BIOGEOCHEMICAL ASPECTS OF EVOLUTION OF SAPROPELITES ACCORDING TO DATA OF MOLECULAR PALAEONTOLOGY

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The earliest organisms living on the Earth appeared under the conditions of oxygen-free atmosphere. Oxygen appeared later, due to the ability for photosynthesis acquired by living organisms. We support the opinion of L. Berkner and L. Marshall that the Earth's atmosphere began to convert into an oxidizing one with traces of oxygen appearing about 2-3 Gyr ago, and that in the Silurian it became aerobic (with the oxygen content similar to the present level) [1]. Procaryotic organisms formed the Earth's atmosphere, whose composition, in its turn, exerted an active influence on the composition, productivity and evolution of living matter. Thus, development of life proceeded in the system: organisms - water - atmosphere - mineral matter.

Development of life may be retraced by the data of molecular palae-ontology, e.g. by the molecular and atomic (isotopic) composition of fossil organic matter (OM), taking into account chemical processes during fossilization of OM and its interaction with environment.

During a long time we have studied more than 50 deposits of con-centrated fossilized carbon of different ages (from recent balkhashite and lake sediments to ancient Karelian shungite, 1.8 Gyr old) attributed to sapropelite type (oil shales, bogheads) (Table). Main structural elements of OM of sapropelites are straight and, in less measure, branched carbon chains, precursors of which were fatty acids and isoprenoid structures, respectively. According to a complex scheme of analysis proposed in [2], bitumoids (extracts) and mineral matter of caustobioliths have been studied using conventional geochemical methodics, and insoluble OM (kerogen) has been subjected to oxidative (nitric acid, potassium permanganate) and reductive (pyrolysis, hydrogenation, thermal dissolution) destruction. Products of destruction have been analysed using chromatographic and spectral methods.

BIOGEOCHEMICAL ASPECTS OF EVOLUTION OF SAPROPELIC FOSSILS ACCORDING TO DATA OF MOLECULAR CHEMISTRY

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Characteristics of Some Sapropelites, %

| Sapropelite	Time of formation	Age, Gyr	Yield of extract (bitumoid)		Elemental composition of kerogen				
			A	C	C	H	N	S	O
Karelian shungite (Russia)	PR	1.8	0.06	0.17	91.8	1.3	1.0	1.1	4.8
Kukersite (Estonia)	O₂	0.46	0.4	0.2	77.4	9.4	0.5	1.5	11.2
Pripyat oil shale (Byelorussia)	D₃	0.36	3.7		69.9	10.4	0.8	3.7	15.2
Ust-Kamenogorsk oil shale (Kazakhstan)	C₃–P₁	0.28	2.3		77.6	7.5	2.5	1.0	11.4
Chagan oil shale (Russia)	J₃	0.14	1.1	0.8	62.5	8.2	1.0	8.7	19.6
Boltysh oil shale (Ukraine)	P₂	0.04	2.0	1.0	68.0	7.3	1.3	1.5	17.7
Novodmitrovo oil shale (Ukraine)	P₃–N₁	0.025	8.3		69.3	10.0	1.5		18.2
Balkhashite (Kazakhstan)	Q		5.0	8.7	77.1	11.1	0.7	0.9	10.2
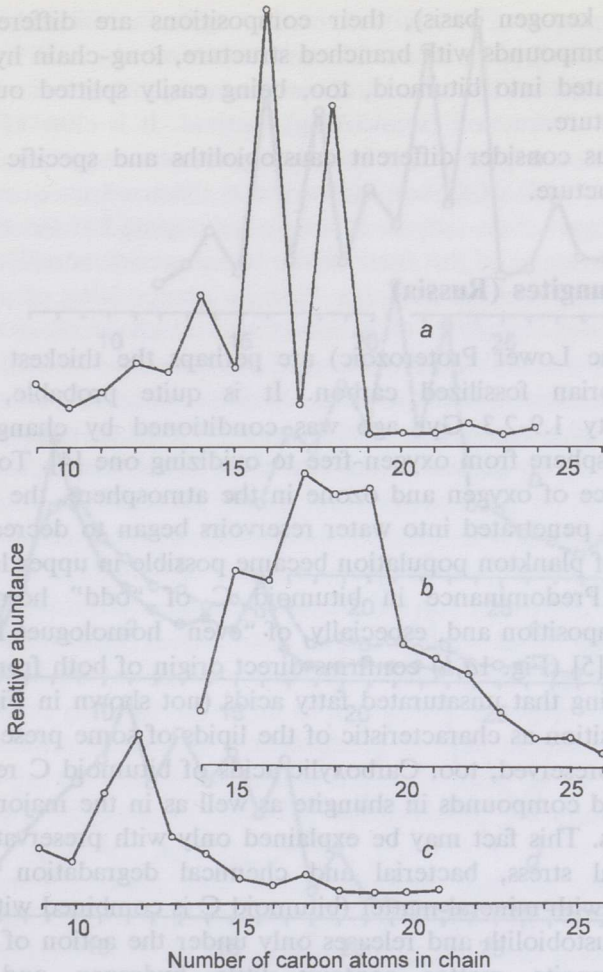
Fig. 1. Composition of *n*-alkane structures of Karelian shungite [5]: *a* - fatty acids of bitumoid B; *b* - *n*-alkanes of bitumoid B; *c* - *n*-alkanes of hydrogenate

As generally known, only the most stable part of living organisms — lipoids consisting mainly of fatty acids — reach the anaerobic stage of diagenesis. Fatty acids with even numbers of carbon atoms in chains are decarboxylated when kerogen is formed, and at the position of the carboxylic group a carbon—carbon bond with the cyclic part of kerogen is formed [3]. As a result, chains of the former fatty acids in the kerogen structure contain odd numbers of carbon atoms. Main source of branched chains in caustobioliths is the phytol chain of chlorophyll which cannot be included into the kerogen structure by the mechanism given above because of its stereo-configuration and the presence of hydroxy-groups. Therefore, branched chains are accumulated mainly in bitumoid. Usually, if bitumoid is syngenetic to kerogen and its content is low

(< 5 % on kerogen basis), their compositions are different because besides the compounds with branched structure, long-chain hydrocarbons are concentrated into bitumoid, too, being easily splitted out from the kerogen structure.

Now let us consider different caustobioliths and specific features of their OM structure.

Karelian Shungites (Russia)

Shungites (the Lower Proterozoic) are perhaps the thickest deposits of the Precambrian fossilized carbon. It is quite probable, that high bioproductivity 1.9-2.3 Gyr ago was conditioned by changing of the Earth's atmosphere from oxygen-free to oxidizing one [4]. Together with the appearance of oxygen and ozone in the atmosphere, the intensity of UV-radiation penetrated into water reservoirs began to decrease and the appearance of plankton population became possible in upper layers of sea water, too. Predominance in bitumoid C of "odd" homologues in n-alkane composition and, especially, of "even" homologues in fatty acid composition [5] (Fig. 1a,b) confirms direct origin of both from plankton. It is astonishing that unsaturated fatty acids (not shown in Fig. 1) of the same composition as characteristic of the lipids of some present plankton species, are preserved, too. Carboxylic acids of bitumoid C represent the best-preserved compounds in shungite as well as in the majority of other caustobioliths. This fact may be explained only with preservation of OM from thermal stress, bacterial and chemical degradation due to its combination with mineral matter (bitumoid C is combined with inorganic matter of caustobiolith and releases only under the action of acids). The bulk of shungite matter contains little hydrogen and is highly metamorphized, aromatic.

