Genetic Aspects in the Generation of Oil Alkanes

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Abstract—Genetic aspects of the generation of oil alkanes suggest that the genesis of oils is controlled by a succession of factors of a single genetic chain, which indicate that the possible sources of oils are certain inorganic components of magmatic fluids, the mineral matter of sedimentary rocks, and the biomass of anaerobes, which is formed when magmatic fluids filter through marine and offshore sedimentary deposits.

INTRODUCTION

Studies of the tectonics and geodynamics of lithospheric continental plates resulted in the discovery of deep-sitting foci of strain and excess pressure near oil and gas fields [1–3]. The partial natural replenishment of oil reserves detected at some oil fields during their development suggests that there is a direct link between oil and gas fields and these foci of strain, at which the excess pressure was relieved and from which magmatic fluids and deep heat penetrated into the sedimentary deposits along a network of fractures, faults, and permeable zones in the crystalline basement. These fractures and faults were produced by ancient seismic–tectonic activity and partly remain active until now, and the fluids maintained reduced conditions favorable for oils generation [4, 5]. The deep fluids were determined to contain complex compounds of heavy elements, including those of U, Au, Pt, Ni, Zn, and other metals, which are insoluble in water and often accompany oil and gas fields [6]. At the same time, the extensive studies of the oceanic floor at the strained rift segments of the continental drift, which are marked by the active release of deep magmatic fluids (so-called black smokers), led to the discovery of highly organized geyser fauna, which flourishes based on the symbiosis of anaerobic bacteria in the practically complete absence of oxygen in the solutions of highly toxic compounds (hydrogen sulfide, ammonia, oxides of carbon, sulfur, nitrogen, and other compounds) at high temperatures, up to 100°C and more [7]. These facts demonstrate that the habitats of anaerobes include not only surface oxygen-deficient environments but also the seafloor and permeable offshore and marine sedimentary deposits [8]. Where magmatic fluids filter through the latter rocks, their pore intergranular space likely becomes favorable for the life of anaerobic bacteria, which are incomparably smaller than pores in the oil-bearing rocks and whose lifetime in the anabiotic state in the absence of nutrients can last for millions of years [9]. Anaerobes are able to rapidly, virtually explosively, proliferate and form, under favorable nourishment and

heating conditions, an original biomass that is commensurable with the reserves of oil and gas fields. Calculations indicate that the number of bacteria equal to 2^n (the minimum size of bacteria is of the order of a few micrometers), which were produced by the mitosis of a single cell (the maximum duration of a singly mitosis cycle is of the order of ~30 min) should exceed the reserves of the Romashkinskoe field (~4 bln. tons) for $n \approx 120$ mitosis cycles, i.e., within approximately 2.5 days. In light of these data and proceeding from the criteria of the catagenetic transformations of oils (proposed by leading geochemists), we focused our research on the development of new approaches to the identification of genetic aspects of oil formation.

EXPERIMENTAL

Our research was based on studying samples of oils of offshore genesis that were not affected by secondary biodegradation processes in the Carboniferous and Upper Devonian deposits of the Romashkinskoe and Arkhangel'skoe fields in Russia and samples of catagenetically more evolved Neogene oils from the White Tiger field in Vietnam (table, Fig. 1). The samples for our research were taken from the core of boreholes and from hydrocarbons outpouring from oil wells. The oil samples from the core were extracted with organic solvents and were then analyzed for the concentrations of alkanes of normal and isoprenoid structure $n(C_{12}–C_{20})$ and $i(C_{14}–C_{25})$, which are used in geochemical studies to determine the degree of the catagenetic transformation of oils. The oil alkanes were separated on a KHROM-5 chromatograph with capillary columns made of stainless steel 0.25 mm in inner diameter and 25 m long, with Apiezon L as the stationary liquid phase and with the use of a flame-ionization detector. The chromatographic separation of oil alkane was conducted at the linearly programed temperature increase of the capillary columns from 100 to 310°C at a heating rate of 4 K/min. The carrier gas was hydrogen. This

