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REDUCED FLUIDS IN THE CRYSTALLINE BASEMENT AND THE SEDIMENTARY BASIN (ON AN EXAMPLE OF ROMASHKIN AND VERKHNE-CHONSKOYE OIL FIELDS)

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ABSTRACT

The paper considers geochemical data on the composition of the reduced fluids that have been found to penetrate the rocks of crystalline basement and sedimentary cover of two regions of the two ancient platforms - East European and Siberian. The study was based on the detailed petrographic research, a wide range of up-to-date geochemical and nuclear physical methods to study the fluid impact on the geological medium, such as thermobarogeochemical, chromatographic, mass spectrometric, bitumen, f-radiographic, instrumental neutron activation and other analyses. The studies have shown that the above fluid systems, which penetrate into the sedimentary rocks from the crystalline basement in petroleum areas, are the complex, multicomponent systems, transporting the elements of lithophilous, chalcophilous and siderophilous groups, which differ in affinity to oxygen and sulphur. Associations of elements in the fluids can only be maintained by organic ligand complexes that permit the transportation of metals over considerable distances through the geological medium. The acquired geochemical and thermodynamic characteristics of the reduced fluids and their differentiation products from the crystalline basement and the sedimentary cover of the southern Siberian and eastern part of the East European platforms indicate that these were formed outside of the sedimentary cover and that the migration was directed upwards.

Keywords: reduced fluids, crystalline basement, oil, bitumen, radioactive elements, trace element, gas-liquid inclusions, granite.

INTRODUCTION

Within the last decade a number of scientific publications emphasizing a leading role of deep fluids in the genesis of hydrocarbons increased significantly. A conception of polygenic naphthydo-genesis assumes that large hydrocarbon accumulations are been formed as a result of synergetic effect of two reduced systems of endogenous systems: endogenous fluids and biogenic organic material of sedimentary rocks. Many aspects of the polygenic oil generation were widely discussed at the Institute of Oil and Gas Problems (the Russian Academy of Sciences) during the International Conference “Genesis of Oil and Gas” taken place in Moscow in 2003.

Among the evidences of participation of deep fluids in formation of oil accumulations are the results of geochemical studies. The long-term study of micro-elemental composition of oil suggests the presence of a wide range of metals in oil. Both the presence and composition of these metals could not be related to rocks of the sedimentary cover.

For example, sometimes the abundances of volatile chalcophile and dispersed elements characteristic of basal and ultrabasic rocks (Hg, Au, Ag, Cu, Re, Se, As, *et al.*) are ten to hundred times higher than the Earth’s crust Clarke values. Moreover, oil contains high-charge and high-ionic lithophilous elements (U, Th, REE, Zr *et al.*) characteristic of alkaline and ultra-alkaline rock complexes [1]. In addition platinoids, among which palladium is predominating, are found in oil. Palladium is commonly predominating over the total of Ru+Ir+Rh. Interrelation between these components is controlling the geochemical classification of oil provinces by platinum metal specialization. The presence of chromium, cuprum, nickel and cobalt in oil in addition to platinoids is indicator of the chemical and metallogeny features of platform hyperbasites [2]. Of much importance is the presence of a sharply defined positive europium anomaly in hondrite-normalized distribution of rare elements in oil that is unusual for host rocks, formation water and organic material [3]. Finally, the inconsistence of isotopic composition of neodymium and strontium enclosed by oil and the isotopic composition of bitumoids of probable oil source rocks is found [4].

Experimental data about the traces of migration of ascending fluids is presented in the geological formations of oil areas and geochemical characterization of these fluids, produced by the analysis of mineral inclusions and differentiation products - bitumen. Discussed are possible sources and conditions controlling formation of such systems [5, 6].

GEOLOGICAL CHARACTERIZATION OF FORMATIONS

The subjects under study are Archaean - Lower Proterozoic rocks of crystalline basement and bottom of the sedimentary cover of the South-Tatarian Arch (STA) of the Volga-Ural anteclise, East European Platform and Nepsky Arch of Nepsky-Botuobinsky anteclise, Siberian Platform (Figures 1, 2). These areas are characterized by the presence of largest accumulations of hydrocarbons - Romashkino field located in the area and Verkhne-Chonskoye field - in the second area.

Outlines of Romashkino oil field (its size is about 65 x 75 km) are located within the limits of granulite-gneiss blocks characterized by a wide spectrum of rocks - crystalline schist, gabbroid, enderbite, biotite - pyroxene gneiss, charnockite, biotite - granite - hypersphenic gneiss, pyroxene - magnetite quartzite, pyroxene plagiogranite, granite, various migmatites, and etc.

Sedimentary geological section consists of terrigenous - carbonate rocks of Devonian, Carboniferous and Permian systems. Its thickness is as much as 1, 6 - 1, 7 km in the most elevated parts of South Tatarsky Arch. It is supposed that deposits of Semilukian horizon (D^{3fm}) represented by carbonate and argillo-carbonate silicified rocks characterized by the 3-5% abundance of organic carbon are major oil-generating complexes within the limits of this area. Oil accumulations are confined mostly to terrigenous reservoirs of the Lower Frasnian stage (D^{3fr}) and to a lesser extent to sandy-aleurolite rocks of the Lower and Middle Carboniferous. Oil density varies from ~ 0.869 g/cm^3 in Devonian deposits up to ~ 0.886 g/cm^3 in Carboniferous deposits, and the content of paraffin varies in the range 2.6-5.4%, sulfur - 1.5-2.1%, tar - 19 - 32 %, asphaltene - 4.3 - 12%.

Submeridional, latitudinal and diagonal faults related to processes taking place in the crystalline basement at the Early Paleozoic stage are predominating among faults identified within the limits of the studied area. The traces of discontinuities are identified from the gabbro - diabase dykes, products of the volcanic activity encountered in the Middle Devonian deposits, and from increased fracturing of rocks. Faults of various ranks are distinctly exhibited in the up-to-date relief. In the sedimentary cover faults are exhibited as flexure - discontinuity zones or structural terraces, they serve as boundaries between sharply replaced facies and sharp changes in the thickness of deposits.

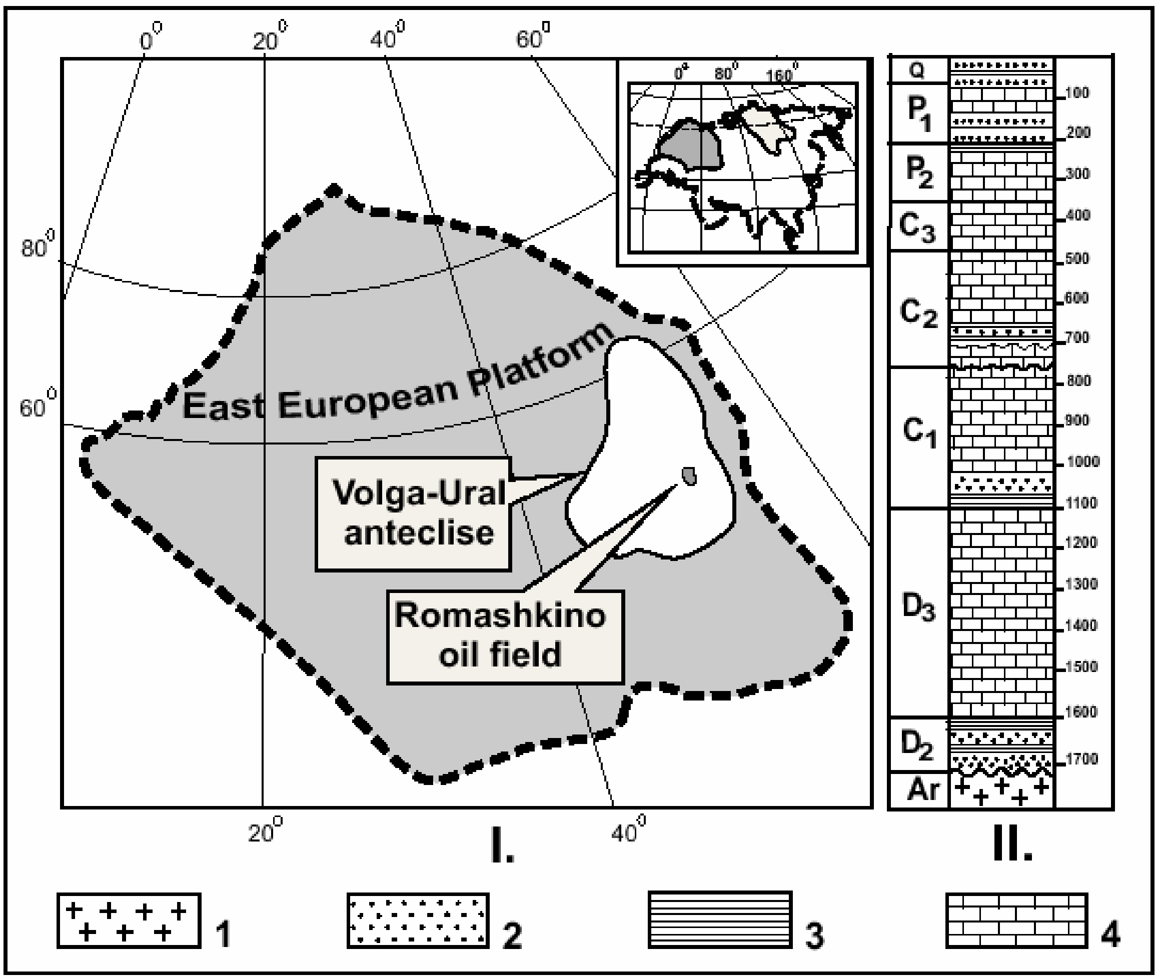

Figure-1. Scheme of location of the South Tatarian Arch and Romashkino oil field on East European Platform. I - scheme of location of the object of study; II - the schematic lithologic-stratigraphical section of South Tatarian Arch; 1: crystalline basement, 2: sandstone and siltstone, 3: clay, 4: limestone.

