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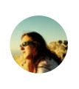

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A preliminary study of methane inclusions in alkaline igneous rocks of the Kola igneous province, Russia: implications for the origin of methane in igneous rocks

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Abstract: Fluid inclusions from the Kovdor, Khibina and Lovozero complexes of the Kola alkaline igneous province have been investigated using microthermometric techniques and PVTX modelling. CH_4 inclusions, found in all three complexes, are always secondary in origin and frequently occur in curvilinear arrays associated with secondary H_2O-dominant inclusions and, in Khibina, CH_4-H_2O inclusions. The secondary nature of the CH_4-bearing inclusions appears to preclude a direct magmatic origin for the methane, which is supported by preliminary C-isotope data which indicate an abiogenic origin. Isochore projections for primary CO_2- and H_2O-dominant inclusions intersect the volatile-saturated, agpaitic, nepheline syenite solidus (at 700 °C), at pressures between 3.5 and 5.5 kbar, compatible with magmatic exsolution of these fluids at crustal depths of between 11-18 km. By contrast, fluid-phase equilibria and the shallow slopes of isochores derived from the PVTX modelling of CH_4-dominant and related inclusions are indicative of trapping conditions at pressures of 0.5 to 1.8 kbar. The close association of CH_4 inclusions with magnetite and late-stage hydrated phases suggests evolution of CH_4 during hydration within a reducing environment. This evolution involved subsolidus Fischer-Tropsch reactions of the type $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$, with the water-produced driving hydration reactions which generated magnetite and more H_2. Methane production is thus a function of vapour-mineral reactions in the C-H-O system operative during late-stage hydrothermal processes and, in particular, is due to two self-reinforcing reaction types linked through a positive feedback mechanism.

Key-words: methane, fluid inclusions, Fischer-Tropsch reactions, igneous processes, Kola, Russia.

Introduction

The origin of methane-bearing fluid inclusions and of higher-order hydrocarbons in igneous rocks is a matter of some controversy. Although rare, methane and other hydrocarbons have been described in fluid inclusions and in evolved gases from a number of magmatic sequences, both volcanic, hypabyssal (*e.g.*, Gerlach, 1980; Gize & MacDonald, 1993; Kelley, 1996), and plutonic (*e.g.*, Larsen *et al.*, 1992; Krot *et al.*, 1994). In particular, they are most commonly found in plutonic rocks from alkaline igneous complexes (*e.g.*, Karzhavin & Vendillo, 1970; Petersilie & Sørensen, 1970; Konnerup-Madsen & Rose-Hansen, 1982; Kogarko *et al.*, 1987; Konnerup-Madsen, 1988; Ikorski, 1991; Salvi & Williams-Jones, 1992; Ting *et al.*, 1994) where the alkaline rocks are a differentiate of a primary, mantle-derived melt.

A variety of mechanisms have been suggested to account for the incorporation of methane and higher-order hydrocarbons into magmatic rocks. One is that the methane is of a biogenic origin and is added to the plutonic rocks during late- and post-magmatic hydrothermal alteration from

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Table 1. Petrography of the major rock types.

ROCK TYPE	SAMPLE NUMBERS	MAIN MINERALS	ACCESSORY MINERALS
Kovdor			
phoscorite	HKB 14,15,16,19	ol, ap, mt, cc	px, phlg, ne
ne-syenite	HKB 9, 10	ne, alk fs, aeg	cancr, ore min
ijolite	HKB 13	ne, px	phlg, cancr, sph, zeo
pyroxenite	HKB 21	dp, phlg, ne	amp, Ti-mt, ol
Khibina			
ap-ne ore	5-K-15, 97-P-187, 6-Yu-60, 6-Yu-63	ne, ap, aeg-aug	Ti-mt, sph, bt, dp
urtite	145-P-85, 1253-153	ne, aeg, alk fs	orth, sulp, ap, eud, mt cancr, natr, sph
foyaite	HX 581-2	fs, zeo	ne, cc, bt, mt, sulp
syenite	211-P-123, HX 1292	fs, ne, px, ks	sph, ap, bt, aen, mt
Lovozero			
lujavrite	146-6	alk fs, ne, aeg	ab, sod, lop, mt
loparite juvite	L-16-19	ne, alk fs, sod, lop aeg, eud	mt, zeo

NOTE: aeg = aegirine, aeg-aug = aegirine-augite, aen = aenigmatite, alk fs = alkali feldspar, ap = apatite, bt = biotite, cancr = cancrinite, cc = calcite, dp = diopside, eud = eudialyte, ks = kalsilite, lop = loparite, mt = magnetite, natr = natrolite, ne = nepheline, ol = olivine, ore min = ore mineral, orth = orthoclase, phlg = phlogopite, px = pyroxene, sod = sodalite, sph = sphene, sulp = sulphide, Ti-mt = titano-magnetite, zeo = zeolite

saline brines circulating in the country-rock reservoir (Gize & MacDonald, 1993). In contrast, Gold (1979) suggested that methane may be a significant component of the upper mantle and was hence likely to be a primary gaseous component of a mantle-derived melt. A third possibility is that the methane is neither biogenic, nor a primary component of the magma (see review by Konnerup-Madsen, 1988), and that methane production is a function of vapour-mineral reactions in the C-H-O system during late-stage hydrothermal processes (Kogarko *et al.*, 1987; Sherwood-Lollar *et al.*, 1993; Kelley, 1996; Berndt *et al.*, 1996; Salvi & Williams-Jones, 1997).

The Kola igneous province of NW Russia has long been known for high concentrations of hydrocarbons in alkaline rocks (Heinrich, 1966; Petersilie & Sørensen, 1970; Sørensen, 1974). In particular, voluminous amounts of CH_4 have been described from the Khibina and Lovozero complexes (Karzhavin & Vendillo, 1970; Kogarko *et al.*, 1987; Ikorski, 1991; Ikorski *et al.*, 1993; Balaganskaya & Pripachkin, 1994; Nivin *et al.*, 1995), some of it in the form of free gases evolved in boreholes or from crushed and heated rock, and some contained in fluid inclusions. However, little detailed work has yet been carried out on the origin and significance of the hydrocarbons. Here we present new fluid-inclusion data and textural observations from three of the alkaline complexes (Khibina, Kovdor and Lovozero) concentrating in particular on the methane-bearing inclusions. These data are used to model P-T trapping paths for the CH_4 fluids with the aim of determining whether their origin is a function solely of mineral reactions associated with late-stage magmatic processes.

Geological setting

The Khibina, Lovozero and Kovdor intrusions are part of the Kola Alkaline Province of NW Russia. The province, covering 100 000 km^2, contains numerous Proterozoic and Devonian alkaline complexes, emplaced into Archaean gneisses and Proterozoic volcanic sediments (Zaitsev & Bell, 1995; Dudkin & Mitrofanov, 1994). The Khibina and Lovozero complexes are neighbouring agpaitic intrusions dated at 377–362 Ma and 371–361 Ma (Kogarko *et al.*, 1995) that are believed to have originated from a single parent magma

Table 2. Bulk chromatographic gas analyses of representative sample from Kovdor and Khibina.

