

A review of the occurrence and origin of abiogenic hydrocarbons in igneous rocks

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Abstract: Reports on the presence of hydrocarbons in igneous rocks have been on the increase and generating greater interest in the scientific community over the last 20 years. Most of the occurrences are due to the incorporation of organic material into the magmatic systems. However, reports on the presence of hydrocarbons formed by abiogenic processes have also increased in recent years, suggesting that these hydrocarbons may not be as rare as previously thought and may have implications for natural gas resources in the future. This paper reviews these occurrences and the models proposed for the generation of these hydrocarbons, in particular the nature of the hydrocarbon-bearing fluids in the alkaline complexes Khibina, Lovozero and Ilímaussaq. The origin of these hydrocarbons remains controversial, whether they are (1) derived directly from the mantle, (2) formed during late crystallization stages by respeciation of a C–O–H fluid below 500 °C, or (3) formed during postmagmatic alteration processes involving Fisher–Tropsch type reactions catalysed in the presence of Fe-oxides and silicates. The reports suggest that a direct mantle origin for the hydrocarbon fluid is unlikely. A model involving near-solidus reequilibration of a C–O–H fluid to a CH₄-rich composition is possible, although only for extreme melt compositions that have large crystallization temperature ranges (i.e. hyperaluminous melts). The Fischer–Tropsch synthesis of hydrocarbons in igneous rocks seems to be a more applicable model for a wide variety of igneous rocks.

The origin of abiogenic hydrocarbons in rocks has recently attracted considerable research interest in geology and applied geology. Most of the Earth's hydrocarbons occur in sedimentary rocks and have been produced from biogenic material during burial and diagenesis (e.g. Schidlowski 1982; Belokon *et al.* 1995). Hydrocarbons in fluid inclusions from metamorphic rocks are also well documented and are thought to have been produced abiogenically through reactions between graphite or bitumen, present in the initial sedimentary rock, and a H₂O-bearing fluid during metamorphism (Holloway 1984; Samson & Williams-Jones 1991; Andersen & Burke 1996). In contrast, fluids associated with igneous rocks are generally CO₂ and H₂O rich (e.g. Roedder 1984; Andersen 1986; Vard & Williams-Jones 1993; Samson *et al.* 1995; Morogan & Lindblom 1995). However, the discovery of large volumes of hydrocarbons in the alkaline intrusions of Khibina and Lovozero of the Kola Peninsula, NW Russia, and Ilímaussaq in Greenland in the late 1950s (Petersilie *et al.* 1961; Petersilie 1962; Petersilie & Sørensen 1970) produced much interest in possible natural gas

resources in igneous rocks. These findings led to the proposition of the existence of potentially large natural gas reservoirs produced abiogenically by streaming of hydrocarbons directly from the mantle (Porfir'ev 1974; Gold 1979; Giardini *et al.* 1982) that ended in the ill-fated Graveberg-1 well drilled into the Siljan Ring Complex, Sweden (Jeffrey & Kaplan 1988; Kerr 1990). The recognition in recent years of the potential for the presence of large hydrocarbon reservoirs in igneous rocks has led to the discovery of many oil–gas fields in igneous and metamorphic basement rocks as well as hydrocarbon occurrences on a smaller scale. The majority of these hydrocarbons are biogenic in origin, having infiltrated through fractures from the surrounding sedimentary source rocks into the igneous assemblage or incorporated into hydrothermal springs associated with igneous terrains (Des Marais *et al.* 1981; Welhan & Lupton 1987; Simoneit 1988; Gize & McDonald 1993; Darling *et al.* 1995; Darling 1998). However, over the last 20 years there have also been many reports emerging on abiogenic hydrocarbons discovered in a variety of igneous rock

types, from ultrabasic and basic rocks (Jeffrey & Kaplan 1988; Abrajano *et al.* 1988, 1990; Larsen *et al.* 1992; Sherwood-Lollar *et al.* 1993; Sugisaki & Mimura 1994; Kelley 1996; Kelley & Früh-Green 2001), to alkaline rocks (Gerlach 1980; Konnerup-Madsen *et al.* 1985; Jeffrey & Kaplan 1988; Ting *et al.* 1994; Salvi & Williams-Jones 1997; Potter *et al.* 1998), mantle xenoliths (Mathez 1987; Krot *et al.* 1994) and hydrothermal gas plumes (Welhan & Craig 1983; Botz *et al.* 1996; Charlou *et al.* 1998).

The proliferation of reports on hydrocarbons in igneous rocks indicates that they may be more widespread than previously thought. However, the origin of these hydrocarbons is still somewhat controversial, as is the mechanism which generated them. This paper reviews the occurrence and composition of abiogenic

hydrocarbons in igneous rocks and will summarize and discuss the models that have been proposed for the origin of these hydrocarbons. Critical evaluation of these models could lead to the possibility of predicting the presence of abiogenic hydrocarbons in igneous rocks and their potential as a natural gas resource in the future.

Abiogenic hydrocarbon occurrences in igneous rocks

The origin of abiogenic hydrocarbons in igneous rocks has been of interest to Russian scientists since the beginning of the 20th century. However, little information on this phenomenon has

Table 1. A summary of reports on abiogenic hydrocarbon occurrences in a variety of igneous rocks

Reference	Rock type	Locality	Interpretation of source
Petersilie <i>et al.</i> 1961	Alkaline ne-syenite	Kola Peninsula	magmatic
Petersilie 1962	Alkaline ne-syenite	Kola Peninsula	magmatic
Zakrzhevskaya 1964	Alkaline ne-syenite	Kola Peninsula	magmatic
Karzhavin & Vendillo 1970	Alkaline ne-syenite	Kola & Siberia	magmatic
Gerlach 1980	Alkaline ne-syenite	Kola Peninsula	late magmatic
Kogarko <i>et al.</i> 1987	Alkaline ne-syenite	Kola Peninsula	late magmatic
Ikorski 1991	Alkaline ne-syenite	Kola & Siberia	abiogenic
Voytov 1992	Alkaline ne-syenite	Kola Peninsula	abiogenic
Ikorski <i>et al.</i> 1993	Alkaline ne-syenite	Kola Peninsula	late magmatic
Nivin <i>et al.</i> 1995	Alkaline ne-syenite	Kola Peninsula	post magmatic
Potter <i>et al.</i> 1998	Alkaline ne-syenite	Kola Peninsula	post magmatic
Petersilie & Sørensen 1970	Alkaline ne-syenite	Kola & Greenland	magmatic
Konnerup-Madsen & Rose-Hansen 1982	Alkaline ne-syenite	Ilímaussaq, Greenland	late magmatic
Konnerup-Madsen <i>et al.</i> 1985	Alkaline ne-syenite	Ilímaussaq, Greenland	late magmatic
Larsen <i>et al.</i> 1992	Gabbro	Skaergaard, Greenland	magmatic
Sherwood-Lollar <i>et al.</i> 1993	Basic shield rocks	Canada & Finland	post magmatic
Sherwood-Lollar <i>et al.</i> 2002	Basic shield rocks	Kidd Creek, Canada	post magmatic
Jeffrey & Kaplan 1988	Granite & dolerite	Siljan, Finland	post magmatic
Salvi & Williams-Jones 1992	Alkaline granite	Strange Lake, Quebec	post magmatic
Salvi & Williams-Jones 1997	Alkaline granite	Strange Lake, Quebec	post magmatic
Welhan & Craig 1983	Hydrothermal	21°N EPR	post magmatic
Neal & Stanger 1983	Ophiolite	Oman	post magmatic
Mathez 1987	Mantle xenolith	Hawaii	abiogenic
Abrajano <i>et al.</i> 1988	Ophiolite	Zambales, Philippines	post magmatic
Abrajano <i>et al.</i> 1990	Ophiolite	Zambales, Philippines	post magmatic
Sugisaki & Mimura 1994	Basic	50 localities	abiogenic
Krot <i>et al.</i> 1994	Mantle garnet	Mir, Siberia	magmatic
Kharmalov <i>et al.</i> 1981	Carbonatite	Kovdor, Kola	magmatic
Ting <i>et al.</i> 1994	Carbonatite	Sukulu, Uganda	abiogenic
Gerlach 1980	Carbonatite	Nyiragongo	late magmatic
Botz <i>et al.</i> 1996	Hydrothermal	Milos, Greece	post magmatic
Kelley 1996	Basalt	SWIR	post magmatic
Kelley & Früh-Green 2001	Basalt	SWIR	late magmatic
Charlou <i>et al.</i> 1998	Hydrothermal	MAR	post magmatic

EPR, East Pacific Ridge; SWIR, South-West Indian Ridge; MAR, Mid-Atlantic Ridge. *Note:* Where 'abiogenic' is listed no further interpretation of the origin was reported. Reports of hydrocarbon occurrences in volcanic rocks, where the hydrocarbons have migrated in from external reservoirs, are not included here.

been accessible outside Russia. Therefore, the presence of abiogenically formed hydrocarbons in crystalline rocks has generally not been noted by western scientists.

