GEOCHEMISTRY

Nature of Specific Geochemical Features of Oil

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Oil and especially the related associated bitumen, in particular, are characterized by high metal contents with a predominance of V, Ni, and Zn that make up a specific "oil" assemblage. Based on the prevalence of one of these metals, we can identify the vanadium, nickel, and zinc types of oil not only in oil fields, but also in large oil provinces of Russia (Fig. 1). The concentration of metals in oils may acquire metallogenic significance. In this respect, vanadium-type oil is particularly productive. For example, 2/3 of vanadium production in the United States is related to its recovery from oil [1, p. 87]. In general, oil of this type contains 0.2–130 ppm V, which is two times higher than the Ni content (0.2–60 ppm) [2]. Solid bitumens (asphaltite, asphalt, and others) are formed in the process of oil degassing. They are characterized by high contents of V and Ni (4500 and 520 ppm, respectively). The concentration of sulfur in oil is one of the factors responsible for high contents of these metals in the oil. According to [2], the V and Ni contents amount to 550–1400 ppm and 120–195 ppm, respectively, in heavy sulfurous oil and maltha [2]. The unique Minas Ragra vanadium deposit in Peru is related to sulfurous oil. The V concentration (~6%) is confined to a vein-shaped asphaltite lode (1 km long and 8–12 m thick) hosted in the Cretaceous rocks. Vanadium occurs as patronite VS_2 in association with Ni and Mo [1, p. 91]. Vanadium is a lithophile (oxyphile) metal. Its sulfide deposit can only be produced by oil with an extremely high content of sulfur. Such oil is widespread in Iran, Venezuela, and Russia (Volga–Ural province). Oil in Venezuela is marked by the maximal V concentrations. Heavy varieties of oil in this country contain 335 ppm V, 80 ppm Ni, and 60 ppm Mo [3, p. 571]. Oils from the Volga–Ural province (Russia), Kazakhstan, Iran, Iraq, Kuwait, Angola, Columbia, and Ecuador are also enriched in vanadium. The V content is two times higher than the Ni content. Oils from West Africa and Indonesia, as well as the

Caucasus and West Siberian province (Russia), are represented by V-poor nickel and zinc types.

In contrast to vanadium oil, oils of these two types are depleted in metals. For example, the nickel-type oil contains 0.3–82 ppm Ni, 0.2–60 ppm V, and 0.3–63 ppm Zn, while the nickel zinc-type oil contains 0.2–6.5 ppm Zn, 0.08–1.2 ppm Ni, and 0.03–0.56 ppm V. Nevertheless, the (V + Ni + Zn) assemblage prevails over other metals in these oils. All types of oil mentioned above are characterized by anomalously high contents of V, Ni, Zn, Cu, Mo, Hg, Au, and other metals reaching economic grades. Gold is recovered from oil in California. The mercury halos above oil pools are used in geochemical exploration.

The specific geochemical features of oil should be taken into account in the analysis of its relations to living substances. One should pay attention to "the optical activity of oil, and the occurrence of porphyrins therein (however, as V and Ni complexes rather than Fe and Mg compounds, in contrast to living substances). Porphyrins occur largely in petroleum oil asphaltenes" [4, p. 494]. Porphyrins of oil and black shales contain bivalent Ni and Cu and tetravalent V [5]. Asphaltenes incorporated into the structures, which definitely rule out the participation of living substances in their formation, are most intriguing. Diamondiferous kimberlite and lamproite pipes, which are confined to ancient platforms with a Precambrian basement (the Clifford rule), are such structures. The ancient age of the basement is correlated with the age of primary diamondiferous rocks (peridotites, pyroxenites, and eclogites) that are in kimberlites as nodules (remnants left after replacement with kimberlitic magma). This age correlation indicates the emplacement of diamondiferous rocks at the early stages of the oldest geosynclinal, orogenic, and platform cycles in the evolution of the Earth's crust. The geosynclinal evolution is characterized by extension of the Earth's crust and mantle that promotes degassing of the Earth's liquid core [6]. The extension also favors the selective migration of hydrogen from the fluid emanations from the core, so that the oxygen-bearing components of these flows prevailed over hydrogen. This process generated acidic water fluids (e.g., $H_2 + 3CO = H_2O + CO_2 + 2C$), which provided the maximal melting of the mantle material. As a result, the sources of dia-