Sample	Rock	He cm³/kg	H_2 cm³/kg	O_2 cm³/kg	N_2 cm³/kg	CH_4 cm³/kg	C_2H_6 cm³/kg	CO_2 cm³/kg	Total cm³/kg
Khibina									
5K15	Ap-ne ore	0.016	0.41	0.13	1.22	8.96	0.31	nd	11.046
97P187	Ap-ne ore	0.003	1.11	0.12	0.86	11.7	0.29	nm	14.083
6Yu60	Ap-ne ore	0.001	0.37	0.11	0.64	0.33	0.04	nm	1.491
6Yu63	Ap-ne ore	0.013	0.39	0.16	0.88	5.52	0.34	nm	7.303
145P85	Urtite	0.7	2.26	0.43	2	75.34	3.07	nd	83.8
1253-153	Urtite	0.2	1.67	0.2	3.48	107.76	nm	nm	113.31
211P123	Ne-syenite	0.003	2	0.18	1.3	18.1	0.9	nm	22.483
HX-1292-2	Ne-ks syenite	0.004	1.27	0.07	0.89	0.013	0.001	0.046	2.294
HX-581-2	Foyaite	0.003	0.81	0.01	1.26	0.049	0.0009	0.84	2.973
HX-581-5	Carbonatite	0.002	4.29	0.037	0.64	0.35	0.25	1.25	6.819
Kovdor									
HKB-1	Ap rock	0.107	0.56	0.014	0.19	0.023	0.003	nd	0.897
HKB-9	Ne syenite	0.011	0.96	0.004	0.34	0.007	0.0002	nd	1.322
HKB-14	Phoscorite	0.003	0.52	0.026	0.26	0.008	0.0004	nd	0.817
HKB-15	Phoscorite	0.021	0.099	0.015	0.18	0.015	0.002	nd	0.332
HKB-16	Phoscorite	0.001	0.034	0.03	0.23	0.004	0.00003	nd	0.299
HKB-19	Phoscorite	0.004	0.112	0.024	0.3	0.004	0.00006	nd	0.444

NOTE: nm = not measurable, nd = not detectable

(Dudkin & Mitrofanov, 1994). Both intrusions consist of nepheline syenites, rocks of the ijolite-urtite series and foyaites. Khibina also hosts large apatite-nepheline ore bodies and a small carbonatite stock whereas Lovozero contains evolved lujavrites and juvites.

Kovdor is a concentric, multiphase intrusion dated at 380 ± 4 Ma (Kogarko *et al.*, 1995) which contains olivinites and pyroxenites, nepheline syenites, rocks of the ijolite-urtite series and abundant phoscorites and carbonatites (Kogarko *et al.*, 1995). Kovdor is adjacent to the Sokli intrusion in Finland (Vartiainen & Paarma, 1979). Both bodies are lithologically similar with abundant phoscorites and carbonatite.

Many of the alkaline rocks show evidence for late-stage hydration, involving the growth of sodic and potassic hydrous phases. The dominant alteration products associated with aegirine-augite, titano-magnetite, apatite, nepheline and eudialyte in rocks sampled for this study are Fe-Ti-biotite, magnetite, aegirine, cancrinite, natrolite, analcime, pectolite ($HNaCa_2Si_3O_9$), natisite (Na_2TiSiO_5), lorenzenite ($Na_2Ti_2Si_2O_9$), lithosite ($HK_3Al_2Si_4O_{13}$) and nacaphite (Na_2CaPO_4F). Although the Kovdor body has experienced little late-stage to post-magmatic alteration the Sokli intrusion has been extensively altered with the development of phlogopitic and serpentinised assemblages and widespread apatite-magnetite and sulphide mineralisation (Vartiainen & Paarma, 1979; Aldous, 1980)

Methodology

This study has concentrated on rocks containing abundant apatite and nepheline as they are the major host minerals for the fluid inclusions, with samples selected for detailed study on the basis of the abundance of fluid inclusions in nepheline, apatite and pyroxenes. Rock types used in the study and their essential and accessory minerals are listed in Table 1. Preliminary gas chromatographic analyses carried out on some of these samples using the method of Ikorski *et al.* (1993) confirm their high gas contents with up to 113 cm³/kg CH_4 being released by sample 1253-153 (Table 2).

Microthermometric measurements were carried out using a Linkam TH600 heating-freezing stage. Calibration with known melting points (Roedder, 1984) and synthetic fluid inclusion standards show that the stage is accurate to ±0.2 °C from minus 100 to 0°C and ± 0.5°C up to 600°C. Most measurements on individual inclusions were reproducible to within ±0.5°C except for Te and Th-CH_4 values which were reproducable to ±1.0°C. A preliminary laser-Raman microprobe study of CH_4-dominant inclusions was carried out at Southampton University using the Microdil-28

Table 3. Microthermometric data.

SAMPLE NUMBER	HOST MINERAL	TYPE	n	Th-CH_4	Th-CO_2		TmCO_2	Te	Tm-ice	Tm-clath	Tm-halite	Th-t		wt%NaCl	average density g/cm^3
HKB 19	Apatite	CO_2	18				-56.6			7 - 8.4		320 - 480	V	3.2 - 5.7	0.48
HKB 19	Apatite	CO_2	21		23.5 - 31	V	-56.6 - -57			5.6 - 9.8		280 - 450	L	0.5 - 8.1	0.3 - 0.4
HKB 9	Nepheline	CO_2	7		31	V	-56.6			4.8 - 10		255 - 292	L	0 - 9.3	0.48
HKB 10	Ne/Aeg	CO_2	17		21.7 - 31	L	-56.6 - -57.2			7.2 - 9.5		320 - 390	L	1 - 5.4	0.3 - 0.37
HKB 14	Apatite	H_2O (L+V+S)	9					-20 - -22.7			170 - 183	270 - 275	L	~31	1.13 - 1.14
HKB 9	Apatite	H_2O (L+V)	11					-25 - -30	-3.6 - -6.5			264 - 324	L	5.8 - 9.8	0.73 - 0.85
HKB 13	Nepheline	H_2O (L+V)	33					-21 - -25	-6 - -13.4			270 - 427	L	9.2 - 17.2	0.67 - 0.9
HKB 21	Nepheline	H_2O (L+V)	24					-21 - -25	-9.8 - -13			365 - 385	L	13.7-16.9	0.8
HKB 21	Apatite	H_2O (L+V)	15					-19.7 - -33.3	-10.5 - -15			279 -439	L	14.5 - 18.9	0.6 - 0.9
HKB 10	Nepheline	H_2O (L+V)	2					-20 - -23	-7			270 - 280	L	10.5	0.9
6-Yu-60	Nepheline	H_2O (L+V)	4					-21				198 - 235	L		
5-K-15	Nepheline	H_2O (L+V)	4					-19.6 - -27.8	-0.7 - -5.2	15		281 - 332	L	1.15 - 8.1	0.7 - 0.75
HX581-2	Nepheline	H_2O (L+V)	23					-15.3 - -29.5	-3.4 - -17.8	11.2-14.4		224 - 349	L	5.4 - 20	0.7 - 0.9
HKB 19	Nepheline	CH_4	2	-82		L									0.17
5-K-15	Nepheline	CH_4	21	-81.8 - -94.6		L									0.17 - 0.28
5-K-15	Nepheline	CH_4	26	-81.3 - -100.5		V									0.04 - 0.13
97-P-187	Nepheline	CH_4	4	-82 - -83		L									0.17 - 0.12
97-P-187	Nepheline	CH_4	14	-81.9 - -86		V									0.09 - 0.15
145-P-85	Nepheline	CH_4	3	-82.2 - -106.6		L									0.17 - 0.32
145-P-85	Nepheline	CH_4	106	-78.4 - -111.3		V									0.03 - 0.15
6-Yu-63	Nepheline	CH_4	2	-82.5		L									0.17
1253-153	Nepheline	CH_4	12	-79 - -85.2		L									0.17 - 0.23
211-P-123	Nepheline	CH_4	1	-83		V									0.13
HX-1292	Nepheline	CH_4	8	-82.5		V									0.15
HX-581-2	Nepheline	CH_4	8	-82.7 - -83		V									0.13 - 0.14
146-6	Nepheline	CH_4	4	-84 - -92.2		V									0.06 - 0.11
146-6	Nepheline	CH_4	6	-82.2 - -84		L									0.17 - 0.2
L-16-19	Ne/Aeg	CH_4	21	-77.7 - -105.2		V									0.03 - 0.15
97-P-187	Nepheline	CH_4:H_2O	5	-81.6- -83.9		V/L		-22.4	-4.1 - -16.5	13.2		340	L	6.5 - 19.8	0.53
5-K-15	Nepheline	CH_4:H_2O	2	-83		V			-9.9			>300			0.53

