

A reassessment of models for hydrocarbon generation in the Khibiny nepheline syenite complex, Kola Peninsula, Russia

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Abstract

Although hydrocarbon-bearing fluids have been known from the alkaline igneous rocks of the Khibiny intrusion for many years, their origin remains enigmatic. A recently proposed model of post-magmatic hydrocarbon (HC) generation through Fischer-Tropsch (FT) type reactions suggests the hydration of Fe-bearing phases and release of H₂ which reacts with magmatically derived CO₂ to form CH₄ and higher HCs. However, new petrographic, microthermometric, laser Raman, bulk gas and isotope data are presented and discussed in the context of previously published work in order to reassess models of HC generation. The gas phase is dominated by CH₄ with only minor proportions of higher hydrocarbons. No remnants of the proposed primary CO₂-rich fluid are found in the complex. The majority of the fluid inclusions are of secondary nature and trapped in healed microfractures. This indicates a high fluid flux after magma crystallisation. Entrapment conditions for fluid inclusions are 450–550 °C at 2.8–4.5 kbar. These temperatures are too high for hydrocarbon gas generation through the FT reaction. Chemical analyses of rims of Fe-rich phases suggest that they are not the result of alteration but instead represent changes in magma composition during crystallisation. Furthermore, there is no clear relationship between the presence of Fe-rich minerals and the abundance of fluid inclusion planes (FIPs) as reported elsewhere. $\delta^{13}\text{C}$ values for methane range from –22.4‰ to –5.4‰, confirming a largely abiogenic origin for the gas. The presence of primary CH₄-dominated fluid inclusions and melt inclusions, which contain a methane-rich gas phase, indicates a magmatic origin of the HCs. An increase in methane content, together with a decrease in $\delta^{13}\text{C}$ isotope values towards the intrusion margin suggests that magmatically derived abiogenic hydrocarbons may have mixed with biogenic hydrocarbons derived from the surrounding country rocks.

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1. Introduction

The discovery of significant volumes (about 28.5 cm³/kg) of hydrocarbon (HC) gas in the Khibiny alkaline complex in the late 1950s (Petersilie, 1960;

Petersilie et al., 1961; Petersilie, 1962; Petersilie and Sørensen, 1970) generated much interest in the possibility of natural gas resources being stored in igneous rocks. As magmatic fluids are commonly CO₂- and H₂O-rich, the reduced composition of the gas phase led to a plethora of models for their origin or genesis (see review of Potter and Konnerup-Madsen, 2003). In principle, hydrocarbon gases in igneous rocks can have

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either a biogenic or an abiogenic origin. Biogenic hydrocarbons in alkaline and other igneous rocks may simply be derived from an organic source in the surrounding country rocks (Whitcar, 1999). The organic matter would be thermally metamorphosed during pluton emplacement and incorporated as thermogenic methane into the magma system. Alternatively, it could have been flushed into the pluton by convective flow of meteoric fluids at a late stage of magmatism (Schutter, 2003), or even later. Three main hypotheses have been proposed to account for the formation of abiogenic hydrocarbons:

- (1) Methane and higher hydrocarbons present in the mantle could be incorporated into magmas during mantle melting (Petersilie et al., 1961; Gold, 1979; Sugisaki and Mimura, 1994). These hydrocarbons may have been preserved in the mantle since the early accretion of the Earth or may have formed by reduction of CO and CO₂ under mantle conditions.
- (2) Hydrocarbons in igneous rocks could be the result of late magmatic respeciation of a primary CO₂–H₂O-bearing fluid (Konnerup-Madsen et al., 1985).
- (3) Post-magmatic mineral-fluid reactions involving the Fischer-Tropsch (FT) synthesis can cause the production of methane and higher hydrocarbons through reduction of magmatic CO₂ during reaction with H₂ produced by hydration of Fe-rich phases at 350 to 400 °C and 0.5 to 2 kbar pressure (Salvi and Williams-Jones, 1997; Potter et al., 2004). FT reactions have also been cited as driving mechanism for hydrocarbon generation at mid ocean ridges where H₂ production results from serpentinisation (e.g. Charlou et al., 1998).

A number of recent papers have highlighted the role of the FT reaction in generating methane and higher hydrocarbons in alkaline igneous rocks (e.g. Salvi and Williams-Jones, 1997; Potter et al., 2004). This model is an elegant one and explains many features of the rock-fluid system in alkaline igneous rocks. However, a number of ambiguities remains that need to be resolved. In this paper, fluid inclusion, petrographic and gas composition data from different rock types of the Khibiny intrusion are presented along with previously published data (e.g. Petersilie, 1962; Galimov, 1973; Voitov, 1992; Potter, 2000; Potter and Konnerup-Madsen, 2003). We highlight data which suggest that the FT reaction may not be as important as previously suggested and reassess existing models in the context of our new data. Earlier studies on the Khibiny pluton (e.g.

Galimov, 1973; Voitov, 1992; Nivin et al., 2005) tended to concentrate on atypical parts of the complex, including the apatite ores and pegmatites of the Central Arch region and the carbonatite body in the eastern part of the complex. Here we concentrate on common rock types that make up most of the Khibiny complex.

2. Geology and occurrence of hydrocarbons at Khibiny

The Khibiny pluton was emplaced during the Devonian (Kramm and Sindern, 2004) synchronously with subsidence of the NE–SW trending Khibiny-Kontozero-Graben. It is the largest apatitic, nepheline syenite body in the Kola Alkaline Province with an exposed area of about 1330 km². It has a ring-shaped structure (Fig. 1) that comprises several phases of emplacement (Kogarko, 1995) and is divided into two, approximately equal, parts by a ring like structure known as the Central Arch. In general, Khibiny consists of a variety of nepheline syenites (khibinite, rischorrite, lujavrite and foyaite), foidolites (ijolite and urtite) and minor alkali syenite plus a small carbonatite stock. Their unusual names are mostly historical and related to arbitrary textural criteria and moderate chemical variations. Khibiny is famous for hosting the World's largest apatite deposits, which are apatite-nepheline-ores concentrated around the central ring and also famous for its diverse minor and accessory minerals, which include eudialyte, titanite and astrophyllite (Yakovenchuk et al., 1999).

Hydrocarbons are present in Khibiny as bitumen, as free gases and as occluded gases in fluid inclusions (Nivin et al., 2005 and references therein). The presence of bitumen in pore spaces and mineral inclusions within nepheline was first reported by Petersilie (1962). Sokolov and Chukanov (in press) describe solid organic substances as a common component of the peralkaline rocks and related pegmatites in Khibiny. The occurrence of free gas leads to continued seepage of methane into mine workings (Nivin et al., 2001). It is trapped in sealed fracture systems and can be released spontaneously by erosion or drilling. Nivin (2002) recorded gas discharge rates of up to 5 l/min from single 2 m long and 40 mm diameter shot-holes.

Most studies of hydrocarbons in the Khibiny pluton have been carried out on fluid inclusions as they present the best-preserved data source. They are mainly trapped as secondary inclusions along healed microcracks and are consistently described as being methane-dominated (e.g. Kogarko et al., 1987; Potter and Konnerup-Madsen, 2003). A more detailed description of these inclusions is given below.

3. Methods

For this study, 60 samples of different rock types from surface outcrops throughout the pluton were collected and located by GPS. In earlier studies (e.g. [Potter et al.,](#)

1998) archived material was used of which the exact sampling locations were unknown.