. During catalytic hydrogenation of shungite in autoclave only a little n-alkanes were obtained (Fig. 1c) in comparison with aromatic hydrocarbons. In their composition "odd" homologues do not predominate and, on the contrary to the above-mentioned regularity, they have longer chains than n-alkanes of bitumoid. We are of opinion that they are of bacterial origin. Aromatic hydrocarbons of hydrogenate have a very special composition: in contrast to analogical products obtained from younger caustobioliths they contain exclusively biphenyl and its mono- and di-substituted derivatives. Formation of biphenyl and 1,2-alkyl-substituted biphenyls is possible through cyclization of aliphatic carbon chains at a moderately high temperature. Judging by the ascertained structural fragments of shungite one can draw the conclusion, that aliphatic chains, mainly saturated and unsaturated fatty acids C_{16} and C_{18}, were the initial matter for its formation.
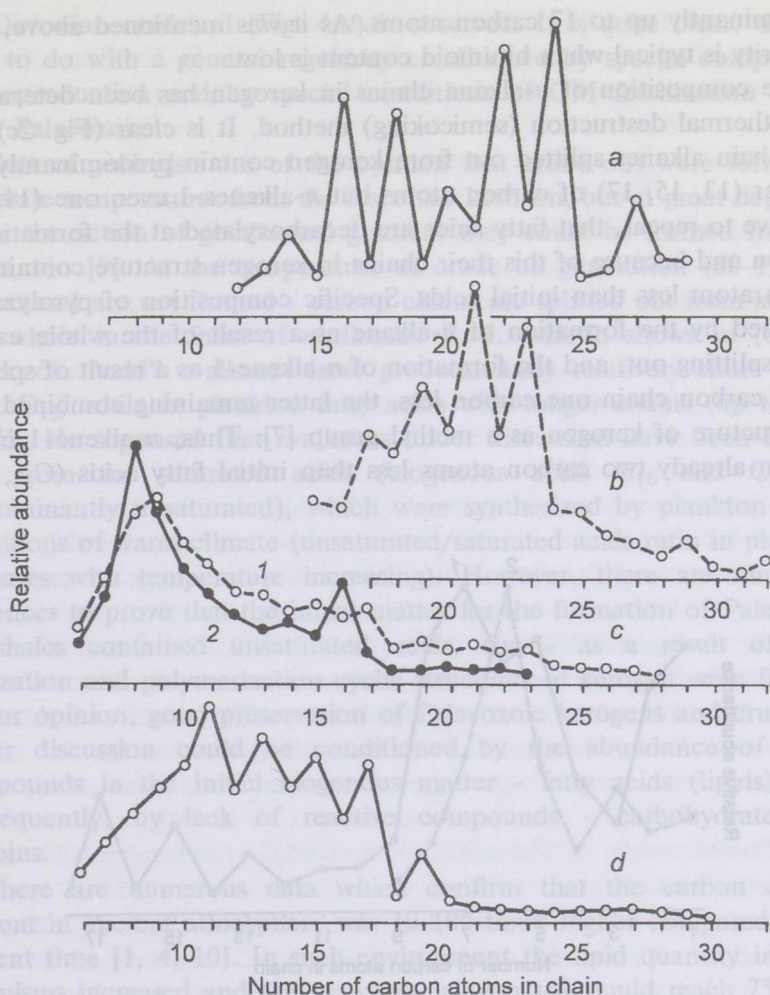
Fig. 2. Composition of *n*-alkane structures of Baltic Kukersite: *a* - fatty acids of bitumoids A and C; *b* - *n*-alkanes (*1*) and *n*-alkenes-1 (*2*) of semicoking oil; *c* - *n*-alkanes of John Creek crude oil (USA, Ordovician) [8] (for comparison)

Baltic Kukersite (Estonia)

Baltic Kukersite (The Middle Ordovician) has much structural peculiarities including an extremely low bitumoid content arising from its allochthonous origin and sedimentation under conditions of oxidizing atmosphere [6]. *n*-Alkanes and fatty acids of bitumoid contain 14-24 carbon atoms in chain (Fig. 2*a,b*) and their composition indicates on the formation of *n*-alkanes ("odd") as a result of decarboxylation of the same "even" fatty acids that are present in bitumoid, too. Carbon chains of *n*-alkanes in bitumoid are longer than those in kerogen, containing

predominantly up to 17 carbon atoms. As it was mentioned above, such regularity is typical when bitumoid content is low.

The composition of *n*-alkane chains in kerogen has been determined using thermal destruction (semicoking) method. It is clear (Fig. 2c) that long-chain alkanes splitted out from kerogen contain predominantly odd number (13, 15, 17) of carbon atoms but *n*-alkenes-1 even one (14, 16). We have to repeat, that fatty acids are decarboxylated at the formation of kerogen and because of this their chains in kerogen structure contain one carbon atom less than initial acids. Specific composition of pyrolyzate is explained by the formation of *n*-alkane as a result of the whole carbon chain splitting out, and the formation of *n*-alkene-1 as a result of splitting out of carbon chain one carbon less, the latter remaining combined with the structure of kerogen as a methyl group [7]. Thus, *n*-alkene-1 chains contain already two carbon atoms less than initial fatty acids (C_{14}, C_{16}, C_{18}).
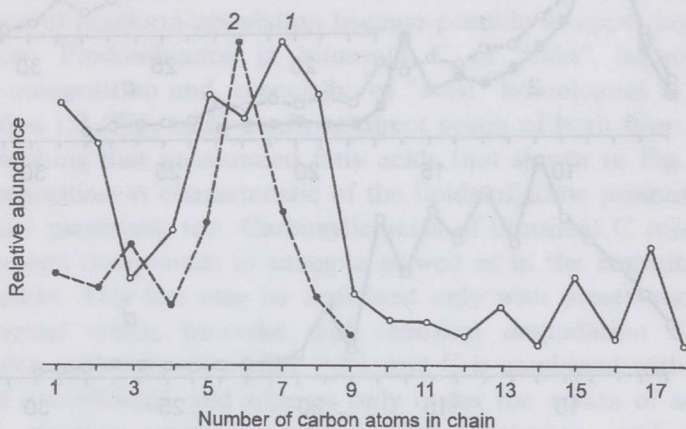

Fig. 3. Composition of 5-alkyl-resorcinols of semicoking oil of Kukersite (*1*) and Pripyat oil shale (*2*)

From a great number of sapropelites studied, the highest "oddness" of *n*-alkanes and "eveness" of *n*-alkenes-1 are established for semicoking oils of two Early Palaeozoic oil shales - Kukersite and the Upper Devonian Byelorussian oil shale (will be characterized in detail below). *n*-Alkane composition of ancient crude oils has analogical peculiarities. R. L. Martin *et al.* [8] have determined the composition of *n*-alkanes in forty Phanerozoic crude oils and established that only in five from them "odd" homologues in the range of C_{11}-C_{19} prevail while the content of long-chain *n*-alkanes is low (Fig. 2,*d*). Those five crude oils belong to the Early Palaeozoic.

