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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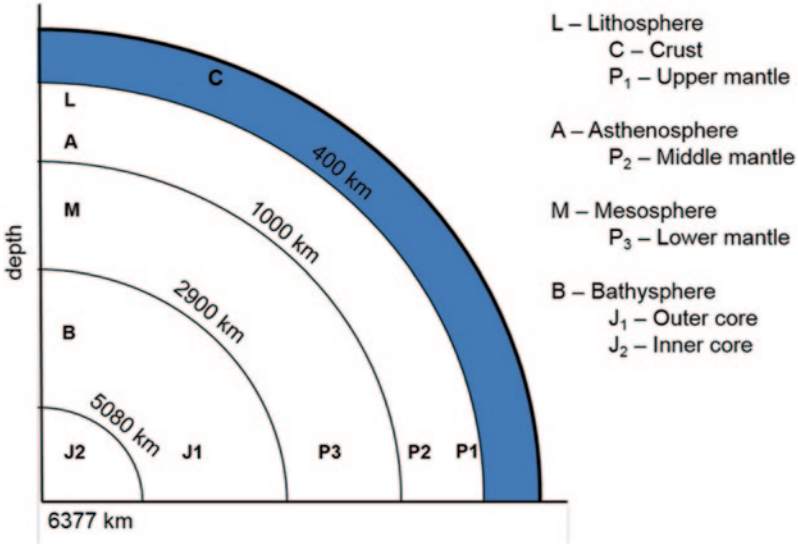

Fig. 1.1 The general structure of Earth

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*.

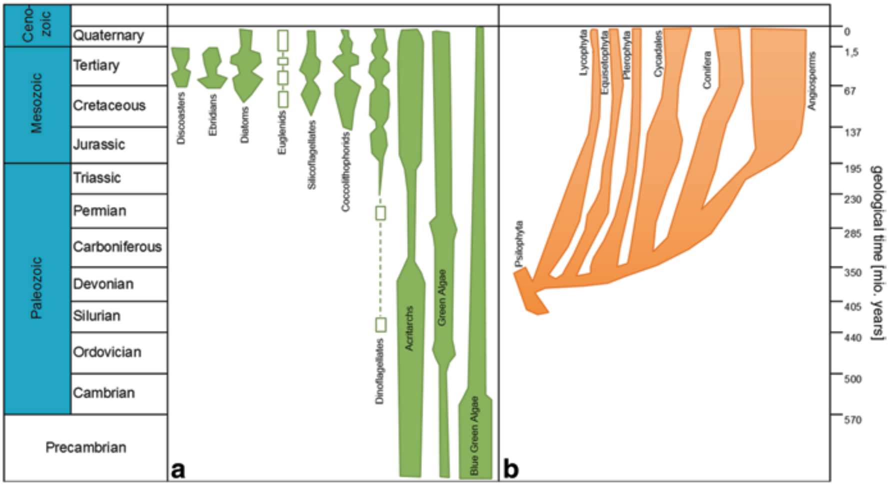

Fig. 1.2 Abundance of certain groups of phytoplankton (**a**), and higher terrestrial plants (**b**) and their total distribution through geological history. (According to Tissot and Welte 1978, 1984)

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

<u>Outline</u>

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:

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

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

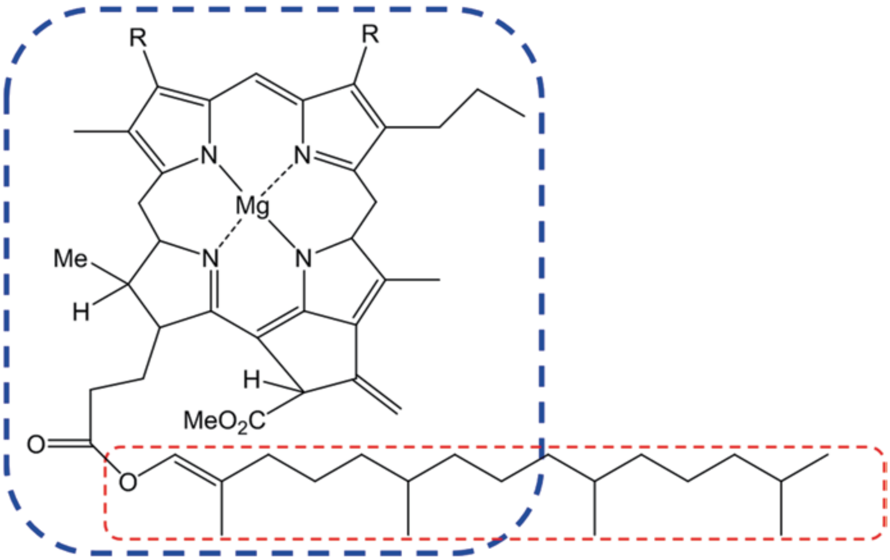

Fig. 1.3 Molecular structure of chlorophyll

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 1.5–7×10^{13} kg in oceans, and 1.5–8×10^{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

