Fundamentals in Organic Geochemistry

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Fossil Matter in the Geosphere

Springer

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Organic Geochemistry is a modern scientific subject characterized by a high transdisciplinarity and located at the edge of chemistry, environmental sciences, geology and biology. Therefore, there is a need for a flexible offer of appropriate academic teaching material (BSc and MSc level) addressed to the variety of students coming originally from different study disciplines. For such a flexible usage the textbook series 'Fundamentals in Organic Geochemistry' consists of different volumes with clear defined aspects and with manageable length. Students as well as lecturers will be able to choose those organic-geochemical topics that are relevant for their individual studies and programs. Hereby, it is the intention to introduce (i) clearly structured and comprehensible knowledge, (ii) process orientated learning and (iii) the complexity of natural geochemical systems. This textbook series covers different aspects of Organic Geochemistry comprising e.g. diagenetic pathways from biomolecules to molecular fossils, the chemical characterization of fossil matter, organic geochemistry in environmental sciences, and applied analytical aspects.

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Preface

In 1933 a four-pages article published by Treibs et al. in the German journal *Angewandte Chemie* pointed for the first time to molecular structures of biogenic origin in fossil matter. This publication opened the door to a new and fascinating scientific field—the Organic Geochemistry.

Since this discipline is located at the interface of geology and organic chemistry its position in academic education is versatile. Organic Geochemistry is part of study programs in chemistry but also in geology, it is located in BSc as well as MSc courses, and students obtain knowledge in this transdisciplinary field in obligatory or optional lessons. The educational experiences of the authors at the University of Belgrade (Serbia) as well as at the RWTH Aachen University (Germany) represent very nicely this complementary character of academic teaching. Organic Geochemistry is on the one hand a facultative lecture in the MSc program of Applied Chemistry at Belgrade University. On the other hand, Organic Geochemistry is teached at RWTH Aachen University as obligatory lecture in geoscientific BSc programes.

In the light of this educational diversity and the obvious need for a very flexible offer of organic geochemical teaching material, the idea arised to create a textbook series for Organic Geochemistry that allows students to pick up those topics in a selectable way, that are useful and essential for their individual studies. Therefore, this textbook series is addressed to BSc as well as MSc students, and to scholars of chemistry as well as geosciences.

The first volume presents an overview on the diversity and properties of fossil material on earth. Organic substances of the Earth's crust are part of one of the major cycles in nature—the carbon cycle. Therefore, this volume focusses on principal aspects about origin and transformation of organic matter in geosphere and, in particular, on the most important forms of fossil organic matter.

Contents

Chapter 1
Origin and Transformations of Organic Matter in Geosphere

Keywords Sedimentary organic matter · Biosphere · Geosphere · Evolution · Blue-green algae · Photosynthetic bacteria · Earth organic matter · Autotrophic organisms · Chlorophyll · Chloroplasts · Glucose · Earth's crust · Sediments · Total organic carbon · Free oxygen · Bound oxygen · Bioproduction · Preservation · Dilution · Diagenesis · Catagenesis · Metagenesis · Metamorphism

To speak about the organic matter in the geosphere means, in fact, to speak about the organic matter in the Earth's crust. This, together with the so-called upper mantle, builds up the lithosphere (Fig. 1.1). It has been estimated that the amount of organic carbon in the biosphere, which has accumulated so far and further transformed in the geosphere, is around 6.4×10^{18} kg. The average annual accumulation of organic carbon in the geosphere since the beginning of life on Earth has been estimated to 3.2×10^{8} kg, which accounts for only about 0.01 % compared to the average annual organic carbon production only in marine environment. Nevertheless, as the organic matter in the geosphere has been accumulating since the appearance of photosynthesis, and then continued during a long geological time (about 2 billion years), its total amount in the geosphere is now about 2000 times larger than the amount of organic matter in the biosphere.

Box 1.1: *General Note*

Knowledge about the origin, amount and forms of organic matter in geosphere is largely the result of searching for an answer to one of the oldest questions of organic geochemistry, the question of the origin of oil. In an effort to better define the origin and manner of oil formation, organic geochemists have proven that the organic substances of the Earth's crust are very heterogeneous in composition, the origin and age, and are part of the organic material of biosphere that has been incorporated in the sediments, and then continued to change through physical, biochemical and chemical processes.

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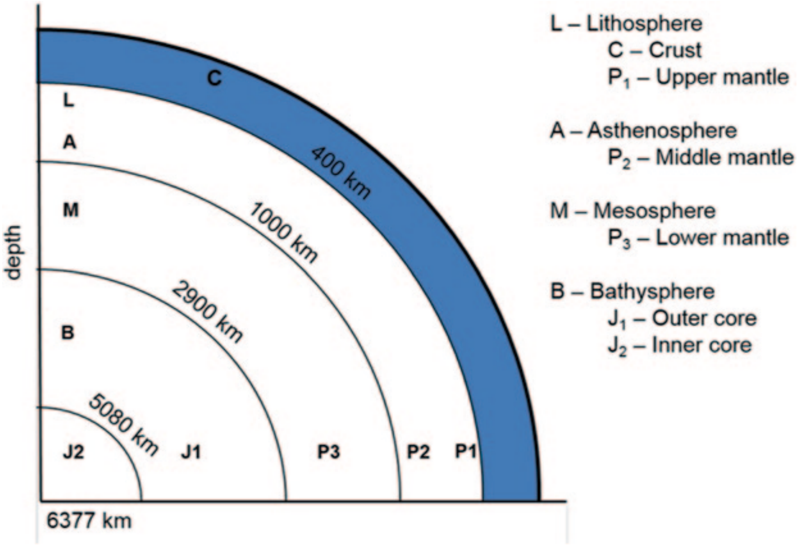

Fig. 1.1 The general structure of Earth

1.1 Evolution of Biosphere

Outline

Sedimentary organic matter originates from the living organic matter and its metabolic products. Considering the genetic relationship between organic matter of bio- and geosphere, the evolution of the biosphere will be shown in detail.

In the Precambrian (about 2 billion years ago) blue-green algae and photosynthetic bacteria were the only producers of organic matter. During the Cambrian, Ordovician and Silurian, dominant source of organic carbon were different marine phytoplankton organisms, bacteria and blue-green algae, until the appearance of terrestrial plants in the Middle Devonian. Even today, marine phytoplankton and bacteria account for 50–60 % of the world production of organic carbon. Abundance of phytoplankton through the geological history of Earth is illustrated in Fig. 1.2a.

The first period of great phytoplankton production in the Precambrian and early Paleozoic, is characterized by blue-green algae as the most primitive unicellular and multicellular plants and some green algae with a cellulose membrane. These algae do not have a membrane reinforced with carbonate or silicate material. The second maximum in the Upper Jurassic, Cretaceous and Tertiary is characterized by algae *Monodophytae*, including *Coccospherales* (*nanoplankton* with calcium carbonate plates in the outer part of the membrane), *Silicoflagellates* (with genuine siliceous skeleton) and *Dinoflagellates* (with the cell wall made up of cellulose or chitin). An important group of phytoplankton in the Cretaceous and Tertiary is represented by siliceous algae, *Diatoms*.

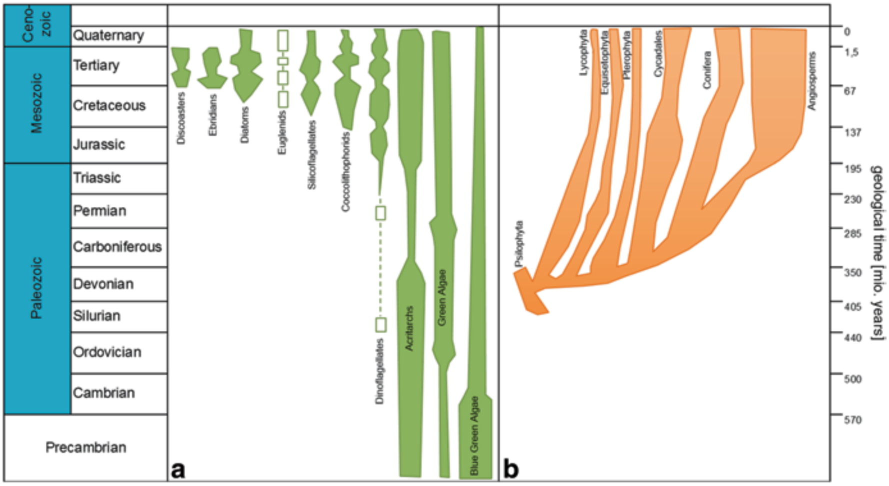

Fig. 1.2 Abundance of certain groups of phytoplankton (**a**), and higher terrestrial plants (**b**) and their total distribution through geological history. (According to Tissot and Welte 1978, 1984)

Fossil remains of bacteria are ineligible for quantification because of microscopic or submicroscopic size and lack of solid particles. However, specimens of fossilized bacteria have been found in all geological times, including the Precambrian. Fossilized bacteria of later periods are often combined with organic matter such as plant tissue and animal and insect residues. Most of fossilized bacteria are genetically similar to today's forms.

Bacteria and blue-green algae are unicellular organisms in which cell protoplast is not differentiated into cytoplasm and a nucleus. Bacteria and blue-green algae, therefore, belong to the *prokaryotes*, unlike all other organisms that are called *eukaryotes* and have a cell nucleus.

Bacteria are metabolically very flexible, what allows them to live virtually everywhere. They can be heterotrophic or autotrophic (with the possibility of photosynthesis without producing oxygen), or both. They are the best example of "evolutionary success". Relying completely on their own adaptability, they were not limited in the survival and development through geological time. The remains of extinct bacteria are second in contribution to organic matter preserved in sediments, after phytoplankton.

Phytoplankton and bacteria are followed by higher plants regarding their proportion in the organic matter of sediments. As it can be seen in Fig. 1.2b, the remains of higher plants in the sediments appear in the Silurian, to be slightly more abundant in the Devonian. Precursors of higher plants evolved in the Precambrian, Cambrian and Ordovician. These are, in order of development, marine blue-green algae, green algae and, finally, higher algae such as seaweed and similar species. The evolution of land plants begins in the Silurian. Based on fossil spores from that time it can be assumed that only a small number of terrestrial plants were distributed then. Their diversity peaked during the Devonian. Also, microfossils of primitive species that belong to the early ferns, which were widely distributed across the continents at that time, were found in the Upper Silurian. Some of them grew also in the marine environment. Primitive plants were probably without leaves and roots, but they certainly had the vascular system.

During the Lower Devonian, other types of ferns also developed. In the Middle Devonian, most probably a sudden evolution occurred and the highest class of vascular plants appeared in their original form. Unlike plants in the Silurian, plants in the Upper Devonian have few leaves and roots. Upper Devonian land flora is very similar to flora of the Lower Carboniferous. During the Lower Carboniferous, the first seed ferns appeared. *Lepidodendrids* become very frequent. During the Upper Carboniferous, this type of terrestrial flora was maximally represented, with a large number of diverse species. Larger shrubs and trees appeared in large quantities during the Upper Devonian and Carboniferous, making thick forests. Huge masses of trees from these geological periods are a precursor to many of today's coal deposits.

An important moment in the evolution of plants occurred during the Lower Cretaceous, when the characteristics of terrestrial vegetation changed considerably by sudden appearance of *angiosperms*, which soon became the dominant type of terrestrial flora. Although the present vegetation consists of greater number of different angiosperms than it was in the Upper Cretaceous, we can say that the same kind of plants still cover large areas of the continents.

1.2 Photosynthesis

Outline

Photosynthesis is the basis for mass production of organic matter in nature. Hence, this process in connection with the photosynthesizing organism will be discussed here, in particular under geological aspects.

The process of photosynthesis uses the energy of sunlight to convert it into chemical energy. During the reaction hydrogen from water and carbon dioxide from the atmosphere are educts for building up organic substance (primarily glucose), releasing oxygen as a by-product. The released oxygen originates from water molecules:

$$6\,CO_2 + 12\,H_2O \xrightarrow{hv} C_6H_{12}O_6 + 6\,O_2 + 6\,H_2O \qquad (1.1)$$

Autotrophic organisms, like green plants, synthesize polysaccharides, cellulose and starch, and all other necessary components, from glucose.

Photosynthesis is the fundamental process that contributes to the mass production of organic matter on Earth. The first primitive organisms that have contributed to the mass production of organic matter were autotrophic, photosynthetic bacteria and blue-green algae, which in their cells contain relatively free, green pigment chlorophyll (Fig. 1.3), capable of absorbing solar energy. In plants at higher evolutionary stage, chlorophyll is concentrated in chloroplasts of green leaves. Chloroplasts are a kind of photosynthetic "factories".

Although the oldest fossils of bacteria and algae were found on South African rocks which are about 3.2 billion years old, it is considered that only 2 billion years

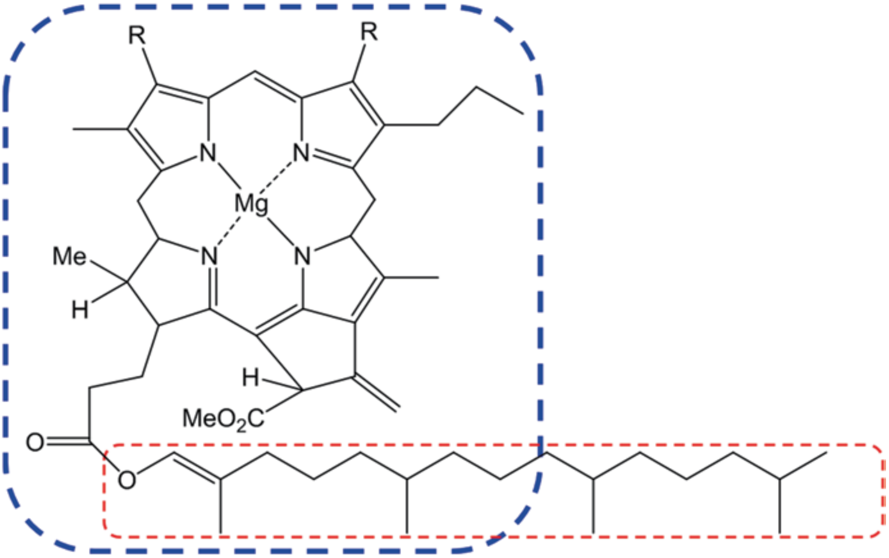

Fig. 1.3 Molecular structure of chlorophyll

ago there was a significant photosynthetic production of organic substances around the Earth. Until then, primitive photosynthetic organisms occurred only sporadically. This is the period when abiogenesis, or chemical evolution, began, with synthesis of organic molecules. The first primitive organisms probably used abiogenically synthesized organic molecules as a source of energy to maintain their metabolism. So, these were heterotrophic organisms because they used abiogenically generated organic matter for their "nutrition". As the population of heterotrophic organisms grew, the amount of abiogenically synthesized organic substances decreased, and photosynthesis gradually became a new source of energy. In other words, heterotrophic organisms became capable of using the energy of sunlight as a supplementary source of energy. Some purple bacteria that exist even today have been among the first ones to show these features. The earliest photosynthetic bacteria were anaerobic ones. This means that during the first phases of photosynthesis development the by-product was not oxygen. Anaerobic bacteria used hydrogen sulphide as a source of hydrogen, so that sulphur was released as a by-product.

Thanks to photosynthesis, and photosynthetic organisms whose populations have suddenly begun to occupy aquatic environment of the planet, the amount of oxygen in Earth's atmosphere was gradually increasing, which until then consisted mainly of hydrogen, methane, ammonia, nitrogen and water. It is believed that oxygen was poisonous to the first primitive organisms, and that the reducing environment was ensured by a considerable amount of Fe^{2+} ion dissolved in water. Fe^{2+} ion bound O_2 produced by photosynthesis, to oxidize to Fe^{3+} ion, which was deposited as an oxide.

Only a relatively narrow area of the total solar radiation can be utilised in the process of photosynthesis, usually one that is visible to the human eye (400–800 nm). Shorter sun's rays, of higher energy, are harmful for living organisms. Different photosynthetic organisms use different parts of the visible spectrum, making it possible for different organisms to live at different depths in a water column.

Some blue-green algae that evolved from photosynthetic bacteria are considered the first organisms to produce oxygen as a by-product of photosynthesis. Although a number of photosynthetic pigments is known, none have ever been as important as chlorophyll. Since autotrophic, photosynthetic organisms, are superior to the heterotrophic organisms, they soon became dominant in the biological world, and the amount of free oxygen in Earth's atmosphere grew continuously for a longer period of time. When photosynthesis has become widespread across the Earth, the conditions were created also for the evolution of higher forms of life.

According to various sources, the average annual amount of carbon in photosynthesized organic matter is $1.5\text{–}7 \times 10^{13}$ kg in oceans, and $1.5\text{–}8 \times 10^{13}$ kg in continental areas. Over geological time scales, production of organic carbon was at the minimum twice: in the Silurian and Triassic, which could be explained by the change in climate or in the amount of available atmospheric carbon dioxide.

Box 1.2: ***General Note***

In the history of Earth, the appearance of photosynthesis is considered one of the most important events. In this process the energy of sunlight is converted into chemical energy, with hydrogen from water building organic substance (glucose) with carbon dioxide from the atmosphere, releasing oxygen as a by-product.

1.3 Accumulation of Organic Carbon

Outline

The conditions for accumulation of organic matter in the geosphere will be introduced and main factors influencing the accumulation are presented. Distributions and amounts of organic carbon of the Earth's crust and free and bound oxygen released by photosynthesis are also discussed.

In order to estimate the total amount of carbon that was involved in photosynthesis over the Earth's history, it is necessary to collect all amounts of organic carbon on Earth, in the ocean water and in sediments. As early as in 1970, it was estimated that total organic carbon and graphite (which originates from organic carbon in the sediments) is about 6.4×10^{18} kg. According to another estimate from 1972, the the total amount of organic carbon is nearly two times higher. However, it includes also "organic" carbon from basalt and other volcanic rocks and the granite and all metamorphic rocks, whose biological origin is uncertain.

Almost the entire quantity of organic carbon on Earth is concentrated in sedimentary rocks. It accounts for a much smaller portion of the total amount of carbon, only about 18 %. Much greater part (about 82 %) is inorganic, carbonate carbon. There is certainly a relationship between organic and carbonate carbon: carbon dioxide from the atmosphere is in equilibrium with carbon dioxide from the hydrosphere. From the aquatic environment, carbonates may be deposited chemically or in a form of some aquatic organisms with calcareous skeleton (conch shells, etc.), building carbonate sediments. On the other hand, carbonate rocks dissolve in water due to equilibrium reactions between CO_3^{2-}, HCO_3^- and CO_2. Primary organic matter is produced by photosynthesis, either directly from atmospheric CO_2, in terrestrial plants, or from CO_2 hydrosphere, in water plants. Terrestrial and marine organic matter, on the other hand, is largely oxidized, so that CO_2 is released back into the atmosphere. Only a tiny quantity of organic carbon of the Earth's crust, including the hydrosphere, is in the living organisms and in soluble form. The largest part of the organic carbon (about 5.0×10^{18} kg) is found in sediments in the bound form. A significant, but still a small part of it (about 1.4×10^{18} kg) is found in metamorphic rocks in the form of material similar to graphite or meta-anthracite (Table 1.1).

Considering that the entire organic carbon in the history of the Earth was produced, directly or indirectly, by photosynthesis, it should be assumed that an adequate amount of oxygen was simultaneously released. It should represent both free and bound oxygen, in the form of oxidized products that are produced during the oxidation of organic and inorganic substances.

Free oxygen is found in the atmosphere and hydrosphere. In the air it accounts for about 20 % by volume, and in hydrosphere, mainly in ocean water, 2–8 mL/L. Bound oxygen is found both in the extinct and in the living organisms, as well as in sulphates (produced by oxidation of various forms of sulphur) and iron oxides that are distributed in the Earth's crust, including the hydrosphere (Table 1.2).

As noted above, the original Earth's atmosphere was reducing. The oxygen produced in the process of photosynthesis was spent for the oxidation of sulphides to

Table 1.1 Organic carbon of the Earth's crust

Source	Amount in 10^{18} kg
Organisms and soluble organic carbon	0.003
Sediments	5.0
Metamorphic rocks of sedimentary origin (60 % of all metamorphic rocks)	1.4
Total organic carbon	*6.4*

Table 1.2 Free and bound oxygen in the Earth's crust and atmosphere (except oxygen in carbonates and silicates)

Source	Amount in 10^{18} kg
Atmosphere	1.18
Oceans	0.02
Biological CO_2	0.16
Soluble marine SO_4^{2-}	2.60
Evaporite SO_4^{2-}	10.20
$FeO—Fe_2O_3$	2.70
Total oxygen	*16.90*

sulphates and Fe^{2+} to Fe^{3+}. The total amount of free oxygen and oxygen bound in this way is estimated at about 16.9×10^{18} kg. The ratio of this amount of oxygen and the estimated amount of organic carbon is similar to the mass ratio of these two elements in the CO_2 molecule: $O_2/C = 16.9/6.4 = 2.64$ ($32/12 = 2.66$). On this basis it can be concluded that most of oxygen, with the exception of oxygen bound to carbonates and silicates, is produced during photosynthesis. Therefore, it was logical that there was a correlation between fossil organic carbon and paleoatmospheric oxygen level.

Box 1.3: *General Note*

Based on data on the total amount of organic carbon in the period when photosynthesis became widespread, it is possible to assess the annual rate of organic carbon accumulation in sediments. It was estimated that the average annual accumulation of organic carbon in the geosphere since the beginning of life on Earth to date was 3.2×10^8 kg, which compared to the average annual production of organic carbon is only about 0.01 %. It is believed that the maximum amount of organic matter that was incorporated into sediments could be as high as 0.1 %. Most of it returned, being degraded by biochemical and physico-chemical processes, and thus recirculated, going mostly to the upper layers of ocean water.

There are known examples of areas in which a much larger amount of organic matter can be preserved. The most famous is the Black Sea in which as much as 4 % of the organic matter is retained in the sediments. Still water, without free oxygen, and without rich benthic life except for anaerobic bacteria, is a highly favourable environment for maximum retention of organic matter in sediments.

1.4 Carbon Cycle in Nature

Outline

The carbon cycle in nature will be explained by considering the formation of sediments rich in organic matter (bioproduction, preservation and "dilution") and transformation of organic matter in sedimentary rocks (diagenesis, catagenesis, metagenesis and metamorphism).

The carbon cycle in nature is illustrated in Fig. 1.4. It is represented by two circular flows. The first, smaller circle (1), which refers to the biosphere, includes about $2.7–3.0 \times 10^{15}$ kg of carbon, with the circulation half-life measured sometimes in days, but sometimes even decades, depending on the lifetime of biopopulations. The second, larger circle (2), which refers to the geosphere, includes the amount

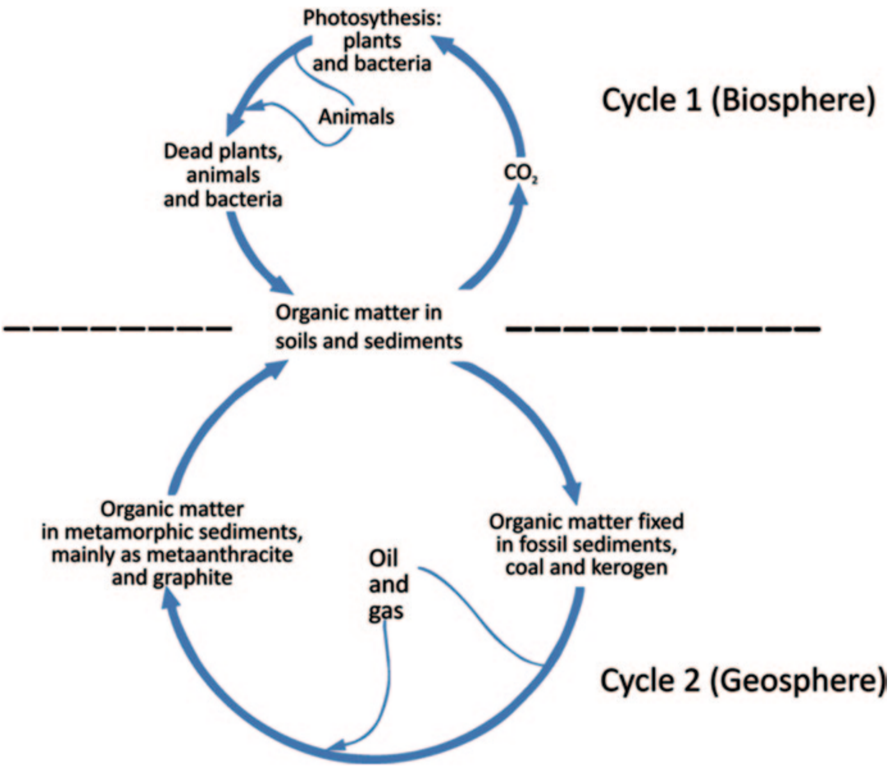

Fig. 1.4 Cycling of carbon in nature. (According to Tissot and Welte 1978, 1984)

of about 6.4×10^{18} kg of carbon with a circulation half-life of several million years. These two circles are connected by a thin bond of around 0.01–0.1 % organic carbon from the biosphere that is permanently incorporated in sediments entering into the geocycle. From the viewpoint of organic geochemistry and petroleum geochemistry in particular, the second cycle is of even greater importance. When organic matter enters the sediment, its further fate is influenced by sedimentation rate and different tectonic disturbances. Namely, subsidence and lowering of sediments to greater depths, or uplift and erosion, will determine whether the organic matter will remain intact, or will be oxidized. Organic matter that, within the geocycle, reaches greater depths due to constant increase of deposit thickness, becomes exposed to diagenesis, catagenesis, metagenesis, and finally metamorphism, which will be discussed later.

1.4.1 Formation of Sediments Rich in Organic Matter

As already mentioned, a very small part of the organic matter of the biosphere (0.01–0.1 %) can be "retained" or "preserved" in sedimentary rocks in the geosphere. As a result of intensive oxidative decomposition of dead organic matter, reinforced by the action of microorganisms, by far the greatest part of it returns to the biological cycle. However, despite this, a small part that avoided the biological cycle during a long geologic time, accumulated in the form of huge amounts of organic material, largely dispersed in fine-grained sedimentary rocks. Clays and shales are richer in organic matter than carbonates, which is, however, richer than the sandstones.

There are three main factors that influence the amount of organic matter that is incorporated in the sedimentary rocks. These are the bioproduction, preservation and "dilution".

1.4.2 Bioproduction

Some of the factors that influence bioproduction are: nutrition, light intensity, temperature, carbonate levels and water. Each of these factors can be further broken down. For example, nutrition depends on the circulation of water, the creation of rocks and their erosion, volcanic activity, paleoclimate and recycling of organic decomposition products.

Food is one of the critical parameters that determine bioproductivity. Shallow seas, with the local circulation of nutrients from decayed organisms and fresh foods of terrestrial origin, are much more productive than the open sea. Distribution of diverse primary photosynthetic production is shown in Fig. 1.5.

Despite the large difference between the total biomass of terrestrial plants (450 billion t) and total biomass of phytoplankton (5 billion t), due to much faster

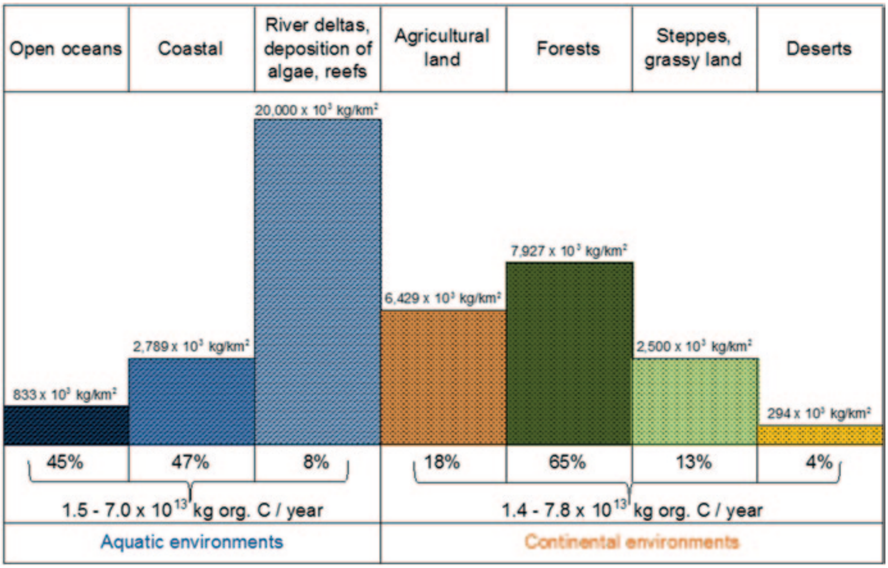

Fig. 1.5 Distribution of photosynthetic primary production

reproduction of lower aquatic organisms, the annual production in both environments is approximately the same. Moreover, due to intense oxidation of terrestrial plant residues in soil, terrestrial organic matter is almost completely oxidized before the residue reaches the sediment.

1.4.3 Preservation

Formation of organic-rich rocks requires depositing of considerable amount of organic material, avoiding processes that take it back into the biosphere. Factors influencing the preservation of organic matter are: the concentration and nature of oxidizing agents, the type of sedimentary organic matter and the sediment accumulation rate. The most important of these three factors are the concentration and nature of oxidizing agents.

Concentration and Nature of Oxidizing Agents

Although a substantial decomposition of organic matter occurs already during the deposition in aqueous media, oxidation is also important in the sediment itself. Figure 1.6 illustrates a typical change in the amount of total organic carbon in oxidizing marine environment. It decreases evenly in the first 300 m depth before it stabilizes at about 0.1 %. This shows that the depth and possibly small organic

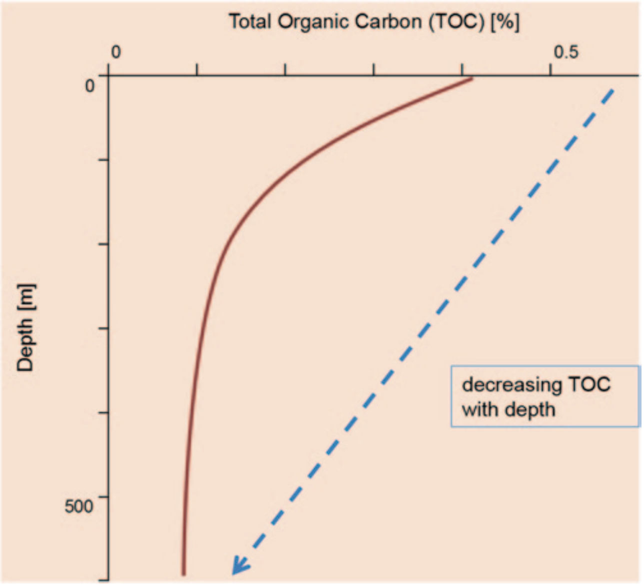

Fig. 1.6 Change of total organic carbon (TOC) with depth

carbon content are the factors that influence the return of organic matter into the biosphere. Microbial activity may decrease at depth, because due to compaction the pores get reduced and the influx of nutrients by water that fills them. On the other hand, the remaining organic matter may have no nutritional value, and the microorganisms stopped taking it as food. Each of these factors may be dominant under different conditions.

Since oxidation processes in water, soils and sediments are mainly a part of biological processes, and most of them need oxygen, the most logical explanation for limiting the oxidative decomposition of organic matter is in the reduction of oxygen. Higher organisms need oxygen to live, although some species can survive with such small amounts as 0.5 mL/L. In comparison, the oxygen content in surface waters is 6 mL/L. If the oxygen concentration is lower, many types of organisms disappear, and some types dwarf, and thus survive in these adverse environments. In environments where the amount of dissolved oxygen is lower than about 0.2 mL/L, the only living beings are those that are called *anaerobes*. These are microorganisms that use sulphate or nitrate ions as electron acceptors in their metabolic processes instead of molecular oxygen. The environment in which they survive is called anoxic. It should be noted that this term does not include environment without oxygen, but the environment with a very small amount of free oxygen.

Anoxic environment is the most important condition for the preservation of organic matter in sediments, because with a limited amount of oxygen changes depend on the anaerobic processes, which, compared to the aerobic ones, are even less efficient and limited to the presence of sulphate or nitrate. Under anoxic conditions, sediments are enriched with organic matter.

It is not always easy to recognize sediments formed under anoxic conditions, because some of the usual indicators of such an environment may lead to error. “Anoxic” sediments always contain a greater amount of total organic carbon, mostly more than 2 %, and as a rule never less than 1 %. However, many sediments deposited in the oxidizing environment may contain a large amount of organic material, especially that which originates from higher plants. Thus, as regards the depositional environment, the values for total organic carbon (TOC) must be taken with caution. Undegraded marine organic matter in sediments is always a good indicator of anoxic depositional environment as marine organic substance is relatively easily used as food by various aerobic organisms. Therefore, its presence in the rocks indicates that biological degradation was stopped prematurely, mainly due to lack of oxygen.

Sediment colour is not always a reliable indicator of depositional environment. All “anoxic” sediments are dark gray or black. However, rocks of black colour are not always rich in organic carbon. Their dark colour may come from the distributed pyrite or similar minerals. The colour should be used only as a negative indicator: if a rock is not expressly dark, it cannot be assumed that it was deposited in the anoxic environment.

Pyrite can also be deceiving. Although pyrite, as it is known, is produced under anoxic conditions, and may indicate a sulphate reduction, its presence is not a sure indication that the seabed environment was anoxic. Such an environment could have been established only after the formation of overlying sediments. In addition, anoxic environment can only be a local phenomenon. Intensive pyritisation of molluscs that live on the seabed confirms that pyrite is not a good indicator of the anoxic seabed at the time of deposition.

Comparison of anoxic conditions at the formation of sediments is particularly important in research of oil deposits. In fact, it was concluded that most of the world's oil was generated in the source rocks deposited under anoxic conditions.

Types of Organic Matter

Different organisms use organic matter of algal origin as food much faster than some other types of organic material, because it contains nutrients that are easily metabolized. It can be argued that this type of organic matter is also very good food for wolverines and birds of prey. It contains a considerable amount of nitrogen and phosphorus, which otherwise are contained in very small amounts in many terrigenous organic materials, especially the woody ones. On the other hand, the phenolic components generated from lignin of terrestrial plants are toxic to many microorganisms, which also limits their degradation. Therefore, at an intense microbial decomposition, algal organic substance disappears first, and material of predominantly terrestrial origin will remain, including cellulose, cuticles and resins, woody part and lignin, which are chemically significantly different to each other. The remaining organic matter, due to the erosion of old rocks, may contain resistant, reworked organic remains, and oxidized organic material which was produced in forest fires.

Sedimentation Rate

Quick sedimentation can significantly contribute to the preservation of organic matter in sediments. For example, it has been proven that the amount of total deposited organic carbon increases with increasing sedimentation rate. It is very easy to conclude that with the rapid sedimentation organic matter is more quickly removed from the zone of microbial decomposition thus reducing the possibility of oxidising and returning to the biosphere.

Rapid filling of the basin occurs with a large influx of inorganic material, inorganic biogenic sediments or organic material. Fast deposition of inorganic materials is characteristic of muddy waters and delta regions. Extremely high accumulation rate of biogenic carbonate and siliceous sediments in areas of high productivity, contribute to the preservation of most of algal remains. Precursor organic matter of coals is also rapidly accumulating, where high concentration of organic material is an ideal condition for the maintenance of oxygen levels low. Fast deposition of organic compounds in the water column is also important, because the intense decomposition occurs during their submersion. A large part of the organic material that reaches the bottom of deep waters is in the form of relatively large grains that are accumulating faster than some phytoplankton species.

Sedimentary organic matter may be *autochthonous*, originating from organisms from the sedimentary environment, *allochthonous*, coming from outside of it, or *reworked*, originating from the decomposition of older sediments.

"Dilution"

Although high accumulation and sedimentation rates contribute to preservation of organic material, the "dilution" of sediments by mineral material can be more significant at very high accumulation rates. Dilution does not reduce the total amount of organic material, but reduces its concentration in the sediment. The outcome is a lower value of total organic carbon in sediment.

The degree of dilution depends on the type and origin of mineral matter. The composition of biogenic sediments in which organic and inorganic material are deposited at the same time, does not depend much on dilution. On the other hand, in oil shales, for example, when the speed of sedimentation is very high, dilution effect is very pronounced.

The Black Sea can serve as an example for conditions that prevail during the formation of organic-rich sediments. In the Black Sea, the main source of organic matter is photosynthesis *in situ*. Unicellular algae play a predominant role in that. The main marine species are, directly or indirectly, dependent on the speed of production. In the entire area covered with water, during the last 2000 years, about 100 g/m^2 of organic material per year was produced by photosynthesis. In addition, a certain amount of organic carbon (less than 10 %) is introduced mainly as detrital material by the Seas of Azov and Marmara and rivers (about one-third of that). Finally, chemosynthesis was a source of organic carbon with estimated annual production of less than 15 g organic carbon/m^2.

The largest portion of the organic carbon that originates in the Black Sea or is introduced into it, oxidizes to CO_2 (in the upper layer of 200 m), thus returning to the biosphere. The amount of carbon that is directly returned to the first carbon cycle accounts for about 80 % of the total amount. A small portion goes to the Marmara and Azov Seas. The remaining part goes to anoxic water below the 200 m of surface, where it undergoes further chemical and microbiological changes.

In the anoxic zone, organic matter oxidized by sulphates slowly and with difficulty, and organic matter that has escaped such oxidation, are in equilibrium with the influx of organic matter from the upper water layer rich in oxygen. A quarter of organic carbon, which entered that area is transferred to the sediment and fossilised, which accounts for about 4 % of the total organic carbon in the Black Sea. This amount is in fact much higher than the average amount of organic carbon which remains in marine sediments. The main reason for the significant preservation of organic matter in the Black Sea is its slow degradation due to lack of oxygen. Quick sedimentation, to some extent, also contributes to the preservation of organic matter. Although, in general, it is difficult to quantify the role of these two factors, in the case of the Black Sea the oxygen deficiency is considered the main cause of significant preservation of organic matter.

In environments such as deltas, quick sedimentation is more important than the impact of anoxic water. For example, the Amazon River adds annually about 10^{13} kg of organic carbon, which is about 100 times more than the annual production in the Black Sea. The Amazon River sediment accounts for about 20 % of total river sediments in the world.

1.4.4 Transformation of Organic Matter in Sedimentary Rocks

As noted above, it is estimated that out of total organic matter from biosphere, after it reaches the surface parts of the geosphere, only 0.01–0.1 % is retained in the sedimentary rocks. The remaining portion is returned to the biosphere.

The transformation of organic substance from geosphere takes place in stages called *diagenesis*, *catagenesis*, *metagenesis* and *metamorphism*. At the very beginning, diagenesis includes changes in the largest portion of the organic matter, the one that returns to the biosphere, and only later the remaining, much smaller portion which remains retained in the sedimentary rock. Therefore, some authors use the terms “early” and “late” diagenesis. Catagenesis and metagenesis are the phases that are specific only for the organic matter of sedimentary rocks. A simplified scheme of these transformations is shown in Fig. 1.7.

As noted above, it is estimated that out of total organic matter from biosphere, after it reaches the surface parts of the geosphere, only 0.01–0.1 % is retained in the sedimentary rocks. The remaining portion is returned to the biosphere. This chapter will address the fate of that small portion of organic matter incorporated into the sediments.

In the first phase, early *diagenesis*, organic matter changes are taking place under mild conditions which are characterised by low temperatures and pressures, while microbial activity is the most intensive one. Basic components of extinct organisms, carbohydrates, proteins, lipids and lignin, after deposition at shallow depths, decompose mainly by the activity of microorganisms. The degree of decomposition depends on the environment in which the sediment is being deposited, especially on its redox properties, but also depends on the toxicity of the environment, as well as the rate of chemical transformations (e.g. poly-condensation) and the protective effects of minerals.

Some parts of the living organic matter are not subject to decomposition, and therefore they retard with no or only small molecular changes. These are usually persistent substances of low chemical reactivity that had a protective role in the living substance (vegetable waxes, resins, some saturated hydrocarbons, etc.).

Most of the degradation products, oligo- and monosaccharides, amino acids and lipids are utilized by microorganisms as their food. In this way, carbon, or CO_2 as a product of metabolic processes, returns to the biological cycle. In addition to CO_2, products of metabolic processes are also H_2O, CH_4, NH_3, N_2 and H_2S. By further

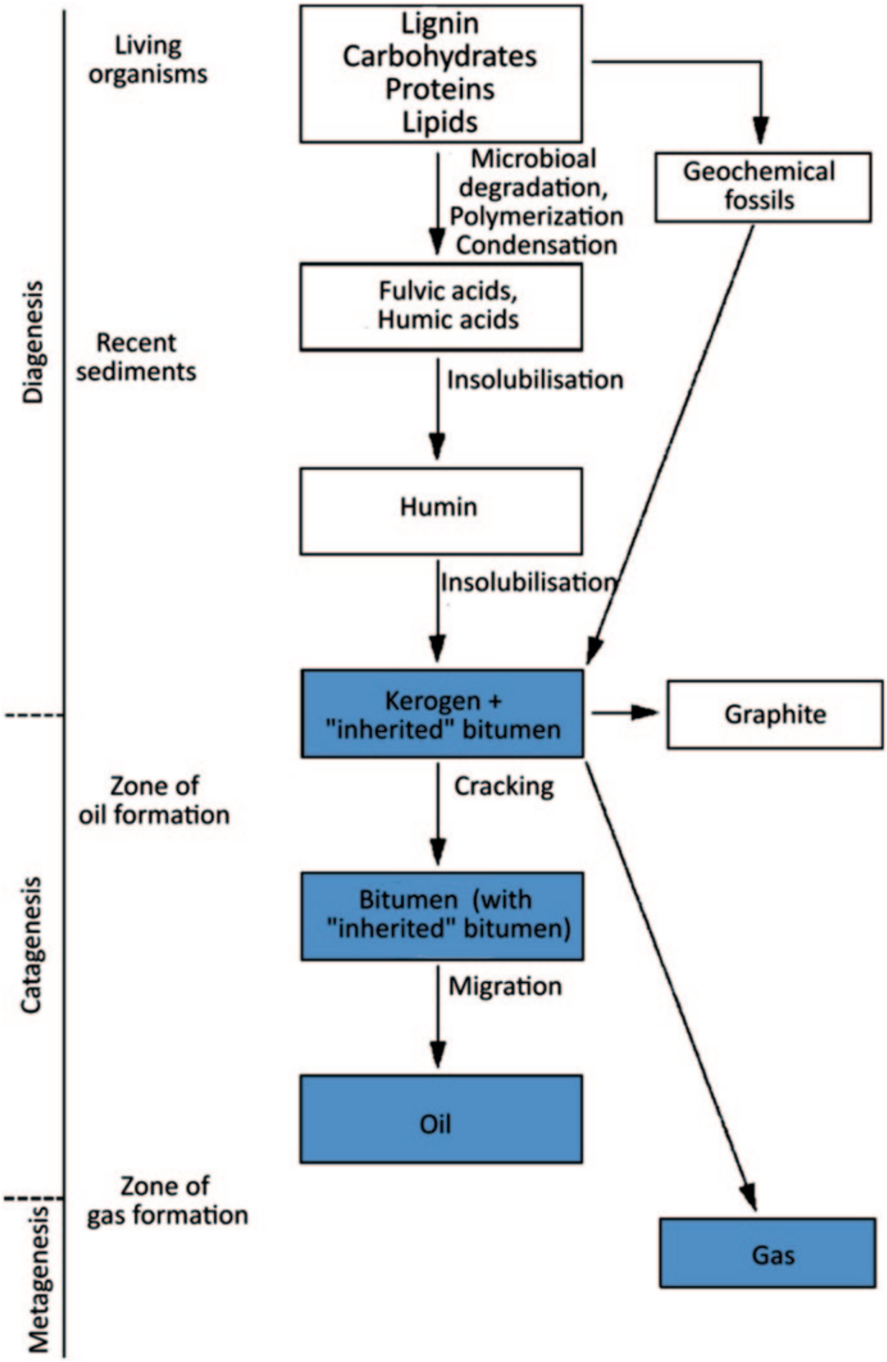

Fig. 1.7 A simplified scheme of the transformation of organic matter in the Earth's crust

oxidation or other chemical process a part of the decomposition products of the organic matter is also converted to the above mentioned degradation products. Much smaller part of it avoids biological recycling or chemical changes, does not break down but builds in sediments. This part presents the main source of sedimentary organic matter. Its transformation in the geosphere starts from the level of formed geomonomers.

In a further, late *diagenesis*, geomonomers polymerise or polycondense to products of the type of fulvic and humic acids, and then humin with increasing molecular weight. Further insolubilisation, releasing carbon dioxide, water, ammonia and methane, leads to formation of kerogen from intermediate geopolymers. Its formation marks the end of diagenesis.

The final and major product of digenetic changes, kerogen, is the insoluble part of organic matter of sedimentary rocks. Apart from it, in a proportionally smaller, soluble part (Fig. 1.7), free hydrocarbons and other lipid compounds can be found as well as substances derived from pigments (isoprenoids, porphyrins) or other metabolites (steroids, terpenoids), which “avoided” polymerisation processes. During the deposition and diagenesis, these compounds largely retain the chemical structure of compounds from the living world, carrying in this way most of the “genetic information” about the precursor organic material. Therefore they are called molecular fossils or biomarkers. The soluble part of the organic matter of sedimentary rocks is called “inherited” bitumen.

By subsidence of initially deposited layers and their further lowering and burial in new sediments, organic matter reaches greater depths, where it becomes exposed to higher pressures and temperatures, and also to the catalytic activity of minerals. Further changes, usually at depths greater than 1000 m, at temperatures of 50–150 °C and pressures of 300–1700 bar, characterise the second phase of the evolution of organic matter in sedimentary rocks called *catagenesis*. Under these conditions, macromolecular kerogen degrades into products that are composed of smaller molecules, soluble in organic solvents, and have the general name of bitumen. So created bitumen is mixed with the inherited bitumen. The degradation of kerogen produces also a considerable amount of gas. Low molecular weight molecules are products of decomposition of C–C bonds, and condensation and defunctionalisation reactions.

Accumulation of bitumen in the sedimentary rocks creates the conditions for its movement/migration. Under favourable conditions, bitumen leaves parent sediment migrating to the reservoir rocks, where it accumulates. Bitumen accumulated in these rocks is oil.

Box 1.4: *General Note*

Taking into account the entire carbon cycle in nature (Fig. 1.4), one can clearly draw a conclusion of the biogenic origin of oil. Earlier abiogenic oil hypothesis by action of water on calcium carbide (at high temperature and pressure), or by action of acid or water on carbides of iron or manganese, are today generally abandoned.

Sedimentary rocks in which sufficient amount of bitumen for the migration is formed or could be formed or in which it has once been formed are called source rocks for oil. The rocks in which bitumen accumulates, as it has been said, are reservoir rocks for oil.

In the final stage of transformation of organic matter in lithosphere, *metagenesis* and *metamorphism*, at depths reaching even ten thousand meters, and under conditions of very high temperatures and pressures, final degradation of kerogen occurs with the release of gas, mainly methane. Kerogen residue is converted to graphite, which represents the end of the last phase of transformation of organic matter in the geosphere.

Besides the larger part of the organic material which undergoes changes resulting from elevated temperature and pressure and catalyst action at greater depths (late diagenesis and catagenesis), a part of the deposited, but already partially modified organic matter remains in the soil, at the surface, and changes in it being exposed to weather conditions (weathering). Finally, evolution of a smaller part of organic matter may be determined also by the change of the site of original deposition as a result of activities of wind or water currents. These changes also assume further decomposition of organic matter to thermodynamically more stable molecules, and the remainder which is usually rich in aromatic structures.

Box 1.5: *General Note*

The form of organic matter in geosphere that has been paid considerable attention in organic-geochemical studies is kerogen. There are many reasons: kerogen is the most common form of organic matter in sedimentary rocks in geosphere, and it is the main ingredient in coals, oil shales, oil source rocks and other rocks with organic matter; second, bitumen, i.e. oil, is produced by kerogen cracking, which means that kerogen is the most important link in the chain leading from the precursor biomass to oil; finally, thanks to its macromolecular nature, kerogen is completely insoluble in organic and inorganic solvents, and represents a specific challenge for the researchers of composition, properties and structure and requires finding of special methods for the analysis. Kerogen is a “link” between different forms of organic matter in geosphere, as they are in close connection with it: either they are on the way to be converted into kerogen (fulvic and humic acids and humin), or are derived from kerogen (bitumen, oil, gas, graphite).

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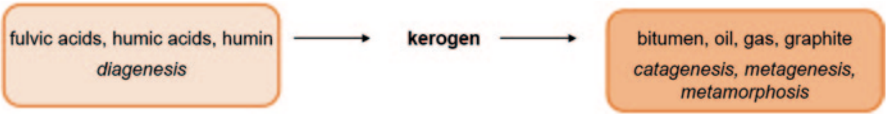
Chapter 2
Main Types of Organic Matter in Geosphere

Keywords Biological markers · *n*-Alkanes · Isoprenoid alkanes · Steranes · Terpanes · Naphthene-aromatics · Composition and structure · Methods · Van Krevelen diagram · Types · Macerals · Source rocks · Maturity · Migration · Reservoir rocks · Oil accumulates · Deasphalting process · Biodegradation · Water washing · Correlation parameters · Aromatics methane · Diagenetic gas · Metagenetic gas · Catagenetic gas · Demethylation

Outline

Most of organic matter forms are either very complex mixtures, or are of the macromolecular nature and complex structure, and in most of them it is possible to distinguish, according to various criteria, between two or more types. The most important types of organic matter in geosphere, bitumen, kerogen, oil and gas, will be discussed in separate chapters.

