An inorganic origin of the "oil-source" rocks carbon substance

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Abstract. On the basis of an inorganic concept of the petroleum origin, the phase relationships of crystalline kerogens of black shales and liquid oil at the physicochemical conditions of a typical geobarotherm on the Texas Gulf Coast are considered. At the conditions of the carbon dioxide (CO_2) high fluid pressure, the process of oil transformation into kerogens of varying degrees of "maturity" (retrograde metamorphism) takes place with decreasing temperature and hydrogen pressure. Kerogen generation in black shale rocks occurs by the sequential transition through metastable equilibria of liquid oil and crystalline kerogens (phase "freezing" of oil). The upward migration of hydrocarbons (HC) of oil fluids, clearly recorded in the processes of oil deposit replenishment in oil fields, shifts the oil ↔ kerogen equilibrium towards the formation of kerogen. In addition, with decreasing of the hydrogen chemical potential as a result of the process of high-temperature carboxylation and low-temperature hydration of oil hydrocarbons, the "mature" and "immature" kerogens are formed, respectively.

The phase relationships of crystalline black shale kerogens and liquid oil under hypothetical conditions of high fluid pressure of the HC generated in the regime of geodynamic compression of silicate shells of the Earth in the result of the deep alkaline magmatism development. It is substantiated that a falling of hydrogen pressure in rising HC fluids will lead to the transformation of fluid hydrocarbons into liquid oil, and as the HC fluids rise to the surface, the HC ↔oil ↔ kerogen equilibrium will shift towards the formation of oil and kerogen.

It is round that both in the geodynamic regime of compression and in the regime of expansion of the mantle and crust, carboxylation and hydration are the main geochemical pathways for the transformation of oil hydrocarbons into kerogen and, therefore, the most powerful geological mechanism for the black shale formations.

Keywords: chemical potentials, phase diagrams, metastable equilibria, hydrocarbons, fluids, oil, kerogen, black shales, oil deposit replenishment, retrograde metamorphism, carboxylation, hydration

Introduction

The origin and evolution of carbonaceous matter of organo-mineralogical associations, widely represented even in ancient Archean geological rocks (Alleon et al., 2019), are fundamental problems. These problems have been reflected in alternative concepts of oil and kerogen formation in black shales, and have proved to be especially relevant in the past few years, due to the fact that black shales has become objects of commercial production. According to the most accepted organic (sedimentary-migration, "biogenic") concept, the formation of oil in carbonaceous oil source rocks is by the degeneration (catagenesis) of kerogen and bitumen under conditions of increasing temperature and increasing burial depth in sedimentary basins (Gubkin, 1975; Tissot, Velte, 1981; Petrov, 1984; Vassoevich, 1986; Hunt, 1996; Tissot, 2003; Kontorovich, 2004; Vandenbroucke, Largeau, 2007; Bjørlykke, 2015). It is believed that fossilized organic matter is the most important and, most likely, the only source of oil in the earth's crust (Kontorovich, Vyshemirsky, 1997; Curiale, Curtis, 2016), and the process of oil generation itself occurs in the main phase (zone) of oil formation ("oil window") at temperatures from 80 to 150–180 °C by thermal and catalytic "cracking" of kerogen and bitumen with the formation of low molecular weight oil components (Tissot, Velte, 1981; Kontorovich, Melenevsky, 1988; Hunt, 1996).

The fundamental work of Richard Helgeson and coauthors (Helgeson et al., 2009) provides a thermodynamic substantiation of a geochemical and

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geological alternative to the traditional nonequilibrium "cracking" paradigm of oil generation in hydrocarbon oil source rocks. This alternative is the incongruent melting of kerogen with an increase in the burial depth of organic matter. The equilibrium phase relationships of oil, bitumen and kerogens of various oxidation states, given in these calculations, are considered on the basis of the "biogenic" concept of naphthide genesis, and it is assumed that the maturation of kerogen and oil formation are inevitable consequences of redox disproportionation reactions caused by progressive (prograde) metamorphism of organic-carbonaceous ("biogenic") raw materials with increasing pressure and temperature. According to this concept, the general sequence of events should look like this: buried organic matter → carbonaceous shales (kerogen, bitumen) → (oil, gas) with a rather unnatural immersion of the original organic matter into the region of high depths, temperatures and lithostatic pressures.

However, the inorganic concept of the origin of oil (Mendeleev, 1949; Kudryavtsev, 1951, 1973; Porfir'ev, 1974; Kropotkin, 1986; Gold, 1992; Letnikov, 2005; Timurziev, 2007; Marakushev, Marakushev, 2008; Kutcherov, Krayushkin, 2010; Simonyan, 2016; Muslimov et al., 2019) postulates a deep inorganic source of oil carbon, instead of a surface biogenic source. Then, with a decrease in temperature and pressure, the sequence of events should go in the opposite direction (the process is opposite to the experimental pyrolysis): endogenous hydrocarbons → (oil, gas) → carbonaceous shales (kerogens, bitumen, asphaltenes) → shungite → graphite (regressive or retrograde metamorphism). In this work, the thermodynamic equilibrium relationships between the phases of liquid oil and solid kerogen of black shales are analyzed, and the sequence of transformation of carbonaceous matter in the process of ascent of deep fluids to the Earth's surface is substantiated.

Methodical approach

The paragenetic analysis of the C–H–O system used in this work is based on the method of thermodynamic potentials (Gibbs, 1950; Korzhinskii, 1959), which makes it possible to study the system of geochemical organomineral facies (areas of thermodynamic stability) (Marakushev, Perchuk, 1966; Marakushev, Belonogova, 2009). The research is based on the Gibbs phase rule, according to which the number of degrees of freedom of an equilibrium thermodynamic system is equal to the number of independent components of the system plus two minus the number of phases. The phase rule is not limited to considering the extensive parameters of the system and therefore is fully applicable to open systems, for which the chemical potential is an independent parameter (Korzhinskii, 1966). Phase equilibria in a system are determined by the equality of

the chemical potential of any component in all phases and are described by phase diagrams that determine the composition and the ratio between the masses of the equilibrium phases. Thermodynamic calculations are based on the assumption that irreversible reactions that control the metamorphic process proceed in accordance with the second law of thermodynamics to a state of metastable equilibrium, which correspond the metastable minimum of the Gibbs free energy for the system. Oils, bitumens and kerogens are considered as substances that have their own thermodynamic characteristics and are capable of forming stoichiometric phases in the phase space of temperatures, pressures and chemical potentials of environmental substances. Accordingly, both light and heavy oils ($C_{8.8}H_{16.9}$, $C_{7.7}H_{14.2}$, $C_{7.6}H_{13.0}$, $C_{7.9}H_{12.2}$, $C_{8.1}H_{11.5}$) can be in stoichiometric phase equilibrium with solid kerogen phases ($C_{128}H_{68}O_7$ and $C_{292}H_{288}O_{12}$), as well as with the hydrocarbon gas phase (alkanes (C_nH_{2n+2}) according to the equations:

$$8.8C_nH_{2n+2} = nC_{8.8}H_{16.9} + (8.8 + 0.35n)H_2,$$
$$7.7C_nH_{2n+2} = nC_{7.7}H_{14.2} + (7.7 + 0.6n)H_2,$$
$$7.6C_nH_{2n+2} = nC_{7.6}H_{13} + (7.6 + 1.1n)H_2,$$
$$7.9C_nH_{2n+2} = nC_{7.9}H_{12.2} + (7.9 + 1.8n)H_2,$$
$$8.1C_nH_{2n+2} = nC_{8.1}H_{11.5} + (8.1 + 2.35n)H_2.$$