Indicators of the degrees of the thermal maturity K_i and the catagenetic transformation K, I, c_α of oils of different ages and their pristane/phytane ratios

| No.	Field	Stratigraphic unit	Age, Ma	Depth, m	Pr/Ph	K_i	K	I	c_α
1	2	3	4	5	8	9	10	11	12
	Oils of Carboniferous deposits at the Romashkinskoe and Arkhangel'skoe fields								
1	Romashkinskoe	Bobrikovian	342	–	0.70	0.76	2.83	1.42	1.99
2	"	"	"	1160	0.70	0.73	1.27	0.62	2.05
3	"	"	"	1198	0.65	0.71	0.91	0.42	2.17
4	Arkhangel'skoe	Tulian	341	1179	0.72	0.66	2.15	0.99	2.17
5	"	"	"	–	0.70	0.75	1.63	0.80	2.04
6	Romashkinskoe	Bashkirian	329	–	0.72	0.78	1.79	0.91	1.97
7	"	"	"	–	0.69	0.79	1.92	0.99	1.94
8	"	Vereian	327	887	0.72	0.84	1.71	0.92	1.86
9	"	"	"	832	0.67	0.75	1.67	0.87	1.92
10	"	"	"	845	0.63	0.76	1.55	0.79	1.96
Average value			334	1012	0.69	0.753	1.743	0.873	2.006
Averaged deviation from the average value			–	–	–	0.033	0.305	0.173	0.080
	Oils of Devonian deposits at the Romashkinskoe field								
1	Zelenogorskaya	Pashian	368	1682	0.81	0.53	1.02	0.36	2.83
2	"	"	"	–1696	0.86	0.56	3.44	1.31	2.63
3	"	"	"	1676	0.86	0.56	1.89	0.73	0.59
4	"	"	"	–	0.66	0.59	0.62	0.25	0.48
5	Minnibaevskaya	"	"	1767	0.85	0.59	3.11	1.26	2.47
6	"	"	"	1750	0.80	0.56	1.35	0.54	2.50
7	"	"	"	–	0.87	0.58	2.03	0.82	2.48
8	"	"	"	–	0.84	0.54	1.49	0.61	2.44
