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Comparison of the contribution of differently depth geological processes in the formation of a trace elements characteristic of caustobiolites

S.A. Punanova[1], M.V. Rodkin[1,2]*

[1]Institute of Oil and Gas Problems of the Russian Academy of Sciences, Moscow, Russian Federation

[2]Institute of Earthquake Prediction Theory and Mathematical Geophysics, Moscow, Russian Federation

Abstract. The article analyzes the correlation dependences between the logarithms of the concentrations of trace elements (TE) in various geochemical environments (oil, coal, fuel and black shales, as well as in clays, organic matter (OM) of various types and biota) in comparison with the average chemical composition of the upper, middle and lower continental crust. At the same time, along with the TE content of oils of the main oil and gas basins – the Volga-Ural and West Siberian ones, the data on the TE content in the so-called young oils were summarized; as such, data on the oil fields of the West Kamchatka oil and gas field and oil manifestations in the area of the caldera of the Uzon volcano were used. Particular attention was also paid to the results of the analysis of the TE composition of the oils of the Romashkino group of fields, as it is possible that they are subject to the influence of deep-seated processes. The correlation coefficients between the studied parameters for the various studied oil- and gas-generating basins, including for the Romashkino group of fields, turned out to be close. For all oils, except for the young oils of Kamchatka and the caldera of the Uzon volcano, a closer connection of their TE composition with the TE composition of the lower crust was revealed. For young oils of the Uzon caldera in Kamchatka, this trend is absent, and a slightly closer relationship is revealed with the average composition of the upper but not lower crust, while for statistically more reliable data on the TE composition of the hydrothermal waters of the caldera of the Uzon volcano, a significantly closer relationship is observed with the average chemical composition of the middle and upper crust. Based on the identified correlations between the TE compositions of oil, caustobioliths and the crust of different levels, conclusions are made about the likely relationship between biogenic and deep processes in the formation of oil and gas fields. According to the authors, the obtained results support the crucially important role in the processes of naphthidogenesis of the upward flows of the low crustal fluids with the dominant source of hydrocarbons from the initial OM of sedimentary basins.

Keywords: trace elements, naphthides, hydrocarbons, earth crust, platform oil and gas bearing basin, correlation coefficients

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It is considered that the process of naftidogenesis is complex, due to the combined interaction of exogenous and endogenous factors. The influence of these processes should be reflected in the composition of microelements (MEs) of oils, which are an important source of information on the processes of oil and gas formation (Gottikh et al., 2008; Punanova, 2004, 2017; Rodkin et al., 2016; Rodkin, Punanova, 2018).

The development of oil and gas fields is a whole complex of necessary measures aimed at the extraction of hydrocarbon (HC) raw materials with maximum effect. At the same time, the knowledge of a huge number of scientific disciplines is used to build a structure model of the deposit, field, oil and gas territory. This includes model programming based on mathematical programs, as well as a broader interpretation of the concept of modeling – mathematical methods of data processing, monitoring in time and space of various properties of hydrocarbons and enclosing strata, the creation of genetic models of oil formation processes, modeling the accounting of deep processes for the possibility of replenishing hydrocarbon resources, the need for geochemical control over development. All these indicators should be taken into account when developing oil and gas fields (Muslimov, 2018; Muslimov, Plotnikova, 2018; Rodkin, Punanova, 2018; Punanova, Rodkin, 2018).

[*]*Corresponding author: Svetlana A. Punanova*
E-mail: punanova@mail.ru

The presented work became possible due to a significant increase in the volume of analytical data on the content of ME in various oils and in other caustobiolites and in rocks. Such progress was achieved in connection with the use of inductively coupled plasma mass spectrometry (ICP-MS), which made it possible to more accurately and quickly determine the concentrations of various MEs in samples (Ivanov et al., 2005, 2013; Maslov et al., 2015; Fedorov et al., 2007; Fedorov et al., 2010). Typical concentrations of various MEs in oils and other caustobioliths (coals and shales), in the upper, middle, and lower continental crust and in living matter differ by several orders of magnitude. In this case, it is more justified to use a logarithmic rather than a linear scale to compare the concentrations of different MEs. We have shown (Rodkin et al., 2016) that the calculation of correlation coefficients for ME concentration values on a logarithmic scale is very useful and informative, this approach is also used in this article.

Correlation between the composition of microelements of various natural reservoirs and the earth's crust

We have analyzed the correlation between the logarithms of ME concentrations in caustobiolites (various oils, coals, oil and black shales), clay rocks, in the upper, middle and lower continental crust and in various types of living matter (biota). When calculating the data used: H.J. Bowen (1966) and V.V. Kowalski (1970) on living matter; M.Ya. Shpirt and S.A. Punanova (2012) on shale, coal and oil; A.P. Vinogradova (1956) on clay; S.A. Punanova (1974) on average ME contents in oils (average sample) and S.R. Taylor, S.M. McLennan (1988) and R.L. Rudnick, S. Gao (2003) on the continental crust. In contrast to the previous analysis (Rodkin et al., 2016), more detailed data were used in this work to differentiate the analysis by three levels of the earth's crust and various types of biota. At the same time, along with the ME content of the oils of the main oil and gas bearing basins of Russia – the Volga-Ural and West Siberian, the contents of the ME in oils of the West Kamchatka oil and gas bearing basin and in oil concentrations in the caldera of the Uzon volcano (Kamchatka) (Beskrovny et al., 1971; Yakutseni, 2005; Kudryavtseva et al., 1993; Dobretsov et al., 2015). If in relation to oils the analysis of the ME concentration is carried out, then in the case of average compositions of caustobioliths and especially of different horizons of the continental crust and clays, this is not entirely correct. For example, the concentration of Fe in the composition of the cortex clearly should not be attributed to the ME region. Bearing this in mind, in the case of the composition of the earth's crust, we will continue to speak not about the ME composition, but about their average chemical composition.