In kerogen of both Kukersite and Byelorussian oil shale the predominance of the same "odd" carbon chains C_{13}, C_{15} and C_{17} as in

the Devonian crude oil (Fig. 4,*d*) is observed. It is quite clear, that we have to do with a general regularity conditioned by special composition of bioproduction and by special conditions of OM fossilization in the Early Palaeozoic.

Most of geologists are of the opinion that crude oils were formed at moderate temperatures from the dispersed kerogen, but at great depths or under the action of geothermal gradient they could be formed from oil shales, too [9]. At the temperature of crude oil generation (60-190 °C) n-alkenes-1 are not formed - carbon chains are splitted out from kerogen as a whole in the form of n-alkanes. R. L. Martin shows in [8] that Palaeozoic "odd" n-alkanes have predominantly relatively short chains (C_{11}, C_{13}) while in plankton fatty acids with longer chains (up to C_{18}) prevail. He supposed that n-alkanes under discussion have been formed only from the saturated acids (biogenous acids C_{16} and C_{18} are predominantly unsaturated), which were synthesized by plankton under conditions of warm climate (unsaturated/saturated acids ratio in plankton increases with temperature increasing). However, there are numerous evidences to prove that the initial matter for the formation of Palaeozoic oil shales contained unsaturated acids, too - as a result of their cyclization and polymerization cyclic structures of kerogen were formed. In our opinion, good preservation of Palaeozoic kerogens and crude oils under discussion could be conditioned by the abundance of stable compounds in the initial biogenous matter - fatty acids (lipids), and, consequently, by lack of reactive compounds - carbohydrates and proteins.

There are numerous data which confirm that the carbon dioxide content in ancient atmosphere was 10-100 times higher compared to the present time [1, 4, 10]. In such environment the lipid quantity in living organisms increased and their content in plankton could reach 75 % on dry weight instead of usual 2-10 %. In their turn, processes of microbiological transformation of lipids, as a result of which n-alkanes with monotonous distribution are formed, were passive. Good preservation of Kukersite, as an exception, could be conditioned by its allochthonous origin [6].

Early Palaeozoic Caustobioliths and the Role of Resorcinol Structures in Their Organic Matter

Phenolic structures are of great significance in the evolution of organic matter on the Earth. As a result of pyrolysis of all sapropelites small quantities of monoatomic phenols (1-3 % on kerogen basis) are formed and their composition is practically invariable irrespective of the

composition of sapropelite OM. We consider carbohydrates to be their precursors. Only during Kukersite pyrolysis much (8-10 % on kerogen basis) diatomic phenols of resorcinol structure with long side chain (1,3-dihydroxy-5-alkyl-benzenes) are formed (Fig. 3, curve *1*). Some quantity of resorcinols (2-3 %) is formed during pyrolysis of Byelorussian oil shales, too [11, 12] (Fig. 3, curve *2*).

In our opinion, Kukersite resorcinols should be of biological origin since in their composition homologues with "odd" side chains (1, 5, 15, 17 carbon atoms) prevail. Phenol and other aromatic compounds are not specific to blue-green algae (cyanobacteria) - the initial bioproducents of Kukersite OM. They are able to synthesize such compounds in small quantities only, and bacteria are able only to accumulate them. Biosynthesis of aromatic structures is characteristic of later stages of living matter evolution. Thus, resorcinols with long side chain (cardol, urushiol) are found in some present higher plants and resorcinols with 1, 3, 5 and 7 carbon atoms in alkyl chain are found in lichens and fungi.

According to ^{13}C NMR-data, about 10 % of organic carbon of Kukersite OM belongs to aromatic structures. However, the question about the presence of resorcinol structures in Kukersite kerogen or their formation during its thermal destruction is still not settled. In the works [3, 6] a hypothesis has been suggested that specific features of Kukersite structure, including the presence of structures-precursors for resorcinols' formation, are caused by its deposition under conditions of oxidizing atmosphere (0.45 Gyr ago there was about 1 % oxygen in it) and from allochthonous origin of Kukersite, i.e. its kerogen has not been formed at the place of its bedding.

According to this hypothesis, polyunsaturated fatty acids C_{20}, C_{22} and C_{24} (*n*-alkane chains of Kukersite kerogen have been formed from the acids C_{14}, C_{16} and C_{18}) have been biogenous precursors of resorcinols. Double bonds in their molecules are isolated and remoted from the carboxyl group. During fossilization of these acids sequential reactions have taken place:

(1) isomerization of double bonds up to conjugation with carboxyl group;

(2) Hydration of double bonds;

(3) Dehydration of hydroxy groups up to oxy ones (oxidative stage);

(4) Cyclization of poly-β-oxo-aliphatic chains through aldol condensation. As a result, cyclic diketones 1-alkyl-1-hydroxy-3,5-dioxocyclohexanes have been formed which, after splitting out of water molecule during diagenesis or pyrolysis, converted into aromatic compounds - 5-alkyl-resorcinols which are able to exist in both enol- (I) and oxo-form (II):

R
|
C
HC   CH
‖ |
C   C
HO   CH   OH

I

R
|
C
H_2C CH
| ‖
$O=C$ $C=O$
CH_2

II
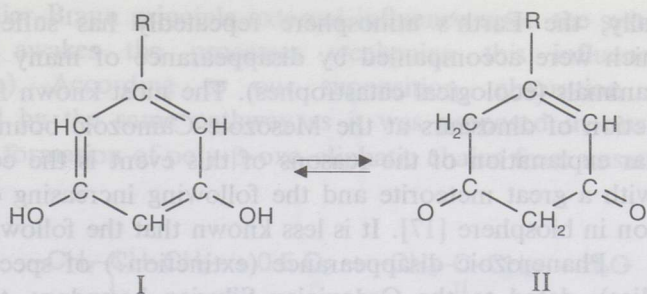
During ^{13}C NMR - spectroscopic analysis of Kukersite and in its pyrolysis products resorcinols occur in the enol-form. In other processes they act as tautomeric dioxocyclohexenes, what testifies the existence of oxo-enol equilibrium of resorcinol structures in Kukersite kerogen.

The oxidative stage of the above-stated process (formation of alkylresorcinols from unsaturated fatty acids) is the key moment which deserves attention. It is supposed that the oxidation reactions were proceeding during transportation of plankton necroma by water flow and were conditioned by a relatively near position of ozone layer to the Earth's surface what, in its turn, made possible the penetration of UV-radiation deep into water and the proceeding of radical reactions of oxidation. It is known that even at the present time in plants of Alpine regions in the active UV-illumination zone poly-β-oxo-structures are formed [13], and CO is formed from plankton in the Ocean at "air-water" interface [14].