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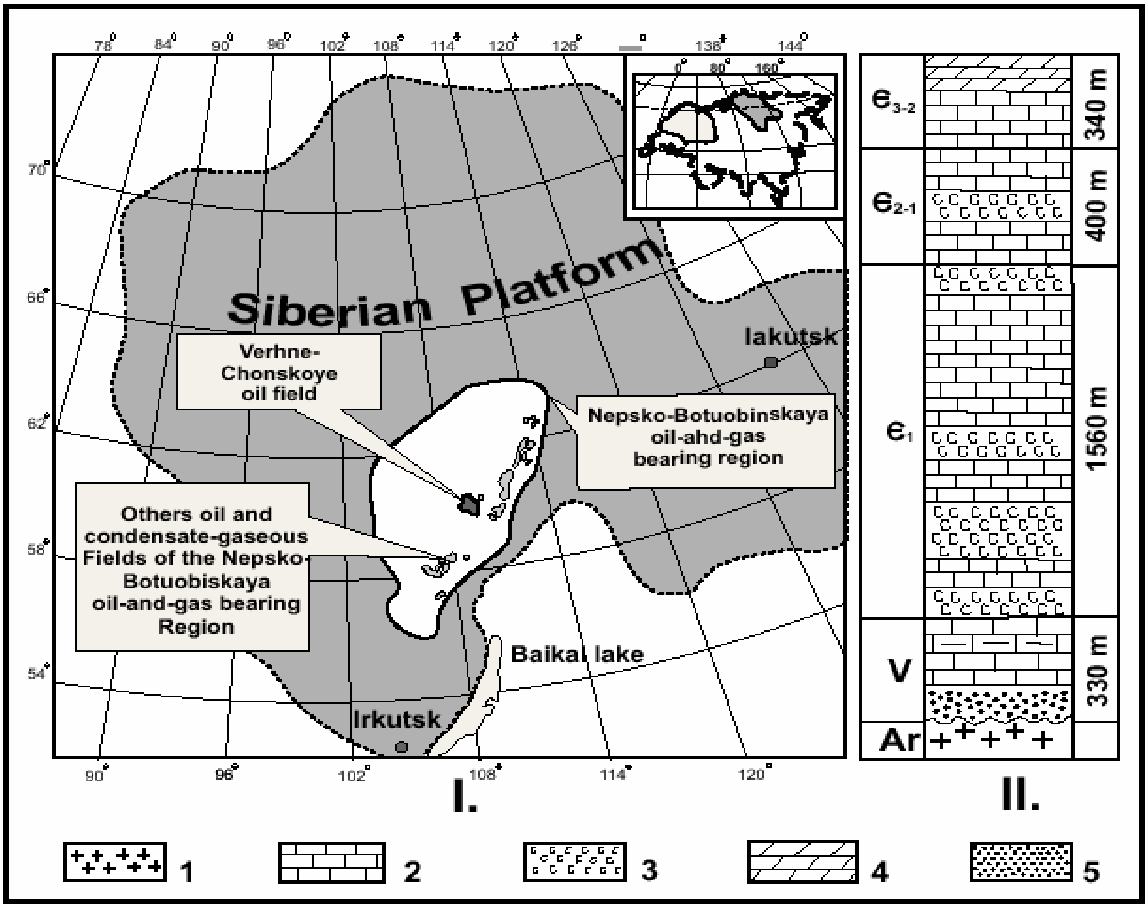

Figure-2. Scheme of location of the Verkhne-Chonskoye oil field on Siberian Platform. I - scheme of location of the object of study; II - the schematic lithologic-stratigraphical section of Nepsky Arch; 1: crystalline basement, 2: limestone, 3: salt-bearing section, 4: marly limestone, 5: sandstone.

Submeridional, latitudinal and diagonal faults related to processes taking place in the crystalline basement at the Early Paleozoic stage are predominating among faults identified within the limits of the studied area. The traces of discontinuities are identified from the gabbro - diabase dykes, products of the volcanic activity encountered in the Middle Devonian deposits, and from increased fracturing of rocks. Faults of various ranks are distinctly exhibited in the up-to-date relief. In the sedimentary cover faults are exhibited as flexure - discontinuity zones or structural terraces, they serve as boundaries between sharply replaced facies and sharp changes in the thickness of deposits.

Sedimentary formations are highly salted, enriched by anhydrites, and practically free of organic matter. That is why Riphean argillites of Baikal-Patomsky depression are considered as possible oil-generating source rocks.

Results of analysis suggest that oils enclosed by the studied formations differ in the character of metal content. Oil of Romashkino field is characterized by accumulation of Cr, Co, Ni, V, Cu, Ga, Nb, Cd, U and substantially high contents of Mo and Re, whereas oil of Verkhne-Chonskoye field is characterized by a low total content of metals and selective accumulation of Zn, Cr, Zr, and Cd. These oils are also different in the relations between volatile elements. Despite a material variation in the content of these elements, it is established oil of Volga-Ural region is enriched by Hg-Te-Re and oil of Nepsky-Botuobinsky anteclise - by As-Se-Sb-Hg-Au [1].

ANALYTICAL METHODS

In this study in addition to detail petrographic analysis we applied methods rarely used in the petroleum geology. Total gas saturation of rocks was studied by thermal gas chromatography. A temperature of heating up of rocks samples was selected in the range of 250°-350^{0}C based on the analysis of decrepitation curves. In specific cases, chemical mass-spectrometry analysis was performed using the MX-1303 device. Relict fluids trapped in minerals were analyzed by thermal using thermobaric geochemistry methods. Geochemical characteristics of fluids were analyzed using water, chloroform and alcohol - benzene extraction. Samples of extraction and bitumen were subject to a preliminary acid decomposition in hermetic autoclaves heated up in a microwave oven MULTIWAVE (manufactured by Anton Paar). Measurements were performed by Elan 6100 DRC with the detection limit of 1-2 mg/ton for heavy and medium elements (U, Th, REE, Rb, Sr and etc.) and 20-100 mg/ton for light and major elements (Li, Be, Ca, and Fe). Volatile chalcophile elements were identified using the instrumentation neutron activation analysis allowing determine the microelemental composition of samples (without preliminary decomposition of sample material) from the spectra produced by fast neutron activation in the experimental nuclear reactor. Measurements were performed by spectrometers including NUC-8100 analyzers and DGDK-50V detectors (germanium - lithium detectors consisting of the super-pure germanium). Activation of polished slices by thermal neutrons allowed estimate the abundance of uranium and specific features of uranium distribution in the studied subjects (by f-radiography) by detecting the traces of ^{235}U induced fission. In this technique, epoxy-based polished sections without the cover glass were packed in lavsan with its inner layer serving as a detector. The radiation dose varied depending on the objective. It was $1.4*10^{16}$ n/cm^{2}s in studying the spatial distribution of metal in rocks and $2.1*10^{14}$ n/cm^{2}s in determining its concentration. After the irradiation, fragments of uranium nuclei were tracked by the etching of the detector in a 40% KOH solution at 60^0C. The association of the tracks with the mineral constituents of rocks and bitumens was studied microscopically. A total of 200 neutron-treated polished sections from the two regions have been studied. The uranium content that serves as a threshold to distinguish between uranium-bearing and uranium-barren bitumens is $(2-4)*10^{-4}$%. Since bitumens are considered in petroleum geology to be the products of oil degradation and alteration, the authors previously studied metal contents in various oil fractions. A maximum uranium concentration of $n*10^{-5}$- $n*10^{-6}$ % has been found in acidic components (asphaltenes) while the total metal content of oils is $n*10^{-7}$-$n*10^{-8}$ %. That is, any alterations in oils cannot result in the uranium accumulation in bitumens higher than $8*10^{-5}$ – $1*10^{-4}$ %. In addition, we applied raster microscope JSM-5300 equipped with Link ISIS spectrometer and transmission microscope JEM-100C equipped with X-ray Kevex-5100 spectrometer. Due to application of these methods we established the spatial association of carbon with lanthanides and actinides, identified zones where elements are redistributed inside bitumen pockets, and determined concentrations of elements both in dispersed and concentrated forms.

RESULTS

The analysis of gas saturation character and relationship between oxidized and reduced components in metamorphic, ultrametagenic, and intrusive rocks of the basement suggests that the presence of hydrocarbons in a gas phase is common for these rocks. Petrographic analysis of core samples performed in addition to the chromatographic analysis allowed to understand the reasons of variation the composition of gas components of the samples. Resulting data presented in Figure-3 and suggests that gases commonly encountered in the studied samples can be subdivided into few groups by gas characteristics.

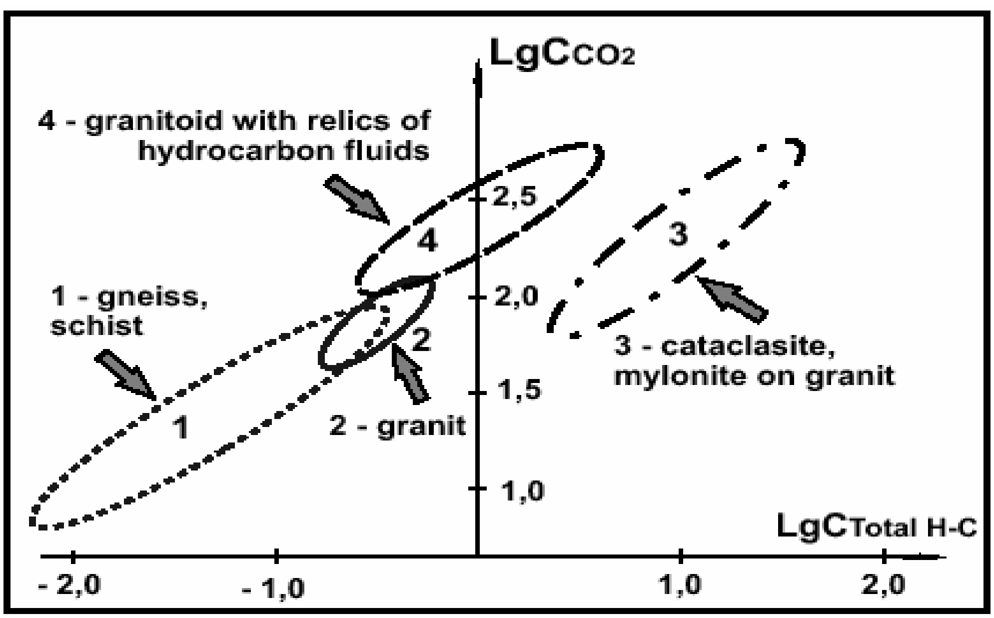

Figure-3. Major genetic types of gas in basement rocks. 1: gneiss, schist; 2: granite; 3: cataclasite, mylonite; 4: granitoid with relics of hydrocarbon fluids.