A summary of recent reports on hydrocarbons in igneous rocks is shown in Table 1, with their interpreted origin. The review by Porfir'ev (1974) listed many early reports of hydrocarbons found in crystalline rocks including many intrusive rocks in Siberia (i.e. Anabar, Timan, Volga, Kamchatka) as well as large hydrocarbon accumulations in the shield rocks of California, the Urals, Ukraine, southern Norway, Arizona and Nevada. He argued that most of these hydrocarbons could be inorganic in origin and that they could come directly from the upper mantle through drainage into deep-seated faults. Petersilie *et al.* (1961), Petersilie (1962), Zakrzhevskaya (1964) and Petersilie & Sørensen (1970) described large volumes of hydrocarbons, (up to 168 cm³ of CH₄/kg of rock), found in the alkaline intrusions of Khibina and Lovozero on the Kola Peninsula and the Ilímaussaq intrusion, Greenland. They interpreted them as magmatic in origin (Table 1). Thermodynamic calculations demonstrated that a CH₄-rich fluid could be stable at magmatic conditions (Karzhavin & Vendillo 1970). Further hydrocarbon occurrences were noted in the alkaline intrusions, Kiyar-Shaltyr and Sredniy-Tatar (Transangaara) in Siberia (Karzhavin & Vendillo 1970; Ikorski 1991). Later investigations of the hydrocarbon inclusions in Khibina, Lovozero and Ilímaussaq linked the trapping of hydrocarbon-bearing inclusions to late- or post-magmatic stages below 600 °C, between 0.5–1.5 kbar (Gerlach 1980; Konnerup-Madsen *et al.* 1985; Kogarko *et al.* 1987; Konnerup-Madsen 1988; Ikorski *et al.* 1993; Nivin *et al.* 1995; Potter *et al.* 1998) (Table 1). Hydrocarbon occurrences in alkaline igneous rocks have been extended to include peralkaline granites and carbonatites with reports of hydrocarbons in the Strange Lake granitic complex, Quebec (Salvi & Williams-Jones 1992; Salvi & Williams-Jones 1997), the Sukulu carbonatite, Uganda (Ting *et al.* 1994) and Nyiragongo crater, Tanzania (Gerlach 1980) (Table 1). The Strange Lake granite contains mixed aqueous-carbonic fluid inclusions that are composed mainly of CH₄, H₂, C₂H₆, CO₂, H₂O and NaCl with smaller amounts of hydrocarbons up to C₆ (Salvi & Williams-Jones 1997). The Sukulu carbonatite contains CO₂, H₂O and CH₄-bearing inclusions. These CH₄-bearing inclusions were also been interpreted as abiogenic in origin and linked to late and post-magmatic processes within the intrusions (Ting *et al.* 1994).

Mathez (1987) described the presence of carbonaceous matter in mantle xenoliths and ultra-basic magmatic cumulates, occurring as films on crack surfaces, and on walls of fluid inclusions. These films were thought to be condensates from volcanic gases during cooling of the host rock. Complex hydrocarbon inclusions were also found in garnet phenocrysts in the Mir kimberlite, Siberia (Krot *et al.* 1994) and are thought to be magmatic in origin, stable at the high pressures where the kimberlite magma formed (~10 GPa) and preserved due to the rapid transportation of the kimberlite to the surface.

The presence of hydrocarbons in basic and ultrabasic rocks was noted as early as 1902 by Mendelyev (see review by Porfir'ev 1974). Neal & Stanger (1983) noted the presence of up to 4.1 vol% CH₄ and 99 vol% H₂ in the gas phase from spring water emerging from the Oman ophiolitic suite. The generation of CH₄ and H₂ was linked with the serpentinization of these basic rocks. This process was also noted in the Zambales ophiolite in the Philippines by Abrajano *et al.* (1990) where CH₄ and H₂ were the dominant gases in seeps coming from the partially serpentinized body. Other authors have reported the presence of hydrocarbons and H₂ in serpentinized basic rocks from carbonic fluid inclusions in mid-ocean ridge basalt (Kelley 1996), in the basic rocks of the Canadian and Fennoscandian shields (Sherwood-Lollar *et al.* 1993, 2002), in dolerite dykes in the Siljan ring complex (Jeffrey & Kaplan 1988), in hydrothermal vents releasing up to 1.45 cm³/kg CH₄ and 38 cm³/kg H₂ at the East Pacific Ridge (Welhan & Craig 1983), and intense CH₄ plumes at the Mid-Atlantic ridge (Charlou *et al.* 1991, 1998). Abundant H₂ was observed in gases in ventilation shafts in the highly serpentinized dunites and peridotites of the Kempirsay intrusion, Siberia (Devirts *et al.* 1993). Larsen *et al.* (1992) described the presence of primary CH₄-H₂O-NaCl fluid inclusions in gabbroic pegmatites in the Skaergaard intrusion, Greenland, and interpreted the CH₄ to have evolved from a magmatic C-O-H fluid during the last stages of crystallization between 655–770 °C at low oxygen fugacities. Similar early CO₂-CH₄-NaCl fluids were found in basalts from the Mid-Atlantic Ridge, implying a similar magmatic origin (Kelley & Früh-Green 2001). Sugisaki & Mimura (1994) analysed hydrocarbons in a range of basic rocks from 50 localities. They proposed three possible origins for these hydrocarbons: (1) they were synthesized by Fischer-Tropsch reactions in the mantle from CO₂ and CO, or (2) they are primeval in

origin, delivered by meteorites during the accretion of the Earth and preserved in the mantle, or (3) they are derived from recycled, subducted biogenic hydrocarbon material.

The nature of hydrocarbon-bearing fluid inclusions in silica-undersaturated alkaline igneous complexes

Khibina and Lovozero complexes, Kola

A more detailed description of the fluid inclusions found in these complexes can be found in Potter *et al.* (1998) or Potter (2000). In summary, the most abundant fluid inclusions in both complexes are hydrocarbon-rich inclusions consisting predominantly of a low-density vapour (0.16 g cm^{-3}). These occur in healed fractures and cleavages within the host minerals (nepheline, apatite, eudialyte, sodalite). Other, less common, associated fluid inclusions consist of a low-salinity, aqueous fluid and rare mixed hydrocarbon–aqueous inclusions. These occur within the same fracture planes as the hydrocarbon-rich inclusions. This implies that the fluids were coeval, but immiscible. The inclusions are secondary in nature and are commonly observed to be present in rock samples that (1) contain titanomagnetite grains showing reaction rims of biotite, aegirine and pure magnetite; (2) contain arfvedsonite grains partially replaced by aegirine; (3) contain hydrated Na/K silicates; or (4) occur as inclusions attached to aegirine microlites (Potter *et al.* 1999).

Microthermometric data from the hydrocarbon-rich inclusions show that the majority of the inclusions are composed of pure CH_4 (critical homogenization temperature of $\text{CH}_4 \sim -82^\circ\text{C}$). Anomalously low CH_4 homogenization temperatures (down to -119°C) indicate the presence of H_2 , confirmed by laser-Raman analysis. Higher CH_4 homogenization temperatures (up to -25°C) indicate the presence of higher hydrocarbons (up to 40 mol% C_2H_6), confirmed by laser-Raman analysis (Potter 2000). The total homogenization temperatures and decrepitation temperatures of the aqueous, hydrocarbon-rich and mixed hydrocarbon–aqueous inclusions occur near the $\text{CH}_4\text{--H}_2\text{O}$ solvus at 350°C (Zhang & Frantz 1992). PVTX modelling of these fluids (i.e. calculating the volumetric and compositional properties of these fluids) infers trapping pressures and temperatures of around 0.5–1.5 kbars (equivalent to 1.5–5 km depth assuming lithostatic pressure) and 350°C (Potter *et al.* 1998).

The Ilímaussaq complex, Greenland

A more detailed description of the fluid inclusions in the Ilímaussaq complex can be found in Konnerup-Madsen *et al.* (1981), Konnerup-Madsen & Rose-Hansen (1982) and Konnerup-Madsen *et al.* (1985). In summary, hydrocarbon-rich gaseous inclusions predominate in all examined minerals from the Ilímaussaq nepheline syenites and in hydrothermal veins considered to have formed from fluids expelled from the late nepheline syenites of the intrusion. Aqueous inclusions are only present in very limited numbers. Mixed hydrocarbon–aqueous inclusions are only very rarely observed in minerals from the nepheline syenites and, in general, there does not appear to be any connection between the hydrocarbon-rich and the aqueous fluids. The few aqueous inclusions observed in minerals from the nepheline syenites are isolated high-salinity inclusions, suggesting that they were entrapped prior to the hydrocarbon inclusions that are largely confined to more or less effectively healed fractures. A minor number of the hydrocarbon gaseous inclusions, however, occur in isolation, are occasionally associated with aegirine microlites in nepheline, and may be of a more primary nature. In the hydrothermal vein minerals, the commonly observed association of highly saline aqueous inclusions and hydrocarbon-rich inclusions indicates the simultaneous entrapment of non-miscible fluids at this stage.

