

Geochemistry of Reduced Fluids from Alkaline Igneous Rocks of the Khibiny Pluton

R. P. Gottikh¹, B. I. Pisotskii², and I. I. Kulakova³

Presented by Academician A. A. Marakushev August 8, 2005

Received August 18, 2005

DOI: 10.1134/S1028334X06020334

Virtually all igneous rocks contain a certain amount of reduced gas components. Alkaline intrusions (e.g., the Khibiny Pluton) serve as the prominent example.

The first sweeping generalizations on gas compositions in nepheline syenite, trachytoid khibinite, ijolite-urtite, rischorrite, malignite, lujavrite, foyaite, and apatite-nepheline ores were been carried out by Petersil' e [1] and Ikorskii [2], who showed that methane (as much as 93%), carbon oxide, and hydrogen are sharply predominant in occluded and free gases, whereas homologs of methane and carbon oxide are subordinate. The subsequent investigations of gas contents in particular minerals in typical igneous rocks of the Lovozero and Khibiny plutons have demonstrated non-uniform distribution of reduced components in minerals on the one hand, and confinement of their highest concentrations to certain mineral species on the other [3]. The highest gas contents in minerals from the Khibiny Pluton are observed in nepheline, alkali feldspar, aegirine, and titanite (listed in the decreasing order). High concentrations of methane are occasionally found in titanomagnetite, analcime, and eudialyte. Various bituminous substances were found in alkaline rocks together with hydrocarbon gases [4].

In this communication, we focus our attention on the formation conditions and geochemistry of reduced fluids retained in rocks of the Khibiny Pluton. We studied samples of aegirine-nepheline-eudialyte from trachytoid khibinite and impersonite from a feldspar-sodalite-natrolite vein hosted in melteigite.

Four groups of inclusions are distinguished by their character of filling and gas composition [5]. The first group comprises sporadic and isolated rounded primary inclusions in nepheline- and apatite-containing carbon dioxide (85–95%), water, hydrogen, and methane in vacuoles (homogenization temperature, T_{hom} from -56.6 to -57.2°C). The second, most abundant group, embraces the methane-rich inclusions (T_{hom} from -81.8 to -111.3°C) with an admixture of heavy HCs and carbon dioxide. These inclusions are closely associated with magnetite (decrepitation temperature 390 – 410°C). The third group is pseudosecondary and secondary water-methane inclusions ($\text{CH}_4/\text{H}_2\text{O}$ 60%, $T_{\text{hom}} = 264$ – 349°C), which were detected only in urtite-hosted nepheline and apatite-nepheline ore. Inclusions of the fourth group consist of heterogeneous water-salt solutions with variable contents of gas phase (20–70%) and homogenization temperature of nepheline-hosted inclusions (196 – 332°C).

We have detected rare isolated groups of rounded gas inclusions in nepheline grains of the pegmatite with numerous aegirine, alkali amphibole, and magnetite crystals. In eudialyte, the fluid inclusions fill variously oriented systems of pseudosecondary fractures that do not extend beyond the mineral. The first system is largely filled with gas inclusions. The second system is filled with heterogeneous gas, gas-liquid, and liquid-gas inclusions. The third system is filled with gas-liquid inclusions (gas 20–30 vol %). The liquid phase of vacuoles consists of yellow resinous-oily components. Such distribution indicates the formation of fluids during several stages in the course of a slow decrease in crystallization temperature. The gas inclusions similar to those in nepheline were formed first. Inclusions with liquid hydrocarbons and their heterocompounds were the latest formations. It is reasonable to suggest that the excess fluid pressure in crystallizing pegmatites and fracturing of the cooling pluton promoted the removal of gases with separation of polar and nonpolar constituents and temperature-controlled segregation of various carbonaceous substances. We studied the geochem-

¹ All-Russia Research Institute of Geological, Geophysical, and Geochemical Informational Systems, Varshavskoe sh. 8, Moscow, 113105 Russia; e-mail: rimgot@mail.ru

² Institute of Oil and Gas Problems, Russian Academy of Sciences, ul. Gubkina 3, Moscow, 117917 Russia; e-mail: pisotskiy@list.ru

³ Faculty of Chemistry, Moscow State University, Leninskie gory, Moscow, 119992 Russia

istry of impsonite, one of the earliest derivatives of such fluids.

