

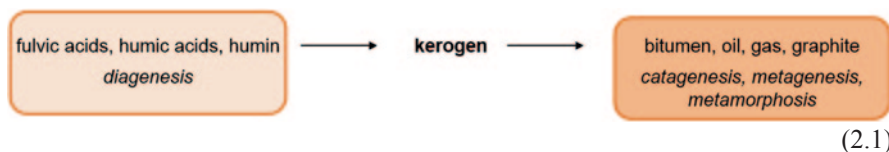
Chapter 2

Main Types of Organic Matter in Geosphere

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:



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.

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, Jovančičević et al. 1996).

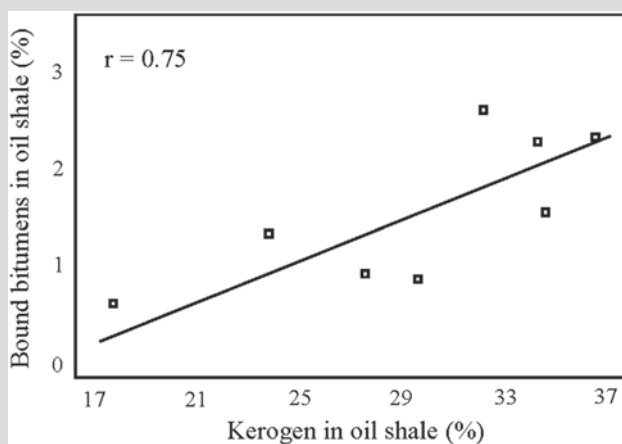


Table 2.1 Bitumen fractions and their main components

Fraction	Components
Saturated hydrocarbons	<i>n</i> -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.

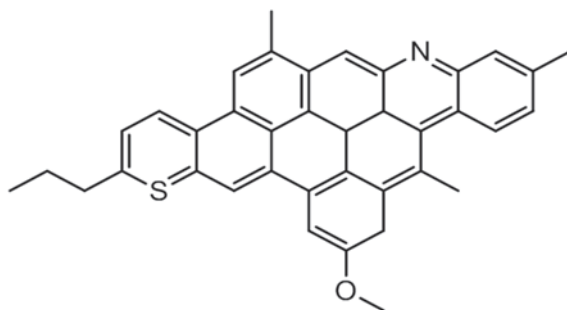


Fig. 2.1 Model of molecular moieties in asphaltenes

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 “bio-markers”.

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
<i>n</i> -Alkanes ($> C_{22}$)	Waxes of terrestrial plants
<i>n</i> -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 (Jovančičević 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 C₂₄–C₃₄ is used:

$$\text{CPI} = \frac{1}{2} \times \left(\frac{\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33}}{\text{C}_{24} + \text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32}} + \frac{\text{C}_{25} + \text{C}_{27} + \text{C}_{29} + \text{C}_{31} + \text{C}_{33}}{\text{C}_{26} + \text{C}_{28} + \text{C}_{30} + \text{C}_{32} + \text{C}_{34}} \right) \quad (2.2)$$

According to the proposal by Philippi from 1965, the C₂₈–C₃₀ 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 (C₂₅–C₂₉ to C₂₅). 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 C₂₅ to C₁₇–C₂₀. 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 fractions 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 C₂₅–C₂₉ to C₁₇–C₂₀. Since in the marine biolipids CPI is about one, and the maximum is at about C₁₇–C₂₀, 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 C₁₇–C₂₀, it cannot be said with certainty whether the organic matter in sediment is of marine origin, or it is matured 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.

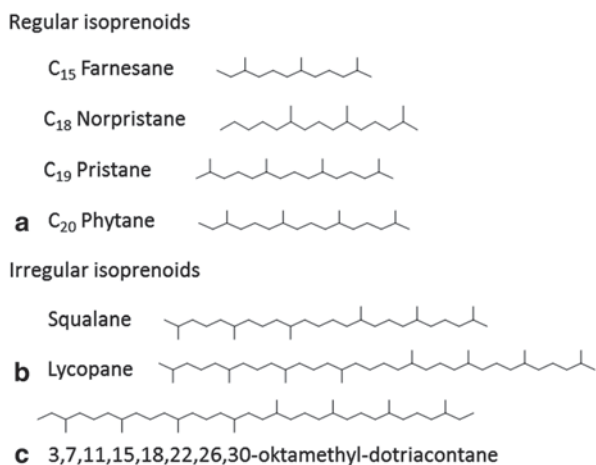
Isoprenoid Alkanes

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.

Fossil Matter in the Geosphere

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