NOTE: Th-Ch_4 = temperature of homogenization of CH_4, Th-CO_2 = temperature of homogenization of CO_2, Tm-CO_2 = melting temperature of CO_2, Te = temperature of the first melt for the H_2O phase, Tm-ice = last ice melting temperature of the H_2O phase, Tm-clath = temperature of melting of clathrate, Tm-halite = temperature of halite dissolution, Th-t = temperature of total homogenization to liquid or vapour, n = numbers of inclusions.

Densities and salinities have been calculated using the FLINCOR program (Brown, 1989) with the exception of CH_4 : H_2O densities estimated from volumetric calculations.

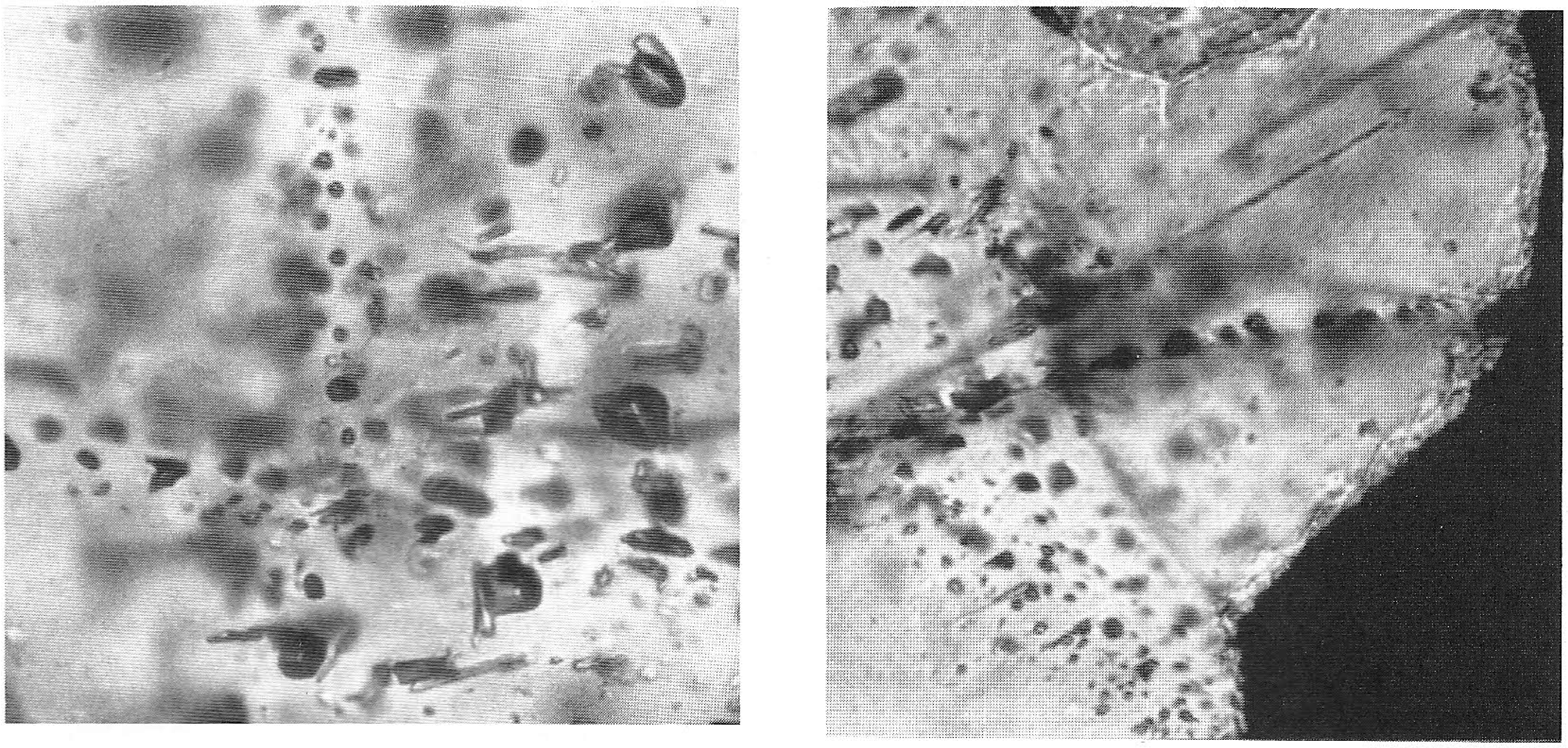

Fig. 1. a) Group of five larger, (>10 µm), relatively isolated CH_4-dominant inclusions and smaller (~5 µm), cross-cutting fracture-bound inclusions in nepheline.

b) Magnetite crystal showing two planar groups of CH_4-dominant inclusions related to it. Note irregular boundary betweeen magnetite and nepheline composed of biotite.

Argon laser system described by Burke & Lustenhouwer (1987). Carbon-isotope analyses were carried out on two samples using the Prism II mass spectrometer and a stepped-heating line at Royal Holloway and Bedford New College, London (Jackson *et al.*, 1988).

Identification and characterisation of fluid inclusion types

The fluid inclusions usually occur in tracks or clusters or as isolated cavities up to 20 m across. They are generally rounded, elongate or negative-crystal shaped. Less commonly they occur in planar arrays and clusters. Four compositional types have been determined on the basis of their shape, distribution, phase properties and changes observed on cooling and freezing: CH_4-dominant, mixed CH_4-H_2O, H_2O-dominant and CO_2-dominant.

CH_4-dominant inclusions occur mainly in nepheline and occasionally in pyroxene from Khibina and Lovozero. They consist of monophase vapour at room temperature with no visible aqueous phase. There are two modes of occurrence. The first is as small fracture-bound inclusions, <10 µm across, that occur in curviplanar trails (Fig. 1a) and are clearly secondary. The second is as negative crystal-shaped inclusions 10–30 µm across, associated with cleavage planes within nepheline. On the basis of their location along cleavage surfaces, these are inferred as also having a secondary origin. Both types are closely associated with magnetite crystals. Trails of fracture-bound inclusions lead off the edges of magnetite grains and the larger inclusions are concentrated in the same vicinity. A reaction rim developed around the magnetite crystals consists of biotite with occasional hematite (Fig. 1b). Initial investigations on altered Sokli phoscorites from Sokli show the same distribution of methane inclusions around magnetite grains. Although hydrocarbon-bearing inclusions have been reported in carbonatites from Kovdor (Kharmalov *et al.*, 1981), CH_4-dominant inclusions are rare in samples studied by us from Kovdor. In this complex gas chromatographic data show low overall abundances of gaseous volatiles and low volumes of hydrocarbons (Table 2).

