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Hydrocarbons and Other Volatile Components in Alkaline Rocks from the Ukrainian Shield and Kola Peninsula

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Abstract—Gas chromatography and other analytical techniques (EMR, PMR, and IR spectroscopy) were used to examine volatile components (CH_4, C_2–C_3, CO_2, CO, H_2, H_2O, and others) in alkaline rocks and minerals from the Ukrainian Shield (eight massifs and dikes of grorudites) and from the Khibina and Lovozero massifs in the Baltic Shield. The alkaline rocks from the Ukrainian Shield are mostly of Proterozoic (1.7–2.1 Ga) age. The alkaline rocks from the Kola Peninsula were confirmed to be rich in methane (21 ± 14 μl/g on average) and other hydrocarbons, whereas the analogous rocks from the Ukrainian Shield are poor in methane (2.1 ± 1.6 μl/g on average at a maximum of 14 μl/g). The latter rocks are richer in CO_2, which is one of the major volatile components of alkaline rocks, including agpaitic nepheline syenites from the Kola Peninsula. The rocks from the Ukrainian Shield often have elevated contents of nitrogen (up to 20 μl/g). The reasons for the differences in the composition of volatile components of rocks from the Kola Peninsula and Ukrainian Shield are as follows: the agpaitic crystallization trends of large massifs in the Kola Peninsula and much less clearly pronounced agpaitic trends in the small massifs in the Ukrainian Shield, the affiliation of these rocks with different complexes, the deeper erosion levels of the Ukrainian alkaline massifs, different ages of these rocks, etc.

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INTRODUCTION

Volatile components may play an important or even decisive role in the genesis of magmatic and metasomatic rocks. Such large massifs of agpaitic nepheline syenites as the Khibina, Lovozero, and Ilimaussaq occurred to bear volatiles of quite unusual composition, first of all, because of their high concentrations of methane (in association with other hydrocarbons), chlorine, and fluorine at subordinate amounts of carbon dioxide and relatively low water concentrations. These massifs are accompanied by large deposits of apatite and trace elements (Zr, Nb, REE, Th, and others).

An unusual feature of volatile components in agpaitic nepheline syenites and related rocks (urtites and ijolites–melteigites) is the coexistence of strongly reduced fluids with assemblages of mafic minerals (aegirine, arfvedsonite, aenigmatite, etc.), which contain more trivalent than bivalent iron. Several researchers believe that the oxidation degree of iron in highly alkaline environments is one of the principal factors controlling the genesis of reduced fluids (hydrocarbons and hydrogen), carbon (graphite and finely dispersed carbon), and concentrated organic matter (anthraxolite, kerite, asphalt, etc.).

Now most researchers are prone to believe that both reduced fluids and organic matter (OM) were produced in agpaitic nepheline syenites during the late magmatic or postmagmatic stages. The reduction degree of the fluid phase thereby increases with decreasing temperature during melt crystallization and the coupled chemical evolution of the coexisting fluid [1]. It is also commonly thought that these reduced fluids are of abiogenic genesis, and their carbon originates from a deep-seated source. One of the mechanisms producing methane is thought to be the reaction between CO_2 and H_2 (at $T = 359°$ C and $P = 0.5$–1.2 kbar) [2].

This publication is devoted to the comparative characterization of volatile components, with emphasis placed onto their hydrocarbon constituents, in the alkaline rocks of the Ukrainian Shield and Kola Peninsula. Our results are the first ones obtained for the rocks from the Ukrainian Shield. Data on contents of volatile components (CH_4, H_2, and CO) were available only for some alkaline rocks from the Azov Sea area, and even these analyses were conducted by different methods [3] and now seem to be out of date.

Inasmuch as volatile components in alkaline rocks from the Kola Peninsula were studied fairly thoroughly, we regarded data on their concentrations as reference material for their comparison with analogous materials on rocks from the Ukrainian Shield. The gas components of analogous rocks were analyzed simultaneously by the same techniques, mostly by gas chromatography of the pyrolysis products of these rocks and their minerals (the methods are briefly described below). We also applied electron paramagnetic resonance (EPR), infrared spectroscopy (IR spectroscopy), and proton magnetic resonance (PMR). Some minerals containing OM were handpicked in UV light and then identified. We examined more than 200 rock and mineral samples: approximately 110 from the Ukrainian Shield and 90 from the Kola Peninsula. The results obtained on these rocks showed fairly significant differences in the composition of the volatile components. The rocks from the Kola Peninsula were sampled mostly at the Khibina Massif and less at the Lovozero intrusion. The materials from the Ukrainian Shield are alkaline and subalkaline rocks and their minerals are from the eight most representative massifs: Chernigovka, Oktyabr'skii, Malaya Tersa, Pokrovo–Kireevo, Southern Kal'chinskii (including the Azovskoe deposit), Proskurovka, Antonovka, and Yastrebetskii. Some samples were from grorudite dikes in the eastern Azov area. The massifs and occurrences contain alkaline rocks broadly varying in SiO_2 concentrations, from ultramafic to acid, and also include carbonatites. Since alkaline rocks from the Ukrainian Shield are not known as broadly as their analogues from the Kola Peninsula and the literature with information on the former is not as widely available, below we present their brief characteristics. The reader can find their more detailed descriptions in [4, 5].

The pyrolysis technique was described in [6, 7]. As usual, we used a water-washed size fraction 0.5–1 mm of samples that was preliminarily dried and crushed in a cast-iron mortar. A 0.3- to 0.6-g sample was placed into a glass reactor ampoule and was step-heated to 1050 or 850°C. The complete composition of the pyrolysis products, including C_1–C_3 hydrocarbons, was analyzed with a temperature step of 200°C. Correspondingly, each sample was characterized by five compositions of the pyrolysis gases that have been formed during each temperature interval and gave, when considered collectively, the composition of the pyrolysis gas within the temperature range of 50 to 1050°C (or 850°C). The heating time was the same for each temperature step: 5 min.

A notable feature of this method was the removal of the pyrolysis products from the hot zone of the reactor by the carrier gas and their concentration in a cryogenic trap, which was a 0.5-m column with a polyadsorbent submerged in liquid nitrogen. Thus, interaction between the components of the gas mixture was thus minimized. The cryogenic trap acts analogously to a locking gate, with all gas components, including methane, stably retained in the cryogenic trap by adsorbent. The gradual heating of the trap results in the separation of the components according to their melting temperatures and in the successive inflow of the melting gases into the chromatograph, where they are further separated in the working column. The use of a cryogenic trap enabled us to determine all major gas components released during the pyrolysis of minerals in a single sample.

BRIEF CHARACTERIZATION OF ALKALINE ROCK MASSIFS AND OCCURRENCES IN THE UKRAINIAN SHIELD

The Ukrainian Shield is a unique province of Precambrian alkaline magmatism and includes approximately 40 known massifs and smaller occurrences (small stocks and dikes) of alkaline rocks, whose location map was published in [4, 8]. The overwhelming majority of alkaline rocks from the Ukrainian Shield are of Proterozoic age, and only the Azov geoblock contains both Proterozoic and Paleozoic (Devonian) alkaline rocks. The Proterozoic alkaline rocks belong to two complexes of different ages [4]: alkaline–ultramafic or carbonatite (2.0–2.1 Ga) and gabbro–syenite (1.7–1.8 Ga).[1] Note that even kimberlites in the inner part of the Ukrainian Shield (near Kirovograd) have a Proterozoic age (1.8 Ga), whereas the Azov (marginal) portion of the territory hosts Devonian kimberlites (exposed not far from the Pokrovo–Kireevo Massif of alkaline rocks of the same age). The reasons for the passivity of the Ukrainian Shield in terms of Phanerozoic alkaline (and flood-basalt) magmatism remain uncertain. At other ancient platforms, including the Baltic Shield, alkaline rocks are predominantly Phanerozoic (Paleozoic, Mesozoic, Cenozoic, and even modern) and include only strongly subordinate amounts (if any) of Precambrian rocks. It is also pertinent to mention that the Khibina and Lovozero plutons differ from the alkaline massifs in the Ukrainian Shield that are compared with them in this publication in having much greater (giant) sizes. Massifs and occurrences of alkaline rocks in the Ukrainian Shield are commonly relatively small, from a few to a few dozen square kilometers. The only exception is the Southern Kal'chinskii Massif of subalkaline rocks (predominantly syenites), whose area ranges (according to the estimates made by various researchers) from 250 to 330 km^2, i.e., this massif is comparable to the Lovozero Massif (650 km^2) and is a few times smaller than the Khibina Massif (1327 km^2).

We believe that the alkaline–ultramafic (carbonatite) complex also includes such massifs as Chernigovka, Proskurovka, and Antonovka, along with small stocks and a dike suite of alkaline–ultramafic

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[1] In our earlier publications, these rock associations were referred to as formations, as was customary in the former Soviet Union. Researchers in the West usually apply (particularly in the literature in English) the term formation to sedimentary or stratified rocks, whereas associations of coeval magmatic rocks are referred to as a complex or massif, as was also adopted in this publication.

rocks (jacupirangites and melteigites) and carbonatite veins. The rocks of this complex were found in the Azov area and in the western part of the Ukrainian Shield.

The most representative massif in the complex is the Chernigovka Massif (which is also referred to as Novo-Poltavka), located in the Azov part of the shield. The area of the massif (together with its fenite aureole) is close to 3 km^2, it has an elongated linear morphology, and consists of alkaline pyroxenites, alkaline and nepheline syenites, and carbonatites. The carbonatites bear ijolite–melteigite nodules (xenoliths). The host rocks (granitoids, charnockites, and amphibolites) of the massifs are extensively fenitized.

The major rock-forming mineral of the alkaline pyroxenites is pyroxene (aegirine–diopside and aegirine–salite), and these rocks contain significant amounts (up to 10–20%) of ilmenite and magnetite and subordinate amounts of subalkaline amphibole, biotite, apatite, calcite, sphene, sulfides, and, often, accessory graphite.

The ijolites–melteigites are particularly interesting because some of their varieties bear hortonolite, a Fe-rich olivine variety (Fa_{70}). When containing elevated amounts of olivine, the melteigites may grade into nepheline–hortonolite rocks. As in the alkaline pyroxenites, the pyroxene of the ijolites–melteigites is aegirine–diopside or aegirine–salite with up to 30% of the aegirine end member. The minor minerals of these rocks are subalkaline amphibole, biotite or Fe-rich phlogopite, calcite, and apatite. The most widely spread accessory minerals are monazite, sulfides, and graphite, with the nepheline–hortonolite rocks containing up to 2.5 wt % of the latter mineral. In contrast to the alkaline pyroxenites, the ijolites–melteigites contain practically no primary magnetite and ilmenite.

The nepheline syenites (canadites) are interesting in that their feldspar is albite at very low (if any) contents of microcline. Biotite is usually the only mafic mineral of these rocks, which may occasionally contain amphibole. The minor and accessory minerals are calcite, apatite, pyrochlore, and sulfides.

The alkaline syenites and related tveitesites consist of K–Na mesoperthitic feldspar and aegirine–salite (with up to 30% of the aegirine end member). The quartz syenites and granosyenites additionally contain quartz. The minor and accessory minerals are apatite, calcite, titanite, orthite, sulfides, molybdenite, and pyrochlore.

The carbonatites are the most compositionally complicated rock group and encompass calcitic (sovites and alvikites), dolomite–calcitic, and dolomitic (beforsites) varieties, along with olivine– (completely serpentinized) and phlogopite-rich rocks, which are referred to as so-called kimberlitic carbonatites. When enriched in apatite, the carbonatites grade into phoscorites. The mafic minerals of the calcitic carbonatites are clinopyroxene (diopside and aegirine–salite), amphibole (hastingsite, edenite, katophorite, and intermediate members of the katophorite–edenite and katophorite–hastingsite series), olivine (in alvikites), phlogopite (occasionally, tetraferriphlogopite), and biotite [which is sometimes rich in Fe, with Fe/(Fe + Mg) = 0.58]. The only mafic minerals of the dolomitic and dolomite–calcitic carbonatites are olivine and phlogopite. The minor and accessory minerals of the carbonatites are magnetite, ilmenite, monazite, zircon, baddeleyite (in beforsites), columbite, pyrochlore, gatchetolite, Ce-fergussonite, sulfides, molybdenite, and others. The rocks often contain graphite. In contrast to carbonatites from other complexes, the Chernigovka carbonatites contain highly ferrous olivine (Fa_{15-70}), which can also be present in the dolomitic carbonatites. Ferrous olivine occurs in association with Fe-rich calcite (up to 1.5–3.8% FeO) and dolomite (up to 6% FeO). Other noteworthy features of these carbonatites is the presence of Ce-fergussonite (second find in the world), which is, along with pyrochlore, gatchettolite, and columbite, of economic importance. The amphiboles belong to an unusual isomorphous series, such as katophorite–hastingsite and katophorite–edenite. The rocks often contain graphite.

The aforementioned and other features of the Chernigovka carbonatite complex can be explained by its abyssal character. This seems to be the world's most deeply eroded carbonatite complex, whose erosion level could be as great as 20 km [9]. The abyssal crystallization conditions (under a relatively low oxygen fugacity) can explain the Fe-rich composition of the mafic minerals (first of all, olivine) and the absence of their alkaline varieties (aegirine, riebeckite, and arfvedsonite), as well as the elevated Fe contents in the carbonates. Magnetite crystallization under these conditions was limited (apatite–magnetite phoscorites are rare and scarce), as also was the crystallization of aegirine and alkaline amphiboles, and bivalent iron was preferably accommodated in mafic minerals and carbonates. These conclusions are consistent with the principle, derived by Roeder and Emslie [10], concerning iron partitioning between silicate and spinel phases in basalts.

The Proskurovka and Antonovka massifs of alkaline rocks are located in the western part of the shield and were discovered relatively recently. They are hosted in unusual granitoids, which are referred to as vinnitsites and consist of plagioclase (at subordinate amounts of potassic feldspar), quartz, garnet, hypersthene, and Ti-rich biotite; i.e., these rocks can be classed with garnet charnockitoids. These granitoids in the outer-contact aureoles of the alkaline massifs are extensively fenitized. The Proskurovka and Antonovka massifs are quite similar, although show certain differences. We attribute these massifs to the alkaline–ultramafic (carbonatite) complex, although no carbonatites have been properly found in them as of yet. The massifs contain relatively sparse apatite–calcite and calcite veins and veinlets, and primary calcite is present in all types of the alkaline rocks.