Microthermometric data on the hydrocarbon-rich inclusions show the earliest entrapped fluids to be composed of pure CH_4 in the nepheline syenites, whereas in the late hydrothermal veins higher contents of e.g. ethane (Th_{CH_4} at -60° to -55°C) are indicated, confirmed by laser-Raman analyses. Homogenization to liquid of the earliest entrapped hydrocarbon-rich inclusions range from -90° to -82°C in minerals from the nepheline syenites, and from -110° to -90°C in the late hydrothermal veins. PVTX modelling infers trapping pressures around 1–2 kbars, equivalent to 3–6 km depth, assuming lithostatic pressure and temperatures of 400° to 600°C for these fluids (Konnerup-Madsen 2001).

Chemistry of abiogenic hydrocarbons in igneous rocks

Bulk gas compositions

Bulk gas compositions of hydrocarbon-bearing fluids in the alkaline complexes Khibina,

Lovozero, Ilímaussaq and Strange Lake have been obtained by mechanical crushing of the rock samples in a vacuum ball mill with the subsequent released gases transported into a chromatograph. Tables 2 and 3 summarize the compositions of the gases in these alkaline rocks along with some borehole gases collected from pressurized pockets within the Canadian and Fennoscandian shield rocks. The majority of the analyses are dominated by CH₄ (80–90 vol%), with higher hydrocarbons decreasing exponentially with increasing carbon number. Hydrocarbons up to C₅ have been detected (Petersilie 1962; Petersilie & Sørensen 1970; Konnerup-Madsen & Rose-Hansen 1982; Voytov 1992; Salvi & Williams-Jones 1997). Methane concentrations can reach as high as 168.7 cm³/kg (Petersilie 1962). Carbon dioxide is either absent or present in small concentrations (up to 4 vol%) (Konnerup-Madsen *et al.* 1979). In the Lovozero samples, H₂ is relatively abundant as the second dominant species after CH₄. This H₂ is present as a free gas in fluid inclusions. Laser-Raman investigations determined that the hydrocarbon-bearing inclusions can have compositions up to 65 mol% CH₄ and 35 mol% H₂ (Potter 2000).

Notable exceptions are analyses 11 and 60 of altered samples that contain distinctly lower CH₄ concentrations and a significant increase in CO₂ in comparison to their unaltered equivalents. This has been attributed to the oxidation of the CH₄ fluid to CO₂ during low-temperature weathering (<150 °C) of the minerals to clays (Petersilie 1962). Other exceptions are analyses 3, 8, 31, 39, 40 and 50. These monchiquite dykes, alkali effusives and early olivine gabbros are dominated by H₂O fluids with low concentrations of gaseous volatiles consisting of CO₂ and CO very different to the fluid inclusion assemblages observed in the other samples. The high H₂ concentrations detected probably came from dissociation of H₂O during crushing, as no evidence from the fluid inclusions suggests that free H₂ gas is present in these samples. Characterization of fluid inclusions in samples 39 and 40 revealed that they contained H₂O-dominant inclusions (Potter 2000). The analyses revealed low gaseous concentrations (<7 cm³/kg) dominated by H₂ and CO₂ that may have come from dissociation of H₂O and decarbonation of carbonate minerals in these samples (i.e. cancrinite and calcite). Analyses from gases from the Canadian and Fennoscandian shield rocks also show high percentage volumes of N₂ and He in contrast to the gas analyses from the alkaline igneous rocks (Table 2).

Stable isotope characteristics

Table 4 shows a summary of the stable isotope results for a number of reports on hydrocarbon-bearing fluids in a variety of igneous terrains. Figure 1 shows the collated $\delta^{13}\text{C}_{\text{CH}_4}$ and $\delta\text{D}_{\text{CH}_4}$ data for a variety of hydrocarbon-bearing fluids in igneous rocks, plotted alongside well-established source fields. The $\delta^{13}\text{C}_{\text{CH}_4}$ results show a large range in values from –3.2‰ to –44.9‰. The majority of examples, however, are in the range of –20‰ to –28‰ (Fig. 1; Table 4). This range of $\delta^{13}\text{C}_{\text{CH}_4}$ results would indicate that the hydrocarbon-bearing fluid is abiogenic in origin (biogenic signatures tend to be more depleted for CH₄). However, the results do not fall within the mantle field (–3‰ to –9‰), so a direct mantle origin is unlikely. The $\delta^{13}\text{C}_{\text{CO}_2}$ results for associated CO₂ fluids range from 0.6‰ to 7.1‰. The CO₂ analysed by Botz *et al.* (1996) was interpreted as originating from marine carbonates ($\delta^{13}\text{C}_{\text{CO}_2} \sim 0\text{‰}$). The $\delta^{13}\text{C}_{\text{CO}_2}$ results of around –7‰ for the CO₂ fluids in the Khibina complex (Potter 2000) and the East Pacific Rise (Welhan & Craig 1983) fall in the mantle field and are interpreted as magmatic in origin. In the Ilímaussaq intrusion, the $\delta^{13}\text{C}_{\text{CH}_4}$ results show a more restricted range in values from –1.0‰ to –7.0‰. The calculated $\delta^{13}\text{C}_{\text{CH}_4}$ of the bulk carbon of the hydrocarbon fluids is $-4.5\text{‰} \pm 1.5\text{‰}$, interpreted to be a clear magmatic/juvenile signature (Konnerup-Madsen 2001).

The $\delta\text{D}_{\text{CH}_4}$ results tend to fall around –110‰ to –135‰ with the exception of gases from the Canadian Shield showing depleted values down to below –400‰. These values plot in the fumaroles and hot springs or juvenile fields on the $\delta^{13}\text{C}_{\text{CH}_4}$ – $\delta\text{D}_{\text{CH}_4}$ plot (Fig. 1). The majority of $\delta\text{D}_{\text{H}_2}$ signatures are extremely depleted with values below –600‰. Such $\delta\text{D}_{\text{H}_2}$ values have been noted in H₂ produced by serpentinization processes in basic rocks (Devirts *et al.* 1993).

The origin of hydrocarbons in igneous rocks

Two possible sources for hydrocarbons in igneous rocks can be envisaged: an organic (biogenic) origin, or an abiogenic origin. Three processes can generally be distinguished for organically derived material: bacterially generated hydrocarbons by either (1) CO₂ reduction or (2) fermentation or as (3) thermogenically derived hydrocarbons. In igneous rocks, biogenic hydrocarbons are generally all thermogenic in nature as the organic matter has been subjected

Table 2. Bulk gas analyses of abiogenic hydrocarbons in igneous rocks, in vol%, from the literature