Several hypotheses of abiogenic origin of hydrocarbon gases and bitumen are known to date. Their formation commonly is referred to the final (postmagmatic) stages of evolution of fluid–mineral systems in peralkaline complexes. Methane may be produced by reaction $C + 2H_2O = CH_4 + O_2$ at a relatively high temperature, as follows from the enrichment of methane in the light carbon isotope ($\delta^{13}C$ from -25 to -27%). This value is close to the isotopic composition of carbon dispersed in igneous rocks after the above reaction [5]. The methane-bearing fluids also could be formed as a result of evolution of the C–O–H system in the presence of graphite that occurs as flakes in these rocks. However, the majority of researchers regard synthesis of hydrocarbons as products of a Fisher–Tropsch reaction in wide ranges of temperature (20 – $700^\circ C$) and pressure (0.001 – 2 kbar) on various catalysts and with structural and chemical control of aluminosilicates [6]. The magmatic carbon dioxide and monoxide, which inherit carbon isotopic composition of the mantle, are, in all probability, the main components of reduced volatiles. This is supported by the enrichment of methane in heavy carbon isotope ($\delta^{13}C$ from -3.2 to -12.8%) [7]. Hydrogen could be produced in a rather wide temperature interval at the end of magmatic crystallization, and afterwards as a result of oxidation of iron [8] and dehydration of fluids in the course of crystallization of eudialyte, arfvedsonite, lepidomelane, alkali amphiboles, and hydration of rock-forming minerals [9]. Temperature and pressure estimates for gas and gas–liquid microinclusions in minerals of the Khibiny and Lovozero plutons reported by different authors based on thermobarogeochemical methods are rather similar ($T = 200$ – $400^\circ C$, $P = 0.5$ – 1.8 kbar). Based on the mechanism of catalytic polycondensation of hydrocarbons, one can assume that the synthesis of liquid bituminous substances in the eudialyte-hosted pseudosecondary inclusions should lead to the formation of hydrogen-free compaction products and molecular hydrogen. The spontaneous character of such a process is provided by thermodynamic conditions favorable for the synthesis of condensation products and aromatic structures from nonaromatic structures and more polycyclic and condensed (in comparison with less condensed ones) structures as a result of hydrogen removal. The mechanism of HC condensation as a function of the initial composition of substances and nature of catalysts has been considered comprehensively in [10]. It has been shown that this mechanism is generally multistage. First, the unsaturated compounds are formed as a result of molecular dehydrogenation of hydrocarbons (except methane) that readily occurs on active catalysts at a temperature below $300^\circ C$. In our case, these compounds are identified as ethane, propane, and butane in igneous rocks. The subsequent processes are represented by the polycondensation of transition olefines, the synthesis of aromatic compounds, and the removal

of both hydrogen and methane. The latter reaction is one of the processes of dehydrogenation and dehydration of compaction products.

The reality of such conversions of gaseous hydrocarbons in the closed system of vacuoles with formation of liquid HCs is also confirmed by chromatographic analysis of gas phases in both nepheline and eudialyte inclusions (Table 1).

The amount of released components increases with the heating of samples, owing to the more complete opening of vacuoles. Nevertheless, the following general trends of their qualitative composition are retained: high content of heavy HCs; abundance of methane and its homologs (including C_7); larger volumes of gases released from eudialyte (relative to nepheline) at any temperature of degassing; noticeable prevalence of unsaturated hydrocarbons over saturated ones, although a part of unsaturated HCs may be formed in the course of cracking of liquid phase; and high concentration of molecular hydrogen (>80 vol % of the total amount of reduced components). Such proportions of the gases may testify to the removal of water and methane in the closed systems of vacuoles. In this case, the inclusion-hosted methane will be a mixture of the primary methane synthesized in the process of crystallization, and transformation of minerals in the closed system and the secondary methane related to polycondensation of olefines. Proportions of both species will shift toward the second species depending on the degree of polycondensation.