The Proskurovka Massif is exposed over an area of about 7 km^2 and is dominated by ijolites–melteigites and nepheline syenites (in roughly equal amounts) at subordinate amounts of jakupirangites and melanocratic rocks like nepheline-free essexites. The ijolites–melteigites and related malignites practically always contain biotite and amphibole of the hastingsite–katophorite series. The clinopyroxene of these rocks is fairly Fe-rich aegirine–salite that contains no more than 30% of the aegirine end member. Fe and Ti ore minerals (magnetite and ilmenite) are usually contained in the ijolites–melteigites in accessory amounts, i.e., these rocks are similar in this sense to the analogous rocks of the Chernigovka Massif. The nepheline syenites are the most diverse and comprise foyaites, miaskites, juvites, and pulaskites. The feldspar of these rocks is a K–Na variety (mesoperthite of anorthoclase composition), and the mafic minerals are biotite, aegirine–salite, and Ca–Na amphibole like Na-rich hastingsite.

The Antonovka Massif has an area of 6.2 km^2 (together with the related fenites) and is dominated by essexites, alkaline pyroxenites, and ijolites–melteigites (in roughly equal amounts, 1 km^2 each) and contains subordinate amounts of nepheline syenites (0.6 km^2). A feature unusual for the alkaline–ultramafic complex is the presence of such rocks as essexites (including their nepheline-bearing and nepheline-free varieties). These are melanocratic rocks made up of aegirine–salite, barkevikite, biotite, albite–oligoclase, and, sometimes, nepheline. The other rock types are jakupirangites, alkaline pyroxenites, iolites–melteigites, and nepheline syenites, which are generally similar to their analogues in the Proskurovka Massif. It should be emphasized that they commonly contain biotite and, often, also amphibole.

The features shared by the Proskurovka, Antonovka, and Chernigovka massifs is the absence of pyroxene rich in the aegirine end member (no more than 30%) and alkaline amphiboles from the alkaline rocks. The most alkaline amphibole is richterite (in the fenites of the Proskurovka and Chernigovka massifs). The alkaline rocks of the Proskurovka and Antonovka massifs are unusually poor in Nb and Zr but bear elevated concentrations of REE (contained mostly in apatite and, more rarely, orthite) and Sr (as is characteristic of carbonatite complexes). There are certain reasons (geophysical, geochemical, and isotopic–geochemical evidence) to hypothesize that the massifs were emplaced in compressional environments (like collisional or subduction). We believe that the massifs are eroded fairly deeply, at least, to a few kilometers; i.e., they have been emplaced into abyssal environments and crystallized at a relatively low oxygen fugacity.

Below we also consider the Oktyabr'skii, Malaya Tersa, Southern Kal'chikskii (together with the Azovskoe rare-metal deposit hosted by this massif), and Yastrebetskii gabbro–syenite massifs of the gabbro–syenite complex. In our opinion, the same complex also includes the Pokrovo–Kireevo Massif, although some researchers [11] regard it as an alkaline–ultramafic–alkali basalt pluton.

The Oktyabr'skii Massif, approximately 34 km^2 in area, is known from the late 19th century (described by J. Morozewich) and is now explored quite thoroughly. The massif consists of subalkaline Ti-augite gabbro (and their derivatives: pyroxenites and peridotites) and alkaline and nepheline syenites (foyaites and mariupolites) and contains scarce vein carbonatites, whose genesis remains somewhat obscure, because the rock association of the Oktyabr'skii Massif and the chemistries of their minerals differ from those in carbonatite complexes elsewhere. The host granitoids in the outer contact zone of the massif were likely not affected by fenitization, as is typical of carbonatite complexes. It was hypothesized that the volume currently occupied by the Oktyabr'skii Massifs could have contained older rocks of a carbonatite complex, including carbonatites themselves, which were then assimilated by the younger alkaline magmas. In any event, primary carbonates are generally atypical of the alkaline rocks of the massif.

In the context of comparison between the rocks from the Ukrainian Shield and Kola Peninsula (and the Ilimausaq Massif), it is interesting to emphasize the agpaitic trend, which was identified in the Oktyabr'skii Massif by one of the authors. The determined and partly inferred genetic succession of the rocks is as follows: subalkaline (Ti-augite) gabbro and their derivatives (pyroxenites and peridotites)–alkaline syenites–taramitic foyaites–mariupolites–aegirine foyaites (dike rocks)–eudialyte-bearing phonolites. The latter rocks are similar in many respects to the foyaites of the Ilimaussaq and Lovozero massifs [12]. Agpaitic rocks are generally scarce in the Oktyabr'skii Massif.

Some noteworthy compositional features of rocks from the Oktyabr'skii Massif, which should be taken into account when the results of the pyrolysis analysis of the gases are interpreted, are as follows: (i) most of the rocks bear hydroxyl-bearing mafic minerals (amphiboles and biotite); (ii) these minerals are absent only from typical (unmodified) mariupolites, aegirine foyaites, and phonolites; (iii) the nepheline-bearing rocks contain sodalite and cancrinite (which are usually younger minerals); and (iv) some rocks (for example, syenites) contain graphite. There are good reasons to believe that the erosion depth of the Oktyabr'skii Massif is insignificant.

The Malaya Tersa Massif is exposed over an area of >40 km^2 (much of this massif is now eroded). The rock assemblage of this massif (gabbro, alkaline syenites, and foyaites) resembles that of the Oktyabr'skii Massif at some principal differences. For example, there are clearly pronounced differences in the compositions of minerals (first of all, mafic minerals) from the alkaline syenites and foyaites of these massifs [4]. Although we assign the Malaya Tersa Massif to the gabbro–syenite complex, this massif shows some petrological, geochemical, and mineralogical characteristics similar to those of carbonatite complexes (such as the presence of fenites, carbonatites, and carbonatite-like rocks, lower Fe# of mafic minerals than those in typical gabbro–syenite massifs, elevated concentrations of Sr and Ba in the young derivatives, etc.). Earlier geochronological data [13] indicate that the massif was formed in two stages: at 2.0 and 1.8 Ga. The earlier stage likely corresponded to the origin of the carbonatite complex itself (which is similar to the Chernigovka Complex), while the younger (gabbro–syenite) complex is thought to be coeval with the Oktyabr'skii Massif. In any event, the alkaline rocks of the massif pervasively contain variable amounts of carbonate (often >1%) and, often, also biotite and amphibole, which causes the presence of H_2O and H_2 in the pyrolysis products. In addition, the foyaites contain zeolites, cancrinite, and sodalite. The youngest derivatives (pegmatoid nepheline and alkaline syenites) contain such minerals as aenigmatite and astrophyllite; i.e., the massif shows evidence of an agpaitic evolutionary tendency.

It is hard to assay the erosion level of the Malaya Tersa Massif as a whole. We cannot rule out that its oldest intrusive phases (carbonatite complex) were significantly eroded, whereas younger rocks were eroded to a depth of a few kilometers, as also was the Oktyabr'skii Massif.

The Pokrovo–Kireevo Massif, >20 km^2 in area, is one of a few Devonian alkaline magmatic bodies in the area. The massif is located in the eastern marginal portion of the Ukrainian Shield or, as several researchers believe, in its junction zone with the Donets Basin folded zone. The most widely spread intrusive rocks of the massif that were analyzed chromatographically include subalkaline (Ti-augite) pyroxenites, malignites, and juvites. The malignites and some juvites are characterized by unusual poikilitic textures (nepheline inclusions in potassic feldspar), which resemble those in the rischorrites of the Khibina pluton. In addition to their high agpaitic coefficient (up to 1.3), an agpaitic character of these rocks also follows from the occurrence of calcic rinkolite in them. Along with clinopyroxene (Ti-augite, aegirine–salite, and aegirine), they contain minor amounts of amphiboles (kaersutite in the pyroxenites and, perhaps, subalkaline amphibole in the malignites–juvites), titanian biotite, and tetraferribiotite. Nepheline in the rocks is replaced by zeolites, and the crushed samples were determined to contain sodalite. Chemical analyses of the rocks indicate that they contain CO_2. The rocks bear overprinted carbonatization zones, and carbonatites (including their volcanic varieties) were found near the massif [14].

The Pokrovo-Kireevo Massif seems to be eroded to a relatively shallow depth, because its surrounding and vein rocks include subvolcanic and volcanic rocks (basalts, limburgites, epi-leucitites, etc.). We also attribute to this complex the dikes of porphyritic Ti-augite pyroxenites in the eastern Azov area (near the village of Andreevka) that are chemically identical to ore pyroxenites of the complex.

The Southern Kal'chikskii Massif is the largest (250–330 km^2) massif of subalkaline rocks in the Ukrainian Shield, with approximately half of its area composed of syenites. The massif also contains much granosyenites and subordinate amounts of mineralized (with ilmenite and apatite) gabbroids. Some researchers consider this massif (including the authors of this publications) to be an eroded syenite–granosyenite analogue of anorthosite–rapakivi plutons of the Korosten or Korsun'–Novyomirgorod types. The syenites of the Southern Kal'chikskii Massif are predominantly two-feldspar fayalite–hedenbergite rocks that pervasively contain ferrohastinsgite and, often, also biotite. The Southern Kal'chikskii Massif hosts the Azovskoe rare-metal deposit, which is a relatively small (slightly more than 3 km^2) differentiated (layered) syenite intrusion with rich REE–Zr ores (britholite, orthite, and zircon). The mineralized syenites are alkali feldspar hypersolvus rocks whose mafic minerals are normally high in Fe (fayalite, hedenbergite, ferrohastingsite, and annite). The rocks usually contain minor amounts of carbonates (rock-forming and REE).

The Yastrebetskii syenite massif, about 4 km^2 in area, is similar to the Azov intrusion and is located 30 km northwest of the Korostenskii anorthosite–rapakivi pluton. The alkali–feldspar syenites of the Yasterbetskii Massif (and the Yastrebetskoe Zr deposit) are generally similar to the analogous rocks of the Azovskoe deposit, but the Yastrebetskii syenite intrusion is much more significantly differentiated due to crystallization differentiation, whose final products were alkaline aegirine and riebeckite syenites and granosyenites. Note that practically all syenite varieties contain variable amounts of hydrous silicates (Fe-rich amphiboles and micas) and carbonates, which release H_2O, H_2, CO_2, and CO when the rocks are heated.

The grorudites of the eastern Azov area were described in [15]. Here it is pertinent to mention only some of their characteristics that are interesting in the context of interpreting the nature of the volatile pyrolysis products. The grorudites can be subdivided into the following two groups, which are clearly distinct mineralogically and chemically: (i) more melanocratic rocks (enriched in aegirine), so-called high-Ti, dike analogues of pantellerites; and (ii) leucocratic low-Ti analogues of comendites. The dikes of the former rocks have northwestern strikes, whereas the bodies of the latter rocks strike latitudinally. Both rock types bear amphibole of the riebeckite series and minor amounts of secondary carbonates, which are the main source of such pyrolysis products as CO_2, CO, and H_2. The grorudites are coeval (400 Ma) with the alkaline rocks of the Pokrovo–Kireevo Massif (see above) and the subalkaline basalts of the Dnepr–Donets ancient rift structure and seem to be derivatives of the latter rocks.

VOLATILE COMPONENTS IN ALKALINE ROCKS

Hydrocarbons (CH_4, C_2–C_3). As was mentioned above, we were particularly interested in these volatile components, and the gas components of the rocks were analyzed largely to elucidate the concentrations of these components. The predominant component of the hydrocarbon gases is methane, with heavier hydrocarbons contained in the gases in lower amounts (from a few percent to 20% of the total of the gases, Table 1), and their relatively high concentrations (up to 50%) were determined in some samples of the foyaites, syenites, and gabbro–diabases from the Malaya Tersa Massif.

Our results confirm earlier data on high concentrations of methane (21 ± 14 μl/g on average) in the nepheline syenites and foidolites from the Khibina and Lovozero massifs (Table 1). At the same time, the alkaline rocks (both Proterozoic and Paleozoic) from the Ukrainian Shield bear relatively low concentrations of this component (2 ± 1.6 μl/g on average), with only the occasional sample yielding concentrations as high as 8–14 μl/g. However, the rocks from the Khibina and Lovozero massifs and from the Ukrainian Shield show very uneven distributions of hydrocarbons. The Kola rocks have the highest CH_4 concentrations of 48 μl/g and about 5 μl/g of other C_2–C_3 hydrocarbons (Table 1).

We failed to identify any systematic tendencies in the distribution of hydrocarbons in the alkaline rocks from the Ukrainian Shield depending on the chemical or mineralogical compositions of these rocks or their affiliation with certain compositions. Elevated methane concentrations are sporadically encountered in various rock types (carbonatites and alkaline and nepheline syenites, pyroxenites, and grorudites). Somewhat elevated (4 μl/g on average) methane concentrations were detected in gabbroids from the Malaya Tersa and Oktybr'skii massifs. It can be concluded that the alkaline rocks of the Proskurovka and Antonovka massifs ubiquitously have very low concentrations of methane and other hydrocarbons, and these concentrations show no local maxima.

To compare these data with analogous materials on the Kola massifs, we analyzed the most alkaline (agpaitic rocks with eudialyte, aenigmatite, and Ca-rinkolite) rocks from the Oktyabr'skii, Malaya Tersa, and Pokrovo–Kireevo massifs of the Ukrainian Shield. However, being chemically and mineralogically analogous or even closely similar to the analogous rocks of the Lovozero, Khibina, and Ilimaussaq massifs, the alkaline rocks from the Ukrainian Shield are very low in hydrocarbon gases.

The alkaline rocks of the Kola Peninsula and Ukrainian Shield also show different temperatures at which hydrocarbons are released from these rocks. While the maximum escape of volatiles (usually methane) from the Kola rocks occurs most often at 450 and even 250°C, the analogous maximum for the Ukrainian rocks is most often shifted to 500–650°C (Fig. 1). The most probable reason for this is the fact that the Lovozero and Khibina rocks contain methane mostly in closed pores (generally in the form of fluid inclusions [16, 17]), whereas the rocks from the Ukrainian Shield can contain methane in the form of chemically bound methyl groups or solid OM. Below we will briefly describe the character and temperature regime of the pyrolitic release of volatile components from rock-forming minerals.