Table 1 presents data on the correlation between the ME composition of clays, coals, oil shales with the chemical composition of the continental crust. Calculations of the correlation coefficients (r) between the logarithms of the average ME contents show a closer relationship between the ME composition of clays, coals, oil shales (obviously upper crustal formations) and the ME composition of the upper continental crust (r = 0.84-0.90) compared to the ME composition lower continental crust (r = 0.79-0.83). The ME composition of black shales has a more significant relationship with the ME composition of the middle crust (r = 0.84). The formation and reformation of black shales takes place at great depths (rather than the formation of oil shales), over a longer period of geological time, and therefore the effect of deep penetrations with a set of so-called deep MEs is more likely.

In contrast, the ME content in oils is more closely correlated with the ME composition of the lower continental crust (r = 0.63) compared with the upper (r = 0.60) and middle (0.58) ones. Moreover, the correlations obtained for the average ME of the oil composition with the crust composition turn out to be significantly lower than the correlations for clays, coals, and shales, which indicates the greater complexity and possible polygenicity of the formation of its ME composition. High correlation dependencies are revealed

Clays and caustobiolites	Continental crust			Biota			
	upper	middle	lower	plants		animals	
				marine	terrestrial	marine	terrestrial
Clays	***0,90**/41	0,85/40	0,83/41	**0,77**/28	0,72/29	0,53/23	0,46/28
Coals	**0,84**/41	0,76/40	0,78/41	**0,78**/28	0,71/29	0,48/23	0,50/28
Black shales	0,82/41	**0,84**/40	0,80/41	**0,78**/28	0,75/29	0,57/23	0,56/28
Combustible shales	**0,84**/35	0,76/34	0,79/35	**0,76**/28	0,74/29	0,54/23	0,55/28
Oil (average)	0,60/37	0,58/36	**0,63**/37	**0,61**/26	0,58/29	0,59/24	0,54/28

*Table 1. The relationship of the ME composition of caustobiolites with the chemical composition of a number of geo-reservoirs. * The value of the correlation coefficient / the number of used values of the logarithms of element concentration; the maximum values in a row are marked in bold.*

between ME compositions of caustobioliths and biota of various origin. The maximum figures (up to 0.78) are characteristic of the relationship between the ME composition of caustobiolites and the ME composition of marine plants. The correlation results definitely indicate that deep components play an important role in the genesis of hydrocarbons.

The microelement composition of oil and its polygenicity

According to (Punanova, 2004; Babaev, Punanova, 2014; Punanova, 2017 and others), most of the ME of oil composition is inherited from the initial organic matter (OM) of sedimentary rocks, as evidenced by the dominant share of the so-called biogenic elements among ME oils a high correlation between the content of ME in oils and the average composition of living matter. Other MEs can be introduced into oil from host rocks and formation water. At the same time, some of the ME oils definitely indicate the presence of a deep source, at least at the level of the lower crust (Gottich et al., 2008).

However, the problem of the ME appearance in oils in connection with deep processes is very polemical. An analysis of the published material on the distribution in oils of elements characteristic of deep magmatic processes, namely As, Sb, Hg, La, and Eu (Nadirov et al., 1984), indicates that the concentration of these elements drops significantly in oils at great depths in the amplification of catagenetic processes. If there was an inflow from the depths, it would be more logical to observe higher concentrations of metals in deep oil samples, and not vice versa. Also the metal content of oils extracted directly from the foundation is controversial. The oils from the deposits in the basement and in the overlying Lower Oligocene in the Vietnamese White Tiger field are characterized by close values of almost all the studied geochemical parameters. The closeness of these oils with respect to the genetic parameter, – V/ Ni < 1, is especially indicative. The prevalence of Ni over V characterizes these oils as weakly transformed (Serebrennikova et al., 2012; Shuster et al., 2018).

Analysis and generalization of the considered material makes it possible to assume the existence of several sources of ME in oils: inherited from living matter (V, Ni, Zn, Cu, U, Fe, Co, As, Mo, Ag, I, Br, B), borrowed from oil from surrounding rocks and formation water (Si, Al, Ti, K, Na, Ca, Mg, Ba, Sr, U) and introduced (As, Hg, Sb, Li, Al, B, lanthanides and REE) along the permeable zones from deep Lower crustal areas of the earth's crust, i.e. polygenic their origin. In this case, the dominant source is the ME composition of the initial OM for oil and the supply of ME that enters the sediment together with the decomposition and transformation products of organisms. We note, however, that the assignment of elements identified in oils to a particular group of sources is very arbitrary. Some "biogenic" elements (V, As, Cu, Fe), under certain geological and geochemical conditions, enter the oil from the environment, while a number of elements (K, Na, Mg, Ca) can be partially inherited from the initial OM. A certain fraction of "abiogenic" elements can also be associated with living matter and with the initial OM (Punanova, 2017).

Confirmation of previous uniform geochemical profile of the ME of oils and living matter composition (Punanova, 2017) is confirmed by the correlation coefficients between the logarithms of the concentrations of the ME average composition of oils and biomass (Fig. 1). For the whole set of 25 ME, r = 0.56. When using data only on biogenic elements V, Ni, Fe, Co, Cr, Zn, As, Pb, Au, and Br, the correlation coefficient is much higher, r = 0.83 (Rodkin et al., 2016). Thus, ME oils are the same witnesses to the organic origin of oil, as are a number of relict hydrocarbon (HC) structures of biogenic origin.

