

The microelement composition of caustobioliths and oil generation processes – from the D.I. Mendeleev’s hypothesis to the present day

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Abstract. The past 2019 is the year of the 150th anniversary of the Periodic Law discovery by D.I. Mendeleev. The international community has recognized it as the International Year of the Periodic Table of Chemical Elements. This initiative was made by the Russian Academy of Sciences, which was supported by UNESCO and the UN General Assembly. The law of D.I. Mendeleev is an interdisciplinary phenomenon, the universal language of communication between scientists – not only chemists, but also doctors, biologists, physicists, geochemists, geologists, and probably many other specialties.

The article presents the features of microelements (ME) distribution in various classes of caustobioliths in connection with the Mendeleev’s Periodic Table. Their comparative assessment was carried out. MEs were identified that are concentrated in oils and shales in increased ore concentrations. Theories of oil generation developed by D.I. Mendeleev and other scientists, possible sources of ME in oils, features of the correlation dependencies of ME of the composition of oils and the Earth’s crust at different levels. The polygenic source of ME in oils is substantiated, which is associated both with sedimentary rocks and organic matter (OM) buried in them, and the occurrence of ME in oils introduced from deep zones of the Earth’s crust. A comparative assessment of ME composition of oil and gas basins and the composition of various geological substances indicate that the bulk of MEs are inherited by oils from OM. High enrichment by moving elements is associated with the migration activity during the formation of oil fields, while the correlation of ME oils with the chemical composition of the lower crust indicates the involvement of lower crustal fluids in this process.

Keywords: Mendeleev’s Periodic Table of Chemical Elements, hydrocarbon, caustobiolith, organic matter, clay rocks, sources of microelements, oil generation, Earth’s crust, clarks composition

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Introduction

There are several generally recognized geochemical classifications of elements, which are based on the Periodic Law of D.I. Mendeleev. Classifications of V.M. Goldschmidt (1923), V.I. Vernadsky (1927), A.E. Fersman (1933), N.A. Solodov (1932), A.N. Zavaritskii (1944) and others subdivide chemical elements according to their geochemical similarity, i.e., on the basis of their joint concentration in certain natural systems (Saukov, 1975).

According to the classification proposed by V.M. Goldschmidt and constructed taking into account the position of elements in the periodic system (such as electronic structure of atoms and ions, the specificity of

affinity for certain anions, the position of this element on the atomic volume curve), all chemical elements are divided into 4 groups: lithophilic, chalcophilic, siderophilic and atmophilic.

V.I. Vernadsky laid down the geochemical facts as the basis of his classification: the history of chemical elements in the Earth’s crust, the phenomena of radioactivity, the reversibility or irreversibility of migration (cyclicality) of elements. According to the classification of V.I. Vernadsky (Table 1), the largest number of chemical elements falls into the group of “cyclic” or organogenes (Vernadsky, 1954). Their geochemical history is expressed in circular processes (cycles), of which living matter is important for the course.

The group of cyclic elements according to V.I. Vernadsky is accepted by us as biogenic in studies on the ME assessment of caustobioliths composition.

No. group	Group	Elements	Number of elements	Content, %
I	Noble gases	He, Ne, Ar, Rr, Xe	5	5.44
II	Noble metals	Ru, Rh, Pd, Os, Ir, Pt, Au	7	7.66
III	Cyclic elements	H, Be, B, C, N, O, F, Na, Mg, Al, Si, P, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ge, As, Se, Sr, Zr, Mo, Ag, Cd, Sn, Te, Ba, Hf, W, Re, Hg, Tl, Pb, Bi	44	47.82
IV	Dispersed elements	Li, Sc, Ga, Br, Rb, Y, Nb, In, I, Cs, Ta	11	11.95
V	Radioactive elements	Po, Rn, Ra, Ac, Th, Pa, U	7	7.61
VI	Rare earth elements	La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	15	16.30

Table 1. Geochemical groups of elements according to V.I. Vernadsky

When studying many ore deposits, N.A. Solodov identified 8 classes of chemical compounds: oxyphilic metals, siderophilic metals, non-metals, noble gases, lanthanides, radioactive elements, noble metals, sulfurophilic metals and metalloid elements.

In the given classifications, the inclusion of the same elements in different groups is not excluded. The classification of A.N. Zavaritskii, who divided the Table of D.I. Mendeleev into 10 blocks: 1) noble gases; 2) rock elements; 3) magmatic emanations; 4) elements of the iron group; 5) rare elements, rare earth elements; 6) radioactive elements; 7) metal ore elements; 8) metalloid and metallogenic elements; 9) platinum elements; 10) heavy halogens (Zavaritskii, 1944). A comparative analysis of caustobioliths using Mendeleev's Table shows in color the separation of elements into classes precisely according to A.N. Zavaritskii.

Comparative assessment of microelements in caustobioliths

More than 60 elements are identified in oil and its derivatives. It seems that only technical limitations prevent the detection in oils of almost all elements of the Periodic Table of Mendeleev. Their concentrations are low, but they carry important information.

As applied to them in petroleum geochemistry, the term microelements (ME) (less commonly "Trace elements" or "Spurenelementen"), introduced by A.P. Vinogradov for Zn, Br, Mn, Cu, I, As, B, F, Pb, Ti, V, Cr, Ni, Sr, found in living matter from 1 to 100 g/t; elements in concentrations from 100 to 1000 g/t were designated by him as macroelements (Vinogradov, 1931, 1956).