Kerogens with relatively high H/C are usually amorphous, but the crystallinity of kerogen increases with a decrease in H/C of kerogen in the process of «maturation», due to an increase in the size of aromatic clusters within the structures. In (Helgeson et al., 2009) it was shown that the consideration of solid solutions of kerogen instead of crystalline components has an insignificant effect on the results of thermodynamic calculations. The idealized kerogen structures considered belong to the C–H–O system, which does not consider nitrogen and sulfur-containing heterocycles – pyrroline, pyrrolidine and thiophene, which are usually stable functional groups of kerogen.

Hydrogen fugacity diagrams were used to calculate the chemical potentials of hydrogen at their corresponding temperatures (Helgeson et al., 2009, Fig. 21, 23), and from the diagram (Helgeson et al., 2009, Fig. 5), at the point of intersection of straight lines, the chemical potentials of gaseous oxygen (μ_{O2} = –402.64 kJ/mol) and hydrogen (μ_{H2} = –15.69 kJ/mol) were determined at a temperature of 150 °C and a pressure of 830 bar, associated with fugacity (f), according to the equations $\mu_{O2} = \mu^0_{O2} + 2.303\ RT\log f_{O2}$ and $\mu_{H2} = \mu^0_{H2} + 2.303\ RT\log f_{H2}$, where μ^0_{H2} and μ^0_{O2} refer to the chemical potentials of gaseous H_2 and O_2 in the standard state, R is the gas constant (8.3145 J/mol·K), and T is the temperature in Kelvin. We used the PT parameters along a typical geobarotherm of the US Gulf Coast from (Helgeson et al., 2009). The reaction equations presented in the diagram (Fig. 5) can be written as a system of algebraic equations:

$14.545P + 3.5O_2 = K + 88.909H_2,$

$P + 8.8O_2 = 8.8CO_2 + 8.45H_2,$

$K + 124.5O_2 = 128CO_2 + 34H_2,$
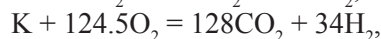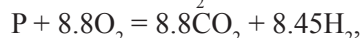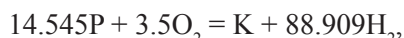
where $P = C_{8.8}H_{16.9}$ (oil), $K = C_{128}H_{68}O_7$ ("mature" kerogen). For each reaction, it is possible to write down the expression of the free energy of the reaction in terms of the energies of formation of these substances. For example: $\Delta G_r = \Delta G_k + 88.909\Delta H_2 – 14.545\Delta G_p – 3.5\Delta O_2$ in a state of equilibrium $3.5\Delta O_2 = (\Delta G_k – 14.545\Delta G_p) + 88.909\Delta H_2$, where ΔG_r is the free energy of the reaction , and ΔG_p and ΔG_k – free energies of formation of oil and kerogen at 150 °C and pressure 830 bar, respectively. Knowing the chemical potentials O_2 and H_2, it is possible to calculate the free energy of the reaction, in this case $\Delta G_r = \Delta G_k – 14.545\Delta G_p$, and so on for each reaction. The resulting system of algebraic equations is solved by the usual substitution method. Thus, we determined the free energies of formation of crystalline kerogen (K_2), liquid oil and water, gaseous carbon dioxide and hydrocarbons: methane, ethane, ethylene, acetylene, propane, butane, hexane, and decane at 150 °C and a pressure of 830 bar (Table).

Results and discussion

The C–O–H composition diagram (Fig. 1) shows the average elemental compositions of organisms in various biological taxa (Vandenbroucke, Largeau, 2007; Ermakov, Kovalsky, 2018), including continental plants, plankton, and algae, which are considered to be the main source of carbonaceous matter of oil source rocks. Kerogen is defined as an insoluble sedimentary organic matter (geopolymer) capable of generating oil, and the study of its elemental composition made it possible to distinguish three types of kerogen, designated in the diagram (Fig. 1) as I, II, and III (Tissot, Welte, 1981). It is believed that the source of organic matter for type I kerogen with a high H/C ratio is lacustrine algae, type II kerogen – marine plankton, algae, terrestrial plants, type III kerogen with the lowest H/C ratio – land plants and animals (Tissot, Welte, 2013; Sephton, Hazen, 2013; Huang et al., 2018). It is generally accepted that with a decrease in the H/C ratio, oil and kerogen «maturation» takes place, and "immature" kerogens transforms into "mature" ones. A schematic representation of the idealized structures of type II ("immature" kerogen) and type III ("mature") kerogens considered in this work is shown in Fig. 2. The composition of five types of

oils, according to (Helgeson et al., 2009), is located on the diagram between the compositions of alkanes and condensed hydrocarbons, and their average composition varies from highly paraffinic (with the highest H/C ratio) to aromatic-naphthenic (low H/C) crude oils in accordance with the Tissot classification (Tissot, Welte, 2013).

The "biogenic" concept postulates that oil, bitumen, shungite, graphite, etc. are formed exclusively from carbonaceous kerogens (decomposition products of biological matter), while in the inorganic concept, on the contrary: oil concentrated in reservoirs as a result of the rise of fluid inorganic hydrocarbon matter, which modifies to form bitumen and kerogen of black shales. In other words, either oil is formed from kerogen (organic concept) or kerogen from oil (inorganic concept). According to the inorganic concept, hydrocarbons are stable exist under high thermobaric conditions and are in a metastable state in the earth's crust and upper mantle (Karpov et al., 1998; Zubkov, 2005; Marakushev and Marakushev, 2006a; Kolesnikov et al., 2017). When they rise to the surface, oil deposits are formed, the retrograde metamorphism of which leads to a constant decrease in the H/C ratio in them. Thus, first of all, light (paraffinic), then heavy (aromatic-naphthenic) oils, "mature" and "immature" kerogens, bitumen, diamandoidoids, asphaltenes and, finally, graphite are formed (Fig. 1). Accordingly, the composition of "primary" highly paraffinic oil should be closest to the composition of alkanes (C_nH_{2n+2}).