Thus, the presence of resorcinol structures in Kukersite may be explained by its specific allochthonous origin and by oxidative conditions of its sedimentation. However, resorcinol structures are also present in terrestrial plants which belong to lower stage of evolution. It is known that the earliest terrestrial plants (mosses and lichens) appeared in the Silurian (0.405-0.440 Gyr ago) simultaneously with the transformation of the Earth's atmosphere from oxidizing into aerobic [15]. Among present plants they are, of course, the most primitive but they are adapted to extremely unfavorable living conditions - sharp fluctuations of temperature and moisture. In addition, lichens may be considered a transitional link between phytoplankton and higher plants - they are a symbiosis of algae and fungi, a classical example of mutualism [16]. It is of interest for us that:

(1) Formation of Kukersite and appearance of lichens are sequential events of the Ordovician-Silurian;

(2) Both Kukersite OM and lichens contain resorcinols and similar to them structures. Such coincidence is a rare fact in biogeochemistry and gives us the basis to put forward a hypothesis about the synthesis of resorcinols by lichens in response to increasing oxygen concentration in the Earth's atmosphere.

Historically, the Earth's atmosphere repeatedly has suffered sharp changes which were accompanied by disappearance of many species of plants and animals (ecological catastrophes). The most known from them is the extinction of dinosaurs at the Mesozoic-Cainozoic boundary. The most popular explanation of the reasons of this event is the collision of the Earth with a great meteorite and the following increasing of iridium concentration in biosphere [17]. It is less known that the following by the importance - Phanerozoic disappearance (extinction?) of species (20 % of all families), dated to the Ordovician-Silurian boundary, took place 0.44 Gyr ago. These time the poisoning with iridium did not precede the extinction of species.

According to the opinion of Estonian geologists [18], extinction of species was conditioned with the global glaciation as a result of which the World Ocean level fell by 50-100 m. At the same time, according to L. Berkner and L. Marshall [1], the concentration of oxygen in atmosphere increased almost up to the present level. A common opinion of evolutionists is: life has appeared in reducing environment and before the appearance of aerobic metabolism in organisms oxygen had been a poison for them. It is quite possible that some organisms of the Early Palaeozoic had no mechanism to protect themselves from the enchanced concentration of oxygen and in aerobic environment they died out. The earliest terrestrial plants certainly had to have a mechanism of protection from oxygen.

It is known that phenolic compounds of hydroquinone type are the components of the respiration system of the higher plants [19]. Their transformations during respiration process may be shown as follows:

R ─ C6H3(OH)2 + 0.5 O2 ⟶ R ─ C6H3O2 + H2O
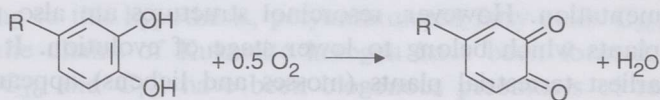
Phenols with hydroxy-groups at 1,2-positions are typical constituents of lignin which is absent in algae but is abundant in higher plants. Fatty acids and other aliphatic compounds are formed in plankton by means of a simple biosynthetic pathway - by joining of two-carbon (acetate) units [16]. Lignin is formed by a more complicated pathway conditioned by the next stage of biosynthesis evolution. In our work, synthesis of phenolic compounds C_6-C_3 [20] must be taken into account.

Simultaneously with decreasing the World Ocean level as a result of the Silurian glaciation [18] discussed above, a considerable reconstruction of shallow ecosystems took place caused by the regression of sea from shelf zones. The appearance of the earliest terrestrial plants should be dated to that time, i.g. lichens as a result of evolution of algae adapted to the living on land. Those mutants have been subjected to the unusual for them action of high concentrations of oxygen. According to the
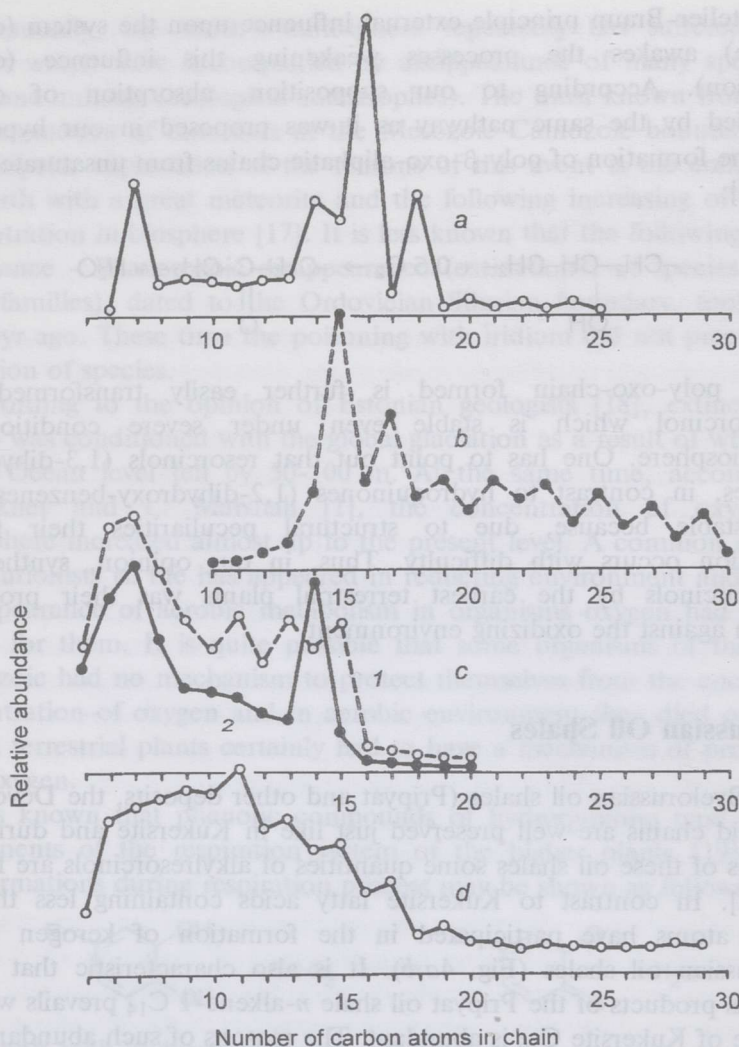
Le Chatelier-Braun principle external influence upon the system (oxygen pressure) awakes the processes weakening this influence (oxygen absorption). According to our supposition, absorption of oxygen proceeded by the same pathway as it was proposed in our hypothesis about the formation of poly-β-oxo-aliphatic chains from unsaturated fatty acids [3]:

$$-CH_2-CH-CH_2- + 0.5\ O_2 \rightarrow -CH_2-C-CH_2- + H_2O$$
$$\quad\quad\ \ |\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad ||$$
$$\quad\quad\ \ OH\quad\quad\quad\quad\quad\quad\quad\quad\quad\ O$$

The poly-oxo-chain formed is further easily transformed into alkylresorcinol which is stable even under severe conditions of palaeobiosphere. One has to point out that resorcinols (1,3-dihydroxy-benzenes, in contrast to hydroquinones (1,2-dihydroxy-benzenes), are more stable because, due to structural peculiarities their further oxidization occurs with difficulty. Thus, in our opinion, synthesis of alkylresorcinols by the earliest terrestrial plants was their protective reaction against the oxidizing environment.