Thus, reactions between components in the course of cooling of igneous rocks and transformation of minerals in closed systems of microinclusions lead to the shift of equilibria toward the reduced gases according to Fisher–Tropsch reactions, but the process is restricted by formation of only methane and its nearest homologs. The crystallization of pegmatites follows a different scenario. The temperature of nepheline composition stabilization in the postmagmatic environment drops from 500 to $360^\circ C$ [2]. Eudialyte becomes stable at an even lower temperature. Thus, conditions become favorable for more complete conversion of hydrocarbons, up to the synthesis of liquid hydrocarbon constituents. In this process, the alkali minerals serve as catalysts. The possibility of this scenario is supported by the geochemistry of bituminous material extracted from inclusions in eudialyte using the well-known technique. The ICP-MS results have shown that bitumens contain a wide spectrum of metals, probably occurring as organometallic complexes (Table 2).

To elucidate a source of metals, we studied the distribution of microelements in nepheline and eudialyte. Data on melteigite and khibinite were taken from [11]. As follows from Table 1 and the figure, the distribution curves and the level of HFSE and LILE concentrations in nepheline, khibinite, and melteigite are rather similar. At the same time, eudialyte is substantially enriched in REE, U, W, Nb, Hf, and Zr. The contents of transition

Table 1. Contents of reduced gas components in nepheline and eudialyte

Gas component	200°C		300°C		400°C	
	Nepheline	Eudialyte	Nepheline	Eudialyte	Nepheline	Eudialyte
H ₂	0.69	1.25	9.18	12.38	40.32	46.80
CH ₄	34.9	109.6	218.6	262.1	1731.2	2130.0
C ₂ H ₆	5.2	18.5	13.5	28.7	350.4	511.7
C ₂ H ₄	8.4	5.7	73.9	106.0	516.1	556.3
C ₃ H ₈	1.1	2.1	6.38	19.8	184.3	245.4
C ₃ H ₆	7.2	13.3	56.9	74.9	422.2	582.4
<i>i</i> -C ₄ H ₁₀	0.2	0.4	0.7	1.8	15.0	22.8
<i>n</i> -C ₄ H ₁₀	0.5	0.9	2.9	8.7	61.6	122.1
C ₄ H ₈	–	105.6	0.2	133.4	0.4	417.0
<i>i</i> -C ₅ H ₁₂	2.8	18.9	19.7	6.7	108.6	133.1
<i>n</i> -C ₅ H ₁₂	3.2	7.3	29.3	10.6	65.6	48.6
C ₅ H ₁₀	4.1	16.9	6.0	35.2	63.0	333.7
<i>i</i> -C ₆ H ₁₄	1.6	2.3	6.7	–	64.9	64.3
<i>n</i> -C ₆ H ₁₄	2.8	2.7	0.9	6.7	2.9	8.0
<i>i</i> -C ₇ H ₁₆ + C ₆ H ₁₂	11.9	2184.2	36.5	920.2	153.2	1930.0
<i>n</i> -C ₇ H ₁₆	0.8	120.6	9.4	80.4	7.7	201.0
<i>i</i> -C ₈ H ₁₈ + C ₇ H ₁₄	37.2	–	47.0	–	193.5	256.9

Note: Hydrogen and hydrocarbon contents are given in cm³/kg and 10⁻³ cm³/kg, respectively.

elements are comparable in all studied samples, and only eudialyte stands out by elevated Mn content. The concentration of microelements in bitumoid is much lower. The geochemical comparison of minerals and bituminous substance has shown that the latter is enriched in W, U, Pb, Mo, V, Cu, and Zn, which make up stable complexes with various organic ligands [8], and depleted in Th, Nb, and REE, which are combined into unstable compounds, mainly with cyclopentadienoid derivatives [12, 13]. However, in any case, the organometallic compounds can form and remain stable only in anhydrous systems, reducing medium, and elevated pressure.