Based on the thermodynamic characteristics of substances from (Helgeson et al., 2009), calculated for the physicochemical conditions of geobarotherm on the shelf of the Gulf of Mexico, a diagram of the chemical potential of hydrogen – temperature was constructed (Fig. 3). This diagram shows the thermodynamic relationships of five phases: "immature" ($C_{292}H_{288}O_{12}$) and "mature" ($C_{128}H_{68}O_7$) pseudocrystalline kerogens (K_1 and K_2, respectively), gaseous CO_2 (g), liquid water (H_2O) and a typical representative of crude oil, liquid alkane 2-methylpentane (2-MP, C_6H_{14}). In this phase space of the C–O–H chemical system, hydrogen, being a chemical potential, passes from extensive parameters to intense ones, and the system becomes two-component (C–O). According to the phase rule, the number of degrees of freedom (C) in an equilibrium thermodynamic system is equal to the number of independent components

Compound	ΔG (kJ/mol)	Compound	ΔG (kJ/mol)	Compound	ΔG (kJ/mol)
Kerogen (c)	-964.78	CO_2 (г)	-395.0	C_2H_6 (г)	-31.79
Oil (l)	-65.35	CH_4 (г)	-23.74	C_2H_4 (г)	-16.1
C_2H_2 (g)	-0.41	C_3H_8 (г)	-39.84	C_4H_{10} (г)	-47.89
C_6H_{14} (g)	-64.0	$C_{10}H_{22}$ (г)	-96.19	H_2O (ж)	-215.6

Table. Free energies of Gibbs formation of crystalline kerogen ($C_{128}H_{68}O_7$), gaseous hydrocarbons and carbon dioxide (CO_2), liquid oil ($C_{8.8}H_{16.9}$) and water (H_2O) at a temperature of 150 °C and a pressure of 830 bar

Fig. 1. Phase diagram C–O–H of the compositions of living organisms (dry matter), oils and kerogens. The atomic amount of oxygen in the substances under study is doubled. Average compositions of five types of crude oils according to (Helgeson et al., 2009) are indicated by large pink triangles in the sequence of decreasing H/C ratio: $C_{8.8}H_{16.9} \rightarrow C_{7.7}H_{14.2} \rightarrow C_{7.6}H_{13.0} \rightarrow C_{7.9}H_{12.2} \rightarrow C_{8.1}H_{11.5}$. Hydrocarbons are dark blue triangles. Stars are the elemental composition of continental and marine plants and animals, plankton and bacteria according to (Vandenbroucke, Largeau, 2007; Ermakov, Kovalsky, 2018). Red circles are the compositions of idealized natural kerogens from (Helgeson et al., 2009). Black squares are the compositions of experimental high-temperature kerogens (Huang et al., 2018). Three groups of kerogens in accordance with the Tissot classification are surrounded by dotted circles and are designated by Roman numerals (I, II, III). Composition of pyrobitumen from (Helgeson et al., 2009), resins and asphaltenes from (Tissot, 2003).

(K) minus the number of phases (Φ) plus two external factors (pressure and temperature): C = K – Φ + 2. Thus, in the system under consideration invariant equilibria are four-phase, monovariant – three-phase, and divariant stability fields (facies) – two-phase (denoted by linear paragenesis). Invariant paragenesis of four phases (points on the diagram at temperatures of 159 and 195 °C) correspond to metastable equilibria:

$$C_{292}H_{288}O_{12} + 119.789H_2O = 37.684C_6H_{14} + 65.895CO_2$$

and

$$C_{292}H_{288}O_{12} = 1.705C_{128}H_{68}O_7 + 12.291C_6H_{14} + 0.033CO_2$$

Each invariant equilibrium is coordinated by four three-phase monovariant equilibria separating the divariant two-phase facies.

Fig. 2. Structures of idealized pseudocrystalline "immature" ($K_1 – C_{292}H_{288}O_{12}$) and "mature" ($K_2 – C_{128}H_{68}O_7$) kerogens according to (Helgeson et al., 2009)

During upward migration into fractured porous rocks the HC fluids, under conditions below their critical PT parameters, become liquid. The HC facies, represented by the paraffinic component of oil, liquid 2-methylpentane (2-MP), occupies a wide area under conditions of a high chemical potential of hydrogen (μ_{H2}) (upper field of the diagram, Fig. 3). When it decreases in the high-temperature region, 2MP hydration with the formation of CO_2, and then 2-MP carboxylation with the formation of "mature" (low H/C ratio) kerogen (K_2) occurs. In general, this chemical process is the sum of a number of reactions leading to a phase transition with the appearance of high-temperature metastable paragenesis of two phases – liquid 2-MP and crystalline "mature" kerogen K_2. With a further decrease in temperature, the liquid hydrocarbon phase disappears with the appearance of a facies with the paragenesis of kerogens K_1 and K_2. In the temperature range below the invariant paragenesis at 159 °C, the transformation of 2-MP into "immature" (high H/C ratio) kerogen (K_1) is mainly determined by the equilibrium of alkane hydration:

$$48.667C_6H_{14} + 12H_2O = K_1 + 208.667H_2.$$

In general, the diagram (Fig. 3) is a thermodynamic model of the transformation of liquid hydrocarbons into carbonaceous matter of black shales in the temperature range significantly higher than those of the traditional oil window, and this temperature range, apparently, can be significantly expanded (eg, Serovaiskii et al., 2020). Thus, during the upward migration of hydrocarbons of oil fluids, clearly recorded, for example, in the manifestation of oil reserves replenishing in the oil deposits (for example, Muslimov et al., 2019), the process of high-temperature fixation of CO_2 and low-temperature hydration of oil hydrocarbons occurs. As a result, "mature" and "immature" kerogenes are formed, respectively.

However, in most naphthide occurrences, the transformation of oil and kerogen occurs mainly at lower temperatures of the "oil window" from 60 to 180 °C (Tissot, Welte, 1981; Vassoevich, 1986; Kontorovich, Melenevsky, 1988; Hunt, 1996; Kontorovich, 2004). Such a decrease in the temperature regime is associated with the difference in the thermodynamic properties of liquid oils and alkanes. The fact is that the facies of the liquid hydrocarbon phase, represented in the diagram (Fig. 3) as pure 2-MP, shifts to the region of lower temperature and hydrogen fugacity as the activity of 2-MP decreases to its activity in the hypothetical oil
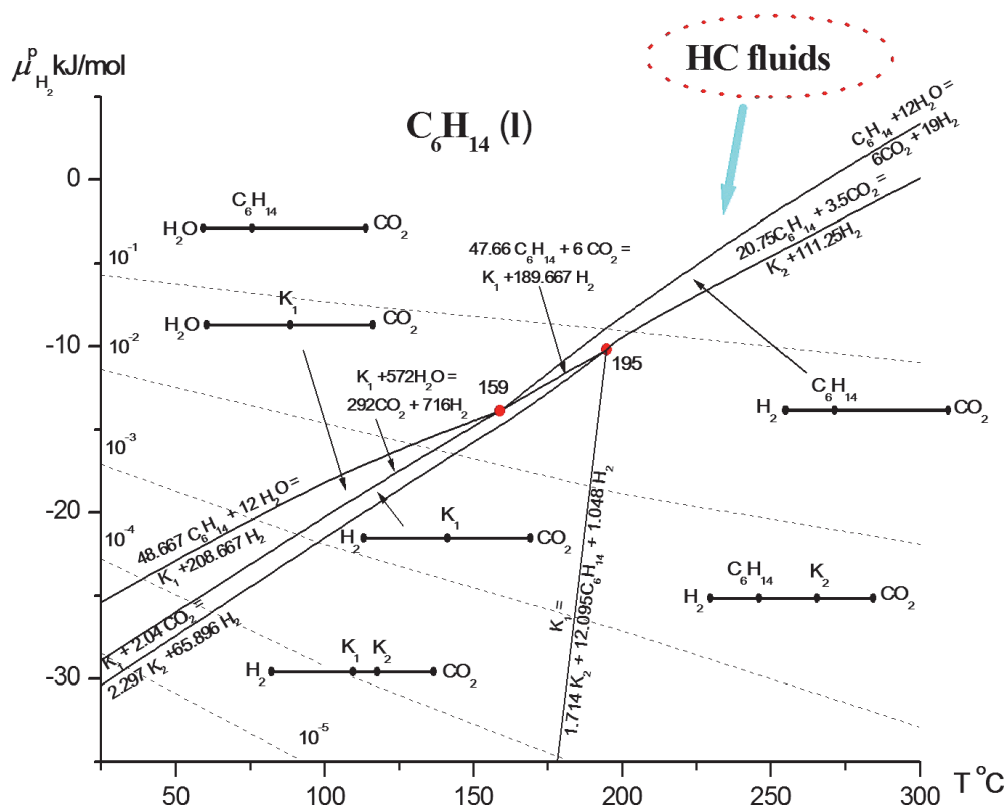