The distribution nature of average ME contents in formation waters (data from more than 1000 analyzes of formation water from oil fields located in various tectonic regions and covering a wide stratigraphic range are used) is similar to the "field" of the element concentrations distribution in organisms and oils (Gulyaeva, Punanova, 1974; Punanova, 2007). To assess the tightness of the relationship, ME correlation coefficients of formation water composition in a number of oil fields and the ME of the main natural geochemical media and various types of rocks of the continental crust were calculated (Table 2). The closest relationship between the ME composition of groundwater is observed with the ME composition of living matter (r = 0.81).

The correlation coefficients of the oil composition with the composition of the upper and lower continental crust (from 0.64 to 0.66) are somewhat smaller in

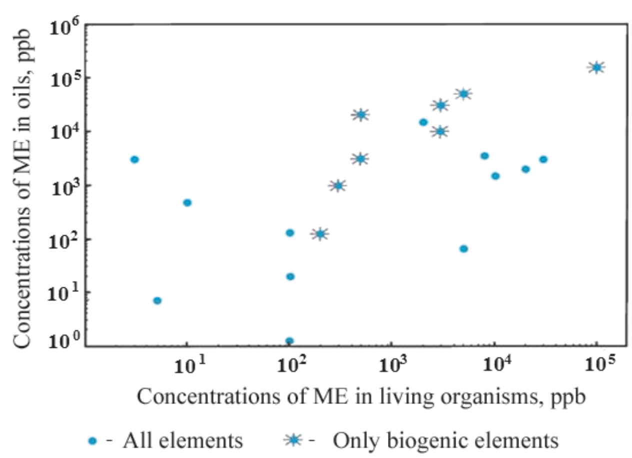

Fig. 1. The relationship between the average concentrations of ME in oils and in living organisms: the concentration values for a number of elements coincide (Rodkin et al., 2016)

Correlation objects	Upper crust	Lower crust	Biota	Oil	Clay rocks	Coals
Formation water	0,66/19*	0,64/19	0,81/23	0,65/16	0,58/17	0,46/17

*Table 2. Correlation between the logarithms of the average concentrations of ME in the formation water of oil fields with the composition of the ME of various geochemical environments (Punanova, Rodkin, 2016). * The value of the correlation coefficient / the number of used values of the logarithms of element concentration; the maximum values in a row are marked in bold.*

magnitude and close to each other (Punanova, Rodkin, 2016). These data are consistent with conclusions based on illustrative material on the close relationship between the composition of ME reservoir water number of oil fields, biota, and oils.

Close values of the ME of the most important elements in the geochemical aspect in oils and black shales with respect to benthos and plankton, as well as in coals with respect to terrestrial vegetation, strongly support the assumptions about their biogenic nature (Fig. 2 a, b).

Indeed, although the magnitudes of these relations are not always identical, the changes in the values in oils, shales, coals and the initial OM occurs symbatically, which indicates their genetic proximity (Shpirt, Punanova, 2012).

From the foregoing, the polygenic composition of the ME oils is quite obvious, determined both by the chemical composition of the initial biological substance and the composition of the deep horizons of the continental crust. Based on these data, a model was constructed for the contribution of the main studied natural reservoirs to the ME composition of oils (Fig. 3). In this case, the contribution of biota dominates in terms of the total concentration of nutrients, and the contribution of the lower crust dominates in terms of the diversity of introduced elements and changes in their concentration.

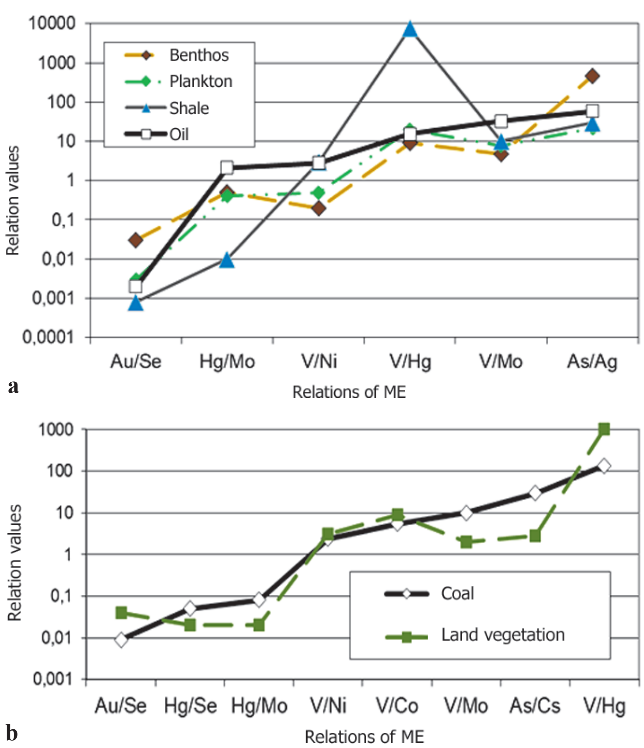

Fig. 2. Relations of ME in oils, shales, benthos and plankton (a); coals and land vegetation (b) (Shpirt, Punanova, 2012)