Analysis #	Sample	CH ₄ vol%	C ₂ H ₆ vol%	C ₃ H ₈ vol%	C ₄ H _{10-I} vol%	C ₄ H _{10-n} vol%	C ₅ H _{10-I} vol%	C ₅ H _{10-n} vol%	HHC vol%	H ₂ vol%	CO vol%	CO ₂ vol%	N ₂ vol%	He vol%	O ₂ vol%
Khibina															
1	Khibinite	90.00	—	—	—	—	—	—	2.15	1.77	1.32	0.19	4.59	—	—
2	Ijolite	89.70	—	—	—	—	—	—	2.53	3.45	4.13	0.19	—	—	—
5	Ne syenite	93.42	1.08	0.24	0.0500	—	—	—	—	0.91	2.30	0.00	2.20	—	—
7	Rischorrite	60.10	4.86	1.19	0.1300	0.3600	—	—	—	5.96	9.34	1.85	16.21	—	—
8	Monchiquite	17.45	0.00	0.00	0.0000	0.0000	—	—	—	30.95	51.60	0.00	—	—	—
9	Malignite	70.30	1.18	0.51	—	—	—	—	—	10.34	15.10	2.57	—	—	—
10	Ijolite	71.96	2.78	0.73	0.0500	0.1500	0.07	0.04	—	1.99	6.77	0.67	14.52	—	—
11	Altered Ijolite	2.06	0.00	0.00	0.0000	0.0000	—	—	—	10.54	16.40	71.00	—	—	—
12	Yukspor mine	79.50	—	—	—	—	—	—	1.90	13.90	—	0.00	4.30	0.00	—
13	Yukspor mine	24.06	—	—	—	—	—	—	0.65	2.40	—	1.90	70.30	0.69	—
14	Yukspor mine	56.00	—	—	—	—	—	—	2.17	2.88	—	2.88	35.98	0.09	—
15	Kukisvumchorr mine	42.09	—	—	—	—	—	—	3.78	1.68	—	0.00	52.31	0.15	—
16	Rasvumchorr mine	91.59	—	—	—	—	—	—	4.68	1.40	—	0.00	1.58	0.54	—
17	Rasvumchorr mine	57.94	—	—	—	—	—	—	4.61	10.04	—	0.00	27.26	0.15	—
12a	Yukspor mine	97.64	0.76	1.52	—	0.0400	0.00	—	—	—	—	—	—	—	—
13a	Yukspor mine	96.10	3.19	0.43	—	0.2800	0.00	—	—	—	—	—	—	—	—
14a	Yukspor mine	96.00	3.32	0.48	—	0.2000	0.00	—	—	—	—	—	—	—	—
15a	Kukisvumchorr mine	91.80	6.28	1.55	0.1100	0.1700	0.08	—	—	—	—	—	—	—	—
16a	Rasvumchorr mine	94.88	4.36	0.58	0.0300	0.1100	0.03	—	—	—	—	—	—	—	—
17a	Rasvumchorr mine	92.58	6.56	0.52	0.0250	0.0270	0.00	—	—	—	—	—	—	—	—
26	Khibinite	95.69	2.93	0.15	0.0005	0.0020	—	—	—	1.16	0.00	0.03	—	0.04	—
27	Khibinite	95.55	3.15	0.16	0.0002	0.0010	—	—	—	1.08	0.00	0.02	—	0.03	—
28	Urtite	96.75	1.93	0.05	0.0060	0.0200	—	—	—	1.16	0.00	0.00	—	0.08	—
29	Rischorrite	90.04	3.59	0.17	0.0040	0.0080	—	—	—	4.02	1.97	0.17	—	0.03	—
30	Foyaite	92.84	1.63	0.13	0.0000	0.0030	—	—	—	5.37	0.00	0.34	—	0.00	—
31	Monchiquite	38.09	0.00	0.00	0.0000	0.0000	—	—	—	61.91	0.00	0.00	—	0.00	—
35	Ap-ne ore	83.79	2.08	—	—	—	—	—	—	7.95	—	0.00	6.16	0.00	—
36	Urtite	95.27	0.00	—	—	—	—	—	—	1.48	—	0.00	3.08	0.18	—
37	Ijolite	89.70	3.28	—	—	—	—	—	—	4.56	—	0.00	2.26	0.19	—
38	Rischorrite	81.17	4.04	—	—	—	—	—	—	8.97	—	0.00	5.83	0.01	—
39	Foyaite	1.69	0.03	—	—	—	—	—	—	27.36	—	28.38	42.57	0.10	—
40	Carbonatite	5.16	3.69	—	—	—	—	—	—	63.27	—	18.43	9.44	0.02	—

Table 2. (continued)

Analysis #	Sample	CH ₄ vol%	C ₂ H ₆ vol%	C ₃ H ₈ vol%	C ₄ H _{10-I} vol%	C ₄ H _{10-n} vol%	C ₅ H _{10-I} vol%	C ₃ H _{10-n} vol%	HHC vol%	H ₂ vol%	CO vol%	CO ₂ vol%	N ₂ vol%	He vol%	O ₂ vol%
Canadian Shield															
61	Sudbury N	12.55	0.07	0.02	—	<0.02	—	—	—	—	—	1.44	79.78	6.12	—
62	Sudbury CCS	74.00	4.21	0.31	—	0.13	—	—	—	7.13	—	0.21	8.77	5.30	—
63	Elliot Lake	54.20	0.11	0.02	—	0.03	—	—	—	—	—	0.11	26.40	19.10	—
64	Timmins	78.55	4.67	0.71	—	0.23	—	—	—	—	—	0.10	14.15	1.59	—
65	Red Lake - Dickenson	41.37	1.30	0.73	—	0.06	—	—	—	—	—	1.11	51.97	3.44	—
66	Red Lake - Campbell	56.35	2.20	0.99	—	<0.01	—	—	—	0.28	—	0.32	31.98	7.87	—
Fennoscandian Shield															
67	Juuka	78.90	0.79	<0.01	<0.01	—	<0.01	—	—	—	12.80	—	0.04	6.32	1.09

1-4 are analyses from Kogarko *et al.* (1987). HHC = C₂-C₅ or C₃-C₅ where individual C_n were not reported. 5-6 are from Petersilie (1962). 7-11 from Petersilie *et al.* (1961). 12-17 are free gas analyses from gas jets in the Khibina mines taken from Voytov (1992). The vol% of the individual hydrocarbons present are displayed in 12a-17a. 18-20 are occluded gas analyses, 21-25 are free gas analyses from Nivin *et al.* (1995). 26-34, 46-50 are from Petersilie & Sørensen (1970). 35-45 are from Potter (2000). 51-53 are from Konnerup-Madsen & Rose-Hansen (1982). 54-58 are from Konnerup-Madsen *et al.* (1979). 59-60 are from Salvi & Williams-Jones (1997). 61-67 are average compositions from Sherwood-Lollar *et al.* (1993). *Note:* the majority of reports of hydrocarbons do not report bulk gas contents.

Table 3. Bulk gas analyses of abiogenic hydrocarbons in igneous rocks, in cm³/kg, from the literature

Analysis #	Sample	Total gas cm ³ /kg	C ₁ H ₄ cm ³ /kg	C ₂ H ₆ cm ³ /kg	C ₃ H ₈ cm ³ /kg	C ₄ H ₁₀ -I cm ³ /kg	C ₄ H ₁₀ -n cm ³ /kg	C ₅ H ₁₀ -I cm ³ /kg	C ₅ H ₁₀ -n cm ³ /kg	HHC cm ³ /kg	H ₂ cm ³ /kg	CO cm ³ /kg	CO ₂ cm ³ /kg	N ₂ + inert cm ³ /kg
Khibina														
1	Khibinite	41.78	—	—	—	—	—	—	—	0.89	0.74	0.55	0.08	1.92
2	Ijolite	33.90	—	—	—	—	—	—	—	0.86	1.17	1.40	0.06	—
5	Ne syenite	176.66	—	1.910	0.400	0.1000	—	—	—	—	1.50	4.05	0.00	—
7	Rischorrite	20.97	—	1.020	0.250	0.0380	0.0760	—	—	—	1.25	1.96	0.39	3.40
8	Monchiquite	25.00	—	0.000	0.000	0.0000	0.0000	—	—	—	6.19	15.32	0.00	—
9	Malapinite	19.33	—	0.230	0.010	—	—	—	—	—	2.00	2.93	0.59	—
10	Ijolite	33.78	—	0.950	0.019	0.0520	0.0270	0.0130	—	—	0.68	2.31	0.23	5.00
11	Altered Ijolite	21.34	—	0.000	0.000	0.0000	0.0000	—	—	—	2.25	3.50	15.15	—
26	Khibinite	54.20	—	1.590	0.080	0.0003	0.0010	—	—	—	0.63	0.00	0.02	0.02
27	Khibinite	44.36	—	1.400	0.070	0.0001	0.0005	—	—	—	0.48	0.00	0.01	0.02
28	Urtite	50.85	—	0.980	0.020	0.0030	0.0110	—	—	—	0.59	0.00	0.00	0.04
29	Rischorrite	11.71	—	0.420	0.020	0.0004	0.0009	—	—	—	0.47	0.23	0.02	—
30	Foyaite	11.46	—	0.190	0.020	—	0.0004	—	—	—	0.62	0.00	0.04	—
31	Monchiquite	0.84	—	—	—	—	0.0000	—	—	—	0.52	0.00	0.00	—
35	Ap-ne ore	139.96	—	0.290	—	—	—	—	—	—	1.11	—	0.00	0.86
36	Urtite	113.11	—	0.000	—	—	—	—	—	—	1.67	—	0.00	3.45
37	Ijolite	45.15	—	1.480	—	—	—	—	—	—	2.06	—	0.00	1.11
38	Rischorrite	22.30	—	0.900	—	—	—	—	—	—	2.00	—	0.00	1.30
39	Foyaite	2.96	—	0.000	—	—	—	—	—	—	0.81	—	0.84	1.26
40	Carbonatite	6.78	—	0.250	—	—	—	—	—	—	4.29	—	1.25	0.64
Lovozero														
3	Alkali effusive	6.69	—	—	—	—	—	—	—	0.01	—	4.37	0.02	—
4	Ne syenite	18.55	—	—	—	—	—	—	—	1.16	—	2.01	0.03	—
6	Juvite	57.80	—	3.400	0.250	0.1500	—	—	—	—	4.80	2.50	0.00	—
32	Syenite	15.37	—	0.630	0.130	0.0016	0.0075	—	—	—	2.10	0.23	0.05	0.01
33	Urtite	19.44	—	1.060	0.590	—	—	—	—	—	1.31	—	0.08	—
34	Foyaite	33.22	—	0.920	0.430	—	0.0800	—	—	—	1.40	—	0.04	—
41	Eud Lujavrite	23.77	—	0.680	—	—	—	—	—	—	1.22	—	0.00	1.15
42	Lop Juvite	8.18	—	0.360	—	—	—	—	—	—	2.12	—	0.00	0.57
43	Lujavrite	7.38	—	0.360	—	—	—	—	—	—	1.82	—	0.00	0.23
44	Foyaite	26.59	—	0.510	—	—	—	—	—	—	1.10	—	0.00	1.21
45	Urtite	28.24	—	1.920	—	—	—	—	—	—	7.84	—	0.00	0.77
Hämaussaq														
46	Augite syenite	15.24	—	0.382	0.036	0.0061	0.0064	—	—	—	1.92	0.00	0.01	0.12
47	Naujaite	60.10	—	5.954	1.049	0.0750	0.1860	—	—	—	3.03	0.00	0.02	1.18
48	Sod Foyaite	5.75	—	0.424	0.077	0.0064	0.0210	—	—	—	0.73	0.40	0.00	0.01
49	Arf lujavrite	4.06	—	0.128	0.008	0.0004	0.0009	—	—	—	2.78	0.00	0.01	0.15
50	Olivine gabbro	2.72	—	0.001	0.002	0.0000	0.0000	—	—	—	2.54	0.00	0.00	0.04