Fig. 3. Diagram of the dependence of the chemical potential of gaseous hydrogen (μ_{H2}) on temperature (T), demonstrating metastable phase ratios of pseudocrystalline kerogens K_1 and K_2, gaseous CO_2, liquid H_2O and a representative of liquid oil – alkane 2-methylpentane (2-MP, C_6H_{14}) in the C–H–O system. Lines are monovariant three-phase equilibria separating the divariant stability fields (facies) of substances. The points indicated by the temperature value are the invariant four-phase equilibria. Thermodynamic characteristics of substances in the P-T conditions of a typical geobarotherm on the shelf of the US Gulf of Mexico from (Helgeson et al., 2009). The CO_2 fugacity determines the fluid ambient pressure of 830 bar. The logarithms of the activity of liquid water ($\dot{I}_2\hat{I}$) and 2-methylpentane (2-MP, C_6H_{14}), as well as solid "mature" (K_2, $C_{128}H_{68}O_7$) and "immature" (K_1, $C_{292}H_{288}O_{12}$) kerogens are equal to one for pure liquid and solid phases, respectively. Parageneses in divariant facies are presented in line diagrams. Dotted lines (10^n) are fugacity isobars of molecular hydrogen.

($C_{8.8}H_{16.9}$), which correspond to the minimum value of Gibbs free energy in stoichiometric phase equilibrium oil ↔ kerogen (Helgeson et al., 2009). In other words, replacement of the hydrocarbon phase with the phase of crude oil (aliphatically enriched oil with an average composition of $C_{8.8}H_{16.9}$, which corresponds to H/C = 1.92 and O/C = 0) has a significant effect on the position of invariant points and monovariant equilibria emanating from them, which move, as shown in the diagram (Fig. 4), to the region of lower temperatures (100 and 128 °C) and chemical potentials of hydrogen. In this temperature regime, with a decrease in the chemical potential of hydrogen, metastable phase transitions of liquid oil into solid "mature" (K_2) and "immature" (K_1) kerogens occur as a result of the processes of CO_2 fixation and hydration of oil, respectively. For example, the high-temperature equilibrium of carboxylation of liquid 2-methylpentane ($20.75C_6H_{14} + 3.5CO_2 = K_2 + 111.25H_2$) (Fig. 3) is replaced by the equilibrium of CO_2 fixation by oil ($14.148C_{8.8}H_{16.9} + 3.5CO_2 = K_2 + 85.548H_2$), which is already observed in the "oil window" temperature range (Fig. 4).

The equilibrium $C_{292}H_{288}O_{12}$ (K_1) = $1.71C_{128}H_{68}O_7$ (K_2) + $8.31C_{8.8}H_{16.9}$ + $15.65H_2$ separates the low-temperature facies with the paragenesis "immature" kerogen (K_1) – "mature" kerogen (K_2) and the high-temperature facies "mature" kerogen – oil (Fig. 4). In

(Helgeson et al., 2009), these phase relationships based on the biogenic concept are interpreted as a process of progressive incongruent melting of "immature" crystalline kerogen with the formation of liquid oil and "mature" crystalline kerogen, occurring with increasing depth and temperature. In our proposed inorganic interpretation, this phase transition with a decrease in temperature below 128 °C at depths of about 3 km can be called a regressive phase "freezing" of the liquid oil phase with the formation of paragenesis of crystalline phases of "mature" and "immature" kerogens. In general, a drop in the temperature and chemical potential of hydrogen leads to the phase "freezing" of liquid oil and its dehydrogenation (carboxylation and hydration reactions) with the formation of solid kerogen phases of various degrees of "maturity" (Fig. 4).

Let's look at the relationship of the three phases – liquid oil, gaseous CO_2 and solid kerogen at a temperature of 150°C on the diagram, the chemical potential of hydrogen (μ_{H2}) – chemical potential of oxygen (μ_{O2}) (Fig. 5). Oxygen and hydrogen in this system are intensive parameters, and, therefore, the considered three-component system C–H–O becomes one-component. In the phase space of these chemical potentials, the metastable paragenesis of three phases – liquid oil, crystalline "mature" K_2, and gaseous CO_2 is an invariant point, whereas monovariant equilibria
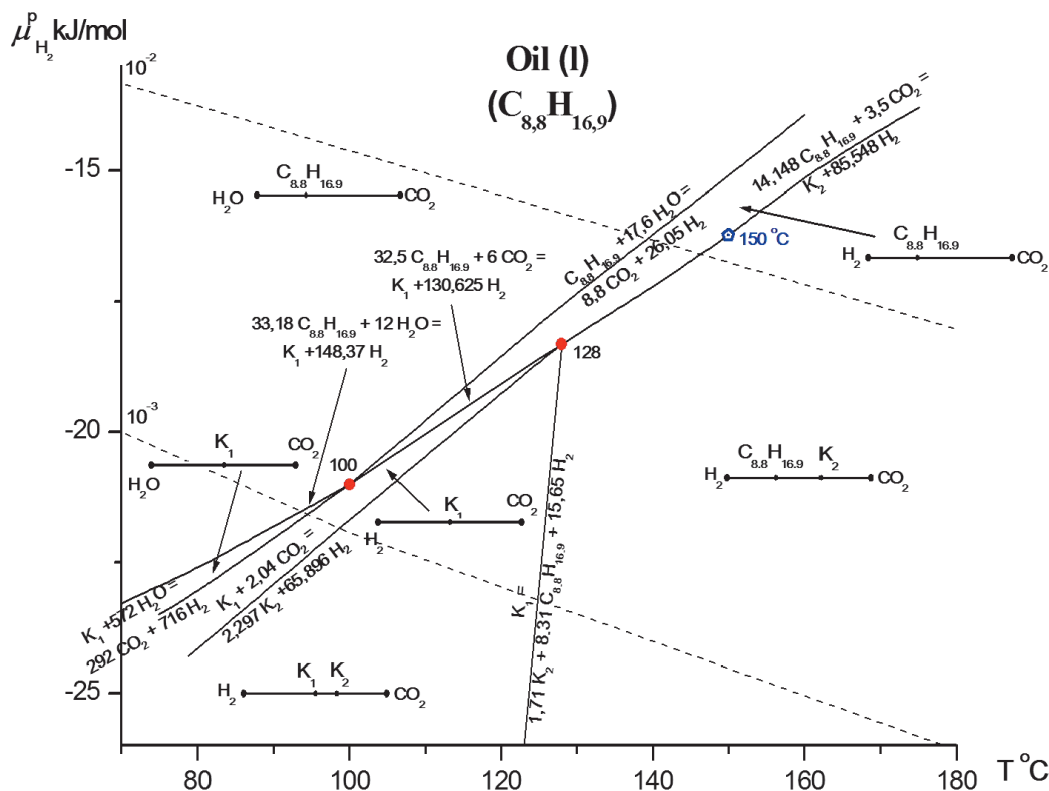