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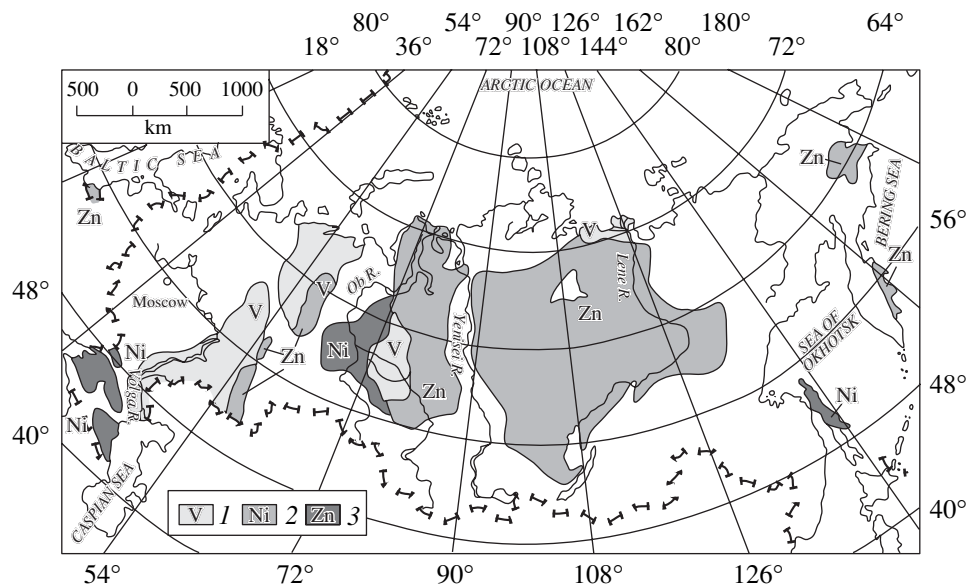
Fig. 1. Oil provinces of Russia classified by predominance of (*1*) vanadium, (*2*) nickel, and (*3*) zinc in oil and bitumen (simplified after I.S. Goldberg [2, p. 64]).

mondiferous magmatism were created at a depth of 200–300 km. Under the influence of fluids, the primary magmas in these sources fractionated and intruded into the Earth's crust in the course of its geosynclinal–orogenic evolution. This model is supported by the CO_2–H_2O composition of fluid inclusions in minerals of normal and low-alkaline mafic–ultramafic rocks, including diamondiferous rocks. These inclusions contain all components of the aforementioned reaction (H_2O + CO_2 + CO + H_2 + N_2).

The extension of the Earth's crust and mantle was followed by compression and folding that stopped emplacement of diamondiferous intrusive bodies for a long period of orogenic–platformal evolution. Magmatism evolved toward an increase in alkalinity only in deep-seated magma sources. However, the sources did not lose structural links with the older diamondiferous intrusions in the Earth's crust. Their fluid impact fostered the remelting of diamondiferous rocks with the formation of kimberlitic and lamproitic magmas, which replaced the older intrusive rocks, inherited their diamond resource potential, and captured their incompletely replaced fragments as nodules. This scenario demonstrates the long-term evolution of the mantle sources in a regime of increasing fluid pressure that stimulated their growth owing to involvement of the mantle substrate with the respective increase in alkalinity of magmas. As compared to the extensional regime, the compressional geodynamic regime more actively prevented selective hydrogen migration from ascending fluid flows and changed the proportions of fluid components toward enrichment in hydrocarbons: $3H_2 + 3CO = H_2O + CO_2 + CH_4 + C$. This reaction was responsible for the hydrocarbonaceous–carbonic fluid regime of kim-

