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Advances in Organic Geochemistry

S.M.Manskaya

Two research fields embraced by the concept "organic geochemistry" are discussed. The first includes works on the abiogenic formation of organic compounds and the second deals with studies on the phenomena involving the formation and transformations of fossil organic matter and its importance in geochemical processes. This branch of geochemistry has been defined by certain Soviet investigators as "geochemistry of organic matter".
The present review deals with modern studies on aminoacids, carbohydrates, lipids, porphyrin structures, carotenoids, aromatic compounds of the type of lignin, and flavonoids in contemporary and ancient deposits in connection with problems of petroleum and coal formation.
On the basis of the investigations described, the author of the review believes it to be possible to define the future tasks in the geochemistry of organic matter and rational procedures for carrying them out.
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1. PRINCIPAL FIELDS OF RESEARCH IN ORGANIC GEOCHEMISTRY

The branch of geochemistry under consideration (organic geochemistry) has been treated in a number of symposia[1,2] comprising papers of a fairly wide variety of types. Some of these are devoted to problems of organic cosmochemistry—the abiogenic formation of organic compounds. Others deal with modern concepts concerning the organic materials in coals, petroleum, and petroleum-bearing rocks. Reports on organic cosmochemistry and on the investigation of organic structures in coals and petroleum, scarace organic substances, and paleontological specimens were presented at the Fourth International Congress on Organic Geochemistry (Amsterdam, September, 1968). It is noteworthy that both natural phenomena characterised by the concept "organic geochemistry" gave rise to two different fields of geochemical research.

In the Soviet literature these two fields are fairly clearly distinguished. The first includes work on the abiogenic formation of organic compounds associated with organic cosmochemistry and problems of the origin of life. The second deals with studies on individual stages in the formation of fossil organic matter and its importance in geochemical processes. This branch of geochemistry has been defined by some Soviet investigators as "geochemistry of organic matter" [3,4].

In the present review it is necessary to consider in the first place the principal features of the first field: the abiogenic formation of organic compounds, the origin of life on earth, and the creation of the biosphere in which fossil organic matter was formed.

Meteorites are important objects for the investigation of organic matter of abiogenic origin. At present numerous data are available, showing the extraterrestial abiogenic nature of the organic material of meteorites[5,6]. A high-molecular-weight of carbon compound with a condensed aromatic structure has been isolated from carbonaceous chondrites[7].

The primary cold matter of the earth's mantle resembles the rocky meteorites. As a result of the rise of the earth's temperature due to radioactivity, readily fusible substances evolved from the earth's mantle in liquid and gaseous forms and formed its outer shells: aqueous (the ocean) and gaseous (the atmosphere)[8-10].

In his monograph Vinogradov[11] describes the probable situation on the earth's surface before the formation of the biosphere. The amount of oxygen in the atmosphere was negligibly small at that time and there was no ozone screen. Life could develop only in the water of the ocean where it was protected from cosmic radiation. Biogenic synthesis was probably preceded by radiogenic and photogenic formation on the earth of complex organic molecules. Oparin's theory of the origin of life[12] is based on the hypothesis of an abiogenic synthesis of primary organic molecules. Oparin and his coworkers performed numerous experiments whereby it was possible to synthesise under laboratory conditions biologically important compounds from ammonia, methane, and formaldehyde under the action of ultraviolet rays and radioactive emission[13-15] †. Aminoacids and nucleotides were synthesised in this way. The abiogenic synthesis of adenosine triphosphoric acid (ATP)—the principal source of energy in all present day organisms—from polyphosphates was achieved under the action of short-wavelength ultraviolet light. Oparin postulates the existence of an enormous number of catalysts which were responsible for the occurrence of a wide variety of reactions in prebiological systems (protobionts).

Nicotinamide adenine dinucleotide (NAD^+) is a universal hydrogen-transfer agent in the living cell. Its presence has been established in all present day organisms; microbes, plants, and animals. It is suggested that NAD^+ was first formed in an early stage of the evolution of organic matter. Similar universal catalysts were also other coenzymes and to an even greater extent enzymes with exclusive specificity and enormous catalytic activity. Thus the enzyme hexokinase accelerates the reaction of ATP with glucose by a factor greater than 10^{11} and alcohol dehydrogenase accelerates the oxidation of alcohol by a factor greater than 10^9. The principal components of all

† Similar experiments were carried out for the first time by Miller [S. Miller, J. Amer. Chem. Soc., 77, 2351 (1955)] [Editorial Note].

these enzymes are proteins. The specificity of enzymes is associated with a strictly ordered arrangement of the aminoacid residues in the polypeptide chain and a definite packing of this chain in the protein molecule. In this connection there arose the hypothesis of the formation in the course of evolution of a "molecular-matrix" apparatus with the properties of polynucleotides[16,17]. Further development of the primary hydrocarbon systems was an important stage in the generation of life.