Microthermometric data (Table 3) show that, for any sample, both the fracture-bound and the isolated CH_4 inclusions have the same range of homogenisation temperatures (Fig. 2a, b) and are therefore interpreted as belonging to the same fluid system. In addition, the homogenisation temperatures are independent of which intrusion the sample is from (Fig. 2d). That some homogenisation temperatures fall above the critical point of CH_4 (–82.1 °C), may be due to the presence of vol-

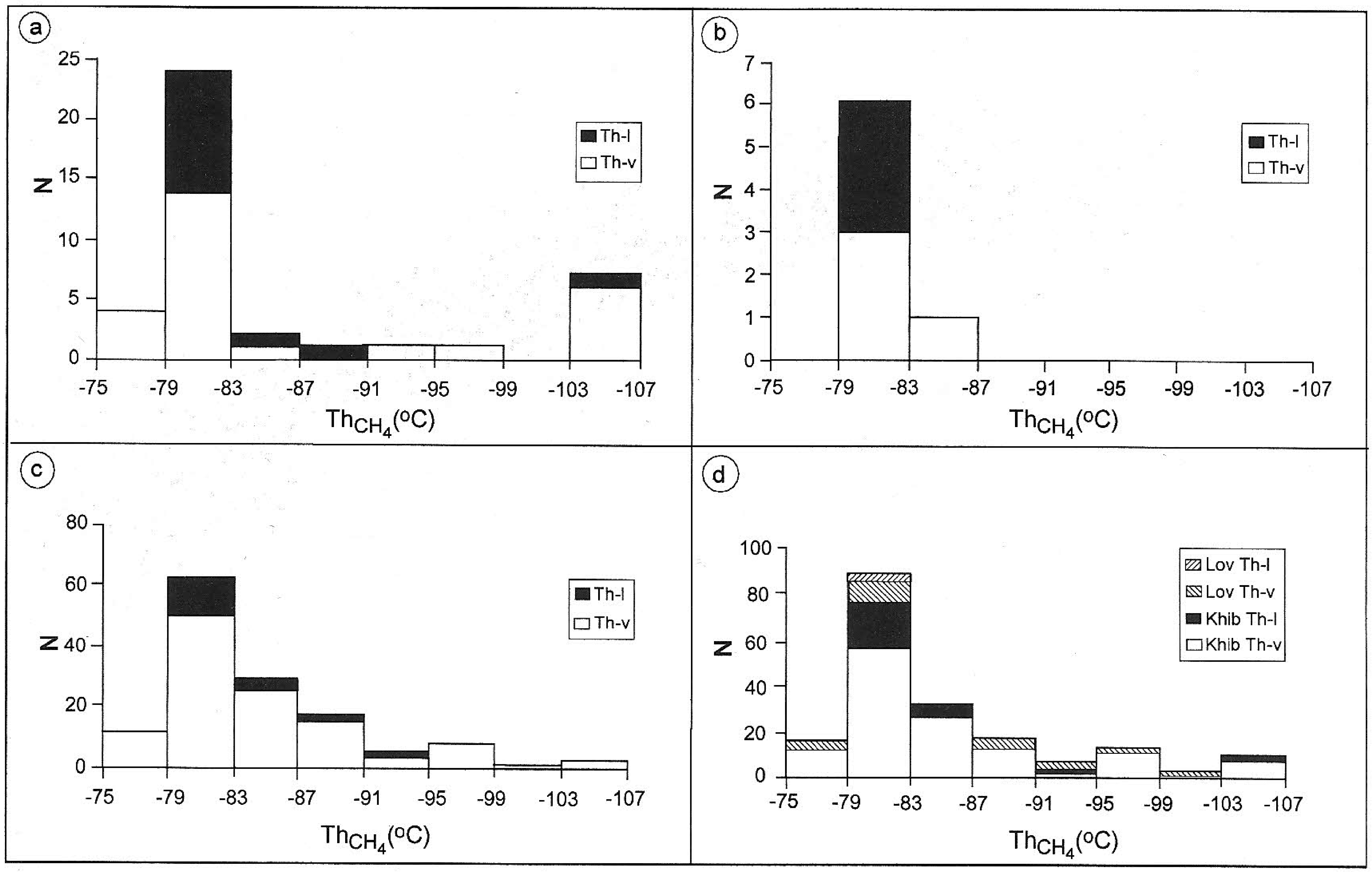

Fig. 2. The temperature of homogenization of methane for CH_4-dominated fracture-bound inclusions (a), large inclusions (b), CH_4-H_2O inclusions (c) and for CH_4-dominant inclusions from Khibina and Lovozero (d).

atiles such as C_2H_6 or CO_2 as suggested from the gas chromatographic analyses (Table 2). Homogenisation temperatures less than –82.1 °C may be due to the presence of N_2 which is present at up to 41.8 vol% N_2 in some of the gas analyses. However, preliminary laser-raman results on three inclusions from Khibina with homogenisation temperatures to vapour at –83.5, –78.7 and –86.5°C failed to detect any of these volatiles. Accurate detection limits for CO_2, C_2H_6 and N_2 can be hard to determine due to various factors but are within the range of a few mole percent (Roberts & Beattie, 1995). The presence of some higher hydrocarbons as possible liquids adhering to the walls of some of the CH_4 inclusions is inferred from UV fluorescence spectroscopy. However, they are extremely rare and, to date, we have been unable to obtain any microthermometric data on them.

Preliminary $\delta^{13}C_{CH4}$ isotopic data have been obtained from two samples rich in CH_4-dominant inclusions. Bulk decrepitation during step heating occurred between 390 and 410 °C. A $\delta^{13}C_{CH4}$ value of –25.4 ‰ was measured for nepheline and pyroxene from Lovozero (sample L-16-19) and of –25.33 ‰ for nepheline from Khibina (sample 145-P-85). These values are typical of hydrothermal fluids (Kiyosu *et al.*, 1992).

CH_4-H_2O inclusions are extremely rare and in this preliminary study have only been found in nepheline in urtites and apatite-nepheline ores at Khibina. They occur within the same curviplanar trails as the fracture-bound CH_4-dominant inclusions. Despite this close association, which may imply immiscibility, the CH_4:H_2O proportion is constant at *ca.* 60 % CH_4 : 40 % H_2O. Thermometric data for these inclusions are limited by their scarcity and because the samples decrepitate before total homogenisation occurs at *ca.* 340 °C. The Th-CH_4 (to L and V) for these inclusions has a small range of –81 to –83.9 °C that is close to the critical point of pure CH_4 (Fig. 2c) indicating both a relatively pure CH_4 component and a density comparable to that of the CH_4-dominant inclusions (Fig. 2c). Two clathrate-melting temperatures were recorded at 13.2 °C (Table 3) which is compatible with published dissolution temperatures for CH_4-clathrate (Zhang & Frantz, 1992). The aqueous component has Tm-ice ranging from

−4.2 to −16.5 °C indicating that the aqueous fluid belongs to the H_2O-NaCl system.