To assess the nature of MEs accumulation in caustobioliths, a comparison was made of 42 MEs in coals, oils (the ash content of which is assumed to be 20% and 0.1%, respectively) and shale (oil and black shale with an ash content of 50 and 80% and an OM content of 20-80% and 8-20%) of the majority of the world's basins (Table 2) (Punanova, 1974; Yudovich, Ketris, 1994, 2005, 2006; Shpirt, Punanova, 2010, 2012; Babaev, Punanova, 2014).

For comparison, the average contents – clarks of elements were used in clay rocks with an ash content of more than 90% and OM less than 8% (Vinogradov, 1962, 1970) and living matter (Kovalskii, 1970; Bowen, 1966).

The degree of ME concentration by caustobioliths (Q_i) and their ashes (Q_i^A) compared with their average contents in clay rocks (K) was taken as the estimated parameters. For the clark value, a correction factor of 1.13 was used, which was not previously taken into account for calculating Q_i^A , which is associated with calcining of clay rocks at a temperature of 550-900 °C, their dehydration, and weight reduction by 12-14%, which leads to a corresponding increase in the ME content in an average of 13% (Shpirt, Punanova, 2007). Oils contain insignificant amounts of mineral impurities (ash content is usually $\leq 0.1\%$), and MEs are concentrated only in organometallic compounds in a relatively small fraction with a high molecular weight, as a result of which the ME content in them is usually low. For these reasons, the concentration of ME in oil is much lower than its average content in clayey rocks. Therefore, ME contents comparison in terms of oil ash, i.e. Q_i^A parameter is more informative.

The large range of changes takes place in the element concentrations in natural objects, significantly increased concentrations of many elements in the caustobiolite ash, the difference in oil ash from the content of ME from coal ash, shale and clay rocks: enrichment of the ash of oils Hg, Mo, Se, Co, Ni, V and depletion of Be, Sc, La, Pb, Zr, Ti (Fig. 1). Such significant differences in a large number of MEs can be explained by different initial organic material (higher and lower ground vegetation for coal and planktonogenic for oils and shales), as well as conditions for further OM conversion (by the redox environment, burial rate, depth and stage of compensation for deflection).

To determine the dependence of ME concentration on their general geochemical characteristics in various types of caustobioliths, the geochemical classification of A.I. Perelman was applied (Perelman, 1989).

MEs	K ₁ – clarks of clay rocks	Q _i			Q _i ^A				Group of MEs*
		Coal	Shale		Coal	Shale		Oil	
			oil	black		oil	black		
Li	60	0.25	1.0	0.52	1.1	1.77	0.57	–	1
Rb	130	0.12	1.07	0.57	0.53	1.95	0.63	2.3	1
Cs	2.0	0.32	2.5	2.35	1.42	4.42	2.57	27.2	1
Sr	450	0.23	0.6	0.42	1.02	0.97	0.46	0.88	1
Ba	800	0.16	0.7	0.625	0.7	1.24	0.69	0.33	1
Be	3.0	0.7	1.0	0.67	3.1	1.77	0.74	0.15	2
Sc	10	0.27	1.5	1.2	1.19	2.65	1.33	0.25	2
Y	26	0.29	1.0	1.0	1.28	1.85	1.11	–	2
Yb	2.2	0.43	–	1.27	1.9	–	1.41	–	2
La	90	0.13	0.4	0.31	0.58	0.7	0.34	0.09	2
Ce	50	0.42	1.6	1.16	1.86	2.8	1.28	–	2
Eu	0.95	0.42	–	1.26	1.86	–	1.4	1.43	2
Nd	26	0.36	–	1.27	1.59	–	1.41	–	2
Sm	4.5	0.38	–	1.2	1.68	–	1.33	–	2
Pr	7.1	0.34	–	0.59	1.5	–	0.65	–	2
Gd	3.8	0.47	–	1.24	2.1	–	1.37	–	2
Ga	20	0.32	1.0	0.8	1.4	1.77	0.88	3.4	2
Ge	1.6	1.5	1.2	1.5	6.6	2.1	1.67	1.32	2
B	100	0.63	1.3	0.56	2.79	2.3	0.62	–	2
Ti	4500	0.36	0.3	0.67	1.59	0.6	0.74	0.00004	3
Zr	200	0.18	0.8	0.6	0.8	1.42	0.66	0.035	3
Hf	3.0	0.4	1.3	1.4	1.77	2.39	1.55	–	3
Th	12	0.32	0.4	0.58	1.4	0.67	0.64	0.08	3
Sn	10	0.11	0.5	0.39	0.49	0.88	0.43	0.012	3
V	130	0.19	1.0	1.58	0.82	1.77	1.75	268	3
Nb	11	0.2	1.6	1.0	0.88	2.74	1.11	–	3
Mo	2	1.2	1.0	10	5.3	1.77	11.1	538	3
W	1.8	1.3	1.2	1.6	5.75	2.1	1.77	–	3
U	3.7	0.59	0.9	2.3	2.6	1.59	2.55	4.8	3
Re	0.0002	< 5	2.5	4500	< 22.5	4.4	4978	–	3
Cu	57	0.2	0.8	1.22	0.93	1.42	1.34	5.7	5
Ag	0.1	0.5	0.8	10	2.2	1.42	11.1	37.2	5
Au	0.003	10	0.7	2.3	44	1.15	2.55	147.5	5
Zn	80	0.35	1.25	1.6	1.55	2.2	1.77	26	5
Hg	0.05	3.0	3.6	5.4	15.9	6.4	5.97	45000	5
Pb	20	0.64	1.1	1.05	2.8	1.95	1.15	0.028	5
As	13	1.45	1.0	2.3	6.4	1.77	2.54	16.9	6
Se	0.6	5	25	14.5	25	44	15.9	427.4	6
Cr	100	0.14	1.0	0.96	0.62	1.77	1.06	4.3	7
Mn	850	0.18	0.6	0.47	0.78	1.06	0.52	0.3	7
Co	19	0.24	1.0	0.95	1.04	1.86	1.04	14.9	7
Ni	95	0.11	0.7	0.74	0.47	1.33	0.81	132	7

Table 2. The degree of caustobioliths enrichment with microelements (Shpirt, Punanova, 2007). * groups by (Perelman, 1989); A dash in the table means that the average content of the element has not been established; MEs are shown in bold are, the enrichment of which is higher than caustobioliths clarke (Q > K), the so-called “typomorphic”¹, characteristic (Yudovich, 1978).