berlitic magmatism that provides emplacement of diamondiferous pipes into the upper zones of platformal structures. The carbonic component of fluids was fixed in carbonates of kimberlites, while hydrocarbons largely migrated and were retaining only in bitumen that occurs as geoides, druses, and veinlets in kimberlites. In geoides of the Udachnaya diamondiferous pipe in the Siberian Platform, the bitumen is composed of asphaltite that is characterized by enrichment in the light carbon isotope ($\delta^{13}C = -34.6\%o$) typical of the oil assemblage, in contrast to the extremely heavy carbon of associated calcite ($\delta^{13}C = +24.5\%o$) [7]. Figure 2 demonstrates the distribution of trace elements in asphaltite (based on [7]) versus their ordinal number with division into even and odd elements. The diagram distinctly shows the oil assemblage (V + Ni + Zn). The high peaks of these elements are considerably higher than those of other trace elements. The high vanadium maximum is especially striking, because this odd element should be less abundant than the adjacent even elements according to the Oddo–Harkins rule. Actually, the V content in asphaltite considerably exceeds the contents of all other trace elements. This indicates an extremely high affinity of vanadium to hydrocarbons and, consequently, its efficient concentration in the processes of their generation.

The second-order maximums in asphaltite fall on Cu, Mo, La, Ce, and Pb. However, their concentrations are markedly inferior to the major (V + Ni + Zn) assemblage. Hence, these metals have an especially high affinity to the oil phase that selectively extracted them from the kimberlitic melt. This is particularly distinct in the case of vanadium, the content of which in asphaltite is much higher than in kimberlite, although asphaltite is
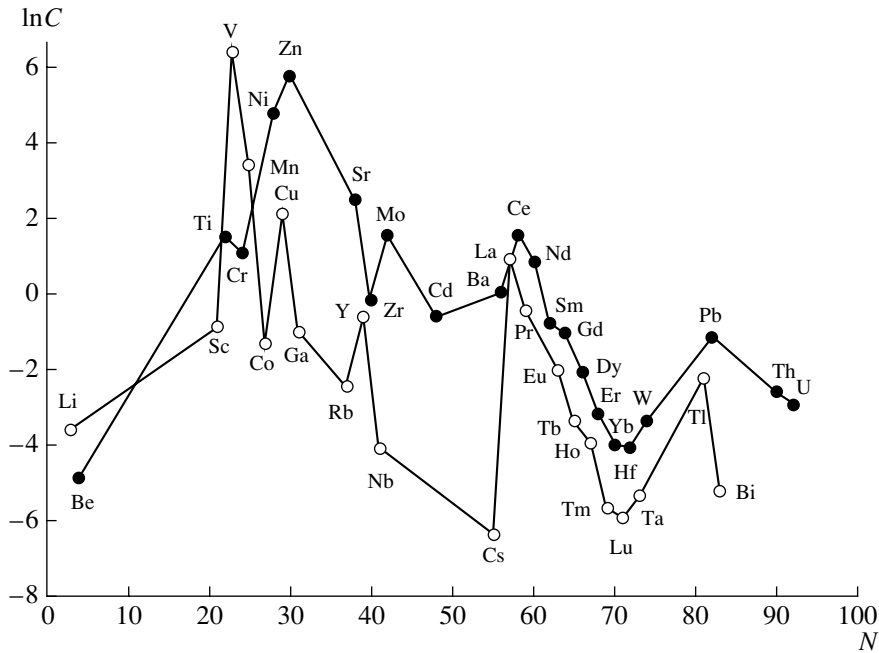
Fig. 2. Geochemical spectrum of asphaltite from the Udachnaya kimberlite pipe in the Siberian Platform. (*N*) Ordinal number of element; (ln*C*) logarithm of trace element content, ppm (after [7]) with subdivision into even and odd elements (filled and open circles, respectively).

depleted in all other trace elements in comparison with kimberlite.

Figure 3 demonstrates the abundance of trace elements in asphaltite from the Aikhal kimberlite pipe in the Siberian Platform. Vanadium and nickel dominate in asphaltite from this pipe, whereas zinc is subordinate. Thus, V and Ni are especially characteristic of the oil assemblage of metals, although oil of the zinc type is also as equally widespread as the vanadium and nickel types. This has been shown above for Russia (Fig. 1). The table compares the trace element compositions of asphaltite and kimberlite from the Udachnaya Pipe. Figure 4 presents the respective geochemical spectrum of kimberlite. The (V + Ni +Zn) assemblage of metals is not recognized in this figure, whereas Ti, Ni, Cr, Mn, and strong bases (Sr, Ba) dominate. Hence, the oil assemblage (V + Ni + Zn) is related to the specific geochemistry of the oil rather than kimberlitic magmatism. The oil fields show a paragenetic relation with the residual bitumen (indicator of oil potential) in kimberlite pipes (Fig. 2).