9	"	"	"	–	0.83	0.67	1.82	0.79	2.30
10	"	"	"	1725	0.81	0.64	2.27	0.95	2.39
Average value			368	1725	0.82	0.582	1.904	0.762	2.511
Averaged deviation from the average value			–	–	–	0.032	0.647	0.264	0.103
	Oils of Early Miocene Neogene deposits at the White Tiger field, Vietnam								
1	White Tiger	Miocene	25	3300–3500	2.05	0.30	0.75	0.19	3.95
2	"	"	"	"	2.51	0.31	1.06	0.25	4.24
3	"	"	"	"	2.47	0.27	0.82	0.16	5.12
4	"	"	"	"	2.31	0.30	0.83	0.20	4.15
5	"	"	"	"	2.18	0.21	0.98	0.20	4.90
6	"	"	"	"	1.50	0.22	0.74	0.15	4.93
7	"	"	"	"	2.00	0.29	0.57	0.13	4.38
8	"	"	"	"	2.21	0.23	0.79	0.16	4.94
9	"	"	"	"	2.15	0.20	0.92	0.19	4.84
10	"	"	"	"	2.20	0.22	1.00	0.19	5.26
11	"	"	"	"	2.23	0.29	0.90	0.21	4.29
Average value			25	3400	2.16	0.258	0.851	0.184	4.637
Averaged deviation from the average value					–	0.038	0.11	0.025	0.396
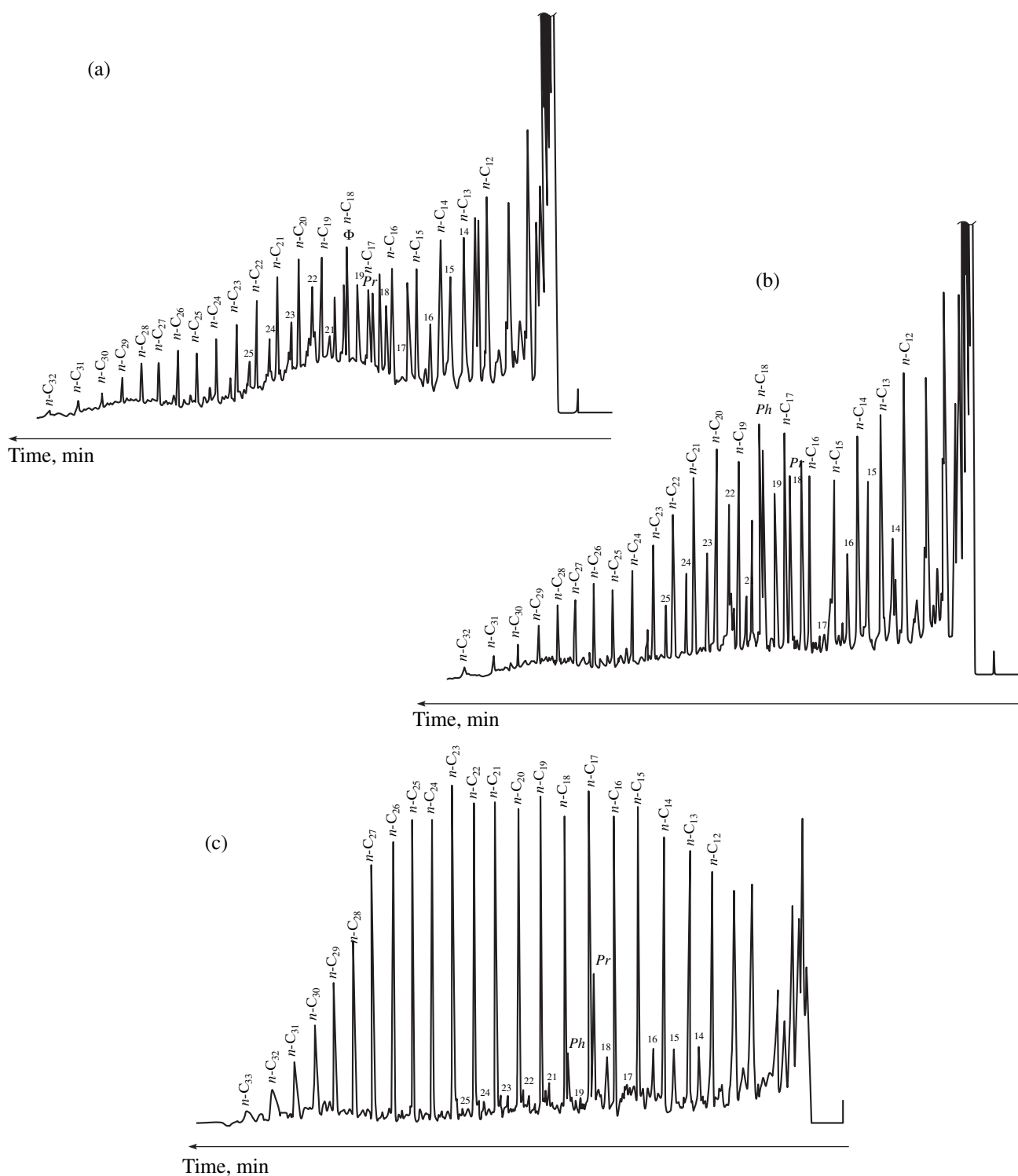
Fig. 1. Typical chromatograms of oils from (a) Carboniferous deposits at the Romashkinskoe and Arkhangel'skoe oil fields in Tatarstan, (b) Late Devonian (Pashian) deposits of the Romashkinskoe field, and (c) Neogene (Early Miocene) deposits of the White Tiger field, Vietnam. Indices n in n-C_n expression denotes the number of carbon atoms in the molecule of n-alkane or n-isoprenane; Pr is pristane and Ph is phytane.