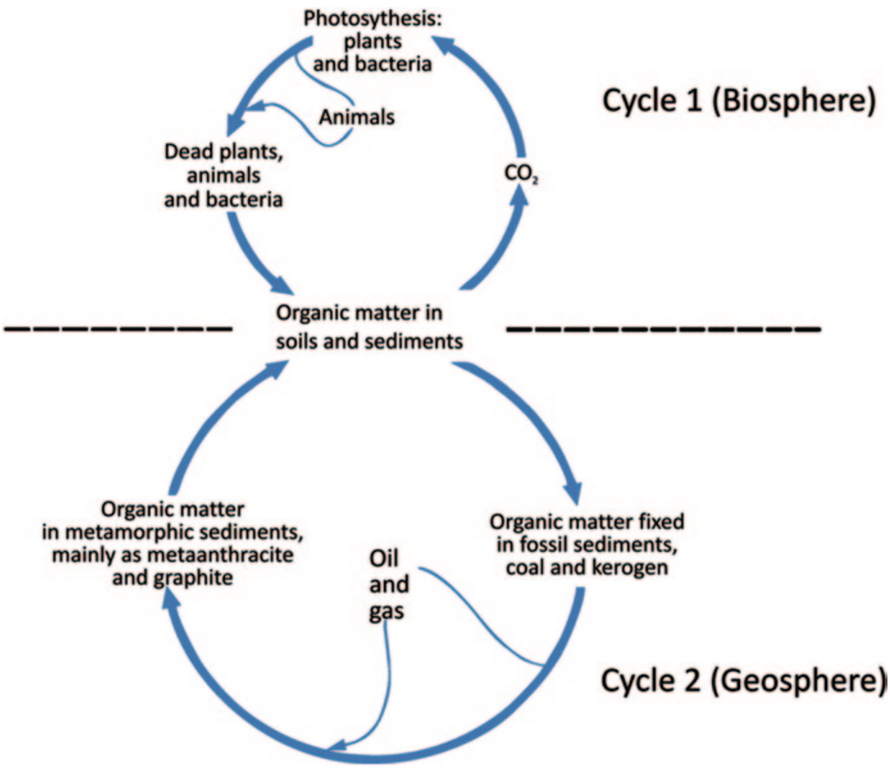

Fig. 1.4 Cycling of carbon in nature. (According to Tissot and Welte 1978, 1984)