Polished thin sections were prepared for petrological and microprobe analysis. Major element compositions were determined using Oxford Instruments ISIS EDS

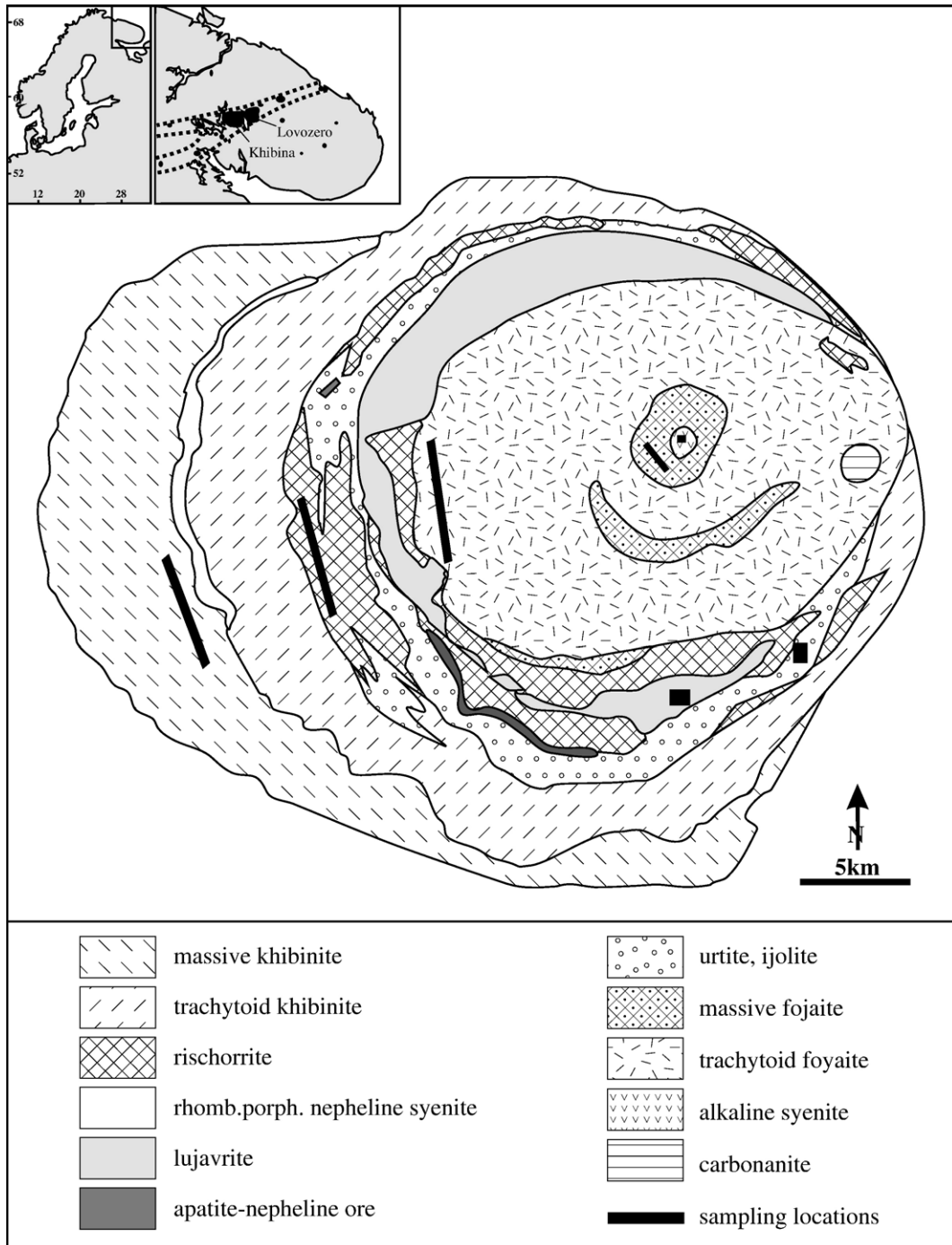
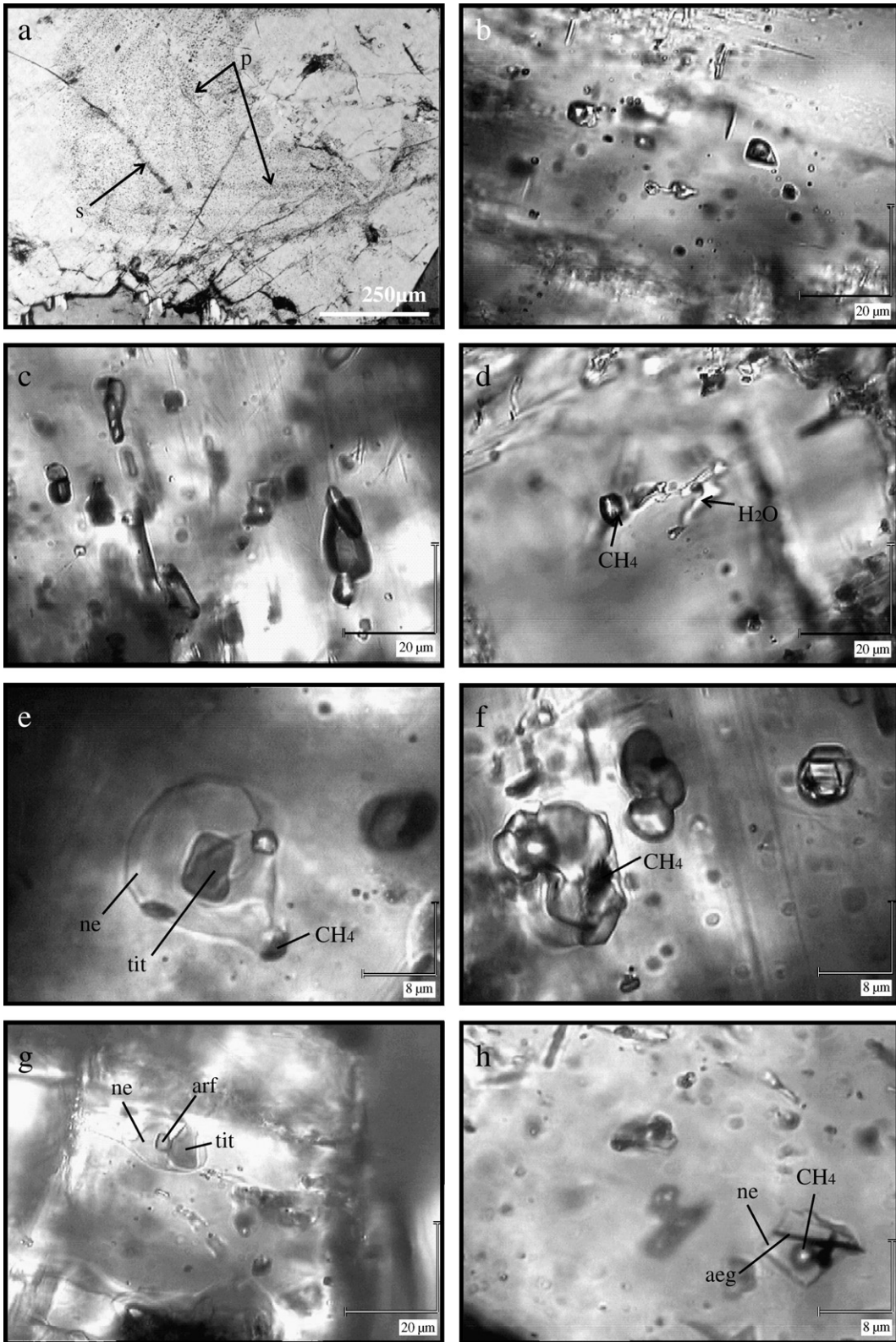


Fig. 1. Simplified geological map of the Khibiny pluton. Samples described here were mostly collected along traverses (bold black lines) or at separate sampling locations (black squares).



mounted on a JEOL 6310 SEM at Kingston University, and a Cameca SX50 WDS microprobe at the Natural History Museum, London.