Fig. 4. Diagram of the dependence of the chemical potential of gaseous hydrogen (μ_{H2}) on temperature (T), showing metastable phase ratios of solid kerogens and crude oil ($C_{8.8}H_{19.9}$) in the C–H–O system in the "oil window" temperature regime. The calculated logarithm of oil activity corresponds to the logarithm of the activity of liquid methylpentane – 0.76 and 0.86 at 150 and 200 °C, respectively (Helgeson et al., 2009). The logarithms of the activity of liquid water (H_2O) and oil ($C_{8.8}H_{19.9}$), as well as pseudocrystalline "mature" ($C_{128}H_{68}O_7$) (K_2) and "immature" ($C_{292}H_{288}O_{12}$) (K_1) kerogens are equal to one for pure liquid and solid phases, respectively. The rest of the designations are shown in Fig. 3.

separate the regions of their thermodynamic stability. Crystalline kerogen, unlike liquid oil and gaseous CO_2, cannot be in paragenesis with liquid water and, therefore, according to (Helgeson et al., 2009), upon instant contact of "mature" kerogen with water under these P-T conditions, it should irreversibly interact with it with the formation of CO_2 or oil. However, the opposite scenario is more likely, when oil hydration occurs. For example, the formation of the considered "mature" kerogen at a temperature of 150°C and a pressure of 830 bar, accompanied by hydrogen degassing, is thermodynamically favorable: $14,545C_{8.8}H_{16.9}+7H_2O = C_{128}H_{68}O_7+95,905H_2$, $\Delta G^p_T = -9.81$ kJ.

With a decrease in the fluid pressure of hydrogen (formation of an oxidizing environment), the liquid oil phase will transform into a solid kerogen phase. In addition, ascending hydrocarbon fluids causing oil inflow into the reservoir (Kasyanova, 2010; Bochkarev, Bochkarev, 2017; Muslimov et al., 2019) will constantly shift the oil ↔ "mature" kerogen balance towards the formation of kerogens and then bitumen, asphaltenes and native carbon (Fig. 1). Such a process is currently observed, for example, in the process of replenishing the reserves of the developed oil fields of the South Tatar arch (Muslimov, Plotnikova, 2019).

According to A.A. Marakushev, the evolution of the Earth (which manifested differently depending on the geodynamic settings prevailing in the crust and mantle) is determined by the impulse degassing of its liquid core along the dislocation structures of solid silicate shells (Marakushev, 1999; Marakushev, Marakushev, 2010; Marakushev and Marakushev, 2010; Marakushev, Belonogova, 2019). The generation of water-carbonic fluids is facilitated by the extention regime of the earth's crust, which reduces fluid pressure due to selective migration of hydrogen, as the most mobile component, from fluids to the atmosphere. As a result, the oxygen components in them become dominant over hydrogen, so that the disproportionation of the components leads to the generation of carbon dioxide aqueous fluids according to the reaction between the components $H_2 + 2CO = H_2O + 0.5CO_2 + 1.5C$.

A significant change in magmatism is associated with the transition to compression regimes of mobile mantle structures, which prevents the migration of hydrogen. The increasing pressure of hydrogen leads to liquation immiscibility in magmas, which creates an antidromic development of magmatism, which is fundamentally different from homodromic, where the composition of volcanic products changes from alkaline to acidic. Hydrogen, which creates the possibility of antidromic magmatic development with a successive decrease in the content of silicon and aluminum in magmas and an increase in the role of ore and other metals, is at
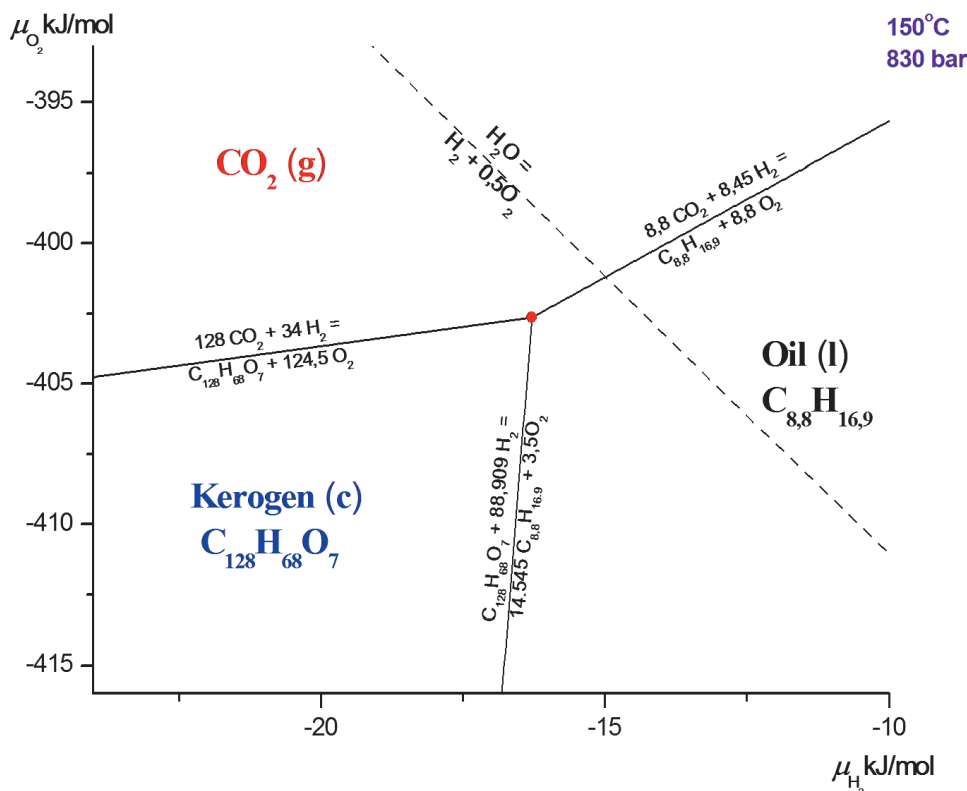