Nepheline is likely one of the major minerals concentrating hydrocarbon gases. We analyzed nine nepheline samples from the Khibina alkaline rocks and four samples from the Ukrainian Shield. As can be seen in Table 2 and Fig. 2, the nephelines from Khibina rocks as a whole have high or elevated methane concentrations (12–90 μl/g) at insignificant amounts (no more than 3 μl/g) of other hydrocarbons (their percentages are slightly lower than in the host rocks). At the same time, nephelines from the Ukrainian Shield and the rocks hosting this mineral are poor in CH_4 (0.9–6 μl/g). All nepheline samples from the Khibina Massif release methane at temperatures of up to 850°C, with maximum releases at 250–450°C. At the same time, three of the four nepheline analyses from the Chernigovka and Oktyabr'skii massifs in the Ukrainian Shield release the greatest methane amounts at 450–650°C, and only one of the samples shows a maximum at 250–450°C. Hence, nepheline is characterized the same temperature ranges of methane release as those of the rocks.

Sodalite is also a mineral concentrating hydrocarbons in the rocks in question (Table 3, Fig. 3). This is a major rock-forming mineral (lujavrites and foyaites) in the Lovozero and Ilimausaq massifs and minor in the Khibina and Oktyabr'skii massifs. As was mentioned above, sodalite was also found in minor amounts in crushed samples of the alkaline rocks of the Pokrovo–Kireevo and Malaya Tersa massifs. This mineral in samples from the latter two massifs luminescences brownish and bluish in UV radiation, which suggests that the mineral is rich in organic matter. Regretfully, we had not enough material to conduct a pyrolitic analysis of this mineral. Its identification with sodalite was confirmed by microprobe analyses (35–39 wt % SiO_2, 21–24 wt % Na_2O, 0.1–3 wt % K_2O, 32–35 wt % Al_2O_3, and 8–9 wt % Cl) and the character of its IR spectra. As was mentioned above, the massifs in which sodalite was found (Oktyabr'skii, Pokrovo–Kireevo, and Malaya Tersa) show agpaitic evolutionary tendencies. The limited amount of analyzed samples (Table 3) led us to conclude that sodalite from foyaite of the Lovozero Massif contains close to 47 μl/g methane, whereas this mineral from the Oktyabr'skii Massif contains 3.9–6.5 μl/g methane. Moreover, while methane is released from the Lovozero sodalite mostly within the temperature range of 250–450°C, this peak for the Okttyabr'skii Massif is shifted to 450–650°C.

Relatively large methane amounts (as in the alkaline rocks from the Ukrainian Shield) were also detected in cancrinite (5.3 μl/g) and zeolites (supposedly, natro-

Table 1. Gas chromatographic data on the pyrolysis products of alkaline rocks from the Ukrainian Shield and Kola Peninsula

Rock (number of analyses)	Volatile components	Volatile components (μl/g) released in discrete temperature ranges (°C)*					
		50–250	250–450	450–650	650–850	850–1050	Total
Chernigovka carbonatite Massif							
Alkaline pyroxenites (3)	CH_4	0	$\frac{0.27{-}0.61}{0.46}$	$\frac{0{-}0.72}{0.4}$	0	0	$\frac{0.51{-}1.30}{0.86}$
	CO_2	$\frac{6.9{-}10.2}{8.8}$	$\frac{27.0{-}49.8}{35.7}$	$\frac{119{-}522}{302}$	$\frac{1517{-}3033}{2399}$	$\frac{0{-}13\,465}{4715}$	>1 wt %
	CO	$\frac{0.14{-}0.65}{0.43}$	$\frac{2.2{-}5.5}{4.3}$	$\frac{1.0{-}2.4}{1.7}$	$\frac{36{-}92}{59}$	$\frac{0{-}1395}{500}$	$\frac{44{-}1448}{566}$
	H_2	0.01	$\frac{1.9{-}6.8}{4.3}$	$\frac{0.9{-}24.0}{11}$	$\frac{19{-}106}{49}$	$\frac{0{-}293}{105}$	$\frac{33{-}425}{169}$
	H_2O	$\frac{0.37{-}0.63}{0.51}$	$\frac{0.07{-}0.18}{0.14}$	$\frac{0.11{-}0.14}{0.13}$	$\frac{0.34{-}0.38}{0.36}$	$\frac{0{-}1.25}{0.45}$	$\frac{1.20{-}2.26}{1.59}$
	C_2–C_3	0	$\frac{0.06{-}0.09}{0.08}$	$\frac{0{-}0.03}{0.01}$	0	0	$\frac{0.06{-}0.10}{0.08}$
Ijolites–melteigites (4)	CH_4	0	$\frac{0.24{-}0.72}{0.49}$	$\frac{0.85{-}1.33}{1}$	$\frac{0{-}0.20}{0.05}$	0	$\frac{1.43{-}1.64}{1.55}$
	CO_2	$\frac{6{-}10}{8}$	$\frac{22{-}248}{93}$	$\frac{109{-}850}{335}$	$\frac{106{-}6925}{4321}$	>1 wt %	>1 wt %
	CO	$\frac{0.2{-}1.2}{0.7}$	$\frac{2.6{-}7.7}{4.5}$	$\frac{2.2{-}28.5}{9.2}$	$\frac{32{-}825}{346}$	$\frac{0{-}1997}{796}$	$\frac{39{-}2501}{1157}$
	H_2	$\frac{0{-}0.09}{0.06}$	$\frac{7.1{-}22.2}{12.5}$	$\frac{41{-}215}{113}$	$\frac{47{-}250}{129}$	$\frac{0{-}285}{91}$	$\frac{102{-}757}{345}$
	H_2O	$\frac{0.40{-}0.81}{0.6}$	$\frac{0.60{-}1.00}{0.76}$	$\frac{0.77{-}2.06}{1.36}$	$\frac{0.92{-}2.39}{1.53}$	$\frac{0{-}3.98}{1.28}$	$\frac{3.4{-}9.7}{5.53}$
	C_2–C_3	0	$\frac{0.05{-}0.17}{0.11}$	$\frac{0{-}0.06}{0.01}$	0	0	$\frac{0.07{-}0.17}{0.12}$
Nepheline syenites (canadites) (4)	CH_4	0	$\frac{0.27{-}2.59}{1.19}$	$\frac{0.07{-}3.68}{1.45}$	$\frac{0{-}1.81}{0.46}$	$\frac{0{-}0.95}{0.24}$	$\frac{0.37{-}8.01}{3.35}$
	CO_2	$\frac{2.7{-}4.7}{3.5}$	$\frac{45{-}126}{69}$	$\frac{77{-}221}{164}$	$\frac{867{-}3151}{2405}$	$\frac{0{-}17\,960}{5790}$	>1 wt %
	CO	$\frac{0.05{-}0.38}{0.14}$	$\frac{1.90{-}2.27}{2.09}$	$\frac{1.2{-}4.2}{2.2}$	$\frac{50{-}1313}{513}$	$\frac{0{-}795}{468}$	$\frac{389{-}2060}{985}$
	H_2	$\frac{0{-}0.01}{0.01}$	$\frac{0.8{-}11.7}{5.4}$	$\frac{17{-}80}{53}$	$\frac{63{-}996}{518}$	$\frac{0{-}783}{305}$	$\frac{120{-}1479}{881}$
	H_2O	$\frac{0.07{-}0.20}{0.12}$	$\frac{0.6{-}1.8}{1.4}$	$\frac{0.5{-}4.7}{2.1}$	$\frac{0.3{-}3.9}{2.1}$	$\frac{0{-}2.8}{1.5}$	$\frac{2.1{-}13.3}{7.2}$
	C_2–C_3	0	$\frac{0{-}0.17}{0.1}$	$\frac{0{-}0.5}{0.2}$	$\frac{0{-}0.01}{0}$	0	$\frac{0.07{-}0.71}{0.32}$
Alkaline syenites (2)	CH_4	$\frac{0{-}0.003}{0}$	$\frac{0.17{-}0.27}{0.22}$	$\frac{0.17{-}1.23}{0.7}$	$\frac{0{-}0.17}{0.08}$	0	$\frac{0.44{-}1.53}{0.99}$
	CO_2	$\frac{4.3{-}26.4}{15.4}$	$\frac{23.1{-}83.7}{53.4}$	$\frac{39.0{-}81.8}{60.4}$	$\frac{410{-}1438}{924}$	$\frac{32{-}1966}{999}$	$\frac{634{-}3470}{2052}$
	CO	$\frac{0.14{-}0.30}{0.22}$	$\frac{3.0{-}5.9}{4.5}$	$\frac{2.2{-}5.3}{3.8}$	$\frac{3.3{-}60.5}{31.9}$	$\frac{0.2{-}52.4}{31.9}$	$\frac{8.7{-}124.4}{66.6}$
	H_2	0.01	$\frac{3.5{-}3.7}{3.6}$	$\frac{8.7{-}29.4}{19.1}$	$\frac{0.9{-}52.0}{26.5}$	$\frac{0.7{-}22.0}{11.4}$	$\frac{13.7{-}107.1}{60.5}$

Table 1. (Contd.)

Rock (number of analyses)	Volatile components	Volatile components (μl/g) released in discrete temperature ranges (°C)*					
		50–250	250–450	450–650	650–850	850–1050	Total
Alkaline syenites (2)	H_2O	$\frac{0.10\text{–}0.12}{0.11}$	$\frac{0.12\text{–}0.15}{0.14}$	$\frac{0.08\text{–}0.11}{0.09}$	$\frac{0.11\text{–}0.12}{0.12}$	$\frac{0.07\text{–}0.13}{0.1}$	$\frac{0.53\text{–}0.56}{0.55}$
	C_2–C_3	0	$\frac{0.04\text{–}0.09}{0.07}$	$\frac{0\text{–}0.22}{0.11}$	0	0	$\frac{0.09\text{–}0.27}{0.18}$
Carbonatites (7)	CH_4	$\frac{0\text{–}0.27}{0.07}$	$\frac{0.17\text{–}4.26}{1.06}$	$\frac{0.03\text{–}1.19}{0.58}$	$\frac{0\text{–}0.17}{0.04}$	0	$\frac{0.20\text{–}6.17}{1.75}$
	CO_2	$\frac{7\text{–}66}{24}$	$\frac{31\text{–}126}{95}$	$\frac{102\text{–}1807}{933}$	>1 wt %	>1 wt %	>1 wt %
	CO	$\frac{0.1\text{–}1.9}{0.5}$	$\frac{1.5\text{–}8.4}{3.4}$	$\frac{1.8\text{–}8.0}{4.6}$	$\frac{46\text{–}2600}{865}$	$\frac{0\text{–}5141}{1567}$	$\frac{94\text{–}6609}{2441}$
	H_2	$\frac{0\text{–}0.09}{0.03}$	$\frac{1.2\text{–}19.1}{7.3}$	$\frac{2.8\text{–}36.0}{13.2}$	$\frac{1.1\text{–}516}{110}$	$\frac{0\text{–}483}{110}$	$\frac{12\text{–}1018}{240.2}$
	H_2O	$\frac{0.07\text{–}1.06}{0.35}$	$\frac{0.13\text{–}0.45}{0.26}$	$\frac{0.08\text{–}1.04}{0.45}$	$\frac{0.09\text{–}1.54}{0.63}$	$\frac{0\text{–}5.1}{0.98}$	$\frac{0.5\text{–}8.1}{2.65}$
	C_2–C_3	0	$\frac{0.06\text{–}0.26}{0.11}$	$\frac{0\text{–}0.11}{0.02}$	0	0	$\frac{0.05\text{–}0.37}{0.13}$
Proskurovka Massif							
Ijolites–melteigites and jakupirangites (3)	CH_4	0	$\frac{0.21\text{–}0.51}{0.37}$	$\frac{0.14\text{–}0.24}{0.17}$	$\frac{0\text{–}0.03}{0.01}$	0	$\frac{0.34\text{–}0.72}{0.56}$
	CO_2	$\frac{3.2\text{–}5.4}{4.2}$	$\frac{10.5\text{–}12.1}{11.3}$	$\frac{85\text{–}169}{129}$	$\frac{523\text{–}1977}{1288}$	$\frac{0\text{–}1428}{883}$	$\frac{708\text{–}3300}{2316}$
	CO	$\frac{0.1\text{–}0.4}{0.2}$	$\frac{1.2\text{–}2.2}{1.7}$	$\frac{0.8\text{–}1.1}{0.9}$	$\frac{18\text{–}597}{213}$	$\frac{0\text{–}139}{60}$	$\frac{21\text{–}739}{276}$
	H_2	$\frac{0\text{–}0.04}{0.02}$	$\frac{0.7\text{–}6.7}{3.8}$	$\frac{6.5\text{–}16.8}{12.5}$	$\frac{11\text{–}194}{77}$	$\frac{0\text{–}168}{59}$	$\frac{36\text{–}385}{153}$
	H_2O	$\frac{0.05\text{–}0.13}{0.09}$	$\frac{0.08\text{–}1.15}{0.57}$	$\frac{0.46\text{–}1.70}{1}$	$\frac{0.3\text{–}1.5}{0.8}$	$\frac{0\text{–}1.5}{0.8}$	$\frac{1.0\text{–}5.9}{3}$
	C_2–C_3	0	$\frac{0.09\text{–}0.12}{0.1}$	0	0	0	$\frac{0.09\text{–}0.12}{0.1}$
Nepheline syenites (5)	CH_4	0	$\frac{0.24\text{–}0.82}{0.46}$	$\frac{0.14\text{–}0.75}{0.36}$	0	0	$\frac{0.48\text{–}1.09}{0.83}$
	CO_2	$\frac{3.5\text{–}14.2}{7.5}$	$\frac{16\text{–}185}{60}$	$\frac{47\text{–}258}{115}$	$\frac{921\text{–}3882}{1714}$	–	$\frac{766\text{–}4339}{1897}$
	CO	$\frac{0.16\text{–}0.38}{0.23}$	$\frac{1.2\text{–}5.9}{2.6}$	$\frac{1.3\text{–}4.3}{2.5}$	$\frac{22\text{–}512}{156}$	–	$\frac{26\text{–}518}{161}$
	H_2	0	$\frac{2.0\text{–}8.8}{4.4}$	$\frac{6.3\text{–}87.0}{33}$	$\frac{11\text{–}237}{123}$	–	$\frac{27\text{–}272}{160}$
	H_2O	$\frac{0.06\text{–}0.47}{0.18}$	$\frac{0.3\text{–}1.6}{0.9}$	$\frac{0.1\text{–}1.0}{0.5}$	$\frac{0.2\text{–}0.7}{0.4}$	–	$\frac{0.5\text{–}3.3}{2}$
	C_2–C_3	0	$\frac{0.03\text{–}0.24}{0.12}$	$\frac{0\text{–}0.10}{0.06}$	0	–	$\frac{0.03\text{–}0.34}{0.18}$
Antonovka Massif							
Alkaline pyroxenites, ijolites–melteigites, and essexites (6)	CH_4	0	$\frac{0.07\text{–}0.88}{0.54}$	$\frac{0.23\text{–}0.87}{0.45}$	$\frac{0\text{–}0.14}{0.05}$	–	$\frac{0.33\text{–}1.66}{1.03}$
	CO_2	$\frac{2.5\text{–}7.6}{4.7}$	$\frac{10.8\text{–}33.8}{23}$	$\frac{49\text{–}272}{149}$	$\frac{1291\text{–}4610}{2822}$	–	$\frac{1353\text{–}4836}{2998}$

Table 1. (Contd.)