Doubly polished wafers of 100–150 μm thickness were prepared for microthermometric and laser Raman microprobe analysis of fluid inclusions. A confocal, multichannel Renishaw laser Raman microprobe RM 1000 with a 514 nm Argon laser and a thermoelectrically cooled CCD detector system was used to determine the composition of the fluid inclusions. The system was attached to an Olympus microscope with lens magnification of $\times 100$ and analytical spot size of 1–3 μm^2 . To correct instrumental drift, silicon and diamond standards were used for regular calibration. The peak positions obtained were reproducible within a range of $\pm 1 \text{ cm}^{-1}$. Fluid inclusion microthermometric analyses were carried out using a Linkam THMS 600 low-temperature heating–freezing-stage attached to an Olympus microscope. Measurements were carried out between -196 and $600 \text{ }^\circ\text{C}$ following the procedure described in Shepherd et al. (1985). The stage was regularly calibrated using the triple point of methane ($-182.5 \text{ }^\circ\text{C}$) in natural fluid inclusions (Beeskov et al., 2005) and the melting point of CO_2 ($-56.6 \text{ }^\circ\text{C}$) in synthetic fluid inclusions. The reproducibility was within $\pm 0.2 \text{ }^\circ\text{C}$.

Gas chromatographic analyses of the hydrocarbons were carried out at the Kola Science Centre, Apatity, Russia based on the method described by Ikorsky (1999). 1 g of handpicked sample material with the grain size range 0.63–0.25 mm was analysed. Prior to analysis, the samples were flushed with helium and crushed on-line in a vibrating ball mill. The helium carrier gas was passed through the mill again after sample crushing and the gas mixture (extracted gas and helium) was sent to the gas chromatograph column for separation and measurements. The composition was calculated by chromatogram peak area estimation.

Isotope data were obtained at the stable isotope laboratory at the University of Lausanne. To release the methane contained in fluid inclusions, the samples were crushed off-line in a vacuum system by hand, using the “pepper-mill” technique of Simon (2001). The mill and interior of the extraction system was previously cleaned with a solution of ultrapure, distilled dichloromethane and subsequently dried at $110 \text{ }^\circ\text{C}$. Gas sampling was performed using a gas-tight syringe and the carbon isotope

composition of the saturated hydrocarbons was measured using a Hewlett-Packard 6890 gas chromatograph coupled to a Thermoquest/Finnigan MAT Delta S isotope ratio mass spectrometer via a combustion interface III under a continuous helium flow (Freedman et al., 1988; Hayes et al., 1990). The GC was operated with a CarboxenTM 1006 PLOT capillary column (30 m \times 0.53 mm internal diameter) for the analysis of CH_4 and CO_2 and a Paraplot Q-HT column for the analysis of higher hydrocarbons, plus helium as carrier gas (linear flow velocity 3 ml/s). After an initial period of 5 min at $35 \text{ }^\circ\text{C}$, the column was heated to $100 \text{ }^\circ\text{C}$ at $20 \text{ }^\circ\text{C}/\text{min}$ followed by an isothermal period of 20 min, and later heated to $220 \text{ }^\circ\text{C}$ at $20 \text{ }^\circ\text{C}/\text{min}$ and held there for 5 min. The samples were injected at $230 \text{ }^\circ\text{C}$. The CuO/NiO/Pt combustion reactor was set at $960 \text{ }^\circ\text{C}$. The performance of the GC/C/IRMS system, including the GC and combustion furnace, was evaluated every 10 analyses by injection of methane and carbon dioxide of known $\delta^{13}\text{C}$ values. The analytical reproducibility, tested by daily replicate analysis of a laboratory standard gas mix is $\pm 0.5\%$.

4. Analytical data

4.1. Petrology and distribution of fluid inclusions in relationship to mineral assemblage and rock type

A major aim of the present study is to test the potential relationships between fluid inclusion population and altered Fe-rich phase assemblages. The main reaction textures associated with the Fe-bearing phases are: fine-grained lorenzenite and aegirine aggregates around aenigmatite; intergrowths of K-rich feldspar and nepheline around biotite; and titanite rimming ilmenite. None of the samples studied here shows evidence for development of fluid inclusion populations along with these mineral textures. There is no evidence of narrow reaction rims of biotite or/and aegirine around magnetite or of reaction rims between magnetite, titanomagnetite and nepheline (c.f. Potter, 2000).

Alkali feldspar shows a perthitic structure, developed by exsolution processes that leave Na- and K-dominated zones. Far more pronounced, however, are zones of albitisation that follow cleavage planes and microfractures in alkali feldspar. These zones are caused by an ion exchange reaction between a Na-rich fluid and alkali feldspar

Fig. 2. Typical appearance of fluid inclusions. (a) Primary fluid inclusions (p) marking growth planes of a nepheline crystal which are cross-cut by secondary fluid inclusion planes (s); (b) isolated cluster of primary mono- and two-phase inclusions; (c) primary fluid inclusions attached to aegirine micro-crysts; (d) necked-down inclusion showing the separation of a water-rich and methane-rich phase; (e–h) melt inclusions in rischorrite. The crystalline components titanite (tit), arfvedsonite (arf), aegirine (aeg), nepheline (ne) and gaseous methane are identified by laser Raman spectroscopy and labelled. All other phases are unknown. Note, the inclusions are hosted in nepheline, therefore the detected nepheline phase within the inclusion might result from scattering of the host mineral.

Table 1
Bulk gas data from the extracted gas of the Khibiny intrusion

Rock type	Sample	CH ₄ cm ³ /kg	C ₂ H ₄ cm ³ /kg	C ₂ H ₆ cm ³ /kg	C ₃ H ₆ cm ³ /kg	C ₃ H ₈ cm ³ /kg	i-C ₄ H ₁₀ cm ³ /kg	α-C ₄ H ₈ cm ³ /kg	n-C ₄ H ₁₀ cm ³ /kg	Σβ-C ₄ H ₈ cm ³ /kg
Khibinite	Kh-03-1	17.10	–	0.730	–	0.075	0.0060	–	0.0150	0.0010
Khibinite	Kh-03-2	13.80	–	0.340	–	0.024	0.0020	–	0.0049	0.0003
Khibinite	Kh-03-3	22.50	–	0.400	0.004	0.035	0.0033	–	0.0069	0.0008
Khibinite	Kh-03-4	36.20	–	1.200	0.007	0.150	0.0120	0.0002	0.0280	0.0017
Khibinite	Kh-03-5	10.90	–	0.650	0.001	0.060	0.0043	–	0.0130	0.0008
Khibinite	Kh-03-6	17.70	–	0.570	0.002	0.056	0.0042	–	0.0088	0.0006
Khibinite	Kh-03-7	12.10	–	0.730	–	0.042	0.0024	–	0.0100	0.0005
Khibinite	Kh-03-8	11.70	–	0.460	0.001	0.038	0.0031	–	0.0087	0.0004
Rischorrite	Kh-03-9	5.97	–	0.950	0.002	0.110	0.0084	–	0.0250	0.0019
Rischorrite	Kh-03-10	32.40	–	1.070	0.005	0.079	0.0063	–	0.0170	0.0014
Rischorrite	Kh-03-11	11.30	–	0.190	0.001	0.012	0.0007	–	0.0026	–
Rischorrite	Kh-03-13	13.90	–	0.580	0.001	0.064	0.0060	–	0.0150	0.0008
Rischorrite	Kh-03-14	4.98	–	0.100	0.001	0.005	0.0003	0.0002	0.0012	–
Rischorrite	Kh-03-42	30.40	–	0.420	0.001	0.026	0.0016	–	0.0050	0.0004
Rischorrite	Kh-03-43	5.40	–	0.100	0.000	0.006	0.0004	–	0.0010	–
Rischorrite	Kh-03-44	98.50	–	3.300	–	0.280	0.0290	0.0015	0.0780	0.0054
Rischorrite	Kh-03-45	0.04	–	0.002	0.001	0.000	–	–	–	–
Rischorrite	Kh-03-48	11.50	–	0.350	0.002	0.024	0.0014	–	0.0042	0.0003
Rischorrite	Kh-03-49	1.10	–	0.018	0.002	0.001	0.0000	0.0003	0.0003	–
Rischorrite	Kh-03-50	0.04	–	0.001	0.001	0.000	–	–	–	–
Trachytoid foyaite	Kh-03-46	16.10	–	0.570	0.002	0.035	0.0025	b.d.	0.0095	0.0004
Trachytoid foyaite	Kh-03-35	4.22	–	0.081	0.002	0.006	0.0005	0.0002	0.0014	–
Trachytoid foyaite	Kh-03-36	0.34	–	0.006	0.001	0.001	0.0000	–	–	–
Trachytoid foyaite	Kh-03-37	5.10	–	0.120	0.004	0.007	0.0003	0.0001	0.0010	–
Trachytoid foyaite	Kh-03-38	2.77	–	0.057	–	0.003	0.0002	–	0.0004	–
Trachytoid foyaite	Kh-03-39	1.30	–	0.026	0.000	0.002	0.0001	–	0.0002	–