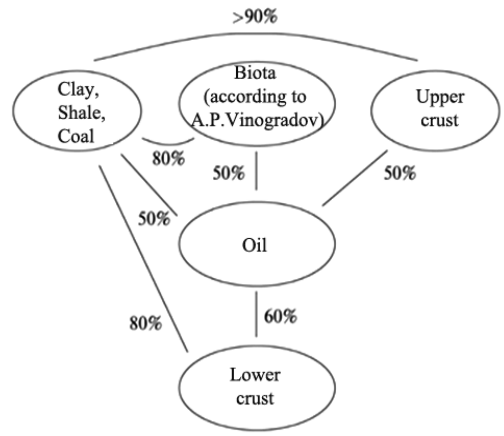

Fig. 3. A simplified model of the magnitude of the contribution-influence (according to the correlation of the chemical composition) of the biota, lower and upper continental crust on the ME composition of oil

Oil features of the Romashkino group of fields

About 20 years ago in Tatarstan, a group of specialists from the Institute TatNIPIneft, Kazan State University, Institute of Organic and Physical Chemistry named after A. E. Arbuzova under the leadership of Academician R.Kh. Muslimova and I.F. Glumov began the study of light migratory hydrocarbon fluids in the deposits located at the beginning of the last stage of development. According to many researchers (R.Kh. Muslimov, I.N. Plotnikova, V.A. Trofimov, R.S. Khisamov, etc.), the so-called “abnormal” wells (with anomalous parameters of productivity) are highlighted in relation to which, on the basis of geological and commercial signs, opinions were expressed about the possibility of their additional recharge by the inflows of deep hydrocarbons.

Various explanations have been proposed for replenishing the reserves of the Romashkino group of deposits (Muslimov, Plotnikova, 2018; and others.). The possible contribution of ME in anomalous zones from deep strata is reported in the works of G.P. Kayukova et al. (2009). These researchers compared the ME contents in oils and bitumen extracted from basement rocks and sedimentary deposits at the Romashkino field. The influence of the ME composition of both the initial OM from sedimentary oil source strata and from deep strata was revealed. It is assumed that the inflow from the basement influencing on the ME composition of the fluids can lead to the disruption of previously established relationships between hydrocarbons and the ME composition of oil. According to the ME indicators, a relationship was found between the types of fluids and the zones of discontinuous disturbances, and a conclusion was drawn about the formation of regional oil-bearing strata of terrigenous Devonian due to the supply and mixing of hydrocarbons from different sources. In Fig. 4 the ratio of the ME indicators of oils from different zones is reflected. The element concentrations in the oils of these two zones practically do not differ from each other. G.P. Kayukova et al. (2009) confirm the same, arguing that the differences are manifested only in the relationships between the ME composition of the oils and the physicochemical properties of the oils. Fields with anomalous wells are characterized by positive high correlation between the hydrocarbon composition, the ratio of resins and asphaltenes, density and sulfur,

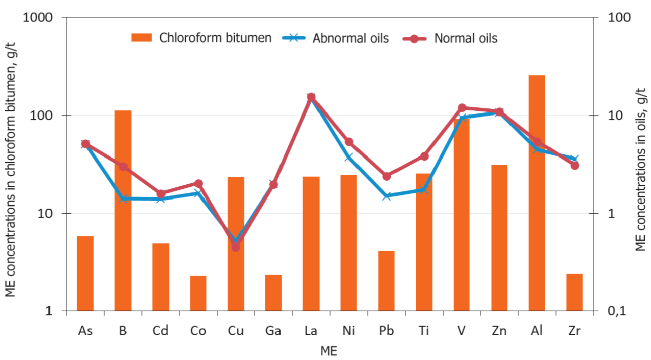

Fig. 4. Comparison of oils from "abnormal" and "normal" Romashkino wells with chloroform bitumen of rocks by ME concentrations (according to analytical data by G.P. Kayukova et al., 2009)

whereas for oils from ordinary wells, which are likely to bear the burden of secondary changes (including the influence of technogenic factors), the absence of such connections is manifested.

Based on HC contents and ratios in naphthides, I.N. Plotnikova and G.T. Salakhidinova (2017) proposed a set of geochemical indicators that allows conducting geochemical monitoring of oils at the developed fields in order to study the process of re-formation of the reservoir during its development and possible replenishment with light hydrocarbons.

V.A. Bochkareva and S.B. Ostroukhova (2012) expressed in their work an interesting concept about the two-phase generation of hydrocarbons filling the deposits of the Romashkino group of fields. It is assumed that in abnormal wells flow rate increases and the composition of oils or gas condensates changes as a result of the young stage of oil generation and their recharge with newly formed oils. At the same time, this second stage of oil generation is associated not with a deep hydrocarbon inflow, but with a younger phase of fluid generation from OM of sedimentary strata.

The table 3 presents the results of evaluating the contribution of different floors of the continental crust to the ME formation of oil composition of the Romashkino group of fields based on calculations of correlation coefficients.