Fig. 5. The facies of liquid oil, pseudocrystalline kerogen and gaseous CO_2 on the phase diagram of the chemical potentials of gaseous H_2 and O_2 at a temperature of 150 °C according to the calculated constants from the data (Helgeson et al., 2009). The fluid pressure in the system is determined by the CO_2 pressure equal to 830 bar, the logarithms of activity (loga) of liquid oil and crystalline kerogen = 1. Lines are monovariant equilibria separating the divariant stability fields of the phases under consideration: gaseous CO_2, solid (K_2, $C_{128}H_{68}O_7$) and liquid (oil $C_{8.8}H_{16.9}$). Point – metastable invariant equilibrium of all three phases. The liquid water facies is located above the dashed line – saturation isopleths.

the same time a factor of increasing in the alkalinity of magmas. Under a high fluid pressure of hydrogen, the hydrocarbons are synthesized ($2CO + 5H_2 = 2H_2O + C_2H_6$, $8CO + 17H_2 = 8H_2O + C_8H_{18}$, etc.) and the oxygen acidic components of fluids ($H_2CO_3 + 4H_2 = 3H_2O + CH_4$, etc.) are decomposed, which creates an alkaline trends in the magmatism. Thus, the origin and formation of oil deposits, obviously, took place under the conditions of the geodynamic regime of compression of the Earth's shells at a high fluid pressure of hydrocarbons originating in the centers of magmatic differentiation. In the history of the Earth, this regime is reflected in the form of the periodicity of oil formation (correlating with the frequency of geomagnetic field inversions) (Kontorovich, Vyshemirsky, 1997; Marakushev, Marakushev, 2008), when ore-bearing metals were deposited together with oil and bituminous phases as a result of evolutionary transformation of the common fluid systems. The metastable equilibrium phase relationships, considered in the diagrams (Fig. 3, 4, 5), are established at a high fluid pressure of CO_2 under conditions that simulate the modern naphthide manifestations of the Gulf of Mexico shelf. Under such conditions, fixation of CO_2, oxidation and hydration of oil components with the formation of shale carbon concentrations took place and are taking place. However, the formation of oil deposits itself apparently took place under conditions of high fluid pressure of hydrocarbons.

Now let us consider the phase relationships of HC fluids, liquid oil and solid kerogen at a hypothetical HC fluid pressure (the sum of partial pressures) 830 bar and a temperature of 150 °C on the diagram of the chemical potentials of hydrogen (μ_{H2}) and oxygen (μ_{O2}) (Fig. 6). In the phase space of these chemical potentials, the metastable paragenesis of three phases – liquid oil, crystalline "mature" kerogen (K_2) and gaseous hydrocarbons – is an invariant point, while monovariant equilibria separate the regions of their thermodynamic stability. Monovariant equilibrium between hydrocarbons and oil at $\mu_{H2} = -15.69$ kJ is the sum of metastable stoichiometric equilibria of individual alkanes with oil with the general formula

$8.8C_nH_{2n} + 2 = nC_{8.8}H_{16.9} + (8.8 + 0.35n)H_2$.
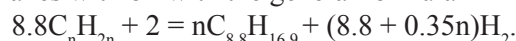
Thus, the composition of the primary oil is close to that of alkanes. It has been shown experimentally that under similar hydrothermal conditions (above the equilibrium of water formation, Fig. 6), n-alkanes are also in metastable phase equilibria with each other (Seewald, 1994).

As the approaches the surface, the partial pressure of hydrogen, as a rule, decreases, which is observed, for example, in oil wells in Eastern Siberia (Levshounova, 1991), and from the diagram (Fig. 6) it follows that a drop in hydrogen pressure in the ascending HC fluids will lead to transformation of fluid hydrocarbons into liquid oil ($C_{8.8}H_{16.9}$). Moreover, as the HC fluids rise to

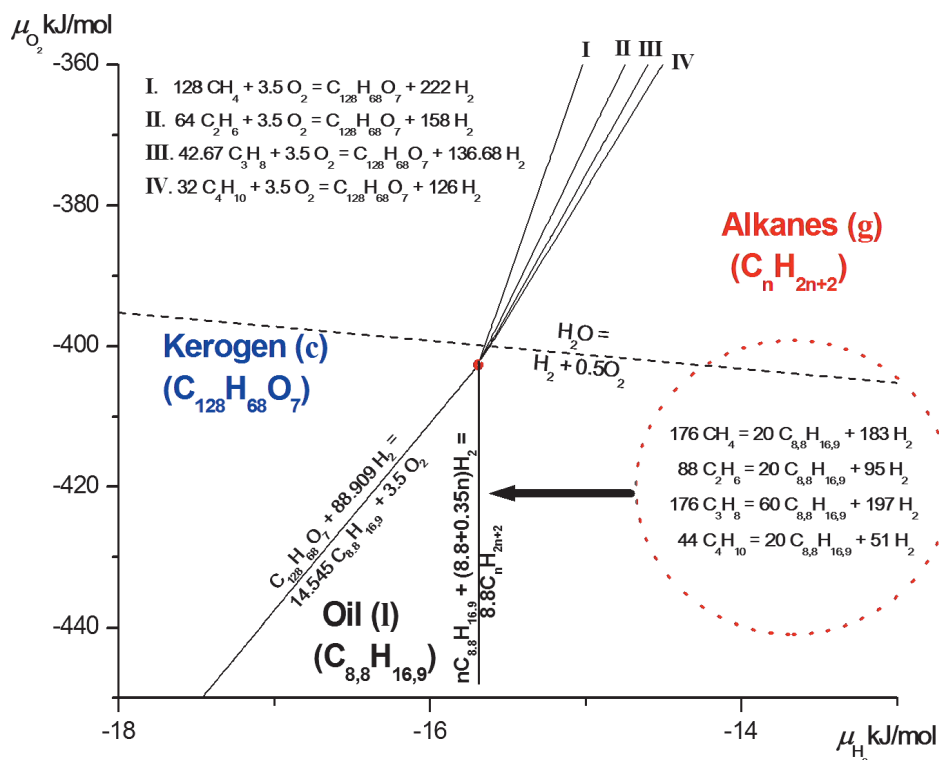*Fig. 6. Facies of liquid oil, pseudocrystalline kerogen and hydrocarbon fluids on the phase diagram of the chemical potentials of gaseous H_2 (μ_{H2}) and O_2 (μ_{O2}) at a temperature of 150 °C. The fluid pressure in the system corresponds to the total partial pressure of hydrocarbon phases equal to 830 bar, the logarithms of activity (loga) of liquid oil and crystalline kerogen are equal to 1. Monovariant equilibria separate the divariant stability fields of the phases under consideration: gas (alkanes, C_nH_{2n+2}), solid («mature» kerogen – K_2, $C_{128}H_{68}O_7$) and liquid (oil, $C_{8.8}H_{16.9}$). The point is their invariant equilibria.*