The first group includes fluids extracted from rocks samples taken within the outline of Romashkino oil field and characterized by the relatively low abundances of CO_2 and HC's and predominance of acid components in the composition of rocks. Ratio CO_2/HC varies from 200 up to 800, and the abundance of hydrocarbons mostly represented by methane does not exceed 0, 550 cm^3/kg. Core samples taken from the basement of Verkhne-Chonskoye field which have a similar composition of rocks are characterized by a ratio CO_2/HC of up to 10-70, abundances of CO_2 limited to 60 cm^3/kg and HC - to 2 cm^3/kg.

The second group includes gases of rocks characterized by a sufficient excess of CO_2 over the total content of HC's (CO_2/HC ranges up to 4000) mostly represented by methane and sharply subordinate number of homologs.

Petrographic studies suggest that gases of the first group are characteristic of gneiss and crystalline schists of various compositions which are disturbed practically by no secondary alterations and can be considered as background gases for the rocks of the studied geological sections.

Gases of the second group are characteristics of migmatites and granitoids which were formed under the action of binary fluids featuring a high partial pressure of CO_2.

Analysis of granitoid slices in the transmitted light allowed identify a few types of inclusions conserved in quartz and feldspar. Encountered are primary gas inclusions where the cryometric analysis identified practically pure carbonic acid (T_{melt} of CO_2 crystals makes -56°C to -57°C). Much more common are primary-secondary and secondary gas inclusions enclosed by microfractures of quartz. Upon freezing these inclusions are converted into a heterogeneous state (Gas + Fluid). Melting of a pre-frozen carbon acid predominantly takes place at the temperature of -56,6 to -56,7°C. This fact points to a high pureness of gases in vacuoles. Homogenization of carbon acid inclusions into the fluid phase takes place at various temperatures ranging from +14,6°C up to +22,1°C, relating to the density of 0,770-0,890 g/cm^3. For a number of inclusions, melting of CO_2 crystals takes place in a range of (-56, 8 - -58°C). This is owed to the presence of inclusions of low-boiling gases - CH_4, which are homogenized into a liquid at the temperature of +8, 2 - +18,6°C. In some vacuoles water solution admixtures are encountered.

Fluid Inclusions in gneisses and granitoids, more or less affected by acid leaching, are characterized by homogenization temperature of 360 - 385^{0}C. Upon freezing gas-liquid inclusions form large amount of CO_2 hydrate. The salt-water phase is represented by NaCl solutions with the $CaCl_2$ admixture (up to 10% of the total volume) and the total salinity of 12.5% (rated to NaCl equivalent).

Most diverse are gases relating to the third group including high abundances of CO_2 and HC's represented by saturated and non-saturated associations. This group of fluid components is encountered in crystalline basements rocks of the South Tatarsky Arc tapped by wells to the depth of 300 to 3500 m. Rocks are mostly represented by granitoids and migmatized gneiss subject to cataclasm and mylonitization. The extent of disintegration of rocks varies from intense crumpling to practically complete disintegration and formation of siliceous- micaceous alteration zones. Disintegration processes took place both without additional supply of material and given intense supply and removal of material.

Petrographic studies allowed trace the tectonic effect on granite-gneisses alteration. The initial stage of alteration is marked by deformation of plagioclase grains and occurrence of damping out mosaic patterns of quartz aggregates, followed by crumpling of rock formations. Crushing phases vary in intensity from the cracking of specific rock-forming minerals to formation of alteration zones of millimetres to a few centimetres in thickness. These zones are filled with the greenish-brown fine-grained material (pseudotachylite) which could be hardly analyzed by microscope and encloses "floating" angular fragments of quartz and feldspar, disintegrated biotite lamellae, and etc.

In course of subsequent alteration and inflow of heated-up solutions into the crushed zones, here the muscovite, sericite (often with magnetite inclusions), pyrite, chlorite, and calcite are produced. In the case of intensive alteration, the mineralogical composition of rocks is changing dramatically. Traces of biotite and amphibole are identified from the presence of earthy aggregates of titanium oxides, and the main rock-forming minerals are replaced for chlorite, sericite and carbonate in various proportions.

In such zone high concentrations of hydrocarbons can be produced as a result of mechanical processes and chemical reactions in the energized environment of the Earth's natural seismicity.

Gases of the fourth group including the increased content of hydrocarbons components are related to rocks relicts of superimposed secondary systems confined to microfractured zones (Figure-4). Consider in detail characteristics of these gases.

When viewed through a microscope of high power, healed microfractures are observed in the polished slices of rocks, mostly in quartz and rarely in feldspar, containing conserved systems of gas, gas-liquid, 3-phase, 2-phase and single-phase liquid inclusions of 10-30 mcm size (Figure-4). The fluorescence in blue, blue-yellow, and light-brown tones is observed in particular vacuoles which are subject to a luminescent illumination. This points to the presence of liquid hydrocarbons of varying composition. These gas-liquid inclusions are being homogenized when heated up in a wide range of the temperature of 40 to 350°C. In some cases when heated up the liquid inclusions began to boil producing bubbles which were preserved when reverting to a room temperature. Simultaneously, particular vacuoles have lost sealing and newly formed fractures were filled with a yellow-brown material. Thus, in the disclosed parts of the Archean - Proterozoic basement of South-Tatarian and

Nepsky Arcs the reduced systems, whose relicts are sealed in rock-forming minerals, migrated through the youngest fractures? This allows identify predominating gas and methane systems and, also, fluids enclosing liquid bitumen material.

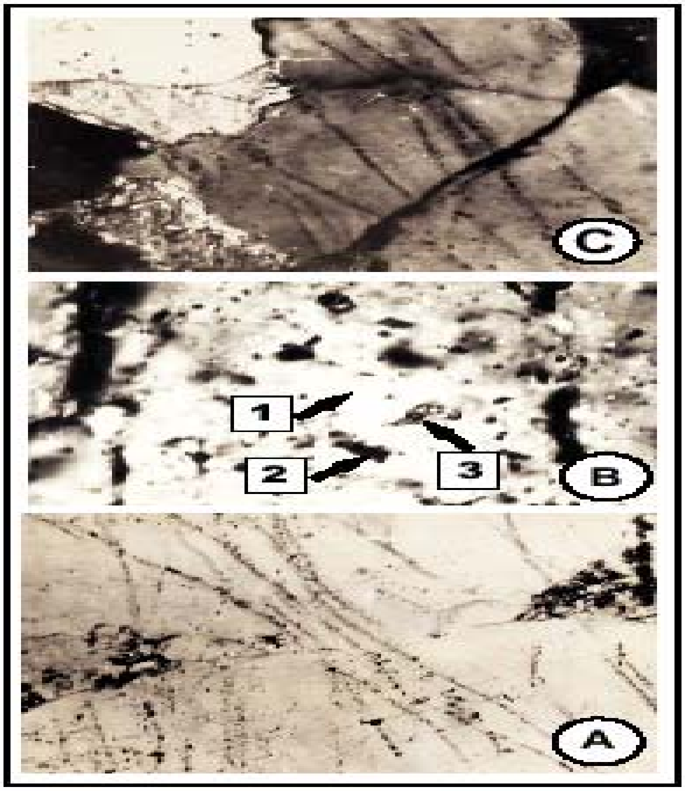

Figure-4. Microcracks with relics of reduced fluids in rocks of crystalline basement and sedimentary cover. A: granite (crystalline basement of South Tatarstan Arch), B: microcrack with inclusions: 1 - quartz of the granite; 2 - vacuoles with liquid hydrocarbons; 3 - three-phase inclusion with liquid hydrocarbons, water-salt solution and bubble of gaseous condensate; C: sandstone (Devonian deposit of South Tatarstan Arch).

Inclusions characterized by a similar composition are also found in rocks of the sedimentary cover. The character of phase equilibrium in the low temperature range is a specific feature of relicts of these fluids. Material of particular vacuoles, which is single-phase at a room temperature, becomes heterogeneous through condensation of the fluid being frozen below -80^{0}C. Also, the inclusions of gas phase are homogenized at the phase conversion temperature of -74.7, -72.5 and -74.0^{0}C, which points to the predominating methane composition of these inclusions. Some of two-phase inclusions filled up to 85-90% contain colorless fluid L_1. When frozen the volume of a gas phase is growing up to 25-30% of the vacuole volume. Next, the second colorless fluid L_2 is being condensed from the gas phase in amounts of ~ 25%. At a temperature below -90^{0}C the volume of fluid L_1 is materially reduced and the fluid is partly crystallized. Fluid L2 is vaporized when heated up to -54 - -52^{0}C. A complete homogenization of inclusions takes place at a temperature of +48 - +53^{0}C.

Some of the inclusions are filled up to 80-90% with a brown liquid. On freezing the limited growth of the gas bubble volume, partial crystallization and “silication” (can be identified from formation of shrink fractures which are closing with growth of the temperature) of the bitumen phase take place. On heating the crystalline phases are being dissolved in bitumoid at +2 to +8^{0}C. The temperature interval of homogenization of inclusions containing hydrocarbon phases ranges from 105 to 145^{0}C.

There are a lot of similar conversions depending on a composition of material in vacuoles. Yet, from the above examples it follows obviously that a portion of the liquid phase of secondary inclusions is represented by heterogeneous hydrocarbon and bitumoid components varying from oil to tar - asphaltene. Chemical mass-spectrometry analysis of a number of samples of quartz taken from the crystalline basement of the studied areas suggests that the portion of HC (C_1 - C_4) in the gas phase in some cases is above 90% at a sharply defined subordinate content of CO_2. Concentration of hydrogen varies from 0.1 up to 18 % vol., and concentration of nitrogen - from traces up to 15% vol.

Apart from gas, bitumen-gas, hydrocarbon and water-hydrocarbon inclusions, some microfractures

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contain gas-liquid inclusions of water-salt solutions. Cryometric analysis has shown that the latter are represented by $NaCl-CaCl_2-MgCl_2-KCl-H_2O$ mixtures and are characterised by various cation ratios at different geological levels. Salt concentrations vary from 6% to 25% of NaCl equivalent. Eutectic temperatures can be as high as 55^0C. The compositional variations in the water-salt phase of the fluids are also indicated by some isolated paragenetic mineral associations in microfractures. The fractures may be filled with chlorite, calcite, sericite and calcite, dolomite, etc. Both fractures and vacuoles are often found to contain pyrite and magnetite. Homogenisation temperatures of vacuoles with the water-salt phase have been found to generally range between 320^0C and 60^0C and to decrease up the geological sequence from the basement to the mean depths of the sedimentary cover. The fluid entry temperatures at the levels that can be reached by drilling substantially differ between the studied regions. The upper portion of the crystalline basement and the lower portion of the sedimentary cover within the Nepsko-Botuobinskaya anteclise of the Siberian Platform are featured by the highest temperatures varying from 300^0C to 190^0C (as determined by more than 150 measurements). At the same time, $T_{hom.}$ of inclusions measured within the basement of the South Tatarstan Arch does not exceed 200-120^0C (by 60 measurements). For instance, $T_{hom.}$ for granitoids from a depth of 4360 m in well 20009 is 220^0C and that from a depth of 2480 m is 150^0C. In some cases, temperatures of fluids entering the sedimentary cover of the South Tatarstan Arch may be high (160-170^0C at a depth of 1785 m and 140-150^0C at a depth of 1250 m in Novo-Yelkhovo-8113) due to the proximity of the well to the fault zone.