The most important types of organic matter in geosphere have already been mentioned. These are the fulvic and humic acids, humin, kerogen (in coal, oil shales, source rocks or scattered in the sediments), bitumen, oil, gas and graphite. All these forms are genetically related and are part of the carbon cycle in nature, or carbon cycle in the geosphere (larger circle in Fig. 1.4). Central place in that part of the cycle belongs to kerogen, because some of these forms are organic substances in geosphere on the way to transform into it while others, however, derive from kerogen:



(2.1)

In the transitional phase (diagenesis → catagenesis), “inherited” bitumen is also found in sediments besides kerogen. So it also holds a “central” place among the most important forms of organic matter in geosphere, although in small quantities.

J. Schwarzbauer, B. Jovančićević, *Fossil Matter in the Geosphere,*
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2.1 Bitumen

Outline

Bitumen represents only a small proportion of the total sedimentary organic matter. However, taking into consideration both the fact that it can be the direct precursor of oil, and that it contains also the inherited bitumen with compounds carrying genetic information, organic-geochemical examination of composition of bitumen of different geological samples and its changes during the geological history is of multiple importance. Therefore, it will be discussed in this chapter.

The total bitumen of sedimentary rocks actually consists of two forms (see Fig. 1.7). One is the so-called “inherited” bitumen. It is composed of lipid molecules which were not incorporated into polymeric materials in type of fulvic and humic acids, kerogen and humin during the diagenesis. The second is bitumen that is derived as a product of catagenetic cracking of the kerogen. These two types of bitumen are combined in the sedimentary rocks during the catagenesis (Fig. 1.7). In “total” bitumen the proportion of the second type is dominating (over 95 %). It is actually main precursor of oil, because it is composed mainly of migrated bitumen derived from kerogen cracking. However, despite this quantitative aspect, inherited bitumen is also of great importance, because it contains many compounds with preserved hydrocarbon skeleton of biological precursors. In this way they carry important “genetic information”. Based on some compounds from the inherited bitumen, and based on composition, structure and abundance of this bitumen, it is possible to draw some important information about the origin of oil. In other words, exploration of the composition of the inherited part of bitumen is of great importance because it contributes to the efficiency of prospective oil and gas exploration.

As mentioned, bitumen is largely formed in catagenesis, by kerogen cracking under the influence of heat, pressure and mineral catalysts. Therefore, it would seem more logical to speak about bitumen only after describing kerogen (about its structure, classification into different types, distribution, methods for analysis). However, since the total bitumen in sedimentary rocks comprises also the “inherited” bitumen which was present in the sediment even before the formation of kerogen, and which merged with “catagenetic” bitumen (Fig. 1.7), both types of bitumen will be addressed here. In the text below, the common term “bitumen” will be used to mean the total bitumen. This term should not be confused with bitumen for roads or with the petrographic notion of bitumen.

Bitumen in the lithosphere may be present in the sedimentary rocks in which it has been formed, in some other sedimentary rock to which it migrated, or it can be found accumulated in large quantities in one place, protected by an impermeable rock. Bitumen accumulated in such a rock is called petroleum, and the rock in which it was accumulated is called “trap”, “reservoir” rock, or “collector” rock for petroleum. Sedimentary rock in which bitumen has been formed, in this case, is called the petroleum “source” rock.

Box 2.1: ***General Notes***

Based on the above it can be concluded that the bitumen and petroleum are similar forms of organic matter, provided that the term bitumen is used for the form to the accumulation in reservoir rock, and the term petroleum for the form in the reservoir rock.

In the organic-geochemical literature, bitumen is defined very simply as an organic substance in the geosphere which is soluble in defined common organic solvents. In all types of sedimentary rocks (including source rocks, oil shales, coals), bitumen occurs as free and as bound bitumen. Free bitumen is extracted from the raw sample (bitumen 1). Bound bitumen is extracted from the sample only after removal of carbonate (bound bitumen 2) and silicate minerals (bound bitumen 3). It is an open question whether the bound bitumen is adsorbed on the minerals, or is adsorbed on the surface of kerogen and thus only "protected" by mineral components.

Box 2.2: ***Case Example***

Bound bitumens—Aleksinac oil shale example

In oil shale of Aleksinac deposit (Serbia), the bound bitumens are most probably adsorbed on the kerogen surface and they are protected by mineral components. The same conclusion was reached when in 20 samples of shales of one profile of this deposit, the quantity of bound bitumens 2 and 3 was correlated with the quantities of kerogen, on the one hand, and the quantities of carbonates and silicates as dominant minerals in shale, on the other hand. Due to the fact that the shale is a very homogeneous mixture of minerals and organic matter, a highly significant positive correlation between the quantities of bound bitumens and kerogens led to the above mentioned conclusion (see figure, Jovančićević et al. 1996).

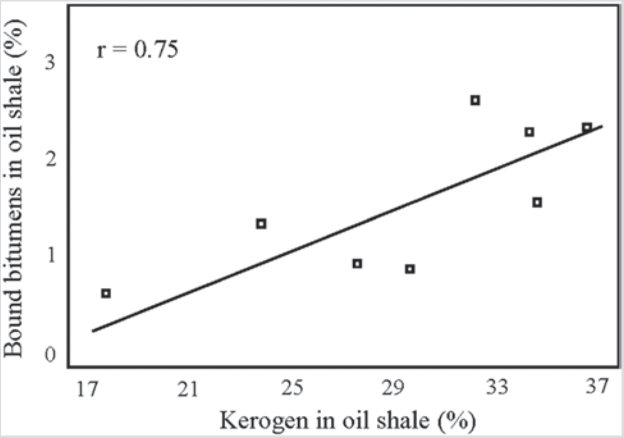


Table 2.1 Bitumen fractions and their main components

Fraction	Components
Saturated hydrocarbons	*n*-Alkanes Isoprenoids and branched hydrocarbons Alicyclic alkanes, including steranes, diterpanes and triterpanes
Aromatic hydrocarbons	Aromatic hydrocarbons Naphthenoaromatic hydrocarbons Small molecules with sulphur
Resins (polar NSO-fraction)	Porphyrins Fatty acids and alcohols Aliphatic and cyclic ketones Sulphuric aliphatic and aromatic compounds
Asphaltenes	Condensed aromatic compounds with a large number of heteroatoms

2.1.1 Composition

Bitumen, the soluble form of organic matter in sedimentary rocks, consists of a high number of different compounds. Some of them are found in relatively large quantities, and others only in traces. In order to investigate the composition more reliably, bitumen is usually first divided analytically into several fractions of different types of chemical compounds (Table 2.1).

The first fraction consists mainly of saturated hydrocarbons: *n*-alkanes, branched hydrocarbons (including isoprenoids), and cyclic and polycyclic hydrocarbons. Saturated hydrocarbons in bitumen have been very well explored so far, as there is a number of reliable analytical methods available for their determination.

The second fraction consists of aromatic compounds and sulphur compounds of small molecular weight. Light aromatic hydrocarbons, such as benzene and toluene, are difficult to determine in bitumen, as they disappear during removal of solvent by which the rock has been extracted. Higher aromatic and naphthenic-aromatic hydrocarbons (compounds formed by aromatization of polycyclic alkanes, the so-called naphthenes), especially those derived from the steroids, were analysed in detail.

The third fraction contains functionalized substances with one or more heteroatoms, dominantly nitrogen, sulphur and oxygen, and is the so-called NSO fraction, polar fraction, or resin. From these fractions, the best explored substance classes were porphyrins, fatty acids and various sulphur compounds.

The fourth, asphaltene fraction, consists of very large molecules highly aromatic in nature, often rich in heteroatoms. Due to their planar structure, asphaltenes tend to set up in "bundles", thus building complex molecules of mass up to about 50,000 Da. Asphaltenes are insoluble in light solvents, and can be separated from bitumen by adding light hydrocarbons such as pentane or heptane. Part of the asphaltene structure is shown in Fig. 2.1.

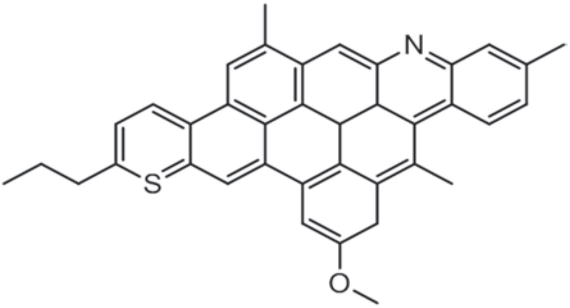


Fig. 2.1 Model of molecular moieties in asphaltenes

Biological Markers

Outline

Initially, only *n*-alkanes, iso-alkanes and anteiso-alkanes, isoprenoid-alkanes, porphyrins, and normal and isoprenoid acids were classified as the biological markers. In the late seventies and early eighties, the introduction of modern instrumental methods of organic analysis to organic geochemical studies, primarily gas chromatography—mass spectrometry analysis, in soluble forms of organic substance in geosphere enabled successful detection of polycyclic alkanes of sterane and terpane types and naphthenic-aromatic compounds. Since then, the interest in these hydrocarbons has been rapidly growing among the organic geochemists. Based on a large number of analyses of biological and geological samples, biological precursor has been presumed for many sterane and terpane isomers in bitumens and oils and paths of their structural and stereochemical changes have been explained. The most important biological markers will be discussed in this chapter.

In the late sixties, compounds that were structurally identical or very similar to compounds that are known to exist in the biosphere were found in bitumens and oils. Such compounds were named “chemical fossils” and they found a wide application in organic geochemical investigations very quickly. Today, in the organic geochemical literature they are often referred to as “biological markers”, or “biomarkers”.

If a compound is to be of interest as a biological marker, it must meet the following requirements: (1) to be stable over a long period of time under the geological conditions, (2) to have hydrocarbon skeleton of specific structure that can be characterized within the known biosynthetic sequences, and (3) not to synthesize in significant quantities by an abiotic way.

The most important biological markers and their biological precursors are listed in Table 2.2.

Table 2.2 Important biological markers and their biological precursors

Biological markers	Precursors
n-Alkanes ($>C_{22}$)	Waxes of terrestrial plants
n-Alkanes (C_{17}, C_{22})	Lipids of algae
Isoprenoids ($<C_{20}$)	Chlorophyll
Isoprenoids ($>C_{20}$)	Lipids or chlorophyll of algae
Porphyrins	Chlorophyll
Steranes	Steroids
Triterpanes	Bacterial triterpenoids
Diterpanes	Constituents of plant resins
Naphthenoaromatic compounds	Steroids, triterpenoids

Box 2.3: *General Notes*

Biological markers are mostly applied to assessment of the origin and degree of maturity of bitumen. They serve as the original parameters due to the fact that during diagenetic and catagenetic changes they preserved the hydrocarbon skeleton which they had in the biosphere. On the other hand, the use of biological markers as maturation parameters is based on the fact that, during the geological history, these compounds are subject to some structural and stereochemical changes that lead to creation of thermodynamically stable geoisomers. The ratio of thermodynamically more stable isomers that were formed and less stable precursors is proportional to the degree of maturity of the total organic matter.

As noted above, the biological markers are present also in oils. However, due to difference in the degree of maturity between petroleum and bitumen in sediments, especially that in recent sediments, the distribution of individual structural and stereochemical isomers of biological markers in them is significantly different. These differences will be discussed in more detail in the section on oil. Here it should be only noted that the source and maturity parameters calculated from the distribution and abundance of biomarkers in bitumens and oils can contribute to detection of petroleum source rocks, assessment of their potentiality, correlation of source rocks and oils, as well as monitoring oil migration routes.

Box 2.4: *Case Example*

Oil—source rock correlation—example of Drmno depression

In the sediments from wells and in the active reservoir rocks from the Drmno depression (southeastern part of the Pannonian Basin) almost all biological markers listed in Table 2.2 were analyzed. Significant similarity was identified both according to maturity and according to the origin, based on which a positive oil-source rock correlation has been defined between the investigated samples of sediments, for the first time within the Drmno depression (Jovančićević et al. 2002).

n-Alkanes

n-Alkanes are a class of organic compounds which was investigated more intensively in the early stages of development of organic geochemistry. In the fifties and sixties, at the beginning of more dynamic development of organic geochemistry, there was a prevailing opinion in the researcher community that *n*-alkanes in geolipids represent simple accumulation of hydrocarbons synthesized in living organisms whose remains have entered into the composition of sediments. Subsequent testing of bitumen in old sediments, and especially of petroleum, have shown a marked difference in the distribution and abundance of *n*-alkanes compared to bitumen in recent sediments, which clearly indicated the transformation of these compounds through the geological history and has led to new investigations in order to explain the origin of *n*-alkanes and mechanism of geogenesis of these hydrocarbons. Sometimes large differences between the *n*-alkane composition of biolipid fractions and oil are expected, since oil represents the total migrated bitumen, and contains mainly *n*-alkanes which occurred by kerogen cracking.

The changes in distribution and abundance of *n*-alkanes that occur during the geological history can be best seen by comparing their distribution and abundance in biolipid fractions, geolipid fractions of recent sediments and geolipid fractions of ancient sediments at a higher level of maturity.

Distribution and abundance are characterized primarily by *n*-alkane maxima, and also the ratio of odd to even-carbon-numbered *n*-alkanes, i.e. CPI values (Carbon preference index). To calculate the CPI, different ranges of *n*-alkanes are used. For example, according to the proposal by Bray and Evans from 1961, the *n*-alkane range of C_{24}–C_{34} is used:

$$\mathrm{CPI} = \frac{1}{2} \times \left(\frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{24} + C_{26} + C_{28} + C_{30} + C_{32}} + \frac{C_{25} + C_{27} + C_{29} + C_{31} + C_{33}}{C_{26} + C_{28} + C_{30} + C_{32} + C_{34}} \right) \tag{2.2}$$

According to the proposal by Philippi from 1965, the C_{28}–C_{30} ratio is used, while some authors use the whole range of *n*-alkanes to calculate the CPI.

It is possible to speak about the direct accumulation of *n*-alkanes in the sediments only in the case of recent sediments of marine origin, since it was found that the distribution and abundance of *n*-alkanes in marine biolipid and in marine

Table 2.3 CPI and *n*-alkane maximum of biolipid main fractions (**a**), geolipid fractions of recent sediments (**b**) and geolipid fractions of the ancient sediments (**c**)

		CPI	Maximum
a	High terrestrial plants	> 10	C_{25}–C_{29}
	Some marine algae	~ 1	C_{17}, C_{22}
	Many marine organisms	~ 1	C_{17}
	Planktons, bacteria	~ 1	C_{17}
b	Terrestrial recent sediments	1.5–2	C_{25}
	Marine recent sediments	~ 1	C_{17}, C_{22}
c	Terrestrial ancient sediments	1–1.5	C_{17}–C_{22}
	Marine ancient sediments	1	C_{17}

geolipid fractions of recent sediments are similar (Table 2.3a, b). However, in recent sediments whose organic matter is of terrestrial origin, during diagenesis and catagenesis, due to maturation changes, there is a large reduction in CPI, (from 10 to 1.5–2), i.e. the enrichment with even-carbon-numbered *n*-alkanes, and a slight shift of maximum toward lower members (C_{25}–C_{29} to C_{25}). Based on this difference it can be concluded that the biological precursors of *n*-alkanes in bitumens of sediments are not only biogenic *n*-alkanes, but also other organic compounds such as saturated and unsaturated fatty acids, alcohols, aldehydes or ketones.

Comparing the distribution and abundance of *n*-alkanes in recent and ancient sediments of terrestrial origin (Table 2.3b, c) it can also be observed that CPI values were reduced from 1.5–2 to 1–1.5, and maxima were shifted from C_{25} to C_{17}–C_{20}. In this case the differences are the result of maturation or catagenetic changes in organic matter and the fact that during catagenesis bitumen is enriched with new *n*-alkanes, which occurred by the thermal degradation of kerogen.

As there is no difference between the distribution and abundance of *n*-alkanes in biolipid and geolipid marine factions in recent sediments (Table 2.3a, b), so there is no difference either between the distribution and abundance of *n*-alkanes in bitumen of recent and ancient sediments of marine origin (Table 2.3b, c).

In summary the following conclusions can be drawn: (1) *n*-alkanes of bitumen of sedimentary rocks only partly derive from biolipid *n*-alkanes; (2) during maturation CPI of *n*-alkanes decrease (10 → 1); and (3) during maturation *n*-alkanes maximum shifts towards lower members, from C_{25}–C_{29} to C_{17}–C_{20}. Since in the marine biolipids CPI is about one, and the maximum is at about C_{17}–C_{20}, the use of distribution and abundance of *n*-alkanes in recent and ancient sediments of marine origin as maturation parameter is limited. In sediments of terrestrial origin, CPI values and maxima of *n*-alkanes can be successfully used as maturation parameters.

Box 2.5: *General Notes*

In an investigated sample of bitumen of an ancient sediment when CPI = 1, and maximum is C_{17}–C_{20}, it cannot be said with certainty whether the organic matter in sediment is of marine origin, or it is maturated organic matter in sediment of terrestrial origin. If the CPI of the investigated sample is, however, slightly above one, and if the *n*-alkane maximum is shifted in only one or a few members over the C_{20}, it can be assumed that the organic matter of the investigated sediment is also partly of terrestrial origin.

Isoprenoid Alkanes

For a high number of isoprenoid alkanes in bitumen of recent and ancient sediments biological precursors have been presumed and paths of their structural transformations during the evolution of organic matter have been explained. Thanks to this fact, it is possible to assess origin, depositional environment and maturation degree of bitumen, based on these isoprenoids and their abundance.

In sedimentary bitumen the identified isoprenoids can be divided into three main types based on the type of isoprenoid coupling. Most of isoprenoids identified in geolipids are characterized by "head-to-tail" isoprenoid coupling (type I). These isoprenoid alkanes are called regular isoprenoids. They include farnesane (C_{15}), isoprenoid with 16 carbon atoms, norpristane (C_{18}), pristane (C_{19}), phytane (C_{20}), and other homologues up to C_{45}. A smaller number of identified isoprenoid hydrocarbons in bitumens of recent and ancient sediments have one "tail-to-tail" coupling in "head-to-tail" coupling series. These isoprenoids are called irregular isoprenoids and include squalane, perhydro-β-carotene and lycopene (type II). Irregular isoprenoid alkanes are also called those isoprenoids that have one "head-to-head" coupling in a series of "head-to-tail" isoprenoid couplings. Isoprenoid of this type, identified in bitumens, is 3, 7, 11, 15, 18, 22, 26, 30-oktamethyldotriacontane. This isoprenoid can be classified as type III. Structures of major isoprenoids are shown in Fig. 2.2.

Farnesane, a regular C_{15} isoprenoid in sediments, occurs during transformation of chlorophyll bacteria, and regular C_{16}–C_{20} isoprenoids during the transformation

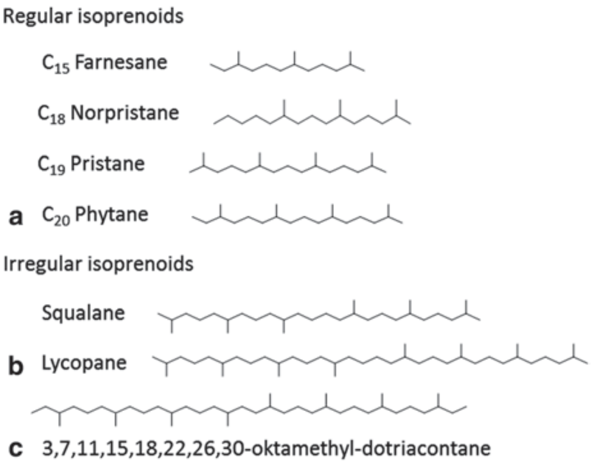


Fig. 2.2 The most important isoprenoids of type I (**a**), type II (**b**) and type III (**c**)

of chlorophyll *a*. Regular C_{21}–C_{25} isoprenoids cannot be related with certainty to the corresponding precursor, while C_{25}–C_{45} isoprenoids have been shown to originate from isoprenoids of a long series of higher terrestrial plants. The irregular isoprenoids of type 2, squalane, perhydro-β-carotene and lycopene, are considered to be of algal origin.

C_{32}–C_{40} isoprenoids with a "head-to-head" coupling, the third type, were identified in different species of bacteria, so these simple organisms are taken nowadays as their source in geolipid factions. Apart from the isoprenoids inherited from living organisms, which are within the composition of bitumen in the diagenetic phase, during the catagenesis bitumen is enriched with new isoprenoid molecules that are formed during the thermal degradation of kerogen.

In most cases there is no simple accumulation of biolipid isoprenoids in sediments, but in the course of geological history, especially during diagenesis, they are structurally transformed into pure hydrocarbons as identified in geolipid fractions. These changes often lead to significant structural changes. An example of biolipid isoprenoid which undergoes changes in the geosphere is botryococcene, a polyunsaturated C_{34}–isoprenoid from the algae *Botryococcus braunii*. During diagenetic and catagenetic changes, botryococcene is converted to the completely saturated botryococcane.

The most important isoprenoids in geolipid fractions are pristane with 19 carbon atoms (Pr) and phytane with 20 carbon atoms (Phyt). They derive from phytol, isoprenoid alcohol of chlorophyll *a*. Changes in phytol in the geosphere are an example of significant structural changes of isoprenoids in sediments. In oxidizing environment, phytol is converted to phytenic acid; by decarboxylation it is converted to pristene, and finally by hydrogenation, to pristane. In the reducing environment phytol is converted to dihydrophytol, followed by dehydration and hydrogenation to phytane. At phytane cracking some lower isoprenoids may be formed. For phytane to be converted to C_{17} isoprenoid alkane, it is necessary to breaking two C–C bonds instead of one. Therefore C_{17} isoprenoid is not found in the sediments, or is found in much lower concentration than C_{16} and C_{18} isoprenoid alkanes.

Phytol is a precursor not only of pristane and phytane, but also of C_{15}–C_{18} isoprenoid alkanes, which was confirmed by thermal cracking of pure phytol under the laboratory conditions as well as in the pyrolysis experiments on kerogen.

Box 2.6: *General Note*

The relative pristane to phytane concentration, the so-called Pr/Phyt-ratio, is one of the best known parameters in organic-geochemical investigations. This ratio is primarily used for determining the diagenetic conditions that influenced the formation of sediment. Higher abundance of pristane in relation to phytane is taken as evidence of deposition of organic substance under predominantly oxidizing conditions. Thus, in coals, pristane is much more abundant than phytane, and the Pr/Phyt-ratio is about three, while in reducing environments (marine carbonates and evaporites), this ratio is less than one.

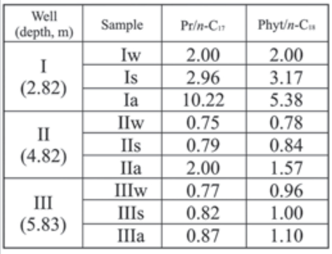
The relative pristane to phytane ratio can also be used in determining the degree of maturity, as it was observed that during the maturation pristane is formed somewhat faster than phytane, which means that in the sediments deposited under the same oxidation-reduction conditions, the Pr/Phy value increases with the degree of maturity.

Box 2.7: Excursus

n-Alkanes and isoprenoids in environmental chemistry

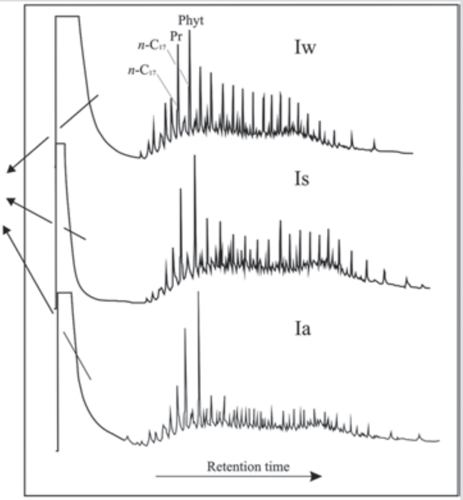
n-Alkanes, pristane (pr) and phytane (phyt) distribution parameters can also be applied in environmental chemistry for identification of different types of organic pollution. For example, comparing the results of gas chromatography (GC) analysis of *n*-alkanes in sewage-polluted river sediments with that of unpolluted sediments, it was shown that *n*-alkane distribution and abundance parameters offer a sound basis not only for the identification of oil derived, but also for non-oil derived organic matter pollution in recent sediments (Jovančićević et al. 1998a).

Microbial degradation of an oil-type pollutant in an alluvial sediment (or in other segments of the environment) can also be estimated on the basis of *n*-alkane, pristane and phytane abundance changes in saturated hydrocarbon fractions. For example, oil-contaminated alluvial groundwater was investigated, taken from three drill-holes (three depths), three times each (<u>w</u>inter ’97/’98, <u>s</u>pring ’98 and <u>a</u>utumn ’98) in the area of an oil refinery. The results unambiguously confirmed that depth-dependent, but obviously existing, biodegradation processes of oil-type pollutants occur in a very short time period (see figure below, Jovančićević and Polić 2000).



Well (depth, m)	Sample	Pr/n-C_{17}	Phyt/n-C_{18}
I (2.82)	Iw	2.00	2.00
	Is	2.96	3.17
	Ia	10.22	5.38
II (4.82)	IIw	0.75	0.78
	IIs	0.79	0.84
	IIa	2.00	1.57
III (5.83)	IIIw	0.77	0.96
	IIIs	0.82	1.00
	IIIa	0.87	1.10

a



b

Polycyclic Alkanes of Sterane Type

Contrary to *n*-alkanes and isoprenoid alkanes, which are predominant compounds in the alkane fraction of most sedimentary bitumens, polycyclic alkanes are contained in only low concentrations. Therefore, qualitative and quantitative analyses of polycyclic alkanes require most modern methods of instrumental analysis, like gas chromatography—mass spectrometry analysis (GC-MS) in the first place.

Box 2.8: *General Notes*

Since most of sterane isomers, identified so far in the sedimentary bitumen and in petroleum, are correlated with biological precursor, and paths of their structural and stereochemical transformations during diagenesis and catagenesis have been almost completely explained, these polycyclic hydrocarbons are very important biological markers. These transformations are described in detail in organic geochemical literature, (for example, Philp, 1985; Waples, 1985 and Peters et al., 2005, see Appendix).

The biological precursors of steranes are mainly steroids found in biolipids of all organisms, particularly animals and higher plants. Prokaryotic organisms such as bacteria and blue-green algae also contain steroids, but in much smaller quantities. The most abundant steroid in animal tissues is cholesterol (C_{27}). A small amount of cholesterol was also found in bacteria. Ergosterol (C_{28}) is most abundant in fungi, but is also found in red algae, while campesterol (C_{28}) is found mainly in higher plants. Sitosterol (C_{29}) and stigmasterol (C_{29}) are typical of higher plants, and fucosterol (C_{29}) is the dominant sterol of brown algae.

Based on the results of a large number of organic-geochemical investigations of bitumen and crude oils of different maturity, the transformation paths of sterane were revealed: different steroids (stanols, stenols, stanons and stenons) of extinct organisms during early diagenesis, by microbiological decomposition at shallow depths and low temperatures and pressures, by various processes of defunctionalisation, are converted into sterenes. During late diagenesis, by hydrogenation and isomerization steranes are converted to diasterenes. On the other hand, the same conditions may lead to aromatization of A or C rings. Finally, at greater depths and at higher temperatures, diasterenes convert to diasteranes, and steroids with aromatic A or C ring, convert to triaromatic steroids, thus ending the process of aromatization. Triaromatic steroids may eventually convert into phenanthrene or its alkyl derivatives. Steranes, diasteranes, steroids with aromatic C-ring, triaromatic steroids and phenanthrene (and its alkyl derivatives), were identified in bitumen and oils. The most important structural and stereochemical changes in steroids in the geosphere are shown in Fig. 2.3.

The characteristic of biolipid steroid isomers is that all the rings are in *trans*-position, so that hydrogen atoms at C_5, C_{14} and C_{17} are in α-position, and methyl groups are bound to C_{10} and C_{13} in β-position. Hydroxyl or carbonyl group is at C_3, and the double bond is between C_4 and C_5, and between C_5 and C_6.

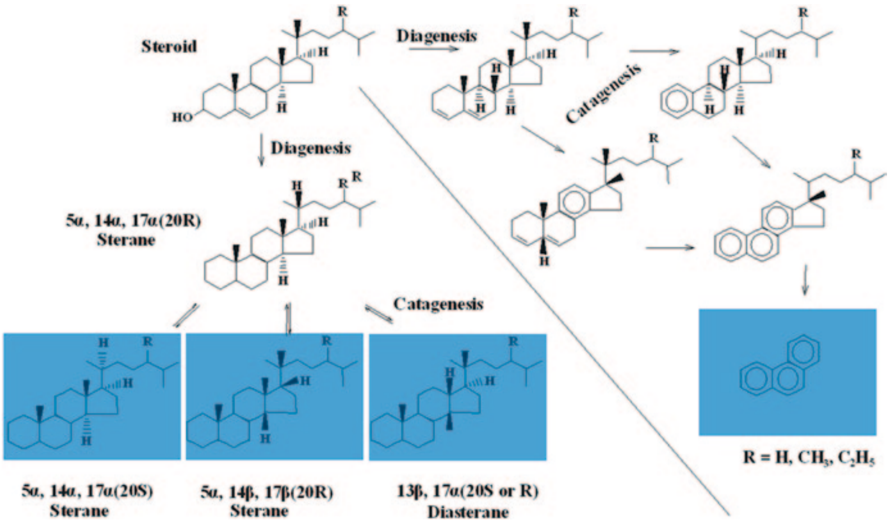


Fig. 2.3 Structural and stereochemical transformations of steroids in the geosphere

During the conversion of sterenes to steranes, 5α(H) and 5β(H) isomers are formed. Their relative abundance ratio is 4:1. 5β(H) is an unstable isomer and is quickly converted into 5α(H) isomer. β5(H) sterane can be identified in sediments only in the early phase of diagenesis.

During catagenesis, structural and stereochemical changes occur in 5α(H), 14α(H), 17α(H) 20R sterane molecules. 5α(H), 14α(H), 17α(H) 20S isomers occur first, and then 5α(H), 14β(H), 17β(H) 20R or 20S isomers are formed.

By moving the methyl groups from C_{10} and C_{13} to C_{14} and C_{15} diasteranes are formed. They occur in fewer numbers of isomers than steranes. Most often they are present in bitumens of ancient sediments and oils as 13β(H), 17α(H) 20R or 20S, and as 13α(H), 17β(H) 20R or 20S in smaller quantities.

C_{27}ααα 20R steranes are predominant in the marine depositional environment, C_{28} ααα 20R in lacustrine, and C_{29}ααα 20R in terrestrial environment, and that interrelationships between these steranes during maturation does not change. Therefore, it is possible to assess the depositional environment, or the species of the deposited organisms based on the distribution of C_{27}–C_{29}ααα 20R sterane. A certain limitation of sterane distribution as a source parameter is that the precursors of C_{29}ααα20R sterane are found, although in much smaller quantities, also in some species of cyanobacteria and blue-green algae.

Based on the abundance of some sterane stereoisomers it is possible to determine the maturity degree of the investigated sample. Relations between thermodynamically more stable geolipid isomers and their less stable precursors are proportional to maturity of the entire investigated organic matter. Based on the sterane parameters it is possible to assess the maturity of both bitumens of ancient sediments and petroleum until the equilibrium is reached at C_{20}, C_{14} and C_{17}: 20S/20S + 20R = 0.50–0.60; ββ/ββ + αα = 0.70. Limitation of the relationships between the sterane isomers as maturation parameters is that sterane diastereoisomerisation is slow, so that it takes a long time to reach equilibrium in spite of the raised temperature. Therefore, in recent, Tertiary basins, isomerisation is incomplete, despite the fact that during the rapid deposition of organic matter high temperatures could have been reached.

Parameters by which it is possible to assess the maturity of organic matter are also the relationships of relative concentrations of diasteranes and 14α(H), 17α(H) 20R steranes. Limitation of these maturation parameters is that the concentration of diasteranes in bitumen depends on the mineral composition of sedimentary rock.

Polycyclic Alkanes of Terpane Type

Outline

For the analysis of terpanes in sedimentary bitumens, and in oils, same analytical methods and same instrumental techniques are applied as for the analysis of steranes. Therefore, along with examining the origin and structural and stereochemical changes of steranes, tests aimed at detecting biological precursors, and transformational paths of tri-, tetra- and pentacyclic terpanes are also presented.

In the alkane fractions of recent sediments tricyclic terpanes are present in traces, or are not present at all. The largest amount of these hydrocarbons is incorporated into kerogen or is in the form of polar fractions of bitumens, resins and asphaltenes, from which it is released during thermal degradation of the sediment. Therefore, only in the alkane fractions of many mature sediments and crude oils tricyclic terpanes are found in the range from $C_{19}H_{34}$ to $C_{45}H_{86}$.

It is believed that the precursor of C_{19}–C_{30} tricyclic terpanes is C_{30}-tricyclohexaprenol. However, this alcohol was not found in living organisms, suggesting that it was formed by abiogenic cyclisation of hexaprenol, which is found in the cells and membranes of algae and bacteria (Fig. 2.4). Precursors of C_{30}–C_{45} tricyclic terpanes are probably higher unsaturated isoprenoid alcohols. An example is solanesol (C_{45}), isoprenoid alcohol of higher terrestrial plants.

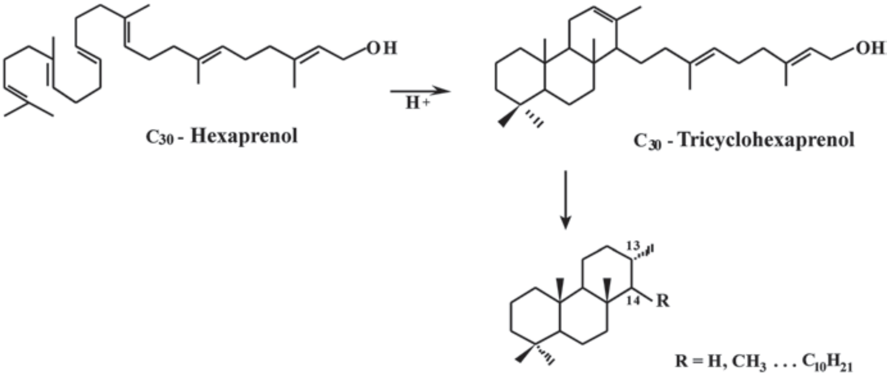
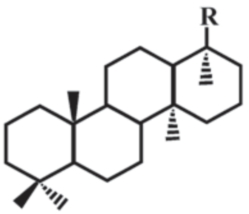


Fig. 2.4 Tentative mechanism of tricyclic triterpanes formation from hexaprenol



R = H, CH_3 or C_2H_5

Fig. 2.5 Molecular structure of tetracyclic terpanes

By analysis of tricyclic terpanes in a number of geological samples, it was concluded that organic matter from saline lacustrine environment and marine organic matter usually contain a greater amount of tricyclic terpanes, where C_{23} terpane is most abundant. In the organic matter of terrestrial origin, these polycyclic hydrocarbons are much less present, and the most abundant among them is C_{20} tricyclic terpane. Regardless of the origin, among the tricyclic terpanes, the least abundant are C_{22} and C_{27} terpanes. Compounds with more than 24 C-atoms exist in the form of a mixture of 22R and 22S diastereoisomers.

During catagenesis, higher members of tricyclic terpanes (C_{23}–C_{25}) are transformed to C_{19}–C_{23} tricyclic terpanes. Having in mind this fact, it is possible to use ratios of higher to lower tricyclic terpane as maturation parameters.

In bitumens of a number of sedimentary rocks of different origin and age, and in the oils, tetracyclic terpanes were also identified in the range of C_{24}–C_{27} (Fig. 2.5).

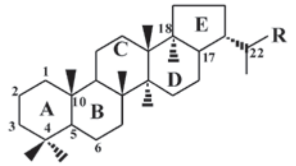
Compared to tricyclic terpanes, tetracyclic terpanes are less abundant in various forms of organic matter in the geosphere. Previous investigations have shown that the most abundant in most samples is C_{24} tetracyclic terpane, that relative concentration of C_{25}–C_{27} homologues in carbonate rocks is higher than in non-carbonate rocks, and that the concentration of tetracyclic terpanes increases with the sample maturity degree.

There are two views on the origin of these hydrocarbons in geolipids. According to the first one, tetracyclic terpanes are formed by thermocatalytic degradation of hopanoids of microbiological origin, and according to the other, tetracyclic terpanes are formed by opening of the E-ring in hopanoids by microbial activity during early diagenesis, and then defunctionalisation during maturation.

According to some authors, the ratio of relative concentrations of C_{24} tetra- to C_{26} tricyclic terpanes can indicate oxidation and reduction conditions of depositional environment of organic matter. When depositional conditions are less reducing, due to increased bacterial activity, concentration of C_{24} tetracyclic terpane increases, and the ratio C_{24} tricyclic/C_{26} tetracyclic terpanes becomes larger.

The most abundant terpanes in alkane factions of geological samples are pentacyclic triterpanes. Most of these geolipid compounds belong to a hopane series (Fig. 2.6).

In geolipid fractions C_{27}–C_{35} hopanes were identified. The most abundant are C_{29} and C_{30} hopanes. C_{40} hopane was also identified in bitumens, but its precursor is not known yet. So far a total of about 150 hopane derivatives were isolated.



R = H **Norhopane**
R = CH_3 **Hopane**
R = C_2H_5, C_3H_7, C_4H_9, C_5H_{11} **Homohopanes**

Fig. 2.6 Molecular structure of hopanes

Initially it was thought that hopanes of geolipids originate from biohopanoids of higher terrestrial plants. Identification of hopanes in geological samples which are not of terrestrial origin encouraged organic geochemists to further investigation to determine biological precursors of these polycyclic alkanes.

The most important discovery in this field was the identification of a tetrahydroxylated C_{35} hopanoid, first in the bacterium *Acetobacter xylinum*, and later in more than one hundred species of bacteria and in blue-green algae. This bacteriohopane is the main component of cell membranes and acts as a hardener in the membranes of microorganisms that are involved in the degradation of organic matter in diagenetic phase. Possible mechanism of geohopane derivation from tetra-oxy-bacteriohopane is shown in Fig. 2.7.

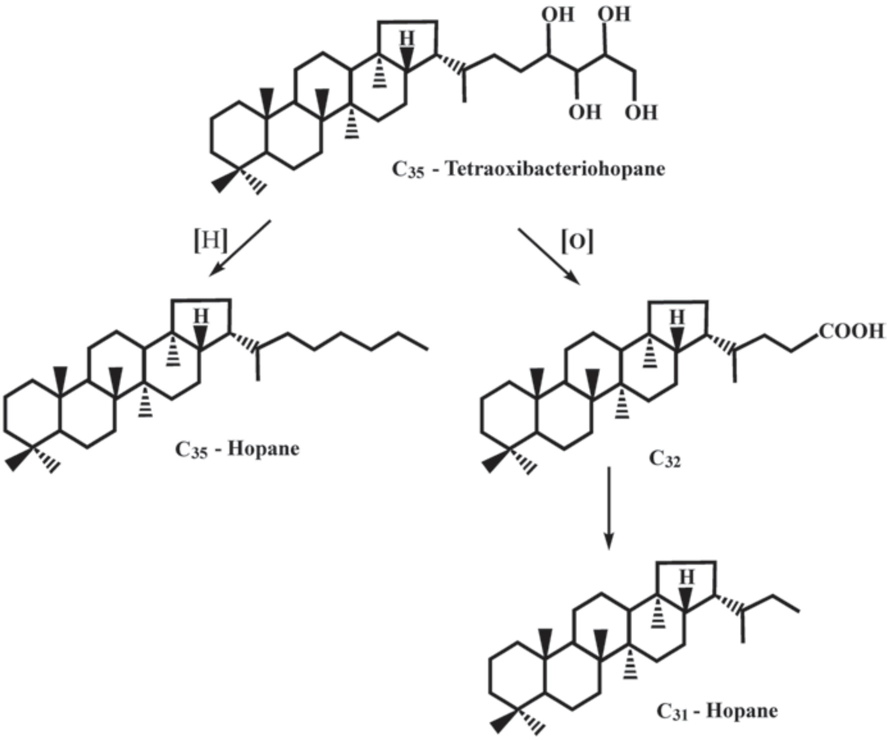


Fig. 2.7 The possible mechanism of genesis of hopanes from tetraoxibacteriohopane

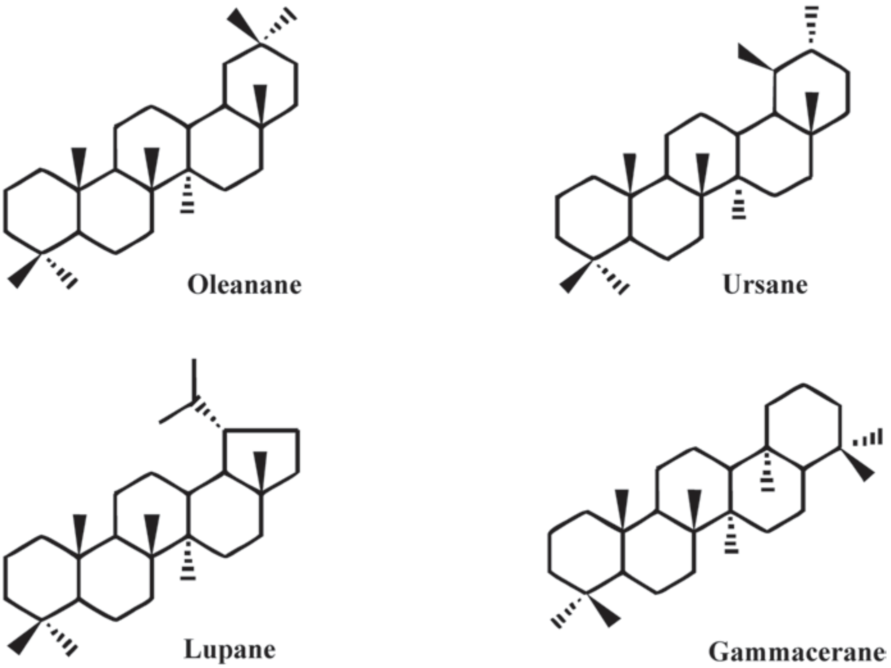


Fig. 2.8 Some types of pentacyclic terpanes identified in sediment bitumens and oils

Precursor of geohopane is also an unsaturated C_{30} hopanoid, the diplopten, which has been identified in ferns, mosses and lichens.

Besides hopane further types of pentacyclic triterpanes appear in alkane fractions of geological samples, such as oleanane, ursane, lupane and gammacerane (Fig. 2.8). Oleanane, ursane and lupane are indicators of terrestrial origin of organic matter of geosphere whereas gammacerane is an indicator for reducing, marine-evaporite depositional environment.

Three diastereoisomers of hopane were identified in geological samples. In recent sediments, 17β(H), 21β(H) 22R hopanes and 17β(H), 21α(H) 22R isomers called moretanes, and in mature sediments and oils also 17α(H), 21β(H) 22R+22S hopanes and 17β(H), 21α(H) 22R+22S moretanes have been identified.

The ratio of moretanes to hopanes in fossil organic matter is used as a maturation parameter. In young, recent, immature sediments, which were not exposed to high temperature, which is necessary for epimerisation of moretane, values of moretane/hopane ratio (0.70–0.85) represent the biogenic composition of the source material, not the maturity.

For epimerisation of moretane to hopane, in addition to high temperature, long enough geological time is required. Some Tertiary oils, which according to other maturation parameters at a high level of maturity, have still relatively high values of moretane/hopane ratio (above 0.1), because the elapsed time was not enough for epimerisation. In oils from the Cretaceous and Jurassic, values of this ratio are below 0.1.

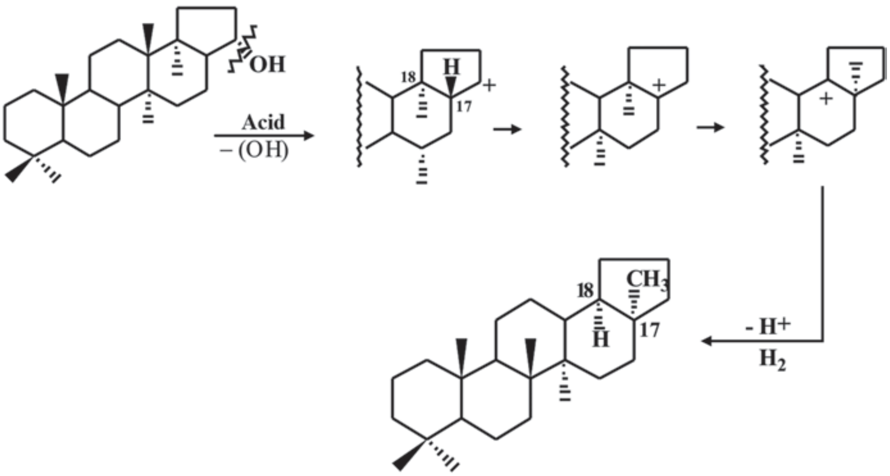


Fig. 2.9 Formation of 18α(H)-trisnorneohopane (Ts) during maturation of organic matter

One of the most important maturation parameters calculated from the distribution of terpane biomarkers is 22S to 22R epimer ratio. Using this relationship as a maturation parameter is somewhat limited because the conversion of 22R to 22S epimer is not complete, but reaches a steady state. At equilibrium the ratio of hopane epimers is: 22R:22S = 40 %:60 %, and in moretane: 22R:22S = 60 %:40 %.

C_{27-}17α(H)-trisnorneohopane (Tm), and C_{27-}18α(H)-trisnorhopane (Ts_{-}) are terpane isomers that can be identified in almost all bitumens and oils. It is believed that the biological precursors of Tm are the same hopanoids which are precursors of all other geohopanes. The thermodynamically more stable isomer Ts, is formed during maturation by moving a methyl group from C_{18} to C_{17}. The reaction mechanism of these changes was proposed firstly in the late fifties (Fig. 2.9).

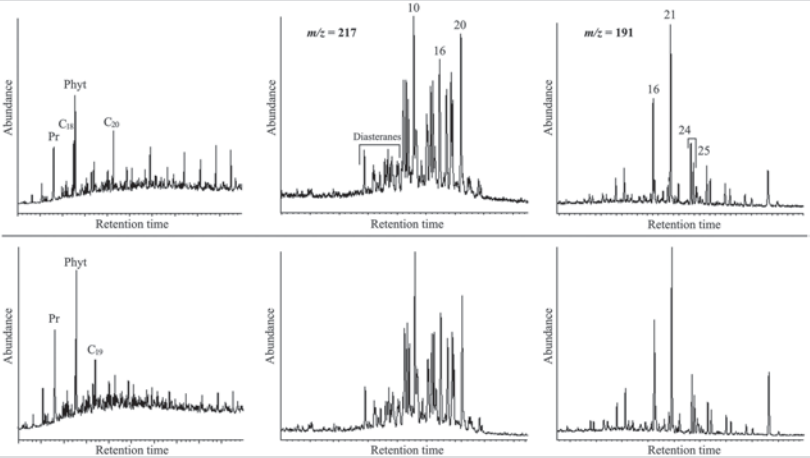
Box 2.9: Excursus

Steranes and terpanes in environmental chemistry

Bearing in mind that any oil in alkane fraction has characteristic distribution of steranes and triterpanes (a kind of “fingerprint”), the distribution of these biomarkers is used as a very useful forensic tool for determining the origin of an oil-type pollutant in the environment, or to determine the cause of an ecological accident.

Polycyclic alkanes of the sterane and triterpane type can be also applied in the environmental chemistry, as a tool for identification of oil-type pollutants in almost all segments of the environment. For example, where *n*-alkanes and isoprenoid aliphatic alkanes of pristane and phytane type are not applicable to oil-type pollution identification (*e.g.* if their biodegradation has occurred in the environment), steranes and triterpanes with highly recognizable distributions of structural and stereochemical isomers in oil can be very useful.

Typical oil sterane and triterpane distributions in the groundwater sample with *n*-alkanes not typical for oil fractions (even-numbered homologues predominance, CPI < 1) and in the sample with degraded *n*-alkanes, are evidence of the presence of oil-type pollution (see figure, Jovančićević et al. 2001, 2003. Identification of marked sterane and terpane peaks will be given in Tables 2.5 and 2.6).



Naphthene-Aromatic Hydrocarbons

From the organic-geochemical point of view aromatic steroids are the most important compounds among the naphthene-aromatics. Since the early seventies these constituents of sediment bitumen and oils have been intensively studied, hence pathways of their formation as well as their structural and stereochemical transformation have been explained in detail. Aromatic steroids are also important biomarkers. Based on their distribution and abundance it is possible to estimate the origin and dominantly the maturity of the investigated sample.

As it has been noted in the discussion of Fig. 2.3, during the diagenesis steroids can be transformed to aromatic steroids. So far, in aromatic fractions of geological samples, C_{20}, C_{21} and C_{26}–C_{30} monoaromatic steroids (aromatic A or C ring), and C_{20}, C_{21} and C_{26}–C_{28} triaromatic steroids were identified.