Rock (number of analyses)	Volatile components	Volatile components (μl/g) released in discrete temperature ranges (°C)*					
		50–250	250–450	450–650	650–850	850–1050	Total
Alkaline pyroxenites, ijolites–melteigites, and essexites (6)	CO	0.15–0.60 0.4	1.4–6.5 3.5	1.0–2.2 1.5	81–360 211	–	99–367 216
	H_2	0	0.8–17.6 5.3	6–81 35	143–563 277	–	175–661 317
	H_2O	0.18–1.66 0.7	0.1–3.4 1.8	0.2–8.6 4	0.5–7.3 3.5	–	1.4–21.0 9.8
	C_2–C_3	0	0.02–0.82 0.38	0–0.21 0.08	0	–	0.02–0.97 0.46
Nepheline and alkaline syenites (3)	CH_4	0	0.16–0.67 0.43	0.25–0.39 0.34	0–0.05 0.02	–	0.41–1.10 0.79
	CO_2	3.0–3.5 3.2	14.6–34.2 21.3	72–127 94	303–5340 3301	–	394–5504 3420
	CO	0.16–0.25 0.22	1.18–3.12 1.89	0.69–2.18 1.6	39–176 95	–	44–180 99
	H_2	0	3.22–6.74 5.3	20–73 47	49–225 130	–	75–304 182
	H_2O	0.10–0.95 0.39	0.09–3.43 1.51	0.08–2.07 0.95	0.09–1.27 0.75	–	0.35–7.7 3.58
	C_2–C_3	0	0.15–0.44 0.29	0.08–0.17 0.13	0	–	0.29–0.52 0.42
Oktyabr’skii Massif							
Subalkaline gabbro and pyroxenites (3)	CH_4	0	0.41–1.36 0.81	0.92–1.77 1.67	0.17–3.61 1.52	0	1.5–7.3 4
	CO_2	5.01–7.76 6.51	15–473 171	51–1668 616	146–992 439	0–224 75	249–2294 1307
	CO	0.38–0.84 0.54	3.25–18.7 8.7	1.5–14.6 6.7	10–236 89.7	0–46 15.4	28–291 121
	H_2	0	9.3–41.5 22.2	50–123 98	232–639 396	0–416 139	324–1187 655
	H_2O	0.08–1.03 0.42	0.08–0.13 0.1	0.43–0.98 0.75	0.83–1.87 1.52	0–4.2 1.4	2.4–7.1 4.2
	C_2–C_3	0	0–0.2 0.04	0–0.08 0.05	0	0	0.08–0.12 0.09
Alkaline syenites (2)	CH_4	0	0.38–0.96 0.67	0.85–1.77 1.36	0.03–0.24 0.09	0–0.03 0.02	1.50–2.76 2.13
	CO_2	11.1–11.3 11.2	38–39 44	194–251 223	1537–2465 2001	274–630 452	2066–3395 2731
	CO	0.68–7.07 3.88	3.39–7.42 5.41	5.47–7.91 6.69	131–193 162	23–55 39	174–260 217
	H_2	0	9.3–12.1 10.7	93–211 152	197–247 222	60–122 91	360–592 476
	H_2O	0.08–1.42 0.75	0.13–0.71 0.42	0.26–0.64 0.45	0.45–0.65 0.55	0.33–0.43 0.38	1.34–3.75 2.55

Table 1. (Contd.)

Rock (number of analyses)	Volatile components	Volatile components (μl/g) released in discrete temperature ranges (°C)*					
		50–250	250–450	450–650	650–850	850–1050	Total
Alkaline syenites (2)	C_2–C_3	0	0.10–0.11 0.11	0–0.01 0.01	0	0	0.11–0.12 0.12
Nepheline syenites (mariupolites and foyaites) and agpaitic phonolites (7)	CH_4	0	0.24–0.85 0.43	0.51–2.45 1.48	0–0.41 0.08	–	0.89–3.20 1.99
	CO_2	4.6–17.8 9.07	18–143 50	22–259 94	30–2219 447	0–384 62	98–2520 663
	CO	0.05–2.71 1	2.03–9.86 6.26	1.76–6.17 3.86	1.25–93 22	2.1–77 11	5.3–118 44.4
	H_2	0	0.73–7.73 4.68	7–161 51	1–321 87	0.9–26 3.8	9–428 147
	H_2O	0.17–0.94 0.51	0.79–2.09 1.23	0.22–0.95 0.53	0.07–1.15 0.4	0.02–0.10 0.02	1.78–3.63 2.68
	C_2–C_3	0	0–0.17 0.05	0.10–0.56 0.2	0	–	0.16–0.56 0.29
Malaya Tersa Massif							
Gabbrodiabases (3)	CH_4	0	0.91–1.33 1.07	0.64–3.79 2.1	0.55–2.14 1.36	–	2.14–7.26 4.52
	CO_2	3.7–6.8 4.9	13.5–20.4 16.5	34–160 112	138–3424 2185	–	189–3611 2318
	CO	0.28–0.87 0.49	3.8–9.3 5.8	1.65–3.61 2.46	12–254 93	–	18–269 102
	H_2	0	5.86–15.2 12	87–367 210	529–976 818	–	631–1332 1040
	H_2O	0.19–0.90 0.48	0.25–0.67 0.4	1.97–4.22 2.91	10–13 11.3	–	13–19 15
	C_2–C_3	0	0.32–0.96 0.65	0.21–0.27 0.24	0	–	0.59–1.16 0.88
Alkaline syenites (6)	CH_4	0–0.55 0.11	0.30–5.73 1.65	0.54–3.82 1.39	0.04–0.92 0.4	–	0.87–11.01 3.53
	CO_2	2.8–21.7 11.5	15–146 47	13–261 116	26–921 317	–	60–1351 491
	CO	0.31–4.09 1.63	2.40–6.20 3.99	1.6–11.2 4.8	12–54 37	–	18–107 48
	H_2	0	4.6–60.4 22.4	73–476 187	122–1273 448	–	205–1753 657
	H_2O	0.09–0.82 0.42	0.13–0.46 0.29	0.12–2.71 0.75	0.79–9.16 2.78	–	1.43–12.85 4.24
	C_2–C_3	0–0.01 0	0.09–0.73 0.3	0–0.18 0.05	0–0.01 0	–	0.12–0.80 0.36
Foyaites (7)	CH_4	0–0.02 0	0.09–0.85 0.41	0.44–1.65 0.98	0–0.14 0.05	–	0.73–2.24 1.44
	CO_2	1.9–6.8 4.7	7–307 90	32–832 335	173–5534 1870	0–130 19	471–6151 2320
	CO	0.11–1.25 0.33	0.87–5.2 2.55	1.06–17.4 5.3	3–182 68	–	11–205 77

Table 1. (Contd.)

Rock (number of analyses)	Volatile components	Volatile components (μl/g) released in discrete temperature ranges (°C)*					
		50–250	250–450	450–650	650–850	850–1050	Total
Foyaites (7)	H_2	0	$\frac{1.97-6.81}{6.6}$	$\frac{17-152}{89}$	$\frac{5-256}{193}$	$\frac{0-38}{5}$	$\frac{31-525}{294}$
	H_2O	$\frac{0.09-0.99}{0.34}$	$\frac{1.34-7.26}{3.17}$	$\frac{0.64-7.26}{3.01}$	$\frac{0.41-3.26}{1.52}$	–	$\frac{2.91-18.31}{8.07}$
	C_2–C_3	0	$\frac{0.07-0.43}{0.28}$	$\frac{0.03-0.71}{0.35}$	$\frac{0-0.01}{0}$	–	$\frac{0.11-1.04}{0.62}$
Southern Kal'chikskii Massif							
Two-feldspar fayalite–hedenbergite syenites (2)	CH_4	0	$\frac{0.21-0.24}{0.23}$	$\frac{0.34-0.58}{0.46}$	0	0	$\frac{0.55-0.82}{0.69}$
	CO_2	$\frac{9-23}{16}$	$\frac{13-628}{321}$	$\frac{63-460}{262}$	$\frac{590-880}{735}$	$\frac{106-109}{108}$	$\frac{1075-1807}{1441}$
	CO	$\frac{0.8-1.7}{1.3}$	$\frac{3.5-29}{16}$	$\frac{1.6-11}{6.5}$	$\frac{17-19}{18}$	$\frac{2.4-3.8}{3.1}$	$\frac{27-62}{45}$
	H_2	0.09	$\frac{9.8-62}{36}$	$\frac{76-109}{93}$	$\frac{12-67}{40}$	$\frac{2.1-3.3}{2.7}$	$\frac{156-185}{171}$
	H_2O	$\frac{0.73-1.41}{1.07}$	$\frac{0.37-0.61}{0.49}$	$\frac{0.71-0.97}{0.84}$	$\frac{0.18-0.56}{0.37}$	$\frac{0.07-0.11}{0.09}$	$\frac{2.49-3.24}{2.86}$
	C_2–C_3	0	$\frac{0-0.05}{0.03}$	0	0	0	$\frac{0-0.05}{0.03}$
Azovskoe deposit							
Alkali feldspar syenites, including Zr–REE ores (12)	CH_4	$\frac{0-0.03}{0}$	$\frac{0.27-1.26}{0.7}$	$\frac{0.68-4.19}{1.77}$	$\frac{0-2.35}{0.33}$	$\frac{0.03-0.89}{0.08}$	$\frac{1.53-6.55}{2.88}$
	CO_2	$\frac{1.8-56.4}{20.9}$	$\frac{33-3302}{548}$	$\frac{60-1627}{419}$	$\frac{22-336}{112}$	$\frac{21-185}{64}$	$\frac{182-4671}{1164}$
	CO	$\frac{0.19-12.6}{2.8}$	$\frac{4-167}{39}$	$\frac{2-122}{33}$	$\frac{7-26}{22}$	$\frac{4-27}{16}$	$\frac{25-262}{113}$
	H_2	0–0.7	$\frac{0.4-97}{32}$	$\frac{33-533}{175}$	$\frac{0.6-4004}{494}$	$\frac{1.2-393}{51}$	$\frac{121-4812}{752}$
	H_2O	$\frac{0.04-5.67}{1.43}$	$\frac{0.06-3.16}{0.79}$	$\frac{0.04-1.93}{0.83}$	$\frac{0.02-4.48}{1.17}$	$\frac{0.04-3.98}{0.45}$	$\frac{0.30-13.64}{4.67}$
	C_2–C_3	0	0.15	0.08	0	0	0.07–0.25**
Yastrebetskii Massif							
Alkaline syenites (4)	CH_4	0	$\frac{0.27-2.27}{1.19}$	$\frac{0.37-6.62}{2.85}$	$\frac{0-0.44}{0.11}$	0	$\frac{0.78-8.89}{4.15}$
	CO_2	$\frac{6.8-66}{31.4}$	$\frac{17-277}{159}$	$\frac{137-8170}{2662}$	$\frac{451-4090}{1972}$	$\frac{0-340}{85}$	$\frac{1325-8965}{4909}$
	CO	$\frac{0.33-7.7}{3.9}$	$\frac{3.6-20}{14.6}$	$\frac{6-148}{46.4}$	$\frac{2.8-1643}{543}$	$\frac{0-101}{25}$	$\frac{41-1813}{633}$
	H_2	$\frac{0.04-12.1}{5.1}$	$\frac{11-158}{80}$	$\frac{67-489}{495}$	$\frac{99-1821}{976}$	$\frac{0-594}{149}$	$\frac{184-2968}{1705}$
	H_2O	$\frac{0.13-3.37}{1.44}$	$\frac{0.29-2.2}{1.22}$	$\frac{0.32-6.0}{3.1}$	$\frac{1.6-6.3}{4.8}$	$\frac{0-1.15}{0.29}$	$\frac{3.45-17.7}{10.9}$
	C_2–C_3	0	$\frac{0.08-0.47}{0.24}$	$\frac{0-0.76}{0.21}$	0	–	$\frac{0.08-1.23}{0.44}$

Table 1. (Contd.)

Rock (number of analyses)	Volatile components	Volatile components (μl/g) released in discrete temperature ranges (°C)*					
		50–250	250–450	450–650	650–850	850–1050	Total
Pokrovo–Kireevo Massif							
Titanaugite pyroxenites (3)	CH_4	0	0.41–0.78 0.53	0.21–0.98 0.68	0–0.08 0.04	–	0.99–1.47 1.25
	CO_2	3.4–3.6 3.5	5.6–18 11.5	64–135 93	436–2108 1076	–	537–2252 1184
	CO	0.28	4.7	1.5	11–43 26	–	17–49 32
	H_2	0	5.8–7.2 6.6	22–31 28	76–166 115	–	114–201 149
	H_2O	0.08–0.27 0.17	0.07–0.16 0.13	0.78–1.26 0.99	1.82–2.61 2.20	–	3.19–3.70 3.49
	C_2–C_3	0	0.19–0.46 0.29	0–0.18 0.08	0	–	0.29–0.46 0.37
Malignites and juvites (7)	CH_4	0	0.23–1.57 0.74	0.10–2.76 1.14	0–0.23 0.08	–	0.55–3.34 1.96
	CO_2	4.8–34 13.4	34–1613 267	94–1430 363	212–>1 wt %	>1 wt %	>1 wt %
	CO	0.11–2.9 0.77	3.6–15.8 8.3	1.1–8.4 4.1	5–457 91.4	–	16–479 104
	H_2	0–7.5 1.0	3.2–13.8 7.1	6–170 59	33–309 149	–	51–488 217
	H_2O	1.1–4.1 1.71	2.3–6.2 4.2	1.1–3.1 2.37	0.9–5.5 2.1	–	6.0–16.2 10.15
	C_2–C_3	0	0.06–0.51 0.29	0–0.28 0.24	0	–	0.33–0.67 0.54
Dike in granite, near the village of Andreevka, eastern Azov area							
Porphyritic titanaugite pyroxenite (augitite)	CH_4	0	2.80	6.78	0.85	–	10.43
	CO_2	6.98	631	128	313	–	1079
	CO	0.30	78.8	4.6	10.8	–	94.5
	H_2	0.45	145	302	533	–	980
	H_2O	2.48	0.44	3.94	17.11	–	28.97
	C_2–C_3	0	1.31	0.16	0	–	1.47
Grorudite dikes, eastern Azov area							
Low- and high-Ti grorudites (analogues of comendites and pantellerites) (8)	CH_4	0–1.43 0.18	0.78–6.65 1.87	0.51–5.09 1.83	0–1.16 0.26	–	1.43–14.35 4.15
	CO_2	5.3–81 33.0	21–169 89	27–165 88	45–449 249	–	130–732 459
	CO	1.4–9.1 4.7	3–28 16	2–18 10	2–83 30	–	35–135 60
	H_2	0.16–0.70 0.45	1.7–17 8.0	1.8–149 60	1.8–216 77	–	17–310 147

Table 1. (Contd.)