According to Oparin's concepts (Ref. 14, p. 56), "a characteristic feature of life is that it is not simply scattered in space but consists of individual very complex systems separated from the outer environment (organisms), which continuously interact with the external medium and the internal structure of which is extremely well adapted to their prolonged existence, continual self-renewal, and spontaneous reproduction under the given conditions of the universe surrounding them".

Vinogradov[11] believes that the formation of complex organic compounds in the water of the ocean, which led to the appearance of organisms, resulted in the first profound transformation in the composition of the ocean and the entire hydrosphere, in the atmosphere, and in many processes occurring on the earth's surface. The mechanism of photosynthesis, which includes the reduction of water with liberation of free oxygen, arose in the course of the evolution of the simplest organism. This led to the accumulation of oxygen in the atmosphere and the formation of the ozone screen so that life became possible not only in water but also on dry land.

Boichenko[18] points out the role of the metal-containing oxido-reductases in the evolution of photosynthesis. With the appearance of manganese in the chloroplast lipids, the oxidation-reduction potential necessary for the evolution of oxygen was attained. The biosphere was at one time investigated on a wide front by Vernadskii[19,20], who found that organisms should be investigated in relation to the medium where they lived or live, i.e. in relation to the earth's crust. This led to a new geochemical problem—the study of the chemical composition of living matter, i.e. the average chemical composition of living organisms in relation to geochemical processes occurring in the earth's crust. A new branch of geochemistry—biogeochemistry—also arose.

The role of organisms or living matter in geochemical properties was studied by Vinogradov[21] on a large amount of material. The elementary chemical composition of sea organisms was determined taking into account their evolutionary development and position in the system of nomenclature. Subsequently the effect of the medium on the elementary composition of organisms was elucidated[22].

Koval'skii[23], who studied the effect of the medium (chemical elements) on metabolism in organisms, concluded that the biochemical or physiological mechanisms of adaption to geochemical conditions are important factors in the evolutionary process. It is suggested that the microelements concentrated by plants may accumulate in structural components of the cells (nuclei, mitochondria, ribosomes) and influence the occurrence of mutations.

As a result of the development of living matter in the biosphere, the products of the decomposition of the organisms, which gave rise to fossil organic matter, also began to accumulate. Vinogradov states (Ref. 24, p. 4) that it is difficult to separate the geochemical role of living matter from the geochemical role of organic substances formed after the death of the organisms. The appearance of deposits of coal, petroleum, lime, and other organic rocks itself altered the face of the earth; later Vinogradov states (Ref. 24, p. 11) "...in order to elucidate the mutual effects in the organic substance—rock system, we must be able to distinguish the individual properties of particular organic molecules. This is why it is necessary to concentrate attention on and to intensify the study of the molecular composition of organic substances, the role of which in geological processes cannot be over-estimated".

New studies on the geochemistry of organic matter show investigations of individual organic compounds and methods of their conversion in natural processes may prove very useful for the solution of many geochemical problems.

Here we may include the following branches of geochemistry: (1) the study of the chemical composition of the organic matter of different types of peat and fresh and seawater deposits together with the biochemical processes occurring in them, which determine the initial stages in the formation of different types of coal and petroleum; (2) the study of the organic fraction of paleontological specimens in order to establish the phylogenetic differences and to elucidate the preservation conditions; (3) discovery of the organic structures responsible for the concentration of rare elements in caustobioliths and other natural materials.

In his examination of the principal problems of the chemical study of the world ocean, Zenkevich[25] attributed considerable importance to the investigation of organic matter. Starting with the postulate that "organic matter is a trigger actuating the diagenetic processes in sea deposits", Zenkevich believes that the first task to be performed is the study of the chemical composition of organic matter in oceanic water and deposits and the determination of the individual organic compounds.

Much serious work, described in symposia, monographs, and individual articles, has been done on the chemical balance of organic matter in the ocean and also on its composition. This includes the studies by Skopintsev[26,27] who developed the hypothesis that the bulk of the dead organisms of the plankton decomposes in the upper layer of the ocean. This hypothesis is confirmed by numerous data on the distribution in the sea of ammonia, nitrates, organic carbon, nitrogen, and phosphorus. Romankevich[28,29] followed the relations governing the distribution of organic carbon and nitrogen in the surface layer and in the bulk of the deposits in the Pacific Ocean. In the deep water part of the Pacific Ocean the degree of mineralisation of the organic matter of the phytoplankton in the water and on the surface of the bottom amounts to 99.93–99.99%.

As one moves away from the foot of the continental shelf to the central part of the ocean, the content of organic carbon and nitrogen in the deposits diminishes to minimal values (0.25% of organic carbon and 0.05% of nitrogen relative to the non-silicate and non-carbonate material of the deposits).

Lisitsyn[30] investigated the present day deposits in the Bering sea. The biomass of the phytoplankton in the Bering sea consists largely (90%) of diatomaceous algae. In this connection the distribution of silicon in the waters and deposits of this reservoir is of definite interest.