Byelorussian Oil Shales

In the Byelorussian oil shales (Pripyat and other deposits, the Devonian), fatty acid chains are well preserved just like in Kukersite and during the pyrolysis of these oil shales some quantities of alkylresorcinols are formed [11, 12]. In contrast to Kukersite fatty acids containing less than 16 carbon atoms have participated in the formation of kerogen of the Byelorussian oil shales (Fig. 4a,b). It is also characteristic that in the pyrolysis products of the Pripyat oil shale n-alkene-1 C_{14} prevails while in the case of Kukersite C_{16} is abundant. The reasons of such abundance are still not known.

By the length of alkyl substituents resorcinols of the Pripyat oil shale (Fig. 3, curve 2) are similar to resorcinols of lichens, but without the "oddness" characteristic of latters. Contrary to Kukersite, specific structural features of the Pripyat oil shales cannot be related to the special facial conditions of sedimentation. They were formed in the Devonian when the oxygen concentration in the Earth's atmosphere was similar to the present one, and other conditions were the same as at the formation of most oil shales [21]. However, inspite of their different genesis for Kukersite and Pripyat oil shale the following common features may be noted: on the one hand, good preservation of fatty acid chains of primary bioproducents uniting these oil shales with the Palaeozoic crude oils (Fig. 4) and, on the other hand, presence of resorcinol structures in both oil shales.

Fig. 4. Composition of *n*-alkane structures of Pripyat oil shale [12]: for *a-c* see Fig. 2; *d* - *n*-alkanes of Kawkawlin crude oil (USA, Devonian) [8] (for comparison)

As a rule, caustobioliths originated from bacterially altered initial matter are characterized by high contents of branched and naphthenic structures and monotonous distribution of *n*-alkanes. Such structures are not abundant in Kukersite, Pripyat oil shale and Palaeozoic crude oils that indicates the passivity of bacterial processes. In our opinion resorcinols present in plankton necroma had an oppressive effect on bacteria.

Bactericidal action of phenols, including resorcinols, is well known [19], just as preserving action of peats, mosses and lichens owing to phenols containing in them. In our opinion, namely phenols of resorcinol type were present in dead plankton from which the Early Palaeozoic oil shales and dispersed kerogen were formed. As a result their further catagenesis crude oils with high contents of "odd" *n*-alkanes were formed. During the formation of crude oils *n*-alkanes were splitted out from kerogen according to the same mechanism as during its semicoking [7].

Thus, good preservation of *n*-alkane chains in some Early Palaeozoic kerogens and in originated from them crude oils is conditioned by the presence of resorcinol structures. As for kerogens of the most Early Palaeozoic oil shales studied, they do not contain resorcinol structures and are considerably altered by bacteria.
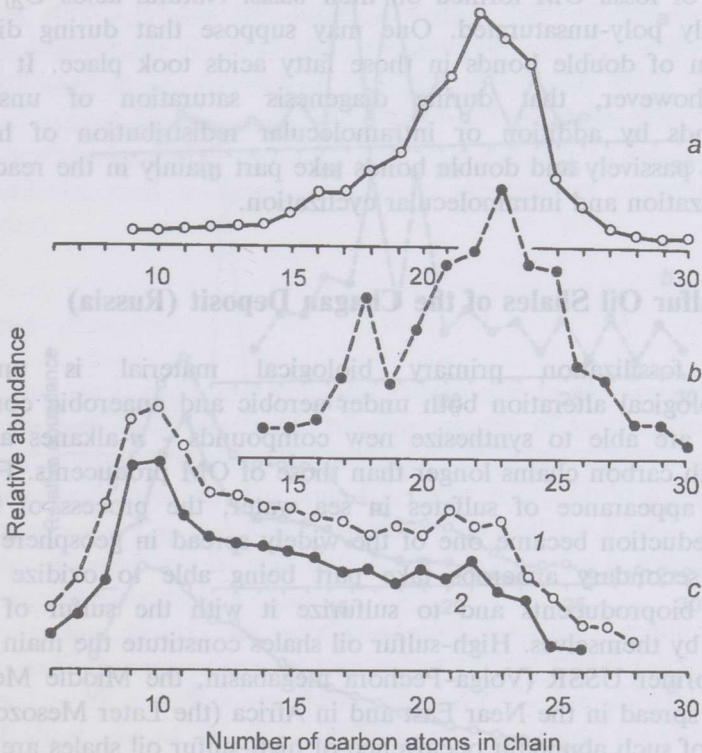
Fig. 5. Composition of *n*-alkane structures of Ust-Kamenogorsk oil shale: for *a-c* see Fig. 2

Kenderlyk Oil Shales (Kazakhstan)

Kenderlyk oil shales of Ust-Kamenogorsk deposit formed in the Later Palaeozoic (Carboniferous-Permian) represent the next interesting example of biogeochemical evolution of sapropelites. Carbon chains in the composition of their bitumoid are already longer (Fig. 5) and "even" fatty acids only slightly prevail in bitumoid so presenting a quite rare case. Carbon chains of kerogen contain up to 23 carbon atoms. Although a little predominance of "odd" chains is observed, it is not so apparent as in some Early Palaeozoic kerogens.

Initial fatty acids for the formation of kerogen of the Kenderlyk oil shales have contained, besides usual C_{16} and C_{18} fatty acids, C_{20}, C_{22} and C_{24} acids, too. The latters are usually present in higher plants, but their contribution into total bioproduction is not considerable just as the quantity of fossil OM formed on their basis. Natural acids C_{20}-C_{24} are exclusively poly-unsaturated. One may suppose that during diagenesis saturation of double bonds in those fatty acids took place. It must be noted, however, that during diagenesis saturation of unsaturated compounds by addition or intramolecular redistribution of hydrogen proceeds passively and double bonds take part mainly in the reactions of polymerization and intramolecular cyclization.

High-sulfur Oil Shales of the Chagan Deposit (Russia)

During fossilization primary biological material is undergone microbiological alteration both under aerobic and anaerobic conditions. Bacteria are able to synthesize new compounds - *n*-alkanes and fatty acids with carbon chains longer than those of OM producents. From the time of appearance of sulfates in sea water, the process of bacterial sulfate reduction became one of the widely spread in geosphere. In this process secondary anaerobs take part being able to oxidize OM of primary bioproducents and to sulfurize it with the sulfur of sulfates reduced by themselves. High-sulfur oil shales constitute the main reserves of the former USSR (Volga-Pechora megabasin, the Middle Mesozoic), they are spread in the Near East and in Africa (the Later Mesozoic). The reasons of such abundant occurrence of high-sulfur oil shales are not still elucidated.