Monoaromatic steroids with an aromatic A ring derive from $\Delta^{3,5}$-steradienes in shallow, immature sediments. Monoaromatic steroids with an aromatic C ring derive from the same precursor, but they are formed at greater depths during the late diagenesis and early catagenesis. During catagenetic changes of organic matter, monoaromatic steroids convert to triaromatic steroids with a methyl group at C_1 or C_4. Increased maturity results in cracking in the side chains of triaromatic steroids, and at the end of maturation changes triaromatic steroids can be converted to a phenanthrene structure with methyl groups on A, B or C rings.

Box 2.10: ***General Notes***

Investigations of a large number of geological samples of different origin and age showed that the distribution and abundance of mono-and triaromatic steroids may be used to determine primarily maturity parameters. The most commonly used are A/B *cis* and A/B *trans* isomer ratios with the aromatic C ring, the ratio of mono- to triaromatic steroids, and the ratio of homologues with shorter (C_{20} and C_{21}) to homologues with longer side chains (C_{26}–C_{28}, and C_{26}–C_{30}).

Source parameters which are determined from the distribution and abundance of aromatic steroids are less reliable, although according to some authors, some ratios of structural and stereochemical isomers of mono- and triaromatic steroids can also refer to the origin and depositional environment of the investigated sample. For this purpose, the ratio of 5β(H) to 5α(H) methyl isomers of monoaromatic steroids (with the aromatic C ring) is applied, as well as relative amount of higher homologues of mono- and triaromatic steroids.

2.1.2 Procedures for Isolation and Analysis of Bitumen

A general procedure for the isolation of different bitumen fractions from samples of sedimentary rock is shown schematically in Fig. 2.10.

Free bitumen is first extracted from dried and powdered sample of dry sediment at a moderate temperature ($< 80\,°C$) within a certain time, using a polar solvent such as chloroform, azeotropic mixture of benzene and methanol or azeotropic mixture of methylene chloride and methanol. Traditionally, Soxhlet extraction is most commonly used for this purpose, but different types of dispersion extraction, microwave or ultrasonic assisted extraction or accelerated solvent extraction methods are also used. In the next phase, carbonates are removed using diluted hydrochloric acid. After drying the residues, the associated bitumen is extracted using the same solvent and in the same manner as for bitumen 1.

Finally, silicate minerals can be removed using a mixture of concentrated hydrochloric and hydrofluoric acids. Following, associated bitumen 3 is extracted from this kerogen concentrate, also using e.g. an azeotropic mixture of methylene chloride and methanol. The overall procedure ends sometimes with a final treatment of the HCl-HF concentrate with lithium aluminium hydride, which removes pyrite as the most abundant sulphide mineral in most sedimentary rocks.

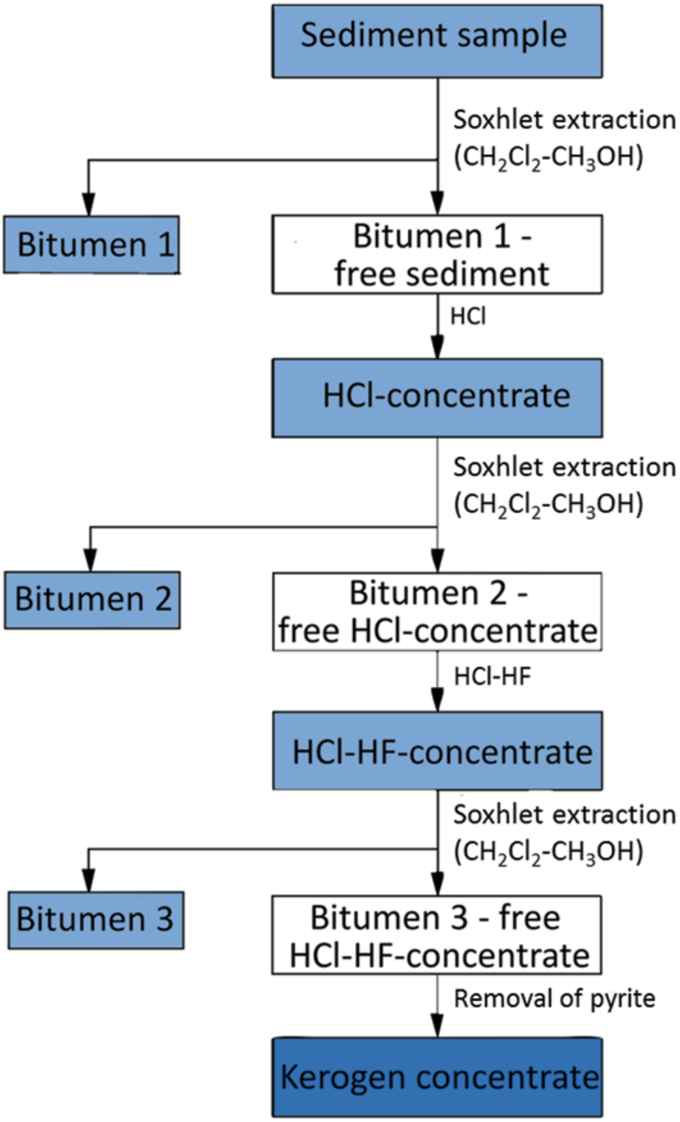


Fig. 2.10 Schematic procedure for the isolation of bitumen from sedimentary rocks

Box 2.11: *General Note*

As already pointed out, bitumen and oil are related forms of organic matter in geosphere. They consist of the same class of organic compounds, only the distribution and abundance of certain structural and stereochemical isomers are different. Therefore, further analysis of free and associated bitumens involves the use of analytical methods and techniques used in the analysis of crude oil.

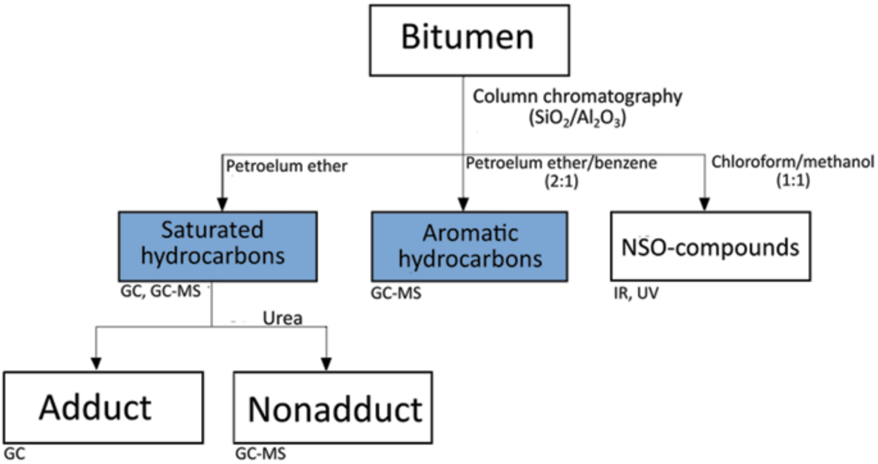


Fig. 2.11 Schematic procedure of analysis of sediment bitumen.(*GC* gas chromatography; *GC-MS* gas chromatography-mass spectrometry; *IR* infrared spectroscopy; *UV* ultraviolet spectroscopy)

The principal analytical approach applied to bitumen is shown schematically in Fig. 2.11. The analysis of bitumen starts normally with the determination of the bulk composition, i.e. isolating and determining the amounts of saturated and aromatic hydrocarbons and NSO compounds. For this purpose column chromatography is applied. Fractions are eluted in order of increasing polarity. First, the nonpolar, alkane fraction (nonpolar solvents as eluents, e.g. petroleum ether or hexane) is eluted, then the slightly more polar fraction containing the aromatic hydrocarbons (medium polar solvents as eluents, e.g. mixture of hexane and benzene), and, finally, the most polar fraction consisting of NSO-compounds (polar solvents as eluents, e.g. mixture of methanol and chloroform).

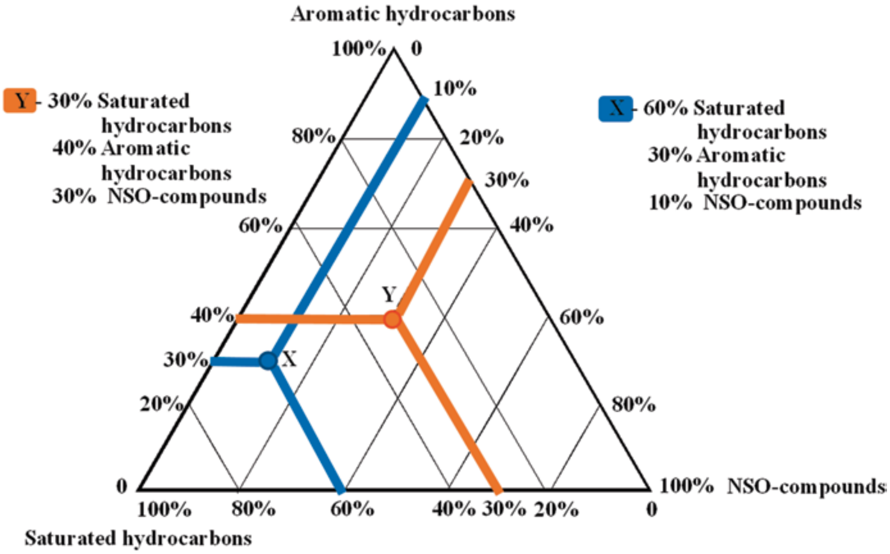


Fig. 2.12 Group composition of bitumen (X and Y are examples) illustrated in a triangular diagram

The results obtained in the determination of bulk composition are shown in a ternary diagram (Fig. 2.12). The sum of the three factions in this diagram is always 100%. The fourth fraction, asphaltenes, specifically singled out in Table 2.1, is difficult to elute due to their macromolecular nature. It represents the remainder on the column and is typically added to the NSO compound fraction at presentation of the results.

In the chapter on the composition of bitumen, it was pointed out that the saturated hydrocarbons are the best investigated fraction. It contains the largest number of compounds with known biological precursor and whose diagenetic and catagenetic transformation pathways have been explained to a satisfactory degree. In other words, most biomarkers are contained in the fraction of saturated hydrocarbons.

Among the aliphatic biological markers most of the attention was paid to *n*-alkanes, which is completely understandable, because *n*-alkanes are not only the most abundant biomarkers in bitumens (and oils), but in most samples it is the most abundant class of organic compounds in general.

n-Alkanes are analysed routinely using gas chromatography (GC-analysis). In bitumens where the *n*-alkanes are predominant in alkane fraction, the homologous series of *n*-alkanes are successfully identified with GC-analysis of the total alkane fraction. Figure 2.13, for example, shows gas chromatograms of aliphatic fractions

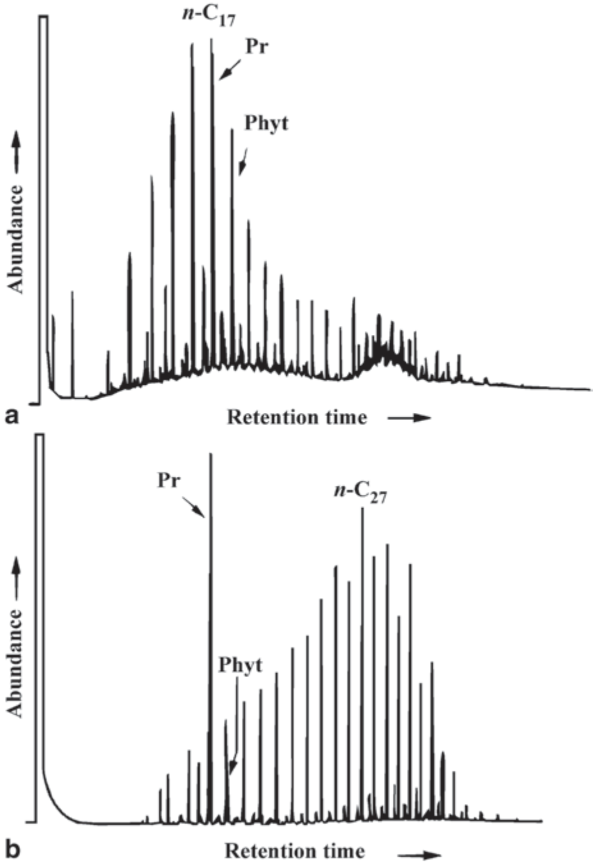


Fig. 2.13 Gas chromatograms of bitumen alkane fractions from recent sediments of predominantly marine (**a**), and predominantly terrestrial origin (**b**)

of bitumen of recent sediments, of both marine (a) and terrestrial origin (b). However, if the proportion of *n*-alkanes is small, i.e. where the *n*-alkane maxima are difficult to identify among the large number of maxima derived from other saturated hydrocarbons (isoprenoid aliphatic alkanes, cyclic alkanes, polycyclic alkanes of sterane and diasterane types, polycyclic alkanes of tri-, tetra- and pentacyclic terpane-types and others), it becomes necessary to isolate *n*-alkanes or concentrate them prior to analysis by gas chromatography. For the isolation of *n*-alkanes from the total mixture of saturated hydrocarbons the most often used methods are: (i) procedure with molecular sieves and (ii) urea adduction. Separation using urea is more often applied. It is based on building of channel *n*-alkane/urea inclusion compounds. As is known, urea crystallizes to form “channels”, which can “receive” only long chain *n*-alkanes and *iso*- and *anteiso*-alkanes. This fraction is called urea adducts. Because of their size, the molecules of other compounds of alkane fraction (branched and cyclic alkanes) do not build urea inclusion compounds and remain in solution. They form a fraction that is usually called urea non-adducts.

For the analysis of the biological markers of sterane, diasterane, tri-, tetra- and pentacyclic terpane types (polycyclic alkanes), gas chromatography analysis is insufficient. In alkane fractions, these compounds are present in very low concentrations and their qualitative and quantitative analysis requires more modern methods of instrumental techniques such as gas chromatography—mass spectrometry analysis (GC-MS). This fraction can be analyzed from a total alkane mixture, or from urea non-adducts.

Gas chromatography—mass spectrometry methods are commonly applied for the analysis of polycyclic alkanes. For an unambiguous identification of substances full scan spectra and corresponding retention times are used, however, for tracing individual groups of geomolecules ion chromatograms are generally used. For this purposes chromatograms of individual and specific ions are extracted from the total ion chromatogram. Table 2.4 provides an overview of the most important classes of

Table 2.4 Characteristic ions for the detection of organic compounds in alkane fractions

Ion (*m/z*)	Class of compounds
71, 85 or 99	*n*-Alkanes
77, 91, 105, 106, 119 or 120	Benzene and substituted benzenes
82 or 83	Cyclohexanes
113, 183 or 197	Acyclic isoprenoids
109, 123, 194, 208, 222 or 236	C_{14}–C_{17} Bicyclic terpenoids
109, 123, 163 or 191	Diterpenoids
123, 163 or 191	Tricyclic and tetracyclic terpanes
149, 163, 177, 191, 205, 219 or 235	Pentacyclic triterpanes
177	Demethylated hopanes
217 or 218	Steranes and diasteranes
231	Methylsteranes
259	Diasteranes

compounds in the fraction of saturated hydrocarbons together with the corresponding specific ions which are used for their identification and quantification.

n-Alkanes and isoprenoid alkanes, pristane and phytane, are analyzed also by gas chromatography—mass spectrometry. As it can be seen from Table 2.4, *n*-alkanes are identified using ions *m/z* 71, 85 or 99 (usually *m/z* 71), and isoprenoids are identified using *m/z* 113, 183 or 197 (usually *m/z* 183). However, a more reliable picture of the distribution of these biological markers in alkane fractions of bitumen (or oil) is obtained on the basis of gas chromatograms (Fig. 2.13).

Sterane is usually identified using ion *m/z* 217, and triterpane using ion *m/z* 191. Typical examples of ion chromatograms of steranes and triterpanes of a bitumen of an ancient sediment are shown in Figs. 2.14 and 2.15, and the corresponding peak identification is given in Tables 2.5 and 2.6.

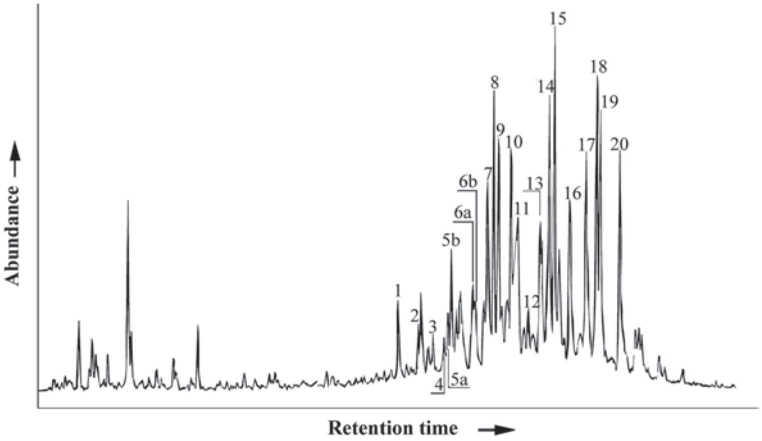


Fig. 2.14 Example of sterane distribution in an ancient sediment as illustrated by the m/z 217 ion chromatogram. (Peak identification is given in Table 2.5)

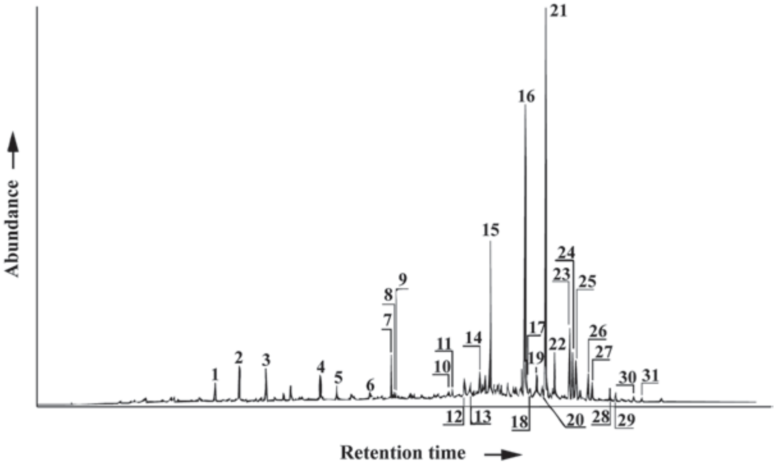


Fig. 2.15 Example of terpane distribution in an ancient sediment as illustrated by the m/z191 ion chromatogram. (Peak identification is given in Table 2.6)

Table 2.5 Identification of the peaks in the chromatogram shown in Fig. 2.14

Peak	Compounds
1	C_{27} 13β(H)17α(H)20(S)-diasterane
2	C_{27} 13β(H)17α(H)20(R)-diasterane
3	C_{27} 13α(H)17β(H)20(S)-diasterane
4	C_{27} 13α(H)17β(H)20(R)-diasterane
5a	C_{28} 13β(H)17α(H)20(S)24(S)-diasterane
5b	C_{28} 13β(H)17α(H)20(S)24(R)-diasterane
6a	C_{28} 13β(H)17α(H)20(R)24(S)-diasterane
6b	C_{28} 13β(H)17α(H)20(R)24(R)-diasterane
7	C_{28} 13α(H)17β(H)20(S)-diasterane + C_{27} 14α(H)17α(H)20(S)-sterane
8	C_{29} 13β(H)17α(H)20(S)-diasterane + C_{27}14β(H)17β(H)20(R)-sterane
9	C_{28} 13α(H)17β(H)20(R)-diasterane + C_{27} 14β(H)17β(H)20(S)-sterane
10	C_{27} 14α(H)17α(H)20(R)-sterane
11	C_{29} 13β(H)17α(H)20(R)-diasterane
12	C_{29} 13α(H)17β(H)20(S)-diasterane
13	C_{28} 14α(H)17α(H)20(S)-sterane
14	C_{29}13α(H)17β(H)20(R)-diasterane + C_{28}14β(H)17β(H)20(R)-sterane
15	C_{28} 14β(H)17β(H)20(S)-sterane
16	C_{28} 14α(H)17α(H)20(R)-sterane
17	C_{29} 14α(H)17α(H)20(S)-sterane
18	C_{29} 14β(H)17β(H)20(R)-sterane
19	C_{29} 14β(H)17β(H)20(S)-sterane
20	C_{29} 14α(H)17α(H)20(R)-sterane

Table 2.6 Identification of the peaks in the chromatogram shown in Fig. 2.15

Peak	Compounds
1	C_{19}-tricyclic terpane
2	C_{20}-tricyclic terpane
3	C_{21}-tricyclic terpane
4	C_{23}-tricyclic terpane
5	C_{24}-tricyclic terpane
6	C_{25}-tricyclic terpane
7	C_{24}-tetracyclic terpane
8	C_{26}22(S)-tricyclic terpane
9	C_{26}22(R)-tricyclic terpane
10	C_{28}22(S)-tricyclic terpane
11	C_{28}22(R)-tricyclic terpane
12	C_{29}22(S)-tricyclic terpane
13	C_{29}22(R)-tricyclic terpane
14	C_{27} 18α(H), 22, 29, 30-trisnorneohopane, Ts

Table 2.6 (continued)

Peak	Compounds
15	C_{27} 17α(H), 22, 29, 30-trisnorhopane, Tm
16	C_{29} 17α(H)21β(H)-hopane
17	C_{29} 18α(H), 30-norneohopane
18	C_{30} 17α(H)-diahopane
19	C_{29} 17β(H)21α(H)-moretane
20	Oleanane
21	C_{30} 17α(H)21β(H)-hopane
22	C_{30} 7β(H)21α(H)-moretane
23	C_{31} 17α(H)21β(H)22(S)-hopane
24	C_{31} 17α(H)21β(H)22(R)-hopane
25	Gammacerane
26	C_{32} 17α(H)21β(H)22(S)-hopane
27	C_{32} 17α(H)21β(H)22(R)-hopane
28	C_{33} 17α(H)21β(H)22(S)-hopane
29	C_{33} 17α(H)21β(H)22(R)-hopane
30	C_{34} 17α(H)21β(H)22(S)-hopane
31	C_{34} 17α(H)21β(H)22(R)-hopane

Since the monoaromatic and triaromatic steroids, which are also important biological markers (Table 2.2), are found in very low concentrations in aromatic fractions of bitumen, their analysis also requires the use of gas chromatography—mass spectrometry. Monoaromatic steroids are analyzed using ion chromatograms *m/z* 253 and triaromatic using ion chromatogram *m/z* 231.

Aromatic hydrocarbons, or simply arenes, are among the most abundant compounds in bitumen and oils. Their concentration can reach up to 50%. The lower limit is about 15%. Mono-, di- and polycyclic aromatic hydrocarbons have been identified. Most often they contain short alkyl substituents and then they are known as alkyl arenes. These hydrocarbons and methods for their identification will be described in detail in the section on oil (Chap. 2.3).

2.2 Kerogen

Outline

The most abundant product of diagenetic processes of organic matter in sedimentary rocks is named kerogen, which represents the most important organic ingredient of sediments. Therefore, it holds a significant place and role in the cycle of organic carbon on Earth. Mostly as a sedimentary organic matter of very specific characteristics, kerogen has always attracted great attention and versatile attention of organic geochemists. Definition, main characteristics, content in the Earth's crust, chemical composition and structure, methods for determining the composition and studying the structure of kerogen will be discussed in this chapter.

The term kerogen defines organic substance not very precious. This name has been used longer times in Scotland first by A. Crum-Brown at testing capabilities of pyrolytic processing of oil shales. Here, the term kerogen has had only a technical meaning. It is derived from the Greek words *keros* and *genos*, meaning "a substance which gives the wax". This name has been survived till today.

Box 2.12: ***General Note***

Kerogen is the name given to a part of organic matter in sediments which is not soluble in conventional organic and inorganic solvents. So, this general definition encompasses not only kerogen dispersed in sediments, but also the insoluble part of organic matter concentrated in coals, oil shales, recent and other fossil sediments.

Main characteristics of kerogen are:

a. it is dominated by macromolecular substances
b. is not a defined compound but it is a complex mixture of organic materials of different composition and origin, and therefore of different chemical nature; and
c. usually, it is in intimate mixture with a large amount of mineral matter.

Quantitative importance of kerogen can be approached from two sides. On the one hand, the kerogen is by far the largest part of the organic matter in sediments. In ancient sediments, coals and oil shales and other sedimentary rocks, the proportion of kerogen in the total organic matter sums up to 95 %, and more. Only in certain types of rocks and sediments, although much less frequently, there is less kerogen and more soluble organic substances. As percentage of soluble organic matter increases with depth, kerogen gradually decreases.

On the other hand, looking at the whole amount of organic matter in the Earth's crust, kerogen is the most abundant of all forms of organic substances. It is believed that, on average, over 80 % of the total sedimentary organic matter is in the form of kerogen. Quantitative kerogen position within the inorganic and the organic part of the sediments is shown in Fig. 2.16.

Estimation of the total amount of sediments, and various types of organic materials in the Earth's crust, has attracted attention of scientists for decades. Estimates have generally relied upon the results of extensive organic-geochemical studies. Estimated amounts of organic materials in sediments have often been expressed through organic carbon. For example, based on Hunts (1979) and Durands (1980) investigation of the total mass of sediments and their average organic carbon content, it was estimated the total amount of organic carbon in sediments at about 1.2×10^{19} kg, which, according to them, accounts for about 10–15 % of total, inorganic and organic carbon of the Earth's crust (Table 2.7).

According to Hunts and Durands estimation, the largest part of the overall amount of organic carbon is kerogen. Quantitative importance of kerogen becomes more apparent by comparing the estimated amount of biomass carbon, carbon dissolved in ocean and atmospheric carbon, with an estimated amount of carbon in the form of kerogen (Table 2.8).

Expressing the estimated amounts of organic matter by organic carbon content factors for conversion to organic matter are needed. However, these factors are different (1.2–1.6), depending on the type of organic material. For kerogen at lower diagenetic stage, values of factors are larger than the values for more mature kerogens. "Elemental" carbon in the rocks, and carbon in carbonates are only partially of organic origin (residues of the thermal decomposition of kerogen, or by-product of biological activity).

Estimation of the total kerogen (10^{19} kg) in different types of sediments are also of interest. The starting point was the fact that every sedimentary rock may contain certain amount of organic matter. In some sediments, it is very small, but there are vast layers of sediments which are composed almost entirely of organic matter. It is estimated that out of the whole amount of kerogen in the Earth's crust, most of it is dispersed in sedimentary rocks, and that 10^{16} kg exist in the form of coals and 10^{17} kg in the form of richer oil shales (Durand 1980). According to these estima-

Table 2.7 Content of organic carbon in the Earth's crust

Forms of carbon in the Earth's crust	Amount (kg)	In relation to the total amount in the Earth's crust (%)
Carbonates in rocks	7×10^{19}	76.05
Carbonates dissolved in the oceans	5×10^{16}	0.05
Organic carbon in sediments	1.2×10^{19}	13.04
"Elemental" carbon (mainly in basalts, granites and metamorphic rocks)	1×10^{19}	10.86

Table 2.8 Content of carbon in biomass, oceans, atmosphere and kerogen

	Amount (kg)
Biomass carbon of living organisms	$0.3–3 \times 10^{15}$
Carbon in the form of CO_2 and organic matter in the oceans	1×10^{15}
Carbon in the form of atmospheric CO_2	1×10^{15}
Carbon in the total amount of kerogen	1×10^{19}

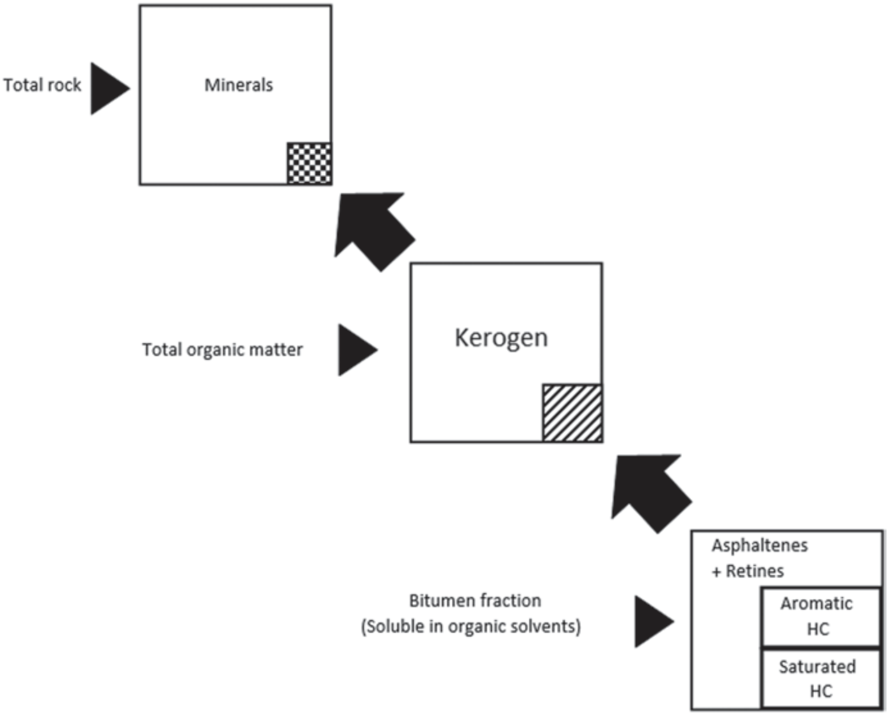


Fig. 2.16 Quantitative kerogen position within the inorganic and the organic part of the sediments (According to Tissot and Welte 1978, 1984)

tions, over 95 % of kerogen is deposited in sediments with less than 5 % organic carbon content, and its total amount in the sediments is nearly 1000 times higher than the estimated total reserves of fossil fuels. The largest amount of kerogen is accumulated in sediments of coastal areas.

Starting from these values, the maximum possible reserves of fossil fuels have also been estimated with a high degree of uncertainty, not considering whether they have already been found or whether they are of economical value. From the standpoint of source rocks for oil and gas, which will be more discussed later, the part of kerogen dispersed in the sediments is considered to be quantitatively the most important. It is further estimated that the total amount of kerogen has the potential to generate naturally (catagenesis, metagenesis) 2×10^{14} kg of gas, 4×10^{14} kg of oil and 3×10^{14} kg of heavy oils and asphalt. It has also been estimated that it is possible to obtain about 5×10^{14} kg of crude oil (“synthetic oil”) from oil shales by pyrolysis, which will also be discussed later.

However, the reserves of fossil fuels found and exploited so far are significantly lower than the estimated ones. In this context it has to be noted that such and similar assessments are characterized by significant uncertainties. As an illustration, the estimations of various authors on the total amount of organic carbon in sediments ranged between 10^{18} and 3.5×10^{19} kg. Therefore, all these estimates are subject to revision and should be understood as estimation of the order of value.

The origin of kerogen was already discussed in the chapter on the evolution of organic matter in sedimentary rocks. The most famous theory on the mechanism of origin of kerogen is expressed in the form of Tissot and Welte degradation-recondensation model (1984), which includes repolimerisation and recondensation reactions of biomonomers, the products of bacterial degradation of biomass, composed of dead autochthonous or allochthonous populations deposited in aqueous media.

However, for explaining the mechanism of the kerogen genesis other models have also been proposed. One of the new models is the model of "selective preservation", which was formulated by Tegelaar et al. in 1989. According to this mechanism, kerogen, or some parts of it occurred by incorporation in the kerogen matrix, very persistent, completely conserved or very little changed biomacromolecular tissues of precursor organisms (algaenanes from algae, bacteranes from bacteria, and cutanes and suberanes from the protective membranes of cells of terrestrial flora).

2.2.1 Chemical Composition and Structure

Outline

Unlike bitumen, whose analysis requires application of classical analytical methods for separation and classical identification instrumental techniques, examination of chemical composition of kerogen and its structure is more complicated work and requires use of a large number of different methods. Therefore, this time these methods (including procedures for sample preparation) will be discussed at the beginning, along with an explanation of the composition and structure.

Methods for determining the composition and structure of kerogen are presented in Table 2.9. However, in most cases the first step in the preparation of natural rock is its isolation in an unaltered, native form. It consists of removing of the bitumen, soluble part of organic matter, and, following, of an extended part of mineral fraction, which is partly an obstacle at determining some constituents. Namely, carbonates interfere in determination of organic carbon, silicates for hydrogen, and pyrite interfere in determining a number of elements.

Due to its insolubility, isolating kerogen by extraction using organic solvents is not possible. On the other hand, its isolation in the native form by removal of mineral part is very difficult and often a insurmountable task, which depends also on the nature of bonds between organic and inorganic substances, especially when it comes to pyrite. Therefore, instead of isolation of completely pure kerogen, usually kerogen concentrates are prepared, whose composition is adjusted to the needs in specific cases.

Table 2.9 Methods for determining the composition and studying the structure of kerogen

Microscopic methods	Microscopy in reflected light
	Microscopy in transmitted light
Physical methods	^{1}H and ^{13}C nuclear magnetic resonance
	Thermogravimetry
	Infrared spectroscopy
	Electron-spin-resonance
	Pyrolytic-gas chromatography-mass spectrometric analysis
	Pyrolysis
	X-ray diffraction analysis
	Electron diffraction analysis
	Ultraviolet and electronic microscopy
Chemical methods	Elemental analysis
	Determination of isotopic composition by mass spectrometric analysis
	Oxidative degradation
	Hydrogenolysis
	Hydropyrolysis
	Hydrolysis
	Reduction

Preparation of Samples for Analysis

Physical methods for the separation of kerogen from the mineral admixtures (flotation, electromagnetic, electrostatic, gravitational, or ultrasound separation, selective "wetting", extraction) have been proved to be insufficient. Although kerogen enriched by using physical methods remained unchanged, the yields of kerogen concentrates were mostly relatively small, and separation was selective, so that, considering the heterogeneity of kerogen, the samples were not representative.

Therefore, for the preparation of kerogen concentrate, chemical methods are most commonly used. For this purpose the sample is ground to a fine powder, and then bitumen is removed by extraction (Fig. 2.10). The next step consists in gradual degradation of greater part of mineral admixtures, usually with diluted hydrochloric acid (removal of carbonates, sulphates, some sulphides, oxides, hydroxides), and then with concentrated hydrofluoric and hydrochloric acid (removal of silicates) at medium heat. In spite of its efficiency, a major shortcoming of using hydrofluoric acid is its unwanted partial reactions also with the kerogen as well as in building insoluble by-products.

In many cases pyrite must be also removed, especially if it is present in large quantities. For removal of pyrite different reagents (nascent hydrogen, lithium aluminium hydride, sodium borohydride, nitric acid, Fe(III)-salts) were used. However, main weakness of using these chemicals is their unintentional reaction also with kerogen leading to significant changes (by oxidation or by reaction with functional groups). Recently, for the removal of pyrite, a more complicated, but better and more efficient, microbiological method has been proposed (removal of pyrite by *Thiobacillus ferrooxidans* bacteria). In the same way, partial removal of silica by *Bacillus circulans* bacteria was also proposed.

Box 2.13: *General Note*

There is still no ideal method for the isolation of the native kerogen. The biggest problem at the preparation of kerogen concentrates is that the used reagents, as it has already been mentioned, can react also with the kerogen (all the more so as the evolutionary stage is lower), changing its composition and structure, and that should not be allowed. In addition, in most cases, reagents are not sufficiently effective, so that a significant amount of mineral impurities remains in the concentrate. Finally, at treatment with hydrofluoric acid, stable, insoluble complex fluorides could be formed, which then have to be removed by special procedure (boric or hydrochloric acid, sodium or ammonium carbonate).

Chemical Composition

Elemental Analysis

Kerogen composition is determined by elemental analysis of homogenized, pulverized and dried sample of kerogen concentrate. For this purpose, usual techniques of organic microanalysis (C, H, N and S) are applied. For a long time there was no appropriate method for direct determination of oxygen, so that in kerogen it was calculated from the difference of total amount and C, H, N and S content. Therefore, the values for the oxygen content were not really reliable, especially in samples with higher content of mineral admixtures. Based on the complex Unterzaucher's method, which assumes pyrolytic conversion of oxygen to carbon monoxide with carbon from the kerogen in an inert atmosphere, methods have been developed for the direct determination of oxygen.

Reliability of the results of elemental analysis depends on several factors, such as type and characteristics of the sample, method of preparation of kerogen concentrate, type and amount of admixtures, the applied analytical methods. Numerous studies have shown that there are significant differences in the results of comparative analyses of reference samples, performed at different laboratories.

Pure kerogen is a fine amorphous dark brown to black powder, of density 0.95–1.50 g/cm^3, with high fluorescence intensity that depends on the type of kerogen. It is mostly composed of carbon (60–90 % ≈ 76 %), hydrogen (1–12 % ≈ 6 %) and oxygen (1–30 % ≈ 11 %), and contains a small amount of nitrogen (0–4 % ≈ 2 %), sulphur (0–12 % ≈ 3.6 %) and some other elements.

Interpretation of the results of elemental analysis will be discussed later.

Mass Spectrometric Determination of Isotopic Composition

Another characteristic of kerogen is the isotopic composition of the stable carbon isotopes ($^{13}C/^{12}C$), which depends on the type of precursor biological material and its subsequent diagenetic and catagenetic changes. The isotopic composition is expressed by $\delta^{13}C_{VPDB}$ values which represents deviation in parts per thousand in relation to a reference, the fossil shell of belemnite (VPDB). In photosynthesis, $^{12}CO_2$ is preferentially assimilated relative to $^{13}CO_2$. Ingredients of different organisms have different isotopic composition of carbon. For example, lipids are enriched with ^{12}C isotope, while amino acids and carbohydrates contain lower proportion of lighter isotopes. Compared to marine plants, terrestrial plants are enriched with ^{12}C isotope. In the formation of kerogen, and during its chemical evolution isotopic fractionation occurs as a consequence of loss of functional groups and polymerisation as well as condensation processes, which allows tracking of diagenetic changes by measuring $\delta^{13}C_{VPDB}$ values. Isotopic composition of kerogen does not change significantly in the catagenetic phase, so that correlation of isotopic composition of carbon in kerogen and bitumen of the same sediment can be used to determine their genetic relationship. This fact is exploited in oil-source rocks correlations, which, as it will be seen later, helps in studying the migration routes of oil and natural gas.

Chemical Structure of Kerogen

Knowing the chemical nature of kerogen is important for several reasons:

a. it is of general scientific interest, because it is the most abundant organic substance in the Earth's crust;
b. learning about its chemical nature contributes to (i) a better understanding of the origin and type of precursor material, to (ii) a better characterisation of life on Earth during the formation of sediments, and to (iii) better knowledge of the environment, the biomass deposition conditions and its subsequent diagenetic, catagenetic and metagenetic alterations;
c. from the practical side, it is of the utmost importance that oil and gas potential of source rocks depends on the chemical nature of kerogen, which, as already stated, is the most important link in the chain leading from biomass to oil and gas (which will be discussed later), and the knowledge of its nature is important in exploration of the oil and gas depositions;
d. kerogen is the main ingredient of organic matter in coals, an important energy and raw material source, and oil shales, a potential alternative source of also large amounts of energy and raw materials; therefore, knowledge of the chemical nature of kerogen contributes to their optimal utilization.

Structurally, kerogen or their specific parts mutually differ very much. The differences are mainly due to their different origins: they originated from different precursor material and under different conditions of sedimentation, but may also be the result of different degree of changes in the Earth's crust.

The contents of functional groups in kerogen are usually inversely proportional to its “maturity” (thermal maturity). Back in early diagenetic stage the loss of some functional groups occurs, which leads also to the beginning of cyclisation and aromatisation processes. In the catagenetic stage, with releasing of low molecular weight molecules cyclization and aromatization continue. In late catagenesis and in metagenesis gas is released leading to a complete aromatization, and later to graphitization.

Because of a possible broad structural diversity of kerogen, a lot of caution is required both in the interpretation of the results of structural studies, and the further use of the structural information obtained. Macromolecular nature, heterogeneity (may consist of parts of very different structure) and the insolubility, and largely the fact that it is in the intimate mixture with a large amount of mineral material, makes the study of chemical structure, and chemical nature of kerogen in general, one of the most complex and the hardest organic-geochemical tasks.

Specific features of kerogen imposed the need to develop and apply methods for its structural study which are different from the methods for analysing the soluble part of the organic matter in sediments, the bitumen. Although chemical methods were once considered as the most useful ones for studying the chemical structure of kerogen. Thanks to the development of powerful instrumental techniques in recent decades, physical and some other specific methods received higher importance nowadays.

The most commonly used methods for studying the chemical nature of kerogen have already been listed in Table 2.9.

Microscopic Methods

Microscopic methods were among the first applied to study kerogen of coals and bituminous shales, and for this purpose they are successfully used nowadays as well. For example, the type of kerogen, as will be discussed in other chapters, can be easily determined microscopically. In studying of the nature of kerogen, it is very useful to investigate thin (in transmitted light) as well as polished (in reflected light) samples of rocks, HCl-HF- and flotation concentrates of sedimentary organic matter.

Optical methods are complementary to other procedures in geological, organic-geochemical and similar surveys. The results of optical measurements allow for the reconstruction of the sedimentation environment and discovering of the great diversity of composition and origin of kerogen. For example, under the microscope it can be seen that kerogen in coals may be of humic nature, deriving from higher plants, or of sapropel nature, originating from algal material. Sediments with less organic matter may have characteristics of oil shales, or source rocks for oil and gas, in which kerogen has predominantly amorphous and only partially recognisable structure. Optical methods can help also in obtaining data on the nature of liquid products that occur at thermal evolution of kerogen, on their origin and migration characteristics, and more generally about the thermal history of the organic matter of sediments.

Investigation of organic matter collected after decomposition of minerals by hydrochloric and hydrofluoric acid, gravity separation or flotation, it is possible in the transmitted light to differ between recognisable and amorphous organic matter. The first, often called ligneous, coaly, humic, or terrestrial organic matter consists of fragments of biological origin, such as plant tissues, lignin fiber, cuticles, resins and microfossils (pollen, spores, algae), while the amorphous organic matter in the form of flakes, powder or agglomerates is unrecognisable and often referred to as colloidal, algal, sapropel or marine. Changes of organic matter can be traced also through changes in color of spores, pollen, algae, and amorphous organic matter with depth, what will be discussed later.

Optical methods, used as the sole methods, have several deficiencies. A more serious deficiency is that in the preparation of test samples a part of organic material gets lost, so that samples are not entirely representative. Therefore, optical methods alone cannot be expected to give a reliable picture of the composition, structure and other characteristics of kerogen.

Physical Methods

Apart from optical methods many other physical methods have been applied in kerogen analysis such as thermogravimetry, infrared spectroscopy, nuclear magnetic resonance, electron spin resonance, diffraction methods, thermal methods, e.g. pyrolysis and pyrolysis—gas chromatography—mass spectrometry analysis and others. Most of these methods are not in routine use.

Thermogravimetric analysis (TGA) and differential thermogravimetric analysis (DTA), usually heating the sample from 25 °C to 600 °C under controlled standard conditions (equipment, heating range and rate, ambient atmosphere, sample size, etc.), are used to simulate changes in kerogen at thermal decomposition and natural production of hydrocarbons and other products in sedimentary rocks. In other words, processes that occur in sediments for a long time (millions of years) at low temperatures (20–200 °C), are simulated in a short time by heating the samples at 300–600 °C. Temperature and rate of decomposition, as well as yields of products depend on the nature of kerogen, its structural type and origin. The obtained decomposition products are tested with other physico-chemical methods.

The general chemical nature of a kerogen, its origin, type of precursor material, as well as maturation changes, may be also assessed by infrared spectroscopic analysis. While all of the infrared spectra of kerogen consist of a limited number of the same, relatively poorly defined broad bands, based on their intensity, they provide raw data on the average abundance of the structural elements in the kerogen, e.g. saturated and aromatic structures, hydroxyl, carbonyl, ester, carboxyl or other functional groups. Advantage of this method is that a small amount of sample can be tested in native form, without any major, complex and complicated preparation.

Based on the fact that in the kerogen stable and free radicals can be found, whose origin, and characteristics depend on the precursor material and its evolutionary changes, electron paramagnetic (spin) resonance (EPR or ESR) is applied for kerogen examination. Although it is possible to obtain only general information with this method, on average, the identified paramagnetism (signal intensity) can be used to assess the origin (nature of precursor biological material) and to explore the potentiality of source rocks and can be correlated with some other chemical or physical characteristics of the investigated samples. Purification of kerogen samples by releasing from minerals with paramagnetic properties with which they are in the mixture, is the biggest problem when using this test method. Its advantage is that it is nondestructive.

From the thermal methods, controlled pyrolysis combined with gas chromatography—mass spectrometry identification of pyrolysis products (Py/GC/MS) is also widely used. In this case, pyrolysis is a simulation of catagenetic changes of kerogen in sedimentary rocks. It turned out that pyrograms are a good basis for assessing the kind of source rock (kerogen type) and its evolution stage (maturity), and the correlation between source rocks and oils. The Py-GC-MS analysis requires only very small amounts of sample.

To investigate structural and some general characteristics of kerogen, Rock Eval method (Rock Evaluation) is used, which involves heating the sample of a sedimentary rock in the absence of oxygen at a certain temperature range (usually up to about 600 °C). With the apparatus, specially designed for this purpose (Rock-Eval pyrolyzer), three maxima are obtained: S_1, S_2 and S_3. Value of the first maximum is proportional to the quantity of bitumen found in the rock. Value S_2 corresponds to the quantity of bitumen that is generated by pyrolysis of kerogen, and finally, the value of maximum S_3 is proportional to the amount of CO_2 generated, and in fact corresponds to the amount of native oxygen in the rock. As a result, this method is often used for the direct determination of oxygen concentration in a sedimentary rock.

Rock Eval pyrolysis is also used for determination of the so-called Maximum Pyrolytic Temperature (T_{max}). It can be a reliable parameter for kerogen maturity, as it has been shown that the temperature of maximum generation of pyrolysates is as high as kerogen is mature. In other words, with increasing maturity of kerogen, the parameter value T_{max} increases. This method will be more discussed in the last chapter of this book.

To investigate structural changes of kerogen, the X-ray diffraction analysis, electron diffraction analysis and electron microscopy are also used.

Chemical Methods—Elemental Analysis

Chemical methods have significantly contributed to the knowledge about the chemical nature of kerogen. For this purpose, oxidative degradation, alkaline hydrolysis and determination of functional groups or cross-connections using specific reagents were the most applied methods in the past.

Since the sediments contain not only insoluble kerogen, but also the inherited bitumen or bitumen generated during catagenesis, which by definition is soluble part of the organic matter, study of the kerogen structure by chemical methods must be preceded by preparation of native kerogen concentrate according to some of the procedures which were discussed before.

One of the shortcomings of chemical degradation methods is that they require a long time. Therefore, for practical application, more general structural characterization of kerogen requires faster and more efficient methods that will meet the needs of organic-geochemical prospecting. One of the most widely used methods that meet this requirement, is also a chemical method: elemental analysis of kerogen (i.e. determination of C, H and O), already described in the chapter on the chemical composition of kerogen.

Although the elemental analysis leads only to the image of the "average" composition and structure of the heterogeneous kerogen and not on the structure of its individual components, it still provides important basic information about characteristics of kerogen and about its background. Moreover, based on the elemental composition it is possible to estimate potential of kerogen to generate hydrocarbons in oil and gas during catagenetic or metagenetic phase.

Many different diagrams were proposed for interpretation of the results of elemental analysis of kerogen in the past. The results are usually interpreted today by entering into a diagram that represents the atomic H/C versus atomic O/C ratio. This diagram was first proposed by Van Krevelen (D.W. Van Krevelen) for characterization of coals, so that all similar diagrams are still called after his name. The interpretation in this way is logical for several reasons. Carbon, hydrogen and oxygen represent the largest part of the kerogen, and it is normal that the interpretation is based on the contents of these elements. On the other hand, when their combination is used, i.e. atomic H/C versus O/C ratio, errors and deviations are smaller than when the results for individual contents of these elements are used.

It was shown that the values obtained for different types of kerogen in the diagram are distributed in three zones (Fig. 2.17), which essentially represent the

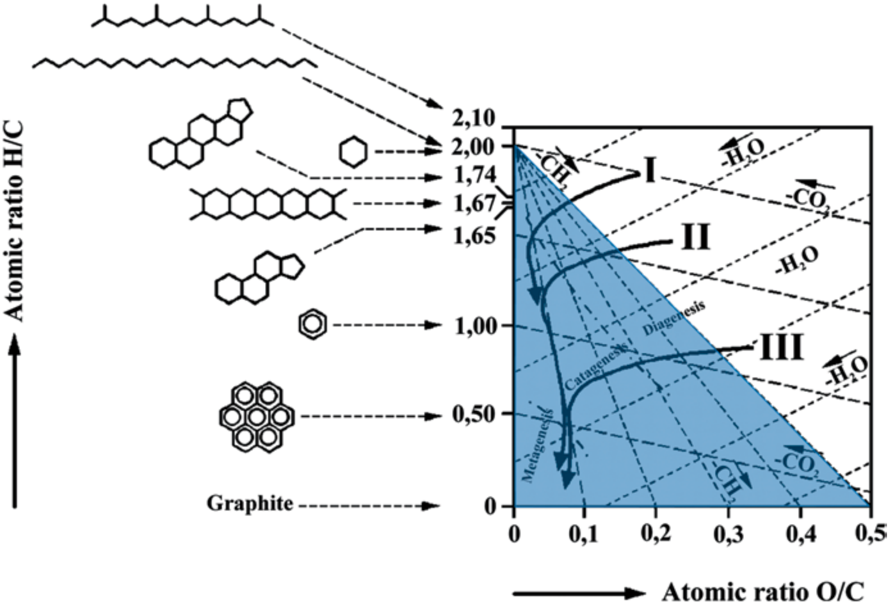


Fig. 2.17 Van Krevelen diagram

three reference kerogen types (I, II and III). As seen from the figure, the evolution changes of the three types of kerogen were followed by reduction in the atomic O/C- versus H/C- ratio, which in all the three cases leads to an increase in carbon content and subsequent convergence to similar values. This is due to the fact that kerogen is not stable at elevated temperatures and pressures at deeper depths, in the absence of oxygen, where oxygen structures are more unstable than the structures rich in hydrogen. In the diagram, straight lines mark the changes represented by loss of CH_4, CO_2 and H_2O. Figure 2.17 illustrates also the general chemical sense of the Van Krevelen's diagram.