¹Ya.E. Yudovich and M.P. Ketris, the authors of this term, no longer use it, believing it is incorrect, and instead proposed the term coaleophilic elements for coal (Yudovich, Ketris, 2002) and oileophilic for oil. According to the author, it's a very successful term that will be used in future works.

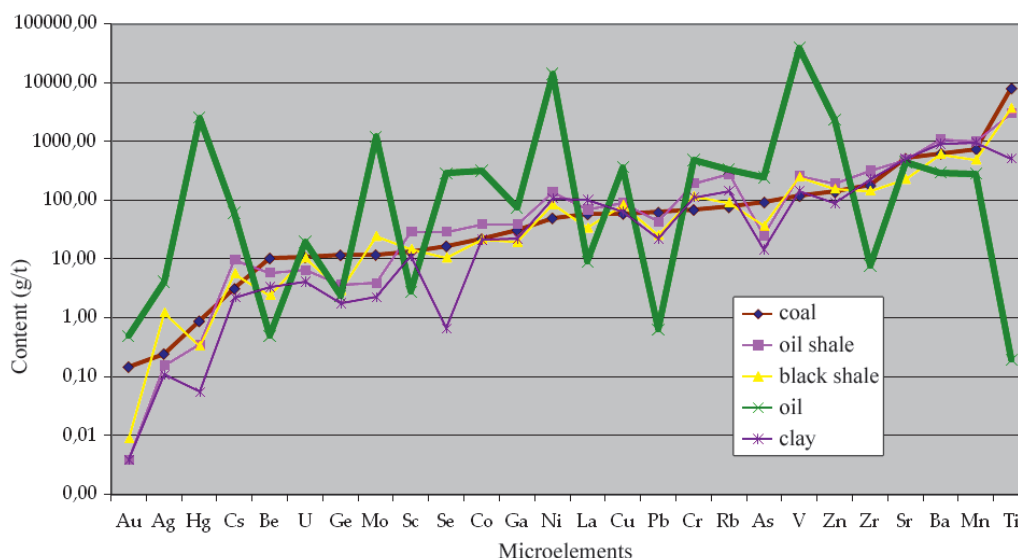


Fig. 1. The average content of microelements in the ash of caustobioliths and clay rocks (ranked by coal)

It was repeatedly used in studies of coal and black shales (Yudovich, Ketris, 1994; 2002; 2005; 2006), with the following ME groups highlighted: 1) typical cationogenic lithophiles; 2) cationic and anionic lithophiles with constant valency; 3) cationic anionic lithophiles with variable valency; 4) typical anionic lithophiles; 5) metals – thiophils; 6) non-metals – thiophils; 7) siderophiles of the iron group.

Table 2 shows a similar grouping of MEs, but group 4 is excluded, since there is no reliable information on the halogen content in oils and coal, and boron is transferred to group 2. Elements are grouped, as a rule, not in accordance with this classification. Traditional geochemical characteristics do not always allow us to explain or predict the degree of concentration of trace elements in caustobioliths, probably due to the fact that during their development the authors do not take into account the specific features of ME interaction with organic components of caustobioliths and, possibly, do not take into account their content in the initial humic or sapropelic material.

By high values of caustobioliths enrichment with microelements, especially oil and black shale ash, ME of groups 5, 6 and 7 (thiophils and siderophiles) – Hg, Se, Au, Ni, Ag, Zn, As, Co, Cr, with the exception of Cu are quite homogeneous. From ME of the 1st group, only Cs is concentrated in caustobioliths. Lanthanides having very similar chemical properties (group 2) differ significantly in their degree of concentration in caustobioliths. This peculiar distribution of individual lanthanides, for example, Eu is also detected for the oils of individual deposits (Gottikh et al., 2009). All caustobioliths are significantly enriched only in Mo and Re (group 3). It should be noted the differentiation in coals of alkali metals and REEs in terms of the Q_i^A coefficients: for Li, Rb, Sc, La, $Q_i^A < K_i$, and for Cs, Y and other lanthanides higher than 1.13 K_i .

Works (Yudovich, Ketris, 2005, 2006), as previous publications of these authors (Yudovich, Ketris, 2002) present calculations of clark concentrations of elements in coals. When replenishing analytical data, these figures are recalculated by the authors. The authors write: “The basis for the calculations was created by M.P. Ketris is a unique Coal Geochemistry Database with tens of thousands of analyzes across all coal basins in the world. This database, continuously updated with new analytical data, made it possible to quickly form fairly homogeneous samples and calculate sample averages, and then evaluate coal clark as the median content in the aggregate of sample averages” (Yudovich, Ketris, 2006, p. 488, authors emphasized).

In our studies of comparing the ME of caustobioliths composition, we rely on the calculations performed by us and published in a number of articles and monographs (Shpirt, Punanova, 2012).

