

Review

# Occurrence Forms, Composition, Distribution, Origin and Potential Hazard of Natural Hydrogen–Hydrocarbon Gases in Ore Deposits of the Khibiny and Lovozero Massifs: A Review

Valentin A. Nivin 

Geological Institute, Kola Science Centre, Russian Academy of Sciences, 14 Fersman Str., 184209 Apatity, Russia; nivin@geoksc.apatity.ru; Tel.: +7-815-55-79-580

Received: 10 June 2019; Accepted: 1 September 2019; Published: 3 September 2019



**Abstract:** The Khibiny and Lovozero massifs—the world’s largest alkaline massifs—contain deposits with unique reserves of phosphorus and rare metals, respectively. The reduced gas content in the rocks and, especially, the ore deposits of these massifs is unusually high for igneous complexes, thus representing both geochemical and practical interests. There are three morphological types (or occurrence forms) of the gas phase in these deposits: occluded (predominantly in vacuoles of micro-inclusions in minerals), diffusely dispersed, and free. All three morphological types have the same qualitative chemical gas composition. Methane is the main component, and molecular hydrogen (which sometimes dominates) and ethane are the subordinate constituents. Heavier methane homologs (up to and including pentanes), alkenes, helium, and rarely carbon oxide and dioxide are present in minor or trace amounts. All three morphological types of gases are irregularly distributed in space to various degrees. Free gases also show a release intensity that varies in time. The majority of researchers recognize that the origin of these gases is abiogenic and mostly related to the formation of the massifs and deposits. However, the relative time and mechanism of their generation are still debated. Emissions of combustible and explosive hydrogen–hydrocarbon gases pose hazards during the underground mining of ore deposits. Therefore, the distinctive features of gas-bearing capacity are an essential part of the mining and geological characterization of such deposits because they provide a basis for establishing and implementing special measures of the gas regime during mining operations.

**Keywords:** gas-bearing capacity of ore deposits; methane; hydrogen; abiogenic natural gases; morphological types of gases; prevention of gas emissions during mining activities; nepheline-syenite massif

## 1. Introduction

The Khibiny and Lovozero nepheline-syenite massifs with foidolites are located in the west of the Kola Peninsula, which belongs to the Arctic zone of Russia. They are unique in terms of their sizes (1327 and 650 km<sup>2</sup>, respectively); their reserves of phosphorus, alumina, zirconium, rare-earth metals, titanium, niobium, and tantalum, which are concentrated in large-scale and extremely large-scale deposits associated with the massifs [1–12]; and their mineralogical diversity (circa 500 and 370 mineral species, respectively) [13]. At present, the Khibiny apatite-nepheline deposits (with extraction from the ore mainly apatite and, to a lesser extent, nepheline and titanite) and the Lovozero loparite (REE–Ti–Ta–Nb) deposit are being mined.

Another peculiar feature of these deposits and their host massifs is an unusually high content of reduced hydrogen–hydrocarbon gases (HHCG) of various morphological types [14–19]. This is in

contrast to gases found in most other igneous complexes, which have CO<sub>2</sub> as the commonest endogenic gas, e.g., [20,21] and references therein. Reduced gases, which are predominantly composed of methane and occluded in vacuoles of fluid inclusions in minerals, are also known to be present in other alkaline massifs (e.g., Kiya-Shaltyrskiy, Koksharovskiy, Zaangarskiy, and Korgeredabinskiy in Siberia and adjacent areas [16]; Ilimaussaq in Greenland [22–28]; and Strange Lake in Canada [29–32]). But only in the Khibiny and Lovozero massifs, free hydrogen–hydrocarbon gases were found in the 1950s [14] and 1980s [33], respectively, to be filling a few systems of conjugated fractures (mainly microfractures) and other cavities in the rocks [15,16,18,19]. Alongside the two main gas types, a transitional type exists between them, namely, diffusely dispersed gases [17]. Previously, such gases were called sorbed or residual gases in open microfractures [16].

The presence of HHCG in the rocks of these massifs is of both scientific and practical interest. Scientifically, it is important to clarify some debated issues, such as the relative time, conditions, key factors, and mechanism of these hydrocarbons' generation in alkaline magmatic systems, as well as to identify the role of reduced fluids as possible agents and indicators of mineral formation, including different ore mineralization [15–19,22–51]. The practical interest is founded on the escape of natural combustible and explosive hydrogen–hydrocarbon gases to the mine air. This factor, among others, complicates the safe processing of these deposits, and gas-bearing capacity has become an integral part of mining and geologically characterizing them [15,16,18,19,33,52].

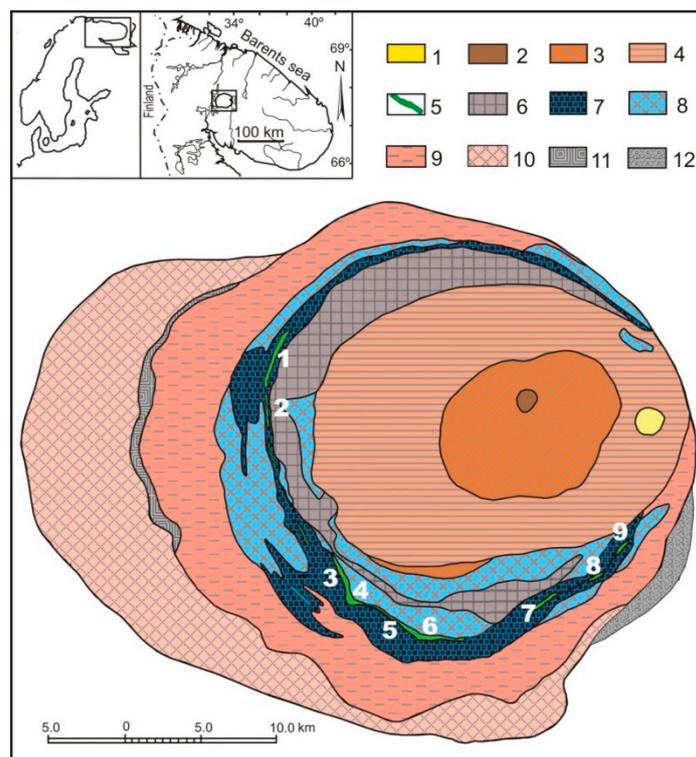
This review systematizes and summarizes references and data, primarily obtained by the author, including unpublished results, on the HHCG occurrence forms, composition, features of spatial distribution, style of emission, origin, and potential hazardousness in the Khibiny and Lovozero deposits.

## 2. Brief Geology

The geological structure, mineralogy, and geochemistry of the Khibiny and Lovozero alkaline massifs and related mineral deposits, which formed between 370 million and 360 million years ago during a burst of Paleozoic tectonomagmatic activity in the eastern Fennoscandian shield, are described in a great number publications, including dozens of monographs [1–7,53–60] and relatively recent papers [8–12,61–73]. Such a vast body of literature permits only the most general information, enough to understand the subject of the article, to be presented herein on the geology of the massifs and related mineral deposits. Here, the names of some rocks that are specific to these massifs are retained in the text, rather than more commonly accepted terms.

### 2.1. The Khibiny Massif and Apatite-Nepheline Deposits

As per the data available, the Khibiny massif is situated in the contact zone of the Archaean granite-gneisses and Proterozoic volcano-sedimentary rocks and has an asymmetric concentrically zoned structure. It is composed primarily of nepheline syenites (Figure 1) that are divided by the rocks of the Main foidolite ring into two parts that are approximately equal in volume: external (khibinite) and internal (lyavochorrite and foyaite), which are distinguished between massive and trachitoid rocks on a provisional basis. Recently, all of these varieties of nepheline syenites have been grouped together as a single intrusion of foyaites. The rocks of the Main Ring are represented by foidolites (melteigite-ijolite-urtite), high-potassium poikilitic (kalsilite)-nepheline syenite (rischorrite), malignite, as well as apatite-nepheline and titanite-apatite-nepheline ores. Late pegmatite and hydrothermal veins, explosive pipes, and alkaline and alkaline-ultramafic dikes also gravitate toward this complex. There is a semicircular zone of foidolites and fine-grained nepheline and alkaline syenites with xenoliths of fenitized volcano-sedimentary rocks in the western part of the massif. A carbonatite complex occurs near the eastern contact of the massif. The core of this complex (circa 1 km in diameter) is composed of calcite-albite, calcite-biotite, aegirine-calcite-biotite rocks, and albite-calcite, biotite-calcite, and manganese-calcite carbonatites. It is surrounded by stockworks of calcite-albite rocks, carbonatites with Ba-REE-Sr mineralization, foskorites, and carbonate-zeolite rocks.

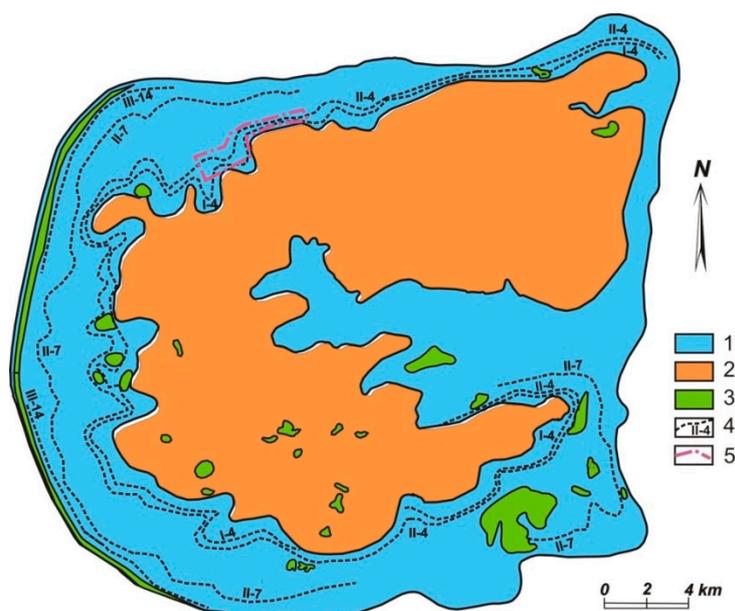


**Figure 1.** Geological sketch map of the Khibiny massif (based on the map of production geological association Sevzapegeologiya). Rocks: 1—carbonatites, 2—alkaline syenite, 3 and 4—massive and trachitoid foyaite, 5—apatite-nepheline ore, 6—lyavochorrite, 7—ijolite-urtite, 8—rischorrite, 9 and 10—trachitoid and massive khibinite, 11—fenitized metavolcanics and foidolites, 12—fenite after granite-gneiss. Deposits (white-colored digits): 1—Partomchorr, 2—Kuelporr, 3—Kukisvumchorr, 4—Yuksporr, 5—Apatite Circus, 6—Rasvumchorr Plateau, 7—Koashva, 8—Nyorpakhk, 9—Oleniy Ruchei.

Apatite deposits and ore occurrences are represented by compact or stockwork-like bodies of apatite-nepheline and titanite-apatite-nepheline rocks (0.01–200 m thick and 0.01–15 km long). They predominantly occur in the apical parts of the Main foidolite ring as three ore fields: southeastern, southwestern, and northern. The largest deposits (Kukisvumchorr, Yuksporr, Apatite Circus, and Rasvumchorr Plateau) are concentrated in the southwestern sector of the Main Ring and, in fact, represent various parts of the same apatite-nepheline rock body (Figure 1). The deposits of the southeastern ore field (Koashva, Nyorpakhk, and Oleniy Ruchei) are made of compact stockworks of lens-/veinlet-like bodies. The Northern sector's deposits (Kuelporr and Partomchorr) consist of individual thin sheet-like apatite-nepheline and apatite-titanite rock bodies. There are mottled, lens-like-banded, blocky, reticulated, impregnated (massive), and brecciated types of apatite ores. Using the underground technique, JSC "Apatit" is presently mining the Kukisvumchorr and Yuksporr deposits in the Kirovsk Mine, as well as the Apatite Circus and Rasvumchorr Plateau deposits in the Rasvumchorr Mine.

## 2.2. The Lovozero Massif and Co-Named Loparite Deposit

The Lovozero massif, located 7 km east of the Khibiny massif, is fully located in the Archaean granite-gneiss. The rocks of the differentiated complex (DC, also known as layered and loparite-bearing) and eudialyte complex (EC) predominate within the recent erosional truncation (Figure 2).



**Figure 2.** Geological sketch-map of the Lovozero massif (based on the map of PGO Sevzapgeologiya). Rocks of the differentiated (1) and eudialyte (2) complexes; poikilitic syenites (3); marker ore horizons (4); mining area of the Lovozero loparite deposit (5).

The DC, in which the ore (loparite) bodies are mainly concentrated, is composed of numerous (up to 200) gently pitching, rhythmically alternating horizons (layers) of lujavrite (trachitoid nepheline syenites of the foyaite-malignite-shonkinite series), massive foyaite, and ijolite-urtite, forming three- and two-member sequences. The thickness of the individual layers varies from several centimeters to dozens of meters. The DC is usually divided into series (I–V or I–VII from top to bottom) consisting of several (up to 16) rhythms. For the marker foidolite horizons, including ore-bearing ones, an accepted nomenclature involves a serial and order number of the horizon from the upper border of the series (for example, I-4, II-7, III-14, etc.).

The EC is generally made up of a slightly differentiated stratum of inequigranular eudialyte lujavrite (eudialyte malignite) that locally changes into foyaite (because of higher K–Na feldspar content) and rarely into foidolite (because of higher nepheline, sodalite, and natrolite amounts). The rocks are enriched with (mangano)eudialyte in quantities ranging from 5 to 10 vol. %, sometimes reaching 90 vol. %.

Both complexes contain numerous variously shaped and sized bodies of poikilitic and inequigranular nepheline, sodalite-nepheline and nosean-nepheline syenites, concordant lens-like or sheet-like xenoliths of olivine basalts, tuffs, and tuffites of the Lovozero Suite, as well as alkaline pegmatites and hydrothermalites.

The sectors of the Lovozero loparite (REE–Ti–Ta–Nb) deposit (DC, I-4, and II-4 horizons) mined out by the Kurnasurt Mine of the LLC “Lovozero Mining and Processing Plant” are located in the northwestern part of the massif (Figure 2). The ore mineral loparite-(Ce), with the formula  $(\text{Na,Ln})(\text{Ti,Nb,Ta})\text{O}_3$ , forms relatively thin and extensive dissemination sheets limited to the boundaries between rhythms. Ore sheets consist of loparite-bearing ijolite (from the upper urtite side) and malignite (from the bottom foyaite side). The richest ores (>10 vol. % of loparite) in sheets I-4 and II-4 have predominantly malignitic and ijolitic composition, respectively. There are no visual geological boundaries in the ore sheets, which are contoured on the basis of the cut-off grade.

### 3. Methods

The methods and approaches used to study the gas-bearing capacity in the apatite and rare-metal deposits and corresponding underground mines are described in [15–19]. It is worth noting that,

compared with the gas-bearing salt and particularly coal deposits, the methods of studying gas-bearing capacity in the ore deposits related to crystalline rocks are poorly established. The mining-hazardous free gases in the undisturbed rock mass mostly remain in a dispersed state and form only local accumulations. Because of the extremely irregular distribution and high mobility of free gases, it is still impossible to reliably define the gas saturation of igneous rocks by direct methods. Various indirect approaches are usually applied to estimate gas amounts, scopes of emission, and excessive pressure in the reservoir, whose features are also mainly hypothetical. We have primarily used the shot-hole method, whereby a horizontal shot-hole with a diameter of circa 4 cm and a depth of circa 2 m was drilled in the wall of a mine opening and pressure-sealed at a distance of 20–40 cm from the mouth immediately upon termination of drilling. One or two thin pipes were passed through a special sealing accessory or cement plug and enabled sampling from the isolated part of the shot-hole channel; samples were then submitted for further laboratory analysis to measure the yield and values of excessive (relative to atmospheric pressure) gas phase pressure using simple facilities. Thus, samples were placed into glass burettes that were pre-filled with saturated sodium chloride solution using a simple original device [16]. To study the irregularity of gas release in the shot-hole channel, a partitioned sampler was applied to determine gasometric parameters in any interval of the shot-hole, except for a short wellhead area. The value of gas with a low yield was calculated on the basis of increases in gas-component concentrations; this usually transpired within the first 10 min after drilling and shot-hole sealing. Free gas (FG) yield above 10 mL/min was measured by a rotameter-type flow-metering device. Indicating pressure gauges were used to measure excessive gas pressure of above 10 kPa. In addition to the specially drilled shot-holes, gasometric observations were made in shot-holes and wells drilled for other purposes, particularly for exploration, and prognostic and discharging wells of the Rock burst prevention service.

To detect gas filtration from the walls of mine openings, a device resembling a metal cone with a base of 350 mm equipped with a gas-sampling nozzle was used. The cone was pressure-tight mounted on the wall for 10–60 min. The gases being released from the rocks were determined by increases in the concentrations of non-air components in the samples.