chromatographic technique allowed us to immediately determine the concentrations of alkanes in crude oil samples [10], without their preliminary dehydration, which facilitated the better preservation of the relations between the concentrations of alkanes of normal and isoprenoid structure in the oils.

In order to minimize the possible dependence of the analytical results on the activity of carbonate carbon in the organomineralic complexes of the carbonate rocks, we analyzed samples of terrigenous rocks [11].

RESULTS AND DISCUSSION

The degree of the catagenetic transformation of oils is assayed in geochemistry based on various criteria, which make use of oil alkanes. The most reliable and informative of them, which were used by leading geochemists: Hunt [12] and Chakhmakhchev [13], and others, are as follows:

$$K_i = \frac{i(C_{19} - C_{20})}{n(C_{17} - C_{18})}, \quad K = \frac{n(C_{12} - C_{20})}{n(C_{21} - C_{35})}.$$

In order to improve the accuracy of the determinations by utilizing the maximum possible number of oil alkanes of normal and isoprenoid structure, which are separated by high-precision gas–liquid chromatography, the author also considered [14] the following ratios, by analogy with K_i and K:

$$I = \frac{i(C_{14} - C_{25})}{n(C_{21} - C_{35})}, \quad c_0 = \frac{K}{I} = \frac{n(C_{12} - C_{20})}{i(C_{14} - C_{25})}.$$

The values of K_i, K, I, and c_0 calculated for the oils of various ages are listed in the table.

For the assessment of the seismotectonic influence on the oil reservoir, the author introduced [15] indicator D, which is based on the values of K, I, and c_0 and reflects the degree of the seismotectonic loosening of the oil reservoir rocks

$$D = \frac{(\Delta K + \Delta I)/2}{\Delta c_0} - 1, \qquad (1)$$

where ΔK and ΔI are the averaged deviations of the indicators K and I of the catagenetic transformations of oils, and Δc_0 is the relative accuracy of the measured c_0 values.

According to the values of D calculated by Eq. (1) and arranged on a nine-grade scale, similar to the Richter scale, the intensity of seismotectonic influence on an oil-bearing stratum in the Neogene, Carboniferous, and Devonian oil reservoir in question is 2.3, 3.7, and 7.6, respectively.

The comparison of the results of the effect of seismotectonic activity during a single megacycle [16] on discrete strata of a single field indicates that the oil reserves contained in various strata of the Romashkinskoe field (before its commission), for example, in the Devonian (in the Pashian reservoir, which contains the main reserves of the field) and Carboniferous deposits, are in strong correlation with the estimated intensity of seismotectonic effect on the strata. This suggests that the oils of the Romashkinskoe field can be genetically related to magmatic fluids.

Deep drillholes through the arch of the Romashkinskoe field penetrated the crystalline basement to a depth of 5099 m and detected deep fluids that contained ~40% carbon dioxide, 21% methane, 5.8% hydrogen, 3.6% helium, and 0.1% heavy hydrocarbons [16]. Calculations indicate that the overall hydrogen content in the fluids is equal to ~11%, including hydrogen chemically bound in methane, which corresponds to practically 100% water (in recalculation to the molecular mass) and suggests that carbon chemically interacted with magmatic water and produced the methane, hydrogen, and carbon dioxide of the deep fluids. The presence of free hydrogen in the magmatic fluids results in reducing conditions and is favorable for the origin of oil. With regard for the occurrence of other possible components, for example, compounds containing sulfur and nitrogen, this composition suggests that fluids from the crystalline basement of the Romashkinskoe field could serve, by analogy with black smokers [7], as the nutritional medium for anaerobic bacterial communities [9].

The K–I plots for the oils in question (Fig. 2) display linear dependences between these parameters [14]. The straight lines are characterized by statistically significant correlation coefficients: 0.99, 0.99, and 0.84 for the Carboniferous, Devonian, and Neogene oils, respectively, at a minimum statistically significant value of 0.74.

The slope angles of the straight lines in the diagrams for the Carboniferous, Devonian, and Neogene oils are $\alpha_1 = 63.3°$, $\alpha_2 = 68.5°$, and $\alpha_3 = 78.9°$. The slope angles for the Parshian oils were determined accurate to $\pm 1\%$.

The linear character of the K–I plots testifies to the preservation of the original proportions in the concentrations of normal and isoprenoid alkanes in the oils, a feature that can be used as a criterion of the absence of the effect of secondary biodegradation on the oil compositions.