Figure 2 shows the degree of ME concentration (Q_i^A) calculated on the ash of caustobioliths. The curves in the graph are ranked by the Q_i^A of oils. The most dramatic differences are observed when comparing the ME contents in oil and clay rocks. A large group of elements is distinguished by which oil ash is significantly enriched in comparison with clay – Co, As, Zn, Cs, Ag, Ni, Au, V, Se, Mo, Hg, Cu. The contents of Ti, Pb, Zr, Th, La, Be are significantly lower than their contents in clays, and the concentrations of Sc, Mn, Ba, Sr, Ge, Rb, Ga, Cr are very close. Concentrations of the majority of MEs in coals are either lower or not statistically different from their average contents in clay rocks (1.13 K_i values) and only statistically higher for Au, Se, Mo, Hg, Ge, As. Significantly less difference in the degree of enrichment of the ME of oil and black shales compared with clay clarks: black shales are enriched in Ag, Se, Mo, Hg, and combustibles are enriched in Cs, Se.

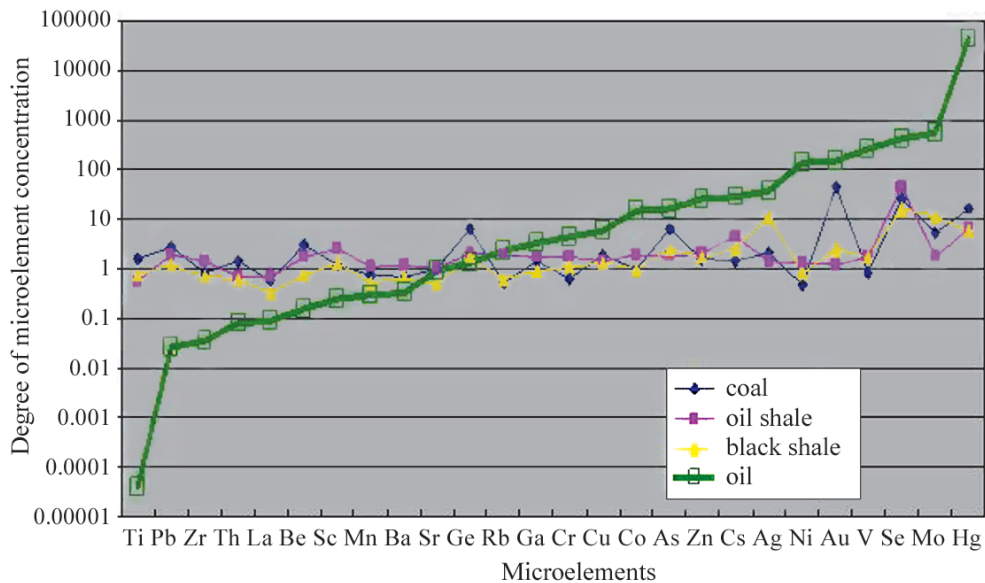


Fig. 2. The degree of microelement concentration in the ash of caustobiolites and shales in relation to clay clarks (ranked by oil)

It can be stated that the same MEs (biophilic elements) are characterized by the highest degree of concentration in all types of caustobiolites, which confirms their genetic unity.

Unfortunately, a number of elements with undefined average data were excluded when plotting. The conclusions obtained are obviously valid only for the average ME contents in caustobiolites, while the comparative indicators for oils, shales, and coals of individual deposits may be different due to the significant difference in the ME contents from the average.

Table 3 shows the “typomorphic” elements, classified by the values of the coefficients $Q_i > 1.4$ and $Q_i^A > 2.0$, in coal, oil shale (combustible and black) and oils, arranged in rows in decreasing Q_i or Q_i^A . MEs with approximately the same values of Q_i or Q_i^A are given in parentheses.

The common “typomorphic” MEs (by dry weight content) for coals and shales (black or combustible) are Au, Se, Hg, Re; coals differ from schists only in “typomorphic” Ge. A significantly larger number of MEs can be considered as “typomorphic” in the value of the Q_i^A parameter, i.e. according to the contents calculated on the ash of caustobiolites. By the number

of “typomorphic” MEs according to this parameter, caustobiolites are located in the sequence: oil (16) > coal (14) > oil shale (12) > black (9). The number of “typomorphic” elements is given in parentheses. Caustobiolites have many common “typomorphic” MEs. In terms of Q_i^A , Ag, Au, As, Hg, Mo, Re, Se, U, W are common “typomorphic” MEs for coals, black shales and oils. According to the Q_i^A parameter, MEs that are “typomorphic” for only one type of caustobiolite can be distinguished, namely: for coal – Ge and Be, possibly Pb, probably Gd; oil shale – Ce, Nb, Sc, Hf; there are no black shales; oils – V, Ni, Co, Cu, Cr, probably Ga, Rb. Therefore, in comparison with other types of caustobiolites, oil ash is the richest ME. It differs both in the number of all “typomorphic” MEs and in the number of “typomorphic” MEs that are characteristic of only one type of caustobiolites considered, which may indicate the complexity and multifactorial nature of oil formation processes.