Much attention has been devoted to the study of the organic matter of present day and ancient sea and continental deposits in connection with the conditions governing the formation of petroleum. Veber[31] attributes particular importance to the study of bitumens in the organic matter of the deposits as a function of the conditions of their formation in the facies.

Rodionova[32] studied by biochemical-bitumenological analysis the composition of the hydrocarbons in more than 2000 rock specimens from the Devonian and Lower Carboniferous periods in the Volga-Ural petroleum- and gas-

bearing region. The results of the chromatographic separation of the individual bitumen fractions enabled her to determine the distribution of hydrocarbons in the organic matter of rocks of different lithological composition and different geological ages.

2. STUDY OF INDIVIDUAL ORGANIC COMPOUNDS IN DIFFERENT STAGES OF THEIR CONVERSION INTO FOSSIL ORGANIC MATTER

The modern theory of the organic origin of petroleum is based on the following concepts: (1) the nature of the materials from which petroleum was derived; (2) the processes and conditions in the formation of petroleum; (3) the migration and accumulation of petroleum[33-35]. The principal compounds in petroleum are hydrocarbons of the methane, naphthene, and aromatic types. Hydrocarbons similar to those detected in petroleum have been found in all sedimentary rocks, ranging from ancient to contemporary deposits[36].

The majority of investigators agree with the hypothesis that the principal biochemical source of petroleum hydrocarbons are fats and fatty acids. Fats included in the group of lipids constitute a mixture of esters of glycerol (a trihydric alcohol) and high-molecular-weight fatty acids. The principal fatty acids entering into the composition of fats are palmitic $CH_3(CH_2)_{14}COOH$, stearic $CH_3(CH_2)_{16}COOH$ oleic $CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$, linoleic $CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$, and linolenic $CH_3CH_2CH{=}CHCH_2CH{=}CHCH_2CH{=}CH(CH_2)_7COOH$.

All living organisms contained the enzymes (lipases) which catalyse the hydrolysis of fats with formation of glycerol and fatty acids. The decarboxylation of fatty acids in the course of their conversion into petroleum hydrocarbons might have occurred in the first place under the influence of bacterial enzymes and also under the action of physical factors—temperature and pressure.

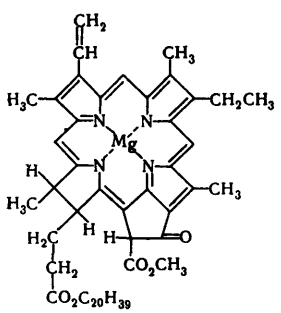
Abelson[37] devoted much attention to kerogen as the most probable source of petroleum hydrocarbons in the course of formation of petroleum from the decomposition products of the phytoplankton. He postulates also the possibility of a secondary transformation of kerogen (the insoluble fraction of the organic matter in ancient deposits). The fatty acids liberated after the death of the phytoplankton interact with other compounds or are acted upon by micro-organisms (depending on the conditions in the medium). In both cases they can serve as the starting material for the formation of petroleum hydrocarbons or an insoluble kerogen complex. The data obtained by Williams[38], who established a sharp decrease of the ratio of fat carbon to the total content of carbon in the organic matter of the deposits compared with its value in algae, are of interest in this connection. Williams determined this ratio as 0.3 for diatomaceous algae and 0.2 for mixed algae. In the organic matter from the deposits taken at a depth of 20 m the ratio is 0.08 and at a depth of 400 m it is 0.02. For the dissolved organic matter at depths of 20 and 400 m, the ratio is 0.004 and 0.003 respectively.

Brooks and Smith[39] determined the relative amounts of hydrocarbons with even and odd numbers of carbon atoms in living plants, coals with different degrees of metamorphism, in different types of petroleum, and in natural gas. They suggested that in many cases the same plants can serve as starting materials for the formation of both coal and petroleum, depending on the biochemical conditions and early diagenesis. Wood gave rise to the formation of humus coal, and small plant particles (leaves and others) containing large amounts of lipids may have been involved in the formation of lake or sea silt. Deposits of this type served as a source for the formation of petroleum. Characteristic differences in the composition of humus and sapropel types of fossil organic matter have been demonstrated[40,41].

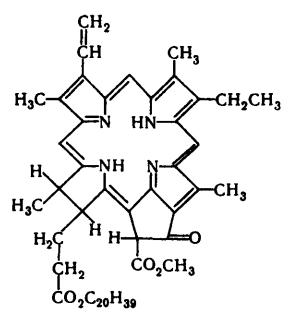
In the hypotheses concerning the genesis of petroleum considerable importance is attributed to pigments: chlorophyll and carotenoids. Porphyrin pigments of the type of chlorophyll were first detected by Treibs[42] in different types of petroleum, asphalts, and tars, which confirmed the theory of the organic origin of petroleum.