The K–I plot for the Pashian oils can be represented in a generalized form by the equation

$$K = a + bI, \qquad (2)$$

where a and b are the constants of the equation (b is the tangent of the slope of the straight lines, and a is the ordinate-axis intercept cut of this straight line). The values of a and b for the Pashian oils are equal to 0.01 and 2.54, respectively. If the value of a in Eq. (2) is neglected (it is close to zero), the equation for the straight line can be written using the value of the polar angle

$$K = bI = I \tan \alpha. \qquad (3)$$

The polar K–I link between the concentrations of $n(C_{12} - C_{20})$ and $i(C_{14} - C_{25})$ alkanes is caused by the single mechanism that produced them and their common source. It follows from the chromatograms in Fig. 1 that the oil alkanes with boiling temperatures of above ~150–200°C mostly have isoprenoid and normal struc-

tures with low concentrations of isomers. In the absence of an abiogenic oil-producing mechanism, the only source of isoprenoid oil hydrocarbons can be organic isoprenoid structures, which can be produced by autotrophic anaerobes, with the latter able, as was mentioned above, to rapidly proliferate under favorable conditions, when the sedimentary rocks are penetrated by magmatic fluids and heated by them. The linear character of the K–I dependences, which was caused by the preservation of the initial proportions of normal and isoprenoid alkanes in the oils, is discernible in the series of oils of different ages and various thermal maturity, i.e., is of universal character. The absence of the biodegradation of the main oil series can be related to the catagenetic transformations of the active or dormant anaerobic bacteria of the oils within the temperature range of their thermal instability.

At the same time, the generation of oil alkanes of n structure could result from inorganic synthesis, according to the Fisher–Tropsch reaction [17], from carbon dioxide and hydrogen, which are contained in sufficient amounts in magmatic fluids with the preferable yield of liquid hydrocarbons of n structure. The facts and considerations presented above suggest that the source of the oils could be of mixed biogenic–abiogenic character, with the involvement of magmatic fluids and the biomass of autotrophic anaerobes produced in this medium.

It also follows from Eq. (3) that, when α tends to zero during the initial stages of oil catagenesis,

$$\lim_{\alpha \to 0} \frac{K}{I} = \lim_{\alpha \to 0} \frac{n(C_{12} - C_{20})}{i(C_{14} - C_{25})} = \lim_{\alpha \to 0} \tan\alpha = 0. \quad (4)$$

As can be seen from Eq. (4), when $\alpha \longrightarrow 0$, the value of K becomes zero, as also does the corresponding sum of n-alkanes ($C_{12} - C_{20}$), but not the value of I and the sum of isoprenanes $i(C_{14} - C_{25})$, which is, in the limiting case, inherited during early catagenetic stages from anaerobic bacteria bearing isoprenoid structures and functioning in sedimentary rocks. At the same time, for oils with the maximum and catagenetic transformation, i.e., at $\alpha \longrightarrow 90°$,

$$\lim_{\alpha \to 90} \frac{I}{K} = \lim_{\alpha \to 90} \frac{i(C_{14} - C_{25})}{n(C_{12} - C_{20})} = \lim_{\alpha \to 90} \cot\alpha = 0. \quad (5)$$

This equation shows that, when $\alpha = 90°$, the value of I becomes equal to zero.

These relations explain the reasons for the relatively low concentrations of isoprenoid hydrocarbons in oils with a high degree of catagenetic transformations.

According to the thermodynamics of a quasi-leak-proof oil-bearing bed, an increase in its temperature should bring about irreversible processes of the catagenetic transformation of the original organic matter with the predominant accumulation of thermally more stable low-molecular oil compounds, including alkanes of normal structure.
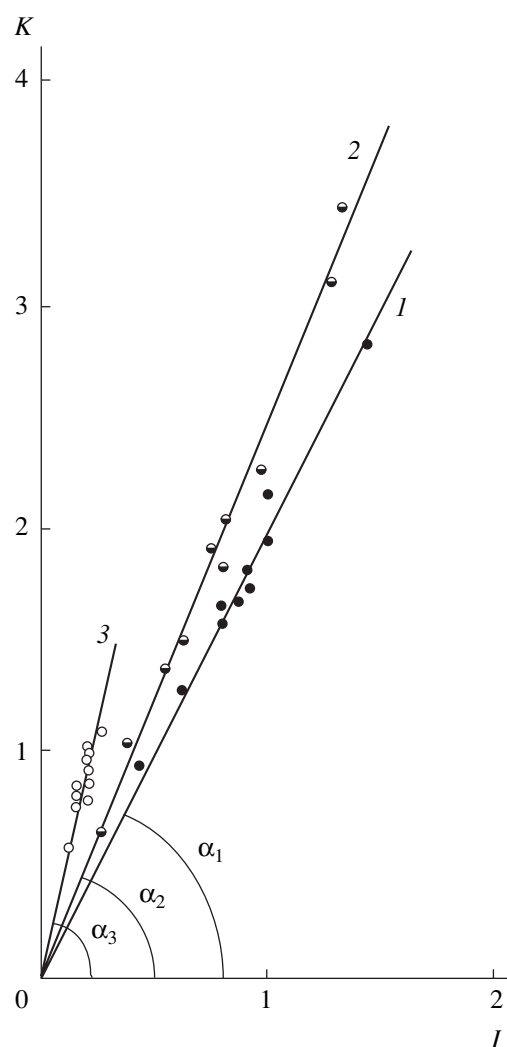