Figures 3 and 4 using the Periodic Table of D.I. Mendeleev present a comparative average characteristic of ME concentration in oil ashes and in black shales relative to clay clarks and taking into

Caustobiolites	“Typomorphic” MEs	
	By dry weight $Q_i > 1.4$	By ashe $Q_i^A > 2.0$
Coal	Au, Se, Hg, Re, Ge, As	Au, Se, Hg, Re, Ge , As, W, Mo, Be , (B, Pb), U, Ag, Gd
Oil shale	Se, Hg, (Re, Cs), (Ce, Sc, Nb)	Se, Hg, (Re, Cs), Ce , Sc , Nb , Hf , B, Zn, (W, Ge)
Black shale	(Zn, W, Ge, V), Re, Se, (Ag, Mo), Hg, (Cs, As, Au, U)	Re, Se, (Ag, Mo), Hg, (Cs, As, Au, U)
Oil	-	Hg, Mo, Se, V , Au, Ni , Ag, Cs, Zn, As, Co , U, Cu , Cr , Ga , Rb

Table 3. “Typomorphic” MEs in various caustobiolites. MEs that are “typomorphic” for only one type of caustobiolite are shown in bold

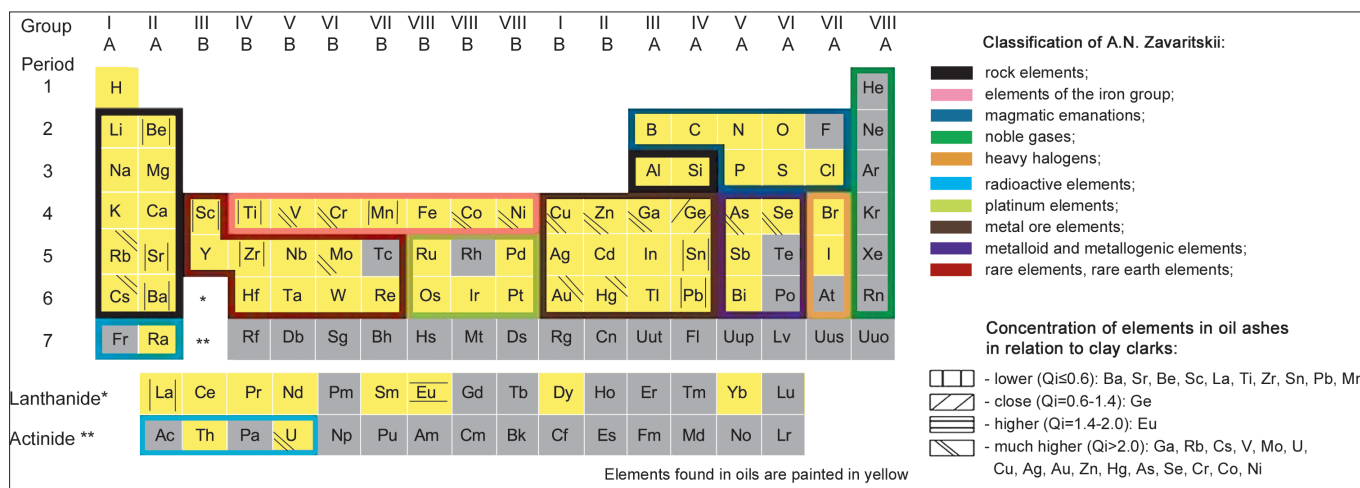


Fig. 3. Element concentrations in oil ashes relative to clay clarks

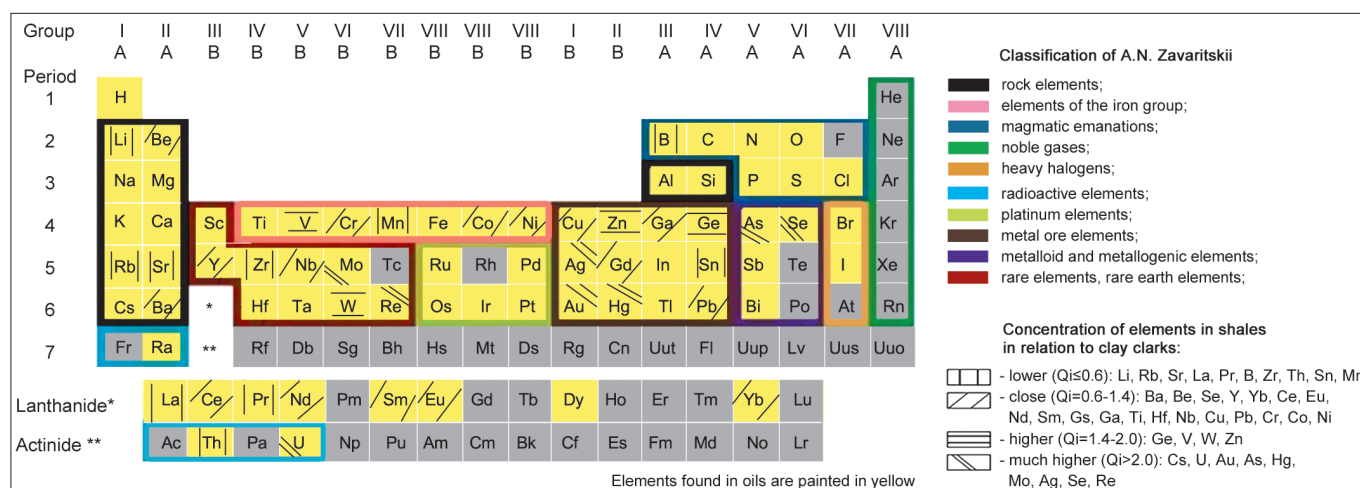


Fig. 4. Element concentrations in oil shales relative to clay clarks

account the classification of elements according to A.N. Zavaritskii. We have identified four gradations of statistical evaluation. An analysis of these data underlines the wide variety of ME composition in caustobioliths. The group of elements enriching caustobioliths includes rock elements, iron groups, metal, rare, metalloid, and radioactive. In terms of enrichment, two groups of elements are distinguished. The maximum values are characteristic of the so-called elements highly mobile under the Earth's crust (Hg, Se, Mo, Sb, As, Cd, Pb, Bi, etc.), which probably indicates the activity of migration processes during the formation of hydrocarbon (HC) deposits.