Geochemical information on the fluid composition has been acquired by studying water-salt, chloroformic and alcohol-benzene extractions from quartz of granites of the Verkhne-Chonskaya Area. Examination of polished sections has indicated high fluid saturation due to abundant microfractures filled with inclusion relics.

After thorough grinding, quartz powder was treated with chloroform and alcohol-benzol and by water extraction. The prepared specimens, contained in superpure quartz ampoules, were exposed to a thermal neutron flux $2\square 10^{13}$ n/cm^{2}s. Instrumental neutron activation and chemical analyses have shown (at their sensitivity thresholds) that the water phase of the fluid apart from cryometrically-detected cations contains Cs and Zn and that its anions include Cl^-, ΣSO_4^{--}, S_2^{--}, HCO_3^-, F^- and Br. The bitumen extract has been found to contain Ce, Hf, Sc, Co, Cr, Sb (0.3-1.5 ppm), Hg (18-30 ppm) and uranium and thorium traces. The content of all the elements in the alcohol-benzol extract was higher than in the chloroformic.

A wide range of microelements has been detected in the bituminous substance by inductively coupled plasma mass spectrometry (ICP MS). It contains highly volatile elements U, Bi, Pb, Hg, Re and Sb and low-mobility hydrolysates Th, REE, Nb and Y along with substantial amounts of V, Cr, Fe, Ni, Cu and Zn (Table-1).

Table-1. Isotopic composition of carbon and oxygen of streak of calcite in crystalline rocks of basement.

Territory of study	Well #	Rocks	Interval, m	$\delta^{13}C$	$\delta^{18}O$	Comments
South Tatarstan Arch	Novo-Yelkhovo-20009	Granitoid chloritizated with garnet	3986-3988	-14,3	+10,6	Calcite-quartz streak
South Tatarstan Arch	Novo-Yelkhovo-20009	Biotite-amphibolite gneiss	4061,1-4062,6	-14,5	+13,6	Calcite streak
South Tatarstan Arch	Novo-Yelkhovo-20009	Biotite-garnet crystalline shale	4153-4155	-13,9	+11,4	Calcite-quartz streak
South Tatarstan Arch	Novo-Yelkhovo-20009	Amphibolite- biotite crystalline shale	4360-4363	-16,4	+11,8	Calcite- sericite streak
South Tatarstan Arch	Novo-Yelkhovo-20009	Biotite gneiss	4827-4829	-16,9	+21,5	Calcite- muscovite streak
North Tatarstan Arch	Priviatskaia-603	Biotite- garnet gneiss	1871-1872	-16,4		Calcite streak
North Tatarstan Arch	Priviatskaia-545	Granitoid	1752-1756	-10,1		Calcite streak
North Tatarstan Arch	Priviatskaia-537	Biotite-garnet gneiss	1860-1865	-12,4		Calcite streak
South Tatarstan Arch	Crim-Sarai-2206	Granitic gneiss	1938-1943	-13,6	+20,8	Calcite streak
Nepsko-Botuobinskaya anteclise	Verhnechonskaia-26	Granite	1620	-17,9	+23,5	Calcite streak
Nepsko-Botuobinskaya anteclise	Verhnechonskaia-64	Granite	1773	-15,2	+19,3	Calcite streak

Migration traces of reduced systems in the crystalline basement of the study areas are also detected by the presence of the bituminous substance in rock fractures.

Luminescence studies of core samples from deep wells of the South Tatarstan Arch have shown bluish-white and yellowish-brown luminescence of the fracture infill, which suggests that this material is of an oily/resinous type. Maximum bitumen concentrations have been recorded at fracture intersections and in rock crushing zones. The organic carbon content in most samples is 0.01-0.09%, in some individual cases reaching 0.15-0.5%, for 0.0003-0.008% to 0.01-0.02% chloroform extraction. Their group composition is dominated by resins and oils and includes minor amounts of asphaltenes. The fractional composition of hydrocarbons in them is very diverse. Some samples include a wide range of hydrocarbons from C_9 to C_{33}, while others contain narrower fractions with different final boiling points. In cataclastic zones, they are enriched with high molecular C_{26}-C_{32} compounds containing notable concentrations of polycyclic structures [7]. Compositionally similar bitumens occur at various depths. The following has been detected by IR spectra: CH_2 groups, CH_3 of paraffin structures, CH_2 groups of paraffin chains, aliphatic ethers, C-C aromatic ring groups and C-O links.

The content of chloroform extracted bitumen in granitoids of the Nepsky Arch is much higher and reaches 0.104-0.178% of the rock mass. Their group composition is dominated by essentially alcohol-benzene resins (~50 mol. %). Oil compositions are dominated by normal C_{13}-C_{33} and isoprenoid C_{15}-C_{21} hydrocarbons [8].

Another geological feature of the areas under study is the presence of hard bitumens in the crystalline basement and in the lower portion of the sedimentary cover, which are confined to microfractures filled with reduced fluid relics. The classification of these carbonaceous substances is based on measured temperatures of the homogenisation of inclusions. The anthraxolite-type substances occur in microfractures with inclusion homogenisation temperatures of 320-270^{0}C. Kerites are characterised by temperatures of 260-210^{0}C and asphaltites by temperatures of 140-80^{0}C. Asphalts are condensed at 140-80^{0}C and the condensate and oil reservoirs are featured by temperatures of 100-60^{0}C.

Carbonaceous substances occupy various positions in the rock structure. In some cases, these are round bodies within rock-forming minerals, and their secondary morphological character is evidenced by their relation to the microfractures filled with gas-liquid inclusions (Figure-5). The zones of cataclasis and intense fracturing represent another source of origin of carbonaceous substances. These zones contain bitumens that form irregular but almost round clots, forcing apart the disintegrated host material and occupying an idiomorphic position. Their paragenesis is characterised by the secondary mineralisation represented by calcite ± chlorite ± sericite ± prehnite ± quartz and ore minerals occurring in various ratios.

A distinctive feature of the bitumens under study is their high metal content. The classification of carbonaceous substances is based on concentrations of various elements. For instance, bulk anthraxolite and kerite samples from the Nepsko-Botuobinskaya anteclise contain 6.2-1.0% thorium, 0.072-0.015% uranium, 0.17-0.013% yttrium and 9,5% total lanthanides according to ICP-MS data. Asphaltites and asphalts contain much smaller amounts of lithophilous elements and higher concentrations of chalcophilous V, Ni, Cr and especially Hg, Sb, Re, As and Se. The content of volatile elements in asphalts is close to that in asphaltenic oils. Concentrations of elements of various geochemical groups for the series "anthraxolite-kerite-asphaltite-asphalt-oil asphaltenes" differ by three to five orders of magnitude.

As carbonisation degrees of carbonaceous substances correspond to fluid entry temperatures, the bitumen composition changes regularly in the geological medium of the regions under study. For instance, anthraxolites and kerites occur in the basement and in the weathering crust of the Verkhne-Chonskaya Area but are replaced by asphaltites and asphalts in the sedimentary cover. The basement of the Romashkino field is characterised by lower fluid entry temperatures and contains only asphaltites while the sedimentary cover contains asphalts.

The examination of highly carbonised bitumen clots from the crystalline basement and weathering crust of the Verkhne-Chonskaya area has indicated high contents of actinides and lanthanides.

Radioactive elements are mainly represented by Th. The Th/U ratio usually exceeds 10 and sometimes reaches 60. Lanthanoids are largely represented by LREEs with the preferential accumulation of Ce. Yttrium is universal. In addition, the bitumen contains Si, P, S, and, less commonly, F and Cl.

The track radiography method applied previously to the study of uranium demonstrated its regular distribution in the carbonaceous material and the lack of secondary epigenetic enrichment (Figure-6). The present study revealed at least two types of Th and REE distribution in the bitumen. In addition to the relatively regular pattern, local concentrations are also widespread (Figure-7). This observation does not refute, however, the inference on the simultaneous influx of hydrocarbons and metals into the examined rock complexes.

The element distribution analysis of bitumen has indicated a rather even distribution of uranium (Figure-7; f-radiography) and both even distributions and local accumulations of thorium and rare earth elements due to the presence of finely dispersed minerals either in the form of very fine aggregates or dispersed in the carbon mass. Figure-8 and Table-2 show the contents and distributions of elements in bitumen clots from granites and the weathering crust of the basement.

Let us consider some examples. Bituminous matter in quartz from granite (thin section 87) is characterized by relatively regular distribution of heavy metals (light field). Similar behavior is also characteristic of C, Th, S, and P. No local accumulations of these elements are observed. The X-ray microprobe analysis using the energy-dispersive spectrometer carried out in two points's revealed close concentrations of elements (Table-2). In both cases, the Th content is high (15- 18%). The contents of Zr and Y are 2.06-2.35 and 1.06-1.18%, respectively. The U and REE concentrations are substantially lower (<1%).We also recorded the presence of P (1.03-1.12%) and S.

The dispersed occurrence mode of thorium is distinctly manifested in the rounded bitumen aggregate

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from granite of the Verkhnyaya Chona field (section 82), where the periphery is marked by relative concentration of heavy elements. This is also reflected to a certain extent in the distribution of carbon, although the latter is generally regular. The distribution of elements was determined in two points. The table demonstrates that the mineralization of bituminous matter is largely determined by thorium, the content of which is as high as 18.29-23.76%. Silica, yttrium, and uranium are present in notable quantities (3.26-4.68, 2.17-2.84, and 1.20-1.58, respectively). The concentrations of rare earth elements (La, Nd, Sa, Gd, and Dy) are <1%. The Ca and P contents are also low. Judging from the oxygen concentrations and composition of trace elements, Th mainly occurs in this bitumen as thorianite dispersion in a carbonaceous matrix (Figure-8).

