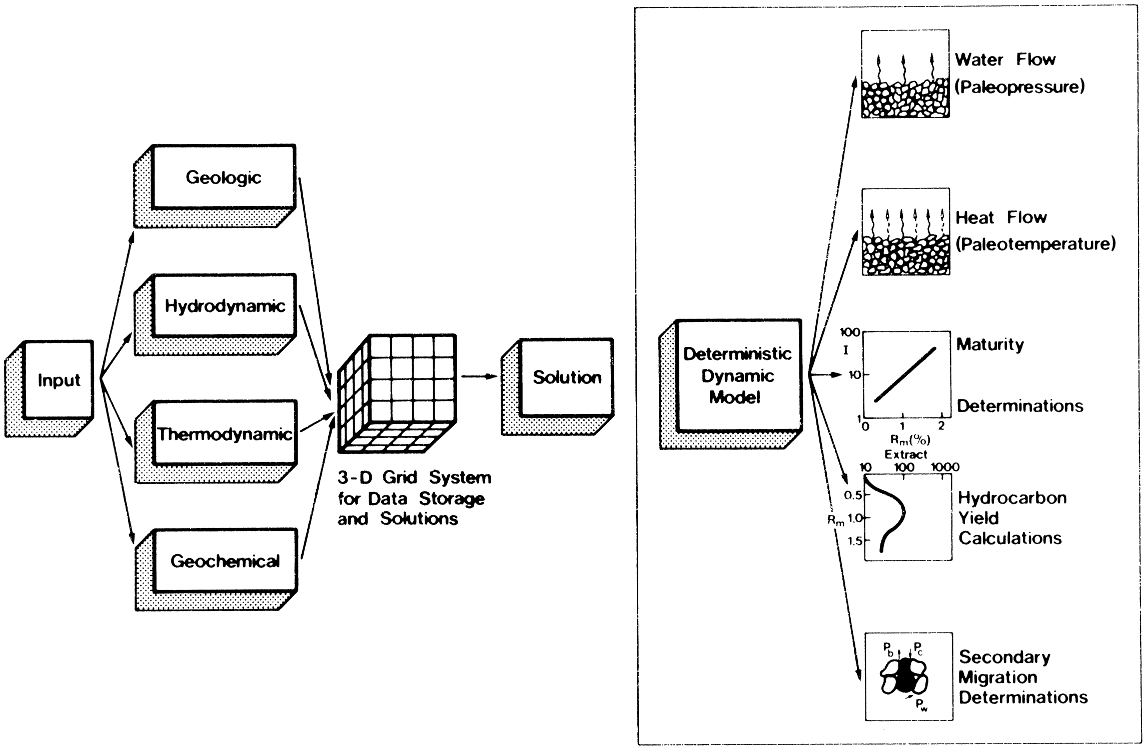


FIGURE 17 Development of a three-dimensional dynamic model. Groups of input parameters and results are schematically shown. [Reprinted with permission from Tissot, B. P., and Welte, D. H. (1984). "Petroleum Formation and Occurrence," 2nd ed., p. 578, Springer-Verlag, Berlin and New York. Copyright 1984 Springer-Verlag.]

Selective degradation of organic matter components during early diagenesis has the tendency to modify (usually increase) C/N ratios. Still, they are commonly sufficiently well preserved in shallow marine sediments to allow a rough assessment of terrigenous organic matter contribution. Care has to be taken in oceanic sediments with low organic carbon contents, because inorganic nitrogen (ammonia) released during organic matter decomposition may be adsorbed to the mineral matrix and add significantly to the amount of total nitrogen. The C/N ratio is then changed to values lower than those of the real marine/terrigenous organic matter proportions. This effect should be small in sediments containing more than 0.3% organic carbon.

2. Hydrogen and Oxygen Indices

Hydrogen indices from Rock-Eval pyrolysis (see Sect. IV.A) below about 150 mg hydrocarbons (HC)/g total organic carbon (TOC) are typical of terrigenous organic matter, whereas HI values of 300–800 mg HC/g TOC are typical of marine organic matter. Oceanic sediments rich in organic matter sometimes exhibit values of only 200–400 mg HC/g TOC, even if marine organic matter strongly dominates. Oxidation during settling through a long water column in these cases has lowered the hydrogen content of the organic matter. Rock-Eval pyrolysis cannot be used for sediments with TOC $< 0.3\%$, because of the so-called mineral matrix effect. If sediments with low organic carbon contents are pyrolyzed, a significant amount of the products may be adsorbed to the sediment minerals and are not recorded by the detector, thus lowering the hydrogen index.