Based on the tabular data, it is possible to note in almost all the samples a slightly higher correlation between the ME of oil composition in the Romashkino group of fields and the chemical composition of the lower and middle continental crust than with

Fields, age	Continental crust			Biota			
	upper	middle	lower	plants		animals	
				marine	terrestrial	marine	terrestrial
Romashkino group of fields, according to analytical data (Ivanov et al., 2013)							
Abdrakhmanovo area, 6 samp.	*0,57/26 ±0,02	0,56/26 ±0,03	**0,59**/26 ±0,02	0,39/23 ±0,18	0,42/23 ±0,11	**0,51**/23 ±0,16	**0,51**/23 ±0,14
Berezovsky area, 5 samp.	0,55/25/25 ±0,02	**0,57**/25 ±0,03	**0,57**/25 ±0,02	0,48/22 ±0,17	0,46/22 ±0,12	**0,65**/22 ±0,16	0,60/22 ±0,15
Romashkino group of fields (satellites oil**), according to analytical data (Maslov et al., 2015)							
Pashian, 5 samp.	0,76/ 60	**0,77** / 54	**0,77** / 60	0,70 / 32	**0,75** / 35	0,71 / 30	0,74 / 34
Dankov.-Lebedyan., 2 samp.	0,74 / 59	**0,76** / 53	**0,75** / 59	0,76 /31	0,80 /34	0,79 /29	**0,81** /33
Kizelovskian, 1 samp.	0,73 / 59	**0,77** / 53	**0,75** / 59	0,76 /31	0,78 /34	0,78 /29	**0,79** /33
Bobrikov.-Radaevsk., 3 samp.	0,73 / 59	**0,77** / 54	**0,75** / 59	0,76 /32	0,80 /35	0,80 /30	**0,81** /34
Tulskian, 1 samp.	0,70 / 60	**0,72** / 54	**0,72** / 60	0,63 /32	**0,72** /35	0,64 /30	**0,72** /34
Average difference***	0	2,2±1,1	1,8±0,5	0	5,2±1,9	0	2,2±2,7

*Table 3. Correlation coefficients between the ME composition of oils of the Romashkino group of fields and the composition of the continental crust and biota. * The value of the correlation coefficient / the number of used values of the logarithms of element concentration; the maximum values in a row are marked in bold; ** Oils of the Chekansky, Tumutuksky and Tumutuk-Chekansky deposits-satellites of the Romashkino oil field; *** % relative to the first value.*

the upper one. The high correlation of the ME composition of the studied oils with the composition of biota is also revealed. Moreover, for oils from Dankovo-Lebedyanian, Kizelovskian, Bobrikovian-Radaevskian and Tulskian sediments, a high connection with biota of plant and animal origin probably indicates a mixed type of the initial organics in these deposits – sapropelic-humic.

Comparative analysis of oil microelements in various oil and gas basins and the earth's crust

It is also of interest to compare the data obtained for the oils of the Romashkino group of fields with the results of a similar analysis for the oils of the West Siberian oil and gas field. Detailed definitions of the ME of the composition of 8 oil samples from the Shaim region are given in (Ivanov et al., 2005; Fedorov et al., 2007; Fedorov et al., 2010), which allows some statistical analysis of them. The Table 4 presents the results of calculations for oil fields of Shaimsky and Sredneobsky districts, which are fairly uniform in oil composition.

We can see good agreement between the calculation results for individual oil samples. The value scatter of the correlation coefficient in all cases is close to 0.05 (no more than 0.1). From here, we take the value 0.1 as the upper estimate of the possible spread for oils of similar composition; in other words, as the maximum "method error". Estimates of the correlation coefficient with the scatter estimate (Table 4) do not reveal significant differences for the upper and lower crust. However, when comparing data on individual samples in 5 cases, the connection with the lower crust appears to be higher, and in 3 cases there are no differences (Table 4, for reasons of uniformity, only estimates the average correlation values). From this it can be supposedly concluded that the statistical relationship between the ME composition of the oils of the Shaim and Central Ob regions of Western Siberia is still slightly higher with the ME composition of the lower crust than with the upper one. Variations in the correlation coefficients of the ME composition of oils with the chemical composition of the lower continental crust are from 0.57 to 0.71, and for the upper – 0.48-0.60. The connection with the composition of biota is also noticeably weaker (0.49-0.61) than the connection with the lower crust.

For comparison, Table 5 shows the results of calculating the correlation coefficients between oils of different oil and gas bearing basins with average

Fields	Continental crust		Biota
	Upper	Lower	
Shaim region			
Severo - Danilovskoe (well 6567)	*0,53/40	0,**64**/40	0,49/26
Danilovskoe (well 2459)	0,60/40	**0,71**/40	0,61/26
Dorozhnoe (well 1746)	0,53/40	**0,66**/40	0,51/26
Ust-Teterevskoe (well 1856)	0,55/40	**0,67**/40	0,49/26
Ubinskoe (well 1236)	0,56/40	**0,68**/40	0,59/26
Lovinskoe (well 9556)	0,48/40	**0,57**/40	-
Central Ob region			
Vostochno-Pridorozhnoe (well 402/2)	0,59/40	**0,67**/40	0,54/23
Kustovoe (well 1182/26)	0,58/40	**0,67**/40	0,53/23
Average	0,55 ±0,04	**0,66** ±0,04	0,54 ±0,05

*Table 4. The relationship between the concentration of ME in the oils of the Shaim and Central Ob regions of Western Siberia with the chemical composition of the continental crust and biota. * The value of the correlation coefficient / the number of used values of the logarithms of element concentration; the maximum values in a row are marked in bold.*

Oils of some oil and gas bearing basins	Earth crust		
	Upper	Middle	Lower
^Dnepr-Donets	*0,54 / 37	0,51 / 36	**0,58** / 37
^Timan-Pechora	0,57 / 36	0,55 / 35	**0,62** / 36
^Volga-Urals	0,59 / 37	0,60 / 36	**0,63** / 37
^Eastern-Siberian	0,57 / 37	0,54 / 36	**0,60** / 37
^Western-Siberian (Shaim region)	0,69 / 33	0,68 / 32	**0,73** / 33
^^Western-Siberian (Shaim region)	(0,60±0,03)/61	(0,58±0,03)/54	(**0,62**±0,02)/58

*Table 5. Correlation of the ME composition of the oils of some oil and gas bearing basins with the average composition of the upper, middle and lower continental crust. * The value of the correlation coefficient / the number of used values of the logarithms of element concentration; the maximum values in a row are marked in bold; according to data (Gottikh et al., 2008); ^^ according to (Ivanov et al., 2005).*

composition of the upper, middle, and lower continental crust, which in most cases appear to be statistically significant (exceeding the value of a possible random spread of 0.1). In all cases, correlation values are maximal of the ME composition of oil with the average composition of the lower continental crust. Let us note that for the oils of the Shaim region (Tables 4, 5), according to different data from different authors, a slightly closer relationship between the ME composition of oil and the composition of the lower crust was also obtained in all cases.