Thus, the coexistence of carbon, phosphorus and sulphur with heavy metals in carbonaceous substances indicates their simultaneous accumulation from a single source. These elements were sourced from the deep fluid systems under study, which is evidenced by the spatial association of bitumens with the relics of superimposed reduced systems and by the dependence of their composition on the fluid entry temperature at various geological levels.

Table-2. Content of the trace-elements in bitumen of the granite and residual soil of the crystalline basement of the Nepsky Arch.

Section 87, p.1

El	Al	Si	P	S	Ca	Y	Zr	La	Ce	Pr	Nd	Th	U	O
El%	0.59	3.73	1.12	0.65	0.72	1.18	2.35	-	0.33	0.21	0.47	18.04	0.79	11.45
Sgm	0.11	0.12	0.13	0.08	0.08	0.48	0.51	0.19	0.21	0.18	0.23	0.47	0.36	0.58
At	2.04	12.4	3.36	1.90	1.68	1.23	2.40	-	0.22	0.14	0.30	7.25	0.31	66.76
Ox	Al_2O_3	SiO_2	P_2O_5	SO_3	CaO	Y_2O_3	ZrO_2	La_2O_3	Ce_2O_3	Pr_2O_3	Nd_2O_3	ThO_2	UO_2	SUM
Ox%	1.12	7.99	2.56	1.63	1.01	1.49	-	-	0.39	0.25	0.55	20.53	0.90	41.58

Section 87 p. 2

El	Al	Si	P	S	K	Ca	Sr	Y	Zr	La	Ce	Nd	Pr	Sm	Gd	Th	U	O
El%	0,54	3.26	1.03	0.74	0.16	0.53	0.71	1.06	2.06	-	0.36	0.41	-	0.33	0.62	15.92	0.37	.65
Sgm	0.10	0.10	0.21	0.07	0.06	0.07	0.33	0.39	0.42	0.15	0.17	0.18	0.14	0.20	0.21	0.37	0.29	0.54
At	2.01	11.60	3.32	2.30	0.42	1.31	0.81	1.20	2.26	-	0.26	0.28	-	0.22	0.39	6.86	0.16	66.60
Ox	Al_2O_3	SiO_2	P_2O_5	SO_3	K_2O	CaO	SrO	Y2O3	ZrO_2	La_2O_3	Ce_2O_3	Nd_2O_3	Pr_2O_3	Sm_2O_3	Gd_2O_3	ThO_2	UO_2	SUM
Ox%	1.02	6.97	2.35	1.84	0.20	0.74	0.84	1.35	2.79	-	0.43	0.48		0.38	0.71	18.11	0.42	38.63

Section 82, p. 1

El	Si	P	S	K	Ca	Mn	Y	Nd	Sm	Gd	Dy	Er	Th	U	O
El%	4.68	0.48	1.05	0.12	0.40	1.14	2.84	0.23	0.55	0.60	0.27	0.22	23.76	1.58	12.42
Sgm	0.20	0.34	0.08	0.09	0.08	0.12	0.52	0.21	0.24	0.34	0.24	0.19	0.53	0.42	1.49
At	14.34	1.33	2.83	0.26	0.87	0.21	2.75	0.14	0.32	0.33	0.14	0.11	8.81	0.57	66.80
Ox	SiO_2	P_2O_5	SO_3	K_2O	CaO	MnO	Y_2O_3	Nd_2O_3	Sm_2O_3	Gd_2O_3	Dy_2O_3	Er_2O_3	ThO_2	UO_2	SUM
Ox%	10.01	1.10	2.63	0.14	0.56	0.18	3.61	0.27	0.53	0.69	0.31	0.25	27.03	1.79	49.58

Section 82, p. 2

El	Si	P	S	K	Ca	Fe	Sr	Y	Nd	Sm	Gd	Dy	Th	U	O
El%	4.61	0.77	1.17	0.20	0.38	0.44	0.59	2.17	0.51	0.46	0.54	0.70	18.29	1.20	12.29
Sgm	0.23	0.49	0.08	0.08	0.08	0.14	0.47	0.53	0.23	0.25	0.30	0.26	0.47	0.37	0.88
At	14.31	2.16	3.18	0.45	0.83	0.69	0.59	2.13	0.31	0.27	0.30	0.37	6.87	0.44	66.98
Ox	SiO_2	P_2O_5	SO_3	K_2O	CaO	FeO	SrO	Y_2O_3	Nd_2O_3	Sm_2O_3	Gd_2O_3	Dy_2O_3	ThO_2	UO2	SUM
Ox%	9.86	1.76	2.92	0.24	0.53	0.57	0.70	2.76	0.60	0.53	0.62	0.80	20.81	1.36	44.29

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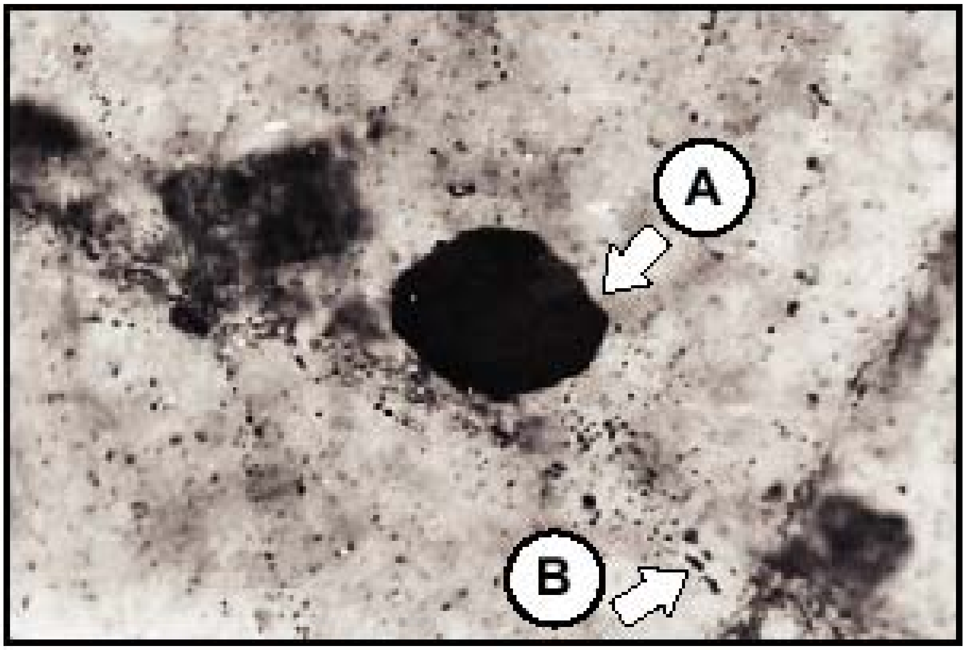

Figure-5. Combination of bitumen's clot and the microfractures filled with gas-liquid inclusions. A: clot of bitumen, B: microfracture filled with gas-liquid inclusions.

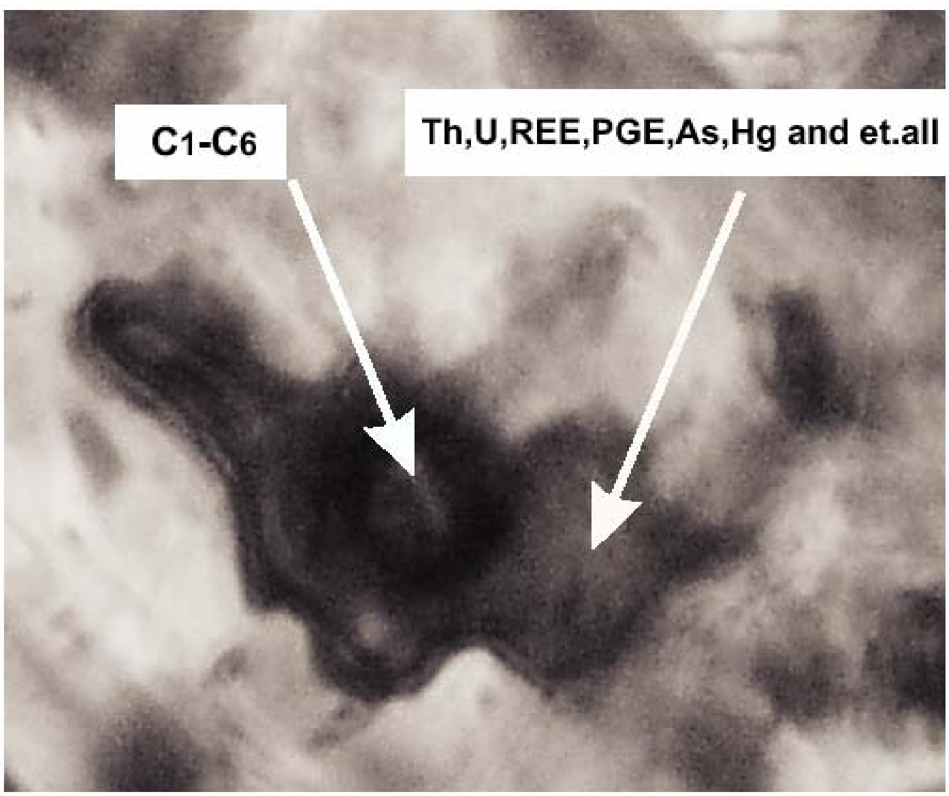

Figure-6. Bitumen from the inclusions.

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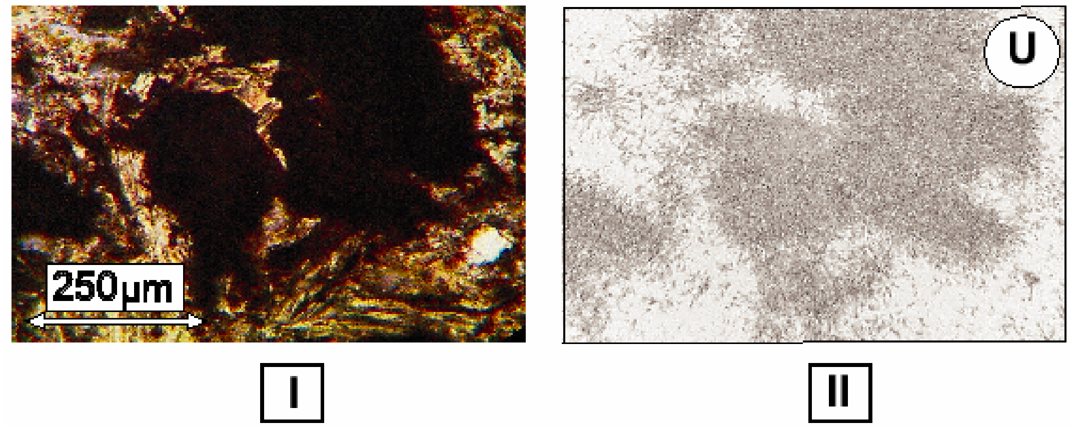

Figure-7. The distribution of uranium in the bitumen. I - photo of thin section, II - detector (f- radiography).