Trachytoid foyaite	Kh-03-40	0.12	–	0.001	0.001	0.000	–	–	–	–
Trachytoid foyaite	Kh-03-41	2.87	–	0.093	0.003	0.008	0.0004	0.0002	0.0012	0.0001
Massive foyaite	Kh-03-51	0.01	0	0.001	0.001	0.000	–	–	–	–
Massive foyaite	Kh-03-52	8.46	–	0.140	0.002	0.008	0.0004	0.0005	0.0019	0.0001
Massive foyaite	Kh-03-53	4.60	–	0.083	0.001	0.004	0.0002	0.0002	0.0007	0.0001
Massive foyaite	Kh-03-54	11.90	–	0.330	0.002	0.025	0.0016	0.0001	0.0042	0.0001
Massive foyaite	Kh-03-55	1.44	–	0.017	0.002	0.002	0.0002	0.0002	0.0005	–
Alkaline syenite	Kh-03-56	0.02	–	0.001	0.001	–	–	–	–	–
Alkaline syenite	Kh-03-57	0.01	–	–	–	–	–	–	–	–
Alkaline syenite	Kh-03-58	0.02	0.0004	0.002	0.001	0.000	–	–	–	–
Alkaline syenite	Kh-03-59	0.01	0.0004	0.002	0.002	0.001	–	–	–	–
Alkaline syenite	Kh-03-60	0.02	0.0003	0.002	0.001	0.000	–	–	–	–
Ijolite	Kh-03-61	21.20	–	0.860	–	0.066	0.0059	0.0002	0.0110	0.0007
Ijolite	Kh-03-62	5.99	–	0.360	–	0.023	0.0028	0.0001	0.0054	0.0003
Ijolite	Kh-03-63	38.20	–	1.480	–	0.230	0.0260	0.0001	0.0480	0.0046
Ijolite	Kh-03-64	29.90	–	1.380	–	0.180	0.0230	–	0.0400	0.0040
Ijolite	Kh-03-65	50.10	–	1.640	–	0.120	0.0150	0.0008	0.0370	0.0025
Ijolite	Kh-03-66	43.80	–	2.030	–	0.180	0.0260	0.0009	0.0450	0.0053
Ijolite	Kh-03-67	40.20	–	1.960	–	0.180	0.0230	0.0002	0.0420	0.0035
Ijolite	Kh-03-68	20.60	–	0.810	–	0.079	0.0071	–	0.0140	0.0007
Ijolite	Kh-03-69	13.30	–	0.450	–	0.043	0.0037	–	0.0110	0.0004
Ijolite	Kh-03-70	0.03	–	0.000	–	–	–	–	–	–
Ijolite	Kh-03-71	4.18	–	0.160	0.001	0.016	0.0014	0.0002	0.0030	0.0002
Ijolite	Kh-03-72	2.20	–	0.075	–	0.006	0.0003	–	0.0007	–
Ijolite	Kh-03-73	1.85	–	0.060	0.001	0.003	0.0002	–	0.0004	–
Ijolite	Kh-03-74	4.46	–	0.150	0.001	0.010	0.0007	0.0003	0.0030	0.0001
lujavrite	Kh-03-17	0.94	–	0.040	–	0.002	0.0001	–	0.0003	–
lujavrite	Kh-03-18	1.05	–	0.043	0.001	0.003	0.0002	–	0.0004	–
lujavrite	Kh-03-19	2.59	–	0.120	–	0.007	0.0003	–	0.0010	–
lujavrite	Kh-03-20	3.58	–	0.130	–	0.006	0.0003	–	0.0011	–
lujavrite	Kh-03-21	2.83	–	0.046	–	0.001	–	–	0.0002	–
lujavrite	Kh-03-22	9.85	–	0.160	–	0.007	0.0004	–	0.0015	–

along cleavages or cracks (Orville, 1963; Brown and Parsons, 1994). This type of alteration is ubiquitous in the Central Arch (Nivin et al., 2005).

4.2. Fluid and melt inclusion study

The majority of fluid inclusions are hosted in nepheline, feldspar and eudialyte. Primary inclusions occur in arrays parallel to growth zones in nepheline and have diameters of up to 5 μm (Fig. 2a). Larger primary inclusions, between 10 and 20 μm in diameter, are found in separate clusters, mainly in nepheline (Fig. 2b). These are mono-phase CH_4 -rich and two-phase CH_4 – H_2O -rich fluid inclusions. A third group of primary fluid inclusions is attached to small aegirine needles (Fig. 2c). They are mono-phase, CH_4 -dominated inclusions with a diameter of 5–15 μm .

The majority of fluid inclusions in the Khibiny rocks are secondary. They were trapped after the rock body cooled and indicate a high level of post-magmatic fluid movement. They are mainly present in fluid inclusion planes (FIPs) and are most common in nepheline crystals but also occur along cleavage planes in feldspar. The FIPs represent healed microcracks and predominantly start and terminate at grain boundaries. Small FIPs start and terminate within mineral grains. Longer FIPs cross-cut several mineral grains and are often aligned sub-parallel to each other. Fluid inclusions in the FIPs vary in size between 5 and 20 μm with a well rounded, elongate or even tabular shape. The majority (c. 90%) of inclusions are mono-phase and methane-dominated. About 10% of the population are two-phase fluid inclusions and consist of a methane-rich gas bubble and brine. There is evidence for necking down with methane and water phase separated into disconnected mono-phase inclusions (Fig. 2d) or two-phase inclusions with different degrees of filling. The water-rich phase was probably commonly consumed during secondary mineral growth, leaving the pure methane phase behind.

Multi-solid inclusions are present in some of the samples studied (Fig. 2e–h). They contain variable proportions of arfvedsonite, titanite, aegirine and nepheline as determined by laser Raman spectroscopy together with unidentified, Raman-inactive phases. We interpret these to be silicate melt inclusions. Some of them contain methane-dominated gas bubbles. Observations of homogenisation temperature were not possible due to a strong degradation, cracking and darkening of the nepheline host at temperatures above 500 $^{\circ}\text{C}$.

4.3. Laser Raman spectroscopy and microthermometry

Primary and secondary fluid inclusions are compositionally similar in terms of microthermometric and

laser Raman data. The majority of the mono-phase fluid inclusions analysed by laser Raman spectroscopy show a methane peak at between 2911 and 2915 cm^{-1} . Low concentrations of ethane and propane have been identified with peak positions of 2954 and 2890 cm^{-1} , respectively. In two-phase inclusions, a broad water peak at c. 3400 cm^{-1} was recorded in the liquid phase, the gas bubbles gave strong methane peaks. No free hydrogen was detected in the fluid inclusions using the laser Raman technique. A broad shoulder, the result of fluorescence produced by the host minerals, was present at higher wavelengths and might have swamped the hydrogen signal.