So, the results of our analysis did not reveal fundamental differences in the nature of the statistical relationships between the ME composition of Romashkino oils and oils of other oil and gas products, as well as a noticeable difference between the ME composition of the anomalous and conventional wells of the Romashkino field (we note, however, that in the second case the comparison results are not completely convincing in connection with a small number – only 12 available values of element concentrations). At the same time, as well as for other oil and gas bearing basins, a relatively closer relationship between the ME composition of oils and the chemical composition of the lower continental crust was revealed.

It is important to note that the change in various concentration samples of presumably biogenic (V, Cr, Co, Ni, Cu, Zn) and deep (Li, Be, La, Sm, Eu) elements (Fig. 5) was uncorrelated. This inconsistency is also not unique to the Romashkino field. We obtained similar conclusions when comparing various genetic groups of MEs for oils from the fields of the Khanty-Mansiysk region (Shuster, Punanova, 2016; Rodkin, Punanova, 2018). The uncorrelated content of biogenic and deep-seated elements in oils convincingly indicates their independent formation from various sources.

In contrast, when comparing distribution of element contents in one putative genetic type of biogenic elements (biogenic in this example), namely V and Ni (Fig. 6 a, b, c), a rather close relationship is observed between the concentrations of these elements in oils of

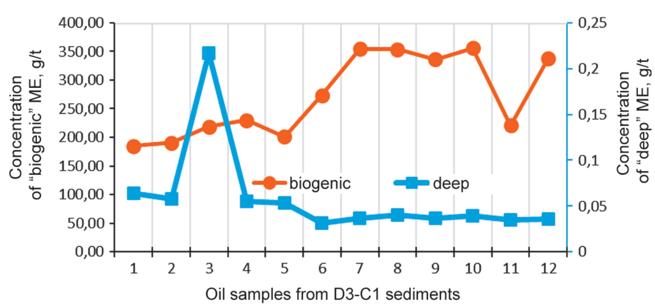

Fig. 5. The distribution model of various genetic types of MEs in oils of different ages from the Romashkino group of fields (according to analytical data (Maslov et al., 2015)); biogenic – ∑ (V, Cr, Co, Ni, Cu, Zn), deep – ∑ (Li, Be, La, Sm, Eu)

different age in oil and gas complexes of the Romashkino group of fields.

The formation of the Romashkino group of fields

Let us note that the possibility of deposit replenishment is consistent both with data on replenishment of the field's reserves and with indications of insufficient hydrocarbon potential of the supposedly oil source formations known here. In view of such insufficiency and, rejecting replenishment of the deposit at the expense of deep sources, academician E.M. Galimov and A.I. Kamaleeva (2015) suggested the migration of hydrocarbons from the area of the Pre-Ural trough to a distance of several hundred kilometers, followed by the final concentration of migrating oil in the Romashkino field. Based on the analysis of oil composition, they concluded that "the probable source of oil from Romashkino and other fields of Tatarstan is the Upper Devonian domanicoids.

Accepting this conclusion, it can be assumed that the source of hydrocarbons are rocks of this type (not only

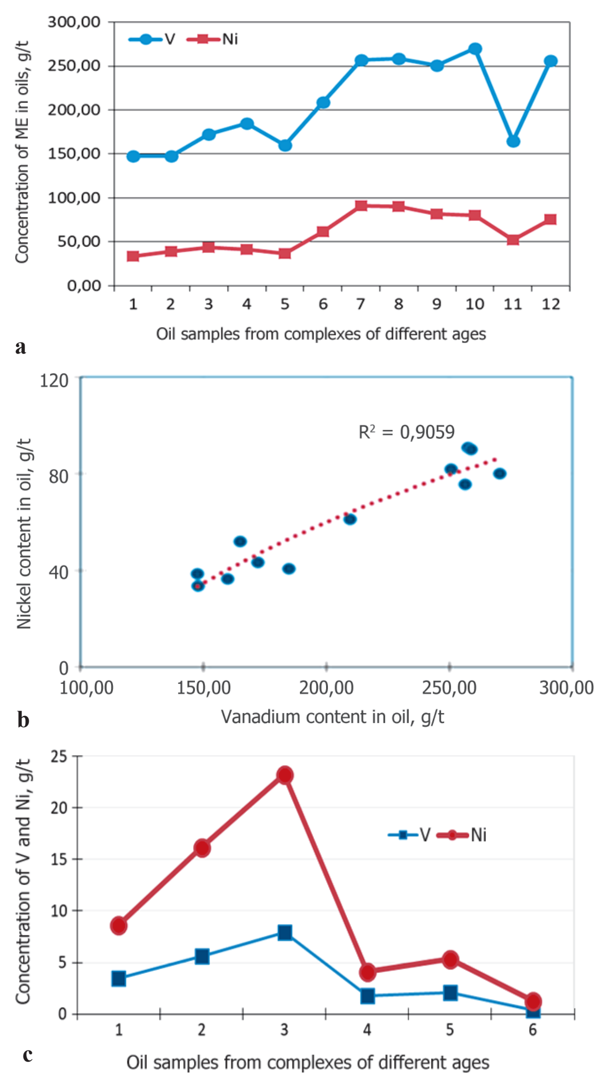

Fig. 6. The ratio of vanadium and nickel in the oils of the Romashkino group of fields: a, b – according to the data (Maslov et al., 2015), c – according to the data (Ivanov et al., 2013)