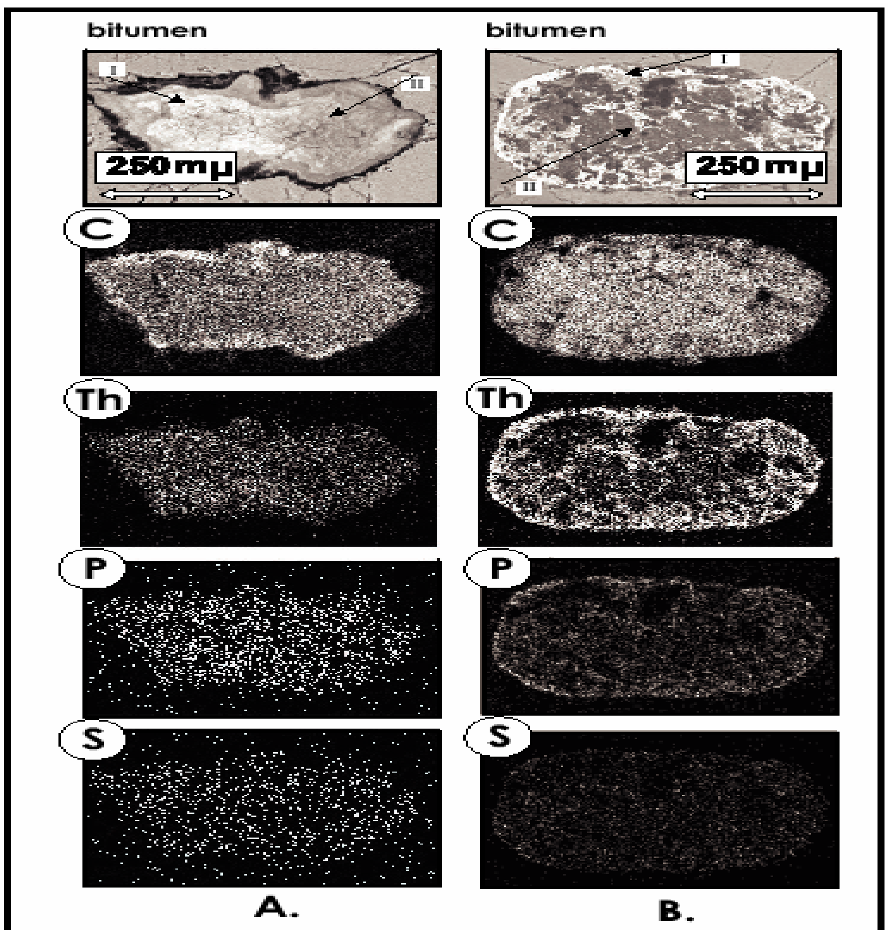

Figure-8. The distribution of some trace-elements in the bitumen. Bitumen in reflected electrons; C, Th, P, S in characteristic X-ray radiation. A: bitumen from residual soil, B: bitumen from granite.

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DISCUSSIONS

The data on the gas saturation of basement rocks and their petrographic composition have indicated the following. Medium- and low-temperature (570-130^{0}C) alterations of the Archaean and Lower Proterozoic crystalline rocks took place under the influence of carbon dioxide/water fluids. Maximum gas concentrations have been detected in granitoids.

Basement rocks have also been found to contain cataclastic and mylonitisation zones at various depths. These are characterised by high concentrations of hydrocarbons with a high percentage of unsaturated compounds (~1/1). Hydrocarbons in such zones were formed in mechanochemical reactions. The mechanism of these processes is based on radical chain reactions on activated surfaces of mineral phases. The crushing of rocks and their crumpling up to a plastic state lead to the appearance of chemically active surfaces and are accompanied by electron emission and other electrophysical phenomena. At the same time, CO_2 and H_2O, required for the formation of organic polymers in the electron medium, are released from the crystal lattice of granites. It has been shown experimentally that mechanochemical reactions mainly produce unsaturated hydrocarbons [9]. The formation of saturated gaseous hydrocarbons, unlike unsaturated ones, is a multistage and more complex process. Its intermediate products are represented not only by chemically active radicals with uncompensated valences but also by olefins.

The above processes could run under tectonic dislocations of any type. In the Volga-Ural anteclise, these mainly took place in the Riphean, during the formation of platform troughs and the stratification of the platform into blocks. Deep wells have penetrated the basement to various depths to find zones of mylonitisation and cataclasis, several to tens of centimetres in thickness, filled with illite, smectite, chlorite and kaolinite [10-12]. Decryptographs show that fluid components are mainly released from the rocks at 450-500^{0}C, in the temperature range of dehydration of micaceous minerals. The zones are characterised by high concentrations of organic carbon and high yields of chloroform extracted bitumen. K-Ar radiometric datings have indicated that the age of minerals from mylonites is 1167.9M years for well 20009 (1927.3-1929.5 m) and 1236.5M years for well 20005 (2888-2889 m). Thus, the formation of major mylonitisation zones and the synthesis of a wide range of hydrocarbons in them took place even before the formation of the South Tatarstan Arch's sedimentary cover.

The gas and liquid hydrocarbon components reside in the rocks under study due to the presence of superimposed, compound, reduced, fluid systems in ancient rock complexes. Relics of these fluids are sealed in secondary inclusions of minerals.

The geochemical and thermodynamic characteristics of the fluids and their differentiation products in the basement and in the sedimentary cover of the regions under study indicate the following. The fluids formed outside the sedimentary cover and migrated upwards. The inclusions are confined to the youngest microfractures in rocks and minerals. Fluid entry temperatures vary upplunge from 320-280^{0}C to 90-60^{0}C in the Nepsky Arch of the Siberian Platform and from 220^{0}C to 50^{0}C in the South Tatarstan Arch of the East European Platform.

The fluids are complex, multicomponent systems. These systems carry a wide range of elements of basic and alkaline parageneses. The elements reside in the fluid in the form of organometallic complexes. Some of these complexes could be formed only at high pressures in a highly reducing environment. The entry of such high-pressure systems into less dense, upper portions of the crystalline basement and lower portions of the sedimentary cover was accompanied by the sudden pressure drop and fluid differentiation. Under new pressure and temperature conditions, low-solubility substances were separated out of the fluid to form hard bitumen. Light component migrated into fractured and porous reservoirs and mixed with biogenic hydrocarbons. Thus, oil (the product of the interaction of endogenous fluids with the organic matter of sedimentary sequences), graphite of the Archaean crystalline complexes and hard bitumens are interrelated elements of the evolution of deep reduced systems. The distribution of microelements in the synthesised substances was governed by the thermobaric characteristics of the fluid and by the stability of organometallic complexes. Figure-9 shows the levels of accumulations of some microelements for the extreme members of the system "kerite - oil asphaltenes" according to the instrumental neutron activation analysis of bitumen and oil from the Pripyat-Dnepr, Timan-Pechora, Volga-Ural and Lena-Tunguska oil provinces.

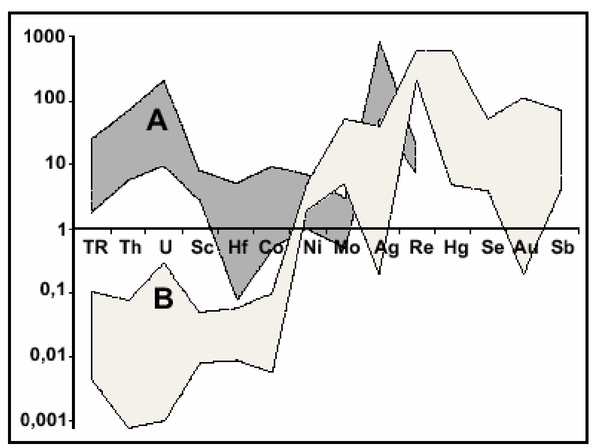

Figure-9. Content of trace-elements in asphaltenes of oil and in kerites of East European and Siberian platforms. A: kerites, B: asphaltenes.

As it appears from the figure, any other mechanism than the proposed one is not likely to explain the accumulation of TR, Th, U, Sc, Hf and Co on the one side and Hg, Se, Au and Sb on the other.

As is known, some elements, such as As, Sb, Hg, Bi, and P, form stable compounds with various organic molecules, including the simplest alkyl and aryl derivatives, and associate practically with any functional groups that are included into the structure of bonded radicals. In addition, they form hydride and fluoride compounds that readily dissolve in organic solvents [14, 15].

Organic chemistry of rare earth elements is more complex. Stability of their organometallic compounds depends on the character of the ligand and the atom of the element. Most widespread are compounds with complex ligands and their derivatives in which metal is associated with hydrogen, nitrogen, sulphur, phosphorus, arsenic and oxygen. Oxygen-containing compounds of rare earth elements with the Ln-0 link are relatively stable, volatile and well soluble in organic solvents. Their thermal decomposition at 260-3200C leads to the formation of oxides [16, 17]. Actinoid organometallic compounds are generally unstable, sensitive to oxygen and can only exist in a highly reduced environment in the presence of organic solvents [17]. Their synthesis and structure have been widely covered in published papers.

When thermobaric characteristics of the fluid change in the process of migration, lithophilous organic compounds are likely to be removed, while stable compounds with As, Sb, Hg, Se and other elements are more likely to remain in the fluid and its derivatives to accumulate in relatively light fractions of liquid hydrocarbons. The presence of radioactive elements in bitumens suggests that the ionizing radiation energy, along with temperature and especially pressure, was one of the factors causing bond breaking in compounds of metals with organic ligands that transported them in the fluid and facilitated the formation of microlites of minerals and their assemblages dispersed in the carbonaceous matrix. In some cases, native elements have also been found. For instance, anthraxolite clots from the basement may contain greyish-yellow spherules consisting of sulphur with small amounts of arsenic, according to microprobe analysis.

If the thorium content is as high as several percent and the uranium content is tenths of one percent, bitumen becomes rounded and idiomorphic in shape relative to the matrix irrespective of the host mineral substratum (biotite, amphibole, feldspar or quartz). As the metal content of bituminous substances decreases, their shapes become more conformable with fractures and pores of rocks.