The products of the decomposition of chlorophyll and haemoglobin in natural materials have been extensively investigated at the present time and the possible pathways in their conversion into petroleum porphyrins have been demonstrated. Orr et al.[43] proposed a mechanism for the conversion of chlorophyll via a number of intermediates into the porphyrin structures of the deposits and petroleum. Among the intermediate decomposition products postulated in the mechanism, pheophytin and phaeophorbide, chlorophyll derivatives without magnesium, have been detected in deposits.

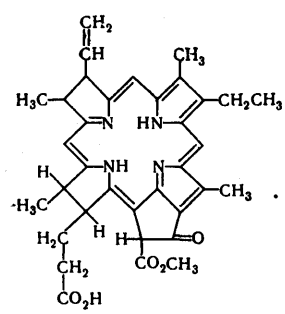
Studies on the organic matter of the present day deposits in the Pacific Ocean, taken from various depths (from 30 to 7500 m), established that chlorophyll decomposition products predominate markedly over unchanged chlorophyll[28]:



chlorophyll a

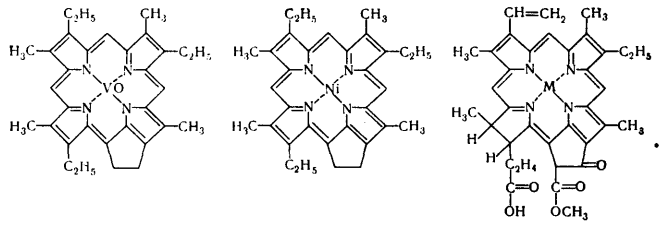


phaeophytin a



phaeophorbide a

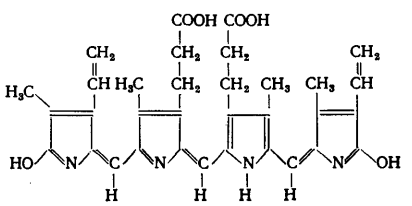
Hodgson et al.[44] demonstrated in model experiments the conversion of phaeophytin and its derivative chlorene into petroleum porphyrins. In sedimentary rocks and in hydrocarbon accumulations porphyrins are encountered mainly in the form of vanadium or nickel complexes. There exists the hypothesis that pigments having the porphyrin structure with a metal atom in the ring (chlorophyll with magnesium, haemin with iron) lose the metal in the subsequent reactions of the organic material. Metal-free porphyrins are encountered in fossil organic matter fairly rarely—probably the interaction of vanadium or nickel with the free porphyrins is relatively rapid:



V-porphyrin Ni-porphyrin Metal-chlorene

Hodgson et al.[45] investigated the distribution of porphyrins and chlorene in polycyclic aromatic compounds in 250 specimens of soils, deposits, and sedimentary rocks of different ages, ranging from the early Precambrian period up to the present day. Ni- and V-porphyrins were detected in all the specimens, which indicates their wide distribution in sedimentary formations. They are found mainly in fine-grained clastic sea rocks with ages ranging from the Tertiary to the Precambrian periods. Chlorenes are encountered predominantly in contemporary deposits and in soils. Fe-Porphyrins have been found in a small number of specimens. Hodgson and coworkers extracted Fe-porphyrin from gilsonite with the aid of methanesulphonic acid and then obtained it in the form of free porphyrin. This enabled them to investigate on models the interaction of porphyrin with nickel, copper, cobalt, zinc, and both divalent and trivalent iron and to obtain complexes of these compounds.

In connection with the importance of the study of porphyrin structures in the geochemistry of organic matter, mention should be made of the pigments in the blue-green and purple algae. These are phycocyans, allophycocyans, and phycoerythrins—complexes of proteins and plant bile pigments. Bile pigments are regarded as derivatives of porphyrins—tetrapyrroles with an open chain. An example of such a pigment is bilitriene which has a blue-green colour:



The blue bilitriene was detected in the blue-green algae *Tolypothrix tenuis* and *Anabaena cylindrica*. The unicellular thermophilic alga *Cyanidium caldarium* accumulates phycocyan, allophycocyan, and chlorophyll when exposed to light[46]. The study of the pigments of the blue-green algae, which are examples of the most ancient organisms on earth, can provide new data for the characterisation of the Precambrian kerogen, recently investigated by Hoering[47]. Paleobotanists demonstrated the existence of the blue-green algae in the Precambrian period[48].

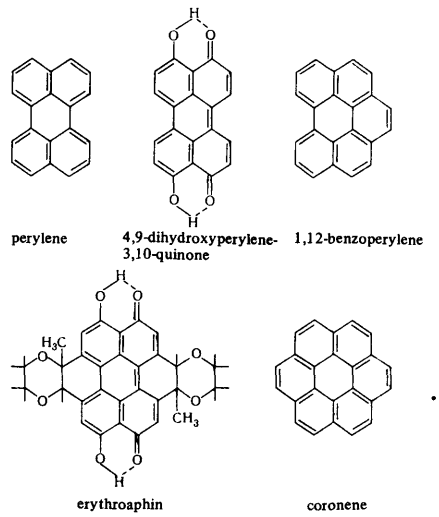
Chlorophyll in green plant leaves is always accompanied by yellow pigments—carotenoids, which belong to the group of isoprenoids. Carotenoids can be divided into two classes: (1) hydrocarbons (carotenes) and (2) xanthophylls—oxygen-containing derivatives of carotenes.