In the composition of *n*-alkane structures of the Chagan oil shale (the Jurassic) fatty acids and *n*-alkanes of bitumoid are well preserved (Fig. 6a,*b*) although their genetical correlation is not quite clear (usual planktonic acids C_{16} and C_{18} and *n*-alkanes C_{17} and C_{19} prevail). On the contrary, carbon chains of kerogen are considerably altered, neither "odd" nor "even" homologue predominances are observed. A similar

composition of *n*-alkane structures of kerogen with concentration maximum at C_8-C_{10} and its following smooth decreasing up to C_{20} (Fig. 6*c*) is observed in all high-sulfur oil shales, particularly in younger oil shales of the Central Asia (the Eocene).

Just like in the overwhelming majority of crude oils, in *n*-alkanes of the Jurassic crude oil from the Darius accumulation (the Near East) [8] no predominance of "odd" chains is observed and its *n*-alkane composition (Fig. 6*d*) is similar to that of *n*-alkane chains in kerogen of sulfur-containing oil shales. We consider this important characteristic of crude oils (absence of the predominance of "odd" *n*-alkanes) being conditioned by bacterial alteration of OM in diagenetical and hypergenetical processes.
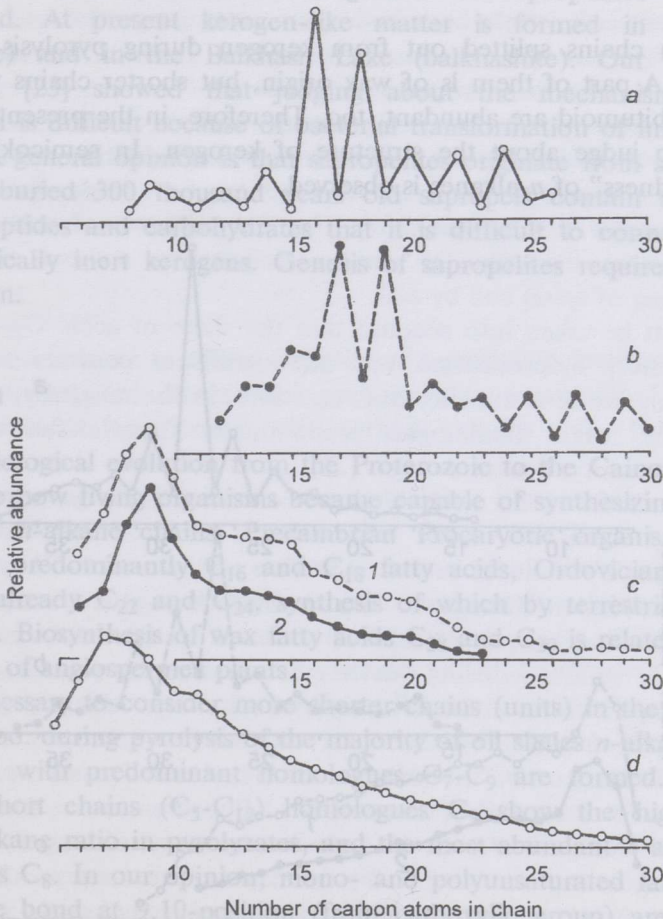
Fig. 6. Composition of *n*-alkane structures of Chagan oil shale: for *a-c* see Fig. 2; *d* - *n*-alkanes of Darius crude oil (Near East, Cretaceous) [8] (for comparison)

Boltysh Oil Shale (The Ukraine)

Beginning from the Later Palaeozoic, the contribution of terrestrial plants into the formation of sapropelites increases, although Procaryotic water organisms remain the main initial material for them. Oil shales of the Boltysh deposit (the Palaeogene) are typical oil shales with high content of terrigenous material. They were deposited in the caldera of volcano or meteorite in freshwater environment. A principal feature of these oil shales is the abundance of long-chain aliphatic structures (Fig. 7*a,b*). Fatty acids of bitumoid are exclusively typical wax acids C_{28}, C_{30}, etc. and it is difficult to explain why shorter fatty acids are not found. Genetical correlation of *n*-alkanes and fatty acids is apparent, and in their composition the characteristics of primary bioproduction are preserved.

Carbon chains splitted out from kerogen during pyrolysis are long (Fig. 7*c*). A part of them is of wax origin, but shorter chains which are absent in bitumoid are abundant, too. Therefore, in the present case it is difficult to judge about the structure of kerogen. In semicoking oil, a slight "oddness" of *n*-alkanes is observed.
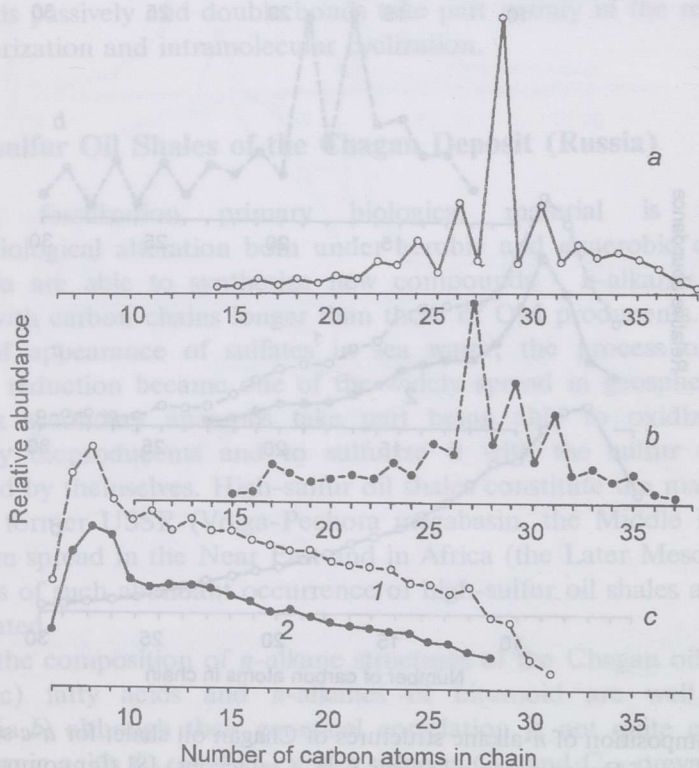

Fig. 7. Composition of *n*-alkane structures of Boltysh oil shale: for *a-c* see Fig. 2

Just like in the case of other sapropelites, in pyrolyzate of the Boltysh oil shale n-alkanones with oxo-group at 2-position or in the middle of chain are present. In Boltysh shale oil n-alkanones are abundant, their "oddness" being higher than that of n-alkanes. Such peculiarities are characteristic of semicoking oils of other oil shales containing terrigenous material, too.

Some oil shales are defined to be similar to the Boltysh ones by the genesis and structure. For example, the Novodmitrovo oil shales [22] were formed in freshwater environment, too, and long carbon chains and oxo-groups are abundant in them.