Kimberlite pipes are permeable structures favorable for the migration of hydrocarbons. Such structures are represented, for example, by the ring-shaped explosion structures at platforms ("astroblemes"). These structures are incorrectly attributed to the fall of meteorites, which have never been detected therein. The occasionally encountered small oil pools hosted in these ring structures (Lake Siljan in the Scandinavian Shield and others) are additional evidence in favor of their endogenic origin. The ring structures serve as conduits

between the Earth's crust and magmatic sources in the mantle. This is eventually expressed in the emplacement of kimberlitic and lamproite pipes, where the primary Precambrian normal and low-alkaline diamondiferous rocks (peridotites, pyroxenites, and eclogites) are juxtaposed with the secondary Phanerozoic diamondiferous subalkali kimberlites and alkali lamproites that contain outliers of primary diamondiferous rocks. In the course of prolonged evolution, magma sources could generate hydrocarbons (e.g., eicosane: $41H_2 + 20CO = 20H_2O + C_{20}H_{42}$) owing to the compression of the mantle material that hampers selective migration of hydrogen from the fluid emanations from the Earth's core. The increase in fluid pressure stimulated replacement of the solid mantle substrate by magmas and their subsequent alkalization. The model of deep generation of hydrocarbons is consistent with their facies characteristic [8], according to which hydrocarbons heavier than methane are formed at high *PT* parameters and transported to the Earth's crust in a metastable state.

Alkaline evolution is typical of platform magmatism. This is especially prominent in volcanosedimentary (trap) depressions, where normal and low-alkaline igneous rocks occur at the base and alkaline rocks are located in the upper part of the section. Both rock associations are separated by carbonate–terrigenous sequences that make up autonomous sedimentary basins. However, like volcanosedimentary depressions, sedimentary basins are connected with mantle sources of alkaline magmas. The hydrocarbon specialization of magma sources is created in the course of this evolu-
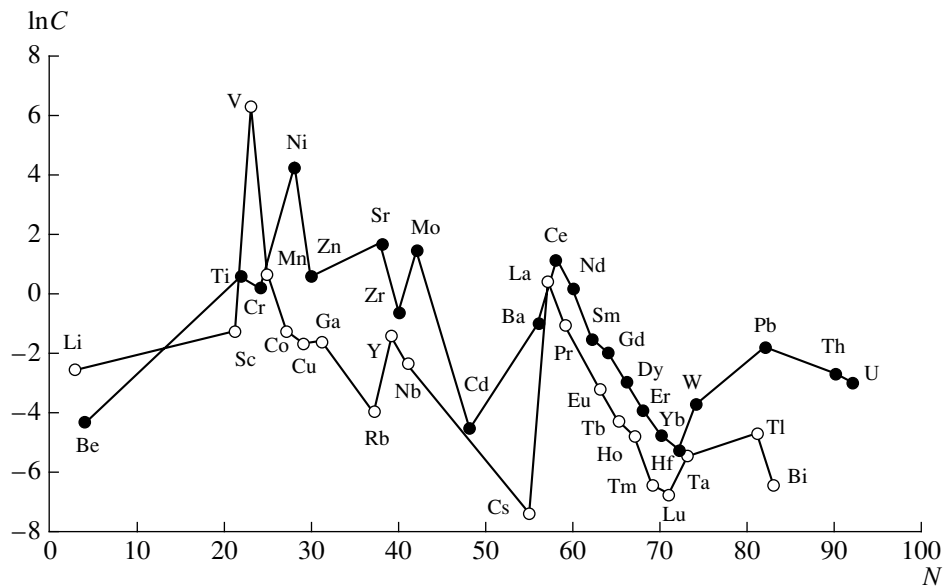
Fig. 3. Correlation of logarithms of trace element contents, ppm, in asphaltite from the Aikhal diamondiferous pipe. See Fig. 2 for legend.
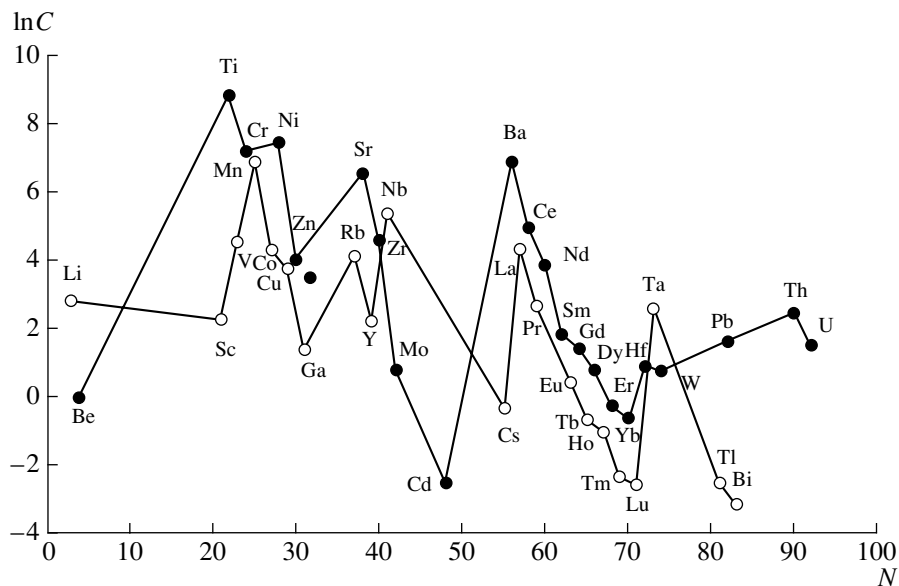