Domanic, but also sub-Domanic deposits), drawn into the area of deep crust overthrust. Such an interpretation corresponds to the model of hydrocarbon generation and their removal to the surface by an upward fluid flow according to the nonequilibrium flow reactor scheme (Rodkin, Rukavishnikova, 2015; Rodkin et al., 2018; Rodkin, Punanova, 2018; Punanova, Rodkin, 2018). The influence of deep fluids on the oil composition of the Romashkino field, which leads to a significant catagenic transformation that is not characteristic of true domanic fluids, is also evidenced by some works of Kazan researchers. Thus, I.N. Plotnikova et al. (2017), on the basis of detailed studies of the geochemical characteristics of Semilukskian bitumen and the Eifelian-Frasnian oil of the terrigenous complex, it was concluded that in the Semilukskian horizon, along with syngenetic scattered OM, there are mobile bitumen identical to the oils of the underlying terrigenous deposits of Pashian and Timanian horizons. In this regard, it is proposed to consider bitumen in the Domanic strata as migratory. The deposits of Domanic facies serve as "an accumulation or accumulation-generation system, the oil deposits of which were partially formed due to oil systems generated in other sources" (Plotnikova et al., 2017). In addition, the works (Petrenko, Galai, 2012) show transfer of both hydrocarbons and ME from the lower layers of the subsoil: there is a qualitative and quantitative transfer of almost all MEs in the vapor-gas medium from zones with high thermobaric bedding conditions to less rigid zones, which is associated with large-scale gas flows from the bowels.

Thus, we believe that the main source of hydrocarbon oils is buried OM; but for massive oil production, it is necessary to study the sedimentary strata with an upward flow of fluids bearing an ME mark about the characteristic depths of formation of this fluid flow. This assumption, in our opinion, allows us to more naturally explain the formation of the Romashkino field, rather than within the framework of long-distance hydrocarbon migration with a small pressure gradient, through a series of fault zones and with the final concentrated collection of migrated hydrocarbons into the Romashkino field. In the framework of naftidogenesis according to the flow-through nonequilibrium reactor scheme, the upward fluid flow carries an ME mark on the depth of its formation. In typical deep crustal zones of a thrust, massive dehydration reactions of thrusts drawn into a thrust occur at the level of the lower crust. It is this that presumably determines the closer correlation between the ME of the composition of typical oils and the average chemical composition of the lower continental crust. At the same time, the presence of a thrust zone also explains the high concentration of hydrocarbons in the fields; in this scheme, the OM dispersed over the area and depth is concentrated along the thrust line.

The proposed source model of the Romashkino field is supported by the interpretation of the seismic section of this field as a zone of deep thrust (Trofimov, 2014). Perhaps the same is also indicated by the results of soil studies conducted over the oil fields of the Volga-Ural oil and gas field (Trofimov et al., 2007). The results of processing a large analyze array (6272 element determination) indicate the possible migration of some metal compounds from the deep zones of the earth's crust. The influence of oil and gas and deep tectonic anomalies observed in the earth's crust and associated with tectonic processes on the change in the ME of the soil composition is revealed. Over tectonic anomalies an increased content of such elements as Li, B, Al, As was recorded, and over oil accumulations – V, Ni, Cu, Mo, Ag. Figure 7 shows the distribution of Li in soils, an element characteristic of magmatic emanations. It can be seen that the abnormal concentrations of Li in soils tend to be consistent with tectonic anomalies, which are possibly the migration routes of lithium and other elements. Above the oil deposits, on average, slightly elevated Li concentrations were also found. However, the latter are not so pronounced.

A close interpretation of the replenishment of the Romashkino field was proposed in the works of V.P. Gavrilova (2007).

A slightly different picture is revealed by the analysis of ME composition of the young oils of Kamchatka and hydrothermal waters of the caldera of the Uzon volcano (according to analytical data by Beskrovnyi et al., 1971; Kudryavtseva et al., 1993; Yakutseni, 2005; Dobretsova et al., 2015). Despite the wide variation in the values of the correlation coefficients for different trials, a number of general trends are detected quite definitely (Table 6).

As for the other types of oils discussed above, a rather high correlation is observed between the ME composition of Kamchatka oils and the average ME

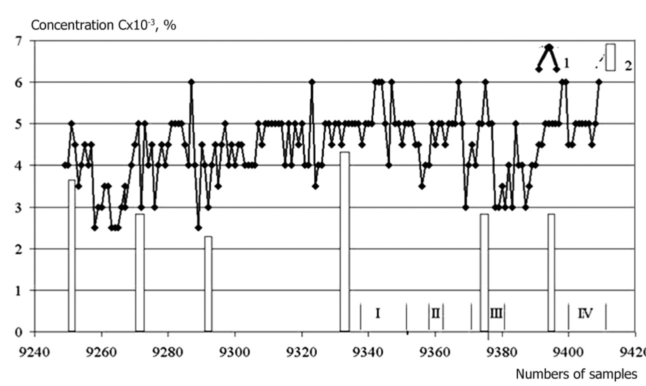

Fig. 7. Comparison of the Li content in the soils of Tatarstan with deep abnormalities and oil content (Trofimov et al., 2007). 1 – Li content in soils; conditional projections on the geochemical profile: 2 – deep anomalies; oil fields: I – Cheremukhovsky; II – Novo-Sheshminsky; III– Summer; IV – Ashalchinsky.