Fig. 2. K–I dependences of polar type for (1) Carboniferous, (2) Devonian, and (3) Neogene oils.

These thermodynamic tendencies should also be manifested in the isoprenane series, for which a decrease in the concentrations in oils with higher degree of catagenetic transformations shifts toward the enrichment in lighter components (table), with the average ratios of the concentrations of the most widespread pristane and phytane, Pr/Ph, increasing with the transition from Carboniferous to Devonian and Neogene oils. Figure 3 illustrates this tendency as a dependence of the average values of this ratio on the degree of the catagenetic transformation of oils c_0. This has the form of an exponential function, which is typical of thermal processes underlying oil catagenesis.

The dependences presented above show that variations in the pristane and phytane concentrations in oils with different degrees of their catagenetic transformations were largely caused by the thermodynamic conditions in the oil reservoir and, thus, do not directly correlate with the composition (humus, sapropel) of the
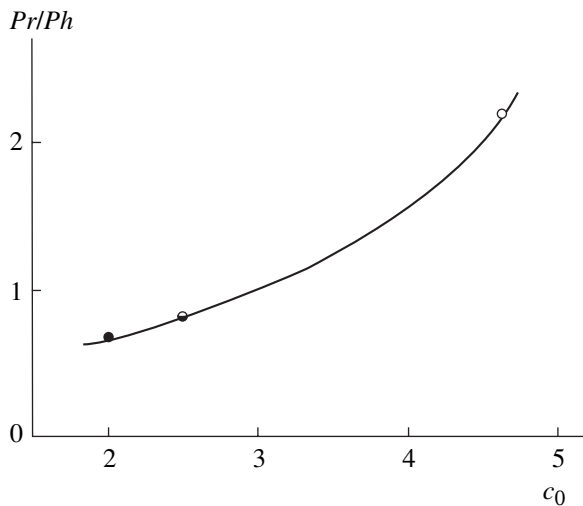
Pr/Ph

Fig. 3. Exponential dependence of the ratio of the concentrations of pristane and phytane in oils on the degree of the catagenetic transformation of these oils c_0. Oils: ●—Carboniferous, ◔—Devonian, ○—Neogene.
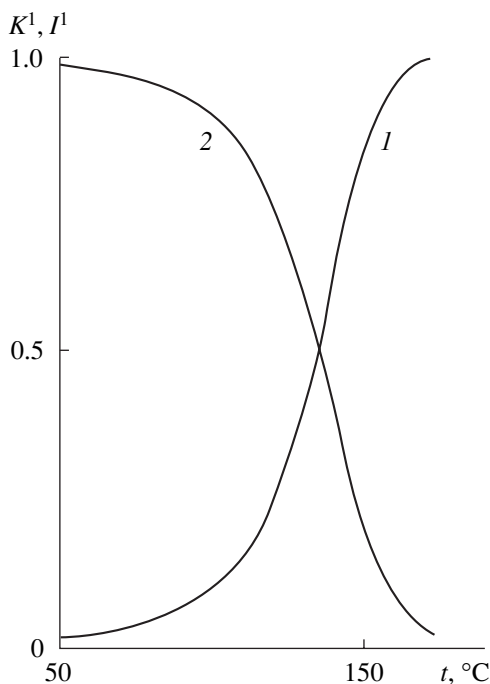
K^1, I^1

Fig. 4. Generation of the (*1*) *n*-alkanes and (*2*) isoprenanes within the temperature range of oil catagenesis.

organic matter disseminated in the rocks. This suggests that the source organic matter (OM) of oils could be of some other genesis, for example, related to autotrophic anaerobes that bear isoprenoid structures [18].