In some cases, the enrichment values are similar to the concentrations of elements in ore deposits, which makes it possible to use caustobiolite deposits in a complex manner, i.e. and as a potential source of a number of ore elements.

This provision indicates the relevance of the instructions of D.I. Mendeleev on the extreme value of oil as a complex chemical feedstock.

Sources of MEs in oils and problems of naftidogenesis

D.I. Mendeleev was a versatile scientist and, along with the development of the Periodic Law and the creation of the Periodic Table of Chemical Elements, was widely known and a significant contributor to other fields of science. October 15, 1876 at a meeting of the Russian Chemical Society D.I. Mendeleev presented a report in which he offered his views on the problem of oil formation. According to his hypothesis, during formation of mountains, water flows deep into the Earth through faults and/or cracks. In the interaction of water with iron carbides under the influence of high temperatures and pressure, iron and hydrocarbon oxides are formed, which rise upward along the same faults and, filling up porous rocks, accumulate and form oil deposits (Mendeleev, 1877). Probably the work of D.I. Mendeleev at the Baku oil fields and in Pennsylvania (USA), as well as his chemical experiments, which testified to the possibility of such processes, reinforced his ideas. Model of D.I. Mendeleev still serves as one of the starting points

of the abiogenic origin of oil hypothesis in its various modifications, and according to (Pikovskii, 2012), the majority of those issues put forward by D.I. Mendeleev are relevant today, and are the subject of study and discussion today.

M.V. Lomonosov is another great Russian scientist and the founder of an alternative biogenic model of oil generation. M.V. Lomonosov was one of the first who drew attention to the problem of the “emergence” of oil. In 1763, in the famous work “On the Layers of the Earth,” he wrote about oil as follows: “Meanwhile, it is expelled by underground heat from prepared coals of brown and black oil matter and appears in different crevices and cavities, dry and moist, filled with water...”. Since it was believed (and is believed) that coals came from plant debris, oil was also attributed to plant origin, “... oil was formed as a result of decomposition of organic matter under the influence of underground heat” (Lomonosov, 1763). Currently, after almost 150 years since the proclamation of D.I. Mendeleev of his views and more than 250 years since the publication of the work of M.V. Lomonosov’s problems of naphthytogenesis are still competing with biogenic and abiogenic models of oil formation. There are also concepts of oil polygenesis (Dmitrievskii, 2008, etc.).

A significant contribution to the development of oil generation models is made by V.I. Vernadsky, I.M. Gubkin, N.B. Vassoevich, A.E. Kontorovich, N.A. Kudryavtsev, P.N. Kropotkin, B. Tisso and D. Velte, K. Peters and J. Moldovan and many, many other researchers.

At the 29th World Congress on Organic Geochemistry held in September in Sweden (All Abstracts EAGE-IMOG, 2019), most of the reports were devoted to the results of studying, at a modern instrumental level, of structural features and the conversion of initial organic material into oil hydrocarbon during diagenesis and metamorphism considering different oil and gas basins of the world. In the framework of the “sedimentary-migration theory”, the source of oil generation is “living matter” (the term of V.I. Vernadsky), which, when immersed and heated in the sedimentary strata, is gradually transformed into “micro-oil” (Vassoevich et al., 1967).

Scattered hydrocarbons, then migrating along the sedimentary stratum under the influence of a stress field and saturating various types of reservoir traps, form deposits. According to V.I. Vernadsky (1954), confirmed by further geochemical studies, the total amount of dispersed oil in the sedimentary shell of the Earth is much higher than the total amount of oil in the fields (Galimov, Kamaleeva, 2015; Tisso, Velte, 1981; Kontorovich, 2004; Neruchev, Smirnov, 2007; Neruchev, 2013; Skorobogatov, Solov’ev, 2013; Mukhametshin, 2019) and others. Within the framework of such a

model, increased OM concentrations in sedimentary rocks are the main factors controlling the oil and gas potential of the basin, heating them to the required temperature (stagewise catagenetic transformation), and the presence of insulating screens fluid supports and trap reservoirs. In this regard, it is worth highlighting a rather vivid statement by V.I. Vernadsky on the unity of shale and oil hydrocarbons: “Two types of deposits for oil accumulations can be noted: 1) accumulation in sedimentary rocks; 2) penetration (saturation) of bituminous shale hydrocarbons. Both types can be considered as parts of the same phenomenon. Being in shale contains the largest masses of oil”. Summing up all his evidence base of the biogenic hypothesis, V.I. Vernadsky came to the conclusion that “the formation of oils is of great importance in transferring the energy of the Sun through living matter to the deeper layers of the planet” (Vernadsky, 1994 a, b)

Existing abiogenic models can describe the synthesis of only some components of oils, but not of all their diversity, not to mention hydrocarbons - chemofossilia-biomarkers. Chemofossilia are fossil biomolecules, their recognizable fragments and genetic analogues, which are undoubted and often found in oils fragments of living matter (Peters, Moldovan, 1993; Vassoevich et al., 1967) and others.

The development of the oil genesis theory led to the development of more complex models of oil generation. Back in 1993, the founders of modern petroleum organic geochemistry B.A. Sokolov and A.N. Guseva (1993) wrote: “Oil and gas are renewable natural resources and their development should be built on a scientifically based balance of hydrocarbon generation volumes and extraction during field exploitation.” These authors draw attention to the high rates of chemical reactions during the destruction of organic matter and its transformation into mobile gas-liquid hydrocarbons (which occurs under certain natural conditions), which are completely incompatible with the rates of sedimentary strata subsidence and their catagenetic transformation due to slow heating. Hydrocarbon fluid motion also occurs at much greater speeds than previously assumed. Oil manifestations in the rift depressions of the Gulf of California (Guyamas field), in the caldera of the Uzon volcano in Kamchatka serve as examples. Under the influence of high temperatures of hydrotherms, from the sedimentary rocks OM, immature oils were formed here, whose age is estimated at several hundred years (Simoneit, 1986; Sokolov, Guseva, 1993; Puanova, Vinogradova, 2017).