Evolutionary processes include various chemical and physical changes affecting certain types of kerogen successively pass under adequate geological conditions. The position on the evolutionary paths indicates not only the differences in the average structures of certain types of kerogen in the initial stage, but also the later gradual chemical changes that converge to newly formed polycyclic aromatic structures with a few functional groups, regardless of the initial chemical structure. Evolutionary paths roughly indicate conditions in the depositional environment, in the case of type I kerogen in the reducing, and type III in oxidizing environment.

The true nature of biomass at the time of deposition, and hence the origin of a kerogen sample can be better assessed if both complementary petrographic and physico-chemical analyses are applied, because the original features of kerogen are changing with the progress of its evolution. In more mature kerogens, assessments of nature are less certain.

In general, type I kerogens are predominantly characterized by aliphatic and type III by aromatic structures, while the type II kerogens consist of variable amounts of aliphatic, alicyclic and aromatic components. Type I kerogen is predominantly of algal origin, type III kerogen originates primarily from terrestrial plants, and type II kerogen is of marine as well as of terrestrial origin (Table 2.10).

However, kerogens represent countless combinations of structural types, including also the possibility that kerogens of the same or similar atomic H/C-O/C-ratio differ structurally. Therefore, neither position determined by elemental analysis nor evolutionary path in the Van Krevelen's diagram cannot be completely sufficient to

Table 2.10 Characteristics of kerogen types I, II and III

Type of kerogen	Characteristics
I	Predominantly aliphatic structures Mainly lipid material of algal origin Amorphous substance, without recognizable remains of organisms Deposited mostly in marine environment and large deep lakes
II	Variable, a mixed structure, with a significant contribution of saturated polycyclic structures Usually marine, and mixed origin, with smaller contribution of terrestrial material Amorphous, sapropel material, the remains of algae, plankton, terrestrial pollen, humic materials Deposited mostly in shallow epicontinental seas
III	Predominantly aromatic structure Primarily derived from terrestrial plants Mainly humic, coaly material

structurally characterise some kerogen with certainty, because kerogens of similar background could tolerate different evolutionary changes, and kerogens of different origin the same ones.

To the original Van Krevelen's diagram was added also the evolutionary curve of type IV kerogen, which shows the composition and changes of reworked, oxidised kerogen of inertinite properties found in some sediments.

Chemical Degradation Methods

For a closer examination of the structure of kerogen chemical degradation methods are used. Considering the insolubility of kerogen, the method that was most commonly used for studying of its structure is degradation to products of low molecular weight both at higher temperatures (hydrogenolysis, hydropyrolysis) and by chemical reagents at lower temperatures (oxidation, reduction, hydrolysis).

Out of all these methods, oxidative degradation was and still is the most widely used. Oxidation converts most of the kerogen into soluble degradation products from which the original structure can be reconstructed. For this purpose, oxidizing agents such as potassium permanganate and ruthenium tetroxide, or sometimes also chromic acid, nitric acid, hydrogen peroxide, mixture of potassium hydroxide and potassium nitrate, ozone, air and pure oxygen were used.

In the first alkaline permanganate degradation procedures two techniques were applied: carbon balance determination, which consisted in complete oxidation of 1 g of kerogen with alkaline permanganate, and bulk oxidation, consisting in the oxidation of a large amount of sediment with solid permanganate. In both cases, products were identified and their yields and types were used for the interpretation of the structure.

To obtain structural information a complete oxidation of kerogen has to be avoided. For this purpose a stepwise oxidation has been introduced. The procedure consists of stepwise addition of small portions of oxidizing agent and separation of oxidation products from the kerogen that have not responded yet, before adding the following amount of oxidant. Advantage of the stepwise oxidative degradation is also in the fact that the products could be tested separately, in steps, which can give more additional structural information on individual components of heterogeneous kerogen.

The research strategy in optimizing the stepwise oxidative degradation was based on the following objectives:

a. for degradation to be as specific and selective as possible;
b. for the yields of oxidation products to be as high as possible, to represent as much of the kerogen as possible; and
c. for the molecular weight of degradation products to be small enough in range that will allow easy and reliable identification by physical methods, but large enough so that they still retain structural characteristics of kerogen, i.e. to be structurally representative.

In this sense, at this point we will describe, as an example, the stepwise degradation method using alkaline potassium permanganate. Advantage of this reagent is that,

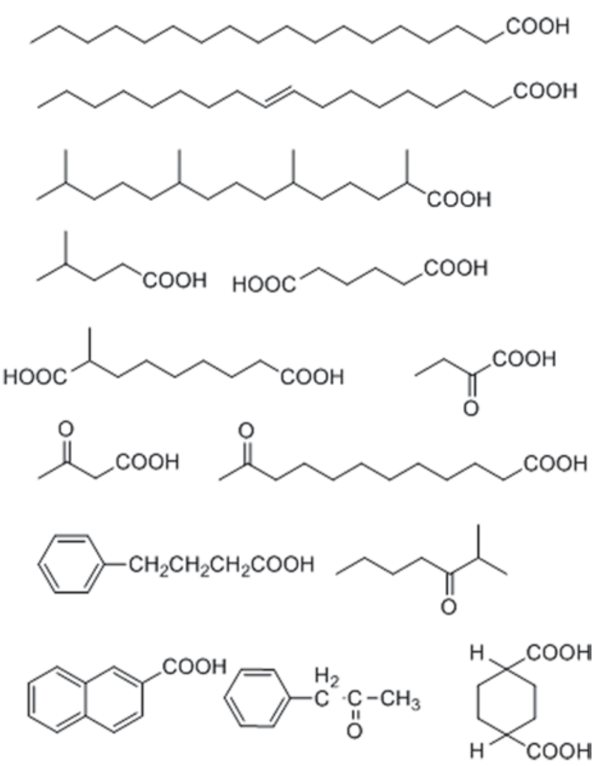


Fig. 2.18 Examples of possible oxidation products of kerogen

with carefully selected stepwise alkaline degradation, it allows timely separation of oxidation products at each stage, making it possible to obtain high yields of structurally relevant products, mainly organic acids that are easy to identify. Examples of possible oxidation products of kerogen are shown in Fig. 2.18.

Box 2.14: *Case Example*

Stepwise oxidative degradation of Kerogen

For example, in one of the first experiments with stepwise oxidative degradation of kerogen in Colorado oil shale (Green River), a significant number of acids in high yields were obtained (see first table below, Vitorović et al. 1994). Their structures were proved by using gas chromatography—mass spectrometry technique.

Detailed gas chromatography—mass spectrometry analysis enables also quantitative assessment of proportion of certain types of acids in oxidation products, as well as structural elements of kerogen, and thus approximate structural comparison of kerogens of different origin and chemical nature, as illustrated by the examples in second table.

Notable differences between types and yields of oxidation products of three samples of kerogen are obvious and significant. Thus, this degradation method was found useful for the interpretation of the general structure of kerogen and a good basis for comparison of kerogens of different origins.

Type of acid	Range
n- Monocarboxylic	C_9–$C3_2$
α,ω- Dicarboxylic	C_6–$C2_9$
Branch dicarboxylic	C_9–C_{15}
Isoprenoid	C_{14}-C_{17}, C_{19}, C_{20}
Alkane-tricarboxylic	C_7–C_{16}
Alkane-tetracarboxylic	C_9–C_{14}
Keto-acid	C_9–C_{11}
Aromatic acids	in low yield

The participation In the total oxidation products of reference kerogen (%)

Type of acid	Green River (USA) oil shale *kerogen type I*	Paris Basin oil shale *kerogen type II*	Mannville (Canada) oil shale *kerogen type III*
Aliphatic *n*- monocarboxylic	28.9	33.2	2.2
Aliphatic α,ω-dicarboxylic	62.1	46.2	4.4
Aliphatic isoprenoid	2.3	0.2	–
Aliphatic keto	–	0.5	–
Alkane-tricarboxylic	4.6	1.1	–
Alkane-tetracarboxylic	2.1	1.2	–
Aromatic	–	17.6	93.4

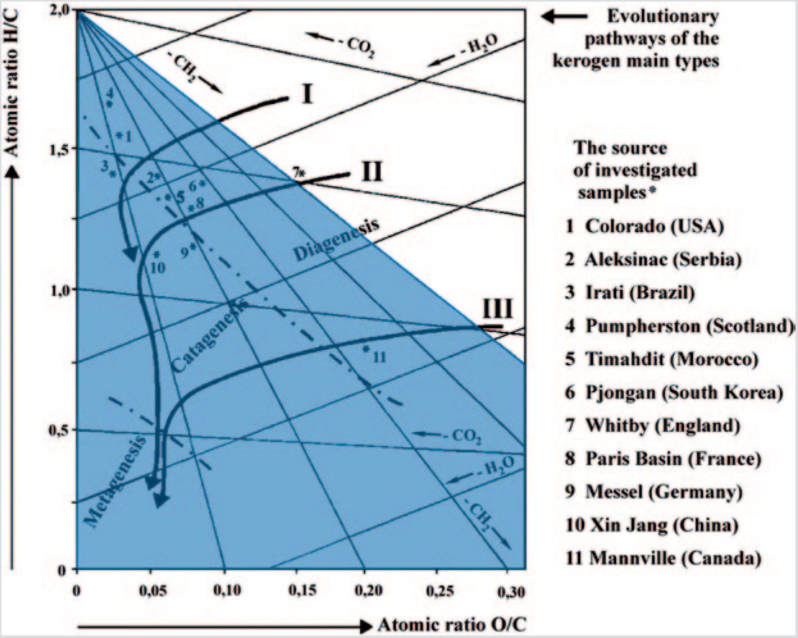
Contrary to Van Krevelen's diagram, the oxidation products indicated much more structural differences among each other. The products of oxidative degradation, as the basis for the characterization and classification of kerogens, enable more precise structural interpretation than the classification based only on the elemental analysis.

Box 2.15: ***Case Example***

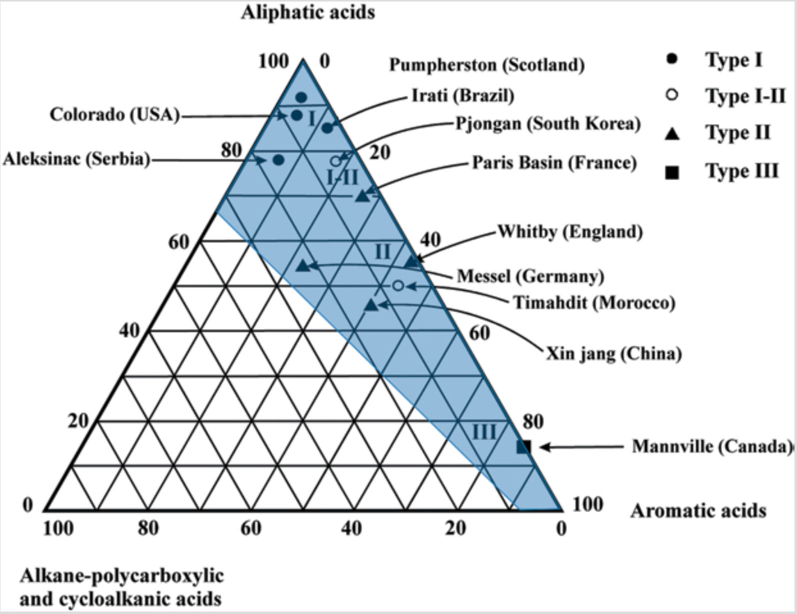
Capabilities of the stepwise degradation method

For example, capabilities of the optimized stepwise oxidative alkaline permanganate degradation method will be illustrated by the results of testing kerogens from 11 samples of bituminous shales of different provenance and apparently different structural types.

On the basis of the elemental analysis of kerogen concentrates and atomic H/C- and O/C-ratios entered into Van Krevelen's diagram, these kerogens were classified as type I, II-I, II and III kerogens (see figure below, Vitorović 1994).



Considering that the three major acid classes in oxidation products, i.e. aliphatic (saturated normal and branched), aromatic (mono- and polycarboxylic), and alkane-polycarboxylic and cycloalkane acids, may be associated with specific but different precursor structures, quantitative assessment of the total yield of these three classes of acids has been entered in the ternary diagram, which was taken as the basis for the specific classification of kerogen. The position in the ternary diagram defines the proportion of certain acid classes in oxidation products of kerogen (see figure below, Vitorović et al. 1991).



It was shown that the difference between type III kerogen, on the one hand, and type I and II kerogens, on the other, was more clearly expressed, whereas the difference between type I and II kerogens was lower, with kerogens of transitional type I-II profiled between them.

Thorough analysis of the diagram shows that kerogens of the same type can show also significant structural differences. Namely, the different positions in the diagram are certainly a reflection of the existing structural differences between the investigated kerogens. Thus, for example, it can be concluded that the kerogen in Green River and Pumpherston shales contains the least proportion of aromatic structures, which indicates the smallest contribution of the terrestrial, and the largest contribution of algal material. On the other hand, the smallest aliphatic and the largest acyclic character of kerogen of Aleksinac shale indicates a greater contribution of bacterial activity.

Possibilities of interpretation of the results of a multistep oxidative degradation of kerogen are not exhausted by the ternary classification diagram. These degradation studies provide a number of other data that open up avenues for further differentiation of kerogens, for example:

a. differences in yields of insoluble acid and undegraded residue indicate a different degree of cross-linking or branching in the structure of the kerogen and different contents of functional groups, but also possible differences in the behaviour of aromatic structures towards the alkaline permanganate, and consequently their properties;

b. different ratios of insoluble acids in relation to acids soluble in ether indicates the length of the hydrocarbon chains in the cross-linked structure of the kerogen or the substituents on the periphery;
c. differences in the relative abundance and distribution of individual members of homologous series, for example, the dominance of a particular member or ordinary or bimodal distributions, indicate the differences in the precursor material from which the kerogens originate;
d. different composition within some acid classes, e.g. the dominance of aliphatic dicarboxylic acids or the dominance of aliphatic monocarboxylic acids in the oxidation product, is substantially indicative for the differences in the aliphatic part of the structure of kerogen; the same can be assumed for the differences in the relations between the mono-, di-, tri- and tetracarboxylic aromatic acids, or the differences between the yields of benzene- and naphthalene-carboxylic acids;
e. the degree and type of changes in the composition of oxidation products in various stages of multistage degradation allow the assessment of homogeneity or heterogeneity of kerogen.

Characterization and classification of kerogen based on the oxidation products obtained by standard optimized multistage alkaline permanganate degradation is a base for considerably more accurate structural differentiation than the classification on the basis of atomic H/C—O/C- ratios only. In this way, it is proved that there may be significant and substantial structural differences even between the kerogens which, based on elemental analysis, look very similar. This conclusion may be of importance in studying the origin of the investigated kerogens, their precursor material, deposition conditions and the geological history, but also in the application of one of the three most important parameters in organic geochemical prospecting for oil and gas deposits, kerogen type, which will be discussed in other chapters of this book.

Recently, as a reagent for studying of the kerogen structure, ruthenium tetroxide has also been used. Ruthenium tetroxide oxidizes alcohols, aldehydes, alkenes, alkynes, and some aromatic compounds to the corresponding carboxylic acids, similar to permanganate. However, in some cases, this oxidant reacts differently than permanganate. One important difference is in the reaction with substituted aromatic hydrocarbons (Fig. 2.19). Another significant difference is the reaction with ethers. The main product of the alkaline permanganate degradation are carboxylic acids. This reagent oxidizes ethers groups to esters and carboxylic acids. Further on, under the used alkaline conditions the already existing kerogen ester bonds are hydro-

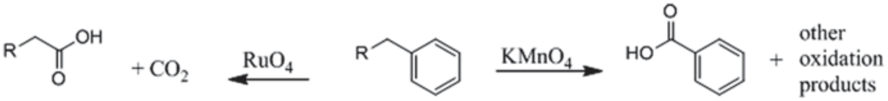


Fig. 2.19 Example of rutheniumtetroxide reactions with substituted (alkylated) aromatic hydrocarbons

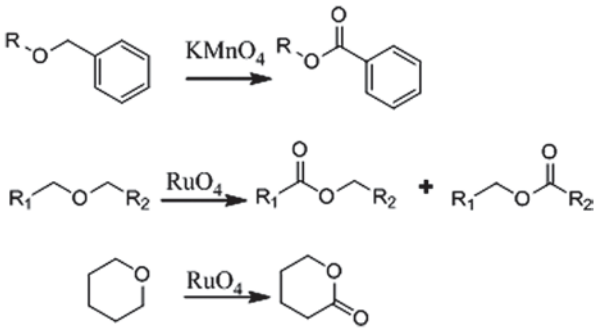


Fig. 2.20 Examples of oxidation of ethers with rutheniumtetroxide

lysed to alcohols and carboxylic acids. Hence, these two formation pathways for carboxylic acids by alkaline permanganate degradation prevents a systematic differentiation of oxidation and hydrolysation products. In contrast, ruthenium tetroxide oxidizes ethers to the corresponding esters, which allows differentiation of the ether structural units from esters (Fig. 2.20). Ruthenium tetroxide preferentially oxidizes aromatic compounds to carboxylic acids and carbon dioxide, converts primary alcohols to acids (over aldehydes), secondary alcohols to ketones and ethers to esters or lactones, but leaves aliphatic and alicyclic parts of the structure unchanged. Therefore, the degradation by ruthenium tetroxide or combined method of hydrolysis/oxidation by ruthenium tetroxide/hydrolysis may be considered as useful complementary methods that allows possibilities for a more complete interpretation of the structure of kerogen.

For the structural study of kerogen further oxidizing agents has been used in the past, but to a much lower extent.

Reconstruction of the kerogen structure based on the oxidation-degradation products is not simple nor complete, mainly because it does not give also quantitative data on the functional groups or the nature of relations between various structural elements. Namely, oxidizing agents most often attack functionalized or adjacent carbon atoms, ignoring the functional groups and cross-links in the kerogen during degradation.

Therefore, specific structural studies of kerogen are devoted to determining the type of cross-linked structure of kerogen, and functional groups. For this purpose, various complementary methods and different reagents, such as concentrated hydroiodic acid (ether links), barium acetate, calcium acetate or aqueous solution of sodium hydroxide (carboxyl groups), acetic anhydride in pyridine (hydroxyl group), sodium hydroxide solution (ester groups), hydroxylamine or formamide (carbonyl groups), bromine reagents (double bonds) and many others have been applied.

For example, in a kerogen sample of Colorado oil shale from Green River formation the distribution of the total oxygen in various functional groups was determined. The results are shown in Table 2.11.

Based on the results obtained by chemical and other methods, different structural models of kerogen were proposed. Originally they were very simple and quite general, and therefore incomplete (Burlingame et al. 1969, Murphy et al. 1970, Yen

Table 2.11 Distribution of oxygen in different functional groups in a sample of Green River oil shale kerogen

Functional group	The percentage of oxygen	
	Relative to kerogen	Calculated on the total oxygen
Carboxylic	1.30	15.3
Ester	2.10	24.7
Amide	0.05	0.6
Carbonyl	0.10	1.2
Hydroxyl	0.40	4.7
Ether	4.55	53.5

et al. 1976). Later, more complex models, based on the study of structure by combined complementary methods, were proposed by Vandenbroucke (cited in Colletta 2003). To simplify, kerogen of the low level of maturity and mature kerogen can be represented as in Figs. 2.21 and 2.22.

However, even the best model cannot fully represent the structural heterogeneity and complexity of kerogen. It has been said that the oxidation methods proved that even kerogens of the same type differ. The "theoretical" oxidation of the most complex proposed structural models of three types of kerogen (Fig. 2.22) was performed to assess the amount and type of carboxylic acids that could be expected as a result of their oxidative degradation by alkaline permanganate. A significant difference between the oxidation products obtained in practice and products of "theoretical" oxidation model of kerogen has been revealed, which indicated the deficiencies and incompleteness of even the most complex structural models of kerogen and, in general, the great difficulty, almost impossibility, to model the structure of kerogens or some parts of their heterogeneous composition more accurately.

The main disadvantage of chemical methods applied to study the chemical nature of kerogen is that they ignore the heterogeneity of kerogen, i.e. presence of different types of kerogen in the same sample.

For defining different types of kerogen, coal petrography terminology was used, which is based on the contents of morphologically defined particles, so called macerals, identified by optical methods. Petrographic investigation and maceral composition of kerogen will be more discussed in the chapter on coals. At this point, the terminology for the characterization of kerogen is compared only generally, based on the elementary analysis or petrographic composition (Fig. 2.23).

Box 2.16: *General Note*

Although the characterization of kerogen based on chemical methods provides a more detailed and accurate structural interpretation and differentiation than the one based on atomic H/C-O/C-ratios, classification on the basis of elemental analysis meets better the practical needs, because it acquires more easily and quickly basic information about a large number of samples (mainly on the type of kerogen). It is of highest importance for the prospective research for oil and gas, because the type of kerogen is one of the most important factors which determine the amount of oil or gas generated in catagenetic or metagenetic stage.

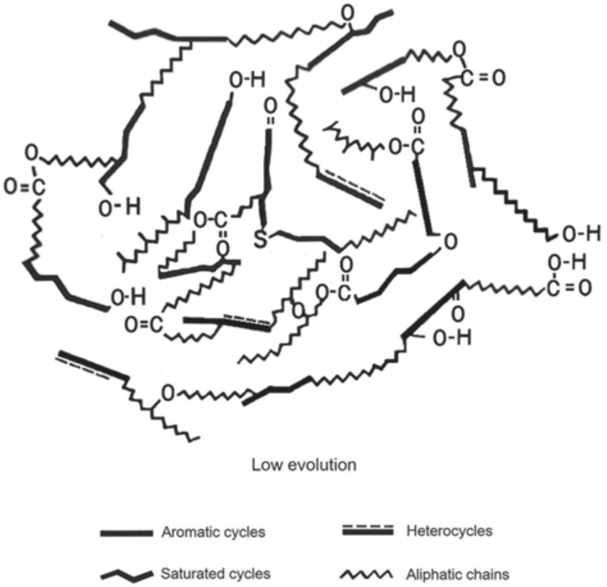


Fig. 2.21 The kerogen of the low level of maturity (According to Tissot and Welte 1978, 1984)

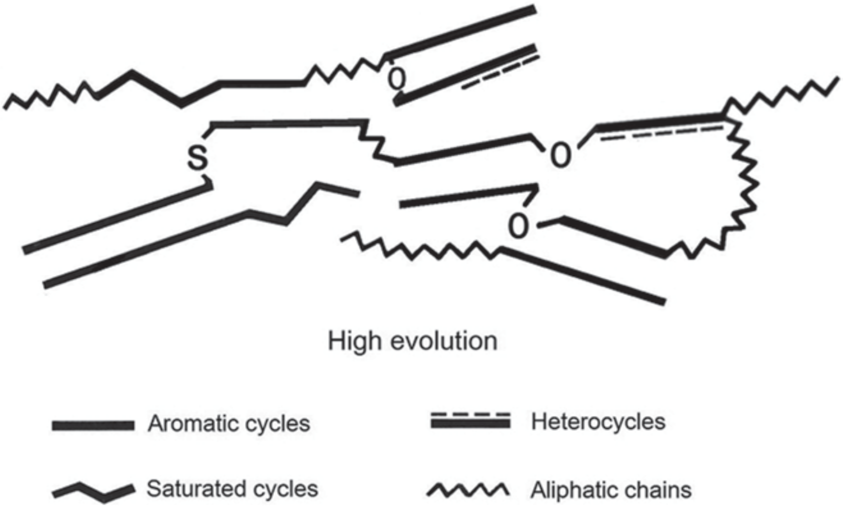


Fig. 2.22 The mature kerogen (According to Tissot and Welte 1978, 1984)

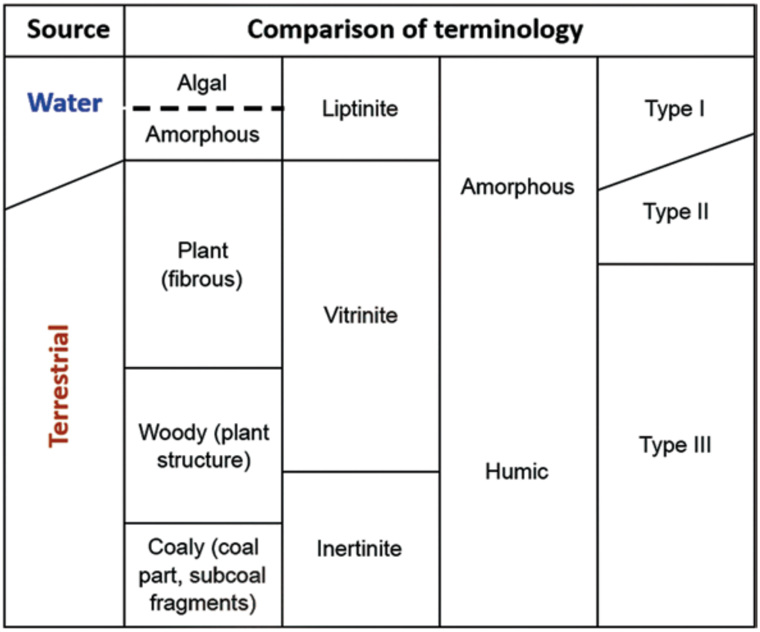


Fig. 2.23 General comparison of terminologies for kerogen characterization. (According to Tissot and Welte 1978, 1984)

2.3 Oil

Outline

Bitumen and petroleum are similar forms of organic matter, considering that the term bitumen is used for the form accumulated in reservoir rocks, and the term petroleum for the form in the reservoir rocks. Description of bitumen composition and method for its analysis at the same time is largely a description of oil and methods for its analysis. Therefore, this is more or less the continuation of the bitumen chapter. Source rocks for oil (with criteria for determining their potential), migration of bitumen, reservoir rocks (with oil changes in them—maturity, deasphalting, water washing and biodegradation) and *correlation parameters* (bulk and specific) will be discussed here. The aromatic hydrocarbons, most relevant to assess the maturity of the oil, will also be described.

From the organic-geochemical point of view oil is one of the final products of transformation of organic matter in sedimentary rocks which can be summarized as follows: in the stage of diagenesis, under the action of microorganisms, *bio*polymers (proteins, carbohydrates, lignin, complex lipids) degrade to *geo*monomers (amino acids, monosaccharides, phenols, fatty acids); geomonomers, if not subjected to further microbial decomposition to even smaller molecules (H_2O, CH_4, NH_3, N_2, and H_2S) polymerize to fulvic and humic acids, then to humin, and finally to kerogen, which is the end stage of diagenesis. Under the influence of heat, pressure and mineral catalysts the kerogen converts to bitumen in the catagenetic phase over a very long period of geologic time. Bitumen and its inherited constituents migrates under certain conditions (primary and secondary migration) from the original (source) to reservoir rocks where it is accumulated as oil. Only in special cases oil may be transferred to a new reservoir rock which is found at yet lower depth (tertiary migration).

Box 2.17: *General Note*

Oil can be characterized to represent migrated and accumulated product of diagenetic and catagenetic transformations of organic matter in sedimentary rocks.

2.3.1 Source Rocks for Oil

Box 2.18: *General Note*

If during catagenetic transformations of kerogen significant amounts of bitumen are generated in a sedimentary rock, and if the amount of generated bitumen allows migration together with the inherited bitumen (possibly to the reservoir rock for oil), this rock is called the “source” or “parent” rock for oil. However, in the organic-geochemical literature, the definition of source rock is broader and vaguer.

The term source rocks for oil was first used by John Newberry back in 1860, only a year after the first well was drilled in Pennsylvania, the United States. Newberry assumed that crude oil originated from oil shale as the source rock.

In the recent organic-geochemical literature, source rock is defined in different ways. The american geochemist Paul Philp defines the source rocks as “sedimentary organic matter-rich rocks, capable of generating crude oil or natural gas”. In one of the best known organic-geochemical monographs, “Petroleum Formation and Occurrence”, Tissot and Welte (Tissot and Welte, 1978) explain that, in a broader sense, the term source rock “means sedimentary rocks that were once able to produce oil, those that now can, and those that will be able to generate petroleum when level of their thermal maturity is at a higher level”. Somewhat earlier, in 1977, Dow (W. G. Dow) defined a source rock as “…sedimentary rock that can generate and expel significant commercial quantities of oil and gas, able to migrate in sufficient quantities to form commercial accumulations”. Ambiguities in the use of the term source rock for oil could be resolved by distinguishing different types of source rocks. Dow proposed a division into several types:

- "*limited*" *source rock* is sedimentary rock that contains all the prerequisites of a source rock except volume; therefore it cannot be defined by geochemical parameters alone, but requires geological criteria, such as layer thickness, density, surface area, etc.;
- "*potential*" *source rock* is sedimentary rock that has the capacity to generate oil and gas in sufficient quantities; however, it has not yet done so because it did not reach the catagenetic phase, or sufficient thermal maturity;
- "*active*" *source rock* is a rock that is in the process of generating oil or gas; this source rock has reached the maturity corresponding to "oil window";
- "*inactive*" *source rock* is a sedimentary rock that was once active but has temporarily stopped generating prior to becoming spent; inactive source rocks are usually associated with areas where tectonic movements (uplift and erosion) have occurred, and would generate hydrocarbons again in a favourable geological environment;
- "*spent*" *source rocks* are sedimentary rocks that have completed the oil and gas generation process and they had high potential once, which, however, was spent over the geologic time.

Classification of source rocks for oil was given by Waples (Waples 1985) in his monograph "Geochemistry in Petroleum Exploration." He classified all the types to "effective", "possible" and "potential" source rocks. An effective source rock is any sedimentary rock that has already generated and expelled hydrocarbons. Possible source rocks are any sedimentary rocks whose potential has not yet been known, but which are capable of generating and expelling hydrocarbons, and potential source rocks are any immature sedimentary rocks known to be capable of generating and expelling hydrocarbons if their levels of thermal maturity were higher. According to Waples a particular stratum could be an effective source rock in one place; a potential source rock in a less-mature area; a possible source rock in an unstudied region. A part of the same sediment might have no source potential at all.

When we analyse a sample of a sedimentary rock in the laboratory, we actually measure its remaining, or untapped source capacity at the present moment. In the organic-geochemical literature this capacity is marked by G. The rock's original capacity is marked by G_0. The difference between G_0 and G represents the hydrocarbons already generated. All the three types of source rocks are characterized by a particular value for G_0. The unused source capacity in the possible source rocks is unknown, and in the potential ones it is reduced to G_0. The amount of generated hydrocarbons (G_0-G) in possible source rocks is unknown, and in the potential ones they do not exist (Table 2.12).

Table 2.12 Primary source capacity of certain types of source rocks

Type of source rock	The initial source capacity	Unused source capacity	Generated hydrocarbons
Possible	G_0	Unknown	Unknown
Potential	G_0	G_0	No
Effective	G_o	G	G_0–G

2.3.2 Criteria for Evaluation the Source Rocks Potential

In oil and gas prospecting studies, one of the most important tasks is to discover oil source rocks. Very often, discovering a source rock is more important than finding a reservoir rock, as source rock can be an effective indicator for the detection of a number of reservoir rocks for oil.

Box 2.19: ***General Note***

Based on the previous organic geochemical investigations of many different types of sedimentary rocks and oils, relevant criteria for assessing the source potential of sediments have been determined. Firstly, a sedimentary rock must contain specific, at least the minimum amount of organic matter. Secondly, in order to classify it as a source rock, organic matter (kerogen) in it must be at a certain level of thermal maturity. Finally, since it is known that some types of kerogen have very little hydrocarbon-generating potential (or do not have it at all), the third essential criteria is that the type of kerogen is favourable.

To be evaluated as a oil source rock all the three mentioned criteria must be fulfilled!

Total Organic Carbon (TOC)

In determining the source potential of sedimentary rocks, total organic matter (soluble bitumen and insoluble kerogen), is a parameter of major priority. It is represented by the total organic carbon content (TOC) that is expressed as weight percent in dry sample of sedimentary rock.

Based on testing a large number of sedimentary rock samples of various ages and from different sites (both oil-generating and non-oil-generating), it was concluded that the amount of 0.5 % TOC should be adopted as the lowest limit of organic carbon content in source rocks. Some organic-geochemical researchers adopted even stricter criteria, so as to take the lowest limit value of 1 %.

The lowest limit for the organic matter content in the source sedimentary rocks depends on their lithological composition. Specifically, it appears that carbonate rocks with only 0.3–0.5 % of total organic matter may be the source rocks for oil. However, values of about 0.5 %, and especially below 0.5 %, must be taken with great caution. There are very rare examples of source rocks with this TOC content. Table 2.13 presents typical ranges of TOC values in the sediments of different source potential.

Increasing total organic carbon content in sediments correlates proportionally with original potential only to a certain limit. Namely, having in mind that at some point the migration of bitumen begins, i.e. bitumen leaves the source rock, it is logical to expect that the total organic matter in a source rock, and thus the TOC, will decrease after a certain period of time. On the other hand, when examining the

Table 2.13 Typical ranges of TOC values in the sediments with different source potentials

TOC (%)	Source material
<0.5	Negligible
0.5–1.0	Possible weak
1.0–2.0	Possible moderate
>2.0	Possible good or excellent

Table 2.14 Limit values of the bitumen content in potential source rocks

Total bitumen	
300–3000 ppm	On crude sample
50–200 mg/g	Of organic matter
5–20 %	On organic carbon

source potential of sedimentary rocks, one must always bear in mind that a large amount of organic carbon may be the result of the presence of organic matter that derived from outside, e.g. from some other rock or as the result of contamination. Such an organic matter is called “allochthonous”, and the organic matter which is present at the site of origin is termed “indigenous” organic matter.

For these reasons it is necessary to determine also the sedimentary bitumen content, or to determine what proportion of the total organic carbon exist in the form of bitumen, and what proportion is in the form of kerogen. If the bitumen content is above the normal limits, doubts about the presence of allochthonous organic matter are reasonable. Limit values for the bitumen content in source rocks, expressed in three ways, are given in Table 2.14.

A bitumen content close to the lowest limit indicates either that this is only a potential source rock or that it is a source rock in which migration has already been completed. Contrarily, if the bitumen content is close to the upper limit, we can assume that this is a rock from which migration has only begun, or is close to this stage. Sedimentary rocks containing organic matter in quantities much above 2 % (e.g. oil shale or coal) are not the source rocks for oil in most cases. There are two possible reasons: either their organic matter is immature, or they contain kerogen type III or IV, with little hydrocarbon-generating potential.

Based on the previous described organic-geochemical analysis methods it has been adopted that a limit of 0.5 % TOC is taken as the basis for selection of samples (a screening approach) for the determination of source potential (regardless of whether it is a possible, potential or effective source rock). In samples with values <0.5 %, further investigations are generally not performed, i.e. organic matter type and maturity level are not determined.

Type of Organic Matter

Just to remember, structure and properties of kerogen have already been addressed in a separate chapter. Methods for studying its structure, including a method for

Table 2.15 The potential of different types of kerogen for hydrocarbon production

Kerogen type	Macerales	The potential for hydrocarbons production
Kerogen type I	Liptinite (alginite)	Excellent potential for bitumen production
Kerogen type II	Liptinite (other macerales)	Excellent/good potential for bitumen production
Kerogen type III	Vitrinite	Weak potential for bitumen production, moderate/good gas potential
Kerogen type IV	Inertinite	Without potential for bitumen and gas production

the determination of elemental composition and classification of kerogen based on atomic H/C- and O/C- ratios, have been also described. From an analytical point of view, these methods are very simple, but they provide important and fundamental results. It can be argued that the classification into types I–IV is actually the basis for studying the composition and properties of kerogen. Position of a kerogen in Van Krevelen's diagram provides a significant amount of information. It enables assessment of the type of precursor material, type of maceral and the maturity level at the time of testing, and prediction of future path of maturation changes. In other words, it is possible to assess how much bitumen has already been produced by some kerogen in the geological past, and how much it can produce in the future. The source potential of kerogen decreases from type I to type IV (Table 2.15).

For assessing a sedimentary rock as a high-quality oil source rock it must contain either type I kerogen or type II kerogen. The rocks that contain type III kerogen cannot be expected to be good oil source rocks. On the other hand, if a rock has been characterized as oil source rock (based on other criteria), then it is possible to assess its type of source rock based on the position of the tested kerogen in Van Krevelen's diagram. For example, if it is at a lower maturity level (high values of atomic H/C- and O/C-ratios), it could be concluded that it is a 'potential' source rock, i.e. rock that will generate bitumen or oil only in the future. On the contrary, if the kerogen is at a higher evolutionary level (lower values of atomic H/C- and O/C-ratios), it can be concluded that it is an effective source rock or source rock at the end of its source potential.

Maturity of Organic Matter

To assess the potential of a sedimentary rock (i.e. the amount of primary generated hydrocarbons), it is necessary to determine the maturity level of the organic matter. To be an effective oil source rock, organic matter maturity (kerogen and bitumen) of sedimentary rocks must be at a level corresponding to the oil window. If the maturity is low, and the sedimentary rock contains more than 0.5 % organic carbon and type I or II kerogen, it could still be a potential source rock for oil. Sedimentary rocks containing organic substance at a higher level of maturity as compared to the oil window are of importance for the prospecting research. These could be rocks that have already spent their source capacity, and in their vicinity there could be found oil in reservoir rocks.

Maturity of Kerogen

In the previous chapter dealing with the chemical properties of kerogen, parameters and methods that are most commonly used for the assessment of its maturity have already been mentioned. Additionally, determination of "vitrinite reflectance" is very useful. The reflectance is determined by comparing the light (monochrome, green, with specific wavelengths) that is reflected from the surface of macerals, with the light reflected from the surface of standard material with known reflectance. Rank or maturity of kerogen is estimated by measuring the *reflectance of vitrinite* (or huminite) particles. This vitrinite reflectance is marked with Rr (%) (e.g. Peters et al. 2005).

Vitrinite reflectance increases with maturity. Based on the current organic petrographic and geochemical investigations it has been shown that the vitrinite reflectance

- in the diagenetic phase (immature source rock) is up to 0.5 %,
- in the early catagenetic phase ranges from 0.6 to 1.3 % (the main oil-generating zone, "oil window"),
- in the catagenetic phase, characterized by the production of wet gas, ranges from 1.3 to 2.0 %,
- and during metagenesis, when methane is generated, it reaches maximum values over 2.0 %.

Vitrinite reflectance in some oil and gas generating stages is shown in Fig. 2.24.

Maturity of kerogen can be monitored directly and through the intensity of fluorescence. It is intense in immature rocks, decreases during diagenesis and most of catagenesis, but disappears entirely at the end of the production zone.

Further on, it is well known, also, that with increasing maturity, spores, pollen and other microfossils progressively change colour, from yellow (early diagenesis), to orange or brownish-yellow (late diagenesis), brown (catagenesis) to black (metagenesis). These changes of colour are expressed by Thermal Alternation Index (TAI). The weakness of this method is that the assessment of the colour changes is a more subjective assessment by the operating researcher. However, careful use of standards of the same palynomorphs significantly contributes to a higher reproducebility and, therefore, reliability. Problems may possibly occur due to lack of proper standards, or more often, lack of pollen and spores in the investigated sample.

Pyrolytic methods are particularly significant for kerogen maturity assessment. Among them, the Rock-Eval method allows quantitative assessment of the rela-

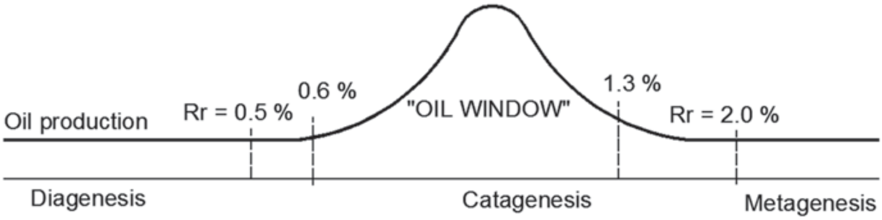


Fig. 2.24 Stages of oil generation

tion between the amount of already generated hydrocarbons and total potential of the sediment. This ratio increases with depth and with increasing the temperature at which the sediment is found. As a maturation parameter, the so-called "Maximum pyrolysis temperature" (T_{max}) is established. As outlined above, the higher the kerogen maturity level, the higher the temperature of maximum generation of pyrolysates. In other words, with increasing maturity of kerogen increases the value of the parameter T_{max}.

Maturity of Bitumen

Investigation of the maturity of bitumen is a very important area of organic-geochemical investigations. Based on the results of many decades of organic-geochemical research, a number of methods for assessing the maturity of bitumen have been defined.

The amount of bitumen in the sediment is an important parameter for the maturity of organic matter. Limit values for the bitumen content in source rocks (shown in three ways) have been given in Table 2.18. In addition, the amount of hydrocarbons in the bitumen, as a sum of fractions of saturated and aromatic hydrocarbons, is a reliable maturation parameter. Previous studies have shown that the tested sample can be an oil source rock if the bitumen contains 20–60 % of hydrocarbons, or if the quantity of hydrocarbons in relation to the total sediment is higher than 100–260 ppm.

The most reliable bitumen maturity parameters are determined from the abundance and distribution of biological markers. Biological markers have already been discussed in the chapter about the composition of bitumen, where it was described how maturation affects the abundance and distribution of *n*-alkanes, isoprenoid aliphatic alkanes and polycyclic alkanes of sterane and triterpane types as the most important biomarkers. It was pointed out that their structural and stereochemical changes do not run to complete decomposition of biological precursors. In fact, in certain phases of the evolutionary changes of organic matter in geosphere equilibrium is reached. Maturation stages have been empirically rather precisely defined. Table 2.16 shows values of vitrinite reflectance (Rr) with equilibrium reached in the most known structural and stereochemical changes of biological markers. If the

Table 2.16 Equilibrium values of important maturation parameters (*n*-alkanes, terpanes and steranes) and the corresponding values of vitrinite reflectance (Rr)

	Equilibrium value	Vitrinite reflectance, Rr(%)
CPI	0.8–1.2	0.6
C_{31} Hopane—22S/(22S + 22R)	0.57–0.62	0.6
Moretane/hopane	0.05–0.10–0.15	0.7
C_{29} Steranes—20S/(20S + 20R)	0.67–0.71	0.8
C_{29} Steranes—ββ/(ββ + αα)	0.52–0.55	0.9

values in this table are compared with Fig. 2.24, it can be easily concluded in which phases of bitumen generation these equilibriums are reached. By interpretation of the values of these maturation parameters it is possible to establish with certainty in which phase of the diagenetic-catagenetic-metagenetic sequence of transformation of organic matter in geosphere is the investigated sample.

2.3.3 Migration of Bitumen

Outline

Movement of bitumen from the site of its generation in the source rock to the reservoir rock, is called migration. The most important issues related to the migration of bitumen are: the time of its commencement and movement mechanism. Even after several decades of intensive research these issues are not fully understood. For both questions several explanations were proposed. An attempt will be made to explain these phenomena in this chapter.

The migration of bitumen starts in the source rock itself. Migration through it is called primary migration. Movement from the source rock to the reservoir is called secondary migration. Bitumen migrates from areas of higher pressure and higher temperature to the area of lower pressure and temperature. In other words, the reservoir rock is situated usually deeper than the corresponding source rock. If the reservoir rock is permeable in its part, there is also a possibility of tertiary migration, or movement of oil to a new reservoir at even lower depths.

Primary migration takes longer time despite the fact that its pathways are relatively short. It is measured in meters, tens of meters, rarely hundreds of meters. Through much larger pores, fractures or fissures, secondary migration is much easier and faster. Secondary migration pathways are much longer and are measured in kilometres and tens of kilometres.

The most important issues related to the migration of bitumen are: the time of its commencement and movement mechanism. Even after several decades of intensive research these issues are not fully understood. For both questions several explanations were proposed.

Commencement of Migration

Among some organic geochemists the hypothesis prevails that bitumen that is produced during kerogen cracking is first adsorbed on the surface of the kerogen itself. During catagenesis the quantity of bitumen increases while the amount of kerogen decreases. The surface of kerogen on which the generated bitumen can be adsorbed is certainly also decreasing, and at one point, when the sites for adsorption are fully "saturated", bitumen will begin to leave the source rock, and its migration will start.

An alternative hypothesis assumes that catagenetic bitumen together with the inherited bitumen is adsorbed on minerals. The increase in its quantity reduces the free space, and at some critical point bitumen will be simply expelled. This expulsion, according to this theory, is the primary migration.

Organic geochemists have tried to define the amount of bitumen that has to be generated in the source rock for migration to commence. As early as in 1978, J.A. Momper presented the assessment "that bitumen should reach concentration of 50 million barrels per cubic mile of the source rock for primary migration to commence". However, bearing in mind that the mineralogical composition of source rocks can vary depending on the physical properties of sedimentary basins, it can be easily seen that these assessments are highly uncertain.

Box 2.20: *General Note*

Under natural geological conditions many phenomena and processes are difficult to define precisely. So when it comes to the commencement of migration, the proposed assumptions in some cases are perhaps more or less justified, and more or less applicable. The only question is which of them is the most suitable in a particular case.

Migration Mechanisms

Primary migration is practically expulsion of bitumen from the rock in which the bitumen is generated, and secondary migration of bitumen takes place through pores, fractures and fissures of conduit rocks primarily with the help of water. Ground water, as much more mobile fluid, significantly helps or, even, practically allows the migration of bitumen to the reservoir rock. However, the issue of migration mechanism is not fully understood yet. Several mechanisms have been proposed. For example, in the form of true solutions or colloidal micelles, the migration mechanism in the form of "globules or droplets", or as "continuous phase".

Migration in the Form of Real Solutions

Bitumen is a mixture consisting mainly of hydrocarbons. Water, as very polar, is a poor solvent of these lipophilic compounds. Lower hydrocarbons can be partly dissolved, but the solubility is considerably decreasing with an increasing length of the carbon chain. Bitumen contains some polar compounds containing nitrogen, sulphur and oxygen (NSO-compounds), which are much better soluble in water. However, their amount is much lower than the amount of hydrocarbons, which account for about 95 %, so that they cannot be expected to contribute significantly to the overall solubility of total bitumen in water. Previous organic-geochemical studies have shown that oil in a reservoir rock contains a significant amount of higher *n*-alkanes, C_{23}–C_{31}, hardly soluble in water, compared to bitumen in the source rock. This fact indicates that the migration mechanism in the form of real solutions cannot be the dominant mechanism of bitumen migration. Still, it would be wrong to exclude this mechanism completely. Its contribution to the migration process can be of greater importance in areas characterized by narrow passages, i.e. small diameters of fractures and pores.

Migration in the Form of Colloidal Micelles

The fact that oil in a reservoir rock often contains a significant amount of higher normal alkanes ($> C_{20}$) compared to bitumen in a source rock, is not logical at a first sight. Not only because the higher *n*-alkanes are hardly soluble in water, but because of the fact that during the migration heavier (and polar) compounds are left behind. According to that, the amount of lower *n*-alkanes in oil should be higher. However, this obvious contradiction may be explained by the fact that NSO-compounds form colloidal micelles in water, which include only *n*-alkanes, especially the higher ones, thus transporting them to the reservoir rock. So, one of possible mechanisms of bitumen migration through sediments may be in the form of colloidal micelles. It is hard to believe that there are environments in which this mechanism is dominant. However, also in this case it would be wrong to exclude this mechanism completely.

Mechanism of "Globules and Droplets" and "Continuous Phase"

Bearing in mind that the secondary migration of bitumen, through a much more permeable environment compared to that characteristic of the primary migration, takes place mainly through pores or fractures, it is possible that the bitumen moves by simply "floating" on the water surface. Depending on the size of these pathways, small aggregates in the form of globules or droplets can be formed on the water surface, or they can be considerably higher, in the form of a continuous phase. In such cases, the interaction between bitumen and water is relatively poor and water does not significantly affect the composition of the bitumen.

As noted above, phenomena and processes in natural geological conditions are difficult to define precisely. Every environment has certain features that are more or less different from the properties of some other environment. Therefore in the case of bitumen migration it is difficult to determine which of these mechanisms had a predominant role. The migration mechanism depends on many different factors, the amount of bitumen, its composition, the amount of water, type of inorganic material, the size of pores, fractures, or fissures, temperature, pressure and depth.

During migration, various changes in the composition of bitumen take place, so that the chemical composition of oil can vary significantly from the bitumen of the source rock. These changes are the result of heavier compounds being left behind or interaction between polar NSO-compounds and the inorganic environment. The intensity of these interactions depends on the length of the migration pathway, but also on the physical and geological properties of sedimentary formation through which bitumen migrates.