1-4 are total gas contents for occluded gases from Kogarko *et al.* (1987). 5-6 are analyses from Petersilie (1962). 7-11 are analyses from Petersilie *et al.* (1961). Analyses 26-34, 46-50 are from Petersilie & Sørensen (1970). HHC = C₂, C₃, 35-45 are from Potter (2000). Note: Bulk gas analyses from other igneous terranes are not reported.

Table 4. A summary of isotopic data reported for abiogenic hydrocarbon-bearing fluids from various igneous terranes

Locality	Type	Origin	$\delta^{13}\text{C}_{\text{CH}_4}$	$\delta\text{D}_{\text{CH}_4}$	$\delta\text{D}_{\text{H}_2}$	$\delta^{13}\text{C}_{\text{CO}_2}$	Reference
Oman	Ophiolite	F-T synthesis~	—	—	-697 to -714	—	Neal & Stanger (1983)
21°N EPR	Hydrothermal	F-T synthesis~	-15 to -17.6	-102 to -126	-388 ± 15	-7 ± 0.1	Welhan & Craig (1983)
Sweden	Siljan dolerite	F-T synthesis	-16.5 to -26.3	—	—	—	Jeffrey & Kaplan (1988)
Sweden	Siljan granite	F-T synthesis	-19.4 to -36.7	—	—	—	Jeffrey & Kaplan (1988)
Philippines	Zambales ophiolite	F-T synthesis~	-6.1 to -7.5	-118 to -137	-581 to -599	—	Abrajano <i>et al.</i> (1990)
Kola Peninsula	Khibina	F-T synthesis	-3.2 to -12.8	—	—	—	Voytov (1992)
Canada & Scandinavia	Shield rocks	F-T synthesis~	-22.4 to -44.9	-133 to -372	-619 to -659	—	Sherwood-Lollar <i>et al.</i> (1993)
Canada & Scandinavia	Shield rocks	F-T synthesis~	-33.0 to -40.7	-390 to -419	—	—	Sherwood-Lollar <i>et al.</i> (2002)
Siberia	Kempirsay Ultramafite	F-T synthesis~	—	—	-744 to -766	—	Devirts <i>et al.</i> (1993)
Kola Peninsula	Lovozero	Post-magmatic	—	-132 to -164	-359 to -629	—	Nivin <i>et al.</i> (1995)
Various	Igneous Rocks	F-T synthesis	-26 to -29	—	—	—	Sugisaki & Mimura (1994)
Milos, Greece	Geothermal	F-T synthesis	-9.4 to -17.8	-104 to -377	—	-0.6 to -1.1	Botz <i>et al.</i> (1996)
Kola Peninsula	Khibina & Lovozero	F-T synthesis	-12.8 to -28.6	—	—	-7.1	Potter (2000)
Greenland	Ilímaussaq	Late-magmatic	-1 to -7	-132 to -145	—	—	Konnerup-Madsen (2001)

Abiogenic mechanisms proposed for the generation of the hydrocarbons: F-T synthesis—Fischer-Tropsch type reactions, ~ related to serpentinization of the assemblage, late-magmatic-closed system fluid respeciation. — not reported.

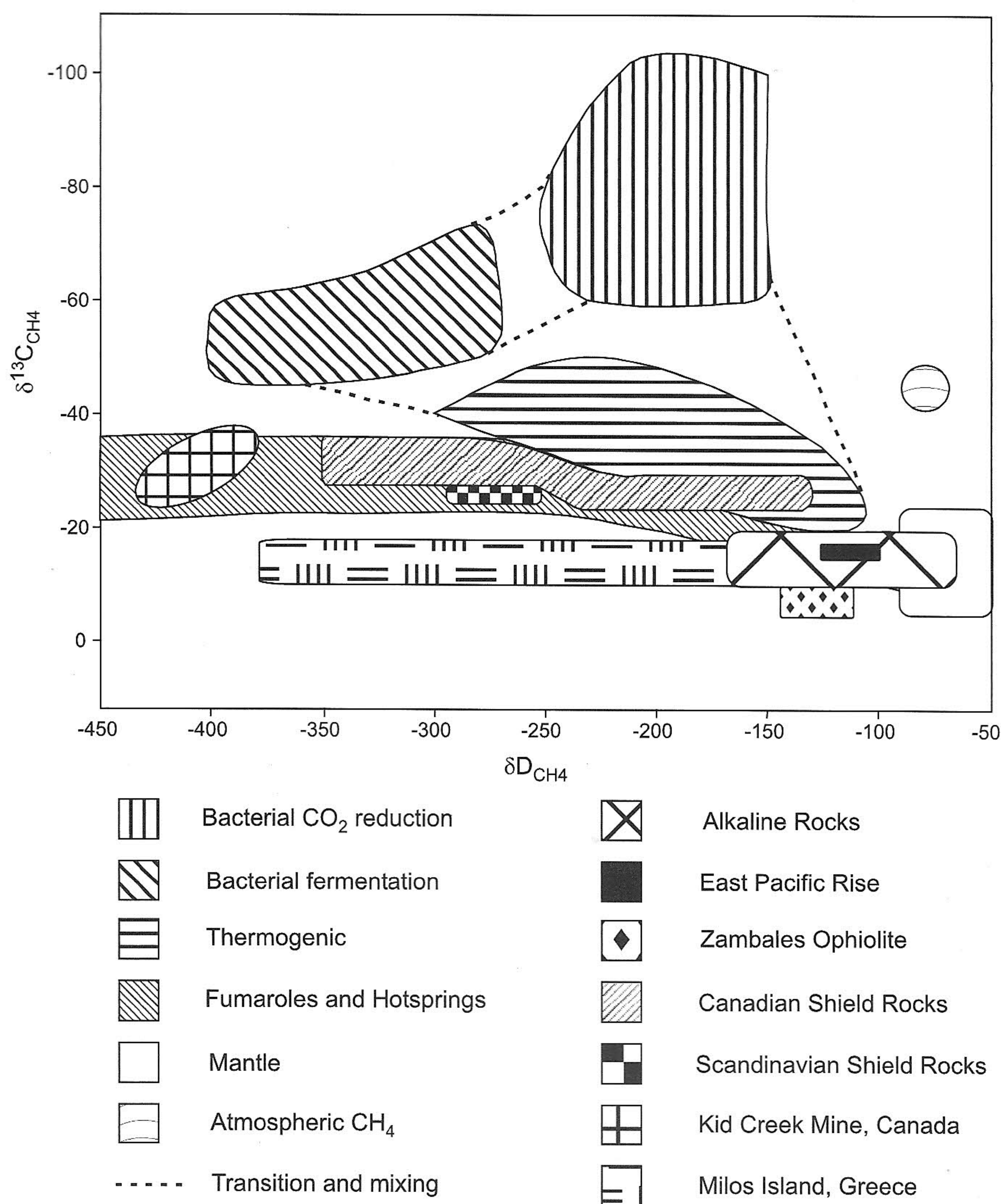


Fig. 1. A $\delta^{13}\text{C}_{\text{CH}_4}$ - $\delta\text{D}_{\text{CH}_4}$ diagram showing where reported abiogenically generated hydrocarbons fall in respect to a number of well-established fields for biogenically generated hydrocarbons and those directly from the mantle. These include the alkaline igneous complexes of Khibina, Lovozero and Ilímaussaq. Data have been taken from Welhan & Craig (1983), Schoell (1988), Abrajano *et al.* (1990), Voytov (1992), Sherwood-Lollar *et al.* (1993, 2002), Nivin *et al.* (1995), Botz *et al.* (1996), Potter (2000) and Konnerup-Madsen (2001).