The inclusions mostly display H1 behaviour as defined by Van den Kerkhof (1988). Homogenisation temperatures of the mono-phase inclusions range from -98 to -62 $^{\circ}\text{C}$. This variation indicates the presence of impurities such as higher hydrocarbons. Most of the methane-dominated inclusions homogenise to vapour, indicating high molar volumes. The homogenisation temperatures of two-phase H_2O – CH_4 inclusions range from 350 to >500 $^{\circ}\text{C}$. Measurements at higher temperatures were not possible due to degradation of the host mineral. The approximate temperatures of first ice melting (-70 to -40 $^{\circ}\text{C}$), hydrohalite melting (-38 to -17 $^{\circ}\text{C}$) and last ice melting (-17 to -1.5 $^{\circ}\text{C}$) indicate a wide salinity range. The aqueous inclusions contain brine with 5 to 20 wt.% salt.

4.4. Bulk gas data

Gas analyses were carried out at the Kola Science Centre, Apatity, Russia on samples of different rock types in order to identify the amount and composition of gases stored in the rocks of the Khibiny complex. CH_4 is the dominant species with concentrations of up to 100 cm^3/kg rock. Higher hydrocarbons are recorded up to C_4 . Their concentrations decrease exponentially with increasing carbon number (Table 1). The results are consistent with laser Raman data where the majority of fluid inclusions contain CH_4 and small proportions of ethane and propane and are similar to those reported in the literature. Other minor volatiles reported in the literature (e.g. Petersilie et al., 1961; Petersilie and Sørensen, 1970; Kogarko et al., 1987; Potter and Konnerup-Madsen, 2003) are CO_2 , CO , H_2 and N_2 .

A comparison of bulk gas data with mineralogy reveals no strong relationship between Fe-rich mafic mineral content and gas content (Fig. 3a). However, there is a positive correlation between bulk gas content and nepheline content (Fig. 3b). This is because nepheline is the most suitable host for fluid inclusions.

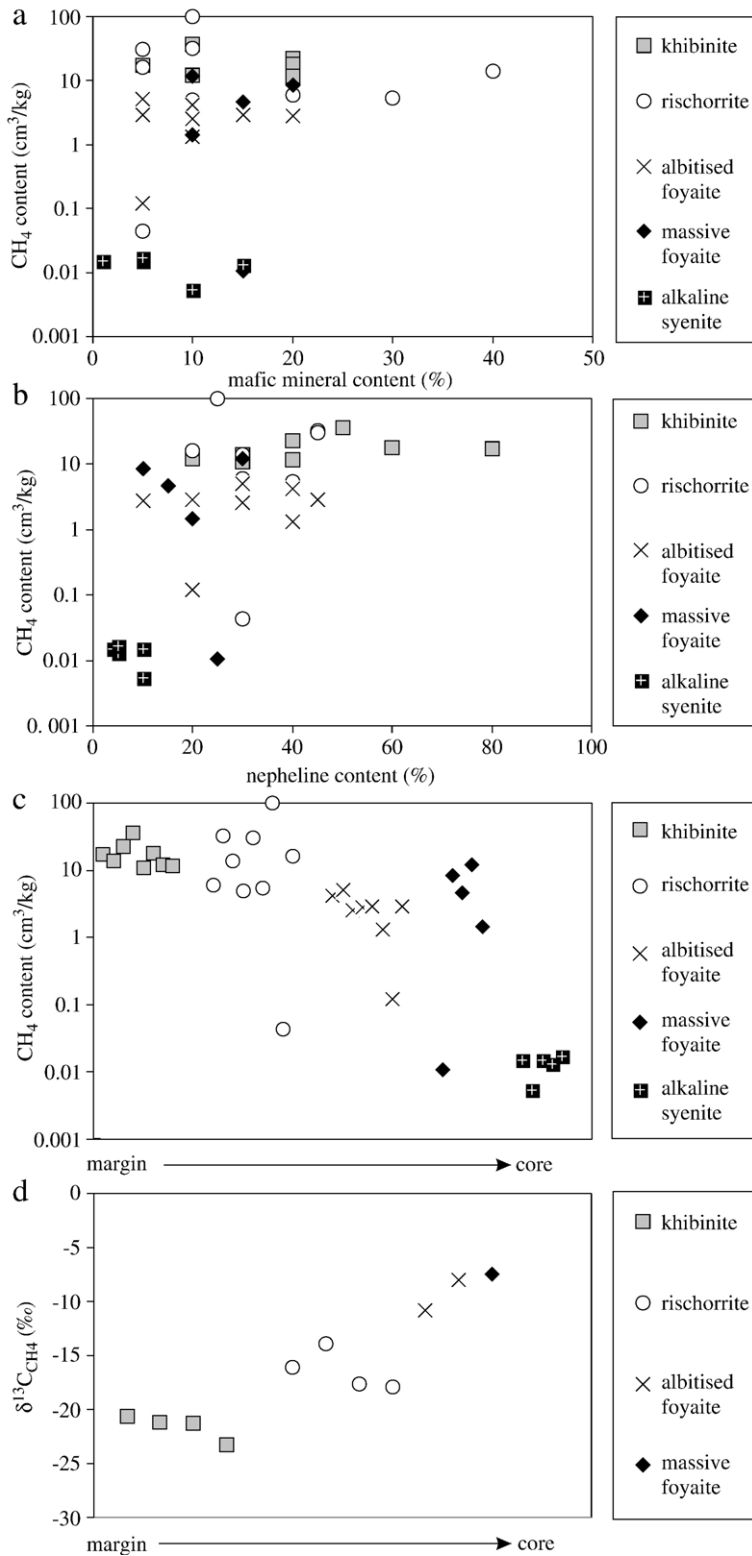


Fig. 3. Methane distribution versus (a) modal distribution of mafic minerals (b) modal distribution of nepheline which is the predominant host mineral for the inclusions and (c) the sampling location from the margin of the complex towards the core. (d) Variation of $\delta^{13}\text{C}$ signatures from the margin of the complex (khibinite) towards the core (foyaite).

Table 2
A summary of published isotope data for the gases of the Khibiny pluton

Publisher	$\delta^{13}\text{C}_{\text{bulk C}}$	$\delta^{13}\text{C}_{\text{CH}_4}$	$\delta^{13}\text{C}_{\text{C}_2\text{H}_6}$	$\delta^{13}\text{C}_{\text{C}_3\text{H}_8}$	$\delta^{13}\text{C}_{\text{CO}_2}$	$\delta\text{D}_{\text{CH}_4}$	Minerals or rocks analysed/location
Galimov and Petersilie (1967)		-3.2					Khibinite
			-12.8				Urtite
			-8.4				Ijolite
			-14.6			-8.5	Fsp from pegmatite
			-8.4			+10.6	Eud from pegmatite
			-13.2				Trachitoid khibinite
			-11.8				Ijolite-urtite
			-19.3				Ijolite-urtite
			-18.2				Ijolite-urtite
			-16.3				Ijolite-urtite
			-19.1				Ijolite-urtite
Galimov (1973)	-7.9						Ne in pegmatite in trachytoid khibinite
	-8.1						Ne in pegmatite in trachytoid khibinite
	-4.6						Eud in pegmatite in middle-grained ne syenite
	-4.3						Ne in pegmatite in middle-grained ne syenite
	-6.1						Aenig in pegmatite in middle-grained ne syenite
	-11.4						Ne with aeg in pegmatite in middle grained ne syenite
	-8.1						Eud in pegmatite in middle grained ne syenite
	-5.3						Ne in pegmatite in titanite foyaite
	-9.2						Ne in pegmatite in rischorrite
	-6.2						Ne in pegmatite in ijolite-urtite
			-12.8	-24.5	-26		
		-3.2	-9.1	25.7			Khibinite
		-7.9	-14.2				

Yerokhin (1978)	-6.5		-82	Eudialyte
	-6.5		-66	
Khitarov et al. (1979)	-10.6	-23.9		Rasvumchorr mine, hole 7, 1967
	-6.5	-11.7		Rasvumchorr mine, hole 7, 1975
Voitov et al. (1990)	-16.5 to -7.7			Rasvumchorr mine
		-12.1		Rasvumchorr mine
		-24		Rasvumchorr mine
	-11.2	-15.6		Rasvumchorr mine
Voitov (1992)			-72	Rasvumchorr mine, hole 7, February 1975, D in CH ₄
			-56	Rasvumchorr mine, hole 7, March 1975, D in CH ₄
			-144	Rasvumchorr mine, hole 7, February 1975; D in C ₂ H ₆
			-173	Rasvumchorr mine, hole 7, March 1975; D in C ₂ H ₆
	-8.7			Rasvumchorr mine, hole 360, August 1986
	-11.2	-15.6		Rasvumchorr mine, hole 360, August 1986
Potter (2000)	-11.44			Urtite, sample 1253-153
	-13.17			Urtite, sample 1253-153
	-8.3			Urtite, sample 1253-153
	-3.28			Urtite, sample 1253-153
	-25.33			Urtite, sample 145-P-85
	-17.82			Urtite, sample 145-P-85
	-12.34			Urtite, sample 145-P-85
			-7.26	Carbonatite, sample Kh28
			-5.58	Carbonatite, sample Kh28
			-3.84	Carbonatite, sample Kh28

The results are given in the standard δ -notation, expressed relative to VPDB and VSMOW in permil (‰).