Vallentyne[49,50] investigated the carotenoids from fresh and sea water deposits; he succeeded in isolating carotenoids from fresh water deposits 20 000 years old. Data on the content of carotenoids in the waters and deposits of the Pacific Ocean were obtained by Romankevich[28].

Kojama et al.[51] investigated plant pigments (chlorophylls and carotenoids) in lake deposits by paper chromatography and spectrophotometry. They established that both the total pigments and their individual fractions decrease in the deposits on the bottom on going from surface to deeper layers.

The study of perylene, a polycyclic aromatic hydrocarbon ($C_{20}H_{12}$) consisting of five rings, is of interest. It has been detected in the distillate from crude petroleum, in present day deposits, and in ancient sedimentary rocks[52]. It has been suggested that biogenic pigments are a source of perylene and other polycyclic aromatic compounds[53,54]. A likely biological precursor of perylene may be the widely distributed quinone, similar to 4,9-dihydroxyperylene-3,10-quinone, isolated from the Ascomycete *Daldinia concentrica*[55]. Another quinonoid pigment similar to perylene—erythroaphin—has been isolated from insects of the family Aphididae[56].

The reduction of these pigments results in the formation of 1,12-benzoperylene and coronene together with perylene:



perylene 4,9-dihydroxyperylene-3,10-quinone 1,12-benzoperylene

erythroaphin coronene

Recent investigations by Douglas and coworkers[57,58], who studied isoprenoid and other hydrocarbons and pigments in coorongite and torbanite and also in the algae *Botryococcus braunii* from which these deposits were formed, are of considerable interest.

In the last 10–15 years the attention of investigators was attracted to the determination of the decomposition products of proteins and carbohydrates in various waters, present day deposits, and organic matter of sedimentary rocks[59,60]. The publication of a large number of papers on this question can be accounted for, on the one hand, by the biochemical importance of these compounds in living

organisms, and, on the other hand, by the relative ease of their determination in fossil organic matter.

The variation of the qualitative composition of amino-acids with preservation conditions, the composition of rocks with which they are mixed, and the geological age of rocks has been investigated. Siliceous shale and argillaceous minerals contain appreciable amounts of amino-acids[60,61]. It has been suggested that the presence in rocks of certain thermostable aminoacids be used as a geological thermometer[62].

Studies on the preservation of aminoacids in the skeletal residues of organisms are of great interest. Abelson[62,63] isolated aminoacids from ancient trilobites of the Ordovician period and peptides from shells and bony residues of the Pleistocene period buried in asphalt. Jones and Vallentyne[59] isolated from the fossil shells of *Mercenaria mercenaria* (Pleistocene), after dissolution of the mineral component, 0.3 g of periostracum fibres—the organic fraction of the shells. The set of aminoacids in this fraction proved to be close in composition to that of the conchiolin of present day shells. Florkin[64] quotes the chemical composition of a typical mother-of-pearl conchiolin found in the fossil shells of the Eocene period (about 60 million years old).

Examples are known of the preservation under geological conditions of collagen and protein characteristic of vertebrate animals and detected in fossil bony residues, horns, teeth, and fish scale[65]. There has been a remarkable discovery of protein of the collagen type in the mummified skin of a fossil amphibian, the geological age of which corresponded to the Lower Permian period (about 200 million years ago)[66].

In most studies on fossil organic matter and the pathways followed in its formation, the carbohydrate content in various natural materials was investigated together with the determination of the aminoacids. The literature on this question has been collected in monographs and reviews[3,67,68]. The studies of Swain and coworkers[69], who determined the monosaccharides in the hydrolysates of fossil residues (Devonian–Permian period) of 25 plant species, are striking. They succeeded in revealing the evolutionary change from the algal polysaccharide rich in galactan to a polysaccharide of the cellulose type characteristic of cordaites.

In many geochemical processes associated to some extent with organic matter, humic substances play a notable role. The term humic substances is not fully defined even when applied to their most thoroughly investigated representatives—humic acids. It is believed that the dark-coloured humic acids are polymeric compounds which dissolve in dilute solutions of alkali and are readily reprecipitated by aqueous acid solutions. Chemically humic acids are characterised as a heteropolycondensate with a high reactivity owing to the presence of active functional groups.

The information about soil humic acids and their chemical composition and properties available at present is extensively described in Kononova's monograph[70]. Humic acids in peat constitute the basis of the organic component of human coal. Humic acids are present in the non-compacted deposits of sea and continental origin constituting in some cases more than 50% of the total organic matter in the rock[60,71].