Rock (number of analyses)	Volatile components	Volatile components (μl/g) released in discrete temperature ranges (°C)*					
		50–250	250–450	450–650	650–850	850–1050	Total
Low- and high-Ti grorudites (analogues of comendites and pantellerites) (8)	H_2O	$\frac{0.88–3.04}{2.01}$	$\frac{0.50–1.45}{0.97}$	$\frac{0.24–1.15}{0.74}$	$\frac{0.10–0.72}{0.37}$	–	$\frac{2.45–6.06}{4.08}$
	C_2–C_3	$\frac{0–0.14}{0.05}$	$\frac{0.21–0.74}{0.39}$	$\frac{0–0.23}{0.11}$	0	–	$\frac{0.27–0.90}{0.55}$
Khibina Massif							
Khibinites (14)	CH_4	$\frac{1.72–16.78}{6.2}$	$\frac{4.4–15.8}{9.0}$	$\frac{1.9–11}{5.3}$	$\frac{0.32–5.5}{1.5}$	–	$\frac{9.9–35.1}{22.0}$
	CO_2	$\frac{4–26}{10}$	$\frac{5.9–74}{37}$	$\frac{3.4–74}{35}$	$\frac{0.8–204}{80}$	–	$\frac{25–308}{162}$
	CO	$\frac{0.2–2.9}{0.8}$	$\frac{1.8–27}{7.0}$	$\frac{1.3–10}{3.6}$	$\frac{0.5–48}{13}$	–	$\frac{8–88}{24}$
	H_2	0	$\frac{2.5–19}{9.3}$	$\frac{9–59}{33}$	$\frac{20–185}{86}$	–	$\frac{31–249}{128}$
	H_2O	$\frac{0.41–2.11}{1.11}$	$\frac{1.16–7.0}{3.77}$	$\frac{0.15–4.13}{1.71}$	$\frac{0.21–2.13}{0.62}$	–	$\frac{3.28–12.53}{7.21}$
	C_2–C_3	$\frac{0–0.67}{0.18}$	$\frac{0.18–1.45}{0.73}$	$\frac{0.07–0.71}{0.29}$	$\frac{0–0.08}{0.01}$	–	$\frac{0.29–2.16}{1.21}$
Urtites (9), melteigites (2), and malignites (1)	CH_4	$\frac{0.63–15.8}{5.46}$	$\frac{1.93–21.3}{9.40}$	$\frac{0.79–8.65}{3.96}$	$\frac{0.04–5.45}{1.67}$	–	$\frac{3.40–47.58}{20.49}$
	CO_2	$\frac{6–45}{22}$	$\frac{15–103}{49}$	$\frac{25–179}{64}$	$\frac{32–291}{114}$	–	$\frac{90–478}{249}$
	CO	$\frac{0.17–2.54}{1.18}$	$\frac{2.7–19}{8.5}$	$\frac{0.7–29}{5.5}$	$\frac{0.9–22}{7.2}$	–	$\frac{7–67}{22.4}$
	H_2	$\frac{0–1.6}{0.4}$	$\frac{0.7–38}{9.5}$	$\frac{0–38}{19}$	$\frac{6–113}{36}$	–	$\frac{15–158}{65}$
	H_2O	$\frac{0.13–3.09}{1.19}$	$\frac{1.39–6.88}{2.55}$	$\frac{0.10–3.30}{0.57}$	$\frac{0.11–0.58}{0.30}$	–	$\frac{1.94–13.2}{4.61}$
	C_2–C_3	$\frac{0–0.34}{0.14}$	$\frac{0.11–2.48}{0.69}$	$\frac{0–0.47}{0.17}$	$\frac{0–0.05}{0.0}$	–	$\frac{0.21–2.89}{1.00}$
Foyaites (5 complete and 11 reduced analyses)	CH_4	$\frac{3.85–20.72}{10.65}$	$\frac{4.23–16.25}{11.23}$	$\frac{3.13–5.39}{4.25}$	$\frac{0.98–2.54}{1.46}$	–	$\frac{13.7–40.22}{27.59***}$
	CO_2	$\frac{3.1–6.6}{4.7}$	$\frac{5.7–63}{22.6}$	$\frac{9–48}{20}$	$\frac{7–50}{33}$	–	$\frac{48–164}{80}$
	CO	$\frac{0.06–1.45}{0.44}$	$\frac{1.6–7.2}{4.5}$	$\frac{1.7–2.2}{2.0}$	$\frac{5.9–30}{11.4}$	–	$\frac{9.4–36}{18.5}$
	H_2	0	$\frac{3.3–14}{8}$	$\frac{27–60}{46}$	$\frac{95–179}{132}$	–	$\frac{126–236}{185}$
	H_2O	$\frac{0.53–2.0}{1.3}$	$\frac{1.14–7.8}{3.61}$	$\frac{0.12–3.78}{1.24}$	$\frac{0.15–0.84}{0.40}$	–	$\frac{1.94–14.4}{6.6}$
	C_2–C_3	$\frac{0.23–1.25}{0.46}$	$\frac{0.46–1.93}{1.02}$	$\frac{0.11–0.59}{0.36}$	$\frac{0–0.03}{0.01}$	–	$\frac{1.06–2.77}{1.86***}$
Lyavochorrites (3)	CH_4	$\frac{4.40–13.61}{7.41}$	$\frac{3.27–17.39}{9.87}$	$\frac{2.23–8.69}{5.55}$	$\frac{0.59–4.83}{2.93}$	–	$\frac{10.29–44.53}{25.76}$
	CO_2	$\frac{16–20}{17}$	$\frac{48–121}{74}$	$\frac{92–123}{108}$	$\frac{59–351}{169}$	–	$\frac{220–525}{368}$
	CO	$\frac{0.4–2.4}{1.66}$	$\frac{0.9–110}{39.2}$	$\frac{1.9–7.1}{4.2}$	$\frac{3.9–17}{9}$	–	$\frac{18–123}{54}$

Table 1. (Contd.)

Rock (number of analyses)	Volatile components	Volatile components (μl/g) released in discrete temperature ranges (°C)*					
		50–250	250–450	450–650	650–850	850–1050	Total
Lyavochorrites (3)	H_2	$\frac{0-1.7}{1.13}$	$\frac{33-172}{77}$	$\frac{34-65}{47}$	$\frac{25-83}{49}$	–	$\frac{120-257}{172}$
	H_2O	$\frac{0.13-1.00}{0.43}$	$\frac{0.68-0.91}{0.76}$	$\frac{0.07-0.22}{0.13}$	$\frac{0.11-0.34}{0.19}$	–	$\frac{1.02-2.47}{1.54}$
	C_2–C_3	$\frac{0.13-0.66}{0.47}$	$\frac{0.68-3.25}{2.03}$	$\frac{0-0.33}{0.21}$	$\frac{0-0.17}{0.10}$	–	$\frac{0.81-4.32}{2.80}$
Rischorrites (2)	CH_4	$\frac{0.25-1.47}{0.86}$	$\frac{1.47-2.50}{1.99}$	$\frac{0.25-1.85}{1.00}$	$\frac{0.62-0.92}{0.77}$	–	$\frac{3.92-5.40}{4.66}$
	CO_2	$\frac{0.39-3.4}{1.85}$	$\frac{3.8-4.7}{4.3}$	$\frac{2.4-2.5}{2.4}$	$\frac{4-15}{10}$	–	$\frac{14-21}{18}$
	CO	$\frac{0.29-3.4}{1.85}$	$\frac{3.8-4.7}{4.3}$	$\frac{2.4-2.5}{2.4}$	$\frac{4-15}{10}$	–	$\frac{14-21}{18}$
	H_2	0	$\frac{3.3-11}{7.2}$	$\frac{13-63}{38}$	$\frac{81-93}{87}$	–	$\frac{98-168}{133}$
	H_2O	$\frac{2.07-24}{13}$	$\frac{5.3-8.7}{7.0}$	$\frac{1.03-2.5}{1.77}$	$\frac{0.58-9.6}{5.1}$	–	$\frac{9-45}{27}$
	C_2–C_3	0	$\frac{0.14-0.23}{0.19}$	$\frac{0-0.10}{0.05}$	0	–	$\frac{0.23-0.24}{0.24}$
Apatite ores (2)	CH_4	$\frac{0.17-0.57}{0.87}$	$\frac{2.31-3.43}{2.87}$	$\frac{0.54-2.46}{1.50}$	$\frac{0.04-0.08}{0.06}$	–	$\frac{4.10-6.50}{5.30}$
	CO_2	$\frac{2.3-7.7}{5.0}$	$\frac{7.4-20}{14}$	$\frac{8.8-87}{48}$	$\frac{6.3-347}{177}$	–	$\frac{25-461}{243}$
	CO	$\frac{0.06-0.37}{0.22}$	$\frac{1.10-3.47}{2.30}$	$\frac{0.98-3.66}{2.32}$	$\frac{0.46-9.4}{4.93}$	–	$\frac{2.6-17}{9.80}$
	H_2	$\frac{0-0.8}{0.4}$	$\frac{3.0-6.4}{4.7}$	$\frac{6.1-80}{43}$	$\frac{3.0-9.6}{6.3}$	–	$\frac{12-97}{55}$
	H_2O	$\frac{0.42-3.87}{2.15}$	$\frac{2.24-3.82}{3.03}$	$\frac{0.49-0.67}{0.58}$	$\frac{0.11-0.14}{0.13}$	–	$\frac{5.03-6.74}{5.89}$
	C_2–C_3	$\frac{0.04-0.28}{0.16}$	$\frac{0.13-0.31}{0.22}$	$\frac{0.04-0.22}{0.14}$	0	–	$\frac{0.21-0.82}{0.52}$
				Lovozero Massif			
Nepheline syenites (4)	CH_4	$\frac{0.30-1.33}{0.86}$	$\frac{3.37-6.65}{4.37}$	$\frac{2.63-11.5}{5.09}$	$\frac{0.15-2.28}{1.08}$	–	$\frac{7-20.8}{11.4}$
	CO_2	$\frac{6.4-22}{13}$	$\frac{17-40}{28}$	$\frac{10-53}{30}$	$\frac{23-80}{48}$	–	$\frac{57-195}{118}$
	CO	$\frac{0.44-2.7}{1.66}$	$\frac{6.8-12}{9}$	$\frac{1.2-8}{3.5}$	$\frac{2.5-7.7}{4.9}$	–	$\frac{14-29}{19}$
	H_2	$\frac{0-1.9}{0.8}$	$\frac{19-69}{47}$	$\frac{53-97}{72}$	$\frac{12-125}{67}$	–	$\frac{136-270}{187}$
	H_2O	$\frac{0.08-5.13}{1.77}$	$\frac{1.34-9.95}{5.0}$	$\frac{0.18-14.37}{4.54}$	$\frac{0.12-4.58}{1.81}$	–	$\frac{1.71-34}{13.1}$
	C_2–C_3	$\frac{0-0.13}{0.05}$	$\frac{0.55-1.62}{1.16}$	$\frac{0.17-3.10}{1.0}$	$\frac{0-0.07}{0.04}$	–	$\frac{0.85-4.73}{2.25}$

Notes: * Numerators—variation ranges; denominators—average values.

** Determined in two samples.

*** Together with 11 additional samples for which reduced single-stage analyses (at 250–850°C) were conducted; the CH_4 concentration is 20.1 μl/g (ranging from 10 to 31 μl/g), and C_2–C_3 is 2.0 μl/g (0.3–3.3 μl/g); C_2–C_3 = $C_2H_4 + C_2H_6 + C_3H_6 + C_3H_8$.

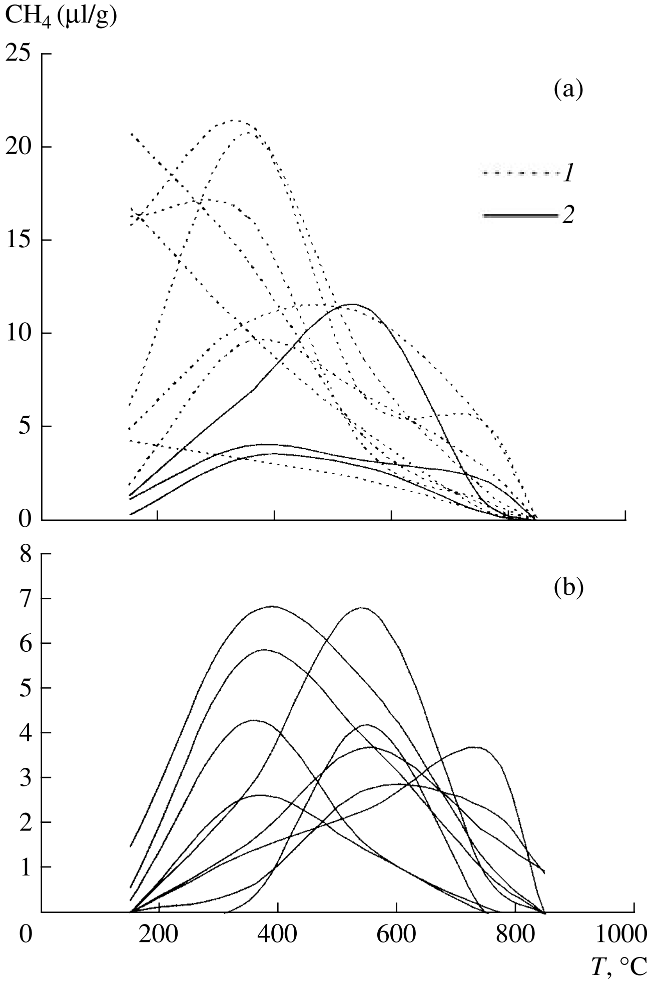

Fig. 1. Methane release (depending on pyrolysis temperature) from the alkaline rocks of (a) the Kola Peninsula and (b) Ukrainian Shield. See Table 1 for data. (*1*) Khibina Massif; (*2*) Lovozero Massif.

lite: 8.5 μl/g) in mariupolites from the Oktyabr'skii Massif.