The source of elements in the reduced fluid may be judged from the chondrite-normalized REE patterns. As follows from the figure, these patterns in khibinite and melteigite are identical ((La/Yb)_n = 32 and 21, respectively). Nepheline from pegmatite is sharply enriched in LREE and is characterized by (La/Yb)_n = 120. The change of physicochemical conditions at the moment of eudialyte crystallization is mirrored in a significant increase in total REE content along with a very low-angle REE pattern ((La/Yb)_n = 2.2). The bituminous material mimics the aforementioned tendency of an insignificant increase in LREE and retention of the Eu* signature (0.9–1.0). LILE and HFSE in bitumoid also inherit the geochemical medium of eudialyte crystallization, except for Nb and Sr, which are gained in the mineral. Impsonite is enriched in U, Sr, and to a cer-

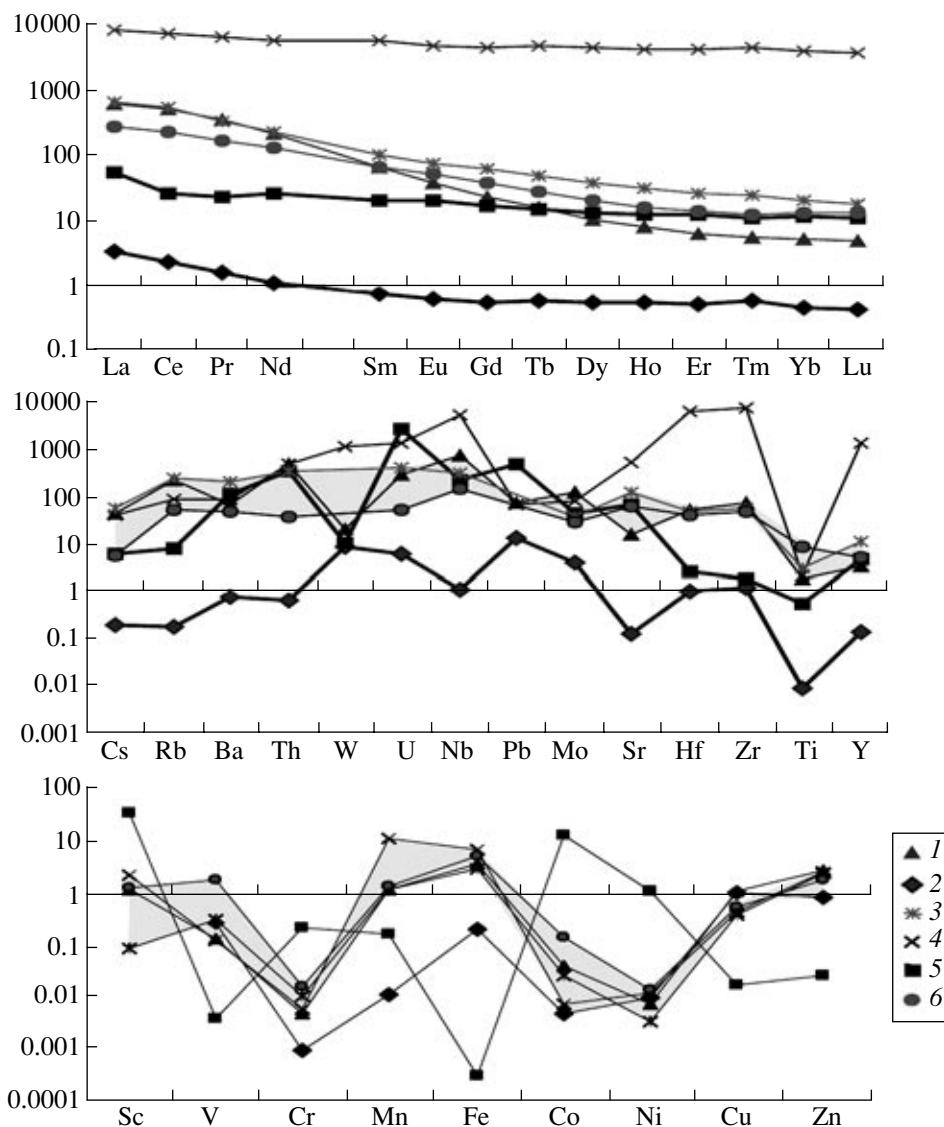
tain extent, Th and depleted in W. Other elements fit the geochemical specialization of the reduced fluid, demonstrating, however, higher concentrations. The distributions of transition metals in rocks, minerals, and bitumoid are broadly similar. Bitumoid is enriched in V, Ni, and Cu. Impsonite formed as a result of fluid fractionation in the open system is characterized by the separation of transition elements and enrichment of bitumen in Sc, Cr, Co, and Ni, whereas V, Fe, Cu, and Zn should be gained in lower-temperature carbonaceous substances (asphalt and maltha).