2.3.4 Reservoir Rocks

Outline

Reservoir rocks are found at shallower depths compared to the source rocks. Therefore, the temperature and pressures in them are generally lower. Also, contact of oil with inorganic environment in the reservoirs is weaker. Despite all this, further changes in the composition of oil still take place in the reservoir rocks. Oil accumulates in reservoir rocks over very long periods of geologic time, measured in millions of years. This long time period compensates for the poorer intensity of changes compared to the intensity of changes of bitumen in the source rocks. First of all, in the reservoir rocks all the maturation changes that have happened also with bitumen in the source rocks are continued. In close connection with maturation is also the deasphalting process. In reservoir rocks, water washing also takes place. Finally, biodegradation can also occur. These oil changes will be discussed in this chapter.

Regardless of the slightly lower temperatures and pressures and a weaker contact with potential mineral catalysts, all the maturation processes that took place in bitumen are continued in the oil reservoir rocks, which leads to an increased amount of low molecular weight compounds, and thermodynamically more stable structural and stereochemical isomers of certain compounds. All previously described maturation changes of *n*-alkanes, isoprenoid aliphatic alkanes, polycyclic alkanes and naphthenic aromatic compounds are continued, if an equilibrium state has not already been reached in the “bituminous stage” (Table 2.16). On the other hand, transformations into compounds of low molecular weight (cracking) are not limited. Therefore, in the reservoir rocks, the amount of gases (C_1–C_4) and condensates (C_5–C_{10}) can increase over time.

Since the amount of lower hydrocarbons increases during the cracking, including pentane, hexane and heptane, which are excellent solvents for the whole oil except for asphaltene, *deasphalting* takes place, i.e. precipitation of asphaltenes in reservoir rocks, and thus the contents of compounds soluble in alkane solvents, saturated and aromatic hydrocarbons and NSO-compounds increases. In organic geochemistry, these three fractions are often collectively referred to as “maltenes”. In addition to asphaltenes and maltenes, oil contains also “volatile components”. These are

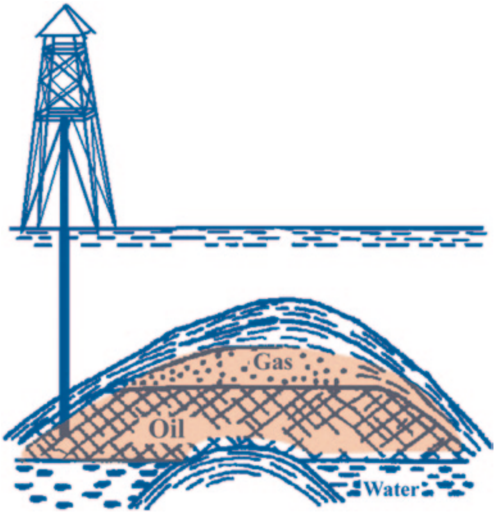


Fig. 2.25 A simplified illustration of the oil reservoir rock

hydrocarbons with approximately less than 12 C-atoms. They mostly “evaporate” during the laboratory investigations of oil, since most analytical methods include experiments at elevated temperatures. Examination of the composition of oil in the laboratory is actually reduced to examination of maltenes, although special methods have been developed also for testing fractions of volatile components.

As explained in the chapter on the migration of bitumen, water plays a crucial role in the transmission of the bitumen from source to reservoir rocks. Therefore, water and above it oil, as it has lower specific gravity, are accumulated together in the reservoir (Fig. 2.25). In the reservoir rocks, oil is in constant contact with water and, therefore, it is subject to continuous water washing for a long time period. Oil as a mixture of dominantly nonpolar hydrocarbons is poorly soluble in water. However, it also contains some compounds that are soluble in water, especially at higher temperatures and pressures. As already mentioned, these are primarily compounds with heteroatoms, nitrogen, sulphur and oxygen, forming the so-called NSO-fraction. Therefore water washing is mostly “washing” NSO-compounds out of the oil phase. Of course, this does not mean that some low molecular weight hydrocarbons cannot be “washed”, although to a much lesser extent.

Another process that can largely alter the composition of oil in the reservoir rock is biodegradation (microbiological degradation). It occurs only in reservoir rocks that contain water as well. Also, previous organic-geochemical studies have demonstrated that biodegradation is possible only in reservoir rocks with the temperature below approx. 70 °C.

Biodegradation of oil in the reservoir rocks is one of the organic-geochemical processes that has been most studied. There are two reasons for that. The first is that biodegradation degrades also *n*-alkanes, hydrocarbons dominant in most of the oils discovered to date. Biodegradation, therefore, completely changes the

Table 2.17 Classification of crude oils based on the degree of biodegradation

Group	Removed hydrocarbons	Degree of biodegradation
1	No	–
2	The lower *n*-alkanes	Minimum
3	More than 99 % of *n*-alkanes	Moderate (I)
4	Alkylcyclohexanes; partially isoprenoids	Moderate (II)
5	All isoprenoids	Moderate (III)
6	Bicyclic alkanes	Medium strong
7	More than 50 % of regular steranes	Strong
8	Steranes changed, a lot of demethylated hopanes	Very strong
9	All regular steranes, domination of diasteranes and demethylated hopanes	The maximum

composition and type of oil. “Paraffin” oil can become so-called “naphthenic” oil. From the standpoint of oil quality this is very important, because it is known that the naphthenic oil distillation processes in refineries can provide much larger quantities of high quality gasoline with high octane number. Another reason is fundamental in nature. Namely, apart from *n*-alkanes, other biological markers (isoprenoids, polycyclic alkanes) can also be degraded by biodegradation, changing the original composition of the oil and reducing the possibility of using biological markers in the investigation of its origin and geological history. It can be concluded that, as regards the processing of oil, biodegradation is a useful process, and from the viewpoint of organic-geochemical fundamental research it is the process that has undesirable consequences.

Biodegradation of oil in reservoir rocks can be of varying intensity (Volkman et al., 1983). Table 2.17 shows the classification of oils in 9 groups, based on the degree of biodegradation, the types of compounds that are microbiologically decomposed, and Fig. 2.26, as an example, shows gas chromatograms of alkane fractions of non-biodegraded oil and oils which were exposed to biodegradation to a different degree.

n-Alkanes are most susceptible to microbiological degradation. Therefore, if oil contains *n*-alkanes in abundance characteristic for oils (*n*-C_{17} and *n*-C_{18} more abundant than isoprenoids pristane and phytane), it can be argued that it was not exposed to biodegradation (Fig. 2.26a). Intensity of biodegradation in the initial stage can be evaluated on the basis of Pr/*n*-C_{17} and Ph/*n*-C_{18} ratios. Figure 2.26b gives an example of the gas chromatogram of alkane fraction of one minimally biodegraded oil, where not even all *n*-alkanes are degraded. Figure 2.26c is an example of biodegradation at a moderate (I) level as the *n*-alkanes are degraded, and isoprenoid aliphatic alkanes are still preserved. Finally, Fig. 2.26d gives an chromatographic example of oil that was subjected to biodegradation at the least moderate (III) level. A precise degree of biodegradation for this oil could be determined by GC-MS analysis of the steranes and demethylized hopanes (Table 2.17).

Box 2.21: *General Note*

n-Alkanes → regular steranes order of degradation as parameter for the stage of biodegradation is not ideal. In other words, it would be wrong to understand that isoprenoids are "waiting" for *n*-alkanes to be degraded, then that the bicyclic alkanes are "waiting" for isoprenoids, steranes, for bicyclic alkanes, etc. Earlier organic-geochemical studies have shown that for example degradation of steranes begins even before the complete degradation of *n*-alkanes. Thus, different biodegradation processes are running also partly in parallel. This fact confirms that biodegradation complicates interpretation of the results of fundamental organic-geochemical studies.

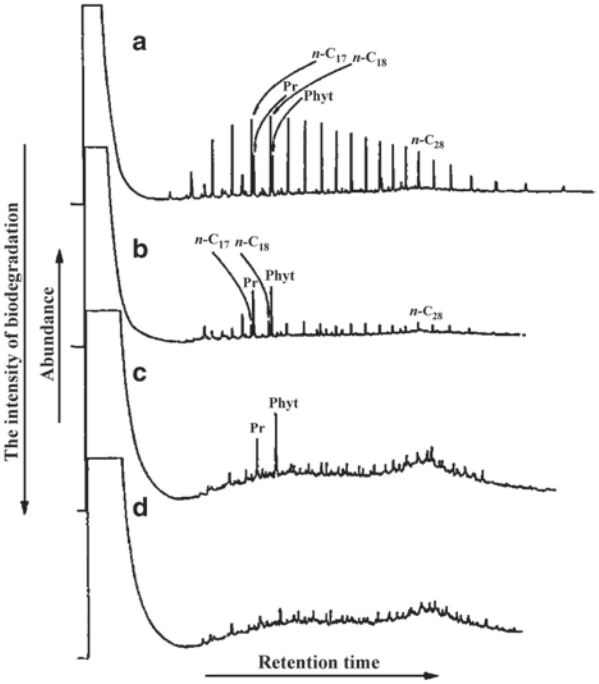


Fig. 2.26 Gas chromatograms of total alkane oil fractions ranked according to the intensity of biodegradation: (**a**) non-biodegraded oil, (**b**) least biodegraded oil, (**c**) moderate (I) biodegraded oil and, (**d**) moderate (III) biodegraded oil

2.3.5 *Factors Affecting the Differences in Composition Between Bitumen and Petroleum*

In the chapter on bitumen it has already been pointed out that bitumen and petroleum are composed of the same types of organic matter, provided that the organic matter *moving to* reservoir rocks is termed bitumen, and *in* reservoir rock—petroleum. They make, or derive from, the soluble part of organic matter of sedimentary rocks and differ from all other forms to which they are genetically related (fulvic and humic acids, humin, kerogen, graphite). However, in the organic-geochemical literature, the two names, without exception, appear often assuming also two different forms of organic matter. The similarity has already been explained. What are the differences between them?

Differences between bitumen and petroleum are the result of processes that affect in the reservoir rock. As noted in the previous chapter, maturation processes are continued in the reservoir rocks and their consequence is deasphalting. As petroleum is subject to water washing, biodegradation may also occur.

As a result of prolonged maturation, petroleum, compared with bitumen, becomes richer in low molecular weight compounds and thermodynamically more stable isomers of biomarkers. Deasphalting leads to reduction of the amount of asphaltenes, and water washing to reduction in quantities of polar NSO-compounds. If petroleum was exposed also to biodegradation, the differences become very significant and are reflected primarily in a small amount of *n*-alkanes, or their complete absence, and in addition, in a lesser abundance and altered distribution of other biomarkers (Table 2.17).

The described differences are related to petroleum and migrated bitumen from which it immediately originated. However, for fundamental, but also for prospecting research, comparison or correlation between petroleum and bitumen that is still found in the source rock is more important. In this case also differences that are the result of water washing, deasphalting and possible biodegradation still exist in the sense that has already been explained. However, when it comes to maturation, the degree of differences depends on whether particular bitumen is a residue that was generated concurrently with petroleum in a reservoir rock, and represents a part that has not migrated, or it is the bitumen, which was generated much later. In the first case, bitumen will be at a higher level of thermal maturity than petroleum, because it "spent" the time in the source rocks at higher temperatures and pressures, and in better contact with the mineral catalysts, compared to the reservoir rocks. In the latter case, the bitumen is at a lower level of maturity, since it has been exposed to heat, pressure and catalysts over a shorter period of time than petroleum which has already gone through migration, accumulation, and "spent" some time in the source rock.

Box 2.22: ***<u>General Note</u>***

In other words, differences in the degree of maturity between bitumen and petroleum in the source rock depend primarily on the type of the source rock. If it is bitumen of an effective (or active) source rock, petroleum is probably more mature. If it is, however, the remainder of bitumen in an inactive (i.e. spent) source rock, bitumen is the one that is more mature.

Besides maturation, deasphalting, water-washing and biodegradation in reservoir rocks, the changes that occur during migration of bitumen from source to reservoir rock also contribute significantly to the differences between petroleum and bitumen. During migration higher molecular weight compounds are left behind and more polar compounds, as a result of interactions with minerals of rocks through which bitumen migrates. Therefore petroleum will always have smaller amount of heavier and more polar NSO-compounds compared to bitumen. Despite the fact that primary migration pathways are shorter than secondary migration pathways, primary migration has much more influence on these differences, because contacts between bitumen and minerals during it are much stronger. Interactions between mineral and organic parts of sedimentary rocks will be more thoroughly explained in a separate chapter.

Understanding of all the mentioned factors is necessary for a successful correlation between petroleum and source rock and potential establishment of genetic relationship among them ("positive oil-source rock correlation"), which is one of the most important organic-geochemical tasks from the prospecting research point of view.

2.3.6 Correlation Parameters

Outline

Bearing in mind the intensity of the changes, as well as the time in which they occurred (geological time, measured in millions of years), large differences between petroleum and the corresponding precursor material are easy to understand. However, despite this, previous organic-geochemical studies of oil, and all other forms of organic matter in the geosphere which are genetically related to it, showed that based on the composition of oil it is possible to assess its origin pretty well and to reconstruct its geological history. When we talk about the geologic history, it primarily refers to the type of depositional environment, intensity of the maturation processes to which the oil was subjected in the source and reservoir rocks, and to the migration and its length, as well as the degree of changes that have taken place in the reservoir rocks. Organic-geochemical parameters for correlation of oils according to origin and geological history (bulk and specific) will be discussed in this chapter.

In order to assess the origin of oil and to reveal its geological history, various organic-geochemical parameters can be used. Depending on whether these parameters are derived from the general characteristics of oil, i.e. from the chemical composition at the level of groups of compounds, or from the composition of the oil on a molecular level, *general* or *bulk*, and *specific* or *molecular* organic-geochemical parameters can be distinguished. In examining a large number of samples, the so-called oil-oil correlation (comparison between many oils on the basis of geochemical characteristics and classification into groups according to origin, maturity and biodegradation), the terms bulk correlation parameters and specific correlation parameters are used. Correlation studies provide a significant contribution to the geochemical definition of a petroleum basin, which is of great importance in the prospecting of oil deposits.

Bulk correlation parameters give a general picture of material and in most cases the values of these parameters depend on all, or nearly all, the factors that determine composition of the oil. Specific parameters are much more sensitive and their value depends on a small number of factors. However, it must be pointed out that the specific parameters whose value depends solely on one factor are very rare. Oil origin, i.e. type of precursor biomass, and thermal maturity degree, have the greatest influence on the bulk, and also on the specific parameters.

Since parameters whose value is affected by only one geochemical factor are very rare, it is clear that for a successful evaluation of the origin and geological history of crude oil the determination of as many as possible parameters (bulk and specific) are necessary. Complementary interpretation of these results is highly important and requires a large organic-geochemical knowledge and experience. Bulk parameters most often give just a clue of importance for the conclusions on the analysed crude oils. Analysis of biomarkers and the determination of higher numbers of specific, molecular parameters, confirm or refute the initial hypothesis, and in fact provide an explanation of the values of bulk parameters. However, given the fact that specific parameter values neither depend only on one geochemical factor, in some cases the bulk parameters still contribute to the final conclusion.

The most common bulk geochemical parameters of oil are: API-gravity, contents of asphaltenes, maltenes and volatile components, bulk composition (contents of saturated and aromatic hydrocarbons and fractions of NSO-compounds), sulphur content and carbon isotopic composition ($\delta^{13}C_{PDB}$). The specific correlation parameters comprise the distribution and abundance of biological markers. As noted above, the most important among them are *n*-alkanes, then isoprenoid aliphatic alkanes (pristane C_{19} and phytane C_{20}), polycyclic alkanes of sterane and diasterane type (C_{27}–C_{29}), polycyclic alkanes of tricyclic diterpane type (C_{19}–C_{30}), tetracyclic diterpanes (C_{24}–C_{27}) and pentacyclic triterpanes (C_{27}–C_{35}) as well as naphthenoaromatic compounds. The biological markers include also porphyrins, which currently do not have significant application in the correlation studies, because the procedures for their identification are complex. On the other hand, the amount of information that is obtained by analysing individual porphyrin structures is relatively small and mainly related to the maturity of oils.

An outline of the best known oil correlation parameters is given in Table 2.18.

Bulk Correlation Parameters

API-gravity

API-gravity is a common measure of oil density and its distillation products. Specific gravity (d) and API-gravity are inversely proportional and their ratio is defined by the following equation:

Table 2.18 Most important group and specific oil correlation parameters

Group correlation parameters	Specific correlation parameters—biomarkers for their calculation
API-gravity	*n*-Alkanes
Content of asphaltenes, maltenes and volatile compounds	Isoprenoids (pristane and phytane)
Group composition (alkanes, aromatics and NSO-compounds)	Steranes (including diasteranes)
Sulfur content	Terpanes
Isotopic composition of carbon ($\delta^{13}C_{PDB}$)	Naphtheno-aromatic hydrocarbons
	Porphyrins

$$\mathrm{API} = 141.5/\mathrm{d} - 131.5$$

Primarily, API-gravity as a measure of the oil density and, therefore, a parameter for its physical or physico-chemical characterization. API-gravity is determined using the given equation, in which the specific gravity (d) is usually determined by standard method, e.g. using a pycnometer.

Previous organic-geochemical studies of oil and other forms of organic matter in the geosphere showed that the value of API-gravity is influenced by (i) some events from the geological history of oil, and (ii) the origin and type of precursor biomass. Hence, the API-density found a significant place in the organic-geochemical correlation studies.

The API-gravity of oil is most influenced by microbiological degradation in reservoir rocks (biodegradation), then maturation, migration and some other changes in reservoir rocks (water-washing and deasphalting), but also by the type of biological precursor.

During biodegradation changes in the chemical composition of oil occur. As noted above, the amount of *n*-alkanes is reduced or completely disappeared followed by isoprenoid aliphatic alkanes. With a more intensive activity of microorganisms the amount of cyclic and polycyclic alkanes becomes also reduced. Anyhow, during the biodegradation processes, the amount of lighter components of oil is lowered, leading to an increase in specific gravity of oil, or reduced API-gravity.

During the maturation processes in the source and reservoir rocks in bitumen or oil, thermodynamically more stable compounds are formed, which includes an increased proportion of low molecular weight compounds. This is primarily related to *n*-alkanes and aliphatic isoprenoids, and since these hydrocarbons are dominant components in most oils, it is easy to understand why the specific gravity of oil islowered with higher level of maturity and the API-gravity increases.

During the migration of bitumen from source to reservoir rocks asphaltenes, NSO-compounds as well as other compounds of higher molecular weight are left behind. This leads to a decrease of specific oil gravity or an increase of the API-gravity during the migration.

In addition to microbiological degradation further processes in reservoir rocks affect the value of this bulk parameter. Water-washing reduces the amount of "heavy" NSO-compounds and aromatic hydrocarbons, which contributes to the reduction of specific gravity or increased API-gravity. During deasphalting, i.e. asphaltene precipitation on reservoir rocks, API-gravity is changed in the same way.

To a certain extent, the type of precursor organic matter also affects the value of API-gravity. Namely, oils formed with significant participation of terrestrial precursor biomass exhibit higher amounts of *n*-alkanes. Higher content of *n*-alkanes contributes to reduction of the specific gravity of oil, i.e. the increased API-gravity.

API-gravity of crude oils is measrued in a relatively wide range with values from 15° to 50°. Following the preceding discussion, oils that were subject to biodegradation are those approaching the lower threshold, and the reason for approaching the upper value of API-gravity can be multifold—maturation, migration, water washing, deasphalting and, lastly, the share of terrestrial precursor biomass. This means that low value of API-gravity (e.g. 15–20°) probably represents an evidence of microbiological degradation. On the other hand, a higher value (e.g. 40–50°) may be the result of a number of geochemical factors and explanation of this value requires the determination of additional bulk and specific correlation parameters.

Asphaltenes, Maltenes and Volatile Components

It has already been pointed out that according to the size of molecules, the components in oil can be divided into three fractions. Highest molecular weight compounds generate the asphaltene fraction. Maltene fraction includes components of medium molecular weight ("C_{12+} fraction"). This fraction is considerably more abundant than the asphaltene fraction and the third fraction of volatile components that include relatively low molecular weight compounds.

Asphaltenes are high molecular weight aromatic compounds or mixtures of compounds with a higher number of condensed aromatic rings and a higher number of heteroatoms, nitrogen, sulphur and oxygen (Fig. 2.3). Most of asphaltenes are formed by cracking of kerogen during catagenesis and in fact they represent the part of the bitumen which contains larger kerogen fragments. Therefore, this fraction largely reflects the properties of kerogen from which it was derived. Asphaltenes in oils are found in small amounts, usually below 1 %.

The most abundant oil fraction are maltenes (usually 60–95 %). It has already been said that it contains various compounds that can be classified into three groups according to the ascending polarity. The first group includes saturated hydrocarbons, the second aromatics, and the third group includes nitrogen, sulphur and oxygen compounds (NSO-compounds). In most cases, saturated hydrocarbons are the most abundant, although there is also a considerable number of samples of crude oils known to be dominated by NSO-compounds or aromatic hydrocarbons. Therefore, it can be stated that the oil composition study is mostly the study of the composition of maltenes, since in maltene fraction are the most important compounds of oil, both from the organic-geochemical as well as an economical point of view.

Fraction of volatile components consists mainly of hydrocarbons with less than 12 carbon atoms. The mere content of this fraction may be useful as an organic-geochemical parameter in the oil-oil type correlation. However, in the fraction of volatile components, there are no important biological markers, and the study of its composition does not represent a significant organic-geochemical task.

The asphaltene content in oil by itself is a very important bulk organic-geochemical correlation parameter. The importance of this parameter is derived primarily from the fact that its value, in comparison with other bulk parameters, is affected by a smaller number of geochemical factors.

Asphaltenes in oil are determined by precipitation with *n*-heptane and filtering using a porcelain Büchner funnel. The maltene content is obtained after removing the solvent from the maltene filtrate. The percentage content of volatile components is calculated from the difference (asphaltenes + maltenes + volatile components = 100 %).

The content of asphaltenes in oil depends on the length of the migration pathway. Namely, during the migration from the source to reservoir rocks, polar and “heavy” asphaltene fraction is left behind, which means that oils, after a long migration pathway, will have smaller quantity of these ingredients. A reduction of asphaltene content is also related to enhanced maturation processes (cracking) in the reservoir rocks due to asphaltene precipitation.

On the other hand, all factors that influence the reduction of maltene components in oil will contribute to the increase of asphaltene content. Such an indirect influence on the contents of asphaltene fraction in petroleum is exerted by biodegradation, which can significantly contribute to reducing the amount of saturated hydrocarbons.

Maltene content is not a significant bulk correlation parameter. Since this fraction contains the most important biomarker compounds, the study of its composition is of great importance for the determination of reliable specific correlation parameters.

Regarding the fraction of volatile components, its contents mostly depends on the intensity of maturation processes in reservoir rocks. As noted above, these processes contribute to cracking of higher hydrocarbons, primarily cracking of higher *n*-alkanes, and thus to the increase in the amount of lower hydrocarbons ($< C_{12}$) and increase in the amounts of volatile components.

Bulk Composition

Bulk composition of oil is presented by contents of alipahtic and aromatic hydrocarbons as well as of nitrogen, sulphur and oxygen (NSO) compounds. Bulk composition of oil is determined in the same way as the bulk composition of bitumen. The procedure has been previously described. Bulk composition can be also illustrated by a ternary diagram. An example is given in the chapter on bitumen (Fig. 2.12).

As a bulk organic-geochemical parameter it is very often used in correlation studies of oils. Application of this parameter today is derived from both the importance in oil-oil-correlation and the fact that its determination involves chromatographic isolating of the different substance fractions, which is an essential analytical preparation step for the identification of biological markers.

Almost all relevant geochemical factors influence the bulk composition of oil. Type of precursor biomass influences in such a way that a higher proportion of terrestrial biomass contributes to the contents of higher members of homologous series of *n*-alkanes, and thus to the increase in the proportion of saturated hydrocarbons compared to aromatics and NSO-compounds. During the maturation process in the source and the reservoir rocks, aromatization of some cyclic and polycyclic alkanes occurs. Hence, maturation and the contribution of terrestrial precursor biomass in the formation of oil have opposite effects on the alkane content. As noted above, during the migration of bitumen from the original to the reservoir rock, NSO-compounds are depleted so that oils, after a long migration pathway, contain a smaller amount of NSO compounds. During biodegradation, however, the *n*-alkane content is reduced. More intense activity of microorganisms in the reservoir rocks may lead to partial or complete disappearance of cyclic and polycyclic alkanes, which together significantly reduce the amount of saturated hydrocarbons compared to aromatics and NSO-compounds. On the other hand, the polar NSO-compounds are removed during water-washing in the reservoir rocks.

These observation show that bulk composition cannot be categorized as specific correlation parameter, and that interpretation of the contents of saturated hydrocarbons, aromatics and NSO-compounds almost always requires additional tests and determining of parameters at the molecular level.

Sulphur Content

Most oils contains relatively little amounts of sulphur, less than 0.5%, although in some oils the amount can reach up to 7%. Most sulphur in oil is found in the asphaltene fraction, where it is incorporated into the ring structures of polyaromatic and polycyclic molecules. Sulphur content in oil may be influenced by depositional environment, degree of maturity and biodegradation, and the length of the migration pathway.

During anaerobic reduction of sulphates in the marine environment, especially if the sediments are depleted in heavy metal ions, a large amount of sulphur can be incorporated into the kerogen. The amount of sulphur in the kerogen derived from organic material is very small as compared to sulphur of sulphate origin. As oil is derived from kerogen, the sulphur content in it will mostly depend on the sedimentary environment and will be higher if the oil originates from the marine environment rich in sulphates and if that environment had conditions for the reduction of sulfates by anaerobic bacteria. Consequently, most oils and bitumens derived from lacustrine source rocks contain only little amounts of sulphur (0.5%).

During maturation, asphaltenes precipitate in the reservoir rocks, while the sulphur content is thereby being reduced. During biodegradation, the sulphur content in oils increases even up to 2–3 times, due to the removal of hydrocarbons. During migration, the asphaltene and NSO-compounds contents are reduced, as well as the sulphur content.

Isotopic Composition

Stable isotope ratios of carbon $^{13}C/^{12}C$, hydrogen $^{2}H/^{1}H$ and sulphur $^{34}S/^{32}S$, are reliable correlation parameters. For the correlation of oils, carbon isotope ratio is most commonly used, while $^{2}H/^{1}H$ and $^{34}S/^{32}S$ are applied for the correlation of gases and organic materials with high sulphur contents.

Carbon isotope ratio is determined by mass spectrometry, after the entire sample is previously converted into CO_2. Comparing this ratio with the corresponding ratio in carbon dioxide from standard carbonate sample (PDB, belemnite from the Pee Dee formation in South Caroline) a conclusion can be drawn on whether the organic material is enriched or depleted in the heavier isotope, ^{13}C. The data are given as δ-values:

$$\delta^{13}C_{PDB} = (^{13}C/\,^{12}C\,\text{sample} - {}^{13}C/\,^{12}C\,\text{standard})/\,^{13}C/\,^{12}C\,\text{standard} \times 1000 \quad (2.3)$$

In biosynthetic pathways there is a tendency of ^{13}C-isotope discrimination. Therefore, organic compounds of living organisms have negative $\delta^{13}C$ values. On the contrary, atmospheric carbon dioxide, the educt of photosynthesis, is enriched with heavier isotope leading to less negative and partially positive values. Carbon isotope ratio values in recent sediments depend on both the isotopic value in the biogenic material (more negative values) as well as on the carbonates (less negative) resulting from the accumulation of CO_2 via bicarbonates in the seas.

The heavier carbon isotope (^{13}C) establishes stronger links than the lighter one (^{12}C) so that all products compared to the organic starting material will be enriched with lighter isotope. This explains the negative $\delta^{13}C$ values in organic substances in marine sediments compared to the values found in organic substances in recent marine sediments.

Ranges of $\delta^{13}C$ values in organic materials are given in Fig. 2.27. For oils it is relatively broad, but oils from the same source rocks and oils derived from the same kerogen exhibit very close values, because $\delta^{13}C$ does not essentially change during the migration and through processes in reservoir rocks. As a result of kerogen transformations, oils have by 2‰ higher negative value compared to the kerogen. These findings allow the use of carbon isotope ratio as a reliable source parameter of oils.

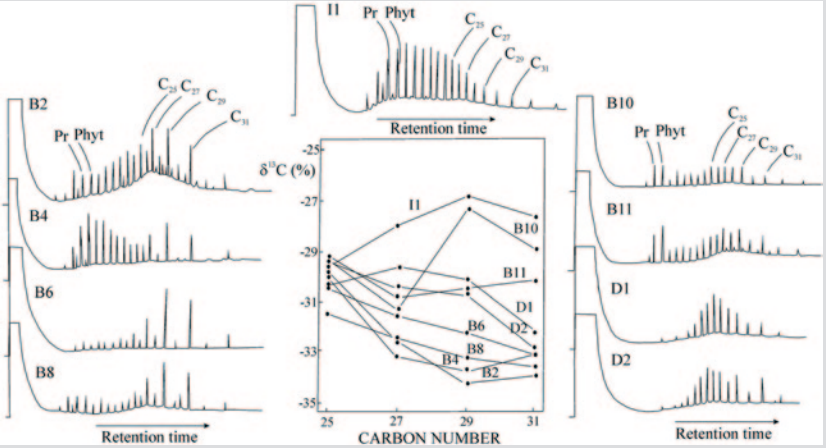
Today, in organic-geochemical practice isotopic analysis is one of the most commonly used methods. Isotope ratios in bulk samples of organic materials (including oil) are determined, then ratios in individual fractions (so-called isotopic profiles), but also ratios in certain compounds in oils (usually in *n*-alkanes).

Box 2.23: Excursus

Carbon isotope ratio in environmental chemistry

Carbon isotope ratio expressed as $\delta^{13}C_{PDB}$ parameter is an unavoidable organic-geochemical parameter that is mostly used in oil-oil correlation. However, having in mind the fact that $\delta^{13}C_{PDB}$ in the whole oil, or some of its compounds (for example, *n*-alkanes) differs from the corresponding values in recent sediments, this parameter can also be used in the environmental chemistry to identify oil-type pollutions.

From the figure below (Jovančićević et al. 1997) it is obvious that sample I1 has $\delta^{13}C_{PDB}$ values for *n*-alkanes C_{25}, C_{27}, C_{29} and C_{31} which are the least negative ones (highest concentration of ^{13}C isotope). In addition to the distribution of *n*-alkanes (CPI about 1), this is also a proof of oil-type pollution in this sample.



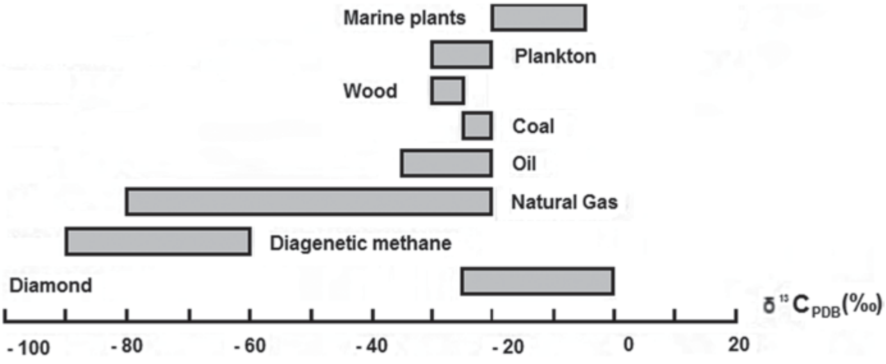


Fig. 2.27 $\delta^{13}C_{PDB}$ values of sediment organic materials

Specific Correlation Parameters

Specific correlation parameters are determined from the distribution and abundance of biological markers. Previous chapters thoroughly addressed the origin of most common biomarkers, *n*-alkanes, isoprenoid aliphatic alkanes, polycyclic alkanes of the sterane and triterpane types (tri-, tetra- and pentacyclic) and their transformation through geological history. Gas chromatography and gas chromatography—mass spectrometry enables to identify a number of structural and stereochemical isomers of these compounds (Figs. 2.13–2.15; Table 2.5 and 2.6) and to calculate the ratios of their relative concentrations, which may serve as a reliable oil correlation parameter. Outline of the most important specific correlation parameters and their dependence on the most important geochemical factors is given in Table 2.19. Besides these, in organic-geochemical literature there are many other parameters, but they are all largely based on the known reactions described also in this book.

Table 2.19 Important specific correlation parameters and their dependence on relevant geochemical factors

	Source		Deposition environment		Maturity	Biodeg-radation
	Marine	Terrestrial	Oxic	Reducing		
CPI	↘	↗	–	–	↘	–
Pr/Phy	–	↗	↗	↘	↗	–
Pr/n-C_{17}	–	–	↗	↘	↘	↗
Phy/n-C_{18}	–	–	↘	↗	↘	↗
C_{31} hopane–22S/(22S + 22R)	–	–	–	–	↗	–
Hopane/moretane	–	–	–	–	↗	–
Ts/Tm	–	–	–	–	↗	–
Oleanane/C_{30} hopane	–	↗	↗	↘	–	–
Gammacerane/C_{30} hopane	↗	–	↘	↗	–	–
C_{29} steranes–20S/(20S + 20R)	–	–	–	–	↗	–
C_{29} steranes–ββ/(ββ + αα)	–	–	–	–	↗	–
C_{27} diaster/C_{27} ster	↘	–	–	–	↗	–
C_{27}αα20R/C_{29}αα20R -steranes	↗	↘	–	–	–	–
Monoaromatic steroids– $(C_{20}+C_{21})/(C_{26}–C_{30})$	–	–	–	–	↗	–
Triaromaticsteroi-dis– $(C_{20}+C_{21})/(C_{26}$-$C_{28})$	–	–	–	–	↗	–
Σ Triarom./Σ monoarom. steroids	–	–	–	–	↗	–

Values of most of the specific parameters depend on the origin (including the depositional environment) and the degree of thermal maturity. According to the outline, given in Table 2.19, biodegradation has a direct impact only on the values of Pr/n-C_{17} and Phy/n-C_{18} ratios. It has already been explained that during the biodegradation *n*-alkanes are degraded (Table 2.17), which leads to an increase in these ratios. However, biodegradation in the initial stages disorganises also the original distribution of polycyclic alkanes of the sterane and terpane types, which contributes to lower efficiency in the use of these biomarkers to assess the origin and maturity degree. In other words, if the oil was subjected to biodegradation in reservoir rock, almost none of these parameters can be reliably used to assess the origin, depositional environment and thermal maturity degree. The exceptions are the parameters that are calculated from the distribution and abundance of mono- and triaromatic steroids that are resistant to microbiological degradation.

In addition, the use of specific parameters has also other restrictions. For example, most of the parameters reach a certain equilibrium value during the maturation, which remains constant although the maturation of oil may continue. The equilibrium values of the most important parameters have been given earlier in Table 2.16.

Box 2.24: ***General Note***

As mentioned in the introductory part of the chapter, none of the specific and particularly bulk parameters depends on only one relevant geochemical factor. Therefore, interpretation of the results correlated with a number of samples of crude oils is a very complex task and requires extensive organic-geochemical experience. It is comparable to putting cubes together in a mosaic: each cube can be placed in several places, but only if placed in the proper place, a true picture will be obtained.

Mineral catalysts in the source and reservoir rocks have different catalytic effects on reactions of individual biomarker molecules, and thus a different impact on the corresponding parameters. For example, transformation of steranes to diasteranes, and transformation of Tm to Ts, cannot take place without the presence of mineral catalyst of silica type. Catalytic activities of minerals influencing reactions such as 20R → 20S steranes, 22R → 22S hopanes and βα → αβ hopanes (moretane → hopane), monoaromatic steroids → triaromatic steroids, C_{26}–C_{30} → C_{20} and C_{21} monoaromatic steroids and C_{26}–C_{28} → C_{20} and C_{21} triaromatic steroids, also exist, but to a much lower extent.

The use of the distribution of C_{27}–C_{29} 14α(H), 17α(H)20R regular steranes is based on the knowledge that C_{27} steranes originate mainly from marine environments, C_{28} from lacustrine, and C_{29} from the terrestrial ones. However, the use of this distribution (in Table 2.19 shown through parameter C_{27}/C_{29}αα 20R—steranes), as a source parameter, also has limitations, because C_{29} steroids are identified also in some biolipid fractions of marine type.

Box 2.25: *Case Example*

Correlation parameters—Pannonian basin oils

Bulk and specific organic-geochemical correlation parameters were determined in oils from oil fields and oil-gas fields in the south-eastern part of the Pannonian basin (a total of 88 samples). Based on their API densities, their sulfur content, asphaltene content, group composition (contents of alkanes, aromatics and NSO-compounds) as well as on the analysis of *n*-alkanes, isoprenoid aliphatic alkanes, pristane and phytane, and polycyclic alkanes of sterane and triterpane types, oils from the entire basin were classified according to the degree of biodegradation (4 groups) and type of precursor biomass (three genetic types). Based on the maturation parameters, their place in the catagenetic sequence of organic matter transformations in the geosphere was defined (Jovančićević et al. 1998b).

2.3.7 Aromatic Hydrocarbons in Oils

Outline

Aromatic hydrocarbons, or simply arenes, are among the most abundant compounds in oils. They do not belong to the biological markers, but from the distribution and abundance of some arene isomers it is possible to determine a number of specific maturity parameters. There is a very large number of different aromatic compounds in oils. It is practically impossible to list all those that have been identified so far. Therefore, at this point, bi- and tricyclic aromatic hydrocarbons will be described in more details, as, according to previous organic-geochemical studies, they are the most applicable, although they are less abundant than the monocyclic ones.

Concentration of aromatic hydrocarbons in oils can reach up to 50 % with a lower limit around 15 %. Mono-, di- and polycyclic aromatic hydrocarbons have been identified in oils accompanied by short alkyl substituted derivatives, the so-called alkylarenes. Additionally, also aromatic hydrocarbons that contains both aromatic and aliphatic rings have been identified. These compounds are called naphthene aromatics, but in oils they are found in very small quantities. Nevertheless, they received higher importance in organic-geochemical studies as useful tool for the assessment of the origin of organic matter in sediments. They belong to the biological markers because their biological precursors and transformation pathways are explained.

Monoarenes (monocyclic aromatic hydrocarbons) are the most abundant group of the aromatic hydrocarbon fraction of most oils. The composition of the aromatic fraction with respect to aromatic basic structures of an average sample of crude oil has been estimated to be as follows: about 67 % benzene-, 18 % naphthalene-, 8 % phenanthrene-, 3 % chrysene- and benzfluorene-, about 2 % pyrene- and only about 1 % anthracene-based substances.

Some genetic pathways of aromatic hydrocarbons from biological precursors to oil constituents have been well explained. However, kinetic, thermodynamic, and catalytic side of these transformations is still not entirely clear. Unlike naphthene aromatics that occur directly from biomolecules (e.g. aromatic steroids, Fig. 2.3), most of alkylarenes in oils occur during catagenetic transformations of kerogen. Therefore they do not belong to the biological markers, and in the previous organic-geochemical studies they did not have significant application for assessment of the origin and depositional environment of the organic matter. Their distribution and abundance are largely used for determining the thermal maturity of oil.

Box 2.26: *General Note*

Oil maturity parameters are based on several types of chemical reactions of aromatic compounds. In the first place, this is transfer (isomerization) of alkyl groups to thermodynamically more stable positions on the aromatic ring, and includes also alkylation-dealkylation processes, mainly methylation and demethylation. Naphthenoarene aromatisation processes are also significant. Finally, some parameters are based on a cracking of the side chain linked to an aromatic ring, whereby alkanes and low molecular weight aromatic hydrocarbons are formed.

These reactions occur also in the kerogen itself. However, they are significantly faster in smaller fragments or individual molecules, released during degradation of kerogen matrix in the later stages of catagenetic transformations. Therefore, maturity parameters which are calculated from the distribution and abundance of aromatic hydrocarbons are of particular importance in oil in which the structural and stereochemical changes in aliphatic biomarkers have already reached equilibrium (Table 2.20: Rr > 0.9 %). Furthermore, having in mind that aromatic hydrocarbons are resistant to microbiological degradation in the reservoir rocks, the parameters

Table 2.20 Most abundant alkylnaphthalenes in aromatic oil fractions

Compounds	Isomers
Methylnaphthalenes (MN)	1- and 2-MN
Dimethylnaphthalenes (DMN)	1,2-, 1,3-, 1,4-, 1,5-, 1,6-, 1,7-, 1,8-, 2,3-, 2,6- and 2,7-DMN
Trimethylnaphthalenes (TMN)	1,2,4-, 1,2,5-, 1,2,6-, 1,2,7-, 1,3,5-, 1,3,6-, 1,3,7-, 1,6,7- and 2,3,6-TMN
Tetramethylnaphthalenes (TeMN)	1,2,3,5-, 1,2,3,6-, 1,2,3,7-, 1,2,4,6-, 1,2,4,7-, 1,2,5,6-, 1,2,5,7-, 1,2,6,7-, 1,3,5,7-, 1,3,6,7-, 1,4,6,7- and 2,3,6,7-TeMN
Pentamethylnaphthalenes (PMN)	1,2,3,5,6-, 1,2,3,5,7-, 1,2,3,6,7- and 1,2,4,6,7-PMN
Ethylnaphthalenes (EN)	1- and 2-EN
n-Alkylnaphthalenes C_{13}–C_{32}	1- and 2-*n*-propylnaphthalene -1- and 2-dodecylnaphthalene

calculated from their distribution can be very useful for assessing the maturity of biodegraded oils.

Bicyclic Aromatic Hydrocarbons

Besides monoarenes bicyclic aromatic hydrocarbons are most abundant constituents in the aromatic fraction of oils. Diarenes are dominated by naphthalene and its alkylated derivatives (up to 90%). In much smaller quantities there are diphenyls, diphenylalkanes, naphthenodiarenes with the maximum number of aliphatic rings rings from 6 to 8.

Alkylnaphthalenes in oils are mainly in the form of methyl-isomers and may contain one to five -CH_3 groups directly bound to an aromatic ring. So far, 1- and 2-methylnaphthalene (MN), and almost all theoretically existing isomers of dimethylnaphthalene (DMN) and trimethylnaphthalene (TMN) have been identified in oils. The structural formula of naphthalene is given in Fig. 2.28, and the outline of the most abundant alkylnaphthalenes in Table 2.20.

Among dimethylnaphthalenes compounds which are predominant in oils are those with substituents on different rings. Also, several isomers of trimethylnaphthalenes (TMN), tetramethylnaphthalenes (TeMN) and pentamethylnaphthalenes (PMN) have been identified in oils. Besides methylnaphthalenes, oils contain also ethyl-naphthalene (EN, α and β), which usually account for 7–10% of total C_2-substituted naphthalenes. In some crude oils, homologous series of C_1- to C_{20}-substituted monoalkylnaphthalenes with unbranched side chain have been identified. Besides tetramethylnaphthalenes and *n*-butylnaphthalenes, C_4-alkylated naphthalene is present in oils in the form of dimethyl/ethyl-naphthalenes and isopropylmethylnaphthalene (norcadalenes; Fig. 2.29).

Besides *n*-pentylnaphthalene and a series of pentamethylnaphthalenes, further 4 isomers of C_5-alkylated naphthalenes have been identified (Fig. 2.30). Among them 1,6-dimethyl-4-isopropylnaphthalene (cadalene) is the most interesting isomer. This compound is found in the resins of higher terrestrial plants. Moreover, the structural relationship between cadalene and biogenic sesquiterpenoids, farnesol and cadinene, is obvious. Some alkylnaphthalenes with a more complex structure, which are believed to originate from terpenoids of higher plants (Fig. 2.31), have also been identified in oils.

Besides alkylnaphthalenes, the less abundant naphthene-naphthalenes were also detected in oils. Molecular structures of best known naphthene-diarenes in oil are shown in Fig. 2.32.

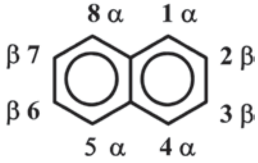


Fig. 2.28 Molecular structure of naphthalene

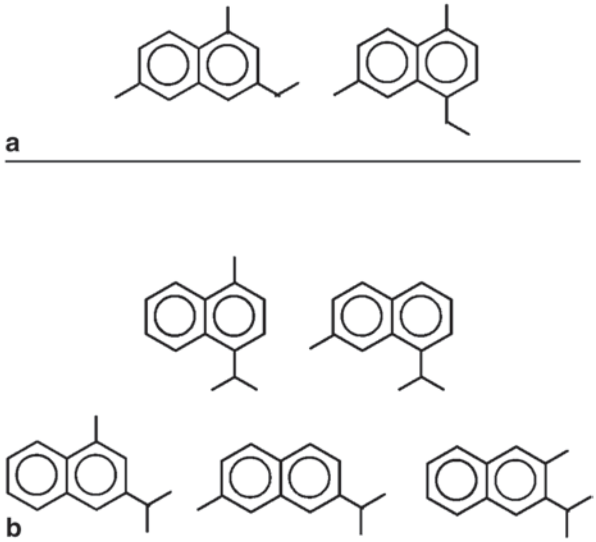


Fig. 2.29 Molecular structures of dimethylethylnaphthalenes (**a**), and norcadalenes (**b**) identified in oils

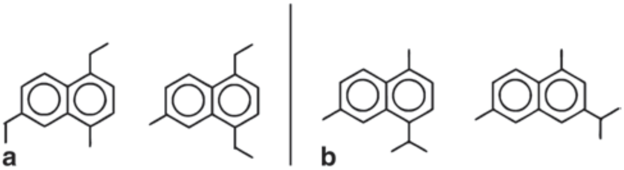


Fig. 2.30 Molecular structures of diethylmethylnaphthalenes (**a**), and dimethyl-*iso*-propylnaphthalenes (**b**), identified in oils

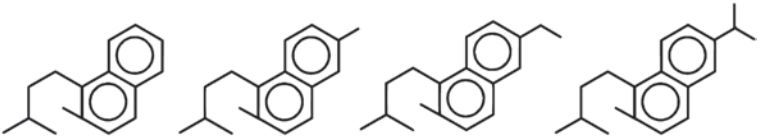


Fig. 2.31 Molecular structures of alkylnaphthalenes identified in oils, which are assumed to originate from terpenoids of higher plants

Genesis of Bicyclic Aromatic Hydrocarbons

As already pointed out, the highest amount of bicyclic aromatic hydrocarbons in oils is formed by kerogen decomposition during catagenesis. Alternatively, organicgeochemical studies have also pointed to some formation pathways of petroleum diarenes from biomolecules (Ellis et al., 1996 and Radke 1987). As an example,

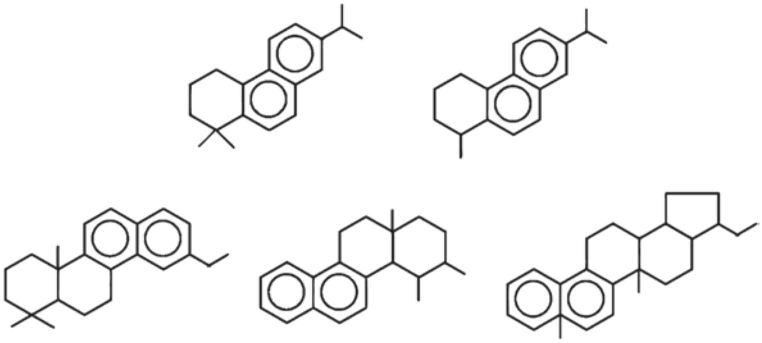


Fig. 2.32 Molecular structures of the most common tri-, tetra- and pentacyclic napthenodiaromatics

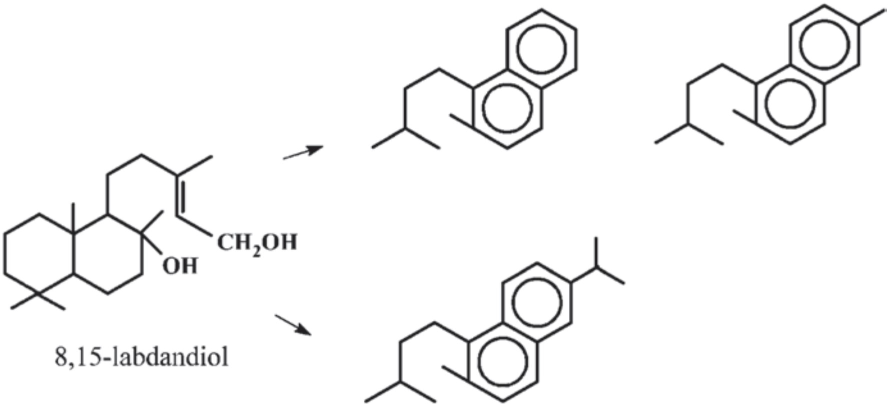


Fig. 2.33 Molecular structures of petroleum diaromatics formed by reductive defunctionalization of 8,15-labdandiol

Fig. 2.33 shows how diarenes can be formed by defunctionalisation of the terpenoid 8,15-labdandiol. Figure 2.34 illustrates aromatisation and degradation of triterpenes with amyrine structure.

Identification of Bicyclic Aromatic Hydrocarbons

Bicyclic aromatic fractions in oil are isolated and purified using column chromatography and thin layer chromatography. Hydrocarbons of this fraction show characteristic absorption maxima around 250 nm in UV-spectra. Diarene concentrates, obtained by conventional chromatographic techniques can be successfully separated to alkylnaphthalenes and derivatives of diphenyls and diphenyl alkanes, using High Performance Liquid Chromatography (HPLC).