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

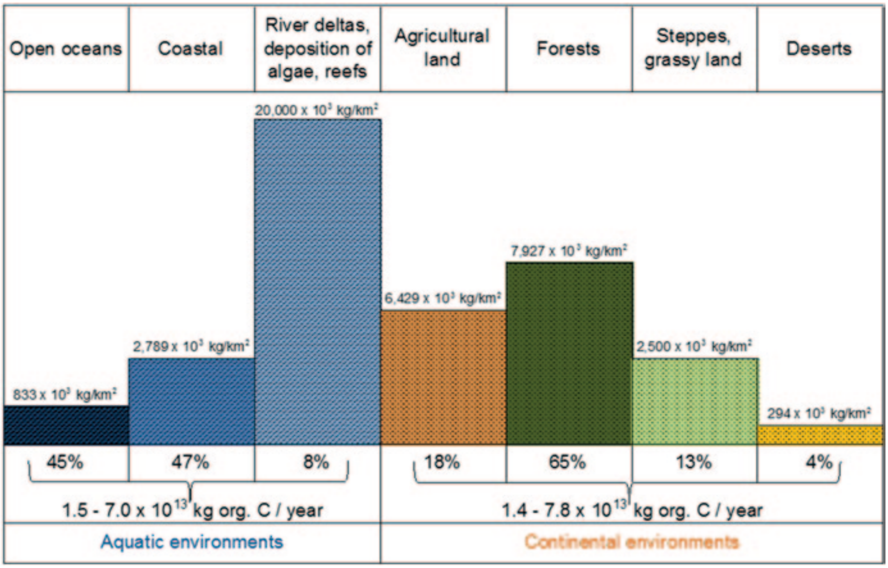

Fig. 1.5 Distribution of photosynthetic primary production

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

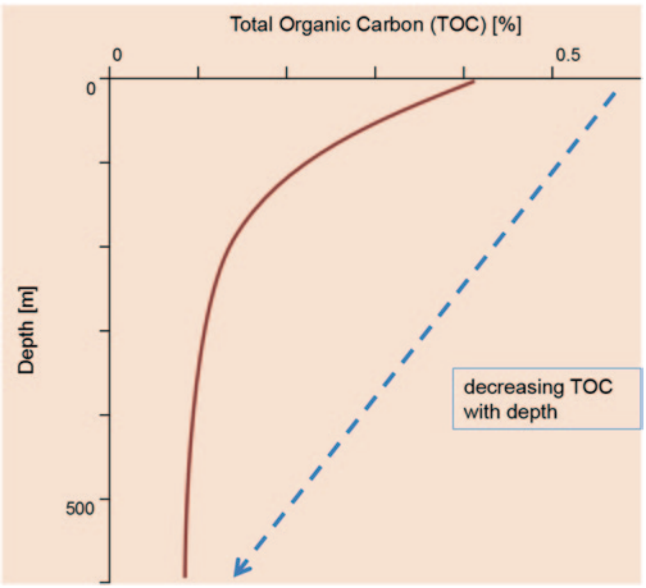

Fig. 1.6 Change of total organic carbon (TOC) with depth

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

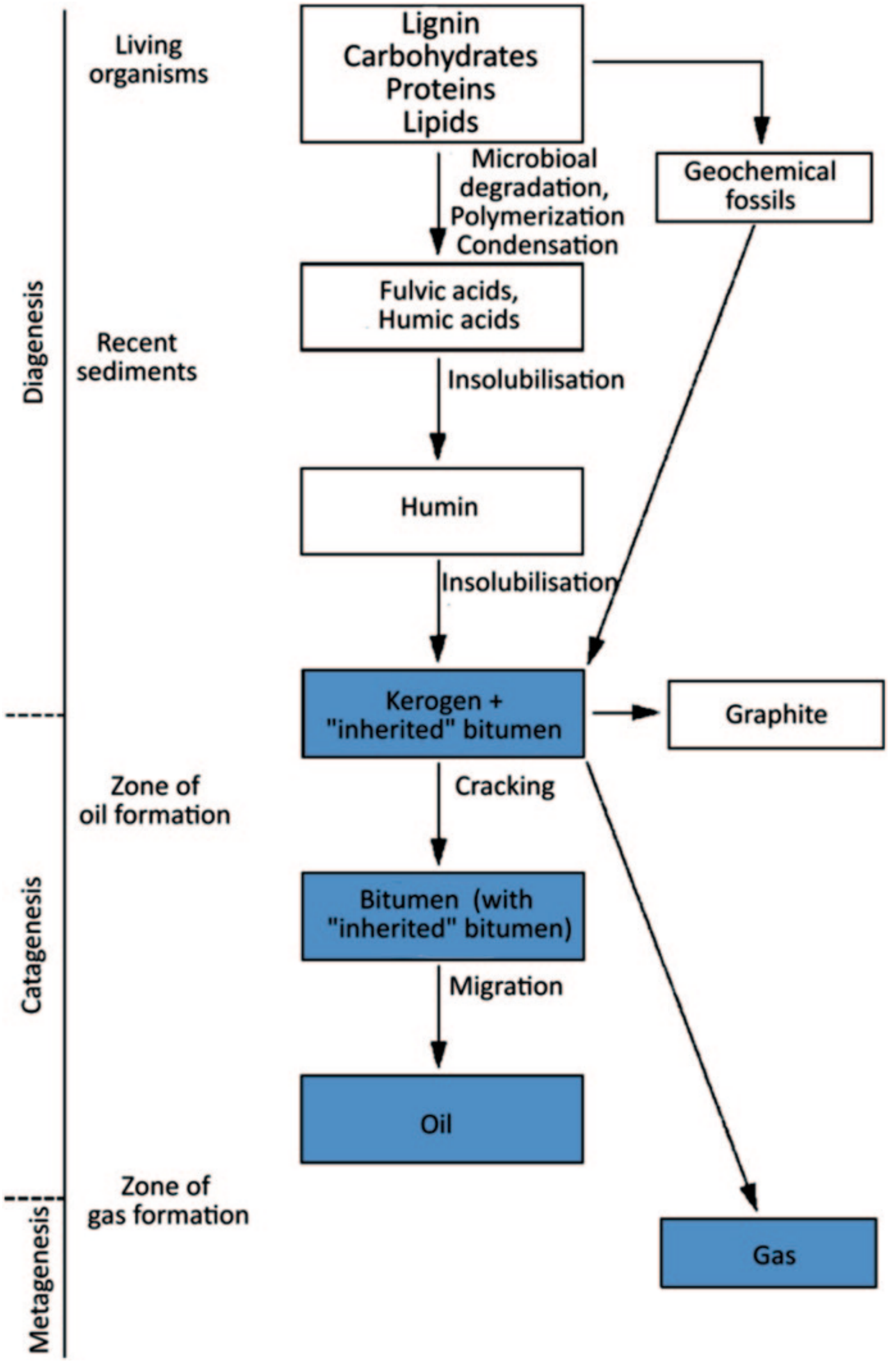

Fig. 1.7 A simplified scheme of the transformation of organic matter in the Earth's crust

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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