H_2O-dominant inclusions occur in three types. *L* + *V* inclusions occur in nepheline and apatite in alkaline rocks from Khibina and Kovdor. In Khibina the *L* + *V* inclusions (sub-type 1) are uncommon and occur as rounded inclusions in nepheline. The vapour-bubble volume in the inclusions is extremely variable, filling from 20 to 70 % of the inclusion. Some rare sub-type 1 inclusions contain a daughter mineral of halite or nahcolite identified on the basis of their characteristic optical and microthermometric properties. They are closely associated with the CH_4-dominant inclusions, and occasionally occur within the same curviplanar trails suggesting that they are secondary in origin and related to the CH_4 fluids. In Kovdor, however, H_2O-dominant inclusions occur as isolated, faceted or rounded cavities approximately 10 µm across (sub-type 2) in nepheline or as clusters within apatite crystals. These have a constant vapour bubble volume of *ca.* 40 %. They are not associated with any other fluid-inclusion type and because of their isolated occurrence are interpreted as being primary in origin. The sub-type 3 are brine inclusions found in apatite-bearing phoscorites from Kovdor. They are not associated with any other fluid inclusion type, occur in clusters in the core of apatite crystals and are typically rounded, faceted or elongate, features which suggest a primary origin. They contain one or more daughter minerals, the most common of which are halite and nahcolite, and have a uniform vapour : liquid ratio.

Microthermometric data for sub-type 1 inclusions have a range in Te from −15.3 to −29.5 °C and in Tm-ice from −0.7 to −17.8 °C (Table 3). Total homogenisation temperatures are near the decrepitation temperature of the inclusions although some decrepitated before homogenisation occurred between 300 and 340 °C. Clathration, observed in a few inclusions, occurs between 11.2 and 15 °C indicating the presence of CH_4. Of the daughter minerals, nahcolite dissolves at between 69 and 100 °C and halite at 160 °C. The Th-total of sub-types 2 and 3 (Table 3) range from 270 to 440 °C. A few inclusions show clathrate formation with a melting temperature of *ca.* 10 °C indicating small amounts of CO_2. The majority of samples show no clathrate or hydrohalite formation. Te values are variable but many cluster at around −22 to −25 °C and Tm-ice ranges from −4 to −15 °C, comparable to fluids in the NaCl-H_2O and NaCl-$NaHCO_3$-H_2O systems (Shepherd *et al.*, 1985). Halite dissolution in sub-type 3 brine inclusions ranges from 170–183 °C, always above the nahcolite dissolution temperature. Sub-type 2 and 3 inclusions show slightly higher Th-total values and lesser variation in Tm-ice and Te than sub-type 1 inclusions.

CO_2-dominant inclusions occur as small, round, isolated inclusions, 5–10 µm across in nepheline, apatite and pyroxene from phoscorites and alkaline rocks at Kovdor. The volumetric proportion of the CO_2-rich phase, compared to the H_2O-rich phase, falls within a narrow range of 85 to 95 % CO_2, suggesting homogeneous fluid entrapment. They are not associated with any other fluid-inclusion type and, on the basis of the isolated occurrence, are interpreted as primary. CO_2 has not been detected in this study in fluid inclusions in Khibina and although gas chromatographic analyses indicate the presence of CO_2 in some samples (Table 2), (Kogarko *et al.*, 1987; Ikorski *et al.*, 1993). Microthermometric data (Table 3) show that Tm-CO_2 clusters at around the critical point for pure CO_2 of −56.6 °C although some spurious values of −60 and −73 °C have been recorded. These could be due to the presence of volatiles, such as CH_4 or N_2. The apatite and nepheline-hosted inclusions show a large range in Th-t-l of 280–450 °C and 255–390 °C respectively.

Interpretation of microthermometric data

The fluid-inclusion data presented here may be modelled within the CH_4-CO_2-H_2O-NaCl ($NaHCO_3$) system. As nahcolite is rare, it is appropriate to consider NaCl as the dominant end-member. The PVTX properties of each group of inclusions were modelled for the simplified CO_2-H_2O-NaCl (Bowers & Hegelson, 1985). H_2O-NaCl (Brown & Lamb, 1989) and CH_4 (Jacobs & Kerrick, 1981) systems using the FLINCOR program (Brown, 1989). Maximum and minimum slopes of isochores for the main inclusion types are shown in Fig. 3a together with the solidus for a volatile-saturated nepheline syenite magma (Edgar & Parker, 1974). Isochores for sub-type 3 brine inclusions have not been plotted, partly because the solubility is likely to be overestimated by the FLINCOR software unless the halite and vapour bubble disappear simultaneously (Brown, 1989), and partly because published PVTX data for $NaHCO_3$-NaCl-H_2O fluids are limited.

The CO_2-dominant inclusions have a mean composition of $xH_2O : xCO_2 : xNaCl = 0.27 : 0.7 : 0.03$. Isochores for these inclusions in alkaline rocks intersect the nepheline syenite solidus at 3–5 kbar at 700°C (Fig. 3a). For CO_2-dominant inclusions in phoscorites from Kovdor, intersection with the carbonatite solidus (Wyllie, 1989) yields entrapment pressures of 2–4 kbar at 600°C. Isochores constructed for the sub-type 2 H_2O-dominant $L + V$ inclusions intersect the H_2O-saturated nepheline syenite solidus at 3.5–5.5 kbar. On the basis of these data, trapping conditions for the primary inclusions in all of the intrusions are inferred to have been at 3-5 kbar. This is close to the estimate obtained independently for Sokli inclusions by Aldous (1980).

Isochores constructed for the CH_4-dominant inclusions intersect the nepheline syenite solidus at <0.5 kbar. In gas-rich inclusions small amounts (up to about 5%) of unrecognised water may be present around the inclusion rim. This water could steepen the slope of the pure CH_4 isochore, but probably insufficiently (Zhang & Frantz, 1992) to imply anything other than a low pressure, and hence shallow depth, of entrapment.

For the CH_4-H_2O inclusions, partial densities of the CH_4-dominant phase range from 0.11 to 0.17 gcm^{-3}. For the aqueous component partial densities, based on salinities in the range of 6.5 to 20 equiv. wt% NaCl, range from 0.7 to 0.98 gcm^{-3}, although due to clathrate formation these salinities will be overestimates (Hanor, 1980). In the absence of total homogenization temperatures, the density and compositions of these inclusions have been calculated using the procedure outlined by Shepherd *et al.* (1985) based on volumetric proportions and partial densities of pure CH_4 and H_2O. The results indicate an approximate molar proportion of 20% CH_4 and 80% H_2O and a density of 0.53 gcm^{-3}. Due to the steep slope of the solvus in PT space (Fig. 3b), homogenisation temperatures for pure CH_4-H_2O inclusions of this density and molar proportion will be *ca.* 350°C, irrespective of pressure (Zhang & Frantz, 1992). The CH_4-H_2O inclusions studied here decrepitated at up to 340°C, close to the solvus temperature. Previous studies of decrepitation pressures in quartz have shown that, for inclusions of a similar size to the CH_4-H_2O inclusions (*ca.* 10 m), decrepitation occurs at about 1.2 kbar (Leroy, 1979; Chryssoulis & Rankin, 1988). In nepheline-hosted inclusions, decrepitation pressures will be lower because of lower internal resistance due to the presence of well-developed cleavage planes. Using 1.2 kbar as the upper pressure limit for decrepitation, and clathrate-melting temperatures of 13.2°C, isochores extrapolated using the data of Zhang & Frantz (1992) yield an entrapment pressure of 0.5–1.2 kbar (Fig. 3b). The H_2O-dominant inclusions spatially related to the CH_4-dominant and the CH_4-H_2O inclusions also homogenise or decrepitate at *ca.* 300–340°C. The extrapolated isochores also give pressures of 0.5–1.1 kbar at these temperatures (Fig. 3b) providing further evidence of the low-pressure entrapment conditions of these secondary fluids.