Feldspars, major rock-forming minerals in nepheline and alkaline syenite in various alkaline complexes, are generally poor in hydrocarbons (Fig. 4). It is interesting that the highest CH$_4$ concentration (13.3 μl/g) was determined in alkali feldspar from marginal (olivine-bearing) syenite from the Malaya Tersa Massif in the Ukrainian Shield, whereas alkali feldspars from the agpaitic nepheline syenites in the Khibina and Lovozero massifs contain as little as 2–8 μl/g methane. Hence, the alkali feldspars examined within the framework of this research do not concentrate hydrocarbons, although some varieties of these minerals described in [16] contained as much as 87 μl/g methane. There also seems to be no clearly pronounced temperature dependence of methane release, although its maximum amounts most often escape within the range of 450–650°C (Fig. 4).

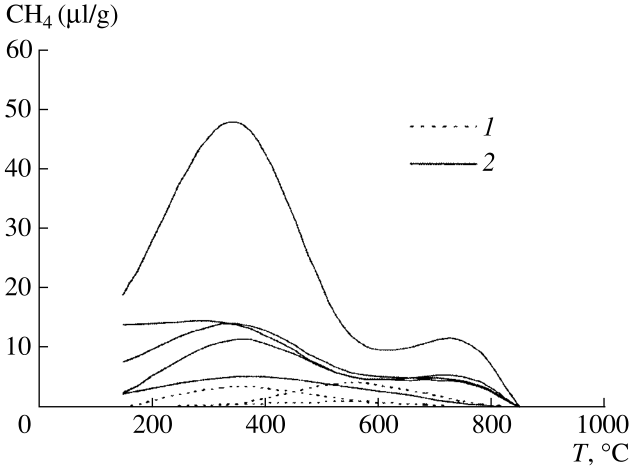

Fig. 2. Methane release (depending on pyrolysis temperature) from nepheline from the alkaline rocks of (*1*) the Ukrainian Shield and (*2*) Khibina Massif. See Table 2 for data.

Roughly equal, or even higher, concentrations of hydrocarbons (4–14, occasionally up to 21 μl/g) were detected in the mafic (biotite, amphibole, and aegirine) and some accessory minerals in alkaline rocks from the Ukrainian Shield and Kola Peninsula (Table 4, Fig. 5). Elevated methane concentrations (26 μl/g) were also detected in a titanomagnetite sample from Khibina urtite. The Khibina and Lovozero alkaline pyroxenes and titanite release maximum methane amounts at 250–450°C, whereas this maximum for aegirine, biotite, amphibole, and zircon in alkaline rocks from the Ukrainian Shield is usually shifted to 450–650°C (Table 4).

The limited amount of statistically treated material available for us suggests the following tendencies: mafic minerals in alkaline rocks from the Ukrainian Shield are generally richer in hydrocarbons than the corresponding rocks, whereas the rocks and minerals from the Khibina and Lovozero massifs show invered relations. The major concentrators of hydrocarbons in the alkaline rocks of the Kola Peninsula are nepheline and sodalite, but the same minerals from analogous rocks from the Ukrainian Shield show no enrichment in hydrocarbons.

Carbon dioxide CO$_2$, a major volatile component of all alkaline and subalkaline rocks in the Ukrainian Shield, is also one of the main gas components in agpaitic nepheline syenites from the Khibina and Lovozero massifs (Table 1). Most earlier publications dealing with natural gases in these rocks [17, 18] did not pay adequate attention to CO$_2$ because the fluids extracted from these rocks with the use of certain crushing techniques were dominated by methane. However, some researchers [1, 19] believed that CO$_2$ and H$_2$O play the leading role during the high-temperature (magmatic) crystallization stage of agpaitic and miaskitic nepheline-bearing rocks, and the fraction of CH$_4$ and

Table 2. Gas chromatographic data on the pyrolysis products of nepheline

Rock, sample no. (number of analyses)	Volatile components	Volatile components (μl/g) released in discrete temperature ranges (°C)				
		50–250	250–450	450–650	650–850	Total
Chernigovka carbonatite Massif						
Biotite–albite nepheline syenite, 280/597	CH_4	0	3.54	1.4	0.14	5.08
	CO_2	3.23	156.4	135.1	1753.4	2048.13
	CO	0.05	1.9	0.8	3.96	6.71
	H_2	0	0.67	1.35	3.78	5.8
	H_2O	0.07	1.29	1.65	0.58	3.59
	C_2–C_3	0	0.14	0.18	0	0.32
Oktyabr'skii Massif						
Pegmatoid, 710	CH_4	0	0.75	1.1	0.31	2.16
	CO_2	11.4	145.9	257.6	640.1	1055
	CO	1.08	3.3	2.7	18.1	25.18
	H_2	0	5.7	64.9	239.1	309.7
	H_2O	0.35	1.7	1.2	1.05	4.3
	C_2–C_3	0	0.11	0.11	0	0.22
Mariupolite, 12/91	CH_4	0	0.68	4.16	1.16	6
	CO_2	6.03	82.1	90.2	161	339.33
	CO	0.16	10.5	4.12	7.1	21.72
	H_2	0	0.86	24	80	104.86
	H_2O	0.59	1.51	1.19	0.39	3.68
	C_2–C_3	0	tr.	tr.	0	tr.
Mariupolite, 22-11/85	CH_4	–	0	–	0.9	0.9
	CO_2	–	143.1	–	–	1763
	CO	–	3.9	–	–	56.2
	H_2	–	0	–	–	161.4
	H_2O	–	0.86	–	2.56	3.42
Khibina Massif						
Urtites (4)	CH_4	$\frac{7.7-19}{10.3}$	$\frac{5.1-48}{20.5}$	$\frac{3.3-12}{7}$	$\frac{0.7-4.5}{5.5}$	$\frac{11.5-90}{43.3}$
	CO_2	$\frac{5.7-11}{8.8}$	$\frac{17-33}{26}$	$\frac{20-160}{86}$	$\frac{36-614}{239}$	$\frac{102-813}{359}$
	CO	$\frac{0.4-1.9}{1}$	$\frac{4.8-13.3}{8.5}$	$\frac{4.5-11.5}{7.8}$	$\frac{1.7-14}{6.8}$	$\frac{17-29}{24}$
	H_2	$\frac{0-0.8}{0.3}$	$\frac{8.3-18.6}{11.5}$	$\frac{26-62}{51}$	$\frac{1.8-61}{26}$	$\frac{37-137}{89}$
	H_2O	$\frac{0.3-1.6}{0.8}$	$\frac{0.4-3.7}{2.2}$	$\frac{0.2-1.0}{0.4}$	$\frac{0.1-0.7}{0.3}$	$\frac{0.9-6.2}{3.7}$
	C_2–C_3	$\frac{0.05-0.29}{0.21}$	$\frac{0.52-1.86}{1.1}$	$\frac{0.26-0.97}{0.65}$	$\frac{0-0.07}{0.02}$	$\frac{1.09-3}{1.98}$
Lyavchorrites (2)	CH_4	$\frac{2.5-12.9}{7.7}$	$\frac{11.5-15}{13.2}$	$\frac{5.2-5.5}{5.3}$	$\frac{4.3-4.5}{4.4}$	$\frac{23-38}{31}$
	CO_2	$\frac{11-14}{13}$	$\frac{38-73}{56}$	$\frac{52-69}{61}$	$\frac{45-79}{62}$	$\frac{182-197}{191}$
	CO	$\frac{0.3-0.6}{0.4}$	$\frac{1.4-20}{11}$	$\frac{2.4-4.1}{3.3}$	$\frac{7.3-8.1}{7.7}$	$\frac{12-32}{22}$
	H_2	$\frac{0.4-0.9}{0.6}$	$\frac{8-32}{20}$	$\frac{11-20}{16}$	$\frac{6.4-14}{10}$	$\frac{27-67}{47}$
	H_2O	$\frac{0.14-0.37}{0.26}$	$\frac{0.3-0.8}{0.6}$	$\frac{0.06-0.11}{0.09}$	$\frac{0.07-0.08}{0.08}$	$\frac{0.76-1.13}{0.95}$
	C_2–C_3	$\frac{0-0.02}{0.01}$	$\frac{0.19-1.66}{0.93}$	$\frac{0-0.32}{0.16}$	$\frac{0-0.11}{0.05}$	$\frac{0.19-2.11}{1.15}$

Table 2. (Contd.)

Rock, sample no. (number of analyses)	Volatile components	Volatile components (µl/g) released in discrete temperature ranges (°C)				
		50–250	250–450	450–650	650–850	Total
Pegmatoid, Koashva (3)	CH_4	13.3–13.8 13.5	13.8–38 22	5.3–6.5 5.9	5.2–13.2 8.1	38–51 43
	CO_2	6.7–9 8	22–31 25	52–63 58	184–334 271	264–389 339
	CO	0.6–1.0 0.8	3.7–5.6 4.5	3.0–3.4 3.2	4.3–8.4 6.3	12–15 13
	H_2	0–1.2 0.6	1.3–7.1 4.4	16–28 22	1.3–24 10	18–39 29
	H_2O	0.12	0.14–0.43 0.27	0.12	0.08–0.26 0.15	0.46–0.69 0.55
	C_2–C_3	0.44–0.71 0.58	0.25–1.65 0.87	0.25	0	0.95–1.68 1.43

other reduced fluid components increases during the late and postmagmatic stages.

Although it is hard to unambiguously interpret our data (Table 1), they demonstrate that significant CO_2 amounts are released already at 50–200–250 to 450°C, i.e., within the temperature range where carbonates should still not dissociate. At temperatures of 450–650°C and higher, the sources of CO_2 can be both dissociating carbonates (first, ferrous- and iron-bearing) and primary high-temperature inclusions. It should be mentioned that already early publications by Petersil'e [18] mentioned CO_2 as a major component released during the heating of ijolites from the Khibina Massif, including the low-temperature region (56–97 vol % at temperatures of 20–400°C). However, this author arrived at the conclusion that CO_2 was most likely formed by the decomposition of secondary carbonates contained in the rocks. At the same time, it was demonstrated later [17] that, when gases are extracted with the use of a vacuum mill, much CO_2 is adsorbed, so that its yield can vary from 0 to 23% of its total amount. This led the authors of that paper to conclude that the absence of CO_2 from the gases extracted by this technique does not necessarily mean that this gas is not contained in the inclusions (if no thermodesorption was applied during gas extraction).

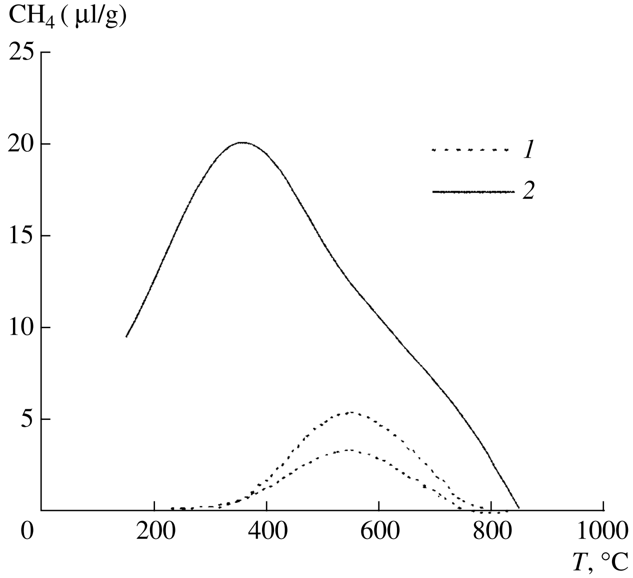

Fig. 3. Methane release (depending on pyrolysis temperature) from sodalite from the alkaline rocks of (*1*) the Ukrainian Shield and (2) Lovozero Massif. See Table 3 for data.

As can be seen from Table 1 and Fig. 6, virtually all alkaline rocks from the Ukrainian Shield have $CH_4 : CO_2$ (CO_2 released at 50–450°C) volumetric proportions of less than 1 : 4. In contrast, most samples form the Khibina and Lovozero massifs have analogous proportions of 1 : 1 to 1 : 4, and many samples have these ratios of less than 1 : 4. Only a few samples have $CH_4 : CO_2$ of 1 : 1 to 2 : 1. Even the most CH_4-rich rocks from Khibina have these proportions no higher than 2 : 1 (Fig. 6). With regard for CO_2 released at higher temperatures (450–650°C), at which calcite still does not dissociate, the fraction of CO_2 in fluid from the alkaline rocks, including their agpaitic varieties, should be even higher.

The occurrence of sodic mineralization and carbonatites testifies to a significant CO_2 concentrations during the formations of the Khibina Massif.

Carbon dioxide was found in the pyrolysis products of practically all minerals of the alkaline rocks, including the low-temperature region (<450°C) (Tables 2–4). The minimum CO_2 concentrations were found in albite from the mariupolites of the Oktyabr'skii Massif and in alkali feldspar from the Khibina lyavchorrite.