the surface, the HC↔oil equilibrium will shift towards the formation of oil. With an increase in the chemical potential of oxygen to –402.69 kJ (metastable invariant equilibrium of all three phases), hydrocarbons are sequentially oxidized to kerogen, with heavy alkanes (with a lower H/C ratio) being oxidized first. In this case, the oxidation of alkanes apparently proceeds through a sequence of reactions with the participation of alkene, alcohol, ketone, and carboxy-intermediates, as shown in experiments (Seewald, 2001). Thus, the high fluid pressure of endogenous hydrocarbons causes their transformation into liquid oil and solid kerogen under the physicochemical conditions of the "oil window". Under these conditions, there is no paragenesis of oil with water (Fig. 6), and therefore any water that is present in the host rock and comes into contact with oil will irreversibly react with it with the formation of "mature" kerogen. In other words, the hydration of oil components is the factor of the irreversibility of the formation of black shale deposits. Since thermodynamics determines the possibility or impossibility of carrying out reactions on a geological time scale, the influence of catalysts on the process should be small. The equilibria presented in the work are the stoichiometric sum of various reactions, the mechanisms and catalysts of which must be considered in a separate study.

Carboxylation and decarboxylation are two main classes of reactions that affect the carbon cycle in the earth's crust (Sheik et al., 2020). The core of the "biogenic" concept of the origin of oil is the transformation of black shale kerogen into oil, during which kerogen decarboxylation occurs with the formation of low molecular weight oil components (e.g., Kissin, 1987). However, the temperature diagrams in Fig. 3 and 4 are interpreted in the opposite direction, as the process of kerogen formation with a decrease in the chemical potential of hydrogen, as a result of high-temperature fixation of CO_2 by oil (equilibrium $14.148C_{8.8}H_{16.9} + 3.5CO_2 = K_2 + 85.548H_2$, Fig. 3) or its components ($20.75C_6H_{14} + 3.5CO_2 = K_2 + 111.25H_2$, Fig. 4). Therefore, the influence of the chemical potential of CO_2 on the phase transformation of oil into kerogen under conditions of high fluid pressure of hydrocarbons should also be very significant.

The facies relationships of three phases – gaseous hydrocarbons, liquid oil and pseudocrystalline "mature" kerogen – are shown in the diagram: chemical potential of hydrogen (μ_{H2}) – chemical potential of CO_2 (μ_{CO2}) (Fig. 7), at a hypothetical total HC pressure of 830 bar. The result of a decreasing in hydrogen pressure of this system is the transformation of fluid hydrocarbons into liquid oil ($C_{8.8}H_{16.9}$), which fixing CO_2 carries out a phase transition
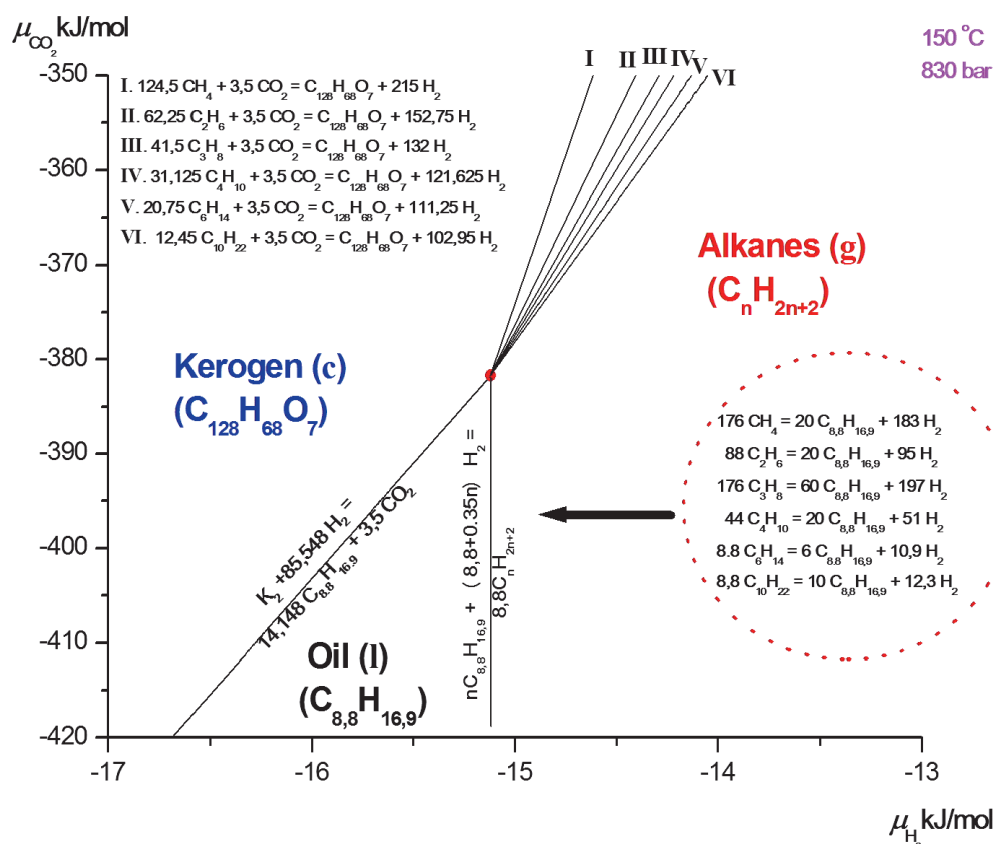

Fig. 7. Facies of liquid oil, pseudocrystalline kerogen and HC fluids on the phase diagram of the chemical potentials of gaseous H_2 (μ_{H2}) and CO_2 (μ_{CO2}) at a temperature of 150 °C. The fluid pressure in the system corresponds to the total partial pressure of alkanes equal to 830 bar, loga of liquid oil and crystalline kerogens = 1. Monovariant equilibria separate the divariant stability fields of the phases under consideration: fluid (C_nH_{2n+2}), solid (K_2, $C_{128}H_{68}O_7$) and liquid oil ($C_{8.8}H_{16.9}$). Point – invariant equilibria of hydrocarbons, kerogen and oil.

from liquid oil to solid kerogen. Direct carboxylation of fluid hydrocarbons with the formation of kerogen occurs at a higher chemical potential of carbon dioxide, and in general, CO_2 fixation is thermodynamically more favorable for heavy hydrocarbons and is accompanied by the release of hydrogen. Thus, in the temperature regime of the "oil window", fixation of CO_2 is apparently the main geochemical pathway for the transformation of oil hydrocarbons into kerogen and, therefore, the most powerful geological mechanism for the formation of black shale formations.