It seems easier to investigate the chemistry of fossilization processes on the example of recent OM deposits. So, genesis of peats is studied well enough. The question about genesis of sapropelites is more complicated. At present kerogen-like matter is formed in Australia (coorongite) and in the Balkhash Lake (balkhashite). Our study of balkhashite [23] showed that judging about the mechanism of its fossilization is difficult because of bacterial transformation of initial algal material. A general opinion is that sapropelites originate from sapropels. But even buried 300 thousand years old sapropels contain so much reactive peptides and carbohydrates that it is difficult to connect them with chemically inert kerogens. Genesis of sapropelites requires further investigation.

Discussion

Studying biological evolution from the Proterozoic to the Cainozoic one can observe how living organisms became capable of synthesizing longer and longer n-alkane chains. Precambrian Procaryotic organisms have synthesized predominantly C_{16} and C_{18} fatty acids, Ordovician marine organisms already C_{22} and C_{24}, synthesis of which by terrestrial plants began later. Biosynthesis of wax fatty acids C_{28} and C_{30} is related to the appearance of angiospermea plants.

It is necessary to consider more shorter chains (units) in the kerogen structure, too: during pyrolysis of the majority of oil shales n-alkanes and n-alkenes-1 with predominant homologues C_7-C_9 are formed. In the range of short chains (C_5-C_{12}) homologues C_9 show the highest n-alkene/n-alkane ratio in pyrolyzates, and the most abundant n-alkane in crude oils is C_8. In our opinion, mono- and polyunsaturated fatty acids with double bond at 9,10-position (from carboxylic group) are distant precursors of hydrocarbons C_7-C_9 in pyrolyzates and C_8 in crude oils.

Thus, saturated alkane chains with 7-9 carbon atoms are the mostly occurring fragments of biogenous n-alkane structures. Double bond is a relatively weak link in chain. Most likely it is not preserved in the

kerogen structure, but at its place, as a result of polymerization (alkylation), a branching of chain is formed. At the first stage of thermal destruction depolymerization of kerogen takes place, double bond is restored and then carbon chain splits out from kerogen just near the double bond. Obviously, restoration of the double bond at the previous place just conditions a high C_9 n-alkene/n-alkane ratio in the products of kerogen pyrolysis.

In bioproduction of present living organisms fatty acids C_{16} and C_{18}, C_{22} and C_{24}, C_{28} and C_{30} with units C_7-C_9 in their molecules are widespread. Then, in the course of biological evolution during more than a thousand million years lengthening of carbon chains was not gradual - joining a growing number of acetate units - but spasmodic: fatty acid molecules became longer by C_6 and C_8 units. At the same time new synthesized compounds acquired quite new properties and biological functions (C_{16} and C_{18} are energy resources, C_{28} and C_{30} are protective cover preventing from environmental action).

Long-chain polyunsaturated acidic radicals in the molecules of glycerides are twisted into spirals owing to the formation of spin-isomers and cis-position of double bond in biogenous fatty acids. Every coil of a spiral contains 6-8 carbon atoms. In the presence of such spiral-like structure, the evolution of carbon chains was realized through the lengthening of spiral coil by coil.

It must be taken into account that the share of acids C_{22}-C_{24} in the total primary bioproduction was not significant contrary to kerogens where they are in abundance and, as a rule, in the range C_{22}-C_{24} neither "odd" nor "even" homologues predominate. These chains in kerogens are of secondary, bacterial origin [24].

The increase in the heteroelement content (O, N, S - see the Table) beginning from the Later Mesozoic is in a considerable degree conditioned by bacterial sulfate reduction and is a common tendency in kerogen evolution during the Phanerozoic. Kerogens become enriched with sulfur and oxygen of sulfates reduced by the bacteria. Since the biomass of sulfate-reducing bacteria contains much proteins (peptides), high-sulfur oil shales differ not only by high content of oxygen (12-20 %) but of nitrogen (1.5-3 %), too.

In the Cainozoic, the number of oil shales formed in freshwater environment increased (Green-River, Boltysh, some Australian oil shales). In kerogens of such oil shales the contents of long carbon chains and nitrogen (up to 1.5-2.5 %) increased. The reasons of the latter phenomenon are not known. During biological evolution the composition of total bioproduction became more complicated has reflected in the structure of kerogens. The bitumoid content increased being conditioned by the appearance in the composition of bioproduction of complex

stereo-configurated long-chain compounds which could not be included into the structure of kerogen.

As noticed long ago, the isotopic composition of organic carbon in caustobioliths became "heavier" from the beginning of the Phanerozoic - $\delta^{13}C$ increased from -30 to -26 ‰ [10]. L. Kodina and E. Galimov consider the appearance of plankton with mineral skeleton (coccolithophorides, etc.) in the Later Palaeozoic the reason of this phenomenon. Mineral skeleton has preserved proteins and carbohydrates from degradation, usually they are easily mineralized during sedimentation under both aerobic and anaerobic conditions. Just proteins and carbohydrates are distinctive by an elevated content of ^{13}C.

It is also possible that more "light" isotopic composition of carbon in ancient kerogens was conditioned by high CO_2 concentration in the Earth's atmosphere of that time. As it was noted above, the increasing of CO_2 concentration induces in algae an abundant formation of fatty acids with lower content of ^{13}C. Moreover, organisms consume ^{12}C for biosynthesis selectively, and so, according to the law of mass action, the excess of CO_2 consumed for photosynthesis, is expected to decrease ^{13}C content in organisms.

Conclusions

Lower Proterozoic up to recent deposits of sapropelitic fossilized carbon have been investigated. During biological evolution spasmodic, i.e. by 6-8 carbon atoms, lengthening of carbon chains of biosynthetic *n*-alkanoic acids is observed.

The most significant biotic event in the Phanerozoic was the transformation of the Earth's atmosphere from oxidizing into aerobic (oxygenous). Plankton and the earliest terrestrial plants (lichens) began to synthesize poly-β-oxo-compounds to protect themselves from enhanced concentrations of oxygen. Later these compounds were converted into phenol (resorcinol) structures by biosynthesis and/or fossilization.

It is shown that kerogen of some Early Palaeozoic oil shales and crude oils are well preserved and they are similar in composition: they contain n-alkane chains up to C_{17}, while *n*-alkanes show a strong "odd" predominance and branched and naphthenic structures are not abundant. A hypothesis has been suggested that these specific features of the structure of kerogens and crude oils are due to the bactericidal action of biosynthetic resorcinol compounds which protected protokerogen from microbiological degradation.

In the Phanerozoic, the composition of kerogens became more complicated, their content of heteroatoms (N,S,O) and bitumoid increased. Also, the "light" carbon isotope composition changed to a

"heavier" one due to the appearance of procaryotic water organisms with a mineral skeleton and/or to the decreasing of CO_2 content in the Earth's atmosphere.