3. Maceral Composition

If the morphological structures of organic particles in sediments are well preserved, organic petrographic investigation under the microscope is probably the most informative method to distinguish marine from terrestrial organic matter contributions to marine sediments by the relative amounts of macerals derived from marine biomass and land plants (see Sect. II.E.1). Many marine sediments, however, contain an abundance of unstructured organic matter which cannot easily be assigned to one source or the other.

4. Stable Carbon Isotope Ratios

Carbon isotope ratios are useful principally to distinguish between marine and terrestrial organic matter sources in sediments and to identify organic matter from different types of land plants. The stable carbon isotopic composition of organic matter reflects the isotopic composition of the carbon source as well as the discrimination (fractionation) between ^{12}C and ^{13}C during photosynthesis. Most plants, including phytoplankton, incorporate carbon into their biomass using the Calvin (C_3) pathway, which discriminates against ^{13}C to produce a shift in $\delta^{13}C$ values of about $-20‰$ from the isotope ratio of the inorganic carbon source. Organic matter produced from atmospheric carbon dioxide ($\delta^{13}C \approx -7‰$) by land plants using the C_3 pathway (including almost all trees and most shrubs) has an average $\delta^{13}C$ value of approximately $-27‰$. Marine algae use dissolved bicarbonate, which has a $\delta^{13}C$ value of approximately 0‰. As a consequence, marine organic matter typically has $\delta^{13}C$ values varying between $-18‰$ and $-22‰$.

The "typical" difference of about 7‰ between organic matter of marine primary producers and land plants has been used successfully to trace the sources and distributions or organic matter in coastal sediments. Unlike C/N ratios, $\delta^{13}C$ values are not significantly influenced by sediment texture, making them useful in reconstructing past sources of organic matter in changing depositional conditions. Figure 18 shows the fluctuations of organic matter $\delta^{13}C$ values in a short sediment core from a tidal flat caused by a variable admixture of eroded peat ($\delta^{13}C = -27‰$) to marine organic matter mainly from diatoms ($\delta^{13}C = -19‰$). If the carbon isotope values of the end members in a two-component system are known, the relative contributions can be easily determined by a simple linear mixing algorithm.

The availability of dissolved CO_2 in ocean water has an influence on the carbon isotopic composition of algal organic matter because isotopic discrimination toward ^{12}C increases when the partial pressure of carbon dixide (pCO_2) is high and decreases when it is low. Organic matter $\delta^{13}C$ values, therefore, become indicators not only of the origin of organic matter but also of changing paleoenvironmental conditions on both short- and long-term scales. For example, the $\delta^{13}C$ values of dissolved inorganic carbon (DIC; i.e., CO_2, bicarbonate, and carbonate) available for photosynthesis varies over the year with the balance between photosynthetic uptake and respiratory production. During spring and summer, when rates of photosynthesis are high, the isotope ratio of the remaining DIC is enriched in ^{13}C. In fall, when respiration is the dominant process, the $\delta^{13}C$ of DIC becomes more negative because organic matter is remineralized.

Fluctuations in the $\delta^{13}C$ values of sedimentary organic matter over the earth's history can, thus, be interpreted in terms of the productivity in the water column and the availability of DIC in a particular geological time period. In a study of sediments from the central equatorial Pacific Ocean spanning the last 255,000 years, it has been demonstrated that the carbon isotopic composition