In summary, on the basis of the entrapment data and primary nature of both the CO_2-dominant and H_2O-dominant fluids (sub-types 2 and 3) we infer that both these fluids exsolved from a parent alkaline magma at *ca.* 600–700°C and 3–5 kbar. Petrographically, there is no evidence to suggest contemporaneous trapping under identical PT conditions as coeval, immiscible fluids. A more likely explanation is that the CO_2-dominant and H_2O-dominant fluids were exsolved as separate phases from the parent magmas at different times under slightly varying PT conditions. The shallow slope of the CH_4 isochores implies trapping at much lower pressures, and hence shallower depths, than the CO_2-dominant and H_2O-dominant fluids (sub-types 2 and 3). The close spatial association between CH_4-dominant, H_2O-dominant (sub-type 1) and CH_4-H_2O inclusions in individual microfractures in Khibina holds the key to their origin as this association implies the presence of two immiscible end-member compositions that were trapped contemporaneously. As the total homogenisation temperatures of the H_2O-dominant inclusions are near to, or slightly greater than, the decrepitation temperatures, the H_2O- and CH_4-rich fluids must have been trapped immiscibly, in the two-phase field of the CH_4-H_2O-NaCl ternary system. The rare presence of nahcolite and halite supports this hypothesis (Lamb *et al.*, 1996). The occurrence of CH_4-dominant, CH_4-H_2O mixed and H_2O-dominant fluid inclusions in the same secondary planes also indicates they were trapped at the same time as immiscible phases at or below the solvus in PTX space for the relevant CH_4-H_2O composition at *ca.* 350°C and 0.5–1.2 kbar. This inference is supported by their decrepitation temperatures of 240–350°C (Fig. 3b) and the low-pressure nature of isochores constructed for the CH_4-dominant inclusions (Fig. 3a).

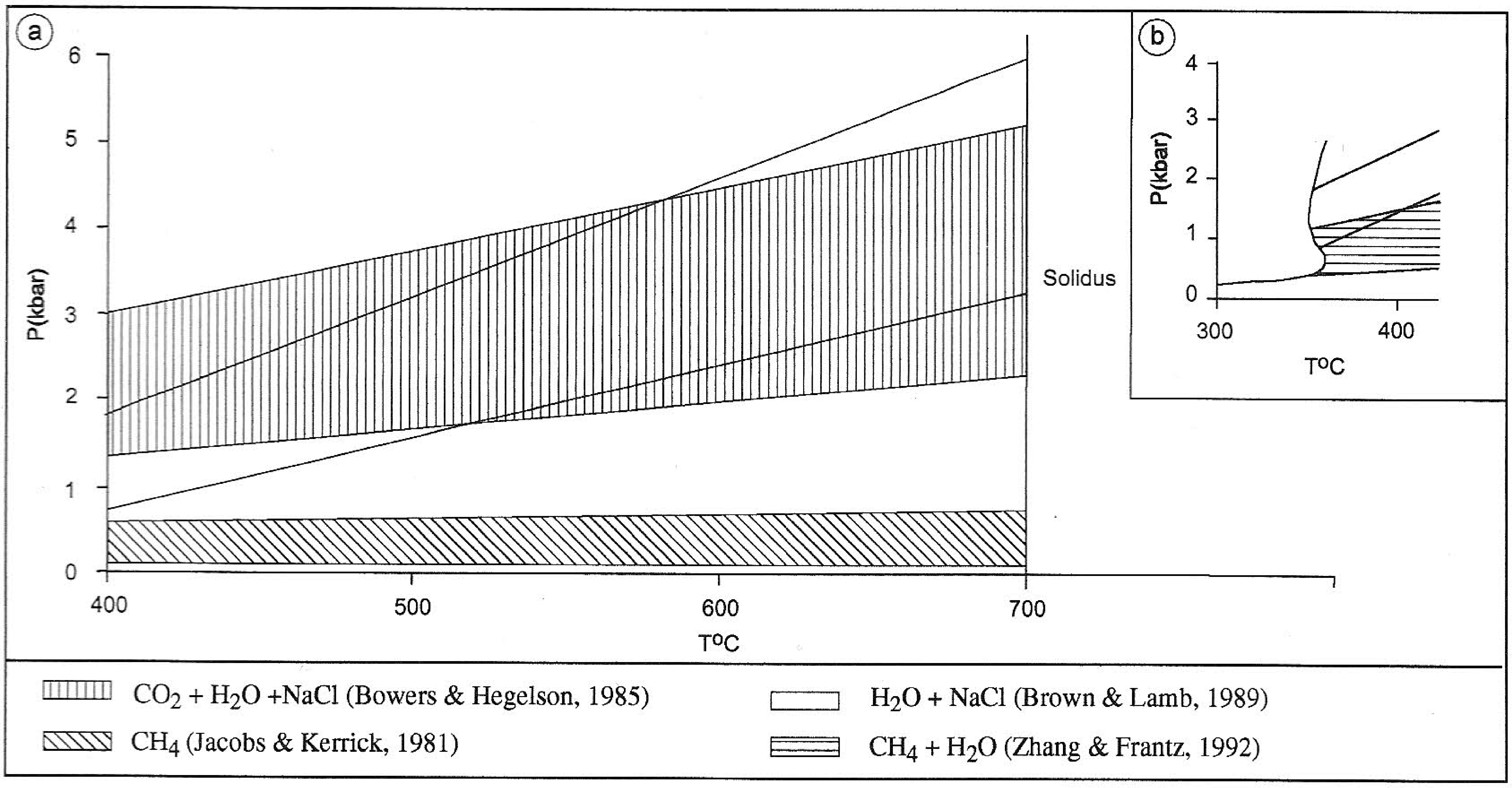

Fig. 3. a) Isochore ranges constructed from minimum and maximum microthermometric properties/densities for the CO_2-dominated, H_2O-dominated and CH_4-dominated. The solidus at 700 °C is taken from the temperature of a volatile saturated nepheline syenite magma (Edgar & Parker, 1974). b) The solvus is estimated for a fluid containing 20 mol% CH_4 and 80 mol% H_2O (Zhang & Frantz, 1992). Isochores intersecting the solvus are estimated from data collected for sub-type 1 H_2O-dominant inclusions and from clathrate melting temperatures for CH_4-H_2O fluids, 13 to 17 °C (Zhang & Frantz, 1992).

Discussion

The low trapping pressures and inferred secondary nature of the methane-rich inclusions in the Kola samples do not support a primary, magmatic origin for the hydrocarbons. Therefore a mantle origin for the methane (*c.f.*, Gold, 1979) is unlikely. In addition, the lack of any biogenic source in the Archaean and Proterozoic country rocks makes the influx of organic-rich brines into the Kola alkaline intrusions unlikely. Hence, methane evolution is likely to have been through some form of abiogenic, low-PT process that involved fluid-mineral interactions.

CH_4-rich fluids can develop through reactions between water and graphite such as:

$$C + 2H_2O \leftrightarrow CH_4 + O_2 \qquad (R1)$$

which usually occur under low- to medium-grade metamorphic conditions (Holloway, 1984; Samson & Williams-Jones, 1991). Gerlach (1980) suggested that pure methane could evolve at low pressures from CO_2 in the presence of graphite. Such an evolution has been modelled in the C-O-H system in equilibrium with graphite by Holloway (1984) and Cesare (1995). A homogeneous CO_2-CH_4-H_2O fluid in equilibrium with graphite will evolve towards either a CO_2-rich fluid or a CH_4-rich fluid, depending on the initial O/(O+H) and $CO_2/(CO_2 + CH_4)$ ratios of the fluid (Fig. 4). The fluid will be homogeneous above the 400 °C isotherm, but will become immiscible and supersaturated in respect to graphite as it cools. Clearly, a CO_2-CH_4-H_2O mixture cannot exist in equilibrium at low temperatures as it will behave immiscibly on cooling.