In the modern version of the oil origin theory, the nonlinear (i.e., strongly thermodynamically nonequilibrium) nature of naftidogenesis is indicated and the contribution of abiogenic sources to the formation of hydrocarbon deposits is allowed (Kontorovich,

2004). In the framework of the fluid dynamic model, the importance of an active fluid regime is emphasized when intense upward and downward fluid flows provide the supply and removal of matter and energy from the focus of oil generation (Sokolov, 1996).

As can be seen from the above, the process of oil formation is complex in nature, due to a combination of exogenous and endogenous factors. In assessing the influence of deep and sedimentary processes on the oil formation, interpretation of the data on the ME composition of naphthides can significantly help.

To date, there is no single, well-defined point of view on the source of ME in oils. The analysis and generalization of a large amount of factual material gives us the opportunity to argue for the existence of three sources of ME in oils – inherited from living matter, borrowed by oil from surrounding rocks and formation water and introduced into permeable zones from deep sections of the Earth's crust, i.e. their polygenic origin (Punanova, 2004; Rodkin, Punanova, 2019).

It has been established that when studying the processes of oil formation, the “biogenic” elements (defined by V.I. Vernadsky, 1954) that are present in oils: V, Ni, Zn, Cu, Fe, Co, As, Mo, Ag, I, Br, B et al. Comparison of the “concentration fields” of a large group of elements in oil, oil ash and living matter showed that it is precisely these “biogenic” elements that show the closest similarity between oil and living matter, but a significant difference from the distribution of elements in clay rocks (Punanova, 2004, 2016). Based on this, it has been suggested that the source of a large group of elements in oils is living matter. The inheritance of the ME composition of oils from the initial OM is confirmed by detailed studies conducted by us in the Volga-Ural, Timan-Pechora, North Caucasus-Mangyshlak, West Siberian and other oil and gas basins. With the “oil – dispersed OM” correlation, the composition of precisely “biogenic” elements shows clear genetic relationships, the oil source strata are diagnosed, the types of OM are differentiated, and parallelism in the stages of their catagenetic transformation is established (Punanova, 2017). Features of the “biogenic” elements distribution in oils are clearly linked to the genetic code of oils, expressed in a specific composition of their biotags.

There are MEs that could accumulate in oil during its interaction with formation water and sedimentary rocks. The metal content of oils is to some extent determined by the enrichment by metals of the surrounding rocks both within the sedimentation basin and in the areas of demolition of terrigenous material, and the presence of ore deposits. These can be rock-forming elements, or elements with variable valency – Si, Al, Ti, K, Na, Ca, Mg, Ba, Sr, U, etc. The exchange of elements between oil and the environment, i.e. borrowing is recorded in the oils of the Timan-Pechora oil and gas deposits, the

South Tajik Depression and other regions and is reflected in model experiments (Punanova, 2017).

The fact that so-called “abiogenic” elements – As, Hg, Sb, Li, Al, B, radioactive, lanthanides, REEs – are found to be very important in oils (Vinokurov et al., 2010). Despite the poor knowledge of these elements and their very low concentration, he points to the possibility of introducing elements into the oil through the fracture zones in the body of the basement formations, to the effect on the composition of oils of the upper and lower continental crusts on the ME, to the probability of hydrocarbon accumulations directly in the deep deposits of the earth bark – in loose basement rocks, in unconventional reservoirs. All this is an additional argument in favor of a wide and comprehensive study of the basement, as an unconventional hydrocarbon storage device and a possible ME supplier.

However, the assignment of elements identified in oils to a particular group of sources – to inherited, borrowed or introduced, is very conditional. Some “biogenic” elements (V, As, Cu, Fe) in certain geological and geochemical conditions enter the oil from the environment, while a number of borrowed elements (K, Na, Mg, Ca) can be partially inherited from the initial OM. The same may apply to abiogenic elements. Some of them can also be associated with living matter and with the original organic matter. However, despite the polygenicity of the source of all MEs in oils, the biogenic complex of elements is different from the composition of the host rocks and magmatic emanations and is dominant. It is paragenetically bound in oils and organisms and initially forms the ME type of oil – vanadium or nickel.

The materials presented above on the polygenic character of ME composition of oils are partly of a qualitative nature, making it impossible to quantitatively compare the contribution of the lower and upper crust components and living matter to the formation of the ME in oils. To obtain quantitative estimates of the close relationship between the ME of the oil composition with various reservoirs and biota, the correlation coefficients between the concentrations of chemical elements were calculated (Rodkin et al., 2016). These studies are described in detail in previous works (Punanova, Rodkin, 2019; Rodkin, Punanova, 2019), in which it was shown that for some oil and gas basins there is a systematically higher correlation between the ME composition of oils and the chemical composition of the middle and lower continental crust than with the upper one (according to analytical data (Fedorov et al., 2007; Taylor, McLennan, 1988)). A more detailed study of oils in fields of the Romashkino group of the Volga-Ural oil and gas basin showed that downstream from the Tula sediments of the Lower Carboniferous to the Pashian sediments of the Upper Devonian, the relationship between the ME