Table 3. Gas chromatographic data on the pyrolysis products of sodalite, cancrinite, and zeolites

Mineral, rock, and sample no.	Volatile components	Volatile components (μl/g) released in discrete temperature ranges (°C)					
		50–250	250–450	450–650	650–850	850–1050	Total
Oktyabr'skii Massif							
Sodalite from pegmatoid, 1m	CH_4	0	0.51	3.31	0.07	0	3.89
	CO_2	15.1	108.8	127.7	443.3	621.5	1316.4
	CO	1.76	6.72	5.42	20.34	51.86	86.1
	H_2	0	1	83.19	72.3	4	160.6
	H_2O	0.5	2.02	1.25	0.23	0.11	4.12
	C_2–C_3	0.14	0.88	0.34	0	0	1.36
Sodalite from pegmatoid mariupolite	CH_4	0	0.55	5.32	0.55	0.07	6.48
	CO_2	4.89	7.6	29.7	43.6	105.7	191.4
	CO	0.03	7.69	2.76	1.79	4.71	17
	H_2	0	1.64	22.96	16.4	0.82	41.81
	H_2O	4.12	19.69	11.87	0.34	0.05	36.07
	C_2–C_3	0	0	2.9	0	0	2.9
Cancrinire from pegmatoid mariupolite	CH_4	0	0.68	3.2	1.43	0	5.32
	CO_2	4.18	11.9	31.3	34.1	18.1	99.5
	CO	0	3.68	2.27	3.09	4.77	13.81
	H_2	0	0.82	32.8	10.9	10.9	55.5
	H_2O	0.62	29.4	53.8	0.14	0.03	84
Zeolite from mariupolite	CH_4	0	0.68	–	7.8	0	8.52
	CO_2	7.17	18.7	–	54.2	30.7	110.7
	CO	0.16	14.6	0	6.6	1	22.3
	H_2	0	9.3	0	77.3	6.2	92.8
	H_2O	10.02	42.2	0	40.9	0.09	93.2
	C_2–C_3	–	–	–	4.92	–	4.92
Lovozero Massif							
Sodalite from foyaite, TS-SH-18-2	CH_4	9.48	20.01	12.37	5.01	0.03	46.88
	CO_2	12.11	63.59	215.21	712.16	2383	3386.1
	CO	20.36	93.16	2.44	23.83	303.3	443.09
	H_2	1.42	81.99	66.61	105.04	94.8	349.9
	H_2O	0.65	10.76	11.3	3.92	0.43	27.1
	C_2–C_3	0.96	1.68	0.45	0	0	3.09

Carbon monoxide (CO) was detected in all analyses of alkaline rocks, in amounts that were usually a few times lower than those of CO_2. In the general case, the concentrations of CO and CO_2 are positively correlated. The alkaline rocks of the Ukrainian Shield contain more CO_2 than CH_4, and the analogous rocks from the Khibina and Lovozero massifs bear comparable concentrations of CO and CH_4, although the former often dominates over the latter, particularly in samples with low CH_4 concentrations. CO released from the rocks and minerals shows certain systematic tendencies, often with two temperature maxima: at 250–450 and 650–850°C or, more rarely, 450–850 or 850–1050°C. The first of these maxima (at 250–450°C) is clearly pronounced in most rock samples from the Khibina and Lovozero massifs at the unsystematic occurrence of the other temperature maximum. At the same time, most samples of alkaline rocks from the Proskurovka and Chernigovka massifs, including their carbonatites, display clearly pronounced maxima of CO release at 650–850 (1000)°C. The mariupolites are characterized by a low-temperature peak, and other alkaline rocks from the Oktyabr'skii and Southern Kal'chikskii (together with the Azovskoe deposit), Malaya Tersa, Pokrovo–Kireevo, Yastrebetskii, and Antonovka massifs usually show both low- and high-temperature maxima, often with the significant predominance of the latter (Table 1).

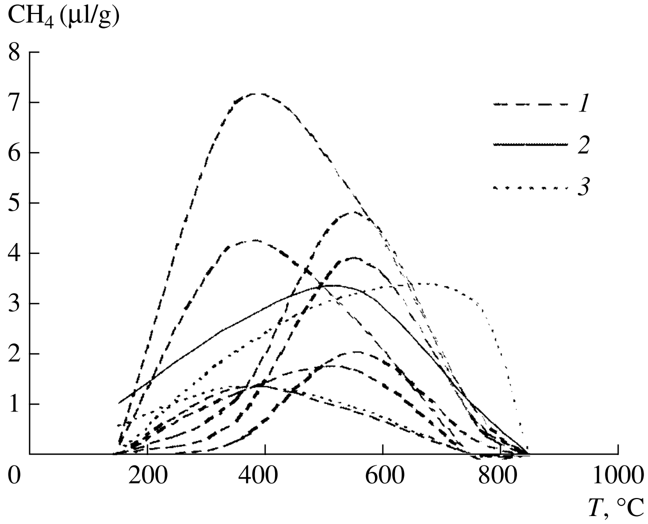

Fig. 4. Methane release (depending on pyrolysis temperature) from feldspars from the alkaline rocks of (*1*) the Ukrainian Shield, (*2*) Lovozero Massif, and (*3*) Khibina Massif.

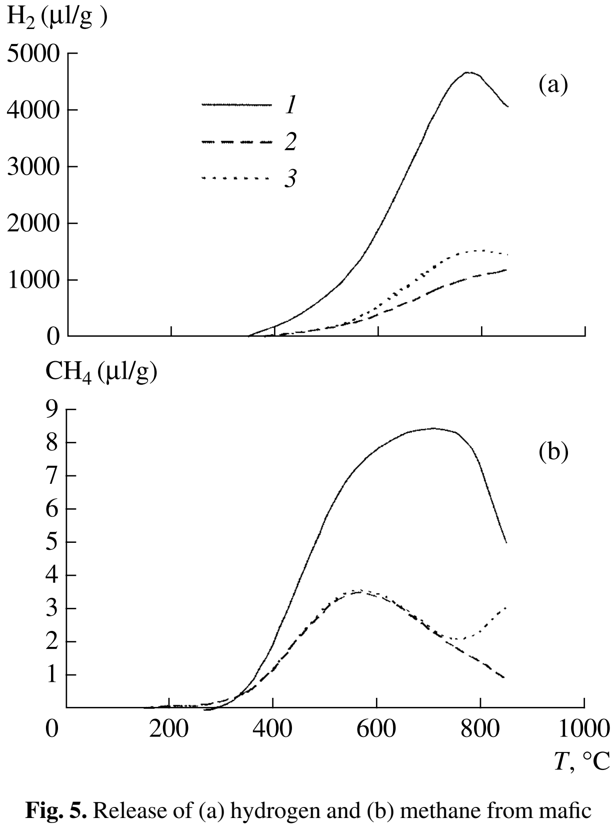

Fig. 5. Release of (a) hydrogen and (b) methane from mafic minerals of the alkaline rocks of the Ukrainian Shield. See Table 4 for data. (*1*) Biotite from syenites of the Azovskoe deposit; (*2*) amphibole, same rocks; (*3*) lepidomelane from albite–lepidomelane rock, Oktyabr'skii Massif.

Note that a clearly pronounced high-temperature maximum of CO release is also characteristic of such rocks from the Ukrainian Shield as syenites, foyaites, and gabbroids, whose mafic minerals have high or elevated Fe mole fractions. Many of these rocks contain carbonates, including their Fe-bearing varieties.

Both of the CO release maxima can also be observed in many samples of nepheline, sodalite, feldspars, and mafic minerals (Tables 2–4).

Hydrogen H_2 was detected in all analyses of the rocks and minerals. It starts to intensely escape from them at temperature above 250°C, and its amount increases with increasing temperature. This is particularly typical of mafic hydroxyl–bearing minerals, such as biotite and amphibole, which start to release hydrogen at temperatures above 450°C, and this process reaches a maximum at 850–1050°C (Table 4, Fig. 5). Maxima of hydrogen release from nepheline, sodalite, and cancrinite often fall onto 450–650 and 20–450°C (Tables 2, 3). The former maximum is more typical of minerals in alkaline rocks from the Ukrainian Shield, and the latter is more characteristic of rocks from the Kola Peninsula. This somewhat resembles the behavior of CO and CH_4, which also show release peaks within the same temperature ranges.

During the pyrolysis of alkaline rocks, the minimum hydrogen amounts were released from leucocratic rocks without mafic hydroxyl-bearing minerals (or with their insignificant contents): mariupolites, urtites, some grorudites, dolomitic carbonatites, and pyroxene alkaline syenites. Most of the analyzed rocks—melanocratic (gabbroids, pyroxenites, and ijolites–urtites), mesocratic, and leucocratic (nepheline and alkaline syenites), with biotite and amphibole—release significant hydrogen amounts (often >100 μl/g) starting at 450°C and ending at 1050°C. Equally high hydrogen concentrations were also detected in the pyrolysis products of most alkali feldspars from rocks of the Ukrainian Shield, and these concentrations are slightly lower in the same minerals from the Khibina and Lovozero massifs. The lowest hydrogen concentrations (5–7 μl/g) were detected in one feldspar sample from Khibina lyavochorrite and in albite from the nepheline syenite of the Chernigovka Massif. Relatively low hydrogen concentrations (26–59 μl/g) were determined in feldspars from mariupolites from the Oktyabr'skii Massif and foyaite from the Lovozero Massif.

Other volatile components (in the pyrolysis products) include H_2O and N_2 and, sporadically, also H_2S and SO_2.

Water H_2O was detected in all of our rock samples, usually in concentrations of a few microliters per gram. However, nepheline-bearing rocks altered by zeolitization and spreusteinization sometimes release as much as 2–4 wt % water. We detected no systematic correlations between the amounts of released water and rock types. The rocks from the Kola Peninsula seem to be generally richer in water than the analogous rocks from the Ukrainian Shield. The elevated water concentrations are likely related to overprinted processes of rock alteration.

Table 4. Gas chromatographic data on the pyrolysis products of some mafic and accessory minerals

Mineral, rock, and sample no.	Volatile components	Volatile components (μl/g) released in discrete temperature ranges (°C)					
		50–250	250–450	450–650	650–850	850–1050	Total
Chernigovka carbonatite massif							
Biotite from nepheline syenite, 280/597	CH_4	0	4.29	3.41	0.03	–	7.74
	CO_2	2.25	19.3	90	3953.9	–	4065.5
	CO	0.27	2.6	2.71	507.3	–	512.9
	H_2	0	0	123	536.6	–	659.6
	H_2O	0.09	0.3	0.37	0.6	–	1.36
	C_2–C_3	0	0.16	0.47	0	–	0.63
Oktyabr'skii Massif							
Lepidomelane from albite–lepidomelane metasomatic rock	CH_4	0	0.48	3.55	2.11	3.07	9.2
	CO_2	3.61	30	37	32	45.3	148
	CO	0.11	3.2	2.55	5.9	19.2	31
	H_2	0	0.41	308.1	1484.4	1484.4	3277.2
	H_2O	0.17	0.68	0.56	0.8	3.03	5.2
	C_2–C_3	0	0.08	0.73	0	0	0.81
Aegirine from mariupolite	CH_4	0	0.34	2.05	0.34	0	2.73
	CO_2	0.01	21.9	58.5	65	69	214.5
	CO	0	5.74	2.76	4.01	0.97	13.5
	H_2	0	4.95	14.9	32.3	4.97	57.1
	H_2O	0.17	2.37	0.37	0.14	0.01	3.06
	C_2–C_3	0	0	0.73	0	–	0.73
Azovskoe deposit							
Biotite from melanocratic syenite, 120/91	CH_4	0	0.68	7.1	8.35	5.01	21.14*
	CO_2	7.43	75.2	143.4	59.9	245.4	531.3
	CO	0.6	16.3	12.7	36.8	319.2	385.3
	H_2	0.01	18.2	1229.8	4573.9	4056.1	9878
	H_2O	0.51	0.68	1.77	5.26	4.78	12.99
Amphibole from the same rock, 120/91	CH_4	0	0.51	3.48	1.87	0.89	6.75*
	CO_2	6.5	40.35	135.4	106.9	106.8	395.9
	CO	0.54	10.29	5.77	18.1	25.7	60.4
	H_2	0	5.44	266.5	999.2	1205.2	2476.2
	H_2O	0.21	0.16	0.6	0.79	9.1	10.84
Yastrebetskii syenite Massif							
Zircon, Borehole 23s, 27.5–30 m	CH_4	0	1.7	4.7	0.03	0.003	6.41
	CO_2	48.1	162.5	298	745.9	58.9	1313.4
	CO	2.71	38.4	15.4	38.6	2.57	97.6
	H_2	0.43	12.6	58.9	18.9	1.3	91.7
	H_2O	0.26	0.32	0.3	0.16	0.13	1.17
	C_2–C_3	0	0.22	0.24	0	0	0.47
Zircon, Borehole 23s, 839.3–840.0 m	CH_4	0.003	0.78	3.51	0.03	0.003	4.26
	CO_2	12.4	56.7	237.4	397.8	40.4	744.8
	CO	1.06	18.7	6.04	4.22	0.3	30.3
	H_2	0.43	27.3	50.6	10.1	1.52	89.6
	H_2O	0.22	0.87	0.92	0.45	0.12	2.56
	C_2–C_3	0	0.14	0.09	0	0	0.24

Table 4. (Contd.)

Mineral, rock, and sample no.	Volatile components	Volatile components (μl/g) released in discrete temperature ranges (°C)					
		50–250	250–450	450–650	650–850	850–1050	Total
				Knibina Massif			
Aegirine from lyavochorrite, 1253-53	CH_4	3.9	7.31	2.6	0.09	–	13.9
	CO_2	11.5	47.7	52.8	59.8	–	171.8
	CO	1.63	5	6.76	13	–	26.4
	H_2	1.71	67.6	107.6	67.6	–	244.6
	H_2O	0.09	0.07	0.04	0.09	–	0.28
	C_2–C_3	0	1.12	0.08	0	–	1.2
Aegirine from lyavochorrite, 1253-45	CH_4	2.3	5.94	2.97	0.01	–	11.23
	CO_2	3.71	12.5	27	43.4	–	86.5
	CO	0.44	2.94	3.68	1.62	–	8.68
	H_2	0.46	7.73	7.73	0.46	–	16.4
	H_2O	0.05	0.04	0.04	0.11	–	0.24
	C_2–C_3	0	0.85	0.05	0	–	0.9
Pyroxene from urtite, 170R-255	CH_4	0	1.24	2.31	1.04	–	4.6
	CO_2	5.5	11.6	9.05	41.9	–	68
	CO	0.28	2.87	1.9	3.23	–	8.3
	H_2	0	5.39	43.7	24.3	–	73.4
	H_2O	0.06	0.04	0.03	0.15	–	0.28
	C_2–C_3	0	0.8	0.11	0	–	0.91
Aegirine from pegmatoid, Koashva	CH_4	0.17	1.28	1.46	1.71	–	4.62
	CO_2	12.4	32.1	86.2	91.6	–	222.2
	CO	0.45	3.9	13.93	13.28	–	31.6
	H_2	0	35.1	143.5	210.8	–	389.4
	H_2O	0.06	0.07	0.04	0.41	–	0.57
	C_2–C_3	0	0.24	0	0	–	0.24
Titanite from urtite, 127k-90	CH_4	0.72	2.05	0.78	0.03	–	3.58
	CO_2	2.9	4.73	5.23	14.3	–	27.1
	CO	1.69	1.93	1.2	0.82	–	5.63
	H_2	0.63	10.1	27.3	1.27	–	39.3
	H_2O	0.05	0.07	0.03	0.06	–	0.21
	C_2–C_3	0	0.05	0	0	–	0.05
Titanomagnetite from urtite, 170R-255	CH_4	1.11	6.88	11.86	6.02	–	25.87
	CO_2	9.71	12.25	19.9	38.5	–	80.4
	CO	0.32	2.11	1.65	2.84	–	6.93
	H_2	0	1.21	26	28.2	–	55.5
	H_2O	0.07	0.06	0.05	0.07	–	0.25
	C_2–C_3	0	0.1	0.03	0.1	–	0.23
				Lovozero Massif			
Aegirine from foyaite, TSSHCH-18-2	CH_4	0.02	2.02	0.72	0	–	2.76
	CO_2	11.38	16.7	29.5	30.4	–	87.9
	CO	3.82	4.14	3.77	1.13	–	12.9
	H_2	0.34	33.9	8.48	0.71	–	43.5
	H_2O	0.08	0.09	0.07	0.07	–	0.3
	C_2–C_3	0	0.85	0.08	0	–	0.93

Note: * Total CH_4 concentration in the rock is 6.54 μl/g (maximum at 450–650°C), the alkali feldspar contains 5.31 μl/g CH_4 (maximum at 450–650°C).