Humic acids may be formed from various organic compounds which enter into the composition of the living population of soils, peats, and silts and which are liberated after the death and breakdown of the organisms. The presence of phenolic components and also nitrogen-containing groupings is characteristic of humic acid. One of the sources of phenolic compounds in humic acids may be their synthesis by micro-organisms from carbohydrates[72,73].

Among phenolic compounds which participate in the formation of humic acids, the most important role belongs to lignin. Lignin is widely distributed in all plants with a vascular system and a mechanical tissue. The involvement of land plant lignins in the formation of soil and peat humic acids is confirmed by the detection of lignin structures in the two materials[74,75].

The role of lignin has been decisive in the formation of the organic component of humus coal and lignites. Brefer[76,77] justly regards lipids and lignins as the most important organic compounds participating in the formation of present day and ancient deposits.

The fundamental outline of the aromatic structure of lignin and the pathways of its formation from photosynthetic products have now been largely elucidated[78]. The complex polymeric lignin molecule is constructed of compounds of the phenylpropane series.

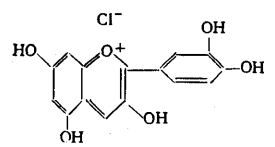
After the death of plants under natural conditions, lignin is acted upon by biological and physicochemical factors in the medium. Under the influence of these factors, depolymerisation processes, i.e. partial rupture of bonds between individual monomers, takes place in the lignin on the one hand and on the other secondary condensation processes occur[79]. The composition of humic acids may include both individual lignin monomers as well as its larger units and also secondary condensed aromatic structures.

The possible pathway of the biological breakdown of lignin and its participation in the formation of humic acids is indicated in the mechanism presented below.

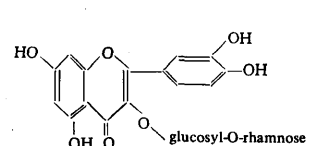
The mechanism shows the sequence of reactions in the biological breakdown of lignin to the monomers. Further reaction leads to the decomposition of the side chain—demethylation and oxidation with formation of protocatechuic acid. Structures of the hydroxy-*p*-benzoquinone type are readily formed from protocatechuic acid in natural processes. The interaction of aromatic lignin structures with nitrogen-containing compounds in the formation of humic acids takes place, according to current hypotheses, after the demethoxylation and oxidation of the aromatic components to quinones[80].

New studies on aromatic soil pigments[81,82], in which the P_g fraction (green pigment) is regarded as a perylene derivative, are of considerable interest. A close genetic relation between these pigments and humic acids is suggested.

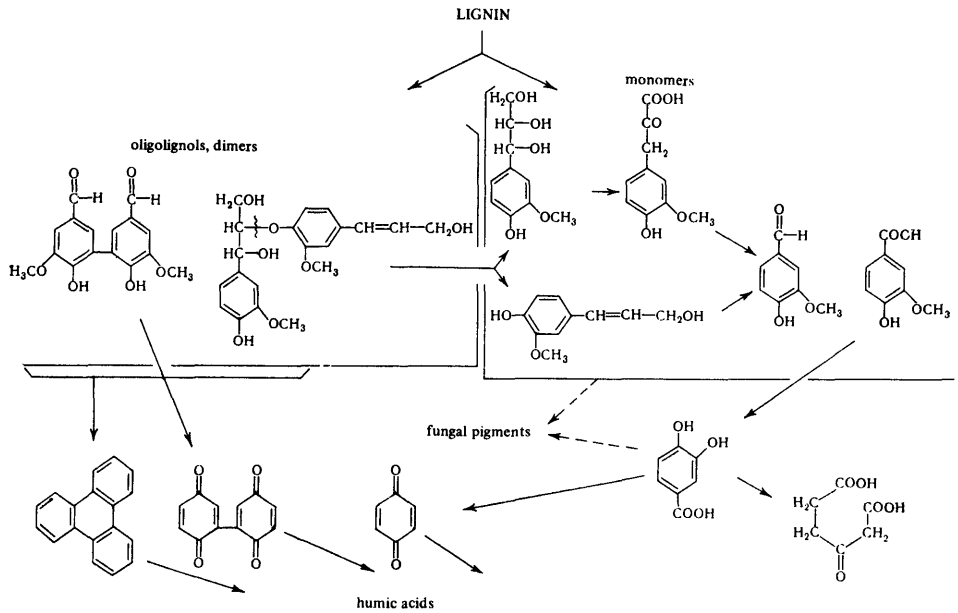
Flavonoids are included among the phenolic compounds fairly widely distributed among plants and undoubtedly participating in natural processes. Flavonoid pigments are a group of water-soluble phenolic glycosides the principal structural unit of which is the flavone skeleton $C_6-C_3-C_6$. Compounds of the type of anthocyanin, which are responsible for the wide variety of raspberry-red and violet tints in various parts of plants, and yellow pigments of the rutin type are known to be present among them:



cyanidine chloride



yutin



Mechanism of the possible geological breakdown of lignin and its participation in the formation of humic acids.