Inasmuch as saturated alkanes of normal and isoprenoid structure do not chemically interact in oils, the linear character of the *K–I* dependences for oils with

various degrees of their catagenetic transformations could be caused by deep processes of the activated state nucleating in the original mixture of biogenic and inorganic compounds during various stages of catagenesis.

Variation in the degree of the catagenetic transformations of oils in the process of catagenesis can be related to variations in the value of c_0 by the differential equation

$$dc_0 = k_\alpha c_0, \qquad (6)$$

where dc_0 is the differential increment of the c_0 value, and k_0 is a temperature-dependent proportionality coefficient. After c_0 is transferred into the left-hand side of Eq. (6), its integration yields

$$\ln\frac{c_0}{c_{0_0}} = k_\alpha, \qquad (7)$$

where c_{0_0} is the initial degree of the catagenetic transformation of oils in the initial temperature segment of oil catagenesis.

In compliance with the Arrhenius equation, the proportionality coefficient k_α in Eq. (7) can be represented in a logarithmic form as a linear dependence on the inverse absolute temperature value

$$\ln k_\alpha = \ln\ln\frac{c_0}{c_{0_0}} = a - \frac{b}{T}, \qquad (8)$$

where a and b are constant for this equation, which are equal to 9.57 and 3331, respectively, and T is the absolute temperature (K).

Equation (8) can also be rewritten in the exponential form

$$k_\alpha = \ln\frac{c_0}{c_{0_0}} = Ae^{-\frac{E}{RT}}, \qquad (9)$$

where A is the preexponential Arrhenius factor, which is related to constant a in Eq. (8) by the expression $\ln A = a$; E is the activation energy of oil catagenesis, $E = \beta R = 6.6$ kcal/mol; R is the gas constant.

The relatively low value obtained for the activation energy of oil catagenesis is characteristic of natural processes, which occur within narrow temperature ranges. The value of constant a in Eq. (8) reflects the increase in the entropy of the original matter during its catagenetic transformations within the temperature range of oil catagenesis, from 50 to 175°C: $\Delta S° = aR = 19$ kcal/(mol grad).

Based on these equations, it was demonstrated in [15] that the vast Romashkinskoe oil field should have been produced without inflow of oils migrating from neighboring fields. Considered together with data on the local scarcity of organic matter and the isofacial thermal maturity of this matter, this highlights the genetic role of deep magmatic fluids in the genesis of this vast oil field.

For parameters $K' = \dfrac{K}{K + I} = \dfrac{c_0}{1 + c_0}$ and $I' = \dfrac{I}{K + I} = \dfrac{1}{1 + c_0}$, which are functions of c_0, the temperature dependences according to Eqs. (8) and (9) are shown in Fig. 4 (curves 1 and 2).

According to the data presented above for K', it can be seen that curve 1 includes segments with notably different increase rates of the concentrations of oil n-alkanes within the temperature ranges of 50–90°C (in which the increase rate is insignificant) and 110–175°C (in which the rates of this increase is at a maximum).

The temperature range of 110–175°C, which is characterized by the most active formation of alkanes, corresponds to the main oil-producing phase [19].