Thus, the eudialyte crystallization medium was a source of HFSE and LILE, whereas organometallic complexes dissolved in liquid hydrocarbons were formed contemporaneously with catalytic polycondensation in the stabilizing mineral. Products of these transformations served as organic ligands for the formation of organometallic compounds. The behavior of transition elements obeys the rule of successive evolution of a magma chamber down to low-temperature stages of mineral formation. The gain of metals in products of fluid fractionation during migration of fluids from the site of their generation into fractures will depend on the composition of the newly formed carbonaceous substances and the stability of the organometallic complexes, which controlled the geochemical signature of the impsonite. Impsonite is markedly enriched in Th, U, Nb, Pb, REE, Sr, Cr, Co, and Ni, and depleted in V, Fe, Cu, and Zn, relative to bitumoid. The composition of the reduced gases and formation of liq-

Table 2. Microelements in rocks, minerals, inclusion-hosted bitumoids, and bitumen (ppm)

Element	1	2	3	4	5	6
Be	9.45	5.73	17.80	1.48	n.d.	22.74
Na	83171	79684	89106.00	79906.00	255.87	5715.92
Sc	1.24	19.5	17.27	34.54	n.d.	0.518
Ti	4140	11820	2516.07	2984.28	11.976	735.648
V	43.6	276	19.44	17.11	38.298	185.800
Cr	34.3	51.4	15.37	19.27	2.969	1.952
Mn	1394.4	1627	1323.42	13598.68	12.234	1583.252
Fe	21980	37170	25760.00	49840.00	1461.73	2470.57
Co	2.84	16	4.48	0.80	0.504	0.519
Ni	7.11	29.1	16.31	26.64	20.577	1.474
Cu	12	18	36.01	13.71	33.278	6.968
Zn	138	105	163.74	151.11	49.355	24.030
Ga	41.2	32.9	66.76	35.84	0.217	1.710
Rb	162	34.4	141.80	55.07	0.118	5.067
Sr	2711	1352	347.99	10981.18	2.873	1492.487
Y	51.2	24.1	15.93	6513.08	0.648	21.213
Zr	638	565	812.46	87579.0	14.03	45.61
Nb	225	110	523.59	3850.60	0.812	167.695
Mo	2.31	1.87	7.79	5.04	0.264	2.742
Cs	1.89	0.19	1.42	1.29	0.007	0.195
Ba	1469	335	502.53	620.43	5.727	835.122
La	163	69.4	154.92	2058.26	0.819	13.264
Ce	352	150	320.54	4743.10	1.499	16.702
Pr	32.9	16.6	34.29	607.02	0.155	2.227
Nd	108	62.2	101.15	2684.20	0.532	10.325
Sm	16.2	10.4	10.46	897.54	0.121	3.226
Eu	4.5	3.04	2.22	268.16	0.037	1.163
Gd	12.8	7.63	4.81	917.61	0.117	3.578
Tb	1.85	1.05	0.61	177.06	0.023	0.558
Dy	9.81	5.26	2.69	1130.75	0.148	3.480
Ho	1.84	0.93	0.46	241.12	0.033	0.716
Er	4.41	2.37	1.07	701.72	0.091	2.030
Tm	0.63	0.32	0.15	113.52	0.015	0.287
Yb	3.45	2.2	0.88	633.74	0.079	1.891
Lu	0.46	0.34	0.12	94.16	0.011	0.284
Hf	15	12.9	16.23	2051.21	0.308	0.851
Ta	9.49	7.98	30.70	370.32	0.064	2.473
W	n.d.	n.d.	0.41	23.40	0.176	0.214
Tl	n.d.	n.d.	0.25	0.34	0.075	0.140
Pb	n.d.	n.d.	14.37	12.30	2.452	90.982
Bi	n.d.	n.d.	0.04	0.07	0.047	0.006
Th	30.7	3.19	42.74	42.07	0.059	28.891
U	8.93	1.08	6.47	29.77	0.135	57.383

Note: (1) Khibinite [11]; (2) melteigite [11]; (3) nepheline; (4) eudialyte; (5) bitumoid from inclusions; (6) impsonite.