CO_2-CH_4 ($\pm H_2O$) mixed inclusions have not been identified to date in any of the Kola samples. Th-CH_4 and Tm-CO_2 data (Table 3) and preliminary laser-Raman investigations indicate the presence of separate pure CO_2 and pure CH_4 fluids. Both could have evolved within a closed system from a complex C-O-H fluid. However, as graphite has not been identified in the inclusions, nor is it present in the surrounding country rocks, the models presented Gerlach (1980), Holloway (1984) and Cesare (1995) may not be applicable to these rocks for which a more complex process involving a multicomponent system may be more appropriate.

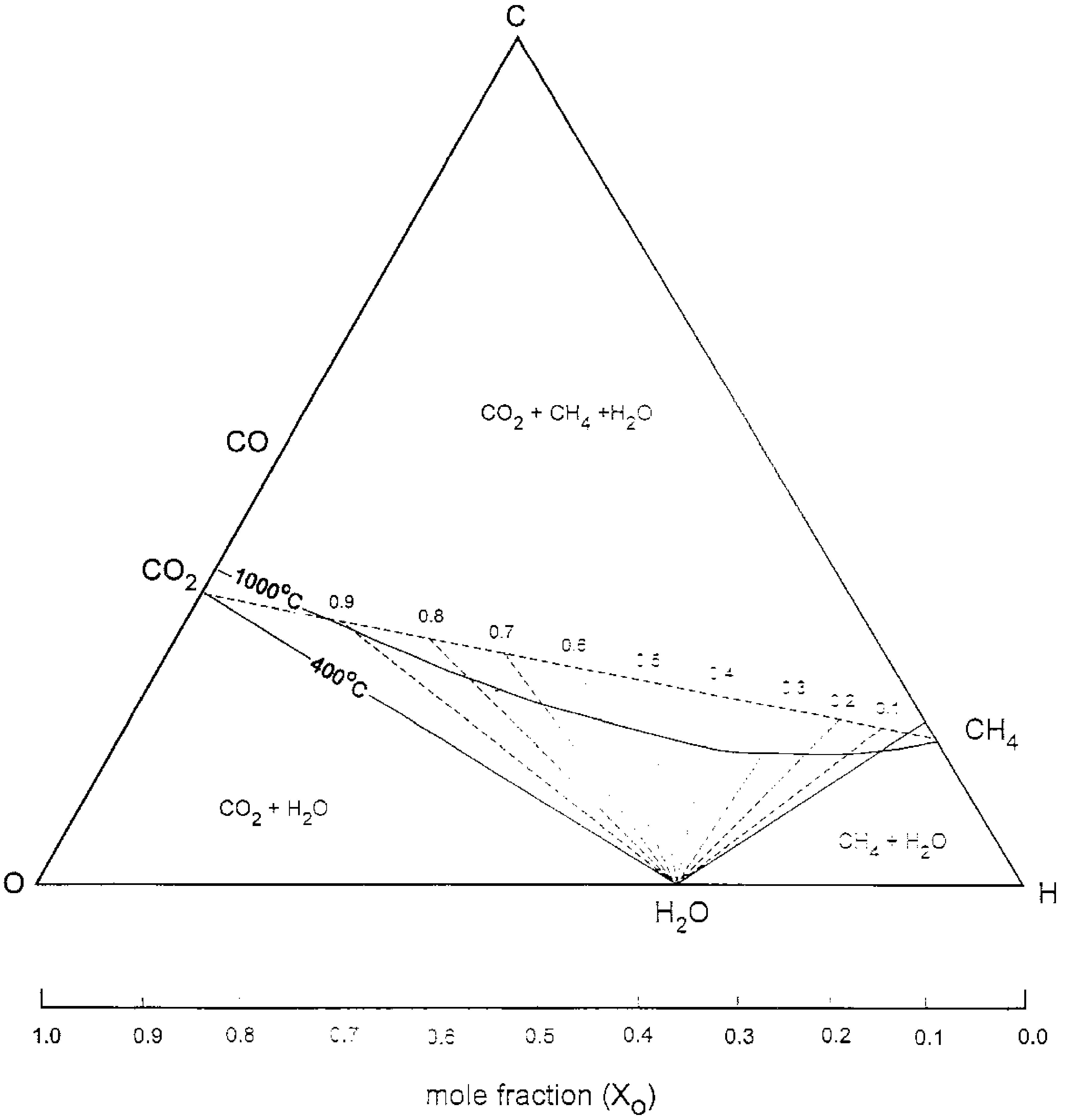

Fig. 4. A schematic C-O-H system showing graphite saturation curves at 1 kbar. Xo = O/(O+H) and the ratios along the CO_2-CH_4 join indicate isopletzs for CO_2/ (CO_2+CH_4). When Xo = 0.3 and $CO_2/(CO_2+CH_3)$ = 0.5 an H_2O-rich liquid will evolve. Any deviation from this value will cause the fluid to evolve to a CO_2-rich or CH_4-rich endmember. Based on Cesare (1995).

A number of authors, most recently Salvi & Williams-Jones (1997), have suggested that the Fischer-Tropsch reaction may play an important role in the production of methane from a CO_2-bearing fluid. The Fischer-Tropsch reaction may be represented by:

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \qquad \text{(R2)}$$

Berndt *et al.* (1996) used this reaction to demonstrate the production of CH_4 during serpentinization of ultrabasic assemblages in which magnetite acted as a catalyst and Salvi & Williams-Jones (1997) argued that higher hydrocarbons may also have formed in alkaline complexes through such a reaction. In many cases the H_2 required to reduce the CO_2 may be provided by reactions operative during late-stage hydration and alteration of the mineral assemblages. Reactions that produce H_2 often described in alkaline and basic rocks (Konnerup-Madsen *et al.*, 1985; Sherwood-Lollar *et al.*, 1993; Kelley, 1996; Salvi & Williams-Jones, 1997) include:

$$\underset{\text{Ol}}{5Mg_2SiO_4} + Fe_2SiO_4 + 9H_2O \rightarrow \underset{\text{Serp}}{3Mg_3Si_2O_5(OH)_4}$$
$$+ \underset{\text{Bruc}}{Mg(OH)_2} + 2Fe(OH)_2 \qquad \text{(R3a)}$$

$$3Fe(OH)_2 \rightarrow \underset{\text{Mt}}{Fe_3O_4} + H_2 + H_2O \qquad \text{(R3b)}$$

$$\underset{\text{Arf}}{3Na_3Fe_4FeSi_8O_{22}(OH)_2} + 2H_2O \rightarrow \underset{\text{Aeg}}{9NaFeSi_2O_6}$$
$$+ \underset{\text{Mt}}{2Fe_3O_4} + \underset{\text{Qz}}{6SiO_2} + 5H_2 \qquad \text{(R4)}$$

The production of H_2 by such reactions may catalyse the Fischer-Tropsch reaction by creating a reducing front suitable for the production of methane (Kelley, 1996; Sugisaki & Mimura, 1994). As the Fischer-Tropsch reaction itself generates H_2O, a positive feedback loop may be established between it and reactions such as R3 and R4, thus perpetuating the cycle of alteration, H_2 production and CH_4 synthesis.