For identification and quantification of bicyclic aromatic hydrocarbons, usually gas chromatography and gas chromatography—mass spectrometry are used. As an example, methyl-, dimethyl- and trimethylnaphthalenes can be efficiently separated by GC analyses as shown in Fig. 2.35. The individual isomers are listed Table 2.21.

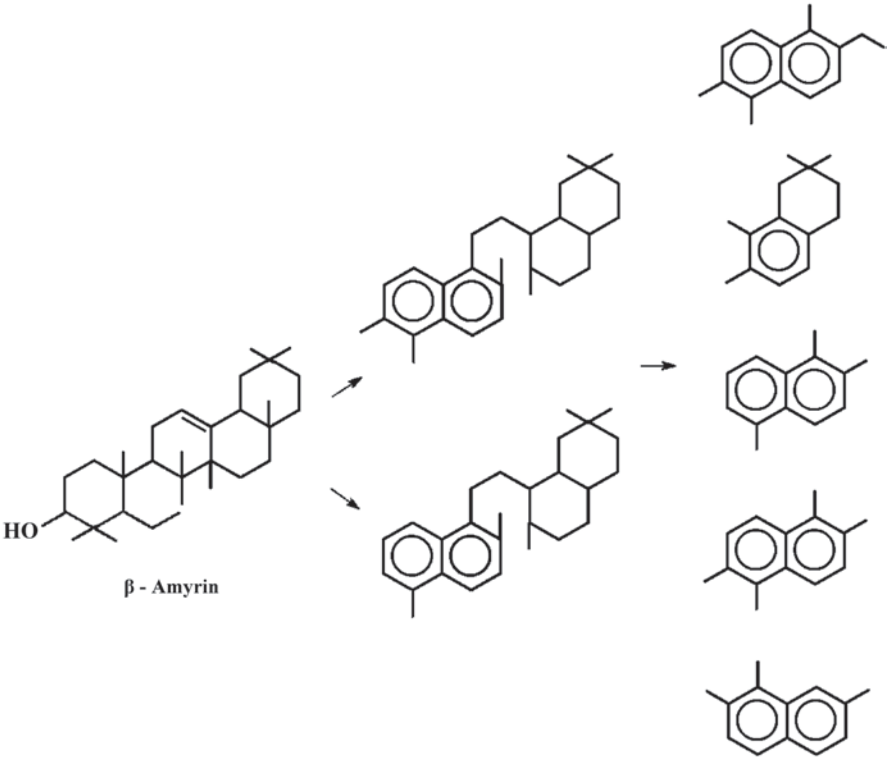


Fig. 2.34 Aromatization and degradation of amyrine forming diaromatics

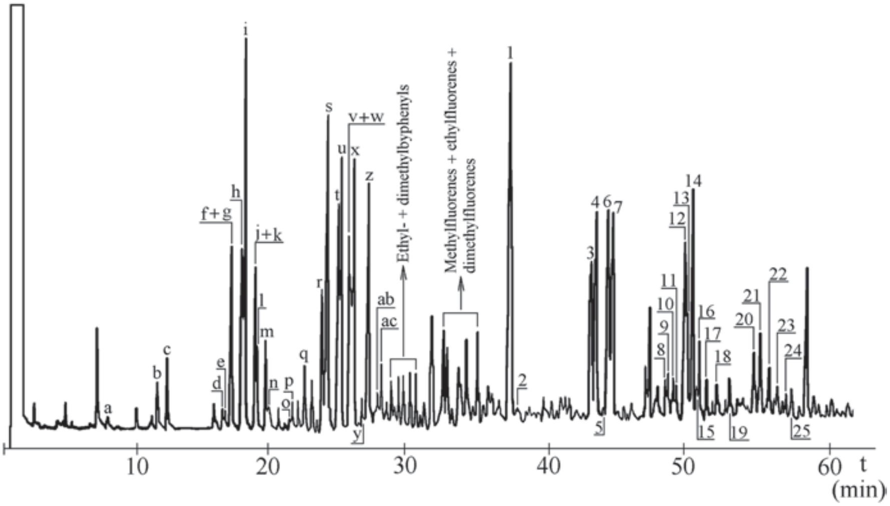


Fig. 2.35 Gas chromatogram of an oil aromatic fraction. (Peak identification is given in Tables 2.21 and 2.25)

Table 2.21 Identification of peaks in the chromatogram shown in Fig. 2.35

Peak	Compound
a	Naphthalene
b	2-Methylnaphthalene
c	1- Methylnaphthalene
d	2-Ethylnaphthalene
e	1-Ethylnaphthalene
f	2,6-+2,7-Dimethylnaphthalene
g	1,7- Dimethylnaphthalene
h	1,3- Dimethylnaphthalene
i	1,6- Dimethylnaphthalene
j	1,4- Dimethylnaphthalene
k	2,3- Dimethylnaphthalene
l	1,5- Dimethylnaphthalene
m	1,2- Dimethylnaphthalene
n	1,8- Dimethylnaphthalene
o	2-Propylnaphthalene
p	1- Propylnaphthalene
q	9,10-Dihydroanthracene
r	1,3,7-Trimethylnaphthalene
s	1,3,6- Trimethylnaphthalene
t	1,3,5-+1,4,6- Trimethylnaphthalenes
u	2,3,6- Trimethylnaphthalene
v	1,2,7- Trimethylnaphthalene
w	1,6,7- Trimethylnaphthalene
x	1,2,6- Trimethylnaphthalene
y	1,2,4- Trimethylnaphthalene
z	1,2,5- Trimethylnaphthalene

For identification of these compounds by GC-MS instrumental technique, the most applicable method is the use of specific ion chromatograms. Characteristic *m/z* values used for ion chromatograms of methyl-, dimethyl- and trimethylnaphthalenes are shown in Table 2.22. An example of such a GC-MS analysis of di-, tri- and tetramethylnaphthalenes is given in Fig. 2.36.

Table 2.22 Characteristic *m/z* values for tracing alkylnaphthalenes by GC-MS analysis

Compound	*m/z*
Methylnaphthalenes	142
Dimethyl- and ethylnaphthalenes	156
Trimethylnaphthalenes	170
Tetramethylnaphthalenes, dimethylethyl- and isopropylmethylnaphthalenes	184
Pentamethylnaphthalenes, dimethyl-*iso*-propylnaphthalenes	198

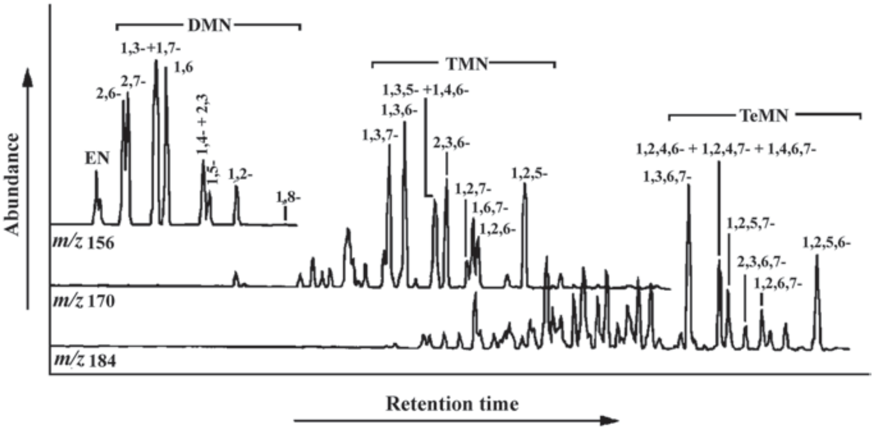


Fig. 2.36 GC-MS analysis of an bicyclic aromatic fraction of oil

Application of Bicyclic Aromatic Hydrocarbons

As already mentioned, the largest proportion of alkylarenes in oils are formed by catagenetic transformations of kerogen. Mostly, they do not belong to the biological markers and organic-geochemical investigations have not found any significant application in assessment of the origin of organic matter. However, their distribution and abundance are used for determination of the degree of thermal maturity of oil.

Most of maturation parameters of bicyclic aromatic fractions are based on the distribution and abundance of naphthalene homologues. During catagenetic transformation of kerogen α-methyl-naphthalenes are formed first by kinetically controlled alkylation reactions of aromatic ring, because of higher reactivity of α- compared to β-positions (Fig. 2.28). Thereafter, the further thermal evolution initiates the movement of methylsubstituents from α- to the thermodynamically more stable β-positions. Therefore, maturity parameters most often represent relations of thermodynamically more stable β- and less stable α-isomers of naphthalene.

Another important maturation process to which aromatic hydrocarbons are subjected in oils is dealkylation. As alrerady illustrated, in the early stage of catagenesis alkylation (methylation) reactions of aromatic rings predominantly occur, what explains the origin of alkylnaphthalenes. These processes are often identified also as transalkylation reactions, given that methyl-isomers of naphthalene, phenanthrene and benzothiophenes may also participate in them. However, with ongoing thermal evolution in oils and bitumens opposite processes also start, such as dealkylation (demethylation) of aromatic hydrocarbons. During this process methyl groups are irreversibly separated in the form of methane (natural gas). Therefore, this process is called methanisation. It is assumed that dealkylation begins only at the stage of "oil window" (Fig. 2.24).

Dealkylation processes are much more pronounced for tricyclic aromatic hydrocarbons and therefore the most important diarene maturity parameters are based on the isomerisation reactions from α to β-isomers. They are outlined in Table 2.23.

Table 2.23 Important maturation parameters based on bicyclic aromatics

Parameter	Formulae
Methylnaphthalene ratio (MNR)	2-MN/1-MN
Dimethylnaphthalene ratio 1 (DNR 1)	1,8-DMN/(ΣDMN in bicyclic aromatic fraction)
Dimethylnaphthalene ratio 2(DNR 2)	(2,6- + 2,7-DMN)/1,5-DMN
Trimethylnaphthalene ratio 1 (TNR 1)	2,3,6-TMN/(1,3,5- + 1,4,6-TMN)
Trimethylnaphthalene ratio 2 (TNR 2)	(1,3,7- + 2,3,6-TMN)/(1,3,5- + 1,3,6- + 1,4,6-TMN)
Trimethylnaphthalene ratio 3 (TNR 3)	1,3,6-TMN/1,2,5-TMN
Trimethylnaphthalene ratio (TMNR)	1,3,7-TMN/(1,2,5- + 1,3,7-TMN)
Tetramethylnaphthalene ratio (TeMNR)	1,3,6,7-TeMN/(1,2,3,5- + 1,2,5,6- + 1,3,6,7-TeMN)
Pentamehylnaphthalene ratio (PNR)	1,2,4,6,7-PMN/(1,2,3,5,6- + 1,2,4,6,7-PMN)
Ethylnapthalene ratio (ENR)	2-EN/1-EN

Tricyclic Aromatic Hydrocarbons

Although tricyclic aromatic hydrocarbons in oils are less abundant than mono- and diarenes, they are of highest importance in organic-geochemical studies using aromatic compounds. These are the best studied aromatic hydrocarbons, from which the most reliable and most numerous maturity parameters have been derived.

Depending on the method of conjunction of benzene rings in triarene molecules, peri-condensed type structures (for example: perinaphthene) and ortho-condensed type (with angular arrangement of rings (phenanthrene) or linear arrangement of rings (anthracene)) can be distinguesshed (Fig. 2.37). The character of ring linkages determines the physical and chemical properties of these compounds and consequently their appearance in oil and other forms of organic matter in the geosphere. Perinaphthene (Fig. 2.37a) is very reactive. Therefore, perinaphthene has been identified only in very small quantities in oils and products of high-temperature pyrolysis of kerogen. On the other hand, phenanthrene and anthracene are stable crystalline compounds, with boiling points at about 350 °C. These two isomers of ortho-condensed type were first identified in products of coal pyrolysis, and later also in extracts of source rocks and oil shales, and in crude oil. Since phenanthrene is thermodynamically more stable than anthracene (Fig. 2.37b, c), the total contents of phenanthrene isomers in oils is up to 50 times higher compared to the total amount of hydrocarbons of anthracene skeleton.

The phenanthrene molecule provides a number of possible alkyl-substitutions and related isomers. Theoretically, there are 5 isomers of monosubstituted phenanthrenes, 30 isomers of disubstituted and even 115 possible isomers of trisubstituted phenanthrenes. In a tricyclic aromatic fraction of oil, the most abundant are phenanthrene and its methyl-derivatives (Table 2.24). Among methyl-phenanthrene (MP) isomers, 1-, 2-, 3- and 9-methylphenathrene are present in significant amounts in oils. As the positions 4 and 5 of the substituents in the phenanthrene molecule are unfavourable because of steric hindrance (Fig. 2.37b), 4-methylphenanthrene is present in oils only in traces.

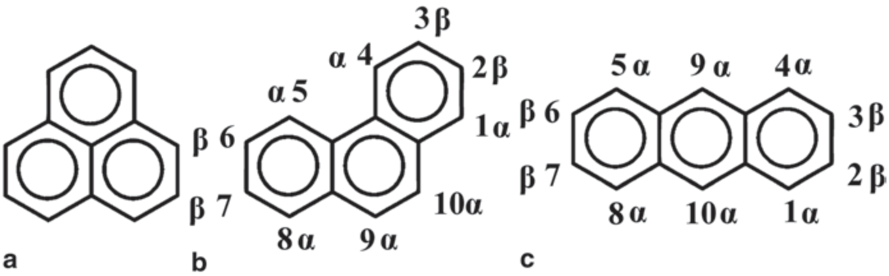


Fig. 2.37 Molecular structures of perinaphthene (**a**), phenanthrene (**b**), and anthracene (**c**)

Table 2.24 Abundant alkylphenanthrenes in oil tricyclic aromatic fraction

Compounds	Isomers
Methylphenanthrenes (MP)	1-, 2-, 3-, 4- and 9-MP
Dimethylphenanthrenes (DMP)	1,2-, 1,3-, 1,6-, 1,7- 1,8-, 1,9-, 2,3-, 2,6-, 2,7-, 2,9-, 2,10-, 3,5-, 3,6-, 3,9-, 3,10- and 4,9-DMP
Trimethylphenanthrenes (TMP)	1,2,3-, 1,2,8-, 1,3,6-, 1,3,7-, 1,3,8-, 1,3,9-, 1,7,10-, 2,3,6-, 2,3,7-, 2,3,10-, 2,6,10-, 2,7,10-, 2,8,10- and 3,8,10-TMP
Ethylphenanthrenes (EP)	1-, 2-, 3- and 9-EP

Also, 16 isomers of dimethyl phenanthrene (DMP) were identified in oils (Table 2.24). Due to steric hindrance (as in methylphenanthrene molecules) 1,4-, 1,5-, 2,4-, 3,4- and 4,10-dimethylphenanthrenes have not been identified in oils.

In tricyclic aromatic oil fractions all four isomers of ethylphenanthrene (EP) have been identified. So far 14 isomers of trimethylphenanthrene (TMP) were identified in oils (Table 2.24). However, as these compounds are difficult to separate also by GC and GC-MS analysis, their use in correlation studies of oils is relatively small. Among the C_4-substituted phenanthrenes, *iso*-butyl, *tert*-butylphenanthrene and 1-methyl, 7-*iso*-propylphenanthrene (retene) have been found in oil. Retene is particularly important with regard to its structural relationship with diterpenoids identified in resins of higher plants.

Anthracene and its alkyl-derivatives are usually found in very low concentrations in oils, what makes it difficult to isolate and identify them. Nevertheless, so far 1-, 2- and 9-methylanthracene, 2-ethylanthracene, 1,8-, 2,3-, 2,6- and 2,7-dimethylanthracene, 2,3,6-trimethylanthracene, 1,3,5,7-, 1,3,6,7- and 2,3,6,7-tetramethylanthracene have been identified in oils.

Naphthenic rings in the tricyclic aromatic hydrocarbon molecules increase the number of possible isomers. So far, alkylated derivatives of seven tricyclic aromatic hydrocarbons containing naphthenic rings have been identified in oils, but only in traces (Fig. 2.38).

The most abundant naphtheno-triarenes in oils are alkyl-derivatives of cyclopentane phenanthrenes or triaromatic steroids. They are particularly significant for their structural similarities with biogenic steroids. Their formation is discussed in the chapter on biological markers (Fig. 2.3).

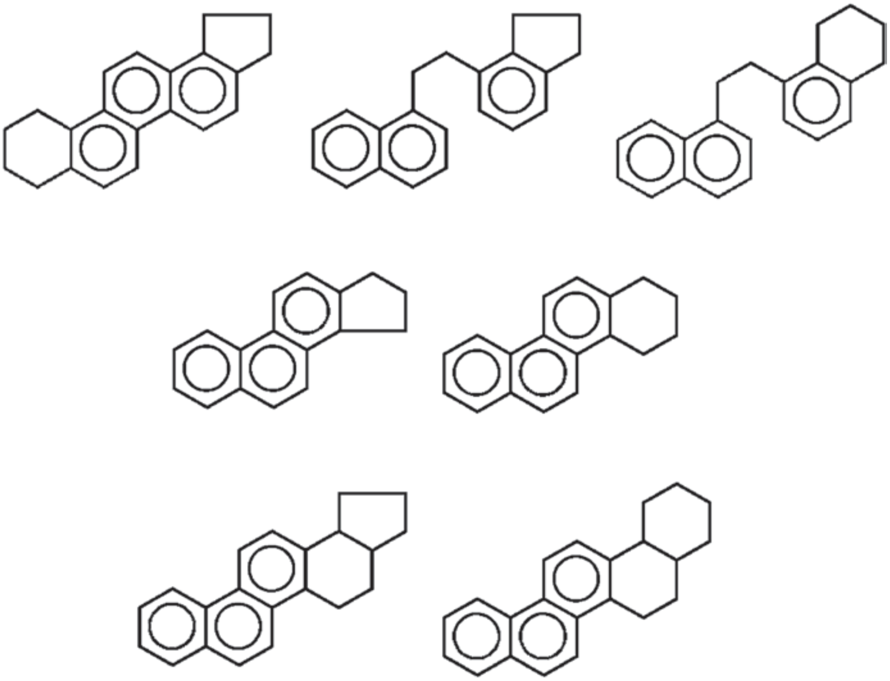


Fig. 2.38 Molecular structures of naphtheno-triaromatics whose alkyl-derivatives are identified in the oil

Genesis of Tricyclic Aromatic Hydrocarbons

Previous studies have shown that living organisms cannot synthesise the tricyclic aromatic hydrocarbons. Furthermore, they have not been identified in the organic matter of recent sediments. Therefore we can conclude that low-molecular weight tricyclic aromatic hydrocarbons (in particular phenanthrene and its methyl isomers as the main components of triarene fraction of crude oil) are not formed by diagenetic processes.

Similar to the bicyclic aromatic hydrocarbons, triarenes also are formed mainly by degradation of kerogen during catagenesis. A number of possible precursors and several transformation mechanisms leading to the the origin of triarenes have been suggested. As an example, Fig. 2.39 demonstrates how alkylphenanthrene and anthracene are formed from polycyclic compounds derived from plants (Schmitz and Bloor 1988). Figure 2.40 presents the molecular structure of phyllocladane which points also to the transformation to triarenes by aromatisation process.

Identification of Tricyclic Aromatic Hydrocarbons

Similar to diarenes, classical methods for the isolation of tricyclic aromatic fraction from oil are column chromatography and thin-layer chromatography. Triarenes

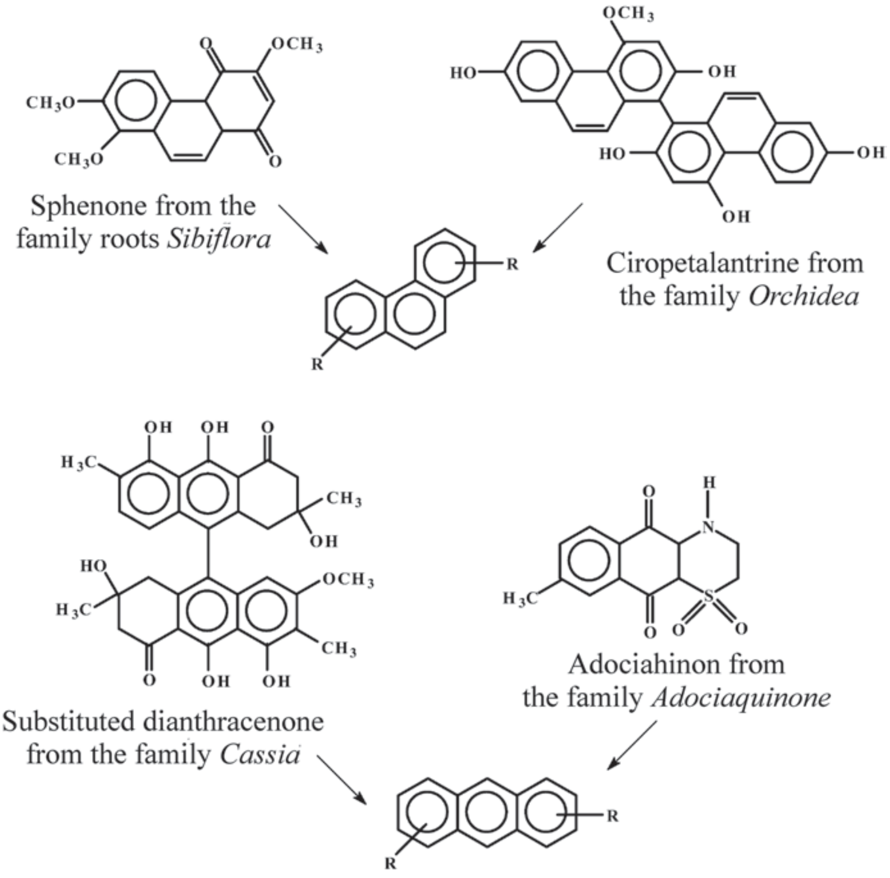
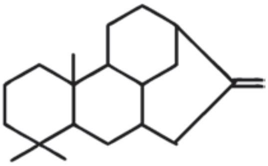


Fig. 2.39 Polycyclic compounds in plant families—possible precursors of alkyl-phenanthrenes and anthracenes in petroleum

Fig. 2.40 Phyllocladane—possible precursor of triaromatics in oils



show characteristic absorption maxima in the UV-spectra in the areas of λ=252–263 nm and 292–307 nm.

Apart from the conventional chromatographic methods, Medium and High Performance Liquid Chromatography (MPLC and HPLC) are used for isolating and purifying of oil triarenes. Crude oil is first separated by MPLC into fractions of saturated hydrocarbons, aromatic hydrocarbons and NSO-compounds. In the aromatic fraction, triarenes are isolated by high performance liquid chromatography. Finally, tricyclic aromatic hydrocarbons can be successfully identified and quantified by gas chromatography (Fig. 2.35, Table 2.25).

Application of Tricyclic Aromatic Hydrocarbons

Parameters based on isomerisation (α→β) and dealkylation reactions of methylphenanthrenes are used for the assessment of thermal maturity of oil and different types of bitumen in sedimentary rocks and coals.

The earliest defined phenanthrene maturation parameter is methylphenantrene index 1

$$\text{MPI }1 = 1.5 \times (2- + 3-\text{MP})/(1- + 9-\text{ MP} + \text{P}) \tag{2.4}$$

Table 2.25 Identification of peaks in the chromatogram shown in Fig. 2.35

Peak	Compound
1	Phenanthrene
2	Anthracene
3	3-Methylphenanthrene
4	2-Methylphenanthrene
5	2-Methylanthracene
6	9-Methylphenanthrene
7	1-Methylphenanthrene
8	9-Ethylphenanthrene + 3,6-Dimethylphenanthrene
9	1-Ethylphenanthrene
10	2,6- + 3,5-Dimethylphenanthrenes
11	2,7- Dimethylphenanthrene + 2- Ethylphenanthrene
12	2,10- + 3,9 + 3,10-Dimethylphenanthrenes
13	1,3 + 1,6 + 2,9-Dimethylphenanthrenes
14	1,7-Dimethylphenanthrene
15	1,9- + 4,9-Dimethylphenanthrenes
16	1,8-Dimethylphenanthrene
17	1,2-Dimethylphenanthrene
18	Ethyl- + Terc.butil- + Isobutylphenanthrene
19	2,6,10-Trimethylphenanthrene
20	1,3,6-Trimethylphenanthrene
21	1,3,7- + 1,3,9- + 2,7,10-Trimethylphenanthrenes
22	2,3,6-Trimethylphenanthrene
23	1,3,8- + 2,3,7- + 2,8,10-Trimethylphenanthrenes
24	Fluorene
25	2,3,10- + 3,8,10-Trimethylphenanthrenes

It is based on isomerisation of α- to β-methylphenanthrene and the possible origin of the 2- and 3-MP by direct methylation of the phenanthrene core. It has been proved that there is a linear correlation between the parameters of MPI 1 and vitrinite reflectance Rr. For bitumens at different degrees of maturity corresponding thresholds were also set (Table 2.26). It should be noted that the MPI 1 is a reliable parameter for the assessment of the maturity of bitumen originated from kerogen type III, in other words, in particular for the assessment of the maturity of bitumens in coals. As a maturation indicator it is less reliable for oils that originated from kerogen types I and II, because of the dealkylation reactions of methylphenanthrenes to phenanthrene at the higher levels of thermal maturity.

Methylphenanthrene index 2, MPI 2, was introduced as an alternative to maturation parameter MPI 1, because 3-methylphenanthrene (value of MPI 1 is based on its relative concentration) at gas chromatography analysis has similar retention time as 1-methyl dibenzothiophene, and it is therefore difficult to detect.

$$\text{MPI } 2 = 3 \times 2 - \text{MP}/(1 - +9 - \text{MP} + \text{P}) \tag{2.5}$$

One of the most commonly used maturation parameters is the methylphenanthrene index 3,

$$\text{MPI } 3 = (2 - +3 - \text{MP})/(1 - +9 - \text{MP}) \tag{2.6}$$

based on isomerisation reactions α-MP→β-MP. The limit values of this parameter for the immature, medium mature and highly mature oils are summarized in Table 2.27.

A recently confirmed maturation parameter is also phenanthrene content in the tricyclic aromatic fraction [P]. It is based on dealkylation processes and the fact that maturation processes of phenanthrene isomers (methylphenanthrenes) lead to the generation of the phenanthrene itself.

Table 2.26 Classification of bitumens according to maturity on the basis of parameters of MPI 1 and Rr

The degree of bitumen maturity	MPI 1	Rr (%)
Immature	0.50–0.60	<0.70
Moderately mature	0.75–0.80	~0.85
Highly mature	>0.92	~0.95

Table 2.27 Values of the parameter MPI 3 for oils of different degree of maturity

The degree of oil maturity	MPI 3
Immature	<0.80
Moderately mature	0.80–1.00
Highly mature	>1.00

Table 2.28 Important maturity parameters of tricyclic aromatic fraction

Parameter	Formula
Methylphenanthrene index 1 (MPI 1)	1,5 × (2- + 3-MP)/(1- + 9-MP + P)
Methylphenanthrene index 2 (MPI 2)	3 × 2-MP/(1- + 9-MP + P)
Methylphenanthrene index 3 (MPI 3)	(2- + 3-MP)/(1- + 9-MP)
Methylphenanthrene ratio 1 (MPR 1)	2-MP/1-MP
Methylphenanthrene ratio 2 (MPR 2)	2-MP/9-MP
Dimethylphenanthrene index 1 (DMP 1)	4 × (2,6- + 2,7- + 3,5- + 3,6-DMP + 1- + 2- + 9-EP)/(P + 1,3- + 1,6- + 1,7- + 2,5- + 2,9- + 2,10- + 3,9- + 3,10-DMP)
Dimethylphenanthrene index 2 (DMPI 2)	(2,6- + 2,7- + 3,5-DMP)/(1,3- + 1,6- + 2,5- + 2,9- + 2,10- + 3,9- + 3,10-DMP)
Phenanthrene Alkylation Index 1 (PAI 1)	ΣMP/P
Phenanthrene Alkylation Index 2 (PAI 2)	ΣDMP/P
Phenanthrene Alkylation Index 3 (PAI 3)	ΣTMP/P
The content of phenanthrene in tricyclic aromatic fraction (%) [P]	P/(ΣMP + ΣDMP + ΣTMP + ΣEP)
The ratio of phenanthrene and anthracene contents	P/A

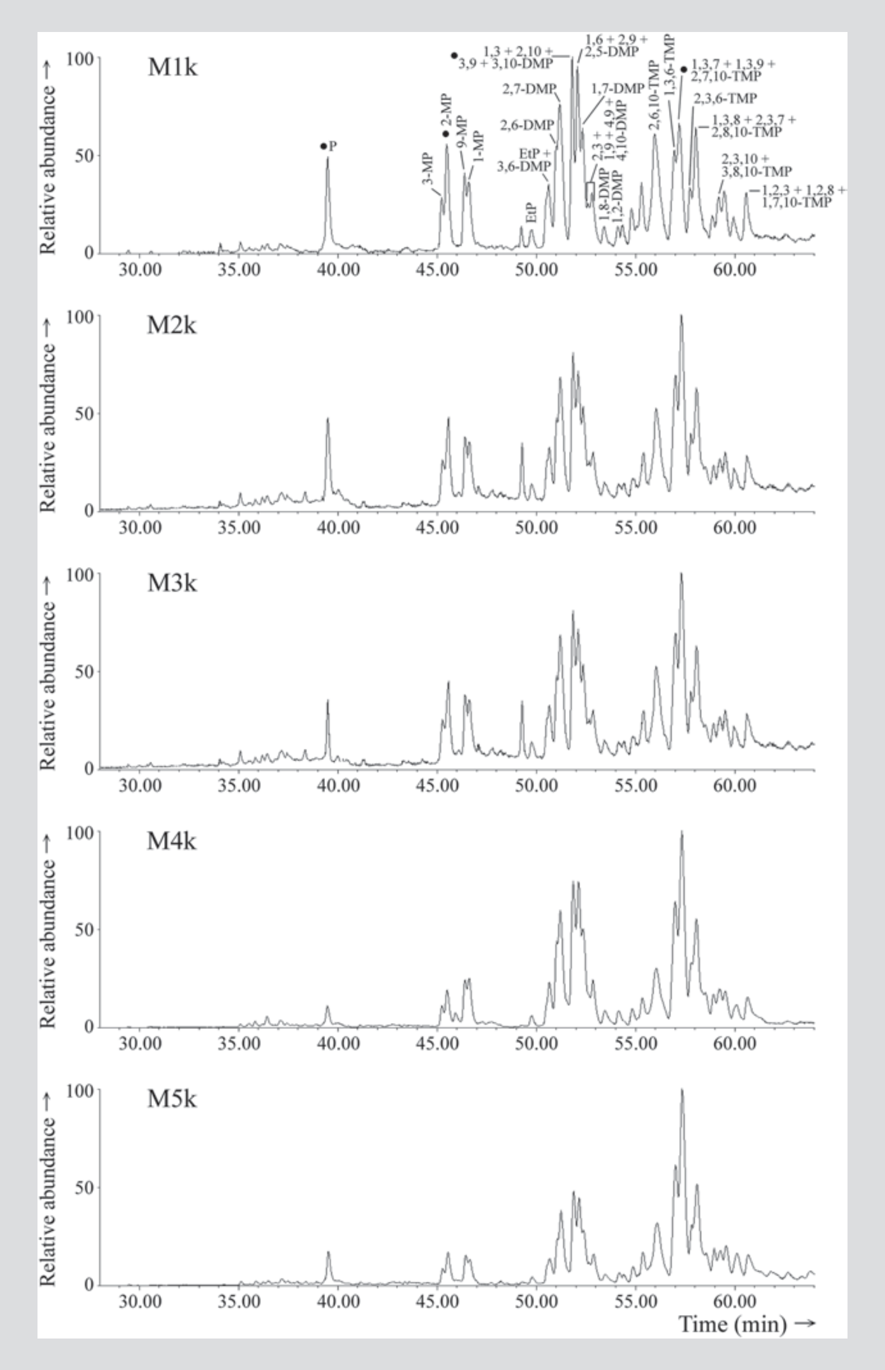
In addition to these parameters, in the organic-geochemical literature there are several other relations between various isomers of tricyclic aromatic hydrocarbons which are used as maturity parameters. They are all based on isomerisation (α→β) and dealkylation reactions of methylphenanthrenes. The most important are summarized in Table 2.28.

Box 2.27: Excursus

Phenanthrenes in bioremediation (environmental chemistry)

In environmental geochemistry as well, phenanthrene (P) and its methyl- (MP), dimethyl- (DMP) and trimethyl- (TMP) isomers are very often examined during monitoring of soil bioremediation processes or of sediment and water contaminated by oil or its derivatives. Bearing in mind that these isomers are more resistant to biodegradation than most other compounds in oil, particularly *n*-alkanes and isoprenoid aliphatic alkanes, their decomposition is proof of the success of bioremediation or biodegradation removal of oil-type pollution.

During the process of natural microbial degradation of oil pollutants (control samples M1k—M5k, see example below), a different trend was observed: the relative concentration of phenanthrene is reduced relative to methyl-phenanthrenes, and dimethyl-phenanthrenes and especially relative to trimethyl-phenanthrenes. Similarly, the concentration of methyl-phenanthrenes is reduced relative to the trimethyl-derivatives (Novaković et al. 2012).


M1k
Relative abundance →
100
50
0
●P
3-MP
● 2-MP
9-MP
1-MP
EtP
EtP +
3,6-DMP
2,6-DMP
2,7-DMP
● 1,3 + 2,10 +
3,9 + 3,10-DMP
1,6 + 2,9 +
2,5-DMP
1,7-DMP
2,3 +
1,9 + 4,9 +
4,10-DMP
1,8-DMP
1,2-DMP
2,6,10-TMP
1,3,6-TMP
● 1,3,7 + 1,3,9 +
2,7,10-TMP
2,3,6-TMP
1,3,8 + 2,3,7 +
2,8,10-TMP
2,3,10 +
3,8,10-TMP
1,2,3 + 1,2,8 +
1,7,10-TMP
30.00
35.00
40.00
45.00
50.00
55.00
60.00
M2k
M3k
M4k
M5k
Time (min) →

2.4 Gas

Outline

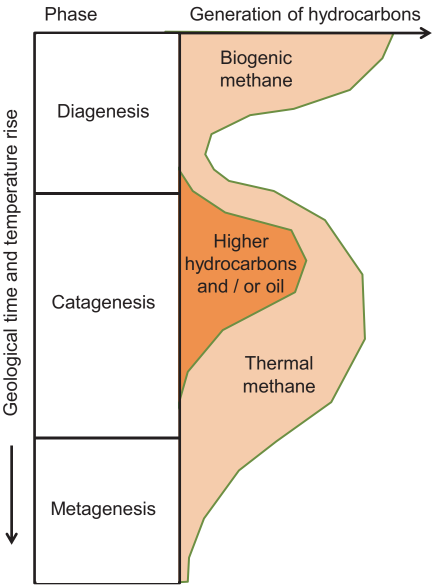
There are two types of natural gas. The first one is derived directly from biological material, as a product of microbiological activity at the beginning of diagenesis. The second type is formed during catagenetic and metagenetic transformations of organic matter in the deeper geosphere. Within the second type, according to the way of formation, several different species can be distinguished. Both types are often termed as natural gas and will be discussed in this chapter.

During diagenesis changes of organic matter occur under mild conditions, that means low temperature and pressure. The main components of extinct organisms, carbohydrates, proteins, lipids and lignin, after deposition, at shallow depths, usually decompose under the activity of microorganisms. Products of decomposition are amino acids, oligo- and monosaccharides, fatty acids, alcohols. Microorganisms consume these low molecular weight substances. Apart from CO_2, the products of these microbial metabolic processes are H_2O, NH_3, N_2, and H_2S, and also methane, CH_4. Thus generated methane is not subject to further changes (Fig. 1.4). It is commonly referred to as biogenic gas, or marsh gas. From gases of organic composition, diagenetic gas contains only methane, and therefore this gas belongs to the so-called "dry" type of gas. Its "inorganic companions" can be CO_2, N_2, NH_3 and H_2S.

In the early stages of catagenetic processes mostly bitumen is formed and the formation rate of gaseous products is low. At the end of the so-called "oil window" the situation changes in favour of gas. During later catagenetic stages and during metagenesis the kerogen is converted to gas under the influence of heat and pressure, which mainly consists of methane. A graphical presentation of the bitumen to gas ratio during the evolution of the organic matter in sediments is given in Fig. 2.41. In addition to methane some higher homologues are formed, primarily C_2-C_4 hydrocarbons. Therefore, catagenetic gas belongs to "wet" type gas.

The ratio of methane to other gaseous products, especially to the C_2–C_4 hydrocarbons, also changes during the evolutionary changes of organic matter in the geosphere. At the beginning of catagenesis the gaseous products are dominated by methane. However, towards the stage of the oil window, which represents the maximum in the bitumen production, the amounts of C_2–C_4 hydrocarbons and other gases increases, so that $C_1/\Sigma C_n$ ratio become slower. From the oil window towards metagenesis this ratio increases again, and finally, in the phase of metagenesis, it reaches a value of nearly 100 % methane content. This tendency is entirely logical if one takes into account that during kerogen cracking (during catagenesis) first larger fragments, and later on smaller and smaller molecules are produced, until at the very end (metagenesis), only methane is generated.

Fig. 2.41 Yield of bitumen and gas during the evolution of organic matter in geosphere



Box 2.28: *General Note*

Natural gas is mostly composed of methane. In diagenetic and metagenetic gas it accounts for almost 100%. In catagenetic gas, besides methane, there are some other gases, mostly C_2–C_4 hydrocarbons, and also some higher ones, which in terms of geological temperatures are also in gaseous state.

At first glance, one might say that metagenetic methane, which is formed in the final stages of organic matter transformation, is identical to diagenetic methane, which is formed in its initial stages. However, there are still differences between them. In fact, it has already been noted that heavier carbon isotope, ^{13}C, builds stronger bonds than the lighter one, ^{12}C. Therefore, the products will be enriched with lighter isotope compared to the precursor. It is therefore entirely logical that the oil, or bitumen, compared to kerogen from which it originates, has higher amount of lighter ^{12}C isotope and so by up to 2‰ more negative value of $\delta^{13}C_{PDB}$ (Fig. 3.27). For the same reason, in the early catagenetic stages the first obtained is gas that is enriched with lighter carbon isotope. Only over time slowly follows cracking and C–C bonds involving ^{13}C, and therefore the amount of heavier carbon isotopes increase in products, and the values for $\delta^{13}C_{PDB}$ of gas become less negative. Previous studies have shown that these values through geological history are changing through history quite uniformly. Typical values for biogenic gas are from −80 to −70‰. In the phase of the oil window, these values for gas are around −40‰, and for gas that is formed in the stage of metagenesis, $\delta^{13}C_{PDB}$ values are about −20 ‰. So the favourable way to distinguish clearly between methane that was formed in the phase of diagenesis and methane that was formed in the phase of metagenesis is an isotopic analysis by determining $\delta^{13}C_{PDB}$ values.

Apart from gas which is derived directly from kerogen, gas is also formed from bitumen by its cracking in source rocks. Finally, gas is also generated by cracking of oil in reservoir rocks. The amount of gas obtained from bitumen in the source rock depends also on temperature, pressure and mineralogical type of rock, but primarily from the time in which bitumen stays in the rock before migration. In reservoir rocks, maturation changes of oil during which low molecular weight compounds are formed (cracking processes) are not practically limited by time. Therefore, the amount of gases (C_1–C_4) and condensates (C_5–C_{10}) in the reservoir rocks is constantly increasing with time, and therefore gas is regularly associated with oil in reservoir rocks (Fig. 2.25).

Finally, the process of dealkylation (demethylation) of aromatic hydrocarbons in oils and bitumens as a source for methane generation should also be mentioned again. During these processes methyl groups are released irreversibly giving methane. This process is called methanisation of oil, and the gas formed in this way may, besides gases formed by cracking of kerogen, cracking of bitumen or cracking of oil, be considered a special type of gas formed during catagenetic and metagenetic transformations of organic matter in the geosphere.

An example that can illustrate the composition of gas that is obtained by cracking of kerogen (simulation of catagenetic and metagenetic processes) is shown in Fig. 2.42, that represents the gas chromatogram of gaseous products derived from pyrolysis of kerogen (type II) at 580 °C. Identification of peaks from Fig. 2.42 is shown in Table 2.29.

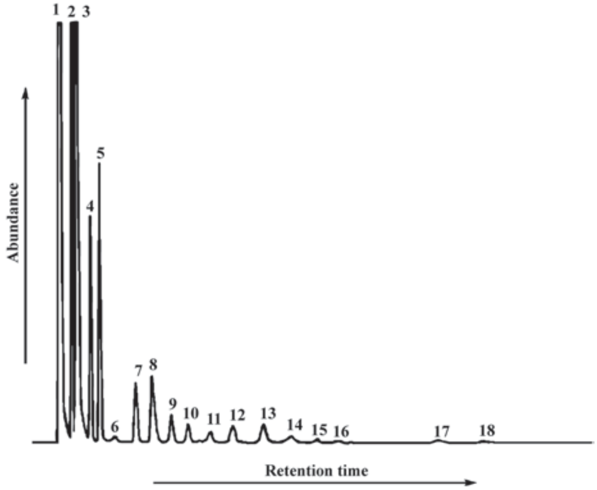


Fig. 2.42 Gas chromatogram of gaseous products of pyrolysis of type II kerogen sample (pyrolysis temperature: 580 °C, pyrolysis time: 50 min, continuous flow pyrolysis under a constant stream of nitrogen). (Peak identification is given in Table 2.29)

Table 2.29 Identification of peaks shown in Fig. 2.42

Peak	Compound
1	Methane
2	Ethane
3	Ethene
4	Propane
5	Propene
6	Isobutane
7	*n*-Butane
8	1-Butene/isobutene
9	*trans*-2-Butene
10	*cis*-2-Butene
11	1,3- Butadiene
12	*n*-Pentane
13	*n*-Pentene
14	*trans*-2-Pentene/2-methyl-1-butene
15	*cis*-2-Pentene
16	2-Methyl-2-butene
17	*n*-Hexane
18	*n*-Hexene

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Chapter 3
Minerals in Sediments and Their Impact on the Changes of Organic Substances in Geosphere

Keywords Silicates · Carbonates · Sulphides · Sulfates · Halides · Certain classes of organic compounds · Free bitumens · Bound bitumens · Pyrolysis of kerogen · Added minerals · Native minerals

3.1 Mineral Composition of Sediments

Outline

Almost all of minerals in the geosphere can be identified in sedimentary rocks. However, at this point there will be more discussion only about silicate, carbonate and sulphide minerals, as they are the most common and most important in studies of the interactions of inorganic and organic matter in sedimentary rocks.

All sedimentary, igneous or metamorphic rocks of the Earth's crust, consist of one or more components which are called minerals. It is estimated that the Earth's crust contains about 2400 mineral species, with about 7000 subspecies. Out of this huge number, only around 150 mineral species and subspecies are of higher importance as they determine dominantly the structure and properties of rocks. In the geological literature these minerals are called *petrogenic minerals*. Mineral species found in ore deposits and which do not have a greater role in the structure of the rocks, are called *ore minerals*.

Box 3.1: *General Note*

In sedimentary rocks, two types of minerals can be distinguished. Allogenic (*allotrios*—strange) or terrigenous (*terra*—earth) compounds are fragments of other rocks, which were formed in an earlier igneous, sedimentary or metamorphic cycle, i.e. before the foundation of the investigated rock. Autogenic minerals (auto—self) are genetically related to the sedimentary rock itself and were formed at the same time.

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Fundamentals in Organic Geochemistry, DOI 10.1007/978-3-319-11938-0_3

From the organic-geochemical point of view, sedimentary rocks are the most significant ones, because almost the entire organic matter in the geosphere is found in them. It has been estimated, that the sedimentary rocks account for only 5 % of the volume of the upper parts of the lithosphere. However, considering only the surface of the lithosphere the sedimentary rocks cover 75 % of the Earth's surface.

Sedimentary rocks are formed from the products of chemical or mechanical transformations of the previously created igneous, sedimentary and metamorphic rocks. They are usually deposited in layers as strata in the area of sedimentation, which covers an area of lithosphere and hydrosphere.

Overview of the major silicate, carbonate, sulphide, oxide and hydroxide, sulphate, haloid and phosphate minerals is given in Table 3.1. This overview contains more details than necessary for the study of organic-inorganic interactions in sediments. But with this more extended form a better picture of the complexity of the mineral composition of sediments can be obtained.

3.1.1 Silicates

Minerals, in whose composition silicon and oxygen are predominant, are called silicate minerals, or simply silicates. They occur not only widespread and abundant in the lithosphere, but also numerous and diverse, despite the fact that their composition comprises a relatively small number of other elements. The existence of a large number of silicate mineral species is possible thanks to special features of silicon and oxygen bound to it.

The silicon ion (Si^{4+}) is surrounded by four oxygen ions (O^{2-}) which are always arranged in the same way. The oxygen ions are at the tips of an imaginary tetrahedron with a silicon ion in the centre (Fig. 3.1). SiO_4-tetrahedron is the basic structural unit of all silicate minerals.

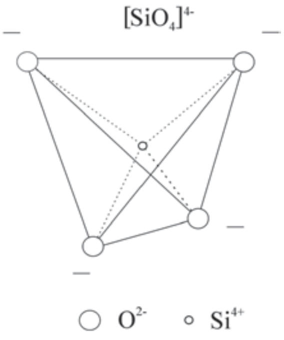
Since the SiO_4-tetrahedron is a negatively charged ion (SiO_4^{4-}), it easily binds to positive ions such as Ca^{2+}, Mg^{2+}, Fe^{2+}, Fe^{3+}, Na^+, K^+, or Al^{3+}. SiO_4-tetrahedra can be bound to each other through a shared oxygen ion. Also, a number of silicon ions in the lattice can be replaced by aluminum ions. Silicates in which at least 10 % silicon ions are substituted with aluminium ions are called aluminosilicates. Thanks to the described features of SiO_4-tetrahedrons, different combinations and forming of different types of silicate mineral species are possible.

According to the type and degree of polymerization of SiO_4-tetrahedrons, the silicates are divided to tectosilicates, phyllosilicates, inosilicates, nesosilicates and soro- and cyclosilicates (Table 3.1). The basic silicon-oxygen groups and ways of bonding between silicon and oxygen in these mineral species are illustrated in Fig. 3.2. For studying the interactions with the organic matter of sediments, the most important are silicon dioxide minerals and feldspars belonging to tectosilicates, and clay minerals that belong to phyllosilicates.

Table 3.1 Important minerals in geosphere

Silicates							
Tectosilicates				*Phyllosilicates*			
Group of SiO_2 minerals	Group of feldspars	Group of feldspathoids	Group of zeolites	Group of mica	Group of chlorite	Group of serpentine	Clay minerals
Quartz Cristobalite Tridimite Opal	K^-, Na^-, Ca—feldspars (Sanidine Orthoclase Albite-Microline Anorthite)	Leucite Nepheline	Natrolite-Heulandite Phillipsite Desmin Chabazite	Biotite Muscovite Paragonite		Antigorite Chrysotile Serpophite Talc	Kaolinite Montmorillonite Nontronite Saponite Illite Vermiculite Glauconite
Inosilicates		*Nesosilicates*				*Soro- and cyclosilicates*	
Group of amphiboles	Group of pyroxenes	Group of olivine	Group of Al-silicates	Group of garnets	Group of epidote		
Anthophyllite Tremolite Actinolite Hornblende	Enstatite Bronzite HyperstheneAlkalinepyroxenes	Forsterite Fayalite	Disthene Andalusite Sillimanite	Pyrope Almandine-Spessartine Uvarovite GrossularAndradite	Epidote	Beryl Tourmaline	
Carbonates							
Group of rhombohedron carbonates			Group of rhombic minerals			Group of Na-carbonates	
Calcite MagnesiteRhodochrosite Dolomite Smithsonite Siderite Ankerite			Aragonite Strontianite WitheriteCerussite			SodaTrona Thermonatrite	
Sulfides							
Pyrite chalcopyrite marcasite melnikovite pyrrhotite							
Oxides and hydroxides							
Oxide of hydrogen	Fe-oxides and hydroxides	Al-oxides and hydroxides	Ti-oxides and hydroxides	Mg-oxides and hydroxides	Mn-oxides and hydroxides	Ba- and Al-oxides	Complex Fe-, Mg-, Al-, Cr-, Zn- and Mn-oxides
Ice	Magnetite Hematite Limonite	Corundum Diaspore Hydrargillite	Brookite Rutile Anatase Perovskite	Periclase Brucite	Psilomelane Pyrolusite	Chrysoberyl	
Sulfates							
Group of barites		Group of Ca-sulfates		Group of alunites		Group of sulfates of salt deposists	
Barite Celestine Anglesite		Gypsum				EpsomitePolyhaliteKainiteGlauberite	
Halides							
Chloride of salt deposits			Group of Ag-, Cu- and Pb—clorides			Fluorides	

Fig. 3.1 Position of silicium and oxygen ions in SiO_4^{4-}—tetrahedron



Group of Silicon-Dioxide Minerals

Silicon-dioxide is found naturally in six crystalline modifications (α- and β-quartz, α- and β-tridymite, α- and β-cristobalite), in one cryptocrystal to microcrystal modification (chalcedony), and may appear also in the amorphous state (quartz glass—lechatelierite). When SiO_2 contains a certain amount of water, it appears in the form of amorphous opal.