Table 3
Isotope data for the gases of the Khibiny pluton from this study

Rock type	Sample	$\delta^{13}\text{C}_{\text{CH}_4}$	$\delta^{13}\text{C}_{\text{C}_2\text{H}_6}$	$\delta^{13}\text{C}_{\text{C}_3\text{H}_8}$	$\delta^{13}\text{C}_{\text{C}_4\text{H}_{10}}$	$\delta^{13}\text{C}_{\text{C}_5\text{H}_{12}}$	$\delta^{13}\text{C}_{\text{CO}_2}$
Khibinite	KH-03-03	-22.4					-15.5
Khibinite	KH-03-03						-14.9
Khibinite	KH-03-04		-18.7	-18.0	-18.7		
Rischorrite	KH-03-10	-12.6					-16.8
Rischorrite	KH-03-42	-14.4	-17.1	-17.3	-17.5		-15.4
Rischorrite	KH-03-44		-18.9	-19.2	-19.7		
Rischorrite	KH-03-46	-13.3	-19.2	-18.9	-19.4		-13.9
Trachytoid foyaite	KH-03-35	-7.4					-13.7
Trachytoid foyaite	KH-03-37	-8.0	-17.5	-19.6			-13.6
Massive foyaite	KH-03-54	-5.4	-14.3	-13.0	-13.2	-14.0	-13.7
Ijolite	KH-03-68	-10.8					-15.2
	Mean	-11.9	-17.6	-17.7	-17.7	-14.0	-14.7
	Range	-22.4 to -5.2	-19.2 to 14.3	-19.6 to 13	-19.7 to -13.2	-14.0	-16.8 to -13.6

The results are given in the standard δ -notation, expressed relative to VPDB in permil (‰).

Therefore, it is likely that the presence of a suitable host mineral for fluid inclusions is more important than the presence of Fe-rich catalyst phases in controlling the bulk gas content in a sample.

The methane content in the samples analysed in this study is highest in the outer, marginal rocks and decreases inwards to very low levels in the core of the complex (Fig. 3c). This is broadly in agreement with the data of Ikorsky (1977) although not with that of Nivin et al. (2005) who report the presence of high post-magmatic fluid fluxes within the Central Arch complex. On the basis of our data, it is likely that a trend of decreasing methane content inward from the margin of the pluton is overprinted by late-stage gas fluxes through the Central Arch. As rock types change towards the core of the intrusion, a number of reasons may explain this observation. These include variations in the modal proportion of those phases most

likely to host CH_4 in fluid inclusions; variations in the modal proportions of Fe-rich phases that may catalyse the FT reaction; variations in permeability permitting access of H_2O ; or, if the methane is not generated in situ, varying distance from the methane source.

4.5. Isotope data

To date, reliable isotopic data from hydrocarbon gases of the Khibiny alkaline rocks are sparse. Previous data from the hydrocarbon-bearing fluids in Khibiny including $\delta^{13}\text{C}_{\text{bulk}}$ data, $\delta^{13}\text{C}$ and δD data for CH_4 and higher HC from free and occluded gases are summarized in Table 2. Our new data from a preliminary study of different rock types show $\delta^{13}\text{C}$ values of -22.4‰ and -5.4‰ for CH_4 . In terms of their spatial distribution, an increase in $\delta^{13}\text{C}$ values from the outer towards the central part of the

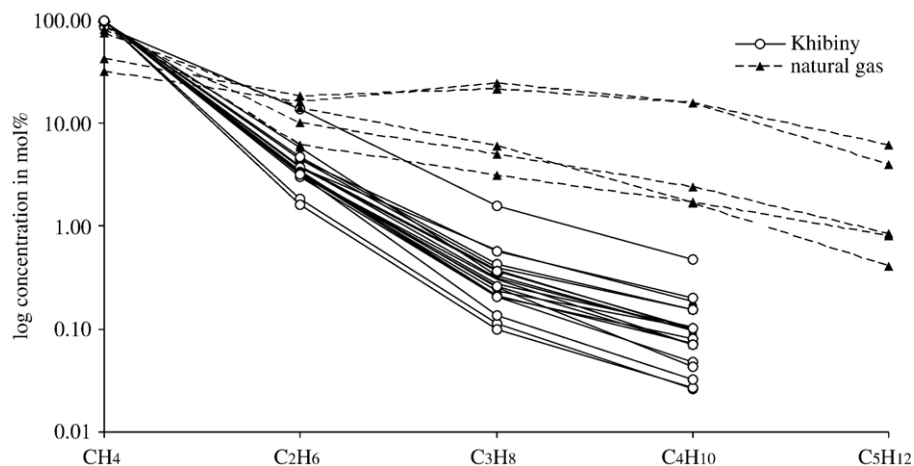


Fig. 4. Log normalised abundance (in mol%) of CH_4 and higher hydrocarbons in the gas phase of the Khibiny complex plotted versus increasing carbon number. For comparison the distribution of a natural gas sample of biogenic origin is shown (from Prinzhofer and Huc, 1995).

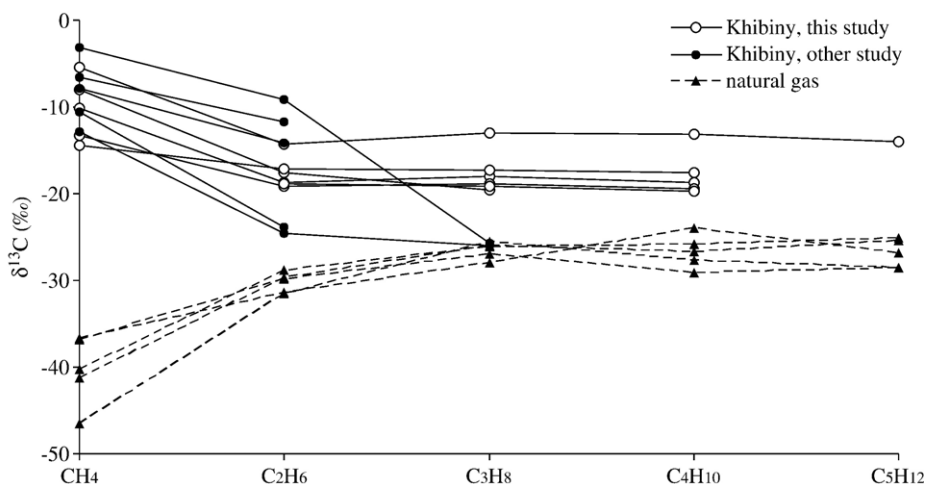


Fig. 5. Isotope distribution of methane and higher hydrocarbons of gas extracted from the Khibiny pluton (Galimov, 1973; Voitov, 1992 and this study) compared with data from natural gas samples (Prinzhofer and Huc, 1995).

complex has been observed (Fig. 3d). Khibinite from the outer part of the complex has a $\delta^{13}\text{C}$ value of -22.4‰ , whereas foyaite from the core of the pluton contains methane with much less negative values from -8‰ to -5.4‰ . The analyses of higher hydrocarbons show a subsequent increase of $\delta^{13}\text{C}$ values with increasing carbon number (Table 3 and Fig. 5).