In plants, flavonoids and lignin are genetically related in their biosynthesis via common precursors, which are phenylalanine and cinnamic acid[83]. Flavonoid pigments are characteristic mainly of higher plants and few are known among spore-bearing plants[84]. Bendz et al and coworkers[85,86] isolated from the green moss *Bryum cryophylum O. Mårt* two anthocyanin pigments. These workers isolated from the cell walls of the sphagnum moss *Sphagnum magellanicum* and *Sphagnum nemoreum* a pigment which they characterised as a copolymer of a flavonoid of the anthocyanin type and lignin structures.

The detection of phenolic acids and flavonoid pigments in the pollen of various plants is of great interest[87,88]. The colour of the pollen ranging from pale-yellow to dark-brown, in various plant species depends on the presence of two types of pigments: flavonoids and carotenoids. Inglett et al.[89] determined in the ether-soluble fraction of pollen tars, hydrocarbons, sterols, and fatty acids. In the alcoholic fraction of defatted pollen they found nitrogen-containing components and about 20 flavonoids including rutin and quercetin.

Lunden[90] reviewed briefly the studies on the chemical composition of the pollen of various plants. Free amino-acids, polypeptides, and proteins have been found in the pollen of the majority of plants.

Considerable amounts of nucleoproteins and deoxyribonucleic acids have been detected. Among carbohydrates, starch, cellulose, pentosans, and reducing sugars were discovered. Lactose was detected in the pollen of *Forsythia*—for the first time in a plant material.

Pollen flavonoids have been separated by chromatography and their spectra have been investigated in the same way as those of chlorophyll and carotenoids.

Fatty acids were isolated from the pollen of five conifer species and analysed by gas–liquid chromatography. Oleic, linoleic, palmitic, and stearic acids were found[91]. The ash content of pollen is 1–7%, potassium predominates in the ash (20–45%), there is frequently much silicon (2–10%), and manganese and titanium have been detected.

After the elimination of fats, proteins, and water-soluble material from pollen, a fairly large amount of non-extractable substances remains in the test samples. In certain pine species between 20 and 57% of such substances were found in the pollen. In the past century these substances were called "pollenins" and the exceptional strength of the outer coats of pollen grains was explained by their presence. Pollenins frequently combine with cutin, also a little investigated substance, which impregnates the outer cell walls of the epidermis of leaves and plant stalks. Matic[92] investigated cutin from the leaves of the agave and concluded that it is a polyester of acids containing 16 and 18 carbon atoms in an unbranched chain and 2 or 3 hydroxy-groups.

In the 1930's pollenin from the pollen of conifers and sporopollenins from the spores of lycopodium were isolated by Zetzsche and Vicari[93]. These substances are resistant to the action of concentrated solutions of alkali and many acids but are oxidised on heating with nitric or chromic acids and alkaline permanganate. Zetzsche et al.[94] isolated sporopollenin preparations from tasmanite and Chulkovo brown coal of the Moscow Basin. The first preparation, which they called tasmanin, had the composition $C_{90}H_{134}O_{15}(OH)_2$ and the second, called bothrodendrin, had the composition $C_{90}H_{111}O_{12}(OH)_9$. Descriptions of these interesting studies have been included in monographs on the chemistry of coal[95,96] but until recently they were not developed any further. The presence of sporopollenins in exine (the outer coat of pollen grains) is responsible for the morphological stability of pollen grains, which made possible the widely familiar spore and pollen analysis. Chemical studies on fossil pollen significantly supplement the microscopic observations. Recently Brooks and Shaw[97] investigated the sporopollenins from rocks of different ages. They believe that the older forms of kerogen are identical in many respects with sporopollenin formed from deposited spores. They believe that the fossil sporopollenins are polymers of carotenoids and their esters, present in the pollen of the initial plants.

They present data on the isolation of aromatic acids from the sporopollenins as a result of alkaline treatment: *p*-hydroxybenzoic, *m*-hydroxybenzoic, protocatechuic, and vanillic.

The information presented above on the chemical composition of present day and fossil pollen suggests the presence in sporopollenins of condensed structures formed from flavonoid compounds and compounds of the lignin type. Their determination in small amounts is quite feasible[98].