The gasometric shot-holes were also applied to qualitatively assess and compare the relative rock mass permeability in the gas-saturated zones and areas in which gas release was not identified. A few closely spaced (0.2–0.5 m) shot-holes were sealed for this purpose. Compressed air from the main line was supplied to the delivery shot-hole at a pressure of 6–7 atm. The pressure rise rate describing the gas permeability of the rocks was observed on a manometer installed in the other receiving shot-holes. Differences in this feature were studied in various ways. If only one shot-hole was available, the rock permeability was judged by the drop in the created air pressure.

More common ideas on the rock gas-bearing capacity, scopes of gas release, and estimates of the absolute and relative gas content in the mines were formed from the large-scale sampling of the atmosphere at both individual mine openings and return vent air currents of mine sites and horizons. The samples were taken by discharging a salt brine-filled 0.25 L bottle.

To estimate the stability of gas release in many shot-holes and wells, multiple measurements were made, but they were occasionally taken at various times. The long-simmering need for continuous monitoring of the FG release dynamics in the deposits under consideration was partially implemented only recently for molecular hydrogen [19,74–76]. Monitoring was performed using a gas analyzer (VG-3) designed by MEPHI, a special design bureau. The device consists of a sensing element with an amplifier, a two-channel metering module, and a power unit. An operating principle of a sensing element is based on the changing electric capacity of the film's metal–insulator–semiconductor structure under the effect of hydrogen, which is occluded by sprayed palladium]. The signal from the sensing element is displayed on the liquid-crystal display and recorded in the non-volatile memory with a preset time interval. The gas analyzer's power is supplied by a 220 V circuit. The hydrogen concentration measurement range in the air was 1–100 ppm at an accuracy of 1 ppm, a relative error of  $\pm 3\%$ , and a memory-recording period of 1 s to 99 h.

Occluded gases from the rocks and minerals were mainly extracted by mechanical sample crushing [15,16,43]. The thermal opening of fluid inclusions was rarely performed [37,77,78], particularly in light of the presence of volatile condensed organic compounds in the rocks [15,35,79].

Diffusely dispersed gases were mainly studied in the core samples of exploratory boreholes. The samples were placed in pressure-tight stainless-steel containers immediately upon drilling and lifting to the surface [16]. The cover of the container is equipped with a bend with a rubber hose and a nozzle with a gasket (made of rubber as well), allowing syringe sampling of the gas that freely escaped from the probe after it was sealed and enabling connection to the pumping system. The sample weight varied from 300 to 800 g. The core from the wells made by the Rock burst prevention service was used less often. The gases were extracted from the core samples some time later (usually a few weeks) after they were sampled in a laboratory environment by vacuum (at room temperature) and/or thermal vacuum (with heating to a temperature of 70–80 °C) degasification [16,17]. Vacuum (relatively low or higher) in the degasification unit was created using a pump. Saturated salt brine solution or mercury was used as a barrier liquid. In some cases, gas, which was released from the samples freely, before its forced extraction, was pumped out of the containers for further analysis.

Valuable information on the nature of the diffusely dispersed gases (DDGs) escaping from the rock mass upon its blasting was obtained during a long experiment that started in the underground mine (Lovozero deposit) and terminated in the laboratory [17]. In this case, immediately upon blasting in the dead-end mine-face, the mine air was sampled. After that, a small portion (42 kg) of blasted rock mass was placed in a 38-L pressure-tight metal container that was then lifted to the surface. The size of the rock fragments represented by foyaite, urtite, and malignite varied from silt to 0.2 m in diameter. At the second stage of the experiment, the composition of the gas–air mixture was occasionally analyzed throughout the day in the container free space without depressurization. Then, the container was opened, ventilated for a few minutes while the rock fragments were mixed, and again pressurized. The third stage of the experiment took two weeks. Another series of container-insulated atmosphere samples were taken during this period. All samples were studied for concentrations of natural methane, hydrogen, helium, and carbon oxide of an obvious technogenic (from the decomposition of a blasting agent) origin.

In other similar experiments, during the observation of blasted rock degasification, the container was regularly depressurized.

The gas phase of all morphological types was analyzed using laboratory chromatographs [15–19,43]. Along with air nitrogen and oxygen, the contents of CH<sub>4</sub>, H<sub>2</sub>, C<sub>2</sub>H<sub>6</sub>, He, and, rarely, CO, CO<sub>2</sub>, methane homologs (up to and including pentanes), and unsaturated hydrocarbons (alkenes), were determined in the majority of the samples. In some cases, only alkanes were analyzed. The total number of analyzable gas components reached 17 in one sample. The minimum detectable concentration of individual gases somewhat varied depending on the chromatograph type and sorbent used, with an average (in vol. %) of 0.0005 and 0.00005 for methane and ethane, 0.00032 and 0.00045 for hydrogen and helium, and 0.013 and 0.042 for carbon oxide and dioxide, respectively. The mean-square deviation of the analysis for individual components was 0.4–0.8 with a variation factor ranging from 2.7 to 4.6 %.

#### 4. Morphological Types of Gas Phase

Since researchers found gases with a hydrogen–hydrocarbon composition uncommon for igneous rocks in the Khibiny and Lovozero massifs, their occurrence forms (morphological types) have been mainly divided into two main groups [15,16]. The first group includes gases that are primarily occluded in vacuoles of fluid and rarely melt fluid-bearing micro-inclusions in minerals (i.e., occluded gases, OGs), which are also known as closed-pore and micro-included gases. Some part of OGs, likely extracted by sample mechanical grinding, was localized in intermineral pores. The second group of gases is represented by free gases (FGs), which are also known as filtering, jet, or spontaneous release gases. Indeed, FGs emanate from the rocks spontaneously, predominantly through filtration, when their accumulations or gas-feed zones percolate to the day surface or are penetrated by a shot-hole, well,

or mine opening. Most often, free gases fill systems of conjugated fractures and other cavities in the rocks of the massif. Along with these two main forms of gas occurrences, many Russian-language studies have recognized so-called “sorbed” or residual (free) gases in open microfractures (RGOM) and gases in closed microfractures (GCM) ([15,16], and references therein). The former gases can be extracted by the thermal vacuum degassing of core samples that were hermetically sealed in containers immediately after their recovery, and the second gases can be released by cracking into several parts of analogous drill-core samples in vacuum (without preparatory hermetical sealing).

Results of our on-location (in an underground mine) and laboratory experiments and observations, as well as the summarization of all available data on the composition, content, conditions, and features of RGOM and GCM emission and extraction, allowed us to qualify such gases as a specific morphological type, namely, diffusely dispersed gases (DDG) [17,18], by analogy with similar gas forms occurring in some other geological settings. In contrast to jet gases, both DDGs and occluded gases fill closed and semi-open, thin and subcapillary microfractures and pores, remaining in an adsorbed state to some extent and migrating predominantly by diffusion [17,18]. In the atmosphere of underground mines, these gases create relatively low background concentrations of hydrogen, helium, and methane that, however, exceed those in the air.

In a way, DDGs are transitional between occluded and free gases. Like FGs, some of them can be released unintentionally but in much smaller volumes and not immediately after breaching the rock mass integrity or rock sampling. Their gradual release occurs as a result of the slow decrease in stress (relaxation) of a rock mass or sample over several days, weeks, or months. Such gases will be minor admixtures to filtering ones in the presence of the relatively long emission of the latter.

The total gas-bearing capacity in rocks and ores is defined by the concentration of all three morphological gas types. However, since the real hazard in the course of mineral deposit mining arises only from the emissions of free gases, the characteristics of this form of gas occurrence is thoroughly described in this paper.

#### 4.1. Occluded Gases

The bulk chemical composition and abundance of occluded gases in the Khibiny and Lovozero rocks and minerals are covered in dozens of publications, including monographs [15,16]. However, only recently, we have managed to systematize the OG chromatographic analyses (mostly unpublished) that have accumulated over the course of over fifty years of research [18]. These analyses are of varying degrees of completeness and were performed using common methods for identifying 2–17 components. In total, about 5000 and almost 700 samples of the ores and enclosing rocks from the Khibiny and Lovozero deposits, respectively, have been analyzed in that way. Herein, all Lovozero samples and about one-third of the Khibiny ones were collected and studied by the author.

Methane is the main component of occluded gases in the rocks of all deposits (Table 1). Molecular hydrogen often predominates at a low total gas content, and methane homologs (up to pentanes), N<sub>2</sub>, O<sub>2</sub>, and He occur in subordinate and trace amounts. Additionally, CO and CO<sub>2</sub>, as well as alkenes, are found in minor and micro-concentrations.

In Khibiny's rocks, the average content of all gas components (except for H<sub>2</sub>) is higher than that in Lovozero's. There are positive correlations between the concentrations of the majority of OG components in all rocks, with hydrocarbon gases showing the closest relationship [18]. Nitrogen and oxygen, which are often believed to have an atmospheric “technical” origin, are also strongly related. However, the correlation between their content and the amount of methane is not in line with such assertions. A significant part, if not all, of N<sub>2</sub> and O<sub>2</sub> is apparently extracted from H<sub>2</sub>O-rich fluid inclusions that are associated with hydrocarbon inclusions. Such an association has been repeatedly described, e.g., in [36,80–83]. Thus, the positive correlation between N<sub>2</sub> and O<sub>2</sub> concentrations in bulk analyses of occluded gases may actually be caused by their common atmogenic nature: they both occur as a result of the air dissolved in paleometeoritic water. Participation of such water in the formation of

Khibiny's and Lovozero's rocks has been confirmed by the isotope composition of oxygen (e.g., [84]) and noble gases ([85] and references therein).

At different degrees of gas saturation, even of the same type of rock, the considered deposits of both types demonstrate the same mechanism of OG distribution. Ore bodies have a relatively low gas content, but increased gas saturation in the subconcordant zones above and below them has been recorded [16,18,35]. The analysis of this zoning as a whole, as well as individual cross-sections, has led to the supposition that it once comprised ore bodies and pegmatites, which were initially more gas saturated. Further, because of the influence of low-temperature gas transformation processes (reduction, polymerization, and polycondensation), the gas concentration could have decreased [18].

**Table 1.** Ranges and median contents of occluded gas (OG) components, cm<sup>3</sup>/kg.

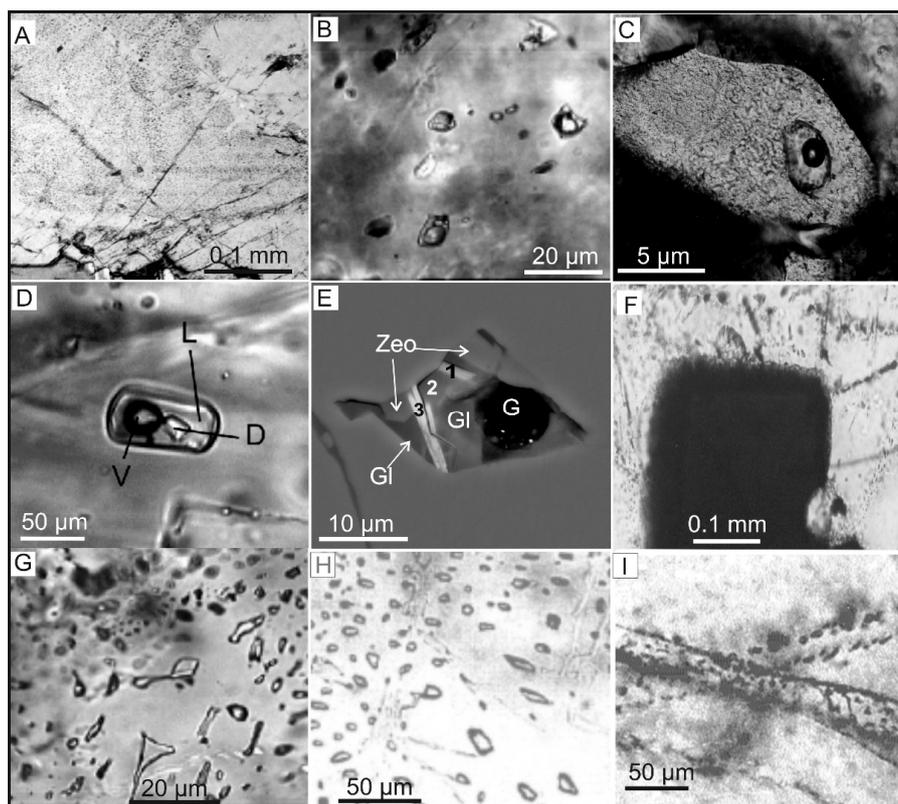
Gas	Number of Analyses	Minimum	Maximum	Median
The Khibiny apatite-nepheline deposits				
CH <sub>4</sub>	5029	0.006	238	8.28
C <sub>2</sub> H <sub>6</sub>	3037	0.00003	8.61	0.44
<sup>1</sup> C <sub>3</sub> –C <sub>5</sub>	1233	0.00005	1.70	0.05
H <sub>2</sub>	4989	0.003	18.11	0.5
He	2627	0.00005	0.43	0.01
N <sub>2</sub>	1508	0.04	14.3	0.89
O <sub>2</sub>	1494	0.0015	1.84	0.08
CO	168	0.00007	3.03	0.005
CO <sub>2</sub>	907	0.00021	4.03	0.06
The Lovozero loperite deposit				
CH <sub>4</sub>	689	0.011	82.2	3.7
C <sub>2</sub> H <sub>6</sub>	676	0.0014	5.58	0.29
<sup>1</sup> C <sub>3</sub> –C <sub>5</sub>	68	0.00032	0.872	0.043
H <sub>2</sub>	664	0.057	25.15	1.34
He	664	0.00011	0.26	0.005
N <sub>2</sub>	665	0.013	6.53	0.43
O <sub>2</sub>	663	0.0034	1.2	0.05
CO	51	0.00013	0.014	0.0015
CO <sub>2</sub>	3	0.013	1.05	0.05



Being practically the only or, at least, the main source of OGs, fluid inclusions in the Khibiny and Lovozero minerals at room temperature are predominantly monophasic (gaseous) or, less often, two- and multiphase; they are subisometric rounded, or, rarely, of elongated tubular or irregular shape [16,36,56,80–83,86] (Figure 3). The prevailing size of fluid inclusions is <15 μk, but in singular cases, it reaches 150 μk. In nature, the majority (circa 90–95%) of observed fluid inclusions appear to be secondary, which are mostly present in so-called fluid inclusion planes (FIPs) that traverse host mineral grains in different directions.

Sodalite, nepheline, K–Na feldspar, and eudialyte are the most essential minerals that concentrate occluded gases (fluid inclusions) in the rocks of both massifs and related ore deposits [36,43,81–83]. Nepheline and feldspar are also important carriers of occluded gases. The increased gas contents are found in analcime, titanomagnetite, and aenigmatite. Gas saturation of all minerals is directly, but to various degrees, related to the total gas content in the rock.

A positive correlation was established between the intensity of post-magmatic alteration of rocks and the OG content in them [16].



**Figure 3.** Primary (A–E) and secondary (F–I) fluid inclusions in minerals of the Khibiny (A–D,F,G) and Lovozero (E,H,I) massifs: A—gas (hydrocarbon-bearing) inclusions along growth zones of a nepheline grain [83]; B and C—gas–liquid inclusions in nepheline [83] and titanite, respectively; D—three-phase (L—H<sub>2</sub>O, V—CH<sub>4</sub>, D—daughter mineral) water-dominant inclusion in nepheline [83]; e—multiphase (Zeo—metanattrolite, G—CH<sub>4</sub>-dominant gas, Gl—gel (high-water glass), 1, 2, and 3—non-identified solid phases) inclusion in nepheline [86]; F—trails of CH<sub>4</sub>-dominant, outward-radiating magnetite grain inclusions in nepheline [81]; G—hydrocarbon-bearing inclusions in nepheline [83]; H and I—CH<sub>4</sub>-dominant inclusions in nepheline and sodalite, respectively.

#### 4.2. Diffusely Dispersed Gases

It was not until recently that systematization made data available for this morphological type of gases [17]. The total contents of DDGs (Table 2) are usually between 1 and 1.5 orders of magnitude lower than that of occluded gases. Only carbon dioxide is found in higher concentrations within DDGs compared with OGs.

Unstable DDG composition and nature of emission are apparently caused and controlled by many factors, including the various natural and physical properties of individual gases, total gas saturation of the rocks, and the geomechanical state of the rock mass or sample.

The dependence of the content and ratios of individual DDG components on the stress–strain behavior of the Khibiny and Lovozero rocks in samples was described in [87,88]. This association is mainly caused by the different intensities of the formation of new fractures and growth of existing cracks, as well as their integration, as a result of the discharge of samples from excessive stresses of various magnitudes. Such three-dimensional self-disintegration of rocks arises from the tectono-caisson effect when the pressure is abruptly relieved ([89] and references therein). Along with an increased gas-bearing capacity, the Khibiny and Lovozero deposits and massifs show high modern geodynamic activity, significant natural and induced seismicity, and poorly distributed tectonic stresses, which are often 10–20 times those of lithostatic stresses (e.g., [90]).

**Table 2.** Composition of diffusely dispersed gases calculated as an air-free mix of continuously present components (the selection with recalculation from [17]).

Variable Min–Max/Median (Number of Analyses), cm <sup>3</sup> /kg			
The Khibiny apatite-nepheline deposits			
Extraction manner <sup>1</sup>	UR	LV	LVH
CH <sub>4</sub>	0.004–7.64 0.07 (32)	0.0007–11.5 0.12 (134)	0.0001–13.92 0.21 (454)
C <sub>2</sub> H <sub>6</sub>	0.0002–2.2 0.014 (20)	0.0001–0.49 0.08 (97)	0.00002–1.96 0.01 (247)
H <sub>2</sub>	0.0001–0.058 0.004 (33)	0.0004–2.40 0.063 (129)	0.001–4.29 0.028 (294)
He	0.0002–0.09 0.004 (36)	0.0006–0.13 0.004 (140)	0.0008–0.17 0.004 (283)
CO <sub>2</sub>	0.07–3.57 0.47 (17)	0.015–3.6 0.22 (77)	0.013–29.7 0.88 (134)
The Lovozero loparite deposit			
Extraction manner <sup>2</sup>	LV	HV	HVH
CH <sub>4</sub>	0.0039–11.0 0.61 (24)	0.0004–0.83 0.04 (12)	0.017–2.01 0.10 (23)
C <sub>2</sub> H <sub>6</sub>	0.002–0.45 0.05 (15)	0.00004–0.04 0.07 (8)	0.0008–0.12 0.01 (21)
H <sub>2</sub>	0.0018–0.99 0.19 (22)	0.00002–0.11 0.0016 (12)	0.001–0.49 0.011 (23)
He	0.003–0.026 0.009 (14)	0.00002–0.004 0.0002 (12)	0.00001–0.006 0.0002 (22)
CO <sub>2</sub>	0.05–1.7 0.3 (5)	0.54–0.92 0.73 (2)	0.008–2.48 0.82 (6)

<sup>1</sup> UR is unintentionally released gases; LV is gases extracted from rock samples at low vacuum without heating; LVH is the same as LV with heating to 80 °C. <sup>2</sup> LV and HV are gases extracted from rock samples in low and high vacuum, respectively, without heating; HVH is the same as HV with heating to 80 °C.

The kinetics of the spontaneously released part of DDGs is different. The most intensive gas emission from core samples placed into pressure-tight containers is observed within the first day after pressurization. In some cases, the gas release stops after this, and in other cases, it gradually fades within a month. Sometimes, the process stops regardless of the amount of gas released. After aeration, removal of geogas components from the sample container, and its subsequent re-sealing, the release of DDGs may resume. These observations indirectly indicate that the emission of gases of this morphotype is due to diffusion, and this process continues until the concentrations of each component are balanced in the air space of the container and in opened microfractures in the samples. The intensity of formation and the opening of microcracks, and therefore, the intensity and duration of gas emission, obviously depend on the rock physical properties and strain–stress state before and during core drilling. Given the extremely low sorptive capacity and gas permeability of the monolith igneous rocks, the predominantly free molecular and surface DDG diffusion in capillary and microfractures is assumed, as distinct from the much more permeable and absorbing sedimentary rocks, in which all types of gas diffusion take place in a complex combination. It was found that much lower quantities of DDGs are spontaneously released and forcibly extracted from core samples taken during the drilling of highly stressed rocks than from weakly stressed sections of rocks. These observations may be particularly explained by the faster self-destruction of more stressed rocks and, correspondingly, sample degasification prior to their placement in a sealed container.

### 4.3. Free Gases

This morphological type of gases was studied in the deposits primarily upon the request of mining and exploration companies for handling applied tasks. Thus, gasometric observations were made in underground mines of the Kukisvumchorr, Yuksporr, and Apatite Circus deposits in Khibiny and of the Lovozero loparite deposit. In contrast, it has been rarely possible to examine free gases in exploratory boreholes. The results of these studies, including by the author, presented mainly in unpublished reports, are published only partially and in most cases only in Russian.

When studying small FG accumulations in igneous rock units, we have most frequently dealt with their mixing with atmospheric air. The proportions of the components in the air–gas mix (AGM) depend on the intensity of the gas emissions from the rock masses, the degree of air-tightness and time of gas accumulation in the shot-hole or other sampled reservoir, the frequency, and other sampling conditions. Examples of real analyzed gas mixtures with relatively slight contamination by air are given in Table 3.

**Table 3.** Chromatographic compositional analysis (vol. %) of natural free gases minimally contaminated by the atmospheric air in shot-holes and boreholes: examples.

Sample	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> –C <sub>5</sub>	H <sub>2</sub>	He	N <sub>2</sub>	O <sub>2</sub>
The Khibiny apatite-nepheline deposits [18]							
9-6	75.0	8.1	0.86	17.6	0.31	1.1	0.1
36	76.6	5.9	0.52	19.0	0.42	8.8	1.3
Nn	79.7	5.2	0.7	2.9	0.22	9.1	2.1
IHS-12	64.6	3.6	<sup>1</sup> n.a.	17.9	0.64	8.9	2.2
360/1190	66.8	3.2	0.32	18.9	0.65	8.2	2.3
721-2	62.3	2.6	0.81	26.5	0.26	7.5	0.8
The Lovozero loparite deposit [19]							
1/51	49.6	2.75	0.14	41.6	0.87	1.4	0.43
14/26	51.4	2.07	0.10	33.0	0.95	9.7	3.0
25/26	57.2	3.23	0.13	29.0	0.75	6.6	1.8
45/21	65.8	6.32	0.37	10.9	1.87	11.7	2.5
110/19	52.6	3.15	0.11	37.0	1.0	4.2	1.15
173/37	34.6	1.28	0.06	57.8	0.89	4.0	0.68

<sup>1</sup> n.a.—not analyzed.

To compare free gases from various and variously sampled ore manifestations, the analytical data are usually recalculated to determine an air-free mix of the defined components. Table 4 demonstrates scattered and average (median) values of the recalculation results on the basis of the methane concentration in air–gas samples. In certain samples, with an increasing degree of air dilution, there is a growth in the spread of values of individual components whose presence is constant. At the same time, the average composition of gases varies insignificantly.

The predominance of free gas collectors in the form of microfractures means that, for free gases, it is common for a combination of filtration (jet) and diffusion gas to escape from the rock mass. Gas bubbling through water is less often observed. Short-term high-flow-rate emissions of gas, flush fluid, and even (although there is no documented evidence) drill-pipes from boreholes have been recorded very occasionally and only in the Khibiny massif. The intensity of gas emissions, depending on the degree of saturation and value of excessive pressure, usually drops within the first dozen minutes after penetration of the reservoir by a shot-hole, well, or mine opening.

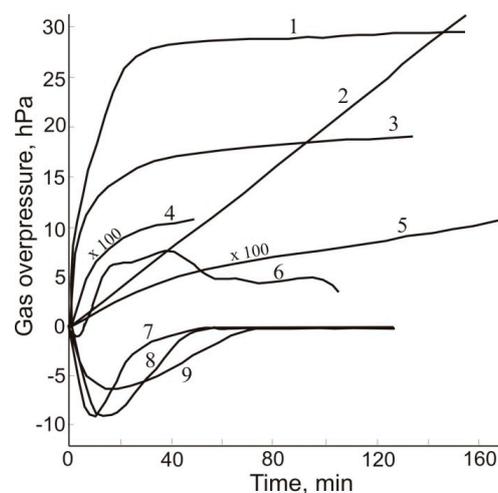
Extensive macrofractures may also drain FG accumulations. The gas emission intensity is particularly characterized by the flow rate of the shot-holes (wells) penetrating the gas-bearing rock mass. Since the flow rate is not constant in time, during field studies, its initial value was usually measured (or calculated by an increase in gas component concentrations) within the first 10 min of the completion of shot-hole drilling.

The flow rate of certain shot-holes (1.8–2 m deep and 40 mm in diameter) and gas seepages has not exceeded 0.5 L/min (5 L/min for boreholes), but values that are 1–2 times lower have predominated. The length of gas emission to the shot-holes varies from a few days to 20 years and more. Various FG

manifestations differ in value and dynamics of varying excessive pressure in relation to the atmospheric pressure (Figure 4). The measured excessive gas pressure ranges from 1 to 100 hPa, rarely higher. Only some estimations show that it may reach a few megapascals [16]. The rarefaction of a gas–air mixture (Figure 4, shot-holes 7–9) to  $-25$  hPa is sometimes recorded within a few dozen minutes of drilling and pressurizing a shot-hole. The latter is caused by intense cracking while drilling the shot-hole in stressed and weakly gas-saturated rocks.

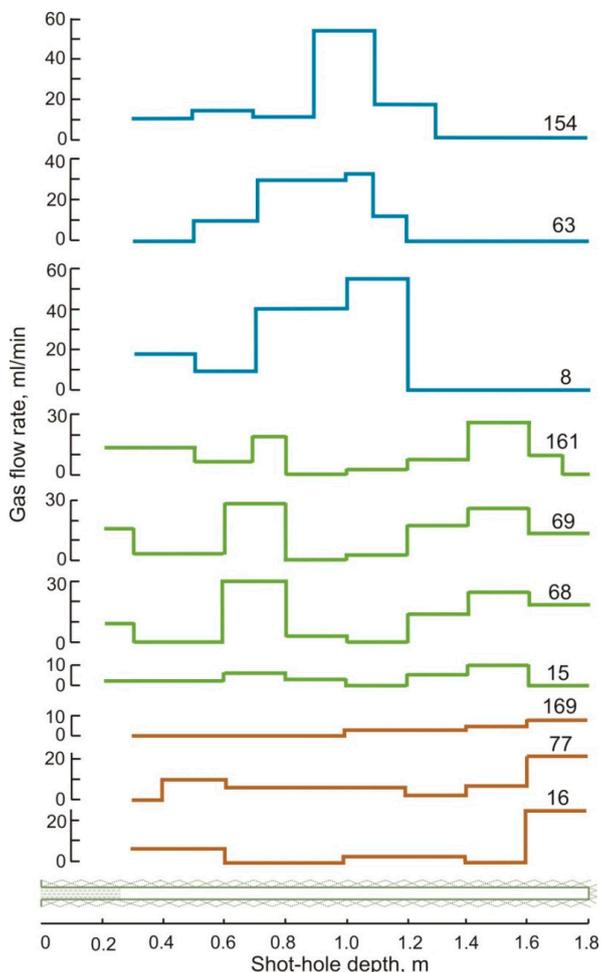
**Table 4.** Composition of free gases calculated as an air-free mix of continuously present components on the basis of the degree of dilution with atmospheric air—CH<sub>4</sub> concentrations in the air–gas mix (AGM).

CH <sub>4</sub> in AGM, vol. %	Variable Min–Max/Median (Number of Analyses), vol. %				
	CH <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>3</sub> –C <sub>5</sub>	H <sub>2</sub>	He
The Khibiny apatite-nepheline deposits					
>50	68–99 87 (12)	0.1–9.5 3.9 (9)	0.2–0.8 0.5 (5)	0.5–29 9 (12)	0.3–2.1 0.7 (6)
<50, >10	56–98 84 (23)	1.2–8.3 5.3 (18)	0.4–2.2 0.7 (9)	0.7–40 11 (23)	0.1–1.6 0.8 (20)
<10, >1	83–94 88 (8)	3.2–7.2 4.4 (4)	0.5–0.5 0.5 (1)	2.8–13.4 9.7 (8)	0.1–0.7 0.6 (5)
<1, >0.1	2.5–99 87 (51)	0.7–22 4.5 (18)	0.2–13 0.6 (17)	0.2–97 9 (8)	0.04–17 0.6 (42)
<0.1	4.9–99 82 (165)	0.5–33 6 (49)	0.2–4.3 0.8 (25)	0.9–92 9 (164)	0.6–32 4 (133)
The Lovozero loparite deposit					
>50	60–73 64 (4)	2.4–6.3 3 (4)	0.1–0.3 0.2 (3)	18–36 32 (4)	0.8–2.6 0.9 (4)
<50, >10	37–92 60 (14)	1.0–3.6 2.4 (11)	0.02–0.2 0.12 (6)	2–61 38 (14)	0.8–3.1 1.0 (13)
<10, >1	18–96 57 (51)	0.2–4.5 1.7(26)	0.04–2.3 0.14 (10)	4–81 40 (51)	0.1–12 1.0 (46)
<1, >0.1	9–99 59 (59)	0.5–6 1.2 (5)	0.02–0.5 0.06 (3)	0.2–90 40 (59)	0.1–3.5 1.0 (57)
<0.1	8–97 65 (285)	0.9–42 15 (26)	1.0 1.0 (1)	1–91 24 (265)	0.3–79 9 (264)

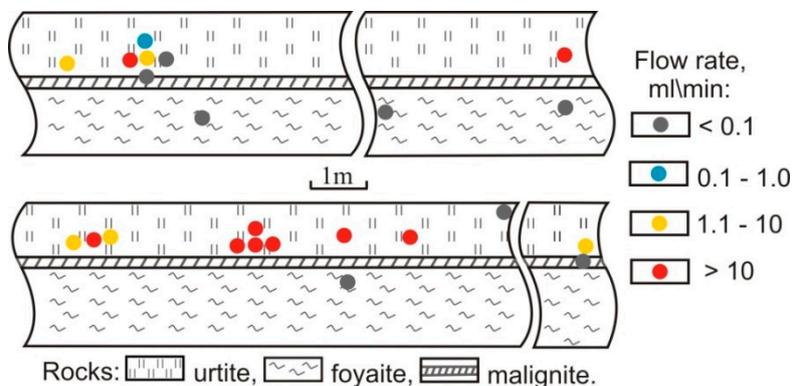


**Figure 4.** Variations in the free gas overpressure in sealed shot-holes (Karnasurt Mine, Lovozero loparite deposit). Time from a shot-hole drilling until the beginning of measurements: 9 months (1), 8 days (2), and 1 min (3–9). From [19], with minor modifications.

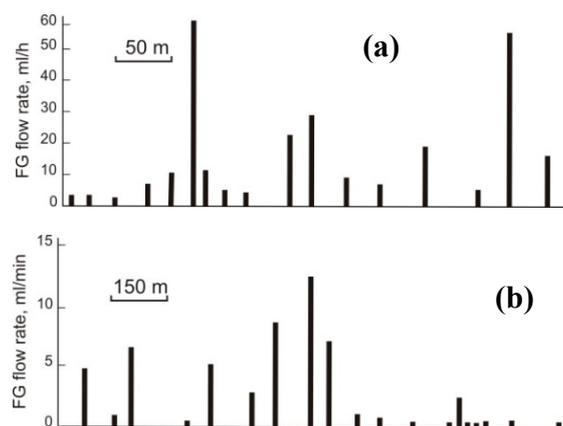
The data on the spatial variations in FG composition and emission intensity in underground mines are fairly scarce. It has not been possible to identify any mechanisms of free gas distribution within the deposits. Only a different-scale spatial irregularity of their localization, as demonstrated in Figures 5–7, has been found.



**Figure 5.** Temporal changes in the gas emission with depth along three (marked with different color) shot-holes in rocks of the Karnasurt site of the Lovozero loparite deposit. Numerals on the right are the number of days between drilling the shot-hole and the gas emission measurement (modified from [19]).



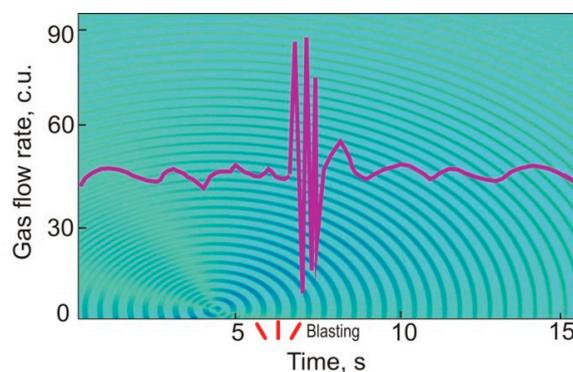
**Figure 6.** Position of horizontal shot-holes with various free gas (FG) flow rates in the walls of Drift 8/25 (up) and Roadway 23-Eastern (down), Karnasurt Mine, Lovozero loparite deposit (from [18], with modifications).



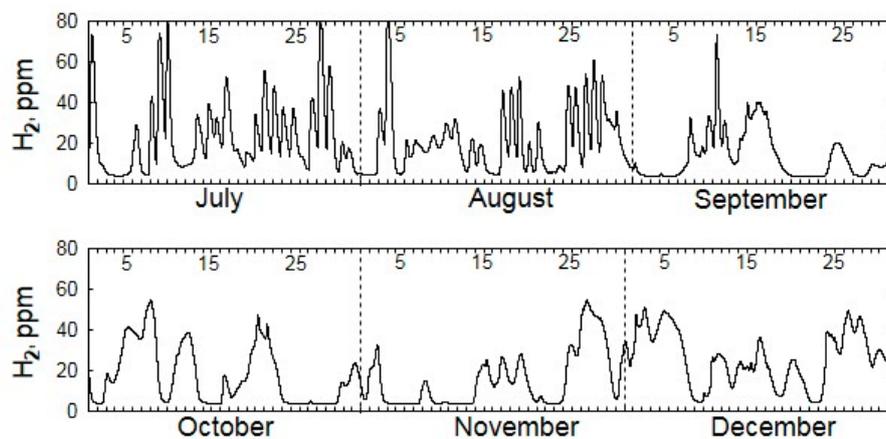
**Figure 7.** Variations in the emission of free gases in individual shot-holes that were drilled in the walls of underground workings that mined (a) in urtite of the Apatite Circus apatite-nepheline deposit (Khibiny, from [18]) and (b) in bedding foyaite of the Lovozero loparite deposit (from [19]). The horizontal axis shows the distance between the shot-holes in the appropriate scale.

Neither the FG content in the natural state of a rock mass nor the sizes of collectors are sufficient for a reliable quantitative estimation. In general, gas manifestations tend to the water-free rock masses with a developed system of microfractures surrounded by almost impermeable blocks of rocks or isolated rock masses that are not interrelated by micro- and macrocavities.

It is natural for free gases to be irregularly localized in space and show instability in time. This is especially true for the dynamics of emission, chemical composition, and isotope composition of gas-forming elements [16,19,75,76,88]. Figure 5 demonstrates the irregular flow rate along the horizontal lengths of shot-holes in the walls of underground mines, and it shows the variability of the flow rate in time or changes in gas emission intensity within the same intervals. The most probable reason for these spatial–temporal variations in the gas flow rate lies in the alternating stress–strain behavior of rocks within each of these areas [88]. Since observations have been made rarely and in various time periods, it is hard to estimate the rate of stress redistribution and gas emission. The very similar distributions obtained with a day’s difference (Figure 5; 68 and 69 days after drilling the shot-hole) only indicate that these changes were not abrupt here. In general, the data of natural gasometric studies in underground mines are indicative of both instantaneous and gradual changes in gas emission dynamics with time [15,16,19,75,76] (Figures 8 and 9). The former can be caused by blasting (Figure 8), whose possible influence on gas release dynamics is well known, such as at Khibiny’s apatite-nepheline deposits, e.g., [91].

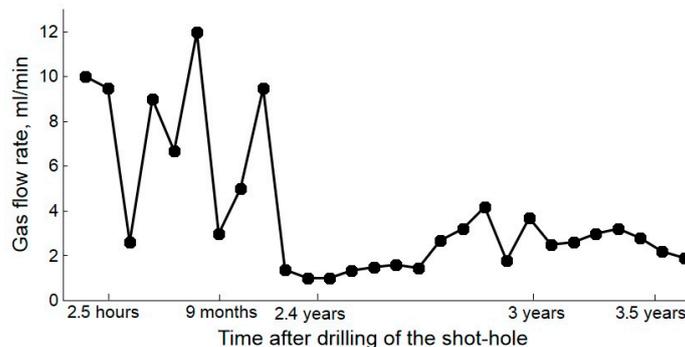


**Figure 8.** Generalized pattern of FG release into sealed shot-holes in response to blasting (from [88], with modifications). Gas discharges were recorded in 12 cases using a rotameter. The conventional moment of blasting at a distant section of the mine is shown under the horizontal axis at an arbitrary time. C.u.—conventional units.



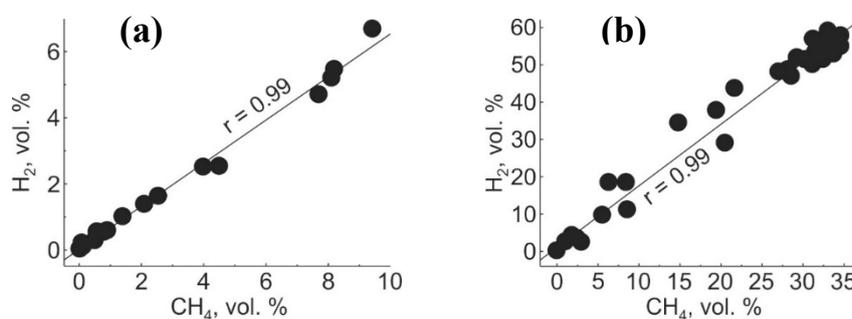
**Figure 9.** Variations in relative hydrogen concentrations in the Karnasurt underground mine (Lovozero loparite deposit) reflecting the FG emission dynamics (fragments of a long time-series [76]).

The attenuation of gas emission over time is most often observed when FG manifestations are relatively intense (Figure 10).



**Figure 10.** Temporal variations in gas flow rate, shot-hole # 25-1 (from [19], with minor modifications).

The FG content variability in the air–gas mixture of each shot-hole (well) is defined by the length of its pressurization, intensity of gas emission, pressure in the collector, time and volume of sampling, etc. The recalculated compositions for an air-free mixture, or at least the ratios of the main components in the same gas flow, are usually fairly constant in time (Figure 11). Rarely, for example, in horizontal boreholes #360 (Rasvumchorr Mine, Khibiny) and #or-1 (Karnasurt Mine, Lovozero), variations in the typically stable  $CH_4/C_2H_6$  ratio are observed [18,19].



**Figure 11.** Ratios of FG-dominating components in exploration borehole #1253, the Kukisvumchorr apatite-nepheline deposit (a), and in shot-hole #173, the Karnasurt Mine, the Lovozero loparite deposit (b).

With varying degrees of justification, various researchers have proposed geodynamic, seismic, hydrogeological, cosmic, and human-induced factors as those that affect the parameters of FG instability. However, because of the irregularity of the performed measurements, it has not been possible to reliably establish other features and patterns of time variations, except for a rarely manifested trend of reducing gas release intensity during the first minutes and/or hours upon penetrating a reservoir.

Recently, during the long-term (52 months) monitoring of molecular hydrogen release from a rock mass due to the excavation of an underground mine in the Lovozero loparite deposit, it was shown that barogenic (atmospheric pressure variation) and human-induced (technogenic explosions) factors are the most important in defining the dynamics of H<sub>2</sub> emanation [75,76]. The contribution of the barogenic factor turned out to be greater and defined the aperiodicity of most of the hydrogen concentration time series, with the corresponding change in pressure being governed by Darcy's law of filtration. The earlier assumed [74] influence of lunisolar tides on gas release dynamics has found no confirmation. The preliminary analysis of the longer time-series of regime observations of the behavior of hydrogen concentration around the Kukisvumchorr and Yuksporrr apatite-nepheline deposits has led to the suggestion that the same factors exert a decisive impact on the emission of gases.

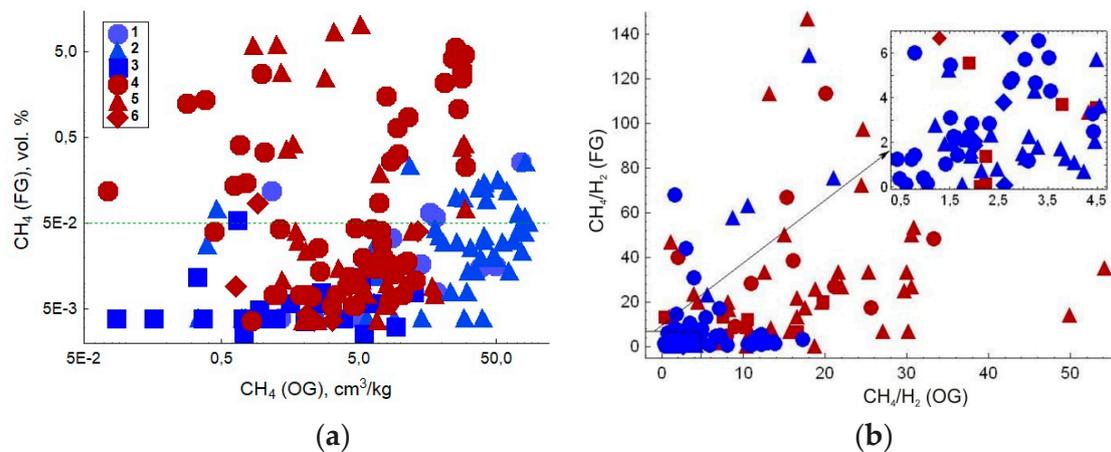
#### 4.4. On the Spatial Relationship of Gas Occurrence Forms

It is immediately clear from the foregoing that when the differentiation between morphological gas phase types is due to the gradual transition of one occurrence form to another in the nepheline-syenite massifs in general and in the related ore deposits in particular, there is some degree of conditionality, especially if the common gas saturation of rocks is low. Thus, some amount of diffusely dispersed gases may be captured in occluded gases and vice versa: i.e., some fluid inclusions, which mix with diffusely dispersed gases, apparently open up as a result of the extensive formation of new microfissures. Spontaneously released gases are represented by both the diffusely dispersed type—which is found almost everywhere in varying but always low amounts in the atmosphere of shot-holes, boreholes, and underground excavations—and (rarely) by the gases that are emitted mainly during filtration because of the pressure differential (referred to as gas jets as per [16] and references therein). The latter can create hazardously increased concentrations of combustible components in the mine air. Gas jets can be recognized (with a certain degree of conditionality) by the presence of measurable excessive pressure and flow rate in the pressurized shot-holes or boreholes that penetrate accumulations or zones of free gas filtration. There are relatively fast-rising concentrations that significantly exceed the background values in the fore-heads of mine excavations after ventilation and removal of natural and industrial gases released during and right after blasting.

Many researchers, including our group, have related diffusely dispersed gases extracted from pre-pressurized core samples and drilling mud and open microfissure residual gases (OMRGs, an earlier term) to free gases. It was also believed that the content of (occluded) gases in the closed rock pores could fairly and definitively describe OMRG and FG distribution because of the strong correlation between these occurrence forms of the gas phase [15,16]. However, for example, the statistical analysis that we tried to carry out on medium hydrogen and methane concentrations, as well as total homologs in 11 petrographic groups (4–145 samples in each) of the Khibiny rocks, revealed no significant coefficients of pairwise homonymous component correlation between the two morphological gas types [17]. The cross-sections penetrated by exploratory boreholes do not always show a spatial interrelation between these gas types [35]. Some studies of the 60s of the last century completely refute any relationship between various gas occurrence forms in these rocks.

When studying the relationship between OG and gases that are inadvertently released to the shot-holes, boreholes, and excavations, it is necessary to compare the specific content of the occluded gases and the volume concentrations of inadvertently released gases in the air–gas mix. Comparison results were provided to prove spatial and genetic relationships of various gas occurrence forms [15,16,64]. However, the correlation between these parameters in gross samples [17,18] turned out

to be weak in some rock groups (Figure 12a). No relationship was observed between the composition of various gas occurrence forms (Figure 12b).



**Figure 12.** Relationships between the occluded and free gas CH<sub>4</sub> concentration (a) and CH<sub>4</sub>/H<sub>2</sub> ratio (b) (modified from [18]). The FG samples were taken from shot-holes 10 min after the drilling and sealing. The OGs were extracted from the rock samples taken near the shot-hole mouths. Symbols: 1—nepheline syenites; 2—foiolites; 3—apatite-nepheline ore of the Khibiny deposits; 4—foyaite; 5—lujavrite; 6—urtite of the Lovozero lopyarite deposit. The dashed line in Figure 12a designates a conditional border below which the predominantly diffusive release of free gases is assumed.

The idea of the spatial relationship and syngenetic nature of various gas occurrence forms in the rocks has long provided a basis for gas-bearing capacity analysis in the deep horizons of the Khibiny apatite and Lovozero lopyarite deposits [15,16]. High content of occluded gases in the rocks penetrated by exploratory boreholes was actually the only criterion for forecasting an increased emission of free gases and gas content in mine excavations toward combustible and explosive natural gas components. However, the available data, part of which are considered in this section, show that a direct but weak dependence takes place only between the distribution of FGs and that of DDGs that are forcedly extracted from rocks or upon their severe destruction [17,18]. The composition and content relationship of occluded gases and inadvertently released diffusely dispersed gases is weaker and almost absent for the localization and intensity of gas jets that create hazardous concentrations of combustible gases in mine openings. Thus, regrettably, it has to be acknowledged that it is still virtually impossible to generate a reliable local forecast of intensive or increased gas releases during the mining of the considered deposits as mining operations expand and deepen.

## 5. On the Origin of HHCGs in Nepheline-Syenite Massifs

Questions on the origin of the reduced gases associated with various magmatic complexes are drawing the attention of many researchers. The genesis of such gases in mafic and ultramafic systems is not a subject of substantial disagreements because it is not linked with magmatic processes. Most authors accept that abiotic methane, CH<sub>4</sub>, in these contexts, was mainly generated by Fischer-Tropsch Type Reactions (FTTR), especially by a specific form of FTTR, namely, the low-temperature (<140 °C) Sabatier reaction, CO<sub>2</sub> + 4H<sub>2</sub> = CH<sub>4</sub> + 2H<sub>2</sub>O, with H<sub>2</sub> produced by serpentinization ([92–96] and references therein). In so doing, there are different (inorganic and organic) possible sources of carbon. Some authors have suggested a deeper source of some of the hydrogen [95,97]. Additionally, Brovarone et al. [98] argued that the H<sub>2</sub> and abiotic CH<sub>4</sub> were produced in high-pressure and high-temperature conditions of mantle lithosphere. In this context, methane can be generated by reactions between rocks and infiltrating fluids enriched in H<sub>2</sub> because of the serpentinization of subducted peridotites and ophicarbonates.

The origin of hydrogen–hydrocarbon gases in the fluid inclusions at the peralkaline Strange Lake granitic complex (Canada) is interpreted with some ambiguity. More often, it is supposed that H<sub>2</sub>

originates from the arfvedsonite replacement by aegirine, and then it reacts with orthomagmatic CO<sub>2</sub> and CO, with the formation of (higher) hydrocarbons by means of magnetite-catalyzed FTTR [29–31,45]. In a recent paper [33], the higher hydrocarbons were considered to be the product of cooling-induced CH<sub>4</sub> oxidation due to the cessation of aegirine-induced changes in arfvedsonite.

Despite the long history of gas studies, mechanisms, conditions, and relative formation time of HHCGs in the rocks of the Khibiny, Lovozero, and Ilimaussaq, nepheline-syenite/foiolite massifs still remain the most debated [18,27,28,34–38,40,41,43–45,71,77,80–83,99,100]. Herein, the nature of the hydrocarbon component in the occluded gases is discussed. Much less attention has been paid to diffusely disseminated and free gases in the previous two decades [17–19,35,74–76,88,100–103]. Reviews (with various degrees of completeness) of the proposed origin hypotheses (from a biogenic to a mantle one) are given in [15,16,18,34,81].

Only a few works have postulated a biogenic origin (thermogenic [44,104] or from the relics of dead organisms introduced by circulating groundwater [105]) of hydrocarbons in nepheline-syenite complexes. Beeskov et al. [36] suggested the existence of a biogenic (at least limited) influence on HC origin in the Khibiny pluton. In this case, primary organic material could have been incorporated into the alkaline magma from the country rocks by either convective fluid flow during emplacement or subsequent percolation of meteoric waters along fracture systems. However, the vast majority of publications in the last two decades (cited above) and early works, e.g., [14–16,22–24], consider these hydrocarbons to be abiogenic. To explain their pre-, early-, late-, or post-magmatic genesis, all processes and mechanisms of abiogenic methane formation studied by Etiope and Sherwood Lollar [93] were involved.

A detailed examination of this complicated issue will be the subject of a special extensive paper. Here, some of the advanced positions outlined in [18] and, in part, [19] are presented. These provisions are based on literature data and the author's (partly unpublished) results of HHCG studies in the Khibiny and Lovozero complexes, including (a) the features of OG, DDG, and FG distribution in the rocks and minerals [16–19,35,43,88,99]; (b) isotope compositions of C, H, and O [28,36,38,45,81–84,106–110], as well as He and Ar [85]; (c) molecular-mass distribution of gaseous alkanes [19,36,43,83,100]; and (d) data on thermobarometry and Raman spectroscopy of fluid micro-inclusions as well as thermodynamic calculations [16,18,23–25,36,40,41,45,71,80–83,86,111–114].

It appears that the carbon and hydrogen isotope compositions of all the morphotypes of reduced gases would be the most informative for solving the problem under consideration. Unfortunately, such data for the Khibiny and Lovozero HHCG are rather poor, unsystematic, and obtained by different studies at different times (the majority of the data are more 20 years old) (Table 5).

In the Khibiny and Lovozero massifs, there is no significant difference in C and H isotope compositions between gases of different morphologic types. Similar to the Ilimaussaq massif [28,115], these HHCGs demonstrate an inverse trend of carbon isotope distribution in certain hydrocarbons compared with the gases of most sedimentary basins and oil-and-gas deposits: carbon is isotopically heavier in methane than in methane homologs. Hydrogen isotopes of gaseous alkanes (at least, in the pair CH<sub>4</sub>–C<sub>2</sub>H<sub>6</sub>) are distributed in the same way. This distribution trend is rather rare. Along with the nepheline-syenite complexes [28,38,45,110], it is characteristic of fumaroles of the Socorro Island, Mexico [116], some gas fields of the northern Appalachian basin [117], and some samples of natural gases from the Tarim basin, China [118]. Another feature of the nepheline-syenite OG isotope composition that is even rarer to observe in nature is methane's richness in the <sup>13</sup>C isotope relative to coexisting carbon dioxide [28,36,38,45]. Such a distribution of carbon isotopes is explained [45] by the kinetic fractionating in abiotic non-equilibrium reactions of methane oxidation, as shown experimentally in [119]. On the δ<sup>13</sup>C<sub>CH<sub>4</sub></sub> versus δ<sup>2</sup>H<sub>CH<sub>4</sub></sub> diagram, the Lovozero OG samples fall into the abiogenic/mantle CH<sub>4</sub> field [45]. According to this work, slightly smaller δ<sup>2</sup>H of the Lovozero FGs (Table 5) can indicate an isotopic exchange with H<sub>2</sub>O. The Khibiny gases, as a whole, differ in their CH<sub>4</sub> isotope composition, with a slightly lower δ<sup>13</sup>C value and higher δ<sup>2</sup>H (Table 5). The former feature could be the result of FTT reactions [45].

Molecular hydrogen of both Lovozero gas morphologic types is characterized by significant fluctuations in  $\delta D$  (from  $-644$  to  $-198$ ‰). Falling within this  $\delta D$  range is molecular hydrogen from different geological settings—in particular, gases from ophiolitic complexes; serpentinite-hosted deep seafloor and continental hydrothermal systems [95,120,121]; fumarole gases [122]; gases from the Witwatersrand Basin, South Africa, Fennoscandian, and Canadian Shields [123]; natural gas from the Ordos Basin, China [124]; as well as gases that originated from mechanical–chemical reactions [125,126].

**Table 5.** Isotope compositions of carbon and hydrogen in the occluded and free gases of the Khibiny and Lovozero massifs.

Component	Gas Type	Concentration <sup>1</sup>	Reference
Khibiny			
$\delta^{13}C_{C1-C5}$	OG	$-13.2$ – $-4.3$	[106,107]
$\delta^{13}C_{CH4}$	OG	$-14.6$ – $-3.2$	[106]
$\delta^{13}C_{CH4}$	OG	$-25.3$ – $-3.3$	[81]
$\delta^{13}C_{CH4}$	OG	$-22.4$ – $-5.5$	[36]
$\delta^{13}C_{CH4}$	OG	$-13.3$ – $-7.6$	[38]
$\delta^{13}C_{C2H6}$	OG	$-24.5$ – $-9.1$	[106]
$\delta^{13}C_{C2H6}$	OG	$-19.2$ – $-14.3$	[36]
$\delta^{13}C_{C2H6}$	OG	$-23.3$ – $-16.1$	[38]
$\delta^{13}C_{C3H8}$	OG	$-26.2$ – $-25.7$	[107]
$\delta^{13}C_{C3H8}$	OG	$-19.6$ – $-13.0$	[36]
$\delta^{13}C_{C3H8}$	OG	$-21.3$ – $-14.1$	[38]
$\delta^{13}C_{C4H10}$	OG	$-19.7$ – $-13.2$	[36]
$\delta^{13}C_{C4H10}$	OG	$-17.4$ – $-16.8$	[38]
$\delta^{13}C_{C5H12}$	OG	$-14.0$	[36]
$\delta^{13}C_{C5H12}$	OG	$-20.6$ – $-19.6$	[38]
$\delta^{13}C_{CO2}$	OG	$-8.5$ – $+10.6$	[107]
$\delta^{13}C_{CO2}$	OG	$-7.3$ – $-3.8$	[81]
$\delta^{13}C_{CO2}$	OG	$-16.8$ – $-13.6$	[36]
$\delta^{13}C_{CO2}$	OG	$-18.6$ – $-14.6$	[38]
$\delta D_{CH4}$	OG	$-118$ – $-50$	[38]
$\delta D_{C2H6}$	OG	$-175$ – $-120$	[38]
$\delta^{13}C_{C1-C5}$	FG	$-19.3$ – $-11.8$	[106,107]
$\delta^{13}C_{CH4}$	FG	$-16.5$ – $-6.5$	[107,109]
$\delta^{13}C_{C2H6}$	FG	$-24.0$ – $-11.7$	[107,109]
$\delta D_{CH4}$	FG	$-82$ – $-56$	[108]
$\delta D_{C2H6}$	FG	$-173$ – $-144$	[108]
Lovozero			
$\delta^{13}C_{C1-C5}$	OG	$-5.3$	[106]
$\delta^{13}C_{CH4}$	OG	$-11.6$ – $-4.7$	[45]
$\delta^{13}C_{C2H6}$	OG	$-17.0$ – $-9.6$	[45]
$\delta^{13}C_{C3H8}$	OG	$-15.9$ – $-7.8$	[45]
$\delta^{13}C_{CO2}$	OG	$-29.9$ – $-16.3$	[45]
$\delta D_{CH4}$	OG	$-164$ – $-132$	[110]
$\delta D_{CH4}$	OG	$-143$ – $-93$	[45]
$\delta D_{C2H6}$	OG	$-211$ – $-147$	[45]
$\delta D_{H2}$	OG	$-629$ – $-198$	[110]
$\delta^{13}C_{C1-C5}$	FG	$-15.7$ – $-7.1$	[110]
$\delta^{13}C_{CH4}$	FG	$-11.8$	[110]
$\delta^{13}C_{C2H6}$	FG	$-15.2$	[110]
$\delta D_{CH4}$	FG	$-167$ – $-162$	[110]
$\delta D_{C2H6}$	FG	$-202$	[110]
$\delta D_{H2}$	FG	$-644$ – $-359$	[110]

<sup>1</sup> ‰, relative to PDB ( $\delta^{13}C$ ) and SMOW ( $\delta D$ ) standards.

The positive correlation between  $\delta D_{H_2}$  and  $\delta D_{CH_4}$  and the unexpected isotope non-equilibrium of undoubtedly coexisting methane and molecular hydrogen in the Lovozero gases were previously pointed out in [110]. For FGs, the latter could be the result of mixing gas components with different isotope compositions when located in isolated areas and fracture systems during their migration. In the case of bulk occluded gases, the intermixture of gas components with different isotope compositions from several generations of fluid inclusions is possible. Although the ability to store molecular hydrogen in the fluid inclusions of peralkaline rocks was proven even for the Precambrian massifs [23–32], it can be assumed that the degree of such preservation is not the same for individual rocks, minerals, and types of inclusions. Furthermore, as is known (e.g., [127]), a light isotope of hydrogen diffuses through the lattices of minerals more easily than deuterium.

Suppose that a homogeneous fluid phase exists and is later divided into liquid (mainly water) and gas components [111]: we [110] estimated temperatures of the isotope equilibrium for  $H_2O-H_2$  and  $H_2O-CH_4$  with  $\delta D_{H_2O}$  equal to  $-50$  and  $-85\text{‰}$  (probable interval of the isotopic composition of magmatic-water hydrogen, e.g., according to [128], and present fissure waters of the Lovozero massif), as well as  $\delta D_{H_2O} -120, -150, \text{ and } -250\text{‰}$  (probable isotopic composition of meteoric waters from relatively high latitudes and so-called organic water). The latter can be a product of organic matter, bitumen, hydrocarbon gases transformed under dehydration, dehydrogenation, oxidation, etc. [129]. Appropriate estimated temperatures of the possible isotope equilibrium vary from  $92$  to  $416$  °C for water with  $\delta D = -50\text{‰}$  and from  $177$  to  $533$  °C with  $\delta D_{H_2O} = -250\text{‰}$ . Methane can be in equilibrium with relatively heavy ( $\delta D = -50\text{‰}$ ) water only. Temperatures of  $CH_4-H_2O$  isotopic equilibrium are always higher than those calculated for  $H_2-H_2O$ .

The analysis of the limited data available on the joint distribution of occluded hydrocarbon gases and recognized tracers of natural fluids such as isotopes of noble gases in the Khibiny and Lovozero rocks revealed that [18] (a) the indicator ratio  $CH_4/{}^3He$  varies from  $7.4 \times 10^6$  to  $8.7 \times 10^{11}$  (with an average value of  $5.1 \times 10^{10}$ ), partially overlapping those typical for both mantle-derived (between  $10^5$  and  $10^8$ ) and crust-derived (from  $10^8$  to  $10^{11}$ ) fluids, and may testify to  $CH_4$  generation by abiotic reduction of the mantle-derived  $CO_2$ , e.g., [130] and references therein; (b) no relationship between the concentrations of  $CH_4$  and  ${}^3He$  is found, whereas in the case of a predominantly mantle source of methane, a positive correlation of these components can be expected; (c) in the Lovozero samples, there is a significant positive correlation of  $CH_4/C_2H_6$  with  ${}^3He/{}^4He$  and a negative correlation with mainly atmogenic  ${}^{36}Ar$  (from paleometeoric water [85]); (d) the coefficients of the pairwise correlation of  ${}^{36}Ar$  with pentanes, ethane, and methane are, respectively,  $0.96, 0.59, \text{ and } 0.45$ . That is, the processes of weighting the composition of hydrocarbon gases, the loss of the fluid phase deep constituent, and the dilution of its atmogenic component probably largely coincide in time and space. An almost in-phase increase in the content of  $CH_4, {}^3He, \text{ and } {}^3He/{}^4He$  and  $CH_4/C_2H_6$  ratios in the fenite of the Lovozero massif compared with the nepheline syenite of the endocontact [85], along with the presence of primary, significant methane inclusions in the magmatic rock-forming minerals [36,45] and the results of thermodynamic modeling [40,113], testifies that, as in the Ilimaussaq massif [27,28,41], methane could be an important species, even of early-magmatic fluid.

One of the main indexes of the nature and formation conditions of gaseous hydrocarbons is the character of their molecular weight distribution (MWD) and degree of the distribution's compliance with the classic Anderson–Schulz–Flory (ASF) distribution [93,131,132]. It is believed that an MWD determination coefficient  $r^2 > 0.9$  may indicate a dominant abiotic component, and  $r^2 > 0.99$  likely refers to almost pure abiotic gas. Additionally, a rather steep graph of the ASF distribution is often considered to be a criterion of HCG abiogenic origin by FTTR, contrary to the flatter MWD in thermogenic gas fields [30,36,82]. The MWD in the Khibiny and Lovozero gases, both occluded and free, corresponds to the ASF distribution and meets the criteria for their abiogenic formation, including that by means of FTTR [19,43,100].

Currently, in aggregate, the above and other data suggest the polygenetic nature of the gases considered, with the complexity and diversity of responses to their formation taking place at all stages

of mineral genesis, starting from the early magmatic stage but predominantly during the late- and post-magmatic stages. In particular, methane in fluid could be generated under the crystallization of aegirine and alkaline amphibole [43]. Another possible gas generation pathway is the interaction between water and graphite, which can form in temperatures ranging from 470 to 360 °C [40,79].

Molecular hydrogen, being the product of magmatic fluid evolution, the main components of which were water and carbon dioxide [40,56,111,113], apparently was also generated in the course of interaction between iron-bearing minerals and aluminosilicates with water during, for example, the formation of aegirine, magnetite, cancrinite, and zeolites [35,80–82,112].

As the temperature decreases and the H<sub>2</sub> content increases in the gas phase, FTTR, such as  $n\text{CO}_2 + (3n + 1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + 2n\text{H}_2\text{O}$ , with the formation of probably most of the HCGs, including methane, have probably occurred under suitable conditions. Apparently, Salvi and Williams-Jones [30] were the first to carry out thermodynamic calculations and point out the possibility of the formation of HCGs in peralkaline complexes in this way. Later, the idea was supported by other authors [35,37,40,80–82]. FTTR are capable of self-sustaining because of the heat release and can be catalyzed and promoted by ferriferous phases, aluminosilicates (especially zeolites) [133,134], as well by microporous hydrous titano-, niobo- and zirconosilicates, with which bituminous matter is constantly associated in the Khibiny and Lovozero massifs [135].

Available data on the isotope composition of carbon from gas components seem to be inconsistent with FTT-synthesis. Thus, the products of such reactions usually demonstrate no reverse trend of  $\delta^{13}\text{C}$  in hydrocarbon gases (e.g., [136] and references therein). However, the experiments referred to in [136] were mainly conducted using Fe and Co catalysts. It may well be that this trend in the agpaite complexes is caused by the fact that the FTTR proceed with other possible above-listed catalysts. Another argument against such reactions in the considered conditions is the presence of an isotopically lighter carbon in CO<sub>2</sub> compared with HCGs [36,38,45]. However, it is worth mentioning here that these publications mean that insignificant amounts of carbon dioxide were extracted from the samples by crushing. The cited researchers fairly state that this CO<sub>2</sub> cannot be the source for HCGs but, to the contrary, may be the product of their oxidation. Taking into account that the most CO<sub>2</sub> extracted from the nepheline syenite and foidolite samples by crushing is sorbed by the crushed material used for analysis (e.g., [16]), small amounts of remaining gas may be depleted by a heavy carbon isotope. When extracting gases from mostly fluid inclusions in the Khibiny and Lovozero rocks by pyrolysis, even under relatively low temperatures (up to 450 °C), the carbonate dissociation should not start, and CO<sub>2</sub> yield is significantly higher than CH<sub>4</sub> [77]. Thus, the issue of the carbon dioxide occurrence form in the rocks remains open. Notably, the isotope analysis of the Khibiny CO<sub>2</sub> extracted by heating has shown that carbon becomes enriched in the heavy isotope when the temperature increases [81].

It may be supposed that the synthesis from initial H<sub>2</sub> and CO<sub>2</sub> can only be part of the complex multistage process of hydrocarbon generation, including the reactions of oxidation and dehydrogenation, polymerization, and condensation, with a rather wide range of varying thermodynamic parameters [37,93,96,131,133,137], but mainly at the post-magmatic stage [43,100]. In the course of such transformations, which are most intense, apparently, in the circulation zones of meteoric waters, both volatile and nonvolatile (condensation products [133]) carbonaceous substances can be obtained at the same time. To the latter, along with amorphous carbon [79] can be included, for example, the numerous micro-segregations of solid organic matter observed in loparite ores of the Lovozero massif that developed in the interstices of rock-forming mineral grains and in the cracks of the grain cleavage [18]. The flow of a certain amount of biogenic organic matter with surface infiltration waters is not excluded, which could be reflected by the carbon isotope composition of methane in the Khibiny [36]. The air dissolved in these waters serves as a source of at least some of the nitrogen and oxygen found in occluded gases (Table 1) and argon with a low ratio of  $^{40}\text{Ar}/^{36}\text{Ar}$  [85].

Molecular hydrogen, in addition to originating from magmatic sources and rock–water interaction, can also be generated during the radiolysis of water and hydrocarbons [126,138–140], as well as during HCG oxidation and dehydrogenation.

If the OG genesis was commonly related to the formation of immediately alkaline magmatic complexes, free gases were often supposed to arrive later (up to present time) from the depth (mantle or long-lived intermediate magmatic hearths) (e.g., [108,109]). During the many years of research on free gases in underground mine openings and during drilling of exploratory boreholes, we have not obtained any significant evidence of their inflow from great depths. However, taking into account an increased density of heat flow in the Khibiny and Lovozero massifs [141] with regard to the enclosing rocks, it is possible that some part of FGs can permeate from the roots of these massifs, in which the conditions may be favorable for the current formation of gas by any of the above-assumed mechanisms. Considering the similarity in chemical and isotope compositions of carbon and hydrogen of gases of various morphological types, specific features of their localization and emission, modern geodynamic and seismic activity of the massifs [90,142], and the possibility of a new formation for HCGs (e.g., [143]) and particularly H<sub>2</sub> [125,126,144,145] under such conditions, it is believed that free gases in the Khibiny and Lovozero deposits mainly represent a mixture of gases in varying proportions. This mixture includes (a) gases remaining in microfissures (in situ) during the consolidation of the massif after being trapped by fluid inclusions and lost during degassing and (b) gases formed by mechanical and chemical reactions, i.e., partial release and concentration of occluded and diffusely dispersed gases under the conditions of the constantly varying stress and strain state of the rock mass [18,19].

The specific features of localization and emission and the type of relationship between the composition and content of gas phase morphological types in the nepheline-syenite massifs have led to the assumption that diffusely dispersed gases, which are, to a certain degree, transitional between OGs and FGs in terms of occurrence in the rocks, are the same in terms of their genesis. It is probable that more significant quantities of DDGs (compared with free gases) were generated immediately during the formation of the massifs and after their consolidation as a result of mechanical rock activation.

Further study is required to better understand the relative time, conditions, and mechanism of the formation of hydrogen–hydrocarbon gases and condensed organic matter in the Khibiny and Lovozero massifs and associated mineral deposits. Cooperation among various interested researchers is needed, as well as the use and combination of modern methods for the systematic examination of the isotopic composition of carbon and hydrogen, including clumped isotopologues of CH<sub>4</sub>, higher hydrocarbons, and CO<sub>2</sub>. Other necessary approaches include the chromatographic compositional analysis of gases, fluid inclusion microthermometric and laser-Raman analyses, and laboratory experiments on the abiogenic synthesis of gaseous, liquid, and solid organic matter using zeolite, niobo-, and zirconsilicates as catalysts and promoters.

## 6. Gas Content of Underground Mine Openings, Basic Principles, and Measures for Gas-safe Mining

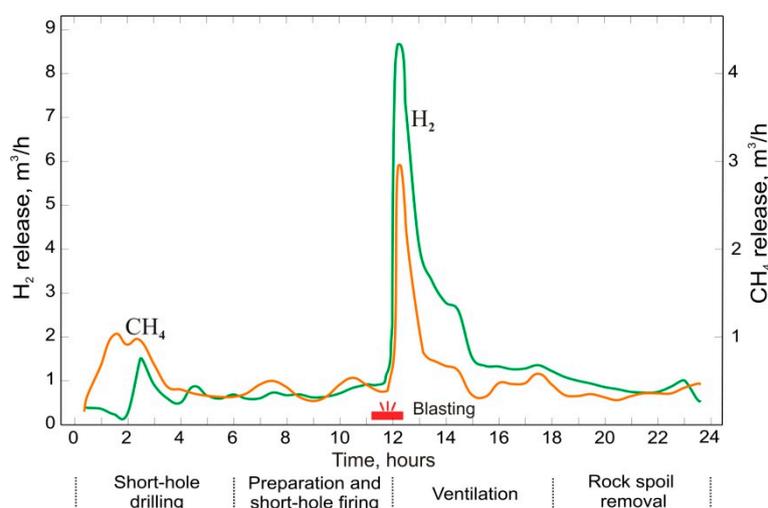
Gas-bearing capacity, which means the total amount of gases of all occurrence forms contained in the natural conditions in the unit of weight or volume for rocks, does not completely (or only slightly) reflect the volume of gases released to the mine air since it depends on gas-bearing capacity and several mining and geological factors. The combustible and explosive gas (CEG) content in the mine air represents a more reliable indicator of whether gas-safe mining operations can be performed. The level of CEG content in the mine atmosphere also reflects the relative state of gas inflow from rocks compared with the amount of air supplied for ventilating mine openings. The relative gas content (RGC) of mine openings, which means the amount of natural gases released as a result of breakage during the blasting of a rock volume unit, is a common gas content indicator in the mining industry. In this research, RGC predominantly reflects the content of free gases in an undisturbed rock mass. Absolute gas content (AGC) of the mine, horizon, block, area, or excavation is an integral indicator of the intensity of gas emission into the mine air: it is the amount of gases emitted from all possible sources during a unit of time.

The study of the gas content of the Khibiny apatite-nepheline deposits was carried out by various scientific organizations and mining services since the 1950s. Relatively recently, a brief review and

generalization of the results of these studies was carried out, as well as the gas-bearing capacity of the deep horizons of the Kukisvumchorr, Yukspor, Apatite Circus and Rasvumchorr Plateau [101,102]. The latter turned out to be close to that for the upper, in a significant part of the already developed, sections of these deposits. Thus, RGC usually does not exceed  $1 \text{ m}^3$  of combustible gases per  $1 \text{ m}^3$  of undisturbed rock, and the AGC of each individual mine in the first few hundreds of cubic meters of CEG per day.

Similar values ( $0.3\text{--}1.1 \text{ m}^3$  of total  $\text{CH}_4$  and  $\text{H}_2$  per  $1 \text{ m}^3$  of rock) describe the RGC of the Lovozero deposit [103,146]. The AGC of individual mining areas in the Kurnasurt Mine varies from the first few dozen to  $180 \text{ m}^3/\text{day}$  for hydrogen and from portions to the first few dozens of cubic meters per day for methane.

During mining operations at the Khibiny and Lovozero deposits, the most intense emission of natural CEG to the mine air takes place immediately after blasting and the outcropping of new surfaces. A remarkably low amount of gases are emitted during the drilling of shot-holes, while clearing blasted rock mass, and from the walls of previously completed mine workings. Figure 13, using the AGC of drifting faces as an example, provides a typical view of the daily variation in this indicator according to the technological stage of mining operations. A similar or identical nature of AGC variations has been revealed for individual mining blocks and areas. Usually, from 40% to 75% of the daily CEG volume is carried off by ventilation airflows within the 6-h forced airing stage. Of this estimate, from 20% to 50% occurs during the first three hours upon blasting.



**Figure 13.** Trend of the absolute gas content (AGC) variation for dead ends during mining operations at the Kurnasurt loporite mine (modified from [18]).

The lower explosive threshold for real natural mixtures of the CEG typical of the considered deposits lies within 4.3–4.7 vol. %. If there is compliance with the accepted ventilation norms, the real concentration of these gases in the mine air does not usually exceed several thousandths of a volume percent, which is several orders of magnitude lower than the explosive threshold. Increased contents of CEG components in the mine air are found in unventilated dead-end mine workings and while excavating the first workings at a certain deposit section, especially those driven from the bottom to the top and/or in free-gas-saturated rocks.

The results of studies of CEG contents in the Khibiny and Lovozero mines indicate that the principles of their gas-safe mining were formulated and appropriate recommendations were given. On the basis of these recommendations and in compliance with the requirements of regulatory documents, together with the experts of mining companies, the authors have developed and implemented some special measures for gas-safe mining during operation in the underground mines of the Kirovsk Branch of JSC Apatit and Lovozero GOK. These safety measures, every existing

edition of which was approved by the federal state supervision authorities, are subject regular revision and amendment (as soon as new gasometric data are obtained or geological setting and mining technology changes).

Since apatite-nepheline and rare-metal deposits generally have the same gas-bearing capacity and conditions and scopes of gas emission, the proposed gas-safe mining measures are also similar and account for the differences in factors such as the composition of free gases, the gas permeability of rock mass, the sizes and geological structure of ore bodies, and mining technological cycles. With due regard to the specific features of the gas-bearing capacity and nature of HHCGs, the absence of intense sudden gas outbursts and bleedings of CEG in the past few decades, and the inactivity of rock and ore dust, it was considered inappropriate to apply the gas regime to the entire underground mine during operations at the deposits in this review. It is recommended to introduce it in accordance with the results of supervision of the mine air composition of some individual mining areas or excavations. Since it is impossible to predict the areas that have increased gas content and local accumulations of free gases, the operating measures primarily come down to supervising the mine air state and optimizing the mine ventilation regime.

After implementing these quite flexible and adjustable (as necessary) safety measures, safe mining during the operation of the Khibiny and Lovozero deposits is ensured for several decades. Examination of various accidents, including injuries and deaths of miners, and emergency situations caused by the combustion and explosion of natural gases in mine openings has shown that these accidents were the result of non-compliance with or serious breach of safety measures.

## 7. Conclusions

The extremely large-scale apatite-nepheline and loparite deposits associated with the Khibiny and Lovozero foidolite-nepheline-syenite massifs, respectively, are also distinguished by reduced hydrogen-hydrocarbon gas content that is higher than usual for igneous complexes. There are three known and spatially weakly related occurrence forms (morphological types) of gases: (i) OGs, which are occluded primarily in vacuoles of fluid micro-inclusions in minerals; (ii) FGs, which fill systems of conjugated fractures and other cavities in rocks and spontaneously emanate, predominantly through filtration, from the rocks when their accumulations are opened; and (iii) DDGs, which fill closed and semi-open, thin and subcapillary microfractures and pores, remain in an adsorbed state to some extent, migrate mainly by diffusion, and are in some sense transitional between OGs and FGs.

The qualitative composition of HHCGs of all three occurrence forms is the same. Although the ratios of the individual gases vary widely, their average relative concentrations, calculated according to the airless mixture, are close. Methane is the main component, molecular hydrogen (sometimes prevalent) and ethane are the subordinate constituents, while heavier homologs of methane (up to and including pentanes), alkenes, helium, and sometimes dioxide and carbon monoxide occur in minor and trace amounts. Gases of all three forms of occurrence are characterized by the multiscale unevenness of their spatial distribution, and FGs demonstrate variations in the intensity of their release over time. Ore ledges of the considered deposits are distinguished by a relatively low OG content, but increased gas saturation in the subconcordant zones above and below them has been recorded. Any regularities of FG localization within the deposits have been identified. Barogenic (atmospheric pressure variation) and human-induced (technogenic explosions) factors are the most important for the dynamics of free H<sub>2</sub> emanation. Unstable DDG composition and the features of their localization and emission are caused and controlled by many factors, including the various natures and physical properties of individual gases, total gas saturation, and the geomechanical state of the rock mass.

The data currently available, in aggregate, suggest a polygenetic nature of the Khibiny and Lovozero HHCGs. Results of analyses highlight the complexity and variety of ways and reactions leading to HHCG formation, which took place not only at all stages of mineral genesis (from early magmatic to post-magmatic) but also after the consolidation of the massifs. In particular, methane in magmatic fluid could have been generated under the crystallization of aegirine and alkaline amphibole,

from the interaction between water and graphite, and, along with higher hydrocarbons, a result of Fischer-Tropsch Type reactions from the initial H<sub>2</sub> and CO<sub>2</sub>. Molecular hydrogen, as the product of magmatic fluid evolution, the main components of which are represented by water and carbon dioxide, was also evidently produced in the course of interactions of iron-bearing minerals and aluminosilicates with water (for example, as a result of aegirine, magnetite, cancrinite, and zeolite formation). Moreover, molecular hydrogen was also apparently formed in the radiolysis of water and hydrocarbons during HCG oxidation and dehydrogenation. Some of the free-phase H<sub>2</sub> may be seismogenic.

Emissions of natural free HHCGs pose hazards during the underground mining of ore deposits because they can create dangerous concentrations of combustible and explosive components in the atmosphere of mine workings. The relative gas content of the deposits is usually a few tenths of a cubic meter (rarely exceeding 1 m<sup>3</sup>) of CEGs per 1 m<sup>3</sup> of an ore or enclosing rock in its natural (undisturbed) state. The absolute gas content of individual underground mines is several hundred cubic meters of total CH<sub>4</sub> and H<sub>2</sub> per day. The identified features of the gas-bearing capacity of the deposits serve as a basis for elaborating and implementing special measures of the gas regime during mining operations.

The collaboration of various researchers and the use of modern methods and approaches are needed for the further comprehensive study of rare igneous complexes of HHCGs in the rocks and minerals of the Khibiny and Lovozero massifs and their associated ore deposits.

**Funding:** This paper was prepared in the framework of State contract No 0226-2019-0051 of GI KSC RAS.

**Acknowledgments:** The author is grateful to Alexandra Rybnikova for text translation from Russian into English and to anonymous reviewers for valuable comments and suggestions.

**Conflicts of Interest:** The author declares no conflict of interest.

## References

1. Eliseev, N.A.; Fedorov, E.E. *The Lovozero Pluton and its Ore Deposits*; Transactions of the Precambrian Laboratory: Leningrad, Russia, 1953. (In Russian)
2. Vlasov, K.A.; Kuz'menko, M.Z.; Es'kova, E.M. *The Lovozero Alkali Massif*; Fry, D.G.; Syers, K., Translators; Oliver & Boyd: Edinburgh and London, UK, 1966.
3. Ivanova, T.N. *Apatite Deposits of the Khibiny Tundres*; Gosgeoltekhizdat: Moscow, Russia, 1963. (In Russian)
4. Onokhin, F.M. *Peculiarities of the Khibiny Massif Structure and Apatite-Nepheline Deposits*; Nauka: Leningrad, Russia, 1975. (In Russian)
5. Kamenev, Y.A.; Mineev, D.A. (Eds.) *New Khibiny Apatite Deposits*; Nedra: Moscow, Russia, 1982. (In Russian)
6. Kamenev, Y.A. *Prospecting, Exploring and Geological Industrial Assessment of the Khibiny Type Apatite Deposits*; Nedra: Moscow, Russia, 1987. (In Russian)
7. Arzamastsev, A.A. *Unique Paleozoic Intrusions of the Kola Peninsula*; KSC RAS: Apatity, Russia, 1994.
8. Kogarko, L.N.; Lahaye, Y.; Brey, G.P. Plume-related mantle source of super-large rare metal deposits from the Lovozero and Khibina massifs on the Kola Peninsula, Eastern part of Baltic shield: Sr, Nd and Hf isotope systematics. *Miner. Petrol.* **2010**, *98*, 197–208. [[CrossRef](#)]
9. Ivanyuk, G.; Yakovenchuk, V.; Pakhomovsky, Y.; Kalashnikov, A.; Mikhailova, J.; Goryainov, P. Self-Organization of the Khibiny Alkaline Massif (Kola Peninsula, Russia). In *Earth Sciences*; Dar, I.A., Ed.; InTech: Rijeka, Croatia, 2012; pp. 131–156. ISBN 978-953-307-861-8.
10. Pakhomovsky, Y.A.; Ivanyuk, G.Y.; Yakovenchuk, V.N. Loparite-(Ce) in rocks of the Lovozero layered complex at Mt. Karnasurt and Mt. Kedykvyrpakhk. *Geol. Ore Deposit.* **2014**, *56*, 685–698. [[CrossRef](#)]
11. Kalashnikov, A.O.; Konopleva, N.G.; Pakhomovsky, Y.A.; Ivanyuk, G.Y. Rare earth deposits of the Murmansk Region, Russia—A review. *Econ. Geol.* **2016**, *111*, 1529–1559. [[CrossRef](#)]
12. Kogarko, L. Chemical composition and petrogenetic implications of apatite in the Khibiny apatite-nepheline deposits (Kola Peninsula). *Minerals* **2018**, *8*, 532. [[CrossRef](#)]
13. Krivovichev, V.G.; Charykova, M.V. Mineral systems, their types, and distribution in nature. I. Khibiny, Lovozero, and the Mont Saint-Hilaire. *Geol. Ore Dep.* **2016**, *58*, 551–558. [[CrossRef](#)]
14. Petersilie, I.A. Hydrocarbonic gases and bitumens in igneous massifs in the central part of the Kola Peninsula. *Dokl. AN USSR* **1958**, *122*, 1086–1089. (In Russian)

15. Petersilie, I.A. *Geology and Geochemistry of Natural Gases and Disperse Bitumens of Some Geological Formations of the Kola Peninsula*; Nauka: Moscow, Russia, 1964. (In Russian)
16. Ikorsky, S.V.; Nivin, V.A.; Pripachkin, V.A. *Gas Geochemistry of Endogenic Formations*; Nauka: St.-Petersburg, Russia, 1992. (In Russian)
17. Nivin, V.A. Diffusely disseminated hydrogen–hydrocarbon gases in rocks of nepheline syenite complexes. *Geochem. Int.* **2009**, *47*, 672–691. [[CrossRef](#)]
18. Nivin, V.A. Gas Components in Magmatic Rocks: Geochemical, Mineragenic and Environmental Aspects and Results. Doctor of Sciences (Geol.-Miner.) Dissertation, Vernadsky Institute of Geochemistry and Analytical Chemistry of Russian Academy of Sciences, Moscow, Russia, 2013; p. 354. (In Russian)
19. Nivin, V.A. Free hydrogen-hydrocarbon gases from the Lovozero loparite deposit (Kola Peninsula, NW Russia). *Appl. Geochem.* **2016**, *74*, 44–55. [[CrossRef](#)]
20. Wallace, P.J. Volatiles in subduction zone magmas: concentrations and fluxes based on melt inclusion and volcanic gas data. *J. Volcanol. Geotherm. Res.* **2005**, *140*, 217–240. [[CrossRef](#)]
21. Fischer, T.P.; Chiodini, G. Volcanic, magmatic and hydrothermal gas discharges. In *Encyclopaedia of Volcanoes*, 2nd ed.; Elsevier: Amsterdam, The Netherlands, 2015; pp. 779–797.
22. Petersilie, I.A.; Sørensen, H. Hydrocarbon gases and bituminous substances in rocks from the Ilímaussaq alkaline intrusion, South Greenland. *Lithos* **1970**, *3*, 59–76. [[CrossRef](#)]
23. Konnerup-Madsen, J.; Larsen, E.; Rose-Hansen, J. Hydrocarbon-rich fluid inclusions in minerals from the alkaline Ilímaussaq intrusion. *South Greenland. Bull. Minéral.* **1979**, *102*, 642–653. [[CrossRef](#)]
24. Konnerup-Madsen, J.; Rose-Hansen, J. Volatiles associated with alkaline igneous rift activity: fluid inclusions in the Ilímaussaq intrusion and the Gardar granitic complexes (South Greenland). *Chem. Geol.* **1982**, *37*, 79–93. [[CrossRef](#)]
25. Konnerup-Madsen, J. A review of the composition and evolution of hydrocarbon gases during solidification of the Ilímaussaq alkaline complex, South Greenland. *Geol. Greenl. Surv. Bull.* **2001**, *190*, 159–166.
26. Markl, G.; Baumgartner, L. pH changes in peralkaline late-magmatic fluids. *Contrib. Mineral. Petrol.* **2002**, *144*, 331–346. [[CrossRef](#)]
27. Krumrei, T.V.; Pernicka, E.; Kaliwoda, M.; Markl, G. Volatiles in a peralkaline system: abiogenic hydrocarbons and F–Cl–Br systematics in the naujaite of the Ilímaussaq intrusion, South Greenland. *Lithos* **2007**, *95*, 298–314. [[CrossRef](#)]
28. Graser, G.; Potter, J.; Kohler, J.; Markl, G. Isotope, major, minor and trace element geochemistry of late-magmatic fluids in the peralkaline Ilímaussaq intrusion, South Greenland. *Lithos* **2008**, *106*, 207–221. [[CrossRef](#)]
29. Salvi, S.; Williams-Jones, A.E. Reduced orthomagmatic C–O–H–N–NaCl fluids in the Strange Lake rare-metal granitic complex, Quebec Labrador, Canada. *Eur. J. Mineral.* **1992**, *4*, 1155–1174. [[CrossRef](#)]
30. Salvi, S.; Williams-Jones, A.E. Fischer–Tropsch synthesis of hydrocarbons during sub-solidus alteration of the Strange Lake peralkaline granite, Quebec/Labrador, Canada. *Geochim. Cosmochim. Acta* **1997**, *61*, 83–99. [[CrossRef](#)]
31. Salvi, S.; Williams-Jones, A.E. Alteration, HFSE mineralisation and hydrocarbon formation in peralkaline igneous systems: insights from the Strange Lake Pluton, Canada. *Lithos* **2006**, *91*, 19–34. [[CrossRef](#)]
32. Vasyukova, O.V.; Williams-Jones, A.E.; Blamey, N.J.F. Fluid evolution in the Strange Lake granitic pluton, Canada: Implications for HFSE mobilisation. *Chem. Geol.* **2016**, *444*, 83–100. [[CrossRef](#)]
33. Ikorsky, S.V.; Nivin, V.A. Free phase gases in rocks of the Lovozero alkaline massif (Kola Peninsula). *Dokl. Acad. Nauk S.S.S.R.* **1983**, *269*, 934–936. (In Russian)
34. Potter, J.; Konnerup-Madsen, J. A review of the occurrence and origin of abiogenic hydrocarbons in igneous rocks. In *Hydrocarbons in Crystalline Rocks*; Petford, N., McCaffrey, K.J.W., Eds.; The Geological Society of London: London, UK, 2003; Geological Society Special Publication; Volume 214, pp. 151–173. [[CrossRef](#)]
35. Nivin, V.A.; Treloar, P.J.; Konopleva, N.G.; Ikorsky, S.V. A review of the occurrence, form and origin of C-bearing species in the Khibiny alkaline igneous complex, Kola Peninsula, NW Russia. *Lithos* **2005**, *85*, 93–112. [[CrossRef](#)]
36. Beeskov, B.; Treloar, P.J.; Rankin, A.H.; Vennemann, T.W.; Spangenberg, J. A reassessment of models for hydrocarbon generation in the Khibiny nepheline syenite complex, Kola Peninsula, Russia. *Lithos* **2006**, *91*, 1–18. [[CrossRef](#)]

37. Gottikh, R.P.; Pisotskii, B.I.; Kulakova, I.I. Geochemistry of reduced fluids from alkaline igneous rocks of the Khibiny Pluton. *Dokl. Earth Sci.* **2006**, *407*, 298–303. [[CrossRef](#)]
38. Potter, J.; Longstaffe, F.J. A gas-chromatograph, continuous flow-isotope ratio mass-spectrometry method for  $\delta^{13}\text{C}$  and  $\delta\text{D}$  measurement of complex fluid inclusion volatiles: Examples from the Khibina alkaline igneous complex, northwest Russia and the south Wales coalfields. *Chem. Geol.* **2007**, *244*, 186–201. [[CrossRef](#)]
39. Schonenberger, J.; Markl, G. The magmatic and fluid evolution of the Motzfeldt intrusion in South Greenland: Insights into the formation of agpaitic and miaskitic rocks. *J. Petrol.* **2008**, *49*, 1549–1577. [[CrossRef](#)]
40. Ryabchikov, I.D.; Kogarko, L.N. Redox potential of the Khibiny magmatic system and genesis of abiogenic hydrocarbons in alkaline plutons. *Geol. Ore Deposit.* **2009**, *51*, 425–440. [[CrossRef](#)]
41. Markl, G.; Marks, M.A.W.; Frost, B.R. On the controls of oxygen fugacity in the generation and crystallization of peralkaline melts. *J. Petrol.* **2010**, *51*, 1831–1847. [[CrossRef](#)]
42. Kendrick, M.A.; Honda, M.; Walshe, J.; Petersen, K. Fluid sources and the role of abiogenic- $\text{CH}_4$  in Archean gold mineralization: Constraints from noble gases and halogens. *Precambrian Res.* **2011**, *189*, 313–327. [[CrossRef](#)]
43. Nivin, V.A. Variations in the composition and origin of hydrocarbon gases from inclusions in minerals of the Khibiny and Lovozero plutons, Kola Peninsula, Russia. *Geol. Ore Deposit.* **2011**, *53*, 699–707. [[CrossRef](#)]
44. Laier, T.; Nytoft, H.P. Bitumen biomarkers in the Mid-Proterozoic Ilimaussaq intrusion, Southwest Greenland—A challenge to the mantle gas theory. *Mar. Petrol. Geol.* **2012**, *30*, 50–65. [[CrossRef](#)]
45. Potter, J.; Salvi, S.; Longstaffe, F. Abiogenic hydrocarbon isotopic signatures in granitic rocks: Identifying pathways of formation. *Lithos* **2013**, *182–183*, 114–124. [[CrossRef](#)]
46. Kerr, M.; Hanley, J.; Morrison, G.; Everest, J.; Bray, C. Preliminary evaluation of trace hydrocarbon speciation and abundance as an exploration tool for footwall-style sulfide ores associated with the Sudbury Igneous Complex, Ontario, Canada. *Econ. Geol.* **2015**, *110*, 531–556. [[CrossRef](#)]
47. Burisch, M.; Gerdes, A.; Walter, B.F.; Neumann, U.; Fettel, M.; Markl, G. Methane and the origin of five-element veins: Mineralogy, age, fluid inclusion chemistry and ore forming processes in the Odenwald, SW Germany. *Ore Geol. Rev.* **2017**, *81*, 42–61. [[CrossRef](#)]
48. Chinnasamy, S.S.; Mishra, B. Genetic implications of fluid-deposited disordered graphite and methane-rich inclusions in the Jonnagiri granodiorite-hosted gold deposit, Eastern Dharwar Craton, India. *Ore Geol. Rev.* **2017**, *89*, 587–593. [[CrossRef](#)]
49. Migdisov, A.A.; Guo, X.; Xu, H.; Williams-Jones, A.E.; Sun, C.J.; Vasyukova, O.; Sugiyama, I.; Fuchs, S.; Pearce, K.; Roback, R. Hydrocarbons as ore fluids. *Geochem. Persp. Lett.* **2017**, *5*, 47–52. [[CrossRef](#)]
50. Lecumberri-Sancheza, P.; Bouabdellah, M.; Zemri, O. Transport of rare earth elements by hydrocarbon-bearing brines: Implications for ore deposition and the use of REEs as fluid source tracers. *Chem. Geol.* **2018**, *479*, 204–215. [[CrossRef](#)]
51. Vasyukova, O.V.; Williams-Jones, A.E. Direct measurement of metal concentrations in fluid inclusions, a tale of hydrothermal alteration and REE ore formation from Strange Lake, Canada. *Chem. Geol.* **2018**, *483*, 385–396. [[CrossRef](#)]
52. Nivin, V.A. The main principles and measures of gas-safe work at the underground mines of the “Apatit” corporation. *Gornyi Zhurnal* **1991**, *8*, 34–36. (In Russian)
53. Gerasimovsky, V.I.; Volkov, V.P.; Kogarko, L.N.; Polyakov, A.I.; Saprykina, T.V.; Balashov, Y.A. *The Geochemistry of the Lovozero Alkaline Massif*; Part 1 and Part 2; Australian National University Press: Canberra, Australia, 1966.
54. Bussen, I.V.; Sakharov, A.S. *Petrology of the Lovozero Alkaline Massif*; Nauka: Leningrad, Russia, 1972. (In Russian)
55. Galakhov, A.V. *Petrology of the Khibiny Alkaline Massif*; Nauka: Leningrad, Russia, 1975. (In Russian)
56. Kogarko, L.N. *Problems of Genesis of Agpaitic Magmas*; Nauka: Moscow, Russia, 1977. (In Russian)
57. Kostyleva-Labuntsova, E.E.; Borutsky, B.E.; Sokolova, M.N.; Shlyukova, Z.V.; Dorfman, M.D.; Dudkin, O.B.; Kozyreva, L.V.; Ikorsky, S.V. *Mineralogy of the Khibiny Massif*; Nauka: Moscow, Russia, 1978.
58. Arzamastsev, A.A.; Ivanova, T.N.; Korobeinikov, A.N. *Petrology of the Khibiny Ijolite-Urtite and Laws of Localization of Apatite Bodies*; Nauka: Leningrad, Russia, 1987. (In Russian)
59. Pekov, I.V. *Lovozero Massif: History, Pegmatites, Minerals*; Ocean Pictures Ltd.: Moscow, Russia, 2000.
60. Yakovenchuk, V.N.; Ivanyuk, G.Y.; Pakhomovsky, Y.A.; Men’shikov, Y.P. *Khibiny*; Wall, F., Ed.; Laplandia Minerals: Apatity, Russia, 2005.

61. Chakhmouradian, A.R.; Mitchell, R.H. New data on pyrochlore- and perovskite-group minerals from the Lovozero alkaline complex, Russia. *Eur. J. Mineral.* **2002**, *14*, 821–836. [[CrossRef](#)]
62. Downes, H.; Balaganskaya, E.; Beard, A.; Liferovich, R.; Demaiffe, D. Petrogenetic processes in the ultramafic, alkaline and carbonatitic magmatism in the Kola Alkaline Province: A review. *Lithos* **2005**, *85*, 48–75. [[CrossRef](#)]
63. Goryainov, P.M.; Konopleva, N.G.; Ivanyuk, G.Y.; Yakovenchuk, V.N. Structural organization of the ore zone of the Koashva apatite–nepheline deposit. *Otech. Geol.* **2007**, *2*, 55–60. (In Russian)
64. Arzamastsev, A.; Yakovenchuk, V.; Pakhomovsky, Y.; Ivanyuk, G. The Khibina and Lovozero Alkaline Massifs: Geology and Unique Mineralization. In Proceedings of the Guidebook for 33rd International Geological Congress Excursion, Apatity, Russia, 22 July–2 August 2008; p. 58.
65. Korchak, Y.A.; Men’shikov, Y.P.; Pakhomovsky, Y.A.; Yakovenchuk, V.N.; Ivanyuk, G.Y. Trap formation of the Kola Peninsula. *Petrology* **2011**, *19*, 87–101. [[CrossRef](#)]
66. Chakhmouradian, A.R.; Zaitsev, A.N. Rare earth mineralization in igneous rocks: sources and processes. *Elements* **2012**, *8*, 347–353. [[CrossRef](#)]
67. Arzamastsev, A.A.; Arzamastseva, L.V.; Zhironova, A.M.; Glaznev, V.N. Model of formation of the Khibiny–Lovozero ore-bearing volcanic–plutonic complex. *Geol. Ore Deposit.* **2013**, *55*, 341–356. [[CrossRef](#)]
68. Ivanyuk, G.Y.; Pakhomovsky, Y.A.; Yakovenchuk, V.N. Eudialyte-group minerals in rocks of Lovozero layered complex at Mt. Karnasurt and Mt. Kedykvyrpakhk. *Geol. Ore Deposit.* **2015**, *57*, 600–613. [[CrossRef](#)]
69. Veselovskiy, R.V.; Thomson, S.N.; Arzamastsev, A.A.; Zakharov, V.S. Apatite fission track thermochronology of Khibina massif (Kola Peninsula, Russia): Implications for post-Devonian tectonics of the NE Fennoscandia. *Tectonophysics* **2015**, *665*, 157–163. [[CrossRef](#)]
70. Kogarko, L.N. Geochemistry of fractionation of coherent elements (Zr and Hf) during the profound differentiation of peralkaline magmatic systems: A case study of the Lovozero complex. *Geoch. Int.* **2016**, *54*, 1–6. [[CrossRef](#)]
71. Marks, M.A.W.; Markl, G. A global review on agpaitic rocks. *Earth Sci. Rev.* **2017**, *173*, 229–258. [[CrossRef](#)]
72. Zartman, R.E.; Kogarko, L.N. Lead isotopic evidence for interaction between plume and lower crust during emplacement of peralkaline Lovozero rocks and related rare-metal deposits, East Fennoscandia, Kola Peninsula, Russia. *Contrib. Mineral. Petrol.* **2017**, *172*, 1–14. [[CrossRef](#)]
73. Rodionov, N.; Lepekhina, E.N.; Antonov, A.V.; Kapitonov, I.N.; Balashova, Y.S.; Belyatsky, B.V.; Arzamastsev, A.A.; Sergeev, S.A. U–Pb SHRIMP-II ages of titanite and timing constraints on apatite–nepheline mineralization in the Khibiny and Lovozero alkaline massifs (Kola Peninsula). *Russ. Geol. Geophys.* **2018**, *59*, 962–974. [[CrossRef](#)]
74. Timashev, S.F.; Nivin, V.A.; Syvorotkin, V.L.; Polyakov, Y.S. Flicker-noise spectroscopy in dynamic analysis of hydrogen evolution in the Lovozero and Khibiny massifs (Kola Peninsula). In *Dynamic Phenomena in Complicated Systems*; MESRT: Kazan, Russia, 2011; pp. 263–278. (In Russian)
75. Nivin, V.A.; Pukha, V.V.; Lovchikov, A.V.; Rakhimov, R.G. Changes in the molecular hydrogen concentration in an underground mine (Lovozero rare-metal deposit, Kola Peninsula). *Dokl. Earth Sci.* **2016**, *471*, 1261–1264. [[CrossRef](#)]
76. Nivin, V.A.; Pukha, V.V.; Lovchikov, A.V.; Rakhimov, R.G. Features and factors of time variations in hydrogen release at Lovozersky rare-metal deposit (Kola Peninsula). *Geochem. Int.* **2018**, *56*, 688–701. [[CrossRef](#)]
77. Kryvdik, S.G.; Nivin, V.A.; Kul’chitskaya, A.A.; Voznyak, D.K.; Kalinichenko, A.M.; Zagnitko, V.N.; Dubina, A.V. Hydrocarbons and other volatile components in alkaline rocks from the Ukrainian Shield and Kola Peninsula. *Geochem. Int.* **2007**, *45*, 270–294. [[CrossRef](#)]
78. Kul’chitskaya, A.A.; Nivin, V.A.; Avedisyan, A.A.; Voznyak, D.K.; Vasyuta, Y.V. Comparison of the results of extracting methane from minerals by mechanical and thermal methods. *Mineral. J.* **2009**, *31*, 84–94. (In Russian)
79. Ermolaeva, V.N.; Chukanov, N.V.; Pekov, I.V.; Kogarko, L.N. The geochemical and genetic role of organic substances in postmagmatic derivatives of alkaline plutons. *Geol. Ore Deposit.* **2009**, *51*, 513–524. [[CrossRef](#)]
80. Potter, J.; Rankin, A.H.; Treloar, P.J.; Nivin, V.A.; Ting, W.; Ni, P. A preliminary study of methane inclusions in alkaline igneous rocks of the Kola igneous province, Russia: Implications for the origin of methane in igneous rocks. *Eur. J. Miner.* **1998**, *10*, 1167–1180. [[CrossRef](#)]
81. Potter, J. The Characterisation and Origin of Hydrocarbons in Alkaline Rocks of the Kola Alkaline Province. Ph. D. Thesis, Kingston University, Kingston, UK, 2000.

82. Potter, J.; Rankin, A.H.; Treloar, P.J. Abiogenic Fischer-Tropsch synthesis of hydrocarbons in alkaline igneous rocks; fluid inclusion, textural and isotopic evidence from the Lovozero complex, NW Russia. *Lithos* **2004**, *75*, 311–330. [[CrossRef](#)]
83. Beeskow, B. The Occurrence, Distribution and Origin of Hydrocarbons in the Khibiny Nepheline Syenite Complex, Kola Peninsula, Russia. Ph. D. Thesis, Kingston University, Kingston, UK, 2007.
84. Pokrovskiy, B.G. *Crustal Contamination of Mantle Magmas According to Isotope Geochemistry*; Nauka: Moscow, Russia, 2000. (In Russian)
85. Nivin, V.A. Helium and argon isotopes in rocks and minerals of the Lovozero alkaline massif. *Geochem. Int.* **2008**, *46*, 482–502. [[CrossRef](#)]
86. Mokrushina, O.D.; Sharygin, V.V. Fluid inclusions in nepheline of the loparite deposit in the Lovozero alkaline massif. In *All-Russian Conference on Thermobarogeochemistry, Dedicated to the 100th Anniversary of the Birth of Prof. Yu.A. Dolgov (1918–1993)*; Mineralogical Museum Named after Fersman, RAS: Moscow, Russia, 2018; pp. 82–84. (In Russian)
87. Nivin, V.A.; Belov, N.I. Correlations between gas-geochemical and geomechanical parameters of alkali rocks at ore deposits. *Geochem. Int.* **1993**, *30*, 34–40.
88. Nivin, V.A.; Belov, N.I.; Treloar, P.J.; Timofeyev, V.V. Relationships between gas geochemistry and release rates and the geomechanical state of igneous rock massifs. *Tectonophysics* **2001**, *336*, 233–244. [[CrossRef](#)]
89. Goryainov, P.M.; Ivanyuk, G.Y.; Yakovenchuk, V.N. Tectonic percolation zones in the Khibiny massif: Morphology, geochemistry, and genesis. *Izv. Phys. Solid Earth* **1998**, *34*, 822–827.
90. Lovchikov, A.V. Review of the strongest rock bursts and mining-induced earthquakes in Russia. *J. Mining Sci.* **2013**, *49*, 572–575. [[CrossRef](#)]
91. Gokhberg, M.B.; Adushkin, V.V.; Voytov, G.I.; Pushkin, M.G.; Krivomazova, N.G.; Zel'dina, B.B. On the reaction of free gases in the Khibiny massif to a powerful industrial explosion. *Dokl. AN USSR* **1989**, *308*, 1082–1086. (In Russian)
92. Proskurowski, G.; Lilley, M.D.; Seewald, J.S.; Fruh-Green, G.L.; Olson, E.J.; Lupton, J.E.; Sylva, S.P.; Kelley, D.S. Abiogenic hydrocarbon production at Lost City hydrothermal field. *Science* **2008**, *319*, 604–607. [[CrossRef](#)] [[PubMed](#)]
93. Etiope, G.; Sherwood Lollar, B. Abiotic methane on Earth. *Rev. Geophys.* **2013**, *51*, 276–299. [[CrossRef](#)]
94. Deville, E.; Prinzhofner, A. The origin of N<sub>2</sub>-H<sub>2</sub>-CH<sub>4</sub>-rich natural gas seepages in ophiolitic context: A major and noble gases study of fluid seepages in New Caledonia. *Chem. Geol.* **2016**, *440*, 139–147. [[CrossRef](#)]
95. Vacquand, C.; Deville, E.; Beaumont, V.; Guyot, F.; Sissmann, O.; Pillot, D.; Arcilla, C.; Prinzhofner, A. Reduced gas seepages in ophiolitic complexes: Evidences for multiple origins of the H<sub>2</sub>-CH<sub>4</sub>-N<sub>2</sub> gas mixtures. *Geochim. Cosmochim. Acta* **2018**, *223*, 437–461. [[CrossRef](#)]
96. Etiope, G.; Whiticar, M.J. Abiotic methane in continental ultramafic rock systems: Towards a genetic model. *Appl. Geochem.* **2019**, *102*, 139–152. [[CrossRef](#)]
97. Zgonnik, V.; Beaumont, V.; Larin, N.; Pillot, D.; Deville, E. Diffused flow of molecular hydrogen through the Western Hajar mountains, Northern Oman. *Arab. J. Geosci.* **2019**, *12*. [[CrossRef](#)]
98. Brovarone, A.V.; Martinez, I.; Elmaleh, A.; Compagnoni, R.; Chaduteau, C.; Ferraris, C.; Esteve, I. Massive production of abiotic methane during subduction evidenced in metamorphosed ophiocarbonates from the Italian Alps. *Nat. Commun.* **2017**, *8*, 14134. [[CrossRef](#)] [[PubMed](#)]
99. Nivin, V.A. Gas concentrations in minerals with reference to the problem of the genesis of hydrocarbon gases in rocks of the Khibiny and Lovozero massifs. *Geochem. Int.* **2002**, *40*, 883–898.
100. Nivin, V.A. Molecular-mass distribution of saturated hydrocarbons in gas of the Lovozerskii nepheline-syenite massif. *Dokl. Earth Sci.* **2009**, *429*, 1580–1582. [[CrossRef](#)]
101. Nivin, V.A. *Estimation of the Ore and Country Rock Gas Content at Deep (down to +10 m) Horizons of the Kukisvumchorr and Yukspor Apatite-Nepheline Deposits Developed by the Kirovsk Mine of JSC Apatit*; Unpublished report; Archives of KSC RAS: Apatity, Russia, 2016. (In Russian)
102. Nivin, V.A. *Estimation of Ore and Country Rock Gas Content of the Plateau Rasvumchorr Deposit*; Unpublished report; Archives of KSC RAS: Apatity, Russia, 2016. (In Russian)
103. Nivin, V.A.; Pukha, V.V. *Additional Study of the Gas Content at Kurnasurt and Kedykoyrpakhk of the Lovozero Rare-Metal Deposit*; Unpublished report; Archives of KSC RAS: Apatity, Russia, 2016. (In Russian)

104. Lyutkevich, Y.M. Statement in the debate at Vsesoyuznyi meeting on the problem of oil origin. In *The Problem of Oil and Gas Origin and Conditions of Their Deposit's Formation*; Gostekhizdat: Moscow, Russia, 1960; pp. 286–289. (In Russian)
105. Guseva, A.N.; Krasil'nikova, M.P. About composition of organic matter in rocks of the Khibiny alkaline massif. *Vestnik MGU* **1960**, *2*, 68–69. (In Russian)
106. Galimov, E.M.; Petersilie, I.A. On the carbon isotope composition in hydrocarbon gases and CO<sub>2</sub> contained in alkaline igneous rocks of the Khibiny, Lovozero and Issimaussaq massifs. *Dokl. AN USSR* **1967**, *176*, 914–917. (In Russian)
107. Galimov, E.M. *Carbon Isotopes in Oil-Gas Geology*; Aeronautics and Space Administration: Washington, DC, USA, 1975.
108. Voytov, G.I. Isotope characteristics of the Khibiny spontaneous gases. *Dokl. AN USSR* **1977**, *236*, 975–978. (In Russian)
109. Voytov, G.I.; Adushkin, V.V.; Gokhberg, M.B.; Nosik, L.P.; Kucher, M.I.; Nikulina, I.V.; Pushkin, M.G.; Zhogina, L.M. About chemical and isotope instabilities of gas jets in Khibiny. *Dokl. AN USSR* **1990**, *312*, 567–571. (In Russian)
110. Nivin, V.A.; Devirts, A.L.; Lagutina, Y.P. The origin of the gas phase in the Lovozero massif based on hydrogen-isotope data. *Geochem. Int.* **1995**, *32*, 65–71.
111. Kogarko, L.N.; Kosztolanyi, C.; Ryabchikov, I.D. Geochemistry of the reduced fluid in alkali magmas. *Geochem. Int.* **1987**, *24*, 20–27.
112. Markl, G.; Marks, M.; Schwinn, G.; Sommer, H. Phase equilibrium constraints on intensive crystallization parameters of the Ilímaussaq complex, south Greenland. *J. Petrol.* **2001**, *42*, 2231–2257. [[CrossRef](#)]
113. Ryabchikov, I.D.; Kogarko, L.N. Magnetite compositions and oxygen fugacities of the Khibina magmatic system. *Lithos* **2006**, *91*, 35–45. [[CrossRef](#)]
114. Marks, M.A.; Markl, G. The Ilímaussaq alkaline complex, South Greenland. In *Layered Intrusions*; Charlier, B., Ed.; Springer Geology: Dordrecht, The Netherlands, 2015; pp. 649–691.
115. Konnerup-Madsen, J.; Kreulen, R.; Rose-Hansen, J. Stable isotope characteristics of hydrocarbon gases in the alkaline Ilímaussaq complex, South Green. *Bull. Mineral.* **1988**, *111*, 567–576.
116. Taran, Y.A.; Varley, N.R.; Inguaggiato, S.; Cienfuegos, E. Geochemistry of H<sub>2</sub>- and CH<sub>4</sub>-enriched hydrothermal fluids of Socorro Island, Revillagigedo Archipelago, Mexico. Evidence for serpentinization and abiogenic methane. *Geofluids* **2010**, *10*, 542–555. [[CrossRef](#)]
117. Burruss, R.C.; Laughrey, C.D. Carbon and hydrogen isotopic reversals in deep basin gas: Evidence for limits to the stability of hydrocarbons. *Org. Geochem.* **2010**, *41*, 1285–1296. [[CrossRef](#)]
118. Liu, Q.Y.; Dai, J.X.; Li, J.; Zhou, O.H. Hydrogen isotope composition of natural gases from the Tarim Basin and its indications of depositional environments of the source rocks. *Sci. China D Earth Sci.* **2008**, *51*, 300–311. [[CrossRef](#)]
119. Kiyosu, Y.; Krouse, H.R. Carbon isotope effect during abiogenic oxidation of methane. *Earth Planet. Sci. Lett.* **1989**, *95*, 302–306. [[CrossRef](#)]
120. Proskurowski, G.; Lilley, M.D.; Kelley, D.S.; Olson, E.J. Low temperature volatile production at the Lost City Hydrothermal Field, evidence from a hydrogen stable isotope geothermometer. *Chem. Geol.* **2006**, *229*, 331–343. [[CrossRef](#)]
121. Suda, K.; Ueno, Y.; Yoshizaki, M.; Nakamura, H.; Kurokawa, K.; Nishiyama, E.; Maruyama, S. Origin of methane in serpentinite-hosted hydrothermal systems: The CH<sub>4</sub>-H<sub>2</sub>-H<sub>2</sub>O hydrogen isotope systematics of the Hakuba Happo hot spring. *Earth Planet. Sci. Lett.* **2014**, *386*, 112–125. [[CrossRef](#)]
122. Tsunogai, U.; Kamimura, K.; Anzai, S.; Nakagawa, F.; Komatsu, D.D. Hydrogen isotopes in volcanic plumes: Tracers for remote temperature sensing of fumaroles. *Geochim. Cosmochim. Acta* **2011**, *75*, 4531–4546. [[CrossRef](#)]
123. Sherwood Lollar, B.; Voglesonger, K.; Lin, L.H.; Lacrampe-Couloume, G.; Telling, J.; Abrajano, T.A.; Pratt, L.M. Hydrogeologic controls on episodic H<sub>2</sub> release from Precambrian fractured rocks e Energy for deep subsurface life on Earth and Mars. *Astrobiology* **2007**, *7*, 971–986. [[CrossRef](#)]
124. Liu, Q.; Jin, Z.; Meng, Q.; Wua, X.; Jia, H. Genetic types of natural gas and filling patterns in Daniudi gas field, Ordos Basin, China. *J. Asian Earth Sci.* **2015**, *107*, 1–11. [[CrossRef](#)]
125. Kita, J.; Matsuo, S.; Wakita, H. H<sub>2</sub> generation by reaction between H<sub>2</sub>O and crushed rock: An experimental study on H<sub>2</sub> degassing from the active fault zone. *Geophys. Res.* **1982**, *87*, 10789–10795. [[CrossRef](#)]

126. Wiersberg, T.; Erzinger, J. Origin and spatial distribution of gas at seismogenic depths of the San Andreas Fault from drill-mud gas analysis. *Appl. Geochem.* **2008**, *23*, 1675–1690. [[CrossRef](#)]
127. Mavrogenes, J.A.; Bodnar, R.J. Hydrogen movement into and out of fluid inclusions in quartz: Experimental evidence and geologic implications. *Geochim. Cosmochim. Acta.* **1994**, *58*, 141–148. [[CrossRef](#)]
128. Taylor, H.P.; Sheppard, S.M.F. Igneous rocks I: Processes of isotopic fractionation and isotopic systematics. *Rev. Mineral.* **1986**, *16*, 227–271.
129. Sheppard, S.M.F. Characterization and isotopic variations in natural waters. *Rev. Mineral.* **1986**, *16*, 165–181.
130. Luo, M.; Huang, H.; Zhang, P.; Wu, Q.; Chen, D. Origins of gas discharging from the Qiangtang Basin in the northern Qinghai–Tibet Plateau, China: Evidence from gas compositions, helium, and carbon isotopes. *JGE* **2014**, *146*, 119–126. [[CrossRef](#)]
131. Sherwood Lollar, B.; Lacrampe-Couloume, G.; Voglesonger, K.; Onstott, T.C.; Pratt, L.M.; Slater, G.F. Isotopic signatures of CH<sub>4</sub> and higher hydrocarbon gases from Precambrian Shield sites: A model for abiogenic polymerization of hydrocarbons. *Geochim. Cosmochim. Acta* **2008**, *72*, 4778–4795. [[CrossRef](#)]
132. Suda, K.; Gilbert, A.; Yamada, K.; Yoshida, N.; Ueno, Y. Compound- and position-specific carbon isotopic signatures of abiogenic hydrocarbons from on-land serpentinite-hosted Hakuba Happo hot spring in Japan. *Geochim. Cosmochim. Acta* **2017**, *206*, 201–215. [[CrossRef](#)]
133. Lapidus, A.L.; Loktev, S.M. Present-day catalytic syntheses of hydrocarbons from carbon dioxide and hydrogen. *Zh. Vses. Khim. O-va im. D.I. Mendeleeva* **1986**, *31*, 527–532. (In Russian)
134. Ione, K.G.; Mysov, V.M.; Stepanov, V.G.; Parmon, V.N. New data on the possibility of catalytic abiogenic synthesis of hydrocarbons in the earth's crust. *Petrol. Chem.* **2001**, *41*, 159–165.
135. Chukanov, N.V.; Pekov, I.V.; Sokolov, S.V.; Nekrasov, A.N.; Ermolaeva, V.N.; Naumova, I.S. On the problem of the formation and geochemical role of bituminous matter in pegmatites of the Khibiny and Lovozero alkaline massifs, Kola Peninsula, Russia. *Geochem. Int.* **2006**, *44*, 715–728. [[CrossRef](#)]
136. Taran, Y.A.; Kliger, G.A.; Cienfuegos, E.; Shuykin, A.N. Carbon and hydrogen isotopic compositions of products of open-system catalytic hydrogenation of CO<sub>2</sub>: Implications for abiogenic hydrocarbons in Earth's crust. *Geochim. Cosmochim. Acta* **2010**, *74*, 6112–6125. [[CrossRef](#)]
137. Sinev, M.Y.; Fattakhova, Z.T.; Lomonosov, V.I.; Gordienko, Y.A. Kinetics of oxidative coupling of methane: Bridging the gap between comprehension and description. *J. Natural Gas Chem.* **2009**, *18*, 273–287. [[CrossRef](#)]
138. Nivin, V.A.; Mel'nik, N.A. Effects of radioactivity on gas-component contents in alkali igneous rocks. *Geochem. Int.* **1990**, *27*, 94–97.
139. Lin, L.-H.; Slater, G.F.; Sherwood Lollar, B.; Lacrampe-Couloume, G.; Onstott, T.C. The yield and isotopic composition of radiolytic H<sub>2</sub>, a potential energy source for the deep subsurface biosphere. *Geochim. Cosmochim. Acta* **2005**, *69*, 893–903. [[CrossRef](#)]
140. Dzaugis, M.E.; Spivack, A.J.; Dunlea, A.G.; Murray, R.W.; D'Hondt, S. Radiolytic hydrogen production in the subseafloor basaltic aquifer. *Front. Microbiol.* **2016**, *7*, 76. [[CrossRef](#)]
141. Levashkevich, V.G. Principles of Geothermal Field Distribution at the Marginal East European Platform. Doctor of Sciences (Geol.-Miner.) Dissertation, Institute of Geochemistry and Geophysics, Minsk, Belarus, 2006; p. 332. (In Russian)
142. Kozyrev, A.A.; Semenova, I.E.; Zemtsovskiy, A.V. Investigation of geomechanical features of the rock mass in mining of two contiguous deposits under tectonic stresses. *Proc. Engin.* **2017**, *191*, 324–331. [[CrossRef](#)]
143. Cherskii, N.V.; Tsarev, V.P.; Soroko, T.I.; Kuznetsov, O.L. *Influence of Tectonic Seismic Processes on the Formation and Accumulation of Hydrocarbons*; Nauka: Novosibirsk, Russia, 1985. (In Russian)
144. Hirose, T.; Kawagucci, S.; Suzuki, K. Mechanoradical H<sub>2</sub> generation during simulated faulting: Implications for an earthquake-driven subsurface biosphere. *Geophys. Res. Lett.* **2011**, *38*, L17303. [[CrossRef](#)]
145. McMahon, S.; Parnell, J.; Blamey, N.J.F. Evidence for seismogenic hydrogen gas, a potential microbial energy source on Earth and Mars. *Astrobiology* **2016**, *16*, 690–702. [[CrossRef](#)]
146. Ikorsky, S.V.; Nivin, V.A. *Study of the Localization, Setting and Scales of Natural Combustible Gas Emissions at the Mines of Lovozero GOK*; Unpublished report; Archives of KSC RAS: Apatity, Russia, 1985. (In Russian)