Fig. 4. Correlation of logarithms of trace element contents, ppm, in kimberlite from the Udachnaya kimberlite pipe [7]. See Fig. 2 for legend.

tion, as may be judged from the unchanged geochemical features of alkaline rocks that contain methane and heavy hydrocarbons (C_2H_6, C_3H_8, C_4H_{10}, C_5H_{12} [9]) in fluid inclusions inside minerals.

The leaching of the granitic–gneissic layer of the Earth's crust by ascending flows of deep fluids rather than sagging of the crust was crucial in the formation of sedimentary and volcanosedimentary (trap) platformal and shelf depressions [10].

Oil pools are commonly localized in specific structures of sedimentary basins controlled by domes, thrust faults, and reverse faults in the crystalline basement, the petroleum potential of which has been demonstrated by the discovery of the White Tiger oil field on the shelf of Vietnam [11]. The formation of oil pools as a result of cooling of the ascending hydrocarbon fluids below their stability level was predated by high-temperature fluid leaching that promoted the formation of cavities filled later with oil, gas condensate, and gas.

Trace element contents (ppm) in (1) kimberlite and (2) asphaltite from the Udachnaya diamondiferous pipe [7]

Even elements				Odd elements			
Element	N	1	2	Element	N	1	2
Be	4	0.992	0.0074	Li	3	17.058	0.0269
Ti	22	7078	4.62	Sc	21	9.689	0.422
Cr	24	1333	2.995	V	23	94.69	615
Ni	28	1761	120	Mn	25	960	30.4
Zn	30	57.754	321	Co	27	76.33	0.2685
Sr	38	716.9	12.3	Cu	29	43.52	8.52
Zr	40	99.525	0.842	Ga	31	4.15	0.362
Mo	42	2.258	4.7	Rb	37	62.146	0.0846
Cd	48	0.08	0.545	Y	39	9.719	0.552
Ba	56	973.8	1.07	Nb	41	211.1	0.016
Ce	58	137.4	4.795	Cs	55	0.749	0.002
Nd	60	48.188	2.364	La	57	77.723	2.53
Sm	62	6.45	0.455	Pr	59	14.629	0.635
Gd	64	4.154	0.3464	Eu	63	1.594	0.132
Dy	66	3.762	0.126	Tb	65	0.513	0.034
Er	68	0.789	0.041	Ho	67	0.359	0.019
Yb	70	0.538	0.0179	Tm	69	0.099	0.0034
Hf	72	2.426	0.0168	Lu	71	0.075	0.0026
W	74	2.182	0.0344	Ta	73	13.492	0.00474
Pb	82	5.194	0.3125	Tl	81	0.082	0.106
Th	90	11.721	0.0744	Bi	83	0.044	0.0053
U	92	4.738	0.0527				