to thermal alteration by the igneous body. The organic material may be leached out of the country rocks by late-magmatic or hydrothermal fluids and found in association with the igneous body (e.g. Welhan & Lupton 1987; Simoneit 1988; Gize & McDonald 1993) or entirely incorporated into and recycled in the magmatic hydrothermal system (Gunter & Musgrave 1971; Des Marais *et al.* 1981; Darling *et al.* 1995; Sakata *et al.* 1997; Darling 1998). Biogenic sources can be distinguished from abiogenic

sources by the $\delta^{13}\text{C}$ values of the hydrocarbons. The pattern of $\delta^{13}\text{C}$ values between the individual hydrocarbon species for hydrocarbons generated by thermal breakdown of organic matter and hydrocarbons generated by abiogenic polymerization processes can be distinctly different. The resulting $\delta^{13}\text{C}_{\text{CH}_4}$ values are generally used to differentiate between the two sources (Sherwood-Lollar *et al.* 2002; Horita & Berndt 1999). Biogenic sources tend to have more depleted $\delta^{13}\text{C}_{\text{CH}_4}$ values (below -30‰),

whereas more enriched $\delta^{13}\text{C}_{\text{CH}_4}$ values indicate an abiogenic origin (Schoell 1983, 1988).

There are three main theories on the abiogenic generation of hydrocarbons, which are not mutually exclusive:

(a) a direct mantle origin (e.g. Petersilie *et al.* 1961; Petersilie 1962; Petersilie & Sørensen 1970; Gold 1979) where hydrocarbons are either synthesized in the mantle via reactions with CO and CO₂, or are present as primeval hydrocarbons delivered by meteorites and preserved in the mantle since the accretion of the Earth (Sugisaki & Mimura 1994);

(b) closed system respeciation of a primary CO₂-bearing fluid during late to post-magmatic stages below 600 °C (Gerlach 1980; Konnerup-Madsen *et al.* 1985; Kogarko *et al.* 1987);

(c) generation of hydrocarbons during post-magmatic mineral–fluid reactions involving Fischer–Tropsch reactions (i.e. serpentinization) (Abrajano *et al.* 1990; Sherwood-Lollar *et al.* 1993; Kelley 1996; Salvi & Williams-Jones 1997; Charlou *et al.* 1998; Potter *et al.* 1998).

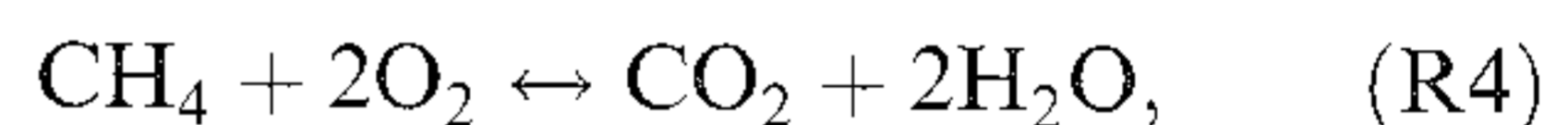
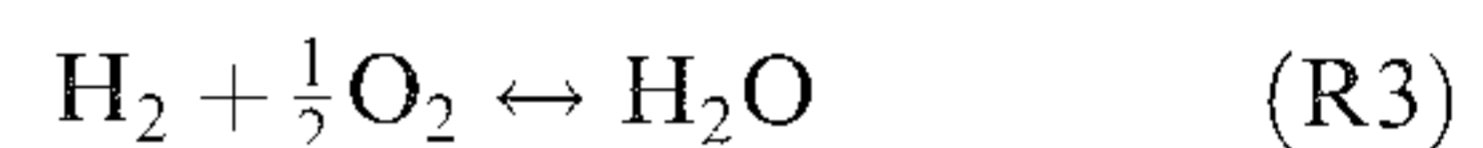
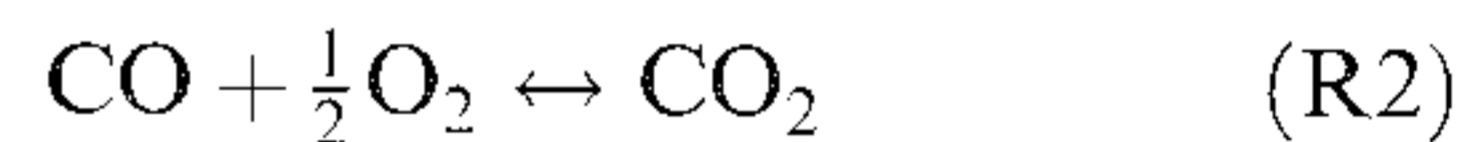
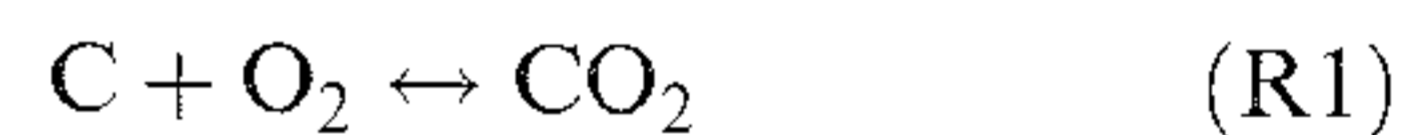
Mantle origin

The potential for exploitable abiogenic hydrocarbon reservoirs outgassing from the primeval mantle was first discussed by Gold (1979). He noted that most hydrocarbons found in igneous rocks have a uniform $\delta^{13}\text{C}$ isotopic signature between -25% and -28% . Although this signature is within the geothermal field, the uniformity of these $\delta^{13}\text{C}$ signatures suggested a common large homogenous source such as the mantle. Petersilie (1962) and Zakrzhevskaya (1964) interpreted the hydrocarbons found in the alkaline intrusions of Khibina and Lovozero as having a primary magmatic origin, and suggested there may be economic accumulations of hydrocarbon gases in deep zones within these massifs. The Graveberg-1 Siljan Ring drilling project was the first well drilled in crystalline rocks. The well was set down in a meteorite impact crater where numerous oil seeps had been observed. Although one hypothesis was that the hydrocarbons observed were generated by the abrupt baking of the surrounding source sediments at the time of impact (Vlierboom *et al.* 1986), the project was funded on the basis of Gold's hypothesis that large reserves of mantle gas might be stored within the crystalline basement (Gold 1979; Kerr 1990). However, only very small concentrations of CH₄ were found in the igneous rocks and these were interpreted as postmagmatic in origin (Jeffrey & Kaplan

1988). More recent fluid inclusion studies on the hydrocarbons found in the alkaline igneous intrusions Khibina and Lovozero have suggested these fluids are secondary and were trapped at temperatures and pressures around 350 °C and 0.5–1.2 kbars, not directly from the mantle (Kogarko *et al.* 1987; Nivin *et al.* 1995; Potter *et al.* 1998). Similarly, a late- to post-magmatic origin for the hydrocarbons in the Ilímaussaq intrusion has been proposed. Therefore, it can be concluded that a direct mantle origin is unlikely.

A late magmatic origin

The majority of abiogenic hydrocarbon occurrences in crystalline rocks have been suggested to be formed by the respeciation of a carbonic fluid in the C–O–H system (Karzhavin & Vendillo 1970; Gerlach 1980; Konnerup-Madsen & Rose-Hansen 1982; Holloway 1984; Kogarko *et al.* 1987; Samson & Williams-Jones 1991; Cesare 1995; Andersen & Burke 1996). In the presence of graphite ($a_{\text{GRAPHITE}} = 1$), the relative proportions of the main volatile species CO₂, CH₄ and H₂O are controlled by the four independent reaction equilibria:



plus



Studies by e.g. Holloway (1984), Huizenga (1995) and Cesare (1995) clearly demonstrated the effects of varying pressure, temperature, oxygen fugacity and activity of graphite for the speciation of a variety of fluids in the C–O–H system. Figure 2 shows schematically some important aspects of the C–O–H system related to the actual concentration of CH₄ to be observed in fluid inclusions.