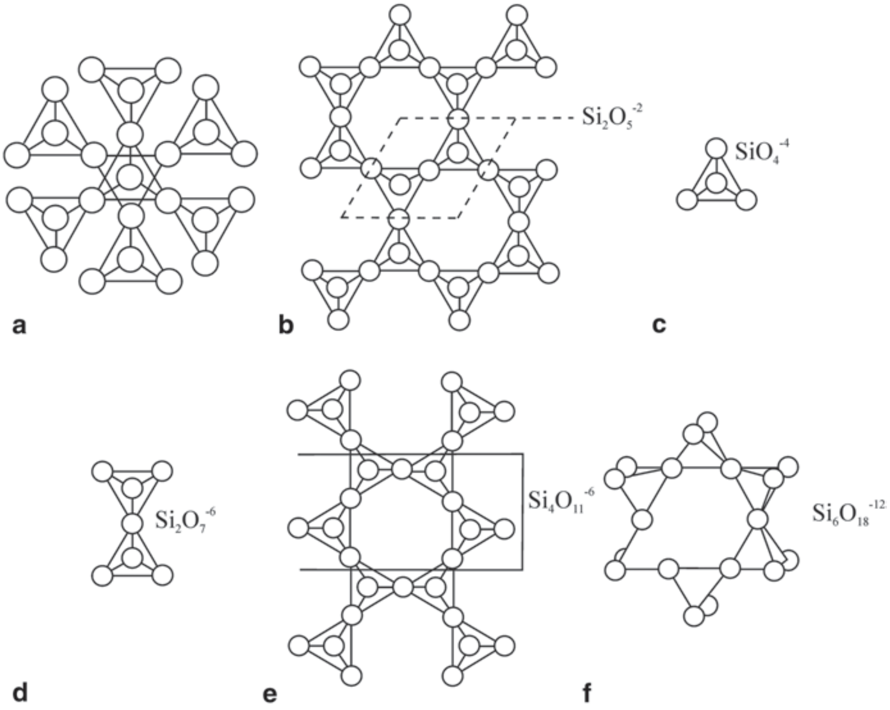


Fig. 3.2 Bonding of silicon and oxygen in tectosilicates (**a**), phyllosilicates (**b**), inosilicates (**c**), nesosilicates (**d**), sorosilicates (**e**) and cyclosilicates (**f**)

Stability of some crystalline modifications depends on heat and pressure. The influence of pressure is thereby less important than the effect of heat. Under the pressure of about one bar certain modifications are stable in the temperature ranges illustrated in the following:

β-quartz	↔	α-quartz	↔	α-tridymite	↔	α-cristobalite	↔	melt
	573°C		870°C		1470°C		1713°C	

(3.1)

Transformations of one form to another in most cases are very slow, even for the geological time conditions. This especially applies to the transformation of α-quartz to α-tridymite and α-tridymite to α-cristobalite. Generally, the rate of transformation largely depends on the crystal lattice of individual modifications (Fig. 3.3).

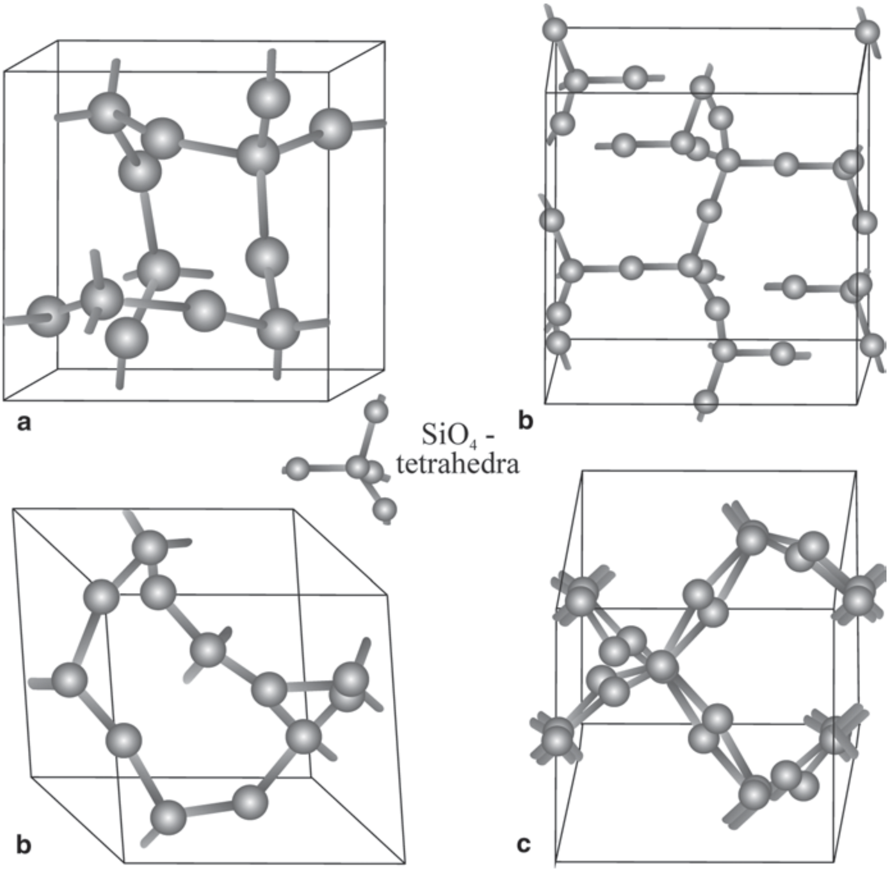


Fig. 3.3 Crystal structures of α-cristobalite (**a**), α-tridimite (**b**), α-quartz (**c**), and β-quartz (**d**), noticeable difference between the crystal structures of α-cristobalite and α-tridimite, and similarity between α-quartz and β-quartz

Table 3.2 Names and composition of isomorphic mixtures of albite and anorthite

Albite	0–10 %	Anorthite
Oligoclase	10–30 %	“
Andesine	30–50 %	“
Labradorite	50–70 %	“
Bytownite	70–90 %	“
Anorthite	90–100 %	“

Quartz is the most important petrogenic mineral from the group of silicon dioxide minerals. According to some estimates, quartz makes up about 12 % of the lithosphere.

Feldspars

In terms of their chemical composition, feldspars are aluminosilicates of potassium ($K_2O \times Al_2O_3 \times 6SiO_2$), sodium ($Na_2O \times Al_2O_3 \times 6SiO_2$) and calcium ($CaO \times Al_2O_3 \times 2SiO_2$) (Table 3.1). Minerals from the group of feldspars usually contain at least two of these elements. Feldspars occur mainly as isomorphous mixture of sodium and potassium or sodium and calcium aluminosilicates.

Feldspar of the first type is called alkali feldspar, and feldspar of the second type is plagioclase. Alkali feldspar occurs in three modifications (sanidine, orthoclase and microline; Table 3.1). Plagioclases are isomorphous mixtures of sodium feldspar—albite and calcium feldspar—anorthite (see Table 3.2).

Structural feldspar lattice is built from SiO_4-tetrahedra connected in all directions. Thereby in every second and fourth SiO_4-tetrahedron, silicon ions can be replaced by aluminium ions, thus becoming a complex structure $/Al_2Si_2O_8/^{2-}$ and $/AlSi_3O_8/^{-}$ that easily bind ions of potassium, sodium and calcium.

Clays

Clay minerals are one of the most important groups of minerals that participate in the formation of sedimentary rocks. They are generally formed by aluminosilicate weathering in the surface layers, although some may be formed by hydrothermal alterations of rocks at relatively low temperatures. The most important clay minerals in this group are kaolinite, montmorillonite and illite.

Kaolinite can be represented by an aggregate formula: $Al_2Si_2O_5(OH)_4$. Silicon and aluminium ions cannot replace each other, but they build separate interchanging layers (Fig. 3.4). Kaolinite is formed by transformation of igneous and metamorphic rocks (mainly acidic) by aluminosilicate weathering (feldspar, feldspathoides or mica). It is formed in acidic environments under oxidation conditions and at low concentrations of Na^+, Mg^{2+} and Fe^{2+}.

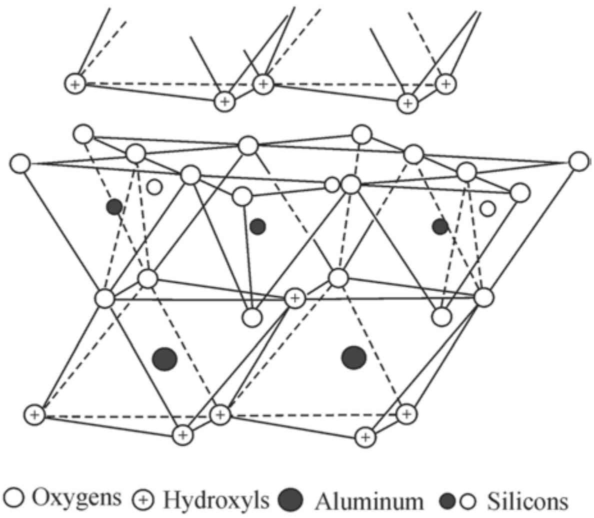


Fig. 3.4 Crystal structure of kaolinite

Montmorillonite is structurally different from other clay minerals. In the structural montmorillonite grid two layers are built up of SiO_4-groups, and between them a layer made of Al^{3+}, Mg^{2+} and Fe^{2+}. Between these “packages” there are water molecules that are weakly bound (Fig. 3.5). Thanks to this structure, it is possible to

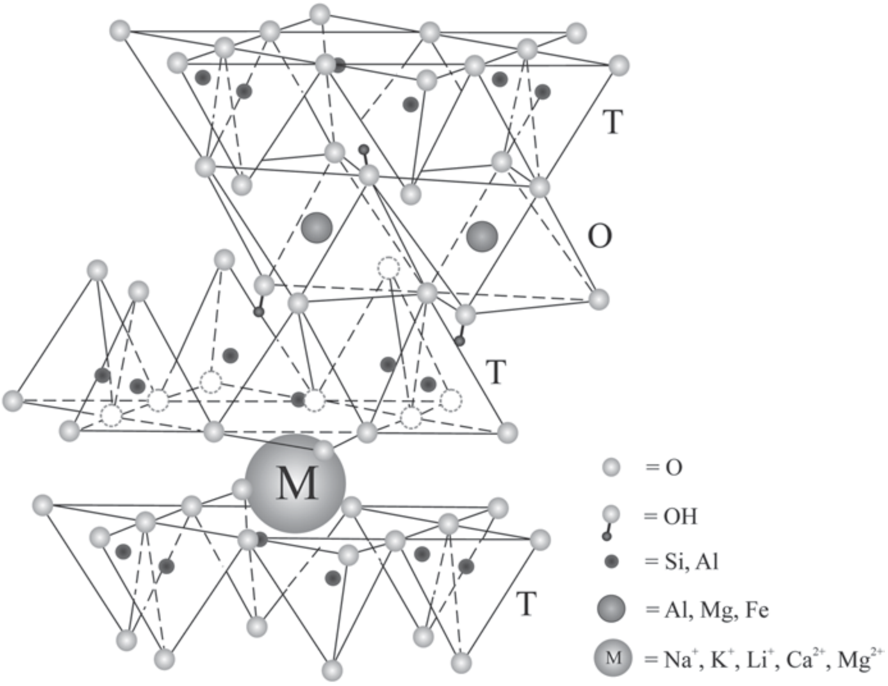


Fig. 3.5 Crystal structure of montmorillonite

easily narrow or expand the space in which water molecules are found. Montmorillonite can lose the interlayer water without disrupting the structure by heating at 100–200 °C, but can just as easily receive it back.

In terms of its chemical composition, montmorillonite is a hydrated aluminosilicate. It can be represented by an aggregate formula: $Al_2Si_4O_{10}(OH)_2 \times 2H_2O$. Part of Al^{3+}-ions can be replaced with Mg^{2+} or Fe^{3+}. Montmorillonite is formed in alkaline environments from solutions which must be rich in Na^+, Mg^{2+} and Fe^{2+}. The more alkaline the environment the easier is the formation of montmorillonite. Therefore, in contrast to kaolinite, montmorillonite is formed also in the marine environment.

Illite is a clay mineral which is formed by transformation of feldspar or muscovite degradation. Chemical composition of this mineral can be represented by the formula: $K_x(AlFe^{3+})_4Si_8 \times Al_xO_{20} \times nH_2O$ where x is less than 2. Instead of Al^{3+}, Mg^{2+} or Ca^{2+} ions may be included.

3.1.2 Carbonates

Carbonates are an important group of petrogenic minerals that are widespread in the lithosphere and comprise a large number of mineral species. They can be divided into two large groups: carbonate minerals without water and other anions and carbonate minerals with water and other anions.

The first group of minerals is subdivided into two further groups: carbonates that crystallize in rhombohedral system and carbonates that crystallize in rhombic forms (Table 3.1). Rhombohedral carbonates are those of calcium, magnesium, manganese, zinc and iron. Rhombic carbonates are built by calcium, strontium, barium and lead. Ions of rhombohedral minerals have smaller diameters than the orthorhombic mineral ions (0.078–0.106 nm compared to 0.127–0.143 nm). Ions of smaller ionic radius are surrounded by six oxygen ions each (coordination number to oxygen is 6), while the ions with larger ionic radius are surrounded by nine oxygen ions each (coordination number to oxygen is 9). Calcium ion is the only one that can be incorporated in both types of crystal lattice, and therefore calcium carbonate is dimorphic.

Carbonates crystallizing in rhombohedral system are more important since they act as petrogenic minerals.

Rhombohedral Carbonates

The general chemical formula of rhombohedral carbonates is MCO_3, where M are the bivalent cations of calcium, magnesium, manganese, iron or zinc. Although all these minerals are morphologically similar, even identical, and structurally completely analogous, there is no possibility of complete isomorphic mixing between all these minerals due to the differences in the ionic diameters (Mg—0.078 nm, Fe—0.082 nm, Zn—0.083 nm, Mn—0.091 nm, Ca—0.106 nm). Only ions that are similar in size can be replaced, so that those that can be mixed are siderite and rhodochrosite, siderite and magnesite, and finally calcite and rhodochrosite. Such a

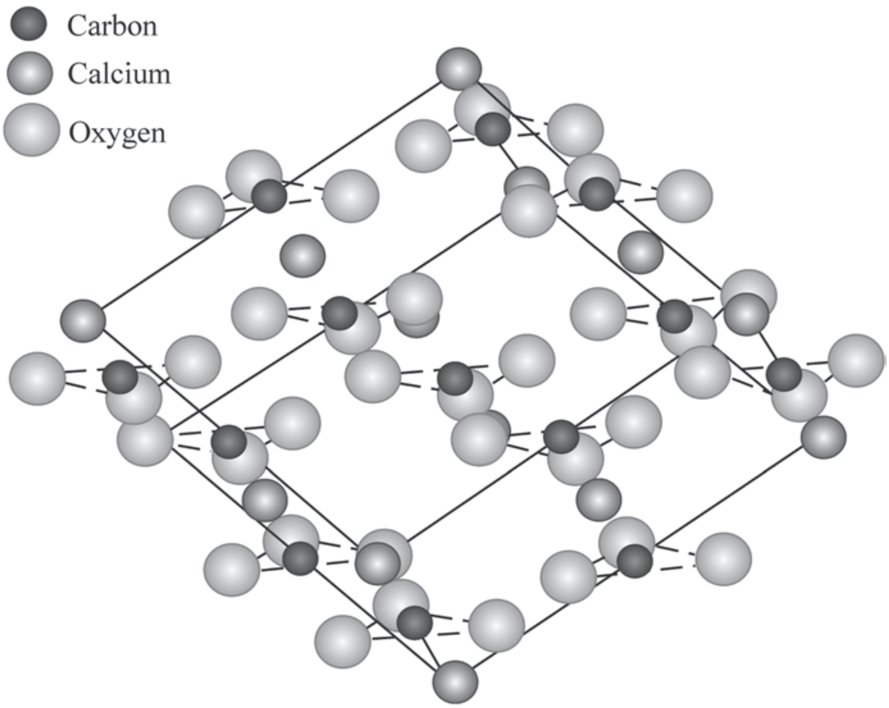


Fig. 3.6 Crystal structure of calcite

dual mineral is dolomite ($CaCO_3 \times MgCO_3$; Table 3.1), in which all magnesium, or portion thereof, may be substituted with Fe or Mn (ankerite; Table 3.1). Due to the large differences in ionic diameters of calcium and magnesium, isomorphic mixing of calcite and magnesite is almost impossible.

Among rhombohedral minerals the most important are calcite, magnesite, siderite and dolomiteas petrogenic minerals. Calcite ($CaCO_3$) is the most widespread mineral from the group of rhombohedral carbonate minerals. It occurs in platy crystals (Fig. 3.6), but builds also aggregates with irregular grain shapes. It is formed in many ways, mostly in the water, at lower temperatures, in the presence of easily soluble $Ca(HCO_3)_2$. In the surface layers of sediments it is dissolved and converted into calcium bicarbonate.

Magnesite ($MgCO_3$) is magnesium carbonate. It occurs in small-grained aggregates of irregular shape. It is formed by hydrothermal alteration of Mg-silicates.

Siderite ($FeCO_3$) is a mineral composed of iron carbonate. It is formed as a product of activity of hydrothermal solutions or cold waters rich in carbon dioxide in minerals with higher iron content. During the surface decomposition it is converted into limonite.

Dolomite ($CaCO_3 \times MgCO_3$) is a double salt known as calcium and magnesium carbonate. It is formed in many ways, often in diagenetic processes, by the influence of magnesium containing solutions on the calciumcarbonate rocks. It can be formed also hydrothermally.

3.1.3 Sulphide Minerals

Sulphide minerals are mostly components of ores, although they are also found in a considerable amount in sedimentary rocks. This is especially true of iron sulfide (FeS_2). Group of petrogenic minerals includes also pyrrhotine (FeS) and chalcopyrite ($CuFeS_2$) (Table 3.1).

Iron sulfide occurs in nature in three modifications: in the tesseral one as pyrite, in the rhombic one as marcasite and the amorphous one as the melnikovite pyrite. The most prevalent among them, and among all the sulphide minerals in general, is pyrite. Under normal conditions, among sulphide minerals only pyrite is stable. Melnikovite is unstable in the amorphous state, which can be quickly and easily converted to pyrite. Marcasite also tends to convert into tesseral—pyrite modification, but that process is slower.

Pyrite crystallizes in a tesseral form of pentagon. As this form is characteristic of pyrite, it is often called also pyritoedron. Pyrite occurs as granular masses and fine-grained aggregates. It is formed in many ways and is found in all kinds of rocks. It is usually generated by hydrothermal processes. During the surface decomposition it is converted into limonite.

3.2 Influence of Minerals on the Alterations of Organic Matter in Sediments

Outline

Microorganisms have a dominant influence on the alterations of organic matter in the geosphere during diagenesis, but temperature and pressure in the phase of catagenesis. Studies of interaction of minerals and organic part of sedimentary rocks have shown in the last 30 years that the influence of minerals on diagenetic and especially catagenetic changes in organic matter is not negligible. It is realised as a catalytic effect, but also by adsorption.

The influence of minerals on organic matter alterations in the geosphere can be considered in two ways, by monitoring the effects of minerals on certain classes of organic compounds that can be found in the geological environment (for example, fatty acids, *n*-alkanes, alcohols, or steroids), or by monitoring the effects of minerals on complex sedimentary organic materials, mostly on bitumen and kerogen. These approaches will be explained in more detail in this chapter.

3.2.1 Interactions of Minerals with Certain Classes of Organic Compounds

One of the oldest known examples regarding the influence of minerals on certain organic compounds i in geological samples is the influence of bentonite on the changes in behenic acid. If behenic acid ($C_{21}H_{43}COOH$) is heated in the presence of bentonite at 200 °C without access of air, n-C_{21} hydrocarbon is obtained. Concentration of all other n-alkanes in the range C_{12}–C_{36} in this case is only about 0.3 %. In this way it is proved that bentonite catalyzes the process of decarboxylation of behenic acid. A similar result is obtained when behenic acid is heated with montmorillonite at 200 and 250 °C. Product of transformation of behenic acid in this case is as well n-C_{21}. Concentration of all other n-alkanes in the range C_{16}–C_{28} is only about 1 %. CPI calculated from the abundance and distribution of these n-alkanes is about 1.5. Thus, in the presence of mineral catalysts generation of n-alkanes are related to dominantly two reactions—decarboxylation of fatty and cracking. Activation energy of decarboxylation in this case is much lower than the activation energy of cracking the hydrocarbon chain (150.7 compared to 194.6 kJ/mol). On the other hand, activation energy of thermal cracking of hydrocarbon chain of behenic chain is 230 kJ/mol. Since this value exceeds the value of activation energy of cracking of behenic acid in the presence of montmorillonite (194.6 kJ/mol), montmorillonite catalyzes this type of reaction, but to a lesser extent than decarboxylation.

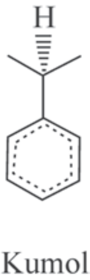
Montmorillonite as the most effective catalyst among all silicate minerals, and among all minerals in sediments in general, has a catalytic effect on the transformations of alcohols. During these catalyzed reactions n-alkanes are also formed. However, the amount of n-alkanes formed in this manner is negligible compared to their total amount in bitumens or in oils.

Catalytic effect of some minerals, especially clay minerals in alkaline aqueous solutions originates primarily from adsorbed Al^{3+}- and Fe^{3+}-ions which act as Lewis acids. Activity of Al^{3+}-ions adsorbed on bentonite is by three orders of magnitude higher than the catalytic activity of Na^{+}-ions adsorbed on the same mineral. Although the activity of catalysts decreases with the increase in water

Box 3.2: *General Notes*

Minerals have an impact on the transformation of n-alkanes. For example, montmorillonite can be an effective catalyst in hydrocarbon cracking reactions thanks to dissociation of interlayer water and presence of ions Al^{3+} and Fe^{3+} that act as Lewis acids on the free mineral surfaces. In this way it is explained why oils originating from silicate dominated source rocks have higher contents of light hydrocarbons compared to oils from carbonate source rocks. However, montmorillonite is more effective as catalyst for cracking of hydrocarbon part of carbonic acids than higher n-alkanes.

Fig. 3.7 Structural formula of kumol



content, Al^{3+}-bentonite is catalytically active also with 40 % water content. Further on, Al^{3+}-bentonite can survive including its catalytic properties under alkaline conditions in which an insoluble hydroxide salt is generated, because Al^{3+} is in equilibrium with the dissolved form. The same interpretation can be applied also to Fe^{3+}-ion.

Water is an important factor determining thermocatalytic properties of clay minerals. It has been shown that it influences *iso*-butane/*n*-butane ratio in products during pyrolysis of behenic acid in the presence of bentonite as mineral catalyst. If the pyrolysis is performed without water, the ratio is higher, and, vice versa, in the presence of water this ratio is around 0.1. So, it could be said that under the conditions of dry pyrolysis, cracking of hydrocarbon part of behenic acid occurs by carboncation mechanism and under the conditions of hydropyrolysis by free-radical mechanism.

Clay minerals have a catalytic effect also on the structural and stereochemical changes of steroids. If cholesterol is heated to 140 °C for 16 h in the presence of these minerals, structural and stereochemical isomers of the corresponding sterane are obtained among which the vast majority (six out of seven) of those that can be identified in bitumens of ancient sediments and petroleum. The highest yield of these isomers is obtained with kaolinite and montmorillonite as catalysts.

An insight into the catalytic mechanism of montmorillonite on the stereochemical changes of sterane can be obtained by studying a simplified molecular analogon. For this purpose cumol can be used due to its structural similarities to steranes (Figs. 3.7 and 3.8).

Stereochemical changes in the cumol molecule adsorbed on a mineral catalyst are explained by hydrogen exchange mechanism. Active acidic centres on the surface of minerals polarize the bond between α-C-atoms and hydrogen atoms in cumol molecule, which leads to further polarization of the link between β-C-atom and connected hydrogen atoms. Thus, hydrogen atom on β-C-atom becomes more acidic. During the hydrogen exchange mechanism the adsorbed cumol molecule passes through a planar “alkene” form, which results in the preservation of configuration at the α-C-atom, and the change in the stereochemical arrangement on the β-C-atom.

When this model is applied to the sterane molecule, stereochemical changes at the individual chiral centres can be explained as follows: sterane molecule reacts

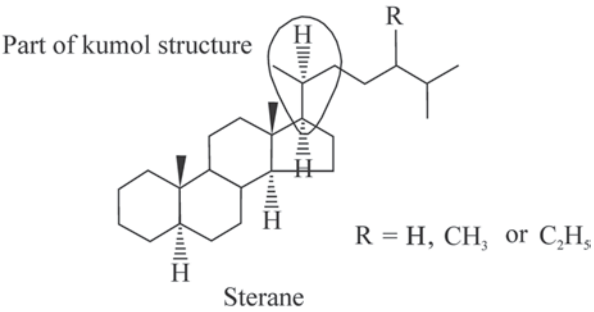


Fig. 3.8 Structural formulas of kumol and sterane

strongest with the mineral catalyst at C_{25}, followed by C_{17}, C_8 and C_{20}. Their adjacent C-atoms are C_{24}, C_{20}, C_{14} and C_{17} (Fig. 3.8). This means that during the interaction of minerals and sterane molecules the fastest stereochemical changes will take place at C_{24}, then C_{20}, C_{14} and C_{17}. Investigation of steranes of a large number of samples of bitumen of sedimentary rocks with different maturity level, led to the same conclusions when it comes to kinetics of stereochemical changes at chiral centres.

The structural and stereochemical changes in fatty acids, *n*-alkanes, alcohols, and steroids are most influenced by silicate minerals or clay minerals from which montmorillonite has the highest impact. However, it is known that calcite ($CaCO_3$) also has certain catalytic effect on transformations of fatty acids and that sulphur has catalytic effect to some extent on structural changes in cholesterol leading to aromatic and naphthenic moieties.

3.2.2 Interactions of Minerals with Geological Organic Materials

Interactions Between Minerals and Bitumens

Box 3.3: *General Note*

Knowledge of methods and intensity of the interaction between mineral components and bitumen of sedimentary rocks, and even the mineral components of reservoir rocks and oil, is of great importance for understanding the changes in organic matter in the geosphere and to determine factors that influence these changes. These findings are almost necessary precondition for a successful correlation of oil-oil and oil-source rock.

The interactions of minerals with bitumen are related to catalytic effects but also to adsorption phenomena. Interestingly, organic-geochemical studies have shown that the composition of bitumen and oil is influenced more by the adsorption effect of minerals. For example, bitumen extraction yields from sedimentary rocks vary depending on the particle size. Highest amounts of bitumen are extracted from fractions of smaller grain size pointing to surface related accumulation.

Additionally, in sediment material of higher grain size bitumen is in the “trap” from which it can be hardly released. Extraction will release bitumen from the larger grain size rocks only from the so-called “open” pores, and a very small amount of bitumen from the “closed” pores. Grinding rocks creates conditions for better access of solvents to bitumen contained in the “closed” pores, which significantly contributes to increasing the yield of extraction.

Under laboratory conditions, bitumen is the most effectively released from the “closed” pores if mineral part of sediment is removed by chemical means creating kerogen concentrates. As already described, carbonates are usually removed with diluted hydrochloric acid, and silicates are removed using a mixture of concentrated hydrochloric and hydrofluoric acids. In this way the bound bitumen is mobilised which can then be extracted with a suitable solvent.

However, under natural geological conditions there are no conditions for the release of the bound bitumen from the “closed” pores of sedimentary rocks, so that only bitumen from “open” pores can migrate. Since it is easiest for minerals of sedimentary rocks to adsorb heavier and more polar compounds, bitumen which migrates (from “open” pores), compared with bitumen which remains in the source rock, is enriched with lighter hydrocarbons. For this reason, the oil in reservoir rock contains higher proportion of the lighter hydrocarbons than the bitumen in the source rock.

The adsorption effect of minerals on bitumen can be estimated by the Rock-Eval method. As already explained, during pyrolysis of sedimentary rocks containing organic matter, according to the Rock-Eval method, three signals, which are marked with S_1, S_2 and S_3 are obtained. Signal S_1, or maximum S_1, originates from the free bitumen, S_2 from kerogen pyrolysis products, and the maximum S_3 from CO_2, so that its intensity is proportional to the amount of oxygen in the rock. However, a part of the S_2 peak derived from associated bitumen. Hydrogen index of the sample (HI—mgHC/g TOC) can be increased up to 40 % as a result of the “release” of associated bitumen.

Adsorption depends to a certain extent on the origin of organic matter. The organic matter derived from terrestrial higher plants is concentrated in larger, “open” pores of the sediment, and the remains of algae and bacteria are adsorbed more in fine, “closed” pores. It could be concluded that in the source rocks, bitumen of algal origin will be retained to a higher extent than bitumen of terrestrial origin.

The best adsorbents are clay minerals, montmorillonite and illite. Carbonate and sulphide minerals have lower adsorption capacities. This means that sedimentary rocks dominated by silicate minerals will adsorb components of bitumen to a higher extent, primarily its heavier and more polar components. As a result of better adsorption on silicate minerals, the primary migration of bitumen through the siliceous sedimentary rocks is significantly more difficult than through carbonate sedimentary rocks. Therefore, oils derived from silicate-type source rocks are enriched with lighter hydrocarbons and have higher values of API-gravity than the carbonate-type oils.

There is another known reason why the oils from siliceous source rocks are enriched with easier and more thermodynamically stable components compared to oils that come from carbonate source rocks. Silicate minerals have also enhanced thermocatalytic properties and higher influence on the maturation changes of bitumen. Although the catalytic effect of minerals on the changes of bitumen is weaker than adsorption, bitumen in the silica type source rock still undergoes significant changes that result from thermocatalytic effects of these minerals.

Clay minerals have more or less catalytic effect on the structural and stereochemical changes of all classes of organic compounds belonging to the group of biological markers. Their effect on *n*-alkanes and steroids has already been discussed. The way and intensity of the catalytic effect of silicate minerals on other biological markers, such as isoprenoid aliphatic alkanes, polycyclic alkanes of triterpane type and aromatic steroids, will be discussed in more detail in the following chapters.

The composition of oil may be also influenced thermocatalytically by minerals in reservoir rocks. For example, silicate can catalyse the reactions of macromolecular asphaltene pyrolysis and thus contribute to increasing the contents of hydrocarbon compounds in petroleum. Theoretically, the silicate minerals in reservoir rocks can act catalytically to almost all the transformations of biological markers that lead to thermodynamically more stable isomers. However, in the reservoir rocks, the contact between oil and a possible catalyst is much weaker than the contact between the catalyst and bitumen in the source rock. Therefore, the catalytic activity in the reservoir rocks is mostly of lower intensity.

Differences in the Composition of Free and Bound Bitumens

Remembering the analytical treatment of sediment material, free bitumen (bitumen 1) can be distinguished from the bound bitumens (bitumens 2 and 3). The first can be extracted directly from a crude sedimentary rock, whereas the other two only after removal of carbonates (bitumen 2) and silicates (bitumen 3). Between these bitumens there are significant differences in the composition as a result of adsorption and thermocatalytic mineral effects. Bitumen 1, as bitumen, which is in the weakest interaction with minerals, has the least amount of polar NSO-compounds, and the highest amount of saturated hydrocarbons. Since the NSO-compounds easily adsorb on minerals, their amount is greater in the bound bitumens. An example of group composition of free and bound bitumens of an Aleksinac oil shale sample is given in Fig. 3.9.

Between these bitumens there are considerable differences in composition of biological markers. As for the *n*-alkanes, bitumen 3 has the lowest CPI-value. It is in the strongest interaction with the silicate catalysts, and therefore in this bitumen maturation changes of *n*-alkanes are most advanced (CPI is tending towards one). Bitumen 1 derived *n*-alkanes have the least uniform distribution (maximum value of CPI). For the same reason this bitumen is dominated by *n*-C_{27}. Example of gas chromatograms of the saturated hydrocarbon fractions of free and bound bitumens of one Aleksinac oil shale sample is given in Fig. 3.10.

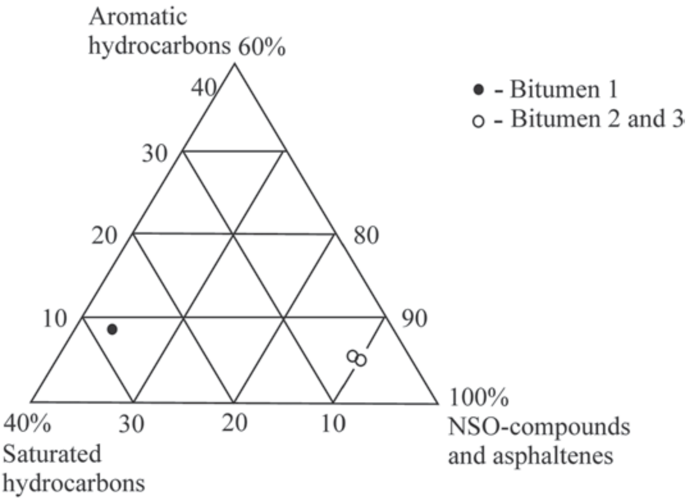


Fig. 3.9 Example of group composition of an oil shale with respect to free and bound bitumens, illustrated by the triangular diagram.

Differences are also visible in the sterane distributions (ion chromatograms of *m/z* 217, Figs. 3.11 and 3.12). In the chromatogram of bitumen 1 there is almost no peak originating from diasteranes, typical geoisomers. They were most intensive in the ion chromatogram of bitumen 3. The same accounts for the peaks originating

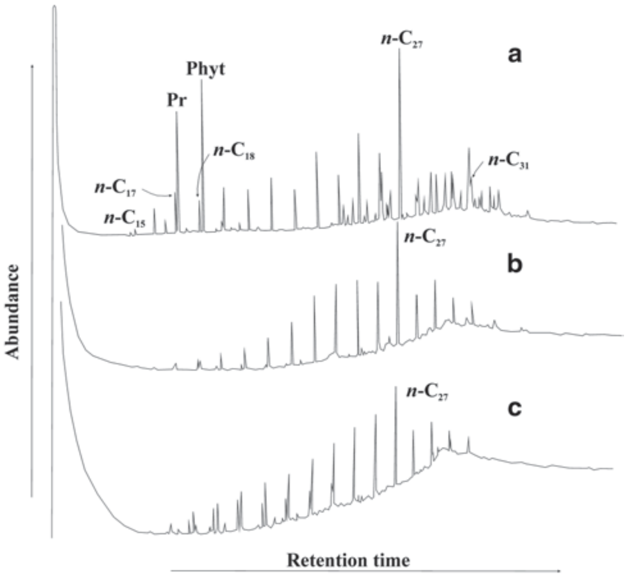


Fig. 3.10 Gas chromatograms of saturated hydrocarbon fractions of bitumen 1 (**a**), bitumen 2 (**b**), and bitumen 3 (**c**), of an oil shale sample

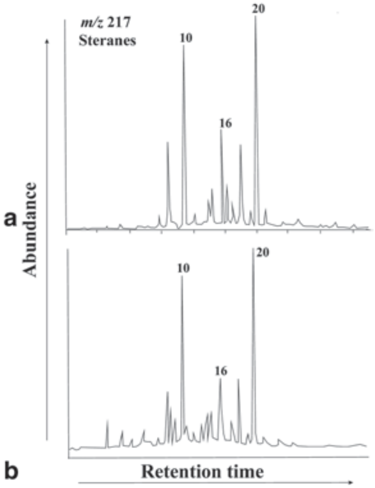


Fig. 3.11 Ion chromatograms *m/z* 217 (steranes) of free bitumen (**a**) and bound bitumens 2 (**b**), of an Aleksinac oil shale sample. (Peak identification is given in Table. 2.5)

from other thermodynamically stable isomers. A stronger interaction of bitumen 3 with silicate catalysts contributes to the increase in the amount of bitumen 3 geoisomers in relation to bitumen 2, especially in comparison with bitumen 1. Furthermore, bitumen 3 contains the largest amount of lower monoaromatic steroids C_{20} and C_{21}, compared to the higher ones C_{26}–C_{30}, and a maximum amount of lower triaromatic steroids, C_{20} and C_{21}, as compared to the higher ones C_{26}–C_{28}.

All differences between the free bitumen and the bound bitumens, as seen for to the group composition and the distribution of biological markers, clearly demonstrate that siliceous minerals have a significant adsorption and catalytic effect on the transformation of bitumen.

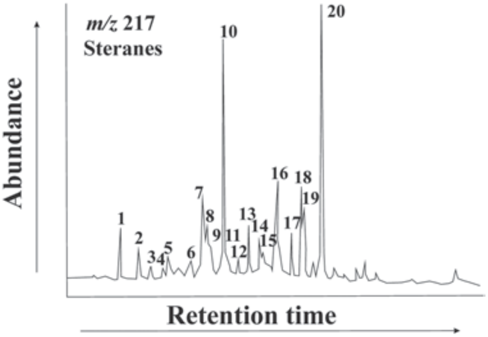


Fig. 3.12 Ion chromatograms *m/z* 217 (steranes) of bound bitumens 3. (Peak identification is given in Table. 2.5)

Interactions Between Minerals and Kerogen

Box 3.4: ***General Note***

Minerals also exert adsorption and catalytic influence on kerogen in sedimentary rocks. However, while the composition of bitumen depends to a great extent on the adsorption properties of minerals, changes of kerogen are largely a consequence of their thermocatalytical activities.

Assessment of the influence of minerals on catagenetic changes in kerogen, or its degradation to gaseous and liquid products, can be made by comparing the experiment with pyrolysis of "pure" kerogen and pyrolysis of kerogen which is "enriched" with various minerals. His approach allows to track differences in the yield of gaseous and liquid products, but also differences in the composition of biological markers. Another approach might be to investigate the effects of native mineral materials to thermal changes in kerogen. To understand the influence of minerals on the thermal changes of kerogen it is useful to consider both approaches.

Pyrolysis of Kerogen in the Presence of Added Minerals

Tannenbaun et al. (1986) presented an example of the pyrolysis results of "pure" kerogen and the kerogen "enriched" with calcite, montmorillonite or illite.

Pyrolysis of "pure" type II kerogen gives a substantial amount of bitumen 1, a much smaller amount of bitumen 2 and C_1–C_9 hydrocarbons. The yield of free bitumen was highest after 100 h. After 1000 h the yield was slightly lower. With added calcite, changes in the yield of products are minimal, and the yield of bitumen 1 is the highest after 1000 h. However, with added montmorillonite, there can be seen significant differences in the yields of pyrolytic products. The amount of bitumen is considerably smaller, while the amounts of C_1–C_9 hydrocarbons and, in particular, bitumen 2, are noticeably higher compared to the amounts that are obtained by pyrolysis of "pure" kerogen. Lower yields of bitumen 1, with concurrent increase in the yield of bitumen 2, are observed when illite is added to the kerogen.

Relative reduction in the yields of free bitumen in the pyrolysis of kerogen with montmorillonite is not due to inhibitory effect of this mineral to the pyrolysis, but, on the one hand, to very pronounced catalytic effect of this mineral on cracking of compounds in free bitumen and on the creation of small molecules that enter into the composition of gaseous products and condensates. On the other hand, this effect can be attributed to adsorption of bitumen on montmorillonite.

Type I kerogen gives a similar result as type II kerogen. However, there are some differences observed. Namely, the yield of bitumen 2 and of C_1–C_9 hydrocarbons is noticeably increased when kerogen is enriched by illite and particularly by montmorillonite. However, pyrolysis of type I "pure" kerogen produces bitumen 1 in a significantly higher yield, the yield of bitumen 1 and 2 together during the pyrolysis of kerogen with montmorillonite is not higher than the yield of these bitumens in pyrolysis of “pure” kerogen. Higher yield of bitumen at pyrolysis of type I kerogen can be explained by the higher potential to create hydrocarbons of type I kerogen compared to type II kerogen.

Montmorillonite and illite have a stronger effect on type II kerogen. This type of kerogen is in a stronger interaction with minerals because of a higher content of heteroatoms (oxygen and sulphur), and thus higher polarity.

The above considerations show how it is possible to assess on a laboratory scale the influence of minerals on the changes of kerogen. The question is whether it is the same under geological conditions, since under natural conditions the temperatures are much lower (temperatures in source rocks range from 50 to 150 °C). On the other hand, the processes occur in a long geologic time period, measured in millions of years. Also the moisture and water content under natural conditions have to be considered. Water reduces the catalytic effect of minerals, which means that in the experiments of “dry” pyrolysis, the catalytic as well as the adsorption effect of minerals is probably stronger than in nature. Therefore, for a more faithful picture, an approach which involves the addition of water is considerably better. The experiments of the so-called “hydropyrolysis” carried out so far, showed, that minerals had somewhat weaker effects on changes in kerogen. However, it does not change the overall conclusion about the catalytic and adsorption effects of silicate minerals, on the changes of kerogen, which lead to the creation of bitumen and gaseous hydrocarbons.

Pyrolysis of Kerogen in the Presence of Native Minerals

The described approaches to study the catalytic effects of minerals on the thermal changes of organic matter in sediments were based on experiments of pyrolysis of some compounds identified in the sediments, or native geologic organic materials, with the addition of certain minerals. This roughly defined the thermocatalytic properties of minerals, but it was not accurately indicated to what extent minerals influence the maturation processes under natural geological conditions. Therefore, it is useful and necessary to define more reliably the influence of native mineral materials on the thermal changes of kerogen. Significant conclusions can be made if one compares the yields and composition of gaseous and liquid products that are obtained by pyrolysis of substrates of different mineralogical composition, obtained by gradual removal of carbonates, silicates and pyrite from a sample of a sedimentary rock. Figure 3.13 presents a diagram of the procedure for obtaining these substrates. The degree of success of demineralization is checked by X-ray analysis of minerals in the initial sample and the obtained substrates (Fig. 3.14).

Pyrolysis in this study is performed usually by heating at 550–600 °C, during 50–60 min in a stream of an inert gas. The yield of gaseous and liquid products is determined separately. Additionally, the stable carbon isotope composition ($\delta^{13}C_{PDB}$) and

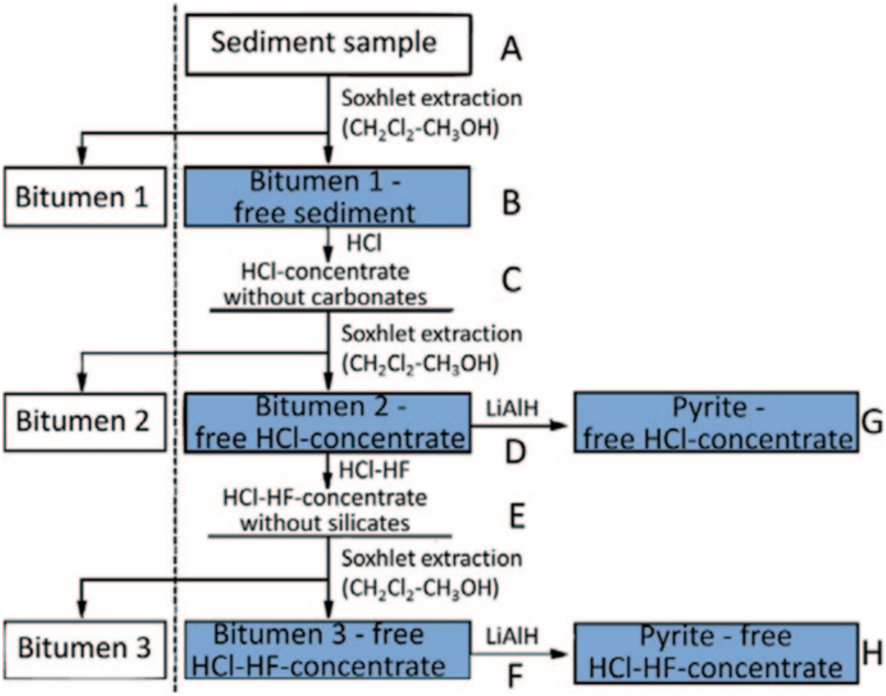


Fig. 3.13 Preparation scheme for obtaining substrates with different mineralogical composition from one sample of sedimentary rock

biological markers (*n*-alkanes, steranes, terpanes and aromatic steroids) are analysed. Comparison of the obtained results may be useful to reach conclusions about the intensity of interactions, as in all the substrates the same kerogen is found, but containing different mineral environment. It is of particular interest to compare the results of pyrolysis of the initial sample and substrates containing only silicate minerals (usually quartz, cristobalite, plagioclase, kaolinite, illite and montmorillonite), with the results of pyrolysis of the substrate that is free of minerals and containing only a certain amount of residual quartz (Figs. 3.13 and 3.14).

It was found that minerals in sediments have very little catalytic effect on the pyrolysis of kerogen. Certain catalytic effect is exerted only by silicate minerals when they are concentrated in a specific substrate. In the previous chapter it was pointed out that these are illite and montmorillonite. They influence to some extent the increase in the yield of gaseous and liquid products, the homolytic bonds cleavage involving the heavier carbon isotope, ^{13}C, the reduction of *n*-alkanes in relation to *n*-alkenes, the formation of thermodynamically stable sterane and triterpane isomers, C_{29} 14α(H), 17α(H), 20S sterane and C_{31} and C_{32} 17α(H), 21β(H), 22S triterpanes of hopane type, and the reactions of cracking of side chains of higher

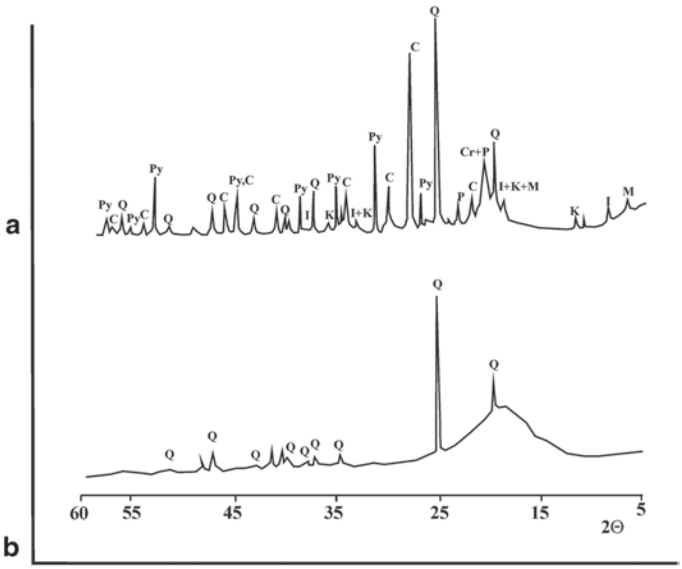


Fig. 3.14 X-ray diffractograms of initial oil shale sample and final substrate obtained according to the scheme given in Fig. 3.13. (*C* calcite, *Q* quartz, *Cr* crystobalite, *P* plagioclase, *K* kaolinite, *I* illite, *M* monnmorillonite, *Py* pyrite)

members of triaromatic steroids, C_{26}–C_{28}, and thereby the forming of C_{20} and C_{21} isomers.

Catalytic effect of native calcite and pyrite is negligible. Pyrite may possibly be a source of sulphur for the formation of organo-sulphur compounds of thiophene type.

Box 3.5: ***General Note***

In the chapter on the differences in composition of free and bound bitumens it was said that native silicate minerals have a significant adsorption and catalytic effect on the transformations of bitumen. On the other hand, the catalytic effect of silicates on the pyrolysis of kerogen is very low. Much more intensive catalytic effect of native silicate minerals on thermal changes of bitumen can be explained by a higher mineral/bitumen mass ratio than the mineral/kerogen ratio in a sedimentary rock and a stronger interaction between the silicate minerals and soluble bitumen than the insoluble kerogen of macromolecular nature.

As a consequence of the described interactions of minerals and fossil organic matter, the most commonly applied organic-geochemical parameters (such as CPI, *n*-alkane distribution, Pr/*n*-C_{17} and Phyt/*n*-C_{18} ratios, sterane and triterpane ratios, mono- and triaromatic steroid parameter), may be applied as reliable maturation correlation parameters only if the investigated samples come from the sedimentary rocks of the same or similar mineralogical composition.

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Chapter 4
Coals

Keywords Coal · Organic—combustible part · Inorganic—mineral part · Genetic classification · Carbonification · Peat · Brown coals · Hard coals · Kerogen · Vitrinite · Bitumen · Carbon · Hydrogen · Nitrogen–sulphur–oxygen substances · Organic substances · Mineral substances · Ash · Vitrinite reflectance · Macerals

Outline

According to some estimates, coal reserves in the Earth's crust represent several tens of times greater accumulation of organic carbon than all the oil and gas deposits together. Hence, the coals are still considered energy and raw material source of immense importance in spite of today's understandably favoured extensive use of oil and gas. Definitions and coal terminology, organic geochemistry of coals, certain major types of humic coals, chemical nature and composition and properties of coals will be discussed here in more detail.

4.1 Definitions and Terminology

The simplest definition describes coal as a black or brownish-black solid combustible organic matter widely used as a natural fossil fuel. To simplify, coal was generated first by partial decomposition of the accumulated extinct plant material under anaerobic conditions, and in the presence of water or under water. Then gradual carbonification took place under high pressure and temperature. Coal is defined as a combustible sedimentary rock, formed from the deposition of the remains of terrestrial, rarely aqueous plants, together with variable, usually small amount of inorganic material (below 50 %).

J. Schwarzbauer, B. Jovančićević, *Fossil Matter in the Geosphere,*
Fundamentals in Organic Geochemistry, DOI 10.1007/978-3-319-11938-0_4

Box 4.1: *General Note*

In the Earth's crust there are various types of coal. They are all made from organic representing the combustible part, and the inorganic, mineral part, which changes during combustion to a limited extent and is mainly left behind in the form of ash. The coal organic matter characterized by a very complex composition consists mainly of insoluble kerogen and small amount (up to several percent) of soluble substance, bitumen.