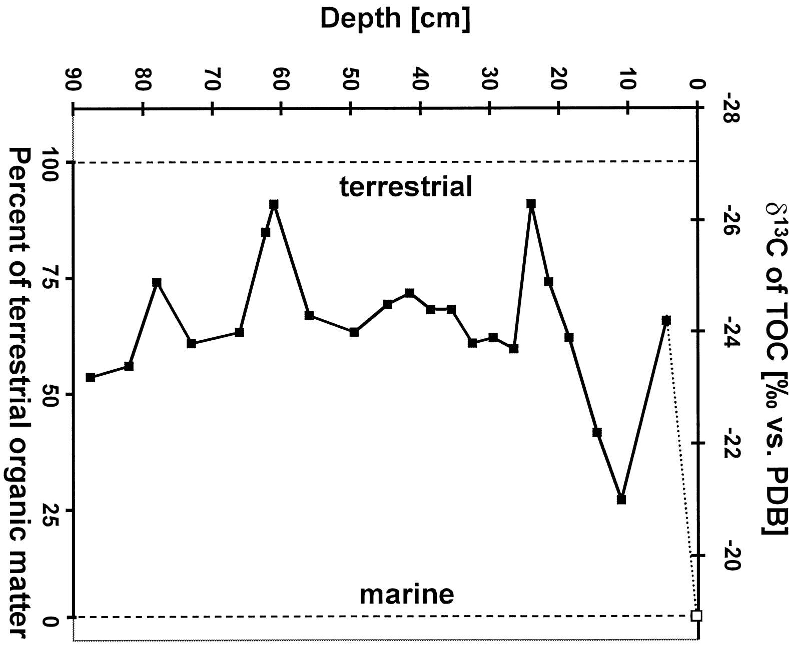


FIGURE 18 Variation of bulk $\delta^{13}C$ values of organic matter in a sediment core from a tidal flat in northern Germany. The variation is due to a variable mixture of marine organic matter ($\delta^{13}C = -19‰$) and of locally eroded peat (terrigenous organic matter; $\delta^{13}C = -27‰$). The relative percentages are calculated using a linear mixing algorithm.

of fossil organic matter depends on the exchange between atmospheric and oceanic CO_2. Changes with time can then be used to estimate past atmospheric carbon dioxide concentrations.

A new type of geochemical information became available with the development of a combined capillary column gas chromatography–isotope ratio mass spectrometry system. This instrument provides the carbon isotope signal ($^{13}C/^{12}C$) of single biological marker compounds in complex mixtures. The resulting data allows assignment of a specific origin to some of these compounds because, for example, the biomass of planktonic algae has a carbon isotope signal completely different from that of land plants or methanotrophic bacteria, due to the different carbon isotope ratios of the carbon sources used by these groups of organisms. This adds another dimension to the understanding of geochemical reaction pathways. The main advantage of the new technique is that a great number of compounds can be analyzed directly within a short time in small quantities and without the need of their tedious isolation.

B. Molecular Paleo-Seawater Temperature and Climate Indicators

1. Past Sea-Surface Temperatures (SST) Based on Long-Chain Alkenones

Palaeoceanographic studies have taken advantage of the fact that biosynthesis of a major family of organic compounds by certain microalgae depends on the water temperature during growth. The microalgae belong to the class of Haptophyceae (often also named Prymnesiophyceae) and notably comprise the marine coccolithophorids *Emiliania huxleyi* and *Gephyrocapsa oceanica*. The whole family of compounds, which are found in marine sediments of Recent to mid-Cretaceous age throughout the world ocean, is a complex assemblage of aliphatic straight-chain ketones and esters with 37 to 39 carbon atoms and two to four double bonds, but principally only the C_{37} methylketones with two and three double bonds **(14)** are used for past sea-surface temperature assessment.

It was found from the analysis of laboratory cultures and field samples that the extent of unsaturation (number of double bonds) in these long-chain ketones varies linearly with growth temperature of the algae over a wide temperature range. To describe this, an unsaturation index ($U_{37}^{K'}$) was suggested, which is defined by the concentration ratio of the two C_{37} ketones:

$$U_{37}^{K'} = [C_{37:2}]/[C_{37:2} + C_{37:3}]. \tag{4}$$

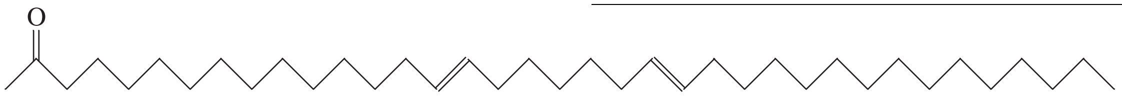
Calibration was then made with the growth temperatures of laboratory cultures of different haptophyte species and with ocean water temperatures at which plankton samples had been collected. From these data sets, a a uniform calibration for the global ocean from 60°N to 60°S evolved and can be used to estimate the ocean surface temperatures in the geological past:

$$U_{37}^{K'} = 0.033T + 0.043, \tag{5}$$

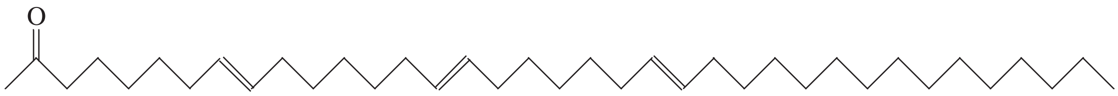
where T is the temperature of the oceanic surface water (SST) in degrees Celsius. The example in Fig. 19 shows pronounced SST variations between the different oxygen isotope stages (OIS) which represent cold (even numbers) and warm periods (odd number). The last glacial maximum (18,000 yr B.P.), for example, falls into OIS 2, the present interglacial (Holocene) is equivalent to OIS 1, and the last climate optimum (Eemian, 125,000 yr B.P.) occurred early in OIS 5.