Naphthides	Biota	Upper crust	Lower crust	Clay	Combust. shales	Black shales	Coals	Averag. oil
Izmennaya, well 10	0,50	0,49	0,38	0,09	0,08	0,03	0,26	0,47
Limanskaya, well 1	0,56	0,63	0,56	0,41	0,39	0,24	0,46	0,56
Bogachevskaya, natural show	0,42	0,62	0,55	0,36	0,33	0,16	0,38	0,52
Bogachevskaya, well 37	0,27	0,28	0,26	0,13	0,13	0,08	0,12	0,52
Dvuhlagernaya, well 50	0,56	0,44	0,41	0,39	0,36	0,31	0,41	0,62
Uzon Caldera	0,57	0,50	0,46	0,30	0,29	0,27	0,34	0,75
Average value and dispersion	0,48±0,12	0,49±0,13	0,44 ±0,11	0,28±0,14	0,26±0,13	0,18±0,11	0,33±0,12	0,57±0,10

Table 6. Correlation of the ME composition of Kamchatka naphthides with the composition of typical geochemical reservoirs as the main potential sources of ME in oils (coefficients were calculated not less than 12 ME)

composition of oils (0.57) and biota (0.48) and low (at a level of 30 % and lower) with other caustobiolites (combustible and black shales, coals) and clays. However, unlike all previously studied oils, the analysis of these data indicates a closer relationship between the ME composition of the oil and the composition of the upper crust, not lower crust. This tendency is especially clearly and systematically seen from statistically more reliable data on the composition of hydrothermal waters (Table 7). It is natural to associate such a difference with the fact that, under the intense thermal regime of the volcanic regions of Kamchatka, dehydration occurs at shallower depths, at the level of the upper and middle, rather than the lower continental crust; accordingly, the upward flow of young mobilized waters formed in this case carries a less deep ME tag.

Sources and basins	Earth crust		
	Upper	Middle	Lower
Well 1	0,38/43*	0,41/41	0,30/43
Termophilny sourc.	0,51/43	0,54/41	0,45/43
Paryaschy sapozhok sourc.	0,52/43	0,54/41	0,47/43
PR NP	0,53/43	0,57/41	0,47/43
Yascheritsa sourc.	0,50/42	0,52/40	0,45/42
OTP lake	0,55/43	0,58/41	0,50/43
Bannoe lake	0,59/43	0,61/41	0,55/43
Vos'myerka Lake	0,54/43	0,55/41	0,49/43

*Table 7. Correlation of the ME composition of the hydrothermal waters of Kamchatka with the chemical composition of the upper, middle and lower continental crust. * Values of the correlation coefficient and the number of elements used in the calculation are given through a dash.*

Conclusion

The nature of the correlation relationships of the ME composition of various oils and other caustobioliths with the average chemical composition of OM and the lower, middle, and upper continental crust is analyzed. The nature of the relationship for the various naphthydogenesis basins studied, including the Romashkino field group, turned out to be close. For all oils, except for the young oils of the West Kamchatka oil and gas bearing basin and oil occurrences in the caldera of the Uzon volcano, a closer relationship with the composition of the lower crust was revealed. For young oils of the caldera, this trend is absent, and for statistically more reliable data on the ME composition of the hydrothermal waters of the caldera of the Uzon volcano, there is a significantly closer relationship with the average chemical composition of the middle and upper crust.

The more significant contribution of the lower and middle crust (compared with the upper) to the ME of the oil composition of the Romashkino field is consistent with the assumption of its modern replenishment from deep horizons. The oils of the Romashkino field are more complex and variable in the composition of ME than the oils of the deposits of many other oil and gas bearing basins. Moreover, the complexity in terms of the ME composition for abnormal wells is maximum.

The results of the obtained analysis testify in favor of a model for the implementation of massive naftidogenesis according to the flow-through nonequilibrium chemical reactor scheme; in this case, the ME composition of the oils is largely determined by the depths of the upward flow of deep waters mobilized during dehydration. In a typical continental thermal regime, this level corresponds to the depths of the lower crust. For the active thermal regime of regions of modern volcanism, such as Kamchatka, this level is shifted to the middle and upper crust.

Work on modeling the influence of exogenous and endogenous processes on the trace element component of the naphthides of the Romashkino group of fields is still unfolding. However, the presented materials, in our opinion, provide significant information for assessing the possibility of the presence or absence of an additional source of hydrocarbons here.

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About the Authors

Svetlana A. Punanova – DSc (Geology and Mineralogy), Leading Researcher, Institute of Oil and Gas Problems of the Russian Academy of Sciences

3 Gubkin st., Moscow, 119333, Russian Federation

E-mail: punanova@mail.ru

Mikhail V. Rodkin – DSc (Physics and Mathematics), Chief Researcher, Institute of Earthquake Prediction Theory and Mathematical Geophysics; Leading Researcher, Institute of Oil and Gas Problems of the Russian Academy of Sciences

3 Gubkin st., Moscow, 119333, Russian Federation

E-mail: rodkin@mitp.ru

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