The V content in oil is as high as 6 kg/t [3]. Vanadium-type oil is geochemically similar to carbonaceous sediments (black shales) that are widespread in sedimentary basins. The mean V content in carbonaceous sediments (205 ppm) is twice as high as in C-poor sedimentary rocks (110 ppm). The anomalous V contents in black shales (up to a few kilograms per ton) have metallogenic importance. Although a weak positive correlation between the contents of vanadium and organic carbon is established, "the concentrating function of living substances with respect to vanadium could not have created vanadium anomalies in black shales" [12, p. 76]. This statement may also be valid for the genesis of oil. It is known that oil pools may be spatially associated with black shales, justifying the term *oil shales*. They clearly demonstrate the effect described above for oil pools (leaching of rocks that increases their porosity before the influx of oil). The formation of black shales was accompanied by a large-scale abyssal input of hydrogen sulfide, which provided sulfide speciation of vanadium (along with oxide and silicate species). The input of hydrogen controlled the carbon isotopic composition of carbonaceous rocks. Black shales (e.g., shungite from Karelia) contain light carbon as a result of its primary hydrocarbon specia-

tion. In contrast, the carbonate rocks that underlie the black shales contain anomalously heavy carbon [13]. The increase in $\delta^{13}C$ is caused by the input of hydrogen into sedimentation basins and the consequent formation of methane: $4H_2 + CO_2 = 2H_2O + CH_4$. Carbon in methane is mainly bound in the light isotope form. Therefore, carbon in carbonates is enriched in the heavy isotope variety. The newly formed methane either migrates or is incorporated into the overlying black shales, resulting in an additionally concentration of light carbon isotope in these rocks.

Thus, the black shales are carbonaceous sedimentary rocks of the vanadium geochemical type. The anomalously high contents of V (up to 2 wt %) and many other metals indicate that the black shales cannot be considered purely sedimentary formations. The metals were supplied by abyssal hydrocarbon fluids, which were responsible for the anomalous light carbon isotopic composition typical of shungite-bearing rocks in Karelia [13]. This feature draws together the formation of black shales and vanadium-type oil, which is close to black shales in many geochemical parameters, such as the isotopically light carbon and anomalously high concentrations of V and other metals. However, the idea of the direct genetic similarity of black shales and vana-

dium-type oil contradicts the traditional interpretation of their relationships. The black shales are commonly regarded as source rocks for oil: "the carbonate-rich source rocks give up vanadium to oil more readily than the substantially clayey sediments" [12, p. 103]. It is traditionally suggested that "the subsidence of black shales to zones with a temperature of 70–100°C produces enormous amounts of oil and hydrocarbon gases" [12, p. 33]. However, in this case, the black shales must be exhausted in comparison with the vanadium oil, whereas the black shales correspond to vanadium oil in terms of positive anomalies of metals. The correspondence is also traced by isotopically light carbon, whereas the hydrocarbon extraction from black shales should lead to their enrichment in the heavy carbon isotope as in rocks underlying shungites in Karelia [13]. However, the invalidity of the traditional concept is indicated by the geological setting of oil pools. Their localization in sedimentary basins is controlled by tectonic dislocations. The oil pools mostly occur either at the base of depressions or in upthrown blocks of the crystalline basement [11]. Therefore, there is no reason to expect source sedimentary units beneath the depressions. A direct relationship between the formation of black shales and oil is evident from the geochemical data. Accumulation of vanadium was most intense in the Cretaceous black shales (590 ppm V, on average) [12]. This is correlated in time with the peak of oil formation on the Earth (71% of oil reserves in Russia fall in Cretaceous oil). All this indicates that the concentration of metals is conjugated with hydrocarbon generation in magma sources. It is also important to note some "feedback," which is expressed in the impact of the hydrocarbon concentration of metals upon magmatism. The Bushveld pluton (Africa) and the Kachkanar intrusive complex (the Urals), where more than half of the world vanadium reserves is concentrated, are indicative in this respect.

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