Figure 2a schematically illustrates the phase relationships for the C–O–H system at some specified pressure and temperature conditions and low oxygen fugacities. Two initial fluid compositions (a and b; Fig. 2a) differ in their initial H₂O/CO₂ ratio. Re-equilibration of composition a (70% H₂O, 30% CO₂) to an oxygen fugacity of QFM-2 will change the initial fluid composition first away from the O apex onto the graphite saturation curve, and then along the graphite saturation curve, with associated precipitation

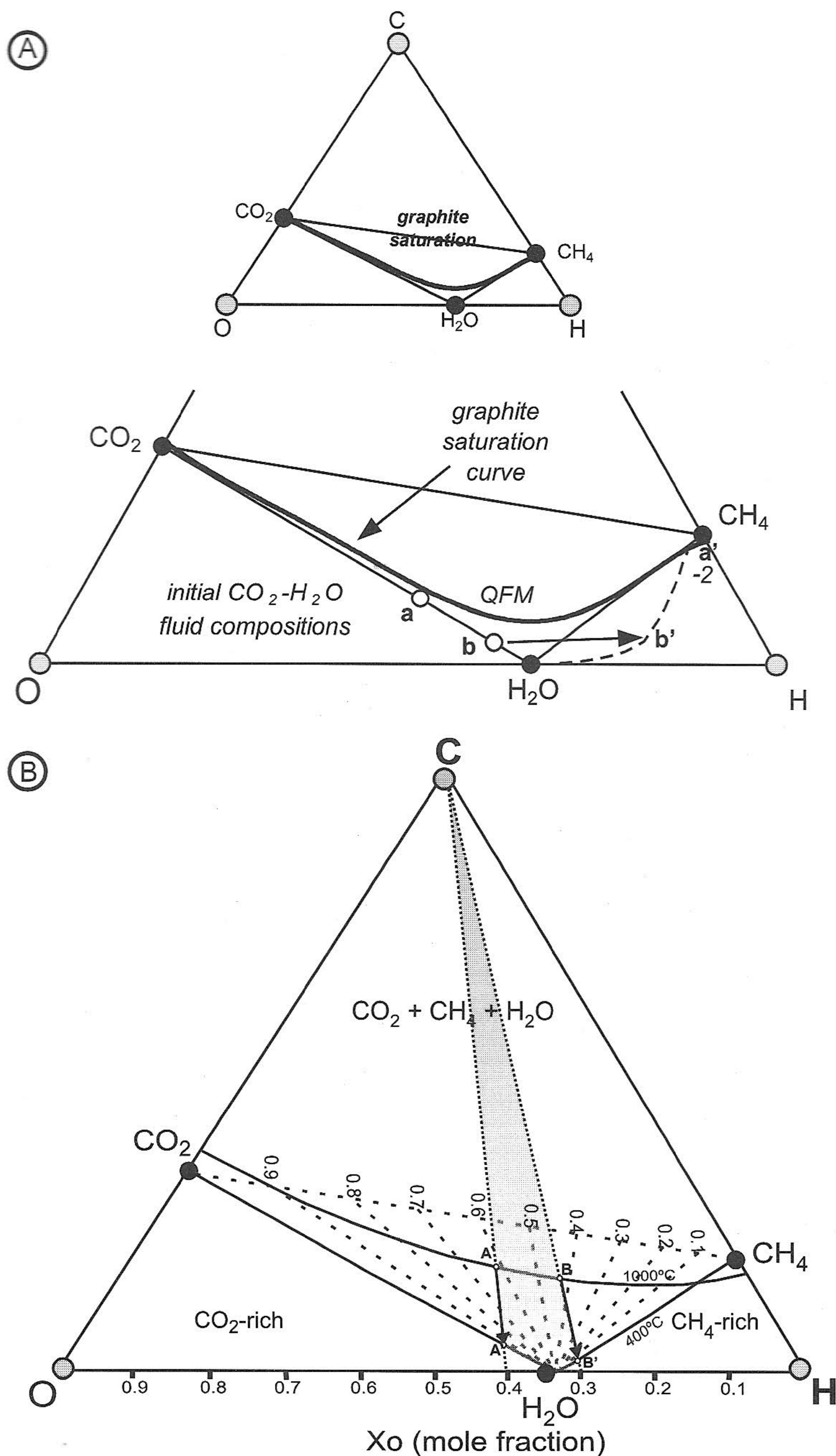


Fig. 2. (a) A schematic diagram showing phase relations in the C–O–H system at fixed temperatures and pressures (500 °C, 2 kbar) demonstrating the evolution of two fluid compositions (a and b) towards CH₄-rich compositions (a' and b') with decreasing f_{O_2} conditions (QFM to QFM-2). (b) Another schematic C–O–H diagram at fixed pressure (1 kbar) showing the down temperature evolution of C–O–H fluids at constant X_o ($X_o = O/O + H$) towards CO₂-rich, CH₄-rich or H₂O-rich compositions depending on initial X_o . The shaded area represents the H₂O-rich fluid region. Paths A–A' and B–B' represent temperature evolution of an H₂O-rich fluid with a minor CO₂-rich or CH₄-rich minor gas phase, respectively. Dashed lines represent CO₂/CO₂ + CH₄ ratio isopleths. See text for further discussion. Based on Konnerup-Madsen (2001), Huizenga (2001) and Cesare (1995). QFM = quartz–fayalite–magnetite buffer.

of graphite, to point **B'** (QFM-2 on the graphite saturation curve). Composition **b**, which is richer in H₂O (90% H₂O, 10% CO₂), will evolve away from the O apex along the arrow until point **b'** without the precipitation of graphite. Thus both compositions will re-equilibrate to CH₄-rich fluid compositions, composition **a** to an essentially H₂O-CH₄ fluid, and composition **b** to a H₂O-CH₄-H₂ fluid. Therefore, a CH₄-rich fluid could evolve in a closed system by re-equilibration from a primary more oxidized CO₂-CH₄-H₂O fluid under geologically reasonable *f*O₂ conditions below about 500 °C, between QFM and QFM-3. The CO₂/H₂O ratio of the initial fluid will determine whether or not graphite precipitates during re-equilibration.

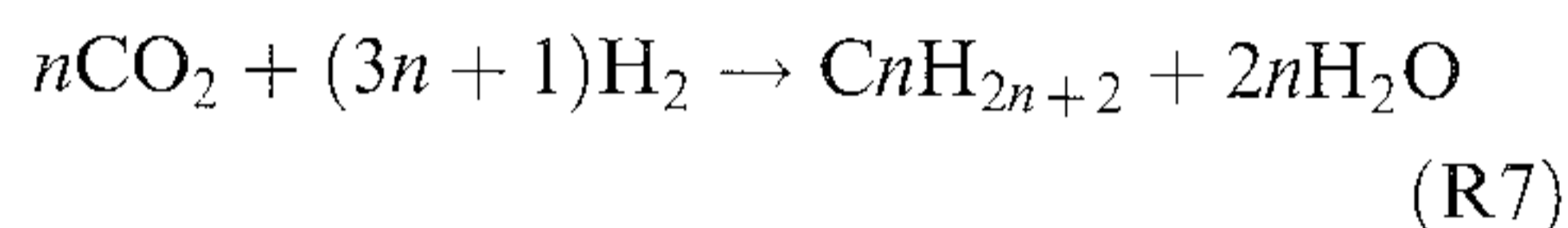
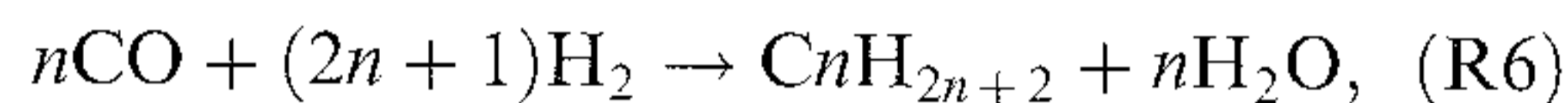
Figure 2b also illustrates schematically how a CO₂-CH₄-H₂O mixed fluid might evolve upon cooling. Depending on the initial X_o ratio (X_o = O/O + H), the C-O-H fluid could evolve to a CO₂-rich fluid (X_o > 0.4), a CH₄-rich fluid (X_o < 0.3) or an H₂O-rich fluid with a minor gas phase (X_o = 0.3-0.4). The X_o ratio remains constant throughout. Upon cooling, the fluid will pass through the graphite saturation curve, resulting in precipitation of graphite and a change in the CO₂/CO₂+CH₄ ratio. Two initial compositions, **A** and **B**, with X_o of 0.3 and 0.4 are shown at 1000 °C. Upon cooling to 400 °C these compositions will evolve to an H₂O-rich fluid. However, the minor gas phase in **A**, at 400 °C, is represented by the intersection of the CO₂/CO₂+CH₄ isopleth with the graphite saturation curve (point **A'**). The minor gas phase would consist of 90% CO₂, whereas, at point **B'**, the final gas phase would consist of 90% CH₄.