Nitrogen N_2 is not a typical component of alkaline rocks, and its concentrations in the pyrolysis products of these rocks from the Khibina and Lovozero massifs are, indeed, very low (<1 μl/g), with only occasional foyaite, khibinite, and urtite samples containing as much as 1–2 and, rarely, 3.3 μl/g N_2. The temperature maximum of nitrogen release falls onto 650–850°C. Nepheline from these rocks contains up to 1.7 μl/g N_2, sodalite 1.5 μl/g, and aegirine 1 μl/g, and these minerals have the same temperature maximum of N_2 release.

The alkaline rocks of the Ukrainian Shield are much richer in nitrogen, with its highest contents typical of such alkali feldspar-rich rocks as the syenites of the Yastrebetskii Massif and Azovskoe deposit and the grorudites of the eastern Azov area. The pyrolysis products of these rocks often contain 1–3, occasionally up to 7–14 and even 20 μl/g N_2, which is released at 850–1050 and 650–850°C. One syenite sample from the Yastrebetskii Massif was determined to contain 180 μl/g nitrogen with its maximum release at 850–1050°C. The maximum N_2 concentrations in the feldspars of the syenites were 7–12 μl/g, and their biotite contained 14 μl/g N_2, which was released at equally high temperatures (650–1050°C). Elevated nitrogen contents were also detected in the amphibole (3.3 μl/g) and zircon (up to 3 μl/g) of the syenites.

Much nitrogen (up to 2.5, occasionally 8 μl/g) was found in the nepheline syenites and ijolites–melteigites of the Antonovka, Proskurovka, Oktyabr'skii, and Chernigovka massifs. This nitrogen was commonly released at high temperatures (650–850, 850–1050, and, more rarely, 450–650°C). Albite from nepheline syenite from the Chernigovka Massif contains 18 μl/g N_2, which was predominantly released within the temperature range of 50–250°C. At the same time, albite (2–3 μl/g), lepidomelane (10 μl/g), and zircon (2.7 μl/g) from the rocks of the Oktyabr'skii Massif released nitrogen mostly at high temperatures (850–1050°C).

Hence, the alkaline rocks of the Ukrainian Shield bear nitrogen concentrations no lower than the methane concentrations, and the former are even higher than the latter in the feldspar-rich rocks. Most samples of alkaline rocks from the Antonovka and Proskurovka massifs contain more nitrogen (up to 5–8 μl/g) than methane (whose concentrations are quite low, no higher than 1.7 μl/g, as was mentioned above). In this respect, the alkaline rocks of the Ukrainian Shield differ from the analogous rocks of the Kola Peninsula. Obviously, the problem of nitrogen in magmatic rocks, including the alkaline rocks of the Ukrainian shield, deserves closer consideration and further exploration.

DISCUSSION AND SOME CONCEPTS CONCERNING THE NATURE OF VOLATILE COMPONENTS IN THE ALKALINE ROCKS OF THE UKRAINIAN SHIELD AND KOLA PENINSULA

Various hypotheses were proposed to explain the genesis of volatile components (first of all, hydrocarbons) in alkaline rocks, from the deep provenance of these components (their origin from the mantle or even core) to their biogenic formation. Not going into details of these alternative hypotheses in this publication, we adhere to the currently most widely spread concept [1, 17] that the composition of the volatiles (CO_2, H_2O, and others) evolved simultaneously with the fractional crystallization of the alkaline intrusions in their magmatic chambers and produced hydrocarbons mostly during the late and postmagmatic stages. The application of such sample-preparation techniques as crushing in ball mills and the subsequent extraction and identification of gases (so-called cold technique) and the release of volatile components during rock heating (pyrolysis) has certain advantages and disadvantages and can distort the actual contents and proportions of the gas components. Nevertheless, it should be mentioned that our results of the analysis of the pyrolysis products of alkaline rocks from the Khibina Massif, first of all, methane, are mostly in good agreement with the data obtained by cold techniques [17]. It is hard to compare the results obtained on other components (H_2, CO, and CO_2) because, on the one hand, they can participate in a variety of chemical reactions with the decomposition of the organic matter during heating, and, on the other hand, we cannot rule out the occurrence of gas components newly formed during the crushing and pulverization of the rock samples [17].

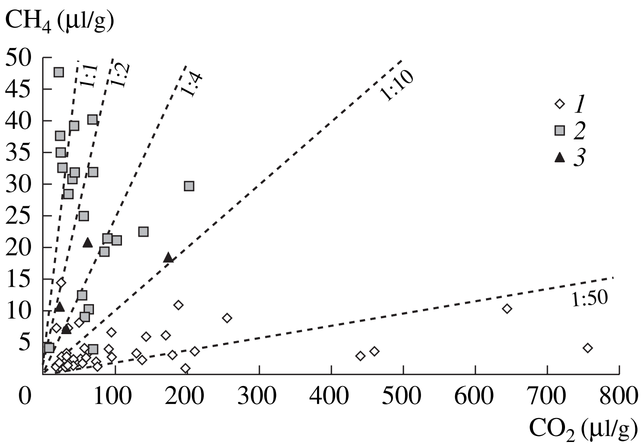

Fig. 6. Proportions of CH_4 and CO_2 concentrations (μl/g) released from alkaline rocks at temperatures of 250–450°C: (*1*) Ukrainian Shield, (*2*) Khibina Massif, (*3*) Lovozero Massif. The diagram shows rocks with elevated CH_4 concentrations. Numerals near the lines correspond to the $CH_4 : CO_2$ ratios.

From this viewpoint, below we propose an interpretation of our results of pyrolysis and other identification methods of hydrocarbons (EPR, PMR, and IR spectroscopy). There are good reasons to believe that the amount of methane extracted by pyrolitic techniques is close to the original concentration of this component in the rocks or to its amount produced by the thermal decomposition of chemically bound methyl groups.

Certain amounts of hydrocarbons can also be lost, if CO, CO_2, and H_2 could be partly produced by decomposing OM. It can also be hypothesized that methane and other hydrocarbons can be generated by reactions between H_2 and CO_2 [2] or in the course of iron oxidation, hydrogen release, and its reaction with carbon dioxide, as was demonstrated in experiments with the heating of basalts [20]. Although we cannot completely rule out such reactions during pyrolysis, we believe that they are not widespread because, otherwise, the biotite- and amphibole-rich rocks from the Ukrainian Shield should have high concentrations of newly formed methane and other hydrocarbons, which is not the case. It is, however, quite probable that these reactions occur in nature during the postmagmatic evolutionary stages of alkaline intrusions, for example the agpaitic Khibina and Lovozero massifs. For some unknown reasons, these reactions did not proceed during the origin of the alkaline rocks of the Ukrainian Shield (or, at least, these reactions were not widespread).

In this paper we do not touch upon the occurrence modes of methane and other hydrocarbons in alkaline rocks. These components were fairly thoroughly studied in the rocks of the Kola Peninsula but are contained only in low concentrations in analogous rocks from the Ukrainian Shield and are studied in them relatively poorly. We still have not reached a consensus on the occurrence modes of hydrocarbons in the rocks of the Ukrainian Shield.

It is even more difficult to interpret the nature of CO_2 in the rocks. Obviously, high-temperature (>650°C) CO_2 is formed predominantly via the thermal dissociation of carbonates and, perhaps, partly by the destruction of OM. At the same time, CO_2 released at temperatures of 250–450°C could also escape from destructed gas–liquid inclusions and be produced by the decomposition of OM. In any event, all alkaline rocks from the Ukrainian Shield, as well as most analogous rocks from the Kola Peninsula, contain more CO_2 (including that released at low temperatures) than CH_4 (Table 1, Fig. 6). Conceivably, pyrolysis at low temperatures is responsible for the bulk of released CO_2 from inclusions, which is close to the amount of this component that was in equilibrium with the melt during the magmatic stage. Earlier experimental research [17] has demonstrated that much CO_2 can be adsorbed, and its degree of recovery is insignificant during the crushing and pulverization of rock samples. The presence of low-temperature CO_2 was previously documented in alkaline rocks from the Khibina Massif [18].

Comparing alkaline rocks from the Ukrainian Shield and Kola Peninsula, it can be concluded that the former are generally much richer in CO_2. As was mentioned above, all of the rock types bear either primary or secondary carbonates. The alkaline magmas that produced the Khibina and Lovozero massifs were likely also enriched in CO_2, as also follows from the younger sodic mineralization of these massifs and from the occurrence of carbonatites in the Khibina Massif. According to chemical analyses, the average CO_2 contents in various Khibina rocks are 0.02–0.62 wt % [21].

Inasmuch as CO_2 and H_2O are the predominant volatile components of magmatic rocks [1, 19, 22] during their high-temperature crystallization stage, it is reasonable to suggest that part of the pyrolitic CO_2 (released before the thermal dissociation of carbonates) was inherited and reflects the composition of the primary fluids.

According to Kogarko et al. [23], reduced gases were produced during the evolution and cooling of the alkaline magmatic system. As the temperature decreased, equilibria in the C–O–H system significantly shifted toward CH_4, H_2, and other reduced gases. Nevertheless, water remains the main fluid component during the postmagmatic stage. Late during the evolution of the alkaline magma, water was actively incorporated in zeolites, which are widespread in the rocks of the Khibina and Lovozero massifs. The dehydration of the postmagmatic fluids was associated with the accumulation of methane, hydrogen, and other gases.

The occurrence of two (low- and high-temperature) maxima of CO release testifies to the existence of two its sources. The high-temperature CO was formed predominantly via the dissociation of Fe-bearing carbonates (and also Mn-bearing carbonates in the carbonatites), while the low-temperature CO was provided by decomposing organic compounds.

An analogous explanation can be proposed for the genesis of the hydrogen. Its high-temperature fractions were produced by FeO oxidation and hydrogen reduction from the OH groups of biotite and amphiboles. Hydrogen could also be generated during the formation of aegirine, magnetite, cancrinite, and zeolites during the late and postmagmatic stages [24]. Some low-temperature hydrogen could also be produced by the thermal destruction of OM.

The other volatiles (H_2O, H_2S, and SO_2) released during the pyrolysis of the alkaline rocks escaped from destructed fluid inclusions and, mostly, were generated by decomposing silicates (micas, amphiboles, zeolites, sodalite, etc.) and sulfides. As was mentioned above, nitrogen, which is often detected in the rocks from the Ukrainian Shield, is particularly interesting in the context of problems discussed in this publication.

Volatile components in rocks from the Ukrainian Shield and Kola Peninsula differ, first and foremost, in their concentrations of CH_4 and C_2–C_3 hydrocarbons, as well as by higher concentrations of CO_2 in the former rocks. There seem to be several reasons for these differences. The main reason is likely the differences between the chemical compositions of the melts and the conditions under which the intrusions were formed. Whereas the Khibina and Lovozero massifs are large intrusions of agpaitic rocks, the intrusions in the Ukrainian Shield are mostly small bodies, and the volumes of their final agpaitic derivatives are insignificant.

Iron contained in most rocks from the Ukrainian Shield is less oxidized than in the analogous rocks from the Khibina and Lovozero massifs. Moreover, most of the compared alkaline massifs of the Ukrainian Shield belong to the carbonatite complex, whose leading volatile component is known to be CO_2. Such alkaline massifs in the Ukrainian Shield as Chernigovka, Proskurovka, and Antonovka are eroded to a significant depth (up to 5–20 km). Many researchers believe that the CO_2 fraction in fluid increases with depth. At the same time, the Khibina and, particularly, Lovozero massifs are eroded to insignificant depths or are hypabyssal intrusions.

Conceivably, the composition of volatile components is somehow correlated with the age of the rocks. Most rocks from the Ukrainian Shield analyzed in the course of our research are Proterozoic (1.7–2.1 Ga). The only exceptions are the Pokrovo–Kireevo Massif and grorudite dikes in the Azov area, which are Devonian, i.e., coeval with the Khibina and Lovozero massifs. However, its seems to be hardly probable that the compositions of the volatiles can be correlated with the rock ages, because the Devonian alkaline rocks of the Ukrainian Shield are poor in methane, whereas the Proterozoic Ilimaussaq Massif of agpaitic nepheline syenites bears as high of a concentration of hydrocarbons as those in the Khibina and Lovozero massifs.

Hence, the principal factors controlling high hydrocarbon concentrations in alkaline rocks should be their oversaturation with respect to alkalis (agpaitic crystallization), the large sizes of the intrusions, and their crystallization near the surface.

CONCLUSIONS

Our chromatographic results confirmed earlier data on high concentrations of methane and other hydrocarbons in the alkaline agpaitic rocks of the Khibina and Lovozero massifs and revealed low contents of these components in alkaline rocks and carbonatites from the Ukrainian Shield. The latter rocks occurred to be richer in CO_2 and to bear elevated to high concentrations of N_2.

There are several principal reasons for these differences in the composition of volatiles from the alkaline rocks of the Ukrainian Shield and Kola Peninsula. The Khibina and Lovozero massifs are large intrusions of agpaitic alkaline rocks, whose rocks are characterized by high degree of Fe oxidation, whereas the massifs in the Ukrainian Shield contain little agpaitic rocks, which appeared in these massifs only during the final evolutionary stages. Moreover, the massifs in the Ukrainian Shield are much smaller than in the Kola Peninsula.

Most alkaline rocks in the Ukrainian Shield affiliate with the carbonatite and gabbro–syenite complexes, whose alkaline melts crystallized according to different mechanisms.

The alkaline massifs of the Ukrainian Shield are eroded to a greater depth than the Khibina and Lovozero massifs.

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