The dependence of the generation of isoprenanes within the temperature range of oil catagenesis (Fig. 4, curve 2) can be regarded in thermal analysis as a thermo-gravimetric line. The first-order temperature derivative of this dependence is presented as an asymmetrical peak AOC (Fig. 5), which is extrapolated to 200°C and reflects the actual process of nucleation during the catagenesis of the activation state centers of the original matter. The same diagram also shows symmetrical peak BOC, which corresponds to the generation of isoprenanes at the complete termination of the aforementioned nucleation at initial catagenetic temperatures of 50–60°C [20]. The comparison of these plots indicates that the left-hand segment of AOC peak is elevated relative to the original left-hand segment of peak BOC to temperatures of about 120–125°C, which suggests a higher thermal stability of some of the original biogenic material during oil catagenesis (shaded area in Fig. 5). Calculations indicate that the relative fraction of anaerobes with the highest thermal stability is approximately 15–20% of their overall mass. It can be seen in Fig. 5 that the maximum decrease in the intensity of the generation of oil isoprenanes, related to the catagenetic transformations of the thermally most stable anaerobes, corresponds to a temperature of ~110°C. As can be seen from the graphical data, the maximum thermal stability of anaerobes participating in the catagenetic process falls into the temperature range of 120–125°C, which is consistent with the microbiological results in [9].

The aforementioned possibility of the generation of significant amounts of organic matter by anaerobic bacteria actively proliferating under favorable conditions (abundant nourishment and the heating of the sedimentary rocks) suggests that the processes related to the genesis of oils can be geologically fast. This also pertains to the stage of the catagenetic transformations of the original matter of oils, as follows from the partial replenishment of the hydrocarbon reserves of some oil fields during their industrial development and in relation to the pathways of deep fluids [4, 5].
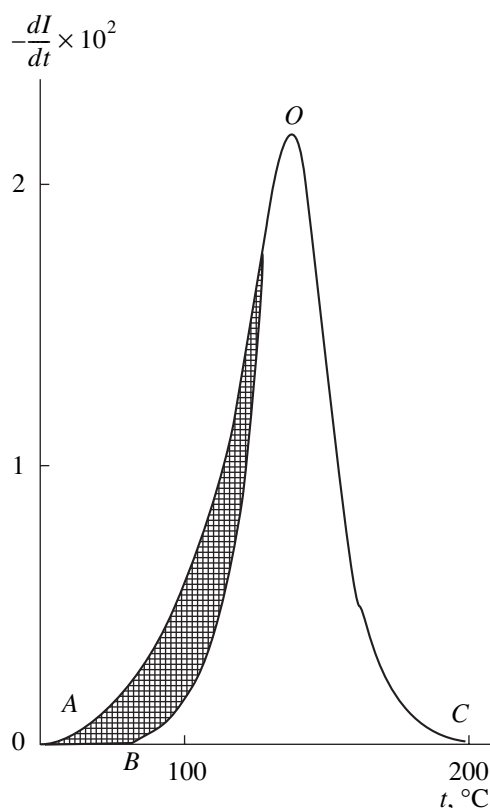

Fig. 5. First-order temperature derivative of the thermogravimetric function of the generation of oil isoprenanes during oil catagenesis.

It is natural to suggest that, if the fluids contain methane, hydrogen, and carbon dioxide, various reactions (for example, analogous to those used in the industrial synthesis of liquid hydrocarbons [17]) can proceed in the pore space of the sedimentary rocks at elevated formation pressures and temperatures.

The comparative analysis indicates that the activation energy of reactions that are utilized in the industrial synthesis of liquid hydrocarbons from carbon dioxide and hydrogen and proceed under favorable conditions and in the presence of efficient catalysts is much (more than thrice) higher than the activation energy of natural processes of oil catagenesis. This practically rules out the possibility that naturally occurring oils can be produced by direct synthesis from fluid components. Synthetic "oil products" contain neither isoprenoids nor naphthene hydrocarbons, which are intrinsic components of natural oils [21].

The facts and considerations presented above highlight genetic relations of oils with deep fluids.

We determined the relative mass of the thermally most stable anaerobes that participate in the generation of natural oil and the temperature of their activity (~125°C).

It is demonstrated that the genesis of oils is controlled by numerous interrelated factors and stages of a

single genetic chain. The source material of oils can be the inorganic components of magmatic fluids and the biomass of autotrophic anaerobes that can be produced at the inflow of magmatic fluids and the heating (under their effect) of marine and offshore sedimentary deposits. These ideas are in agreement with the results of independent X-ray diffraction studies [22], which have demonstrated that the major source of oil hydrocarbons is polynaphthene structures produced by the polymerization of organic compounds of mineral or biogenic genesis. Along with isoprenoid structures, these compounds are contained in the complex biomolecular compounds of anaerobes [8, 9, 23].

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