Therefore, Figure 2 clearly demonstrates how an early C-O-H fluid could evolve to a CH₄-rich composition below 500 °C. This model can be readily applied to CH₄ generation in metamorphic terranes (Holloway 1984), but for magmatic systems unusually low solidus temperatures are required. More recent studies on the hydrocarbons present in the alkaline intrusions Khibina, Lovozero, Ilímaussaq and Strange Lake have indicated that these hydrocarbon-bearing fluids could have been trapped during the final stages of crystallization of these intrusions (Gerlach 1980; Konnerup-Madsen *et al.* 1985; Kogarko *et al.* 1987; Salvi & Williams-Jones 1992), and in particular the Ilímaussaq intrusion, which during final solidification stages evolved into a hyper-aggpaitic melt. These melts have the necessary low solidus temperatures (down to 450 °C) required to evolve a CH₄-rich gas phase due to high concentrations of volatiles (i.e. F, Cl) (Konnerup-Madsen 1988).

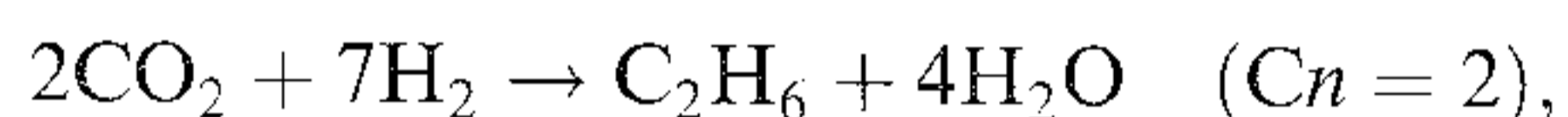
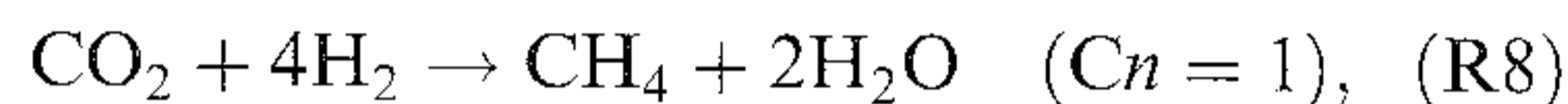
Post-magmatic origin

Finally, abiogenic hydrocarbons could be generated during post-magmatic hydrothermal alteration from Fischer-Tropsch types of reactions between an exsolved magmatic CO₂-dominant fluid and H₂ produced from hydrothermal reactions (Abrajano *et al.* 1988; Szatmari 1989; Abrajano *et al.* 1990; Sherwood-Lollar *et al.* 1993, 2002; Sugisaki & Mimura 1994; Kelley 1996; Salvi & Williams-Jones 1997; Potter *et al.* 1998, 1999).

The disequilibrium Fischer-Tropsch reaction has been well known as a way of producing hydrocarbons from combustion of coal in industry (Anderson 1984; Szatmari 1989). Fischer-Tropsch synthesis involves a series of step reactions, which can be represented by equations such as:



For CO₂-dominant initial fluid compositions, these reactions can be simplified to:



The Fischer-Tropsch reaction is catalysed in the presence of group VIII metals, Fe-oxides, Fe-silicates and hydrated silicates (Lancet & Anders 1970; Porfir'ev 1974; Pommier *et al.* 1985; Szatmari 1989) and may therefore be a mechanism for the production of CH₄ and higher hydrocarbons in natural rocks. The production of CH₄ in ultrabasic and basic rocks during serpentinization processes has previously been attributed to this mechanism (Porfir'ev 1974; Abrajano *et al.* 1988, 1990; Szatmari 1989; Sherwood-Lollar *et al.* 1993; Sugisaki & Mimura 1994; Kelley 1996), the H₂ needed being provided during serpentinization of the primary mineral assemblage. Serpentine and brucite tend to exclude Fe²⁺ ions from their lattices and the Fe²⁺ is partially oxidised to Fe³⁺ and incorporated into magnetite. H₂ is generated in this reaction, due to the dissociation of H₂O and oxidation of the ferrous ions through reactions such as:



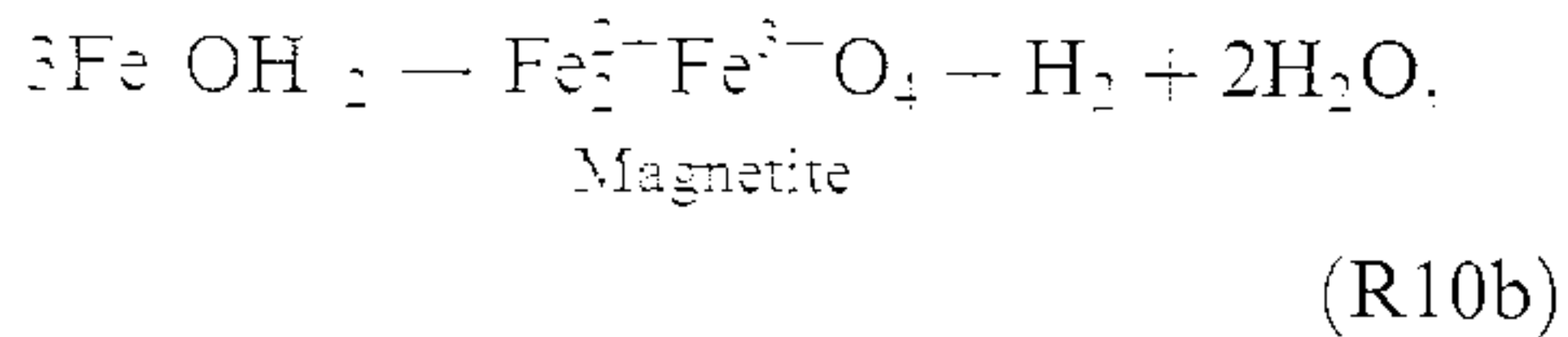
Forsterite Fayalite



Serpentine

Brucite

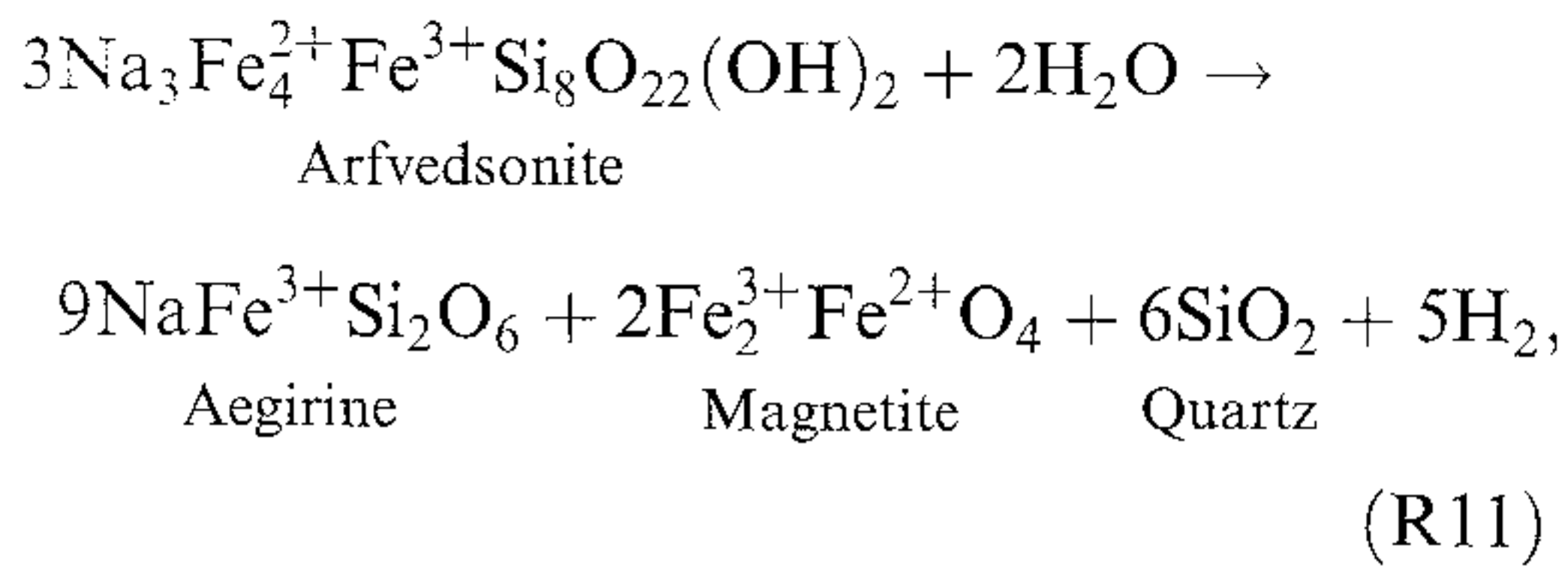
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