composition of oils and the composition of the crust of various levels is steadily increasing. Moreover, the magnitude of the correlation of the ME composition of oils with various geo reservoirs and the chemical composition of biota is noticeably smaller than for coal and shale, which apparently indicates a more complex multifactorial nature of naphthydrogenesis. In this case, a high correlation between the ME composition of the studied oils and the composition of both marine and terrestrial biota ($r = 0.81$) is revealed. Moreover, the relation between the ME composition of oils and the ME composition of terrestrial biota is somewhat higher, which corresponds to the data on the mixed type of the initial organics in these deposits – sapropelic-humic. The number of elements by which the correlation coefficients of concentration logarithms were calculated was different in different cases, but always quite large, varying from 30 to 50. When comparing biogenic (V, Cr, Co, Ni, Cu, Zn) and conditionally deep (Li, Be, La, Sm, Al, Eu) elements in the satellite oils of the Romashkino group of fields (according to analytical data (Maslov et al., 2015)), as well as in the oils of the Abdrakhmanovsky and Berezovsky areas (according to analytical data (Ivanov et al., 2013)), uncorrelated changes in various samples of the concentrations of these two groups of elements were established. On the contrary, when comparing the nature of the distribution of element contents in one putative genetic group, biogenic, namely V and Ni, there is a close relationship between the concentrations of these elements in the oil and gas complexes of different age in the Romashkino group of fields. The uncorrelated changes in the concentrations of biogenic and deep elements with a fairly high correlation of changes in the concentrations of elements within these groups indicates the independent supply of biogenic and deep elements from various sources, and the total concentration of biogenic elements is about 3 orders of magnitude higher, which reflects the crucial role of OM in the oil formation (Punanova, Rodkin, 2019).

Other regularities of the correlation between the ME of the oil composition and the composition of the Earth's crust were obtained using the oils of the West Kamchatka oil field and oil manifestations of the Uzon volcano caldera (according to analytical data (Dobretsov et al., 2015)). Higher correlation coefficients of the oil composition with the composition of the upper crust, not lower one, are noted here. It seems that the traced characteristics of the correlation can be explained by oil ontogenesis in the studied mineral water bodies, which are caused by the peculiarities of geodynamics and the tectonic structure (Kravchenko, 2004). Research of N.B. Vassoevich, V.I. Sokolov, K. Peters, J.M. Moldovan, A.A. Petrov, V.A. Chakhmakhchev, V.F. Kamyranov, A.K. Golovko et al. showed that in the sedimentary section of the Earth's crust, according to the vertical

evolutionary zonation of hydrocarbon formation and transformation due to changes in depth, temperature gradient, pressure and type of initial organics, the composition of hydrocarbon systems generated in the bowels is transformed – from heavy oils to light and condensates. Thus, oils of increased catagenic transformation are more susceptible to deep processing and are characterized by a set of ME associated with lighter oil components, some of which are probably associated with deep processes in the bowels of the Earth, with the products of mantle emanation in areas of its activation and high geodynamic stress. Often, the abnormal enrichment of oil in the hypereogenesis zone of V, Ni, Mo, Re, Cd, Hg and other elements can be explained by their endogenous input under the influence of intrusions and hydrothermal accumulations of asphalt bitumen mainly within the folded areas (Ural, Koryak-Kamchatka, Andean, Apennine and etc.) and the introduction of Hg, Cd, Sb into oil with gas emanations in the zones of deep faults (the Pre-Carpathian Trough, California basins, etc.). Oil deposits of this type, as a rule, of vanadium metallogeny are associated with active geodynamic zones of the reformation and relocation of tectonic structures (Goldberg et al., 1990; Yakutseni, 2005; Punanova, 2017). The oils of these oil and gas regions are characterized by relatively higher correlation coefficients of the ME composition of the lower crust compared to the upper. On the other hand, the oils of the main oil formation zone and early generation oil bear the influence of the upper sedimentary crust to a greater extent, contain more elements associated with the starting organic material: V, Ni, Mo, Co, etc., and exhibit higher correlation dependencies of its ME composition in the upper crust compared to the lower crust (Punanova, Rodkin, 2019; Punanova, 2019).

Conclusion

Thus, the distribution of MEs in various classes of caustobiooliths in connection with the Periodic Table of D.I. Mendeleev was characterized, their comparative assessment was carried out and MEs were identified that are concentrated in oils and shales in elevated, sometimes ore concentrations. The interpretation of hydrocarbon deposits as a production resource as well as of a number of ore elements additionally justifies the relevance of D.I. Mendeleev indication on the extreme value of oil as a complex chemical feedstock.

Theories of naftidogenesis and the contributions of D.I. Mendeleev are briefly described. Analysis of the ME of oil compositions of various oil and gas basins, the Earth's crust of different levels and biota suggests that the bulk of the ME is inherited by oil from OM rocks, which confirms the organic source of hydrocarbon oil. High enrichment with moving elements also indicate the activity of migration processes during the formation of

hydrocarbon accumulations, while the high correlation of ME oils with the chemical composition of the lower crust indicates the involvement of lower crustal fluids in the migration process. These new data on the influence of the Earth's crust composition of at various levels on the ME characterization of oils emphasize the complex nature of oil formation and the influence of deep processes.

A deeper introduction of a large amount of factual material on the composition of microelements of naphthides into the system of the Periodic Law of Chemical Elements is to be made, which will open up perhaps still unknown pages of this connection and will help to correctly solve the most important issues of petroleum geology and geochemistry.

It is important to continue developing naftidogenesis theory, is not constrained by the restrictive framework, and it goes clearly along the lines that were predetermined many years ago: M.V. Lomonosov pointed to the source – the substance – the living, and D.I. Mendeleev – on thermodynamics, the influence of deep-seated processes that supply heat to transform organics. A microelement tag of caustobioliths confirms the validity of these views.

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