Coals are usually classified according to origin (genetic classification), the degree of carbonification (rank), or according to technical usage. According to the origin, coals are classified as humic or sapropelic coals, and according to the carbonification level, roughly, as peat, brown or hard coals. According to the technical usage, they can be divided into steam coal, chemical-technological coal and metallurgical coal.

4.2 Conditions for the Formation of the Deposits—Organic Geochemistry of Coals

Most coals originate mainly from the remains of predominantly terrestrial, higher plants. Most of it is deposited in terrestrial or coastal wetland areas. During deposition and decomposition the precursor material has been exposed to bacterial activity from the beginning. After deposition and subsequent increasing compaction with higher and higher depths plant remains underwent a series of complex physical, biochemical and chemical diagenetic and catagenetic changes. Most of the organic matter was transformed into kerogen, and by gradual carbonification organic matter was converted to coals of different rank (peat, brown coal, bituminous coal, anthracite and meta-anthracite). Categorisation of coals involves different types, starting from virtually unchanged plant material and peat, continues with various types of brown and bituminous coals to finish with anthracite, and graphite.

Characteristic for the formation of coal depositions is an abundant relatively pure organic material remained at the site of deposition, which is then gradually turned into one of the coals.

As outlined above, there are three main types of coal distinguished according to the origin: humic, sapropelic and humic-sapropelic coals (liptobiolites) different both according to the composition and properties.

Humic coals include many species, ranging from peat to all other types derived by further carbonification. Major organic component of most of the humic coals is a lustrous dark brown to black material, derived from the humification of woody tissue. Humic coals, with type III kerogen, are rich in terrestrial plant material. The evolutionary processes are characterized by increasing carbon content (carbonification) and loss of oxygen functional groups. Characteristic of humic coals is also stratification.

Sapropelic coals are mostly homogeneous (amorphous) and dull. Their kerogen is type I. They are rarely found, and were formed in the reducing environments of shallow wetlands, ponds or lagoons, by sedimentation of the remains of lower plants and fine-grained mud. They are not characterized by peat stage, but by diagenetic changes typical of reducing conditions in organic-rich sediments. They can also contain minor amounts of allochthonous organic matter and mineral matter. This category includes so-called "boghead" coals, also called torbanites (with plenty of algal residues), and sapropelic coals, so called "cannel" coals (with large spore content).

Certain major types of humic coals will be discussed in more detail.

4.2.1 Peat

Peat is pale brown to dark brown. Freshly extracted peat contains more than 70 % moisture, and the air dried 15–40 %. Ash can vary within wide limits (1–20 %). Lower calorific value of the absolutely dry peat is about 21,000 kJ/kg, and of air dried to 16,000 kJ/kg. Peat as a fuel is important only at local level. Only in some parts of the world it is used also as power station fuel. It can be used as fertilizer because it contains humic substances that have a stimulating effect on plant growth.

Peat is derived from deposition and humification of large amounts of extinct indigenous plant material, products of primary photosynthetic production of higher plants, coastal marsh, shrubby and woody vegetation, and, possibly, some algal remains, deposited spores and pollen and other resistant alochtonous plant material. The first thin layers of peat were formed in the Devonian (Paleozoic). The amount and rate of biomass growth, and the evolutionary degradation processes, were directly dependent on climate conditions and paleorelief. Production of biomass increased with the increase in temperature and moisture concentration (e.g. in tropical wetland forests). However, today peat bogs also can be found formed in colder climates. The formation of peat bogs sometimes depended on the tectonic conditions: in suitable depressions biomass could be slowly but continuously deposited and subsided.

Concurrently with the deposition of plant residues, various biochemical and geochemical processes start, accompanying mechanical comminution and compaction of material. On the surface itself, in oxidizing conditions, processes take place rapidly, and later, after coverage with new plant material and standing water the environment becomes predominantly reducing. At the surface, the environment is neutral or slightly acidic, while pH decreases, so that the environment becomes more acidic with the increased depth. Depending on the chemical conditions, different types of bacteria and fungi are developed. Microbial activity decreases with sediment depth, and biomass composed of the remains of bacteria and fungi, along with their non-gaseous metabolites, becomes part of the overall organic sediment. There is an obvious similarity between the diagenesis of organic matter during the formation of peat and brown coals and diagenesis of organic matter in soil and other sediments. In all cases, at the end, most of the organic material is converted into kerogen.

Humic substances are the most typical component of peat. A part of the organic matter is soluble in alkaline aqueous solvents (fulvic and humic acids), and another part is insoluble (humin and kerogen). The changes are taking place in two stages: in the first one, comminuted plant material decomposes—depolymerises, with the help of microorganisms into simpler structural units of aromatic, phenolic and carboxylic nature, and in the second stage they are randomly repolymerised and condensed. Humification processes are very complex and include not only structural changes but also changes in elemental composition. In the composition of peat there remain also lipid substances originating from the leaves, spores, pollen, fruits and resins of higher plants that are resistant to microorganisms.

There are peat bogs up to several hundred meters thick. Some of them are considered to derive from deposition that lasted continuously up to a million years. Today, the thickness of peat bogs grows at a rate of about 1 mm per year. To complete formation of a peat bog it is essential that the deposited biomass is covered with water to prevent oxidation and more complete decomposition. Efficiency of converting biomass to peat is relatively small: it is estimated that less than 10 % of the precursor plant material is converted into peat. Its largest part is broken down either during the formation of a peat bog or upon deposition. As can be concluded from the previous presentations, such efficiency is still significantly higher compared with the efficiency of the accumulation of organic matter in fine-grained aquatic sediments, during the formation of source rocks, and it also depends on the nature of the organic material.

4.2.2 Brown and Hard Coals

The largest deposits of coals were formed in coastal wetlands and deltas or around the vast freshwater lakes. Major coal formations originate from the Paleozoic (Carboniferous, Permian), Mesozoic (Triassic, Jurassic and Cretaceous) and Cenozoic (Paleogene, Neogene) as summarized in Table 4.1.

After the formation of peat bogs further chemical and physical changes of organic matter occur with increasing temperature and with increasing pressure at higher and higher depths. They represent the essence of carbonification, and genesis of various types of brown coals, and then to the bituminous coals and anthracite. In different degrees of carbonification, different coal ranks are formed.

The contents of preserved plant residues decrease with increasing degree of carbonification. Basic chemical changes of organic substance during carbonification are condensation, polymerization and aromatization (continued humification processes) and loss of oxygen, sulphur and nitrogen functional groups. The main physical changes during carbonification consist in reducing the moisture content, increased density, reduced porosity and increase in the index of refraction.

Brown coals exhibit brown to dark brown colour and can be of different degree of maturity, ranging from soft brown coal (lignite) with a clear wood structure to older hard brown coals with similarities to bituminous coals. Soft brown coal (lignite) accounts for about 50 % of worldwide coal reserves. Brown coals are often found near the surface and can be exploited by open pit mining. By dry pyrolysis at lower temperatures, brown coals rich in resins can be processed to mineral oils,

Table 4.1 Main areas of coal deposit formation

	North America	Europe	Far East	Southern Hemisphere
Cenozoic				
Piocene	+	+	−	−
Miocene	−	++	−	+
Eocene	++	+	++	−
Mesozoic				
Cretaceous	++	−	++	++
Jurassic	−	−	++	++
Triassic	−	+	−	++
Paleozoic				
Permian	−	−	−	++
Carboniferous	++	++	−	−

++ very abundant, + abundant, − non

paraffin, semicoke and other products. Moisture content in pit brown coal is sometimes as much as 50–60 %, and drying processes reduce it down to 12–18 %. Calorific value of the richest brown coals is 25,000–30,000 kJ/kg, and of the poorest sometimes only 8500–10,500 kJ/kg.

Hard coals are black and more or less lustrous. Except for direct combustion, hard coal is used as raw material for production of coke, "lighting" gas, tar and other products. Based on the content of volatile components flame, gas-flame, gas and lean and fat coke coals can be distinguished. Fat coals are suitable for obtaining coke or gas for lighting, gas-flame and gas coals are used for firing at reverberatory furnaces and for production of gas for lighting. Heating value of bituminous coal (without moisture and ash) ranges between 30,000–35,000 kJ/kg, and anthracite, about 35,000 kJ/kg. The moisture content in hard coals is 3–5 %. At combustion they leave 5–10 % ash.

Chemical evolution of coal was thoroughly defined by Van Krevelen over elemental composition expressed in form of atomic H/C-O/C-diagram. This diagram, which bears the author's name, was first proposed by Van Krevelen for the characterization of coals, and later, as already mentioned in Chap. 2, it was used for the characterization and definition of the evolutionary stage of kerogen and other types of organic sediments (Fig. 2.17). Comparing the corresponding H/C–O/C-diagrams similarity between the kerogen and humic coals, and type III kerogen in general becomes obvious, which points to the similarity of their precursor materials (terrestrial, vegetative) and partly to the similarity in depositional environment and early diagenetic processes.

It was found that the hard coals may be a source of large quantities of natural gas, sufficient for the formation of commercial accumulations. On the contrary, it has been proved that in catagenetic phase, only small amounts of liquid hydrocarbons are generated from the coal.

4.3 Chemical Nature of Coals

The general nature of different types of coals was studied by chemical and physical methods, and on the basis of these studies a number of different chemical structures of coal were proposed. Figure 4.1 exemplifies several models of the structure of highly volatile bituminous coals and anthracite. However, none of the proposed general models can fully define the chemical nature of certain types of coals. The structure of brown and bituminous coals is characterized by aromatic centres with more or less functional groups (methyl-, hydroxyl-, carboxyl-, keto-, amino- and others) interlinked by alicyclic and methylene bridges. There is a high similarity between the model of the kerogen structure of coal and models of kerogen structures of some other types of sedimentary rocks but a more pronounced aromatic structure of coals. Characteristic of all models are alicyclic or aromatic nuclei, cross-linked by bridges and substituted by functional groups, a major difference in the nature of

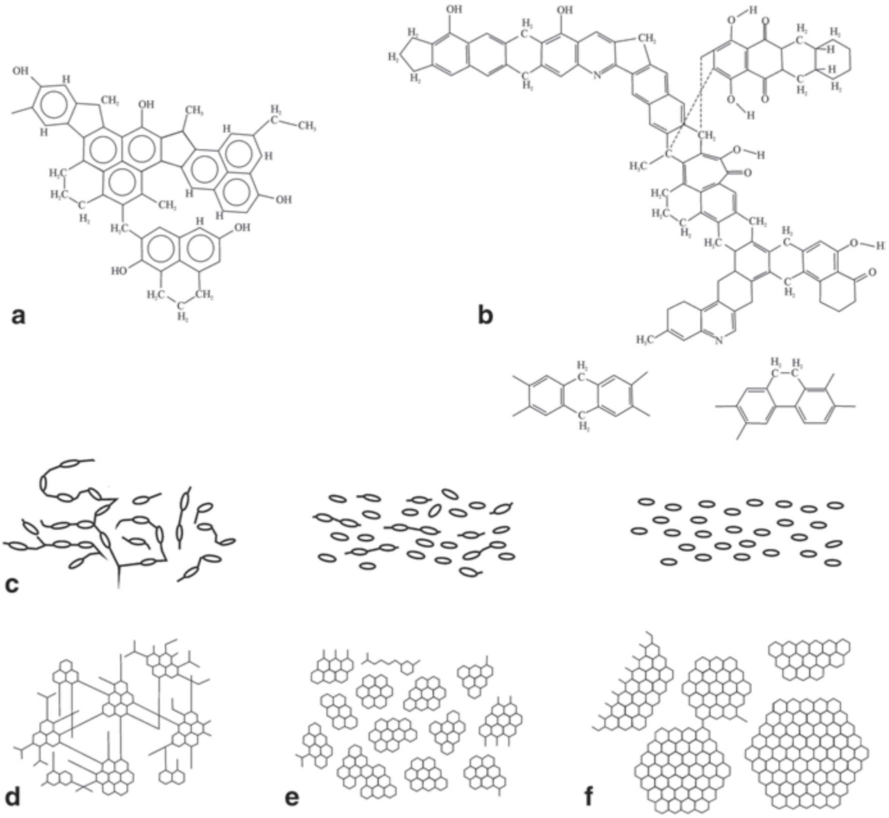

Fig. 4.1 Models of principal coal structure based on chemical and physicochemical investigations (**a**–**c**: assumptions about the structure of vitrinite in coals of different rank; **d**–**f**: assumptions about the general structure of coals of different rank; **d**—highly volatile, **e**—medium-volatile bituminous, f—anthracite). (According to Tissot and Welte 1978, 1984)

bridges, i.e. cross-links. In kerogens of lower evolutionary degrees, cross-links in the form of aliphatic chains are longer than in coals. Bridges in kerogen of coals are shorter, sometimes functionalised, and are often also cyclic or alicyclic in nature.

4.4 Composition and Properties of Coals

Carbon, hydrogen, oxygen, sulphur and nitrogen are the main elements of organic substances of all classes of coals. The amount of heteroatoms as well as the type and content of functional groups depend on the coal rank. Nitrogen occurs in the form of primary, secondary and tertiary amines heterocyclic pyridine-type rings. Sulphur appears in the form of thiols, sulphides as well as thionaphthyl and thiophene rings. The contents of oxygen functional groups (carboxyl, ketone, hydroxyl, phenol, ether and others) decrease with the degree of carbonification.

Mineral admixtures of coals are ballast and during combustion they remain as ash. Mineral part consists mostly of silicon dioxide and oxides, sulphates, carbonates, phosphates, chlorides or sulphides of calcium, magnesium, aluminium, iron, titanium, sodium or potassium. Inorganic sulphur, usually in the form of pyrite, is an almost permanent component of the coals.

Coal rank is usually defined by general parameters such as moisture content, content of volatile substances (without moisture and ash) and vitrinite reflectance (in reflected light), or other appropriate chemical and physical parameters, such as carbon and hydrogen content and calorific (heating) value. Ranking of coals is summarized in Table 4.2.

Different criteria for classification and categorisation of coals are applied in the world. However, it was shown in practice that none of the parameters individually, (in particular when applied alone) is completely reliable for defining all types of coals. Carbon content increases with the degree of carbonification. Moisture and heating value are especially important for the characterisation of brown coals, because they are used as fuel. The contents of volatile substances and sulphur, and vitrinite reflectance (which will be discussed below) are important characteristics of hard coals, which are used as raw material for coke production. The contents of carbon and hydrogen and volatile substances characterise the best low-volatile bituminous coals and anthracite.

In investigation of coals petrographic methods play an important role. Petrographers study composition, structure and texture of the coal in transmitted and reflected light. The main task of coal petrography is to define the petrographic component, the so-called macerals. Macerals are defined as the components of coal that can be identified under a microscope and distinguished according to morphographic optical properties (colour, reflectance, fluorescence). Three main groups of macerals are:

- liptinites (exinites) that originate from residues of plants rich in lipids (resins, waxes, spores, leaf cuticles, algae);
- huminites (brown coals) or vitrinites (hard coals), which are more or less modified ligno-cellulosic material that originates from terrestrial plants, and

Table 4.2 Ranking of coals according to some general parameters

Rank of coal	Rr (%)	Carbon (% C)	Volatile matter (%)	Moisture in the deposit (%)	Calorific value (kJ/kg)
		50			
Peat					
---------				~75	
Lignite		60			
	~0.3		~53		17000
---------				~35	
			~49		25000
				~25	
Brown coal					
	~0,5	75	~45		30000
---------				~8-10	
			30		
Bituminous coal					
	~2,2	90			35000
---------			10		
	~4,0 11,0				
Anthracite		100	0		
Graphite					

- inertinites, consisting of reworked and oxidised plant material rich in carbon, occurring in coals of different rank which are of more aromatic structure, and originate from the biological oxidation or forest fires, as well as from the reworked materials derived from older sediments.

Thus, coal petrography deals with macroscopically and microscopically recognisable components of coals and they are defined based on maceral composition (genetic type) and by measuring vitrinite reflectance (coal rank). The reflectance is determined by comparing the light (monochrome, green, with specific wavelengths) that is reflected from the surface of maceral, with the light reflected from the surface of a standard of known reflectance. The reflectance is given as Rr (%). Approximate vitrinite reflectance values of different coals are given in Table 4.2 below. Rank or maturity of kerogen of coals is estimated by measuring the reflectance of vitrinite or huminite particles.

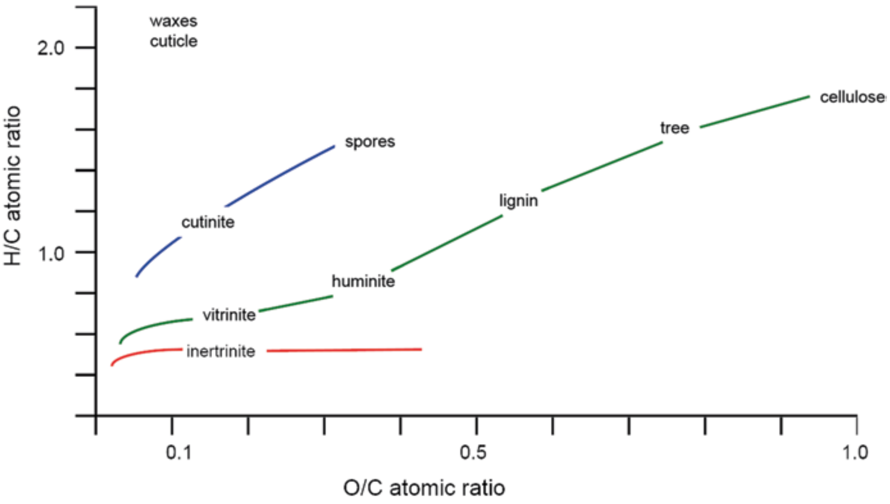

Fig. 4.2 Selected plant materials and coal macerals contrasted in a Van Krevelen diagram. (According to Tissot and Welte 1978, 1984)

Liptinite easily transmits light, fluoresces intensively and has weak reflectance. Huminite and vitrinite particles are angular, sometimes with the structure of cells, with medium light transmittance and reflectance, and usually have a weak fluorescence. Inertinite is also in a form of angular particles, with high reflectance, no fluorescence, opaque in the transmitted light, and of granular texture.

Huminite is the most common ingredient of brown coals and vitrinite of hard coals. Aromaticity of huminite and vitrinite increases with coal rank. Huminites of hard brown coals contain about 70 % of aromatic carbon atoms, in comparison with anthracites with over 90 %. In huminite at the stage of brown coals there are still visible cellular tissues of wood and bark in the mixture with humic substances. With increased degree of gelification (in the early phase of diagenesis) cellular structure changes: cell walls are swelling, and pores and cavities are filled more with humic substances of unrecognizable structure. Starting from the lustrous hard brown coals, i.e. coals of higher rank, huminite is marked as vitrinite.

The proportion of aromatic structures in liptinite increases with the rank of coal. Inertinites are generally containing more aromatic structures than liptinites.

A relatively good correlation between the petrographic (morphological) characteristics of coal macerals and their origin, chemical composition and the evolutionary stage has been established. However, in organic matter dispersed in sediments this correlation is not valid in the same quality.

Evolution and chemical changes of the main components of biomass towards the corresponding macerals during coalification or carbonification may be approximately followed also through the diagram similar to Van Krevelen's H/C–O/C-diagram (Fig. 4.2). Chemical and evolutionary changes of coal are the most similar to evolutionary path of type III kerogen. During carbonification, low-molecular hydrocarbons are released, primarily methane (which is formed in the highest amounts in the phase of medium volatile hard coals), but also inorganic products such as water and carbon dioxide, and to a much lower extent, also heavier, low volatile hydrocarbons.

Macerals of huminite and liptinite groups are not defined solely by reflection but also by intensity of fluorescence or electron microscopical analyses. Change of fluorescence of liptinite macerals from green through yellow to red is used to evaluate the maturity of coals and is particularly useful in examining the genesis of lower rank coals, and organic matter of other sediments. Colour of spores and pollen in the transmitted light can also be used as a maturity parameter.

Box 4.2: Excursus

Coal as a raw material for obtaining "synthetic oil"

Coals contain organic matter in quantities above 50 %, partially till 90 %. Since coal contains, almost always, type III kerogen with a very low potential for generating liquid hydrocarbons it is (despite the high contents of organic matter) not used as a raw material for obtaining "synthetic oil". Indeed, dry distillation processes (heating at a temperature of about 1200 °C without oxygen) are very often performed in the industry, but not with the aim to obtain "oil" as the main product, but primarily with the intention to obtain coke, artificial coal of very high calorific value.

However, in the past there have been attempts to use coal as raw material for obtaining synthetic oil as main product. That refers to periods characterized by high demand for oil and the countries rich in deposits of brown and hard coal. This was the case in Germany during the Second World War: heating the brown coal in the absence of air produced "synthetic oil". It was obtained from type III kerogen and therefore the yields were very small (only a few percent of the original total organic matter). Despite this low yields the process was profitable, primarily due to the fact that the "residue" was, still, sedimentary rock with significant proportion of organic matter, and it was enriched with something that is now called "fixed" or "dead" carbon. Therefore, the calorific value of the "residue" was higher than that of the original coal material.

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Chapter 5
Oil Shales

Keywords Homogeneous mixtures · Inorganic materials · Organic materials · Oil shales · Ölschiefer · Burning shales · Bituminous · Oil shale deposits · Lakes · Shallow seas · Organic-mineral complexes · Immature kerogen · Bitumen · Mineral materials · Silicates · Carbonates · Pyrite · Kerogen · Bitumen · Pyrolysis · Synthetic oil · Semicoke · Gaseous products · Fischer retort

Outline

Oil shales have always attracted attention as a source of energy and industrial raw materials and in recent time as a very interesting substrate in fundamental organic-geochemical studies. Definition and oil shale terminology, organic geochemistry of oil shales, composition (inorganic and organic parts) and usage of oil shales will be discussed here in more detail.

5.1 Definition and Terminology

According to the most general definition, oil shales are clayey-marley-carbonate sedimentary rocks, with more or less organic matter content. Oil shales are homogeneous mixtures of inorganic and organic materials. They are widespread distributed but differ enormously with respect to inorganic and organic fractions, as well as their complex and variable composition. For this type of sedimentary rocks there is no suitable geological or chemical definition, but it is usually based on the economic-technical explanation.

However, all oil shales have the following common features that can be incorporated into a more detailed definition:

a. at dry distillation, i.e. when heated without access of air (pyrolysis), the main useful product is crude oil of hydrocarbon composition (once referred to as tar, and nowadays as synthetic oil);
b. most of the organic matter of oil shales occur in the form of kerogen, and is not soluble in organic and inorganic solvents; and
c. the content of mineral substances is usually very large.

J. Schwarzbauer, B. Jovančićević, *Fossil Matter in the Geosphere,*
Fundamentals in Organic Geochemistry, DOI 10.1007/978-3-319-11938-0_5

The term oil shale corresponds to the French, “schiste bitumineux” and to the German the “Ölschiefer”. In Russian oil shales are called “горючиесланцы” (“burning shales”). Sometimes the English term “bituminous” shale is used.

Box 5.1: *General Note*

The term oil shale may mislead those who are not professionals in this area, suggesting that it is maybe an oil-impregnated rock. This, however, is not the case because most of its organic matter is in the form of insoluble kerogen from which oil can be extracted only by thermal processing. It happened that even experts have a wrong idea of the “oil shale”, believing that, since they are “oil-impregnated”, it is possible to easily separate organic matter from mineral admixtures by simple extraction.

5.2 Conditions for the Formation of Oil Shale Deposits—Organic Geochemistry of Oil Shales

Oil shales are formed during more than 500 million years in almost all geological periods (Fig. 5.1). Oil shale deposits have usually been formed:

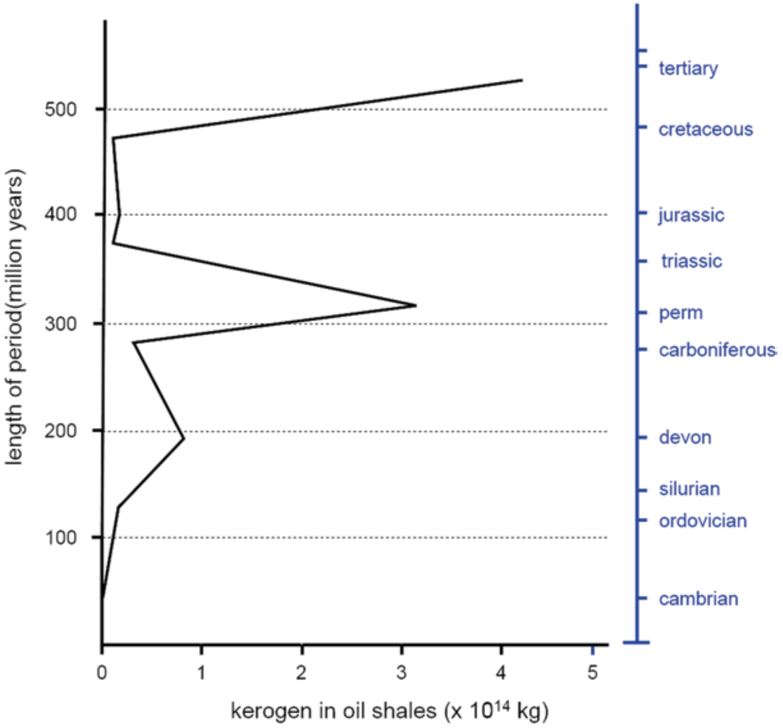


Fig. 5.1 Oil shale deposits in different geological periods

- in large lakes, particularly those that were formed during the formation of mountains; mineral part of these shales is marly or clayey-carbonate;
- in shallow seas, where they formed a relatively thin layer several centimetres (or meters) to several tens of meters thick, but in a very large area; in this case the mineral part is mainly composed of silicon dioxide and clay, and possibly carbonates; and
- in small lakes, swamps, lagoons and flooded areas where coal strata have also been formed, so that the shale deposits often occur in the overlying or underlying coal beds.

Typical characteristic of oil shales is a fine stratification with alternating layers of mixed organic and mineral material (organic-mineral complexes) and pure mineral material. Stratification indicates calm sedimentary conditions in which the minerals are precipitated from solution (carbonates) or are applied in the form of very fine particles (e.g. clay minerals) and alternate seasonal deposition. The deposits and reservoirs of oil shales are mostly superficial or shallow. Their kerogen, regardless of the age of sediment, is usually immature, but the layers of shale may be found at greater depths at which the source rocks for oil are formed.

Based on the composition and structure of kerogen of oil shales, and in particular on the basis of biological markers in the corresponding bitumen, it is possible to link the organic matter with biolipids of flora and fauna, plant and animal precursors, and thus to explain the origin of sediments, depositional conditions, diagenetic and possibly other transformations.

5.3 Composition of Oil Shales

The composition of oil shales is schematically shown in Table 5.1.

5.3.1 Inorganic Matter

Inorganic material appears usually in great excess. The ash content ranges between 33 and 90 %. It is rarely below 60 %, although there are known examples that some

Table 5.1 Tabular description of oil shale composition

The organic material	Bitumen (resolvent)	In a homogeneous mixture
	Kerogen (insoluble in organic and inorganic solvents)	
The inorganic material	Silicates, carbonates, pyrite and other mineral materials	

organic-rich sediments, such as Australian torbanite, exhibit only a small amount of ash (5 %). In the mineral part of various oil shales, clays (montmorillonite, illite, etc.), quartz, feldspar, carbonates (calcite, dolomite, siderite), pyrite, and rarely also nacholite ($NaHCO_3$), throne ($Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$), different phosphates, gypsum and some other minerals were identified (see Table 3.1). The moisture in oil shales is usually small.

5.3.2 Organic Matter

The organic matter of oil shales seems to account for smaller part of the sediment, only a few to several tens of percent (> 2 %), most typically 10–30 %. In some cases (for example in kukersite), organic matter content can reach more than 50 %. As noted above, most of the organic matter of oil shales is in the form of insoluble kerogen (up to over 95 %), and less is in the soluble form.

Optical examination of oil shale kerogens of different origin has shown that some of them are composed almost exclusively of algal material, while others represent a mixture of amorphous substance and recognizable organic remains. The main algal kerogen types are derived from freshwater-brackish algae, *Botryococcus*, which have been widespread from Precambrian to the present time, and from a variety of marine algae. In nature, it is difficult to find sediments with organic material that comes from only one species of organism.

Most of the organic material is usually in the form of amorphous kerogen, based on the H/C–O/C-ratio classified into several types, in the mixture with a small amount of defined organic residues. Amorphous material, which is often called sapropelic, is the result of microbiological transformation of biomass during the formation of sediment. In a homogeneous mixture with the mineral material it makes the world's richest accumulations of oil shales in the USA and Brazil.

The organic part of the shales may derive from planktonic organisms, and the microorganisms that inhabit sediments that have just been deposited. The composition of oil shale organic matter depends on the type of kerogen. Therefore, it ranges within wide limits. Carbon content is within the limits of 60–90 %, and hydrogen is usually high, so that the H/C ratio range from 1.25 to 1.75. Oxygen content is different, and O/C ratios are within the limits of 0.02–0.20.

Oil shale kerogens are most often type I and II. Contents of type III kerogen originating from higher plants, is lower. Type I kerogens are characterised with high contents of long aliphatic chains, and type II kerogens also with the contents of alicyclic and partly aromatic material. Differences in the composition and structure of oil shale kerogen are mainly due to differences in the precursor material, but also of various degrees of degradation of organic residues during the deposition of sediment.

Inorganic and organic materials of oil shales are sometimes intimately mixed so that it can be distinguished hardly under a microscope. Furthermore, they cannot be effectively separated from each other from homogeneous mixtures by physical methods. Since they are relatively accessible, and regarding the huge reserves, oil shales were and still are of great interest as a substrate for various organic-geochemical, chemical, technological and other types of research.

5.4 Use of Oil Shales

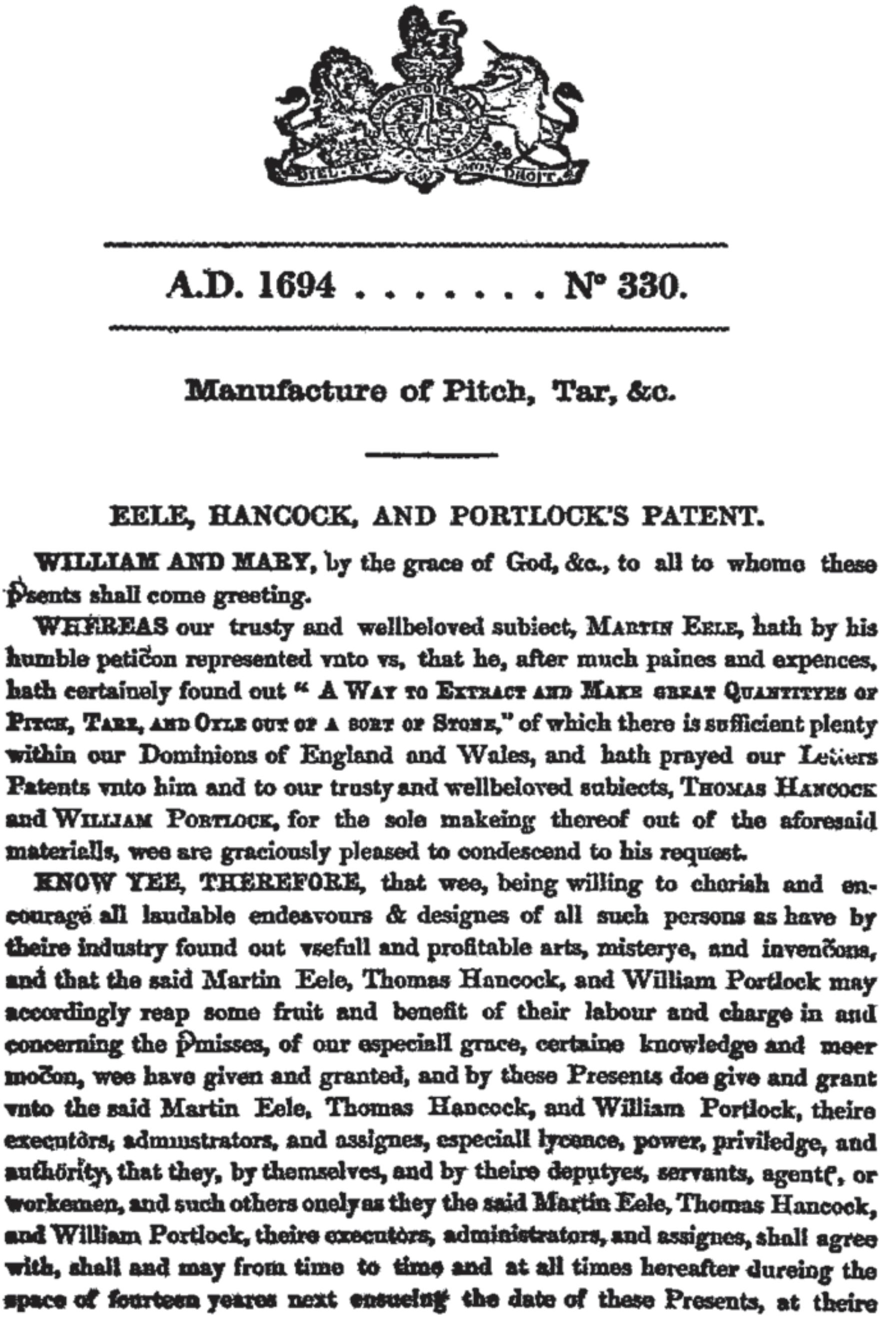
The history of shale processing is very old. The first mention of the possibility "of obtaining large amounts of resin, tar and oil from one type of stone" is found in the British patent no. 330 of 1694 (Fig. 5.2).When the oil shale is heated without access of air to about 500 °C (pyrolysis), organic material (mainly kerogen) decomposes to oil, some gaseous products, and solid residue, rich in carbon, which is left with the mineral material in the form of semicoke.

Production in almost all industrial plants (although with relatively small capacities) in which oil was produced from oil shales was suspended, primarily because the pyrolytic processing is expensive and creates serious environmental problems, so that fuels derived from shales could not compete with fuels from oil. Therefore, oil shales today are still only a potential alternative source of energy, and the study of technological procedures for their processing have been intensified or suspended depending on the seriousness of the world's "energy crises" and movement of oil prices in the world market.

Based on the previously reported data on the quantitative importance of kerogen in the Earth's crust (Fig. 2.16), it can be estimated that about 10^{17} kg of kerogen exist in the form of richer oil shales. From this quantity about 5×10^{14} kg of crude oil, so called "synthetic oil" can be obtained theoretically by pyrolysis. As it is evidently a huge energy potential oil shale is still attracting attention as a prospective source of energy and raw materials.

Pyrolysis is the basic and the most important possibility of its economic exploitation. Pyrolysis of oil shales can be compared with catagenetic processes of kerogen at the appropriate depths in the Earth's crust. Pyrolytic decomposition of oil shale kerogen in retorts is much faster due to much higher temperature compared with the temperature in the sediments in catagenetic zone, and therefore, the kinetics of pyrolysis reactions in the industrial furnaces is very different from the kinetics of reactions that occur in source rocks in geological time at much lower temperatures. The processes that occur during heating of shale kerogen in industrial furnaces are similar to processes during the laboratory simulation of geological changes of kerogen, e.g. during thermogravimetric analysis of sediment or testing by similar laboratory methods. As a result of the mentioned differences, crude oil obtained from oil shales differs significantly by composition from bitumen from source rocks and natural oil.

Finally, it should be noted that the oil shales and source rocks for oil differ in organic matter content. As it will be seen later, sediments, even with only about 0.5 % organic carbon can be conditionally considered as source rocks for oil and oil shale should contain a significantly greater amount of organic matter to be of interest for the pyrolytic processing, i.e. must contain more than the amount which would serve



A.D. 1694 . . . . Nº 330.

Manufacture of Pitch, Tar, &c.

EELE, HANCOCK, AND PORTLOCK'S PATENT.

WILLIAM AND MARY, by the grace of God, &c., to all to whome these ꝑsents shall come greeting.

WHEREAS our trusty and wellbeloved subiect, Martin Eele, hath by his humble peticõn represented vnto vs, that he, after much paines and expences, hath certainely found out "A Way to Extract and Make great Quantityes of Pitch, Tarr, and Oyle out of a sort of Stone," of which there is sufficient plenty within our Dominions of England and Wales, and hath prayed our Letters Patents vnto him and to our trusty and wellbeloved subiects, Thomas Hancock and William Portlock, for the sole makeing thereof out of the aforesaid materialls, wee are graciously pleased to condescend to his request.

KNOW YEE, THEREFORE, that wee, being willing to cherish and encourage all laudable endeavours & designes of all such persons as have by theire industry found out vsefull and profitable arts, misterye, and invencõns, and that the said Martin Eele, Thomas Hancock, and William Portlock may accordingly reap some fruit and benefit of their labour and charge in and concerning the ꝑmisses, of our especiall grace, certaine knowledge and meer mocõn, wee have given and granted, and by these Presents doe give and grant vnto the said Martin Eele, Thomas Hancock, and William Portlock, theire executõrs, administrators, and assignes, especiall lycence, power, priviledge, and authõrity, that they, by themselves, and by theire deputyes, servants, agentꝭ, or workemen, and such others onely as they the said Martin Eele, Thomas Hancock, and William Portlock, theire executõrs, administrators, and assignes, shall agree with, shall and may from time to time and at all times hereafter dureing the space of fourteen yeares next ensueing the date of these Presents, at theire

Fig. 5.2 First page of the patent from the year 1694 as an energy source of the pyrolysis itself. Difference appear also in the organic matter maturity. As already mentioned, oil shale kerogen, regardless of the age of sediments, is immature, or is in the phase of early catagenesis (about 0.70 % Rr).

Box 5.2: Excursus

The most significant deposits and examples of shale processing industry

Oil shales are more widespread than it is generally realised, but the larger and richer deposits of great potential are found only in a relatively small number of countries: USA, Brazil, UK (Scotland), Russia, Estonia, France, Spain, South Africa, Australia, China and Serbia. As an illustration of their richness it can be stated that in only one, by the way very well-known deposit in the USA, Green River formation in Colorado, the estimated reserves of organic matter are approximate to the total world oil reserves.

At the first half of the nineteenth century, so before the first large oil deposits were found by drilling in Pennsylvania, shale processing industry was recorded in France (Autun 1838–1957 and St. Hilaire 1943–1948), Scotland (1848–1963), Kashpir (Russia, 1860–?), Canada (1860), Germany (Messel 1884–1963, Württemberg 1938–1949), Australia (1865, 1947–1952), Brazil (1881, 1897–?), New Zealand (1900–1911), Switzerland (1915), Soviet Union (Estonia 1921–, Slance 1952–), Sweden (1921, 1941–1960), Spain (1922–1966), China (1929–), South Africa (1935–1962), USA (a pilot plant in 1944) and Israel (a pilot plant in 1952).

Considering their potential importance, the main approaches to thermal processing of bituminous shales should be understood. The classical way of processing is the aboveground dry distillation. The shale rock is first mined, crushed, and then heated to a certain temperature in the absence of air (pyrolysis). For this type of processing, a number of different types of special furnaces—retorts (the term "retorting", used for shale processing, has been derived from it) were used or tested. Retorts differ very much from each other in structure, mode of heat transfer and other technical details. Possibilities for heating the shale in retorts are also different: outside, through walls, or directly in the retort, by combustion of a part of shale or with a gaseous or even solid heat carrier. Aboveground processing is expensive, because the entire mass of rock is moved from the deposit, then it is all heated, absorbing a large amount of heat, to obtain only a relatively small amount of crude oil. Most of the shale is remains as a solid semicoke residue, from which the major problems originate, especially from the viewpoint of environmental protection. Namely, the semicoke is easily powdered and spread by wind, and contains sulphides that, when exposed to atmospheric influences, break down polluting the air. On the other hand, washing admixtures contaminates waters. Above all, in order to make savings in transportation, shale must be processed on site, often under conditions that are not much favorable, e.g. in areas where water is scarce and far from consumption centres.

Another option of processing is the underground pyrolysis. In this case, the sediment is not mined, but it is processed in the deposit ("*in situ*"). More than a few decades ago, extensive research of underground distillation was conducted, aimed at addressing the problems encountered with conventional aboveground processing of oil shale, such as environmental protection, high mining costs, disposal of semicoke. The essence of this type of processing is as follows: shale remains in the deposit, there it is crushed (by controlled explosions), and then in so built-up underground "retorts" of large dimensions it is heated by some suitable heat carrier. Oil is collected in collection channels and reservoirs and pumped from there. The biggest problems with these procedures are in the preparation of underground retort, control of the movement of "fire front" and in the relatively small yields of oil, i.e. low overall exploitation of shale organic matter. Technological procedures for thermal processing of oil shales are being tested also nowadays.

The yield of crude oil depends on the richness of raw material (organic matter content), type of kerogen and mineral composition, and also the technology applied. Calculated on the total amount of organic matter, it could be expected with the use of pyrolysis getting the yields of crude oil from 20 % to a maximum of about 65 %.

In a laboratory, the potential of oil shale is estimated by common standardised technical analysis, pyrolysis in the aluminium retort by Fischer. Schematic display is shown in Fig. 5.3. Measured quantity of crushed shale (normally 50 g) is heated

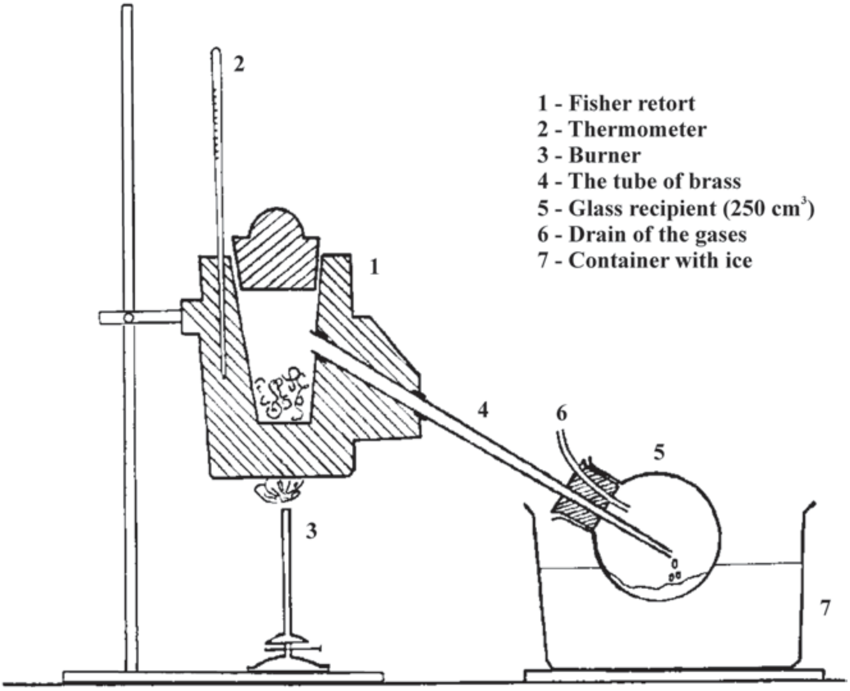


Fig. 5.3 A standard Fischer apparatus for oil shale investigation

in a retort programmed with speed within half an hour to 520 °C, and heating at this temperature is continued for another 15 min. Liquid products (crude oil and water) are caught in a bubble immersed in an ice bath. For corrections, the water content is determined according to Dean-Stark.

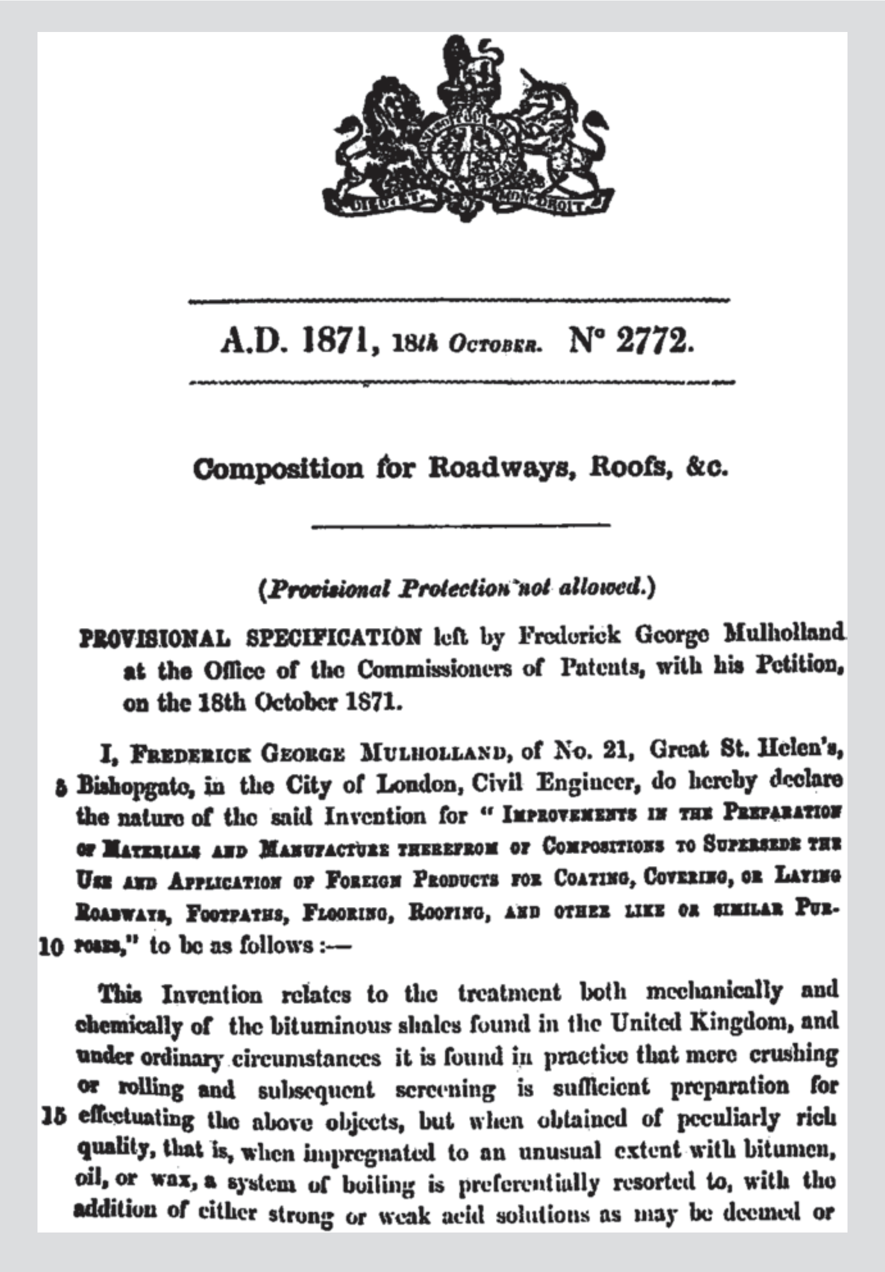
The lower yield limit for the economical processing of oil shales is about 2.5 % of oil. However, in practice it was proven that it is necessary for the limit yield to be at least about 5 %.

The crude oil may contain up to 2 % nitrogen, up to 8 % sulphur and 30–50 % of unsaturated compounds. This crude material is processed to produce gasoline, diesel oil, heating oil, lubricating oil, bitumen (asphalt residue), petroleum coke, various resins and waxes (paraffin) and other less important products. As it has already been mentioned, in addition to oil, gas and semicoke are also obtained by pyrolysis.

Box 5.3: Excursus

Oil shales can have multiple use

Given the specific composition and properties of oil shale, many other possibilities for its utilisation were studied, either as energy source or as raw material. The possibility of processing by gasification, use in cement and brick industry as a supplemental fuel and raw material, use as filler in asphalt mixes, application in the production of electricity by direct combustion, applications as petrochemical feedstock (e.g. to obtain organic acids by kerogen oxidation), obtaining rare elements from the ashes, obtaining substances with antibiotic action, obtaining low-cost adsorbents etc. The example of patenting mixtures for roads and roofs with oil shale as a component, back in 1871, is shown below.



A.D. 1871, 18*th* October. N° 2772.

Composition for Roadways, Roofs, &c.

(Provisional Protection not allowed.)

PROVISIONAL SPECIFICATION left by Frederick George Mulholland at the Office of the Commissioners of Patents, with his Petition, on the 18th October 1871.

I, Frederick George Mulholland, of No. 21, Great St. Helen's, Bishopgate, in the City of London, Civil Engineer, do hereby declare the nature of the said Invention for "Improvements in the Preparation of Materials and Manufacture therefrom of Compositions to Supersede the Use and Application of Foreign Products for Coating, Covering, or Laying Roadways, Footpaths, Flooring, Roofing, and other like or similar Purposes," to be as follows :—

This Invention relates to the treatment both mechanically and chemically of the bituminous shales found in the United Kingdom, and under ordinary circumstances it is found in practice that mere crushing or rolling and subsequent screening is sufficient preparation for effectuating the above objects, but when obtained of peculiarly rich quality, that is, when impregnated to an unusual extent with bitumen, oil, or wax, a system of boiling is preferentially resorted to, with the addition of either strong or weak acid solutions as may be deemed or

Appendix

Proposed Literature for a More Detailed Study of Organic Geochemistry

Books

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