The distribution of radioactive elements in different carbonaceous compounds implies a substantially higher stability of uranium-organic complexes in reduced systems as compared with their thorium-organic counterparts. This is evident from the sharp decrease in the Th/U value in bitumen at 220-190^{0}C (transition from kerite to asphaltite) primarily due to the sharp decrease in the Th content and wide development of U-bearing bituminous compounds in the vertical geological section (up to 3-5 km).

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F-radiography allows the tracing of the vertical migration of fluid systems in the geological medium. On the Siberian Platform, these rarely penetrate above the Cambrian salt deposits other than through major faults. Within the South Tatarstan Arch, uranium-bearing bitumens are found in the Devonian and Carboniferous. Figure-10 shows the provisional geological section of the studied regions, which features the impregnations of bituminous substances in rocks and the corresponding detectors with the tracks produced by the fragments of uranium nuclei and indicates the fluid migration paths.

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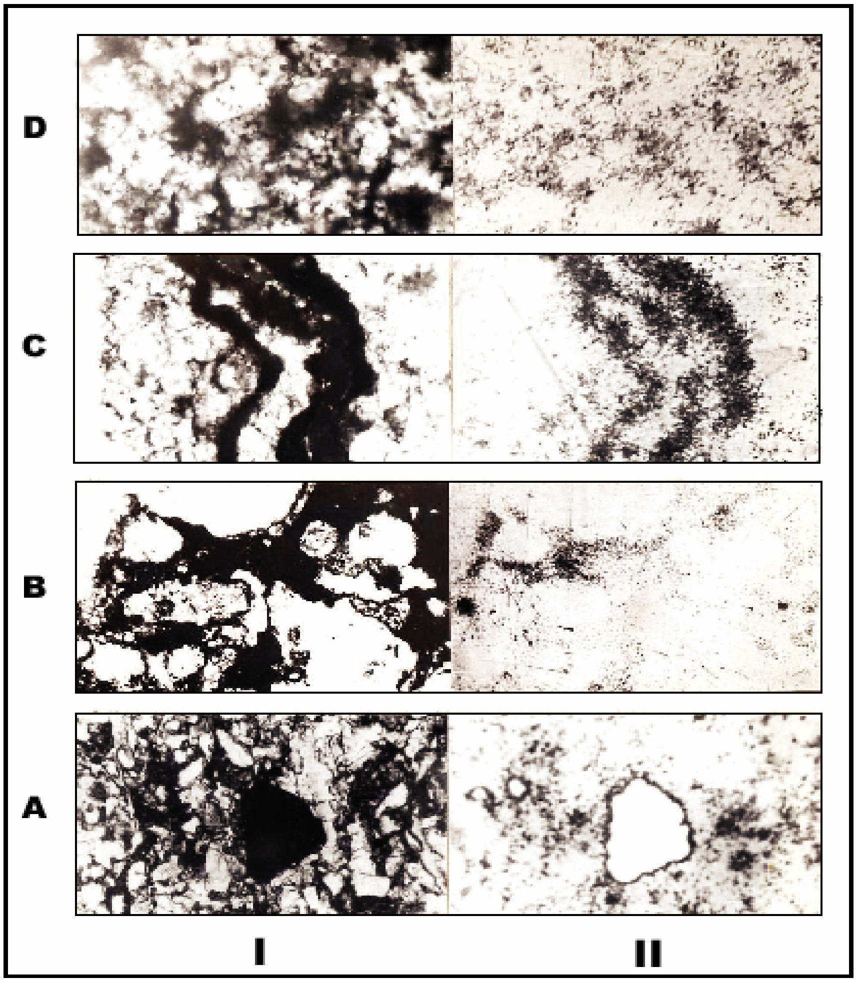

Figure-10. The traces of the migration of fluids marked out by the uranium-containing bitumen. (I - photo of thin section, II - detector): A: granite of crystalline basement; B: sandstone of the Devonian deposits; C: dolomite of the Devonian deposits; D: limestone of the Carboniferous deposits.

The source of the reduced fluids is unknown and is out of the scope of this paper. However, this problem is yet to be solved by integrated geochemical and geodynamic studies. Geochemical characteristics of oil show that the sources of the fluids that participate in oil generation are more likely to be represented by gas emissions of high-alkalinity basic and ultrabasic melts during their crystallisation [1, 2, 19, 20].

The analysis of deep geophysical data clearly indicates the association between the formation of depressions in the continental crust and the oncoming rising of the mantle substratum [21, 22], i.e. deep magmatism that causes the intrusion of the mantle magma into the lower crust. Mantle magmatism creates surface depressions and is reflected in eruptions of basalts and intrusions of diabase dykes. The development of volcano-sedimentary complexes is followed by a long hiatus in volcanism and by the formation of sedimentary deposits. The structural analysis of trappean depressions of the Central (Appalachian), Southern (Karu, Parana, Kaokoveld) and Northern (Labrador, Greenland, Brito-Arctic) Atlantics shows that the end of the evolution of sedimentary basins was marked by alkaline magmatism [23]. It is obvious that alkaline magmatism was reflected not only in magmatic intrusions but also in the fluid exchange between layers.

Ultramafite and mafite intrusions in the consolidated crust are in most cases stratified. In recent years, the large-scale stratification of magmatic complexes was explained by the periodic, repeated entry of fresh doses of melt into the magmatic chamber and their mixing with the earlier intruded magma [24-26]. As a result, igneous complexes constantly grew in volume. Their final size largely depended on the lifetime of the given magmatic system as well as on the further imposition of inherited endogenous events within relatively local areals.

The composition of magmas often changed with time from tholeitic to alkaline. This was caused by the evolution of the zone of decompressive melting above the hot spots and by the inflow of alkaline fluids into the chambers. The alternation of tholeitic and subalkaline basalts within the Siberian Platform may indicate the nearly simultaneous formation of the Permian/Triassic magmas [27]. That is, stable differences in sources and compositions of basalt melts observed throughout the period of trappean magmatism are quite obvious.

Thus, magmatic pulses on platforms created the multistage character of magmatism, both in time and in space, and the observed chemical differences. The intrusion of magmas and their stratification due to convection were followed by the final stage of the intrusion's development. This was accompanied by substantial losses of thermal energy and by the concentration of a major portion of the fluid and incoherent elements in the upper part of the magmatic chamber. The composition of separated magmatic fluids of the C-O-H-N-Cl-F-S-P system can vary depending on the chemistry and the stable depth of their sources. This mainly occurs due to the binding of hydroxyl in minerals of overlying rocks and the dramatic growth of the ratio of hydrogen to oxygen compounds. The fluids can thus form reduced systems. Under high thermodynamic parameters of the migration of gas systems, microelements were apparently transferred together with chlorine, fluorine, sulphur, phosphorus and simple hydrocarbon radicals. At temperatures below 400□C, the fluid composition became more complex due to the active synthesis of hydrocarbons in the reaction of hydrogen with carbon dioxide and monoxide. This was also accompanied by the decomposition of some inorganic metal complexes. All these processes led to the formation of more complex compounds with organic ligands.

The effect of the mantle/crust matter exchange on the structure of the consolidated crust within major oil areas will be explained below. The output data of deep high frequency seismic sounding at 30-40 Hz on a section of the Granite line, crossing the northwestern portion of Romashkino, have revealed the complex, hierarchical structure of the Earth's crystalline crust and upper mantle [18] A major seismic amplitude-frequency anomaly with three branches in the lowermost portion of the consolidated crust is observed at a depth of 110-60 km (Figure-11). High seismic reflection and absorption factors within these anomalies indicate a high layering degree of the geological medium at the given lithospheric levels.

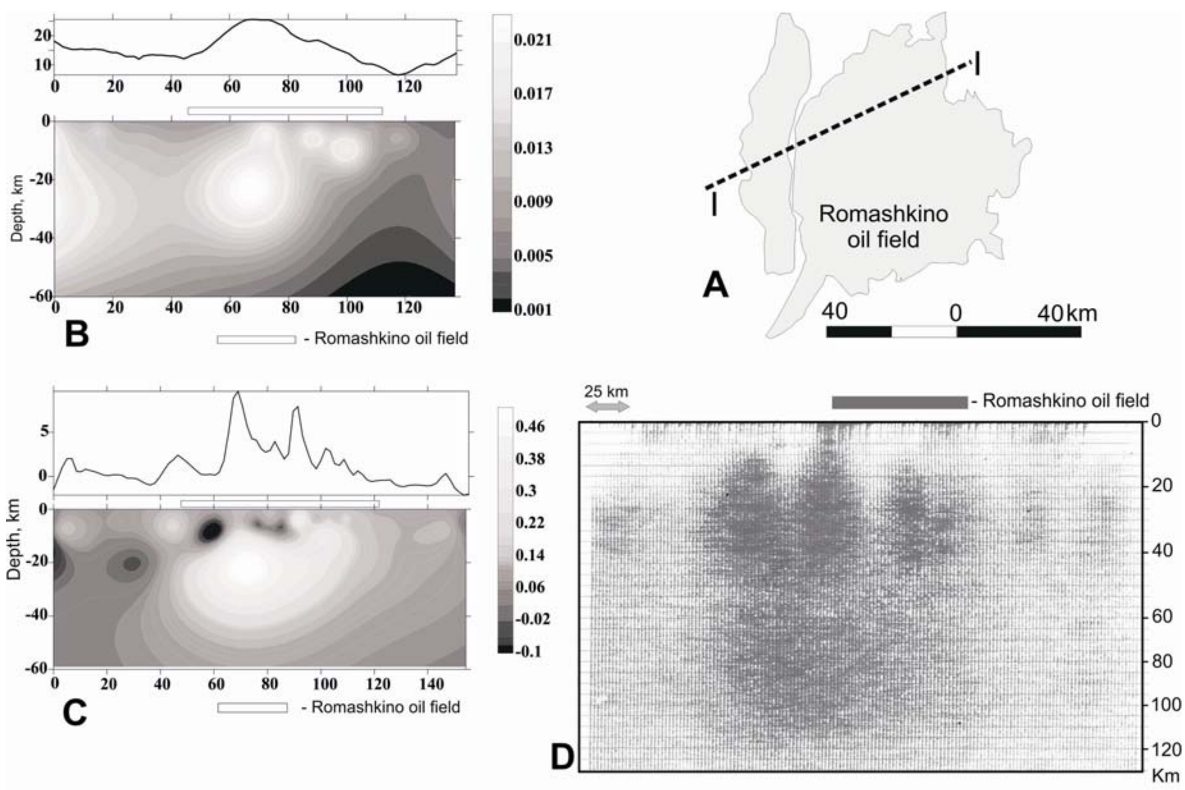

Figure-11. Geophysical description of the mantle/crust matter within the Romashkino oil field. A: location of the deeper cross-section on the Romashkino oil field, B: gravitational field (cross-section I-I), C: magnetic field (cross-section II-II), D: seismic dynamic section along the deeper seismic line "Granite" in high-frequency range of the spectrum 30-40 Hz.