2. ACL Index Based on Land Plant Wax Alkanes

In marine sediments, higher-plant organic matter can be an indicator of climate variations, both by the total amount indicating enhanced continental runoff during times of low sea level or of humid climate on the continent and by specific marker compounds indicating a change in terrestrial vegetation as a consequence of regional or global climatic variations. Long-chain *n*-alkanes are commonly used as the most stable and significant biological markers of terrigenous organic matter supply. The odd-carbon-numbered C_{27}, C_{29}, C_{31}, and C_{33} *n*-alkanes, major



$C_{37:2,}$ heptatriaconta-15E,22E-dien-2-one



$C_{37:3,}$ heptatriaconta-8E,15E,22E-trien-2-one

14

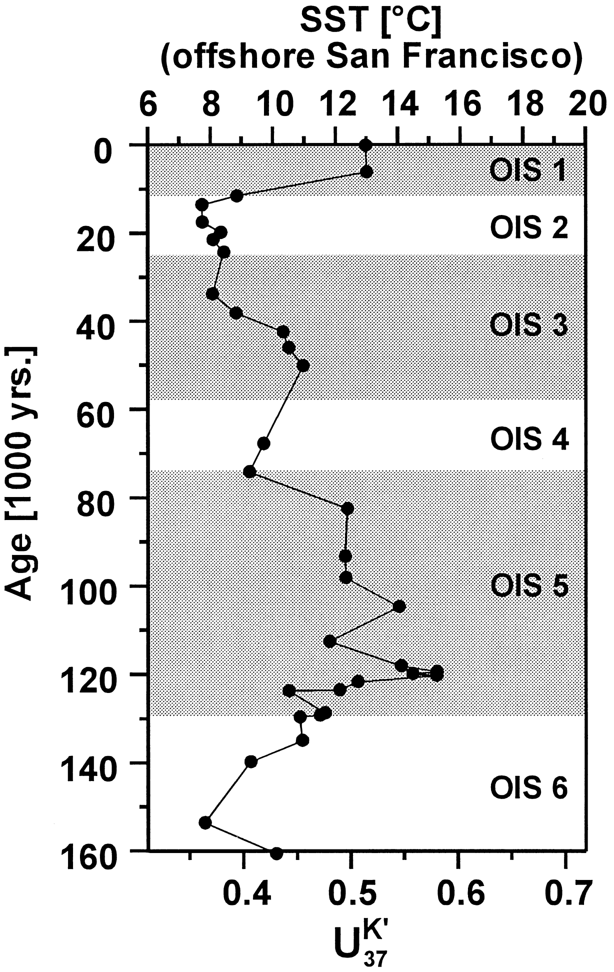


FIGURE 19 Changes of paleaosea surface temperatures (SST) on the California continental margin during the last 160,000 years estimated from the relative proportions of di- and triunsaturated long-chain ketones extracted from deep-sea sediments recovered by the Ocean Drilling Program.

components of the epicuticular waxes of higher plants, are often preferentially enriched in the marine environment.

The carbon-number distribution patterns of *n*-alkanes in leaf waxes of higher land plants depend on the climate under which they grow. The distributions show a trend of increasing chain length nearer to the Equator, but they are also influenced by humidity. Based on these observations, an average chain length (ACL) index was defined to describe the chain length variations of *n*-alkanes:

$$\mathrm{ACL}_{27-33} = (27[\mathrm{C}_{27}] + 29[\mathrm{C}_{29}] + 31[\mathrm{C}_{31}] + 33[\mathrm{C}_{33}])/ \\ ([\mathrm{C}_{27}] + [\mathrm{C}_{29}] + [\mathrm{C}_{31}] + [\mathrm{C}_{33}]), \qquad (6)$$

in which $[\mathrm{C}_x]$ signifies the concentration of the *n*-alkane with x carbon atoms. Sedimentary *n*-alkane ACL values were demonstrated to be sensitive to past climatic changes. In Santa Barbara basin (offshore California) sediments from the last 160,000 years, the highest ACL values were found in the Eemian climate optimum (125,000 yr B.P.). The ACL variations recorded the climatic changes on the continent, because vegetation patterns on the continent responded rapidly to climatic oscillations, which were often characterized by drastic changes of temperature and precipitation. In addition, changes in continental precipitation significantly affected the degree of erosion and the transport of terrigenous detritus to the ocean.

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