3. THE ROLE OF ORGANIC MATTER IN THE MIGRATION AND CONCENTRATION OF CHEMICAL ELEMENTS

Numerous data are now available confirming the importance of organic matter in the migration and concentration of chemical elements[3]. The detection in the organic matter in rocks or in paleontological residues of the decomposition products of highly polymerised natural compounds (aminoacids, aromatic structural units of lignin and flavonoids, and compounds with porphyrin structures) enables us to postulate not only the individual stages in the reactions of these compounds but also the possible conditions for their interaction with metals. Earlier the various ways in which uranium, germanium, vanadium, molybdenum, copper, gold, and other elements accumulated in the organic matter of sedimentary rocks were characterised by the present author[3]. An example of such a process is the distribution of germanium and other metals in fossil coals. Ratynskii and Glushnev[99] noted an increased zinc and lead content in fractions of coal material having the minimal density and relatively rich in components of the exine group (pollen and spores). Their experimental investigations led to a quantitative assessment of the bond between a number of metals and the organic component of the coal material. The following affinity series was established: Ge > W > Ga > Be > Nb > Mo > Sc > Y > La > Zn > Pb.

Earlier Ratynskii and Shterenberg[100] established that germanium is concentrated in the vitrain fraction of coal. The vitrain fraction of coal is formed mainly as a result of natural transformations of polymeric lignin molecules. Structures containing ortho-hydroxyquinonoid groupings responsible for the accumulation of germanium and other rare elements in the organic matter of coals at the peat stage of their formation can be readily formed from lignin in natural processes[101].

It has been noted[102] that the enhanced concentrations of rare elements (germanium, uranium, vanadium, and others) in coal inclusions are associated with plant tissues in fossil wood and bark. It is known that the chemical compositions of the cell walls in the bark and wood of present day plants and also the compositions of extractable substances differ considerably[103]. In this connection it is important to elucidate which of these compounds were involved in the formation of coal inclusions and the concentration of rare elements in them.

It is noteworthy that the organic content of silicon-impregnated inclusions in coal strata known as coal balls, large opal-containing lens-shaped discs found in brown coals[104], has not been investigated. Only isolated chemical studies on mineralised plant residues have so far been made.

An organic fraction in an amount of 0.1–0.2% has been isolated (and investigated) from silicon-impregnated wood of conifers (Cretaceous) and stalks of a lycopodium species—genus Lepidodendropsis (*Lepidodendropsis kazachstanica Senk*, Devonian period)[105]. After alkaline nitrobenzene oxidation, small amounts of aromatic aldehydes derived from lignin were discovered in the organic fraction. Knoche and Ourisson[106] extracted with a benzene–methanol mixture an organic fraction (3 mg) from argillaceous inclusions in sand deposits containing residues of the horsetail *Equisetum brongniarti*. Chromatography on silica gel of the extract led to the determination of the following compounds: n-tricosane, n-pentacosane, and n-nonacosane, which are characteristic of the present day horsetail *Equisetum sylvaticum*.

Recently data have been published characterising the mutual effects of the organic matter and the mineral components in sedimentary rocks and paleontological residues. One may include here the studies on the formation of framboids with participation of sulphate-reducing bacteria: these investigations have been reviewed critically by Kizil'shtein[107]. It was found that the aminoacid composition of shell conchiolin differs in the mineralised and non-mineralised layers[108].

Long et al.[109] showed experimentally that montmorillonite minerals act as acid catalysts in the condensation of aromatic compounds to cyclic structures. The observations on present day organisms are of interest. Thus Werner[110] established appreciable differences in the nucleoside-phosphate metabolism of the diatomaceous alga *Cyclotella cryptica* cultivated in a medium with and without $Si(OH)_4$. Drum[111] observed the formation and distribution of opal in the cell walls of the birch when birch twigs were kept in sodium metasilicate solution for 12–24 h.

The study of reactions of this type may prove useful for the elucidation of the form in which chemical elements are combined with fossil organic matter.

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The results of modern investigations presented in this review suggest the future tasks in the geochemistry of organic matter and rational methods for their fulfilment. One of such tasks is the study of the individual organic compounds in present day and ancient deposits, in fossil coals and coal inclusions, and in the organic fraction of mineralised plant and animal residues. It is essential to investigate it in greater depth lipids, porphyrin structures and carotenoids and aromatic compounds of the type of lignin and flavonoids in the course of their biosynthesis in present day organisms. The knowledge of the accompanying enzymic reactions and the intermediates formed will help elucidate the transformations of these compounds in the course of their conversion into fossil organic matter.

One may expect that studies of this kind will lead to the discovery of new possibilities for elucidating the nature of complex natural formation such as kerogen, land and sea humus, and sporopollenins.

The next important task is to establish the specific structures of the organic compounds responsible for the concentration of rare elements in the organic matter of peats, coals, and shale. Experiments on models play a significant role in the solution of this problem.

No less important is the investigation of organic compounds in paleontological residues. The chemical study of paleontological specimens by modern microchemical and physical methods will help discover new aspects of the evolution and phylogeny of organisms. Another aim of studies of this kind is to elucidate the geochemical and paleoclimatic conditions in which the residues of the organisms were preserved and their chemical composition was

transformed. The study of the corresponding organic compounds is phylogenetically similar present day organisms is one of the ways in which this problem may be solved.

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Vernadskii Institute of Geochemistry and Analytical Chemistry, USSR Academy of Sciences, Moscow