Conclusion

The genetic relationship between the carbonaceous matter of rocks and oils is obvious; however, the geological spatial direction of the process of its transformation remains controversial, although there is not a single compelling argument in favor of the formation of oil from buried organic (biogenic) matter. On the other hand, the concept of deep inorganic origin of hydrocarbons of oils and black shale deposits is based on numerous facts:

a) The presence of obviously abiogenic hydrocarbons in meteorites, planets and satellites of the Solar System (Kissin, 2003; Lunine, Lorenz, 2009; Marakushev et al., 2010, 2013; Glein, Shock, 2013; Malysheva, 2019; Bowling et al., 2020 ; Mastrogiuseppe et al., 2020);

b) The tendency for the location of oil and gas deposits over rift zones and faults associated with mantle structures (Syvorotkin, Pavlenkova, 2013; Timurziev, 2013; Muslimov et al., 2019; Pavlenkova, 2018; Astafiev et al., 2019);

c) Replenishment of oil reserves in deposits and upward migration of hydrocarbons through the basement into the sedimentary basins (Muslimov et al., 2004; Gavrilov, 2008; Kasyanova, 2011; Zou et al., 2013; Goryunov, 2015; Gottikh et al., 2014; Bochkarev, Bochkarev, 2017; Muslimov et al., 2019; Muslimov, Plotnikova, 2019);

d) Association of oil deposits with helium and other trace gases, presumably of mantle origin (Levshounova, 1991; Jenden et al., 1993; Pinti, Marty, 2000; Dmitrievsky et al., 2018, 2019);

e) Gas-liquid HC inclusions in Archean quartz (Touret, 2003; Schreiber et al., 2017), metamorphically altered ophicarbonates (Huang et al., 2017), minerals of alkaline rocks (Potter, Konnerup-Madsen, 2003), minerals of basement granitoids of the oil and gas bearing areas (Shnip, 1997);

f) Metallogenic specificity of oils and black shales (Marakushev, Marakushev, 2006 b, c; Gottikh et al., 2012; Marakushev et al., 2012; Henderson et al., 2019; Sanz-Robinson et al., 2020);

g) Relationship between oil and ore formation (Zubkov, 2010; Kusov, 2011; Letnikov, 2013; Lurie,

2013; Marakushev et al., 2012, 2014);

h) The existence of giant superdeep oil deposits at depths of more than 10 km in various oil world basins (Sephton, Hazen, 2013; Ivanov, 2018).

i) Localization of a number of oil deposits in crystalline basement rocks (Areshev, 2004; Marakushev, Marakushev, 2008; Kutcherov, Krayushkin, 2010; Starostenko et al., 2011; Punanova, 2019; Skvortsov, 2020).

Hydrocarbons accompanying the pulsed hydrogen degassing of the Earth are synthesized in deep alkaline magma chambers under conditions of high pressures and temperatures, which is fundamentally substantiated as in theoretical ones (Kudryavtsev, 1973, 2013; Porfir'ev, 1974; Kropotkin, 1986; Karpov et al., 1998 ; Gold, 1992; Letnikov, 2005; Marakushev, Marakushev, 2006, 2008; Zubkov, 2009; Marakushev, Marakushev, 2010; Kutcherov, Krayushkin, 2010; Marakushev et al., 2014) and in experimental (Kenney et al., 2002; Mukhina et al., 2017; Kolesnikov et al., 2017; Kucherov, Serovayskiy, 2018; Tao et al., 2018; Sokol et al., 2019, 2020; Serovaiskii, Kutcherov, 2020) studies. Aquatic fluids coexist with HC fluids originating in deep magma chambers, which, reaching the crust at depths of about 50 km, transform into an oil fluid (Serovaiskii et al., 2020), which seeps to the surface along faults and cracks (migration channels) and forms oil and gas deposits in rocks of the most diverse lithological composition, genesis and age. In the "biogenic" and in the deep-inorganic concepts of the origin of oil, the direction of the process is fundamentally different – oil from the kerogen of black shale ("oil source rocks") or vice versa. The performed thermodynamic analysis is consistent with the concept of deep inorganic origin of oils, bitumen and kerogens of black shales. When the temperature drops below their critical values, hydrocarbons pass from the fluid phase into the liquid phase ("embryonic" oil), which is transformed into crude oil. Further decrease in temperature and chemical potential of hydrogen leads to stoichiometric equilibrium phase "freezing" of liquid oil with the formation of solid kerogens and bitumen (Fig. 4). It means, hydrocarbons, closed in a trapped reservoir, form an oil reservoir, then oil migrates into fractured porous shale rocks. Then, with a decrease in pressure, temperature and the chemical potential of hydrogen, liquid oil turns into "mature" kerogen, and then into "immature". This occurs as a result of the high-temperature process of CO_2 fixation and low-temperature hydration of oil hydrocarbons, which are the main geochemical pathways of oil transformation into kerogen. Thus, the generation of kerogen in black shale rocks is an irreversible process of oil transformation, in which there is a sequential transition through metastable equilibria between oil, bitumen and kerogens in the geological time interval of the rise of deep fluids.

We assume that the insoluble carbon matter found in carbonaceous chondrites ("mature" kerogen) (Kissin, 2003; Matthewman et al., 2013) was formed in the same way from hydrocarbons in the interior of their parent bodies. Nevertheless, the results and achievements of domestic and foreign scientists cited in the introduction, based on the organo-biogenic concept of naphtide genesis, are undoubtedly of great scientific importance. For example, numerous data on experimental pyrolysis of black shale and bituminous organic matter demonstrate P-T conditions for the kerogen → oil transformation with an analysis of intermediate stages, and suggest possible catalysts that affect the rate of the entire process and individual reactions. On the basis of such studies and geological observations, the concept of the main phase of oil formation ("oil window" model) (eg, Kontorovich, Melenevsky, 1988; Tissot, Welte, 1981) was developed, and was used in this article for the analysis of the genesis of oil and black shale formations.

While recognizing the inorganic origin of oil, it is necessary to emphasize the importance of biological factors in the process of its evolution (e.g., Gold, 1999). First, the formation of deposits is due to the large-scale replacement of sedimentary rocks of platform and shelf depressions with oil (and partly crystalline rocks of the basement) with partial capture of their bacterial and plant components. In addition, most heavy oils are the result of underground microbial anaerobic biodegradation of paraffinic oil (e.g. Cheng et al., 2019; Seitz et al., 2019) over long geological periods of time. Oil is essentially a bio-inorganic "broth" of a mixture of endogenous hydrocarbons, microorganisms and their metabolites that form complexes with metals, which enter into numerous reactions or are their catalysts. Weak, medium and high degrees of biodegradation lead to different chemical types of oils (Punanova, Vinogradova, 2016). Bacteria initially remove low molecular weight n-alkanes, followed by heavy n-alkanes, branched alkanes, cyclic alkanes, and aromatic hydrocarbons, although in some cases this sequence is violated (Liu et al., 2020). Starting with alkanotrophic microorganisms, numerous trophic networks form the structure of oil, including the formation of specific biomarkers (e.g., Lurie, 2019), while its composition is almost completely determined by the upward migration of hydrocarbons synthesized under high thermobaric conditions of the earth's interior.

Acknowledgements

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