Many of the Kola alkaline plutons show evidence for late stage alteration related to hydration.

In particular, Kogarko *et al.* (1987) noted the association of methane inclusions with hydrated minerals such as natrolite, analcime, ussingite ($HNa_2AlSi_3O_9$) and pectolite in Khibina and Lovozero. The alteration of arfvedsonite to aegirine (R4) is a feature of some samples from Kola where samples rich in methane often have aegirine-augite as a dominant mineral. This reaction may have contributed to the formation of H_2. Similarly, the hydration of nepheline to cancrinite produces H_2 as a product of the reaction:

$$\underset{\text{Ne}}{3NaAlSiO_4} + 2H_2O + Na^+ \rightarrow \underset{\text{Cancr}}{Na_4Al_3Si_3O_{12}(OH).H_2O} + 0.5H_2 \qquad (R5)$$

and the hydrothermal alteration of aegirine-augite, titano-magnetite and nepheline to Fe-Ti-biotite, aegirine and magnetite will also produce H_2 by the reaction:

$$\underset{\text{Aeg-aug}}{2(Ca,Na)FeSi_2O_6} + \underset{\text{Ti-mt}}{2(Fe,Ti)_3O_4} + \underset{\text{Ne}}{NaAlSiO_4} + 2Si^{4+} + K^+ + 4H_2O \rightarrow$$

$$\underset{\text{Bt}}{KFe_3(Al,Ti)Si_3O_{10}.(OH)_2} + \underset{\text{Mt}}{Fe_3O_4} + \underset{\text{Aeg}}{2NaFeSi_2O_6} + Ca^{2+} + 3H_2 \qquad (R6)$$

Magnetite is a product of reactions 3, 4 and 6. The close association of CH_4 inclusions with magnetite in the Kola rocks provides supporting evidence for the operation of one or more of these reactions in the production of CH_4.

The potential relationship between methane generation and hydrothermal alteration is also shown by phoscorites from Kovdor and Sokli. Those from Kovdor show little alteration of olivine to serpentine and little or no methane is found in them based on the present study. By contrast, our initial investigations of samples from Sokli which show evidence of alteration to serpentine and phlogopite have identified the presence of methane.

In Khibina, rasvumite (KFe_2S_3), which replaces aegerine-augite at a late stage, has been replaced by bartonite ($K_6Fe_{20}S_{26}(S,Cl)$). As the overall valency of Fe decreases from 2.5 in rasvumite to 2.27 in bartonite (Czamanske *et al.*, 1981), the presence of these sulphides are indicative of a decrease in fO_2 and an increasingly reduced nature of the late-stage fluids consistent with production of H_2 and CH_4 during hydration.

Overall, our preferred model for the formation of methane in the alkaline rocks at Kola is that methane was produced during late-stage hydration of the primary igneous mineral assemblages. Hydration generated H_2 in the presence of magnetite, and thus triggered respeciation of a CO_2-H_2O fluid through the Fischer-Tropsch disequilibrium reaction. The association of both fracture-bound and isolated methane inclusions with magnetite provides compelling evidence for the simultaneous operation of the H_2-producing and CH_4-producing reactions. The scarcity of secondary H_2O inclusions and the dominance of pure CH_4 inclusions, and the link between hydrothermal alteration and methane production presented here is, in agreement with the suggestion made by Kogarko *et al.* (1987), that the H_2O may have been removed from the late-stage CH_4-H_2O-rich fluid into the lattices of the secondary hydrated minerals. CH_4 and H_2O act immiscibly at low temperature (*c.f.*, Zhang & Frantz, 1992). It follows, therefore, that much of the H_2O was incorporated directly into the late-stage hydrated minerals, a pure CH_4 gas would remain to dominate the secondary fluid inclusions with only a small population of H_2O-rich inclusions.

The source for the H_2O is conjectural. It could be a remnant from the primary magmatic H_2O-dominated fluid. Alternatively, it could have been a by-product of the Fischer-Tropsch synthesis. The latter alternative is favoured on the basis of δD isotope data on methane and water extracted in a vacuum ball mill from whole-rock samples from the Lovozero intrusion (Nivin *et al.*, 1995). Values of δD_{CH4} at −130 to −165‰ and δD_{H2O} at −600 to − 650‰ were obtained. These extremely light signatures are similar to those measured by Sherwood-Lollar *et al.* (1993) from methane and water inclusions in serpentinised ultramafic rocks in the Canadian shield, (δD_{CH4} *ca.* −135‰ and δD_{H2O} *ca.* −600‰). They are considered as diagnostic of methane and water produced during serpentinisation processes (Sherwood-Lollar *et al.*, 1993), that involve Fischer-Tropsch synthesis, (Kelley, 1996; Sugisaki & Mimura, 1994) and are atypical of natural magmatic or connate waters (Nivin *et al.*, 1995).

The $\delta^{13}C_{CH4}$ data from the Lovozero and Khibina massifs have signatures that, at *ca.* −25‰, are typical of hydrothermal fluids (Kiyosu *et al.*, 1992). However, if the CH_4-dominant fluid was produced from a CO_2-rich fluid by Fischer-Tropsch synthesis, fractionation of $\delta^{13}C$ will have occurred. Bottinga (1969) calculated the fractionation factor between CO_2 and CH_4 for a range of temperatures. At the inferred low temperatures and pressures, of *ca.* 350 °C and <1 kbar, at which the CH_4 fluids were trapped, the fractionation factor would be 21–22‰ with a shift towards a lighter signature for $\delta^{13}C_{CH4}$ (Bottinga, 1969). Given the magnitude of this fractionation factor, the $\delta^{13}C_{CO2}$ signature of the primary, magmatic CO_2-dominant fluid would have been about minus 4‰. This value falls within the fields of mantle carbon (Mattey *et al.*, 1990) and carbonatite (Deines, 1989). The $\delta^{13}C_{CH4}$ results obtained in this study are close to the figure of *ca.* –27‰, which defines a large variety of peridotites and xenoliths that contain hydrocarbons (Sugisaki & Mimura, 1994). The Fischer-Tropsch synthesis has been suggested as a mechanism for the production of hydrocarbons from these environments as well (Sugisaki & Miruma, 1994). If this is so, the carbon-isotope data are consistent with a suggestion that secondary methane is a frequent abiogenic product of the hydration of alkaline and mafic igneous rocks at high crustal levels.

The recognition in this, and other studies, that Fischer-Tropsch reactions are important in producing methane suggests that such reactions may produce significant amounts of abiogenic methane through mineral-fluid equilibria in crystalline rocks undergoing alteration at high crustal levels. That methane is scarce in the unaltered rocks of the Kovdor complex but present in the altered rocks of the neighbouring Sokli complex suggests that alteration is a requirement for methane production. The close association of methane inclusions and magnetite in fracture arrays has two implications for this process. Firstly, that fracture systems are important in encouraging movement of reduced fluids throughout the complexes. Secondly, that there is likely to be a positive feedback mechanism between the Fischer-Tropsch reactions which produce CH_4 and H_2O and the hydration reactions which reduce the system further and produce magnetite and H_2 to further drive the Fischer-Tropsch reactions. It is clear on the basis of fluid inclusion studies, PTVX modelling, and isotopic data that the extreme abundance of methane in alkaline rocks of the Kola province can be explained without resort to models involving graphite or to the incorporation of biogenic methane from country rocks. Neither does the methane abundance require the direct extraction of methane from the mantle.

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