The gravity and magnetic fields have been analysed in this survey line section at 1:200 000 scale [19]. Data inversion was performed by 3D wavelet decomposition. An apparent density section from the M surface to a depth of 18-25 km features two high-density zones of different orders. The most intensive one branches in the upper crust into a series of smaller sources. The magnetic section of the Earth's crust features

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heterogeneous zones with the boundaries between them. A vast area of magnetised rocks, in contrast to the more differentiated gravity field, is traced between depths of 40 km and 20-25 km in the central portion of the studied survey line section.

The analysis of the obtained data shows generally good correspondence between amplitude-frequency, gravity and magnetic anomalies in the consolidated crust below the given portion of the Romashkino field. These reflect structural and compositional heterogeneities in the crystalline substratum and are, in the authors' view, caused by the intrusion of basite/ultrabasite magmas.

CDP data from the Batholite deep survey line, crossing the Nepsky Arch, indicate the elevation of the M surface in the zone containing hydrocarbons and the presence of groups of reflected waves [28]. The strongly stratified, 30-km thick portion of the Earth's crust indicates the presence of mafite-ultramafite intrusions. It should however be noted that, according to deep geophysical data, the Earth's crust has a classic three-part structure outside oil zones both in the Volga-Ural region and within the southern Siberian Platform. It is characterised by a low diversity of rocks and by a common behaviour of potential fields.

CONCLUSIONS

Gas and liquid hydrocarbon components mainly occur in crystalline basement rocks of ancient platforms penetrated to a depth of more than 3000 m due to deep degassing processes. The traces of the upward migration of fluids are sealed in the geological sequence, including the sedimentary cover, within secondary inclusions of rocks and minerals.

The fluids are complex, reduced, multicomponent systems that transport lithophilous, chalcophilous and siderophilous elements. The presence of microelements in the bituminous phase of inclusions indicates that metals mainly occur in the complexes containing organic ligands.

During the evolution of the fluid systems under new pressure and temperature conditions, low-solubility substances were separated out of the fluid to form hard bitumen, and the lighter components migrated into the overlying fractured and porous rocks. The high metal content of carbonaceous substances and their compositional variations governed by homogenisation temperatures of the inclusions suggest that they are not the products of the decomposition of oil fields.

The constant presence of uranium in the fluid and its differentiation products allows the tracing of the systems' migration ways from the crystalline basement to oil-saturated reservoir zones of the sedimentary cover

The known geochemical properties of bitumen and oil - high platinum content, specific distributions of rare earth elements, that are not characteristic of the upper crust formations, as well as $^{143}Nd/^{144}Nd$ and $^{87}Sr/^{86}Sr$ isotopic compounds, which are out of balance with the organic matter of sedimentary rocks - suggest that hydrocarbons are accumulated in the presence of cooling high-alkalinity mafite-ultramafite intrusions.

This logically corresponds to the distribution of seismic anomalies and magnetic and gravity fields in the consolidated crust below the South Tatarstan and Nepsky arches of the Romashkino and Verkhne-Chonskoye oil fields.

The analysis of the magmatic evolution on platforms reveals its alkaline trend due to the impeded degassing of magmatic sources at depth and the inflow of new doses of alkaline fluids or melts into them. Further evolution of the zones of partial melting of the substratum led, in the authors' view, to the generation of oil-forming fluids and their transportation into the Earth's upper crust. Their interaction with the surrounding rocks in turn led to the formation of oil accumulations.

Thus, oil is the product of the interaction of deep, reduced fluids with the organic matter of sedimentary sequences. Oil, graphite of the Archaean crystalline complexes and hard bitumens are interrelated elements of the evolution of deep, high-enthalpy systems.

REFERENCES

[1] Gottikh R. P., Pisotsky B. I. and Zhuravlev D. Z. 2008. Geochemistry of Oil and Possible Sources of Its Trace Elements. DAN. Vol. 420 [in Russian].

[2] Marakushev A. A., Pisotsky B. I., Paneyakh N. A. and Gottikh R. P. 2004. Geochemical Characteristics of Oil and Origin of Oil Fields. DAN. 398(6): 295-299 [in Russian].

[3] Vinokurov S. F., Gottikh R. P. and Pisotsky B. I. 2000. Integrated Analysis of Distribution of Lanthanides in Asphaltenes, Waters and Rocks for Studying the Conditions of Oil-Field Formation. DAN RF. 370(1): 183-186 [in Russian].

[4] Gottikh R. P., Pisotsky B. I. and Zhuravlev D. Z. 2006. Role of Endogenous Fluids in the Formation of Carbon-bearing Rocks in Petroleum Provinces. DAN RF. 412(4): 524-529 [in Russian].

[5] Kolesnikov A., Goncharov A.F. and Kutcherov V.G. 2009. Methane-Derived Hydrocarbons Produced Under Upper Mantle Conditions. Nature Geoscience. 2(8): 566-570.

[6] Kutcherov V. 2006. Class Transition of Crude Oils under Pressure. International Journal of Thermophysics. 27(2): 67-473.

[7] Atanasyan S. V. and Burova E. G. 1985. Bitumens in the Crystalline Basement Rocks. In: Geochemical Studies of the Migration of Hydrocarbon Systems. Moscow, Nauka Press. 77-87 [in Russian].

[8] Rabotnov V. T., Kulibakina I. B. and Arefiev O. A. *et al*. 1980. Relic Hydrocarbons in the Crystalline

ARPN Journal of Earth Sciences

Basement of the Siberian Platform. DAN. 252(5): 1207-1210 [in Russian].

[9] Chersky N. V., Tsarev V. P. and Soroko T. M. 1982. Effect of Seismotectonic Processes on the Alteration of the Mineral Organic Matter. Yakutsk [in Russian].

[10] Korolev E.A., Kamaleeva A.I. and Plotnikova I.N. 2012. Mineralogocal Indicators of Fluid Dynamic Activity in the Crystalline Basement of an Oil and Gas Field. Geochemistry International. 50: 964-973.

[11] Nourgaliev D.K., Muslimov R.Kh. and Sidorova N.N. *et al*. 2006. Variation of i-butane/n-butane ratio in oils of the Romashkino oil field for the period of 1982-2000: Probable influence of the global seismicity on the fluid migration. Journal of Geochemical Exploration. No. 89.

[12] Plotnikova I.N. 2008. New data of the present-day active fluid regime of fractured zones of crystalline basement and sedimentary cover in the eastern part of Volga-Ural region. International Journal of Earth Sciences. No. 97.

[13] Plotnikova I.N. 2006. Nonconventional hydrocarbon targets in the crystalline basement, and the problem of the recent replenishment of hydrocarbon reserves. Journal of Geochemical Exploration. No. 89.

[14] Kochetkov K. A., Skondinov A. P. and Zemlyanskii N. N. 1975. Antimony and Bismuth. Methods of Elemental Organic Chemistry. Nauka, Moscow [in Russian].

[15] Makarova L. G. and Nesmeyanov A. N. 1975. Mercury. Methods of Elemental Organic Chemistry. Nauka, Moscow [in Russian].

[16] Bochkarev M. N., Kalinova G. S. and Zakharov L. N. *et al*. 1989. Organic Derivatives of Rare Earth Elements. Nauka, Moscow [in Russian].

[17] Nesmeyanov A. N., Nikishina T. V. and Nogina O. V. *et al*. 1974. Subgroup of Copper, Scandium, Titanium, Vanadium and Chromium. Lanthanoids and Actinoids: Methods of Elemental Organic Chemistry. Nauka, Moscow [in Russian].

[18] Muslimov R. Kh. 2004. The role of new geological ideas in development of old oil producing regions in the first quarter of the XXI century. Oil and gas geology. Materials of the Interregional Conference. 2-10 [in Russian].

[19] Gottikh R. P., Pisotsky B. I., Nurgaliev D. K. and Zhuravlev D. Z. 2005. Genetic Aspects of the Formation of the Romashkino Field. National Geology. No. 3. pp. 3-13 [in Russian].

[20] Gottikh R. P., Pisotsky B. I. and Zhuravlev D. Z. 2000. Geochemical Features of Bitumen and Oil Bearing Rocks in Some Petroleum Provinces: Isotope Ratios of Nd and Sr. DAN RF. 375(1): 85-88 [in Russian].

[21] Deep Structure of the USSR Territory. 1991. Moscow, Nauka Press [in Russian].

[22] Egorov A. S. 1998. Deep Structure and Geodynamics of the Lithosphere in Northern Eurasia According to Geological and Geophysical Modelling Along Russian Geotraverses. St. Petersburg, VSEGEI Russian Geological Research Institute [in Russian].

[23] Makarenko G. F. 1997. Periodicity of Basalts, Biocrises and Structural Symmetry of the Earth. Moscow, Geoinformmark [in Russian].

[24] Hatton C. J. and Sharp M. R. 1989. Significance and origin of boninite-like rocks associated with the Bushveld Complex. In: Crawford A.J. (Ed). Boninites. London. Unwin Human. 174-203.

[25] Lambert D. D., Walker R. J. and Morgan J. W. *et al*. 1994. Re-Os and Sm-Nd isotope geochemistry of the Stillwater Complex, Montana: Implications for the petrogenesis of the J-M Reef. J. Petrol. 35(6): 1717-1753 [in Russian].

[26] Sharkov E. V. 2006. Formation of Stratified Intrusives and Associated Mineralisation. Moscow, Nauchnyi Mir. p. 364 [in Russian].

[27] Almukhamedov A. I., Medvedev A. Y. and Zolotukhin V. V. 2004. Compositional Evolution of Permian/Triassic Basalts of the Siberian Platform in Time and Space. Petrology. 12(4): 339-353 [in Russian].

[28] Detkov V. A., Valchak V. I., Gorunov and N. A. *et al*. 2007. Some features of the Earth's crust and upper mantle structure of the southern part of the Siberian platform in Batolin and Altai-Severnaya Zemlya sections. Models of the Earth's crust and upper mantle by deep seismic profiling. International Symposium, St. Petersburg. 22-30 [in Russian].