5. Discussion—models for methane generation in alkaline igneous rocks

Several models have been suggested for the accumulation of methane in igneous rocks. These can be grouped into biogenic and abiogenic models. Many workers (e.g. Gold, 1979; Larsen et al., 1992; Krot et al., 1994; Berndt et al., 1996; Salvi and Williams-Jones, 1997; Potter et al., 1998; Konnerup-Madsen, 2001; Markl et al., 2001; Sherwood-Lollar et al., 2002) have stressed the potential likelihood of the abiogenic evolution of methane in igneous rocks, although there remains a debate as to whether this would occur at an early-, late- or post-magmatic stage of the crystallisation history. Here, we re-evaluate various models of methane generation and assess their applicability to the Khibiny pluton.

5.1. Abiogenic origin

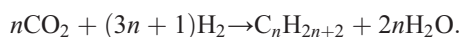
Two critical chemical criteria support an abiogenic origin for the HC gases of the Khibiny pluton. Firstly, the carbon number distribution shows a log-linear relationship between the molar amount of the alkane and its carbon number. New bulk gas data presented in this paper confirm the log-linear trend from C_1 to C_4 with concentrations

decreasing from 100 to 0.01 mol% (Fig. 4). This trend is close to that predicted by the Schulz-Flory distribution (Anderson, 1984) which is a simple statistical model that is a good indicator of an abiogenic origin of the hydrocarbons, as the higher HCs are formed via polymerisation. In contrast, biogenic alkanes have a shallower slope when plotted on the same diagram. Similar results have been found in other alkaline rock complexes such as Lovozero (Potter et al., 2004), Ilímaussaq (Konnerup-Madsen, 2001) and Strange Lake (Salvi and Williams-Jones, 1997).

Secondly, the $\delta^{13}\text{C}$ data set for methane and the higher HC from the Khibiny pluton shows values that decrease from CH_4 towards the higher homologues (Fig. 5). The systematically higher $\delta^{13}\text{C}$ values for CH_4 compared to those of the higher hydrocarbons in the same fluid samples are consistent with an inorganic polymerisation process whereby the heavier hydrocarbons are synthesised from methane (Des Marais et al., 1981). This is common in high-temperature abiogenic hydrocarbons (Voitov, 1992) and supports an abiogenic origin for the gases in the Khibiny pluton. Gas samples from a natural (biogenic) gas source would show the opposite trend, with $\delta^{13}\text{C}$ values increasing towards the higher C numbers (Prinzhofer and Huc, 1995).

5.1.1. Post-magmatic origin via Fischer-Tropsch synthesis

Hydrocarbons in alkaline rocks including the Khibiny complex could be generated by Fischer-Tropsch synthesis according to the general chemical reaction:



CH_4 is produced when $n=1$ and higher hydrocarbons when $n>1$. The H_2 needed for the reaction is probably

released by hydrothermal alteration of Fe-rich minerals (Salvi and Williams-Jones, 1997; Potter et al., 1998, 2004). However, a number of petrologic features suggest that the importance of the FT reaction in generating CH₄ and higher hydrocarbons in Khibiny may be overstated. Here we highlight a number of criteria suggesting that methane occurrence may not be the result of a simple, closed system behaviour.

5.1.1.1. The entrapment problem. It was suggested by Potter et al. (1998, 2004) that trails of CH₄-bearing fluid inclusions terminate at the margins of hydrated Fe-rich minerals as the result of hydration and associated FT reactions. This termination, or pinning, of FIPs is interpreted as the result of fracturing of the host minerals due to volume expansion of the Fe-phase. However, in the samples studied here, FIPs are a general feature of fractured rocks. They are most pronounced in nepheline and feldspar and no obvious relationship between their abundance and the presence or absence of altered Fe-rich phases has been observed. Hence, there is no strong reason to infer that they were produced during methane production by FT synthesis.

Consequently, microthermometrically derived temperatures and pressures of fluid entrapment do record conditions of fluid migration and secondary trapping, rather than those of methane generation.

5.1.1.2. The alteration problem. A number of hydrothermal reactions (not always balanced) involving the breakdown of phases such as arfvedsonite, nepheline and augite have been cited as linked to FT synthesis (Salvi and Williams-Jones, 1997; Potter and Konnerup-Madsen, 2003; Potter et al., 2004). The precise nature of the reaction chemistry is best determined by reaction textures.

Although arfvedsonite breakdown is commonly cited, we see no textural evidence to suggest that the association of arfvedsonite with aegirine is related to hydration and excessive accumulation of fluid inclusions around the mineral assemblage. We do not find aegirine rims developed around arfvedsonite, nor do we find other evidence of arfvedsonite alteration. The observed increase in Na and Fe and decrease in Mg and Ca from core to rim of arfvedsonite crystals is very typical for igneous fractionation.

Similarly, the augite breakdown reactions cited by other workers involve mineral assemblages which we have rarely found in the Khibiny massif. The reaction may well generate small amounts of methane through an FT reaction. However, the rarity of the complete reaction assemblage means that it is unlikely to have been responsible for the production of large volumes of methane in the complex. Either the reaction has not oc-

curred, or it has gone to completion almost everywhere which is unlikely. The hydration of nepheline to cancrinite (Potter et al., 1998; Potter and Konnerup-Madsen, 2003) is a potential CH₄-producing reaction. Our new, whole rock bulk gas data confirm a positive correlation between cancrinite content and methane concentration. This is most pronounced in the cancrinite-rich rischorrite sample Kh-03-44 which has a methane content of nearly 100 cm³/kg. However, there is no evidence for a large population of fluid inclusions in these samples. As basic cancrinite may be considered to be a member of the zeolite family (Hassan and Grundy, 1983) it offers a means of gas storage. Therefore, cancrinite can be considered to be a strong adsorbent that incorporates gases such as methane in their crystal structure but is not necessarily linked to CH₄-production.

In many samples methane-rich gas bubbles are attached to a small aegirine needle, mostly within a matrix of nepheline (Fig. 2c). Although this could be the result of an in situ FT reaction on aegirine, a more likely explanation for this texture is the “water glass” phenomenon where gas bubbles in an immiscible H₂O–CH₄ fluid are preferentially attached onto the surface of a small aegirine needle within the late magma/crystal-mush. This would be consistent with the presence of a methane-rich fluid in a crystallising magma and a primary origin for these fluid inclusions.

5.1.1.3. The CO₂ problem. The heterogeneous distribution of methane in the Khibiny complex could be a function of a number of factors. The presence of suitable host minerals, such as nepheline and feldspar, is an obvious control. However, if the FT reaction is the critical driver of methane generation, the distribution of methane in the complex should be related to the availability of Fe-rich minerals needed to catalyse the reaction, the supply of H₂O to drive the hydration reactions and the availability of primary CO₂ in the source rocks. The complex should thus include regions with high CH₄ concentrations, where all the “reactants” needed for FT reactions were present, as well as regions with high CO₂ concentrations where the FT reaction has not taken place, either due to the lack of anhydrous Fe-rich minerals or suitable amounts of late-stage H₂O-rich fluids. However, gas analyses from the Khibiny complex reveal fluids dominated by CH₄ with CO₂ present only in altered samples (Potter and Konnerup-Madsen, 2003) and no inverse relationship between CO₂ and CH₄ content. In fact, no evidence for a primary CO₂-rich magmatic fluid has been found, all identified primary fluid inclusions are CH₄-dominated. Finally, we stress that methane generation through the FT synthesis can only operate in an almost closed system. Too much H₂O

flux will ultimately flush out not just the CO₂ but also all the CH₄ produced. The post-magmatic methane generation from a primary CO₂-rich fluid seems therefore unlikely.