REFERENCES

1. *Berkner L., Marshall L.* Oxygen and evolution // Earth and Universe. 1966. No 1. P. 32-39 [in Russian].
2. *Klesment I.R.* A complex scheme for investigating the organic structure of oil shales // Oil Shale. 1984. V. 1, No 1. P. 58-68 [in Russian with English Abstract].
3. *Klesment I.R.* The role of fatty acids in the formation of some sapropelites // Organic matter of recent and fossil sediments. - Moscow, 1974. P. 122-129 [in Russian].
4. *Walker J.C.G., Klein C., Schidlowski M.* Environmental evolution of the Archean-Early Proterozoic Earth // Earth's earliest biosphere: Its origin and evolution. Princeton, N.J., 1983.P. 260-290.
5. *Bondar E.B., Klesment I.R., Kuusik M.G.* Investigation of the structure and genesis of shungite 1. The composition of extracts and thermal dissolution and hydrogenation products // Oil Shale. 1987. V. 4, No 4. P. 377-393 [in Russian with English Abstract].
6. *Klesment I.R.* On the genesis of the Baltic oil shales // Oil Shale. 1985. V. 2, No 1. P. 12-22 [in Russian with English Abstract].
7. *Klesment I.R.* On the formation of paraffins and olefins during the low-temperature decomposition of the Estonian oil shale kukersite // Khimiya Tvyordogo Topliva. 1973. No 3. P. 112-119 [in Russian].
8. *Martin R.L., Winters J.C., Williams J.A.* Distributions of *n*-paraffins in crude oils and their implications to origin of petroleum // Nature. 1963. V. 199. P. 110-113.
9. *Urov K.E., Klesment I.R.* Conversion of kukersite during the slow thermolysis in rock dumps // Proc. of Estonian Academy of Sciences. Geol. 1974. No 6 [in Russian with English Abstract].
10. *Kodina L.A., Galimov E.M.* Formation of carbon isotope composition of "humic" and "sapropelitic" organic matter in marine sediments // Geokhimiya. 1984. No 1. P. 1742-1756 [in Russian].
11. *Urov K.E., Liström A.J.* On the composition and properties of kerogen of the Byelorussian Pripyat oil shales according to data of thermal destruction // Khimiya Tvyordogo Topliva. 1979. No 5. P. 86-92 [in Russian].
12. *Urov K.E., Klesment I.R., Pobul L.J. et al.* New data on organic matter of the Upper Devonian oil shales of Byelorussia // Oil Shale. 1985. V. 2, No 2. P. 41-56 [in Russian with English Abstract].
13. *Eglinton G., Hamilton R.J.* Leaf epicuticular waxes // Science. 1967. V. 156, No 3780. P. 1322-1335.

14. *Vangerski P.J.* Cycle of organic carbon in the Ocean // Ekologiya morya. 1986. Is. 24. P. 3-24 [in Russian].

15. *Bardunov L.V.* The most ancient at the land. - Novosibirsk, 1984 [in Russian].

16. *Villee C., Dethier V.* Biological Principles and Processes. - Moscow, 1975 [translated in Russian].

17. *Wilde P., Berry W.B.N.* Iridium abundances across the Ordovician-Silurian stratotype // Science. 1986. V. 333. P. 339-341.

18. *Kaljo D.L., Nestor H.E., Pxlma L.J., Einasto R.E.* Later Ordovician glaciation and its influence on ecological transformations in the Baltic platform basin // Major biotic events in the Earth's history: Abstracts of the 32nd Session of Palaeontologic Society. - Tallinn, 1986 [in Russian].

19. *Zapromyetov M.N.* Fundamentals of phenol compound biochemistry. - Moscow, 1974 [in Russian].

20. *Manskaya M.S., Kodina L.A.* Geochemistry of lignin. - Moscow, 1975 [in Russian].

21. *Azhgirevich L.F.* Regularities of distribution and formation of fossil fuels. - Moscow, 1986 [in Russian].

22. *Urov K.E., Liström A.J.* Comparative organic matter characteristics of oil shale and brown coal of the Novodmitrovo deposit of the Ukraine // Khimiya Tvyordogo Topliva. 1980. No 1. P. 94-100 [in Russian].

23. *Klesment I.R., Pobul L.J., Nappa L.A.* Composition of Balkhashite and questions of sapropelite genesis // Organic matter of recent and fossil sediments. Moscow, 1985. P. 67-71 [in Russian].

24. *Urov K.E.* On the composition and genetic types of aliphatic structures in organic matter of oil shales // Sedicahytes at different stages of lithogenesis. - Moscow, 1982. P. 153-158 [in Russian].

Supplement

As a result of the following investigations on oil shales, a remarkable specimen of sapropelites has come to light. It is the Anabar oil shale (Russia) formed in the Early Silurian (0.44 Gyr ago). Its planktonogenous kerogen (type I) is of low maturity and similar to Kukersite kerogen by composition although this shale is of autochthonous genesis.[1]

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[1] *Bondar E. B., Bityukov M. M., Kuusik M. G.* Peculiarities of oil shale deposition in the Silurian. 1. Characterization of Anabar oil shale (Low Llandovery) and its extracts composition // Oil Shale. 1990. V. 7, No 3-4. P. 193-205 [in Russian with English Abstract].

The composition of semicoking oil of both oil shales are similar including high content and composition of alkyl-resorcinols.[*2]

Geochemical parameters indicate the deposition of the Anabar oil shale in oxidizing environment in spite of which it is of high OM content (68.6 %) and posesses high petroleum-generation potential (shale oil yield 58.8 % on OM). It is obvious that we have to do with a corroboration of the hypothesis of bactericidal action of phenolic compounds preserving OM from degradation. In addition, 1,2- and 1,4-dihydroxybenzenes could act as antioxidants, too, promoting the preservation of biogenous matter in sediments.

In contrast to Kukersite, the isotopic composition of organic carbon of the Anabar oil shale is "heavy" ($\delta^{13}C$ for kerogen is -23.9 ‰ contrary to -32.0 ‰ in Kukersite). This fact was related by the authors of [*2] to the decreasing of CO_2 concentration in the Earth's atmosphere taken place in the Early Silurian: in the conditions of CO_2 deficiency phytoplankton was compelled to reassimilate isotopically heavy CO_2 evolved by itself during respiration.

Dephenolated shale oil and phenol fraction (half of them alkylresorcinols) of both oil shales differ in $\delta^{13}C$ value by 4-5 ‰. It was supposed that "light" isotopic composition of carbon of alkylresorcinols resulted from the abiogenous oxidation (the kinetic isotope effect took place) of their precursors - polyunsaturated fatty acids in the conditions of (1) a long-term contact of protokerogen with atmospheric oxygen in case of allochthonous Kukersite, and (2) a swift oxygen concentration's increasing in the Earth's atmosphere taken place in the Early Silurian, in case of autochthonous Anabar oil shale.

[*2] _Bondar E. B., Kuusik M. G., Bityukov M. M._ Peculiarities of oil shale deposition in the Silurian. 2. The composition of insoluble organic matter of Anabar oil shale (Low Llandovery) by thermal destruction data // Oil Shale. 1991. V. 8, No 3. P. 238-248 [in Russian with English Abstract].