Distribution of microelements in rocks, minerals, and organic matter: (1) nepheline, (2) bitumoid, (3) khibinite, (4) eudialyte, (5) impsonite, (6) melteigite. REE contents are normalized to chondrite C1 [14] and contents of other elements are normalized to the primitive mantle (PM) [15].

uid bituminous material are determined by reactions between components under closed conditions of inclusions. The synthesis of liquid hydrocarbons is possible only at the final stages of pegmatite formation, when the respective minerals are stabilized. Not all alkaline and alkaline ultramafic plutons contain considerable amounts of methane and its homologs, to say nothing of more complex compounds. Therefore, one should suggest that the formation of these hydrocarbons in the course of consolidation of various massifs is related not only to the saturation of magma chambers with gases, but also to the degree of their openness with respect to hydrogen. If the systems are relatively closed ($3\text{H}_2 + \text{CO} = \text{CH}_4 + \text{H}_2\text{O}$), we deal with the situation discussed in this communication and typical of the Khibiny,

Lovozero, and Kiya-Shalyr plutons. If the systems loses a great amount of hydrogen ($\text{H}_2 + 3\text{CO} = \text{H}_2\text{O} + \text{CO}_2 + 2\text{C}$), the abiogenic synthesis of hydrocarbons and their compaction is ruled out. This is exemplified by graphitization of rocks in the Guli Complex, Osino-Kitoi, and other plutons.

REFERENCES

1. I. A. Petersil'e, *Geology and Geochemistry of Natural Gases and Dispersed Bitumen in Some Geological Complexes of the Kola Peninsula* (Nauka, Moscow, 1964) [in Russian].
2. S. V. Ikorskii, *Geokhimiya* **15**, 1625 (1977).
3. V. A. Nivin, *Geokhimiya* **40**, 976 (2002) [*Geochem. Int.* **40**, 883 (2002)].

4. V. N. Florovskaya and V. G. Melkov, in *Mineral Resources* (Gosgeoltekhizdat, 1962), No. 5, pp. 83–86 [in Russian].
5. J. Potter, A. H. Rankin, P. J. Treloar, et al., *Eur. J. Mineral.* **10**, 1167 (1998).
6. A. L. Lyapidus and S. M. Loktev, *Zh. Vsesoyuzn. Khim. Ob-va* **31**, 527 (1986).
7. E. M. Galimov and I. A. Petersil'e, *Dokl. Akad. Nauk SSSR* **176**, 914 (1967).
8. A. A. Marakushev, in *Localization of Mineral Resources* (Nauka, Moscow, 1985), Vol. 14, pp. 211–221 [in Russian].
9. L. N. Kogarko, C. Costoliani, and I. D. Ryabchikov, *Geokhimiya* **24**, 1688 (1986).
10. A. P. Rudenko, I. I. Kulakova, and S. Ya. Kurganova, in *Scientific Principles of Catalytic Conversion of Hydrocarbons* (Naukova Dumka, Kiev, 1977), pp. 164–207 [in Russian].
11. A. A. Arzamastsev, F. Bea, L. V. Arzamastseva, and P. Montero, *Geokhimiya* **43**, 80 (2005) [*Geochem. Int.* **43**, 71 (2005)].
12. A. N. Nesmeyanov, T. V. Nikishina, O. V. Nogina, et al., *Subgroup of Copper, Scandium, Titanium, and Chrome. Lantanoids and Actinoids: Methods of Organometallic Chemistry* (Nauka, Moscow, 1974) [in Russian].
13. M. N. Bochkarev, G. S. Kalinina, L. N. Zakharov, et al., *Organic Derivatives of Rare Earth Elements* (Nauka, Moscow, 1989) [in Russian].
14. N. H. Evensen, P. J. Hamilton, and R. K. O'Nions, *Geochim. Cosmochim. Acta* **42**, 1199 (1978).
15. S.-S. Sun and W. F. McDonough, *Geol. Soc. London Spec. Publ.* **42**, 313 (1989).