5.1.2. Early-magmatic origin from a mantle source

Methane may form inorganically at mantle conditions of >30 kbar and >1200 K from carbonate species, such as FeCO₃ or MgCO₃, in the presence of H₂O at oxygen fugacities buffered by iron-bearing phases near the wuestite–magnetite f_{O2} buffer (Scott et al., 2004). Experimental data suggest that such conditions may be widespread in the mantle and that methane at pressures of up to 1 GPa could be the dominant C-bearing fluid phase under reducing conditions in the mantle (Kenney et al., 2002). Ryabchikov et al. (1981) documented very low oxygen fugacities for rocks of mantle origin: olivines from tholeiite basalts and titanium garnets from alkali rocks. Strongly reduced conditions, compared with the crust (QFM), are also believed by Pasteris (1987) to exist in portions of the upper mantle and several studies by, amongst others, Ryabchikov et al. (1981), Eggler and Baker (1982), and Olafsson and Eggler (1983) imply that f_{O2} variations in the mantle would permit different fluid speciation in different regions or materials in the upper mantle. Hydrocarbons traced back to their mantle source have also been found in garnets from the Mir kimberlite pipe (Krot et al., 1994) and Markl et al. (2001) indicated that methane is the stable fluid phase in the low-f_{O2} asthenospheric mantle which appears to be the source of the Ilímaussaq parental melts.

On the basis of δ¹³C values of –3.2‰ to –12.8‰, Petersilie (1962) also suggested a magmatic origin for hydrocarbons in the alkaline rocks of the Khibiny pluton. He interpreted the ¹³C enrichment, similar to that in diamonds, carbonatites and CO₂ of deep-seated origin, as implying a juvenile carbon source (Petersilie and Sørensen, 1970). As an incompatible compound, primary mantle CH₄ could easily be incorporated into mantle derived magmas.

Our observations of silicate melt inclusions which contain methane bubbles (Fig. 2e–h), the attachment of primary methane-rich gas bubbles to aegirine needles (Fig. 2c), and the presence of primary fluid inclusions along growth zones in nepheline (Fig. 2a) support the hypothesis of magmatic CH₄-rich fluid.

5.1.3. Late-magmatic origin via respeciation of a C–O–H fluid

A late-magmatic origin was proposed to explain methane generation in the Ilímaussaq complex by Kon-

nerup-Madsen (2001) and in gabbroic pegmatites within the Skaergaard complex (Larsen et al., 1992). At temperatures <500 °C this involves the respeciation of a carbonic fluid in the C–O–H–graphite system (Huizenga, 2001) under magmatic conditions of QFM to QFM-3, consistent with a volatile-rich, agpaite magma. These conditions of methane generation are restricted in terms of temperature and chemical composition of the magma. As the Khibiny intrusion contains, apart from the carbonatite, only pure hydrocarbons without any trace of CO₂, it is unlikely that C–O–H-respeciation can be solely responsible for HC production throughout the complex. A further limitation of the model is that, although there is a clear mechanism for CH₄ production through respeciation, the production of the higher hydrocarbons cannot be readily explained. It is therefore unlikely to be a viable mechanism for HC generation in the Khibiny complex.

5.2. Biogenic origin

The host rocks into which the Khibiny complex was emplaced are Archaean granite gneisses and Proterozoic volcanic-sedimentary rocks (Sørensen, 1970; Kogarko, 1995). In the North and South-East the pluton intrudes into Archaean gneisses and in the South and West into the Early Proterozoic Imandra-Varzuga greenstone belt. The greenstone belt comprises an alternating sequence of sedimentary and extrusive volcanic rocks represented by mafic and silicic schists, quartzites, carbonaceous and graphitic schists and metamorphosed limestone and dolomites. Petersilie (1962) described bitumens and low methane contents from some of the schists in the greenstone belt. Mature organic material is present in rocks of the same age in the nearby Lake Onega area (Karelia, NW Russia). Dated at 2 Ga, this constitutes one of the most remarkable accumulations of organic carbon from the Palaeo-Proterozoic. The carbon occurs in the form of shungite, which is a black, non-crystalline, semi-metallic material that contains >98% C (Melezhik et al., 2004). The total carbon reservoir is estimated to exceed 25 × 10¹⁰ t. It was accumulated within a volcanic continental rift setting, developed on the rifted eastern margin of the Archaean Baltic shield. It is thus likely that the carbonate and graphitic schists that enclose the Khibiny pluton contain primary organic material some of which could have been incorporated into the pluton either during convective fluid flow during emplacement or during subsequent percolation of meteoric waters along fracture systems. The origin of hydrocarbons could thus be explained by involvement of organic matter from the sedimentary rocks.

Both, the spatial distribution of CH₄ and its isotopic composition (Fig. 2c and d) suggest that there may have been an, at least limited, biogenic influence on HC origin within the Khibiny complex. The CH₄ content increases towards the margin of the complex and δ¹³C values decrease toward the margin of the complex. Both these trends are consistent with mixing of methane abiogenically produced within the complex with biogenic methane introduced from the country rocks.

A simple mass balance equation can be used to calculate the relative proportions of the biogenic and mantle components present in the methane gas phase. It uses the analysed isotopic composition of the gas phase itself together with estimates of the isotopic compositions of the two end member components. The equation, governing the isotopic composition of the total carbon in the rock, can be expressed as:

$$F_{\text{shu}}m_{\text{shu}} + F_{\text{mantle}}m_{\text{mantle}} = F_{\text{sample}}$$

where F is the designated δ¹³C value of shungite, mantle and the sample and m denotes the molecular mass fraction of C from the two sources. The calculation is based on the overall average δ¹³C value of –32‰ of shungite (Melezhik et al., 1999) and the assumption that the measured δ¹³C value of the innermost sample Kh-03-54 with –5.4‰ represents the uncontaminated mantle composition. On the basis of these values, the biogenic contribution may be up to 10% in the trachytoid foyaite, up to 30% in the rischorrite and up to 64% in the khibinite.

6. Conclusion—towards a model for CH₄ generation in alkaline rocks

On the basis of the data presented here, together with those elsewhere in the literature, no single simple mechanism is responsible for methane generation within the alkaline rocks of the Khibiny complex. The presence of primary methane-dominated fluid inclusions, melt inclusions containing a methane-rich gas phase, bulk gas data, and the isotopic composition of CH₄ are consistent with an early, abiogenic, magmatic origin. Hence, a reduced carbonic fluid present in the mantle could be a source for the abundant HC gases in the Khibiny complex. However, enhanced CH₄ levels and low δ¹³C values suggest that the outer rocks of the complex have a greater biogenic component than those further inwards. This implies the possibility of a marginal biogenic overprint on what is essentially an abiogenic signature.

We find the model of widespread HC generation through a post-magmatic FT type reaction to be untenable. There is little doubt that such a reaction

could have operated in some parts of the pluton. Given the correct phase assemblage, the presence of Fe-rich phases, a primary CO₂ fluid, and incipient hydration, then CH₄ and the higher hydrocarbons could have been formed in situ by an FT reaction. However, over the intrusion as a whole an FT type reaction is unlikely to have been important. In particular, there is no evidence for the widespread, strong alteration of mafic mineral assemblages required to produce the H₂ needed to drive the FT reactions, nor is there evidence in the fluid inclusion population for the presence of a primary CO₂-rich magmatic fluid. Primary fluid inclusions are dominated by CH₄. There is no correlation between the presence of Fe-rich phases and high methane contents as predicted for the FT reaction.

In addition, FIPs are widespread throughout the complex and are not related to alteration of Fe-rich assemblages. They are interpreted as fluid pathways and hence, the fluid inclusion entrapment at low P and T corresponds to conditions of HC migration, but not to their generation.

FIPs document a high post-crystallisation permeability that accommodates high fluid flow. It is possible to envisage a situation in which abiogenically derived fluids migrate through the fracture system upwards within the complex and mix with biogenic fluids from the surrounding country rocks that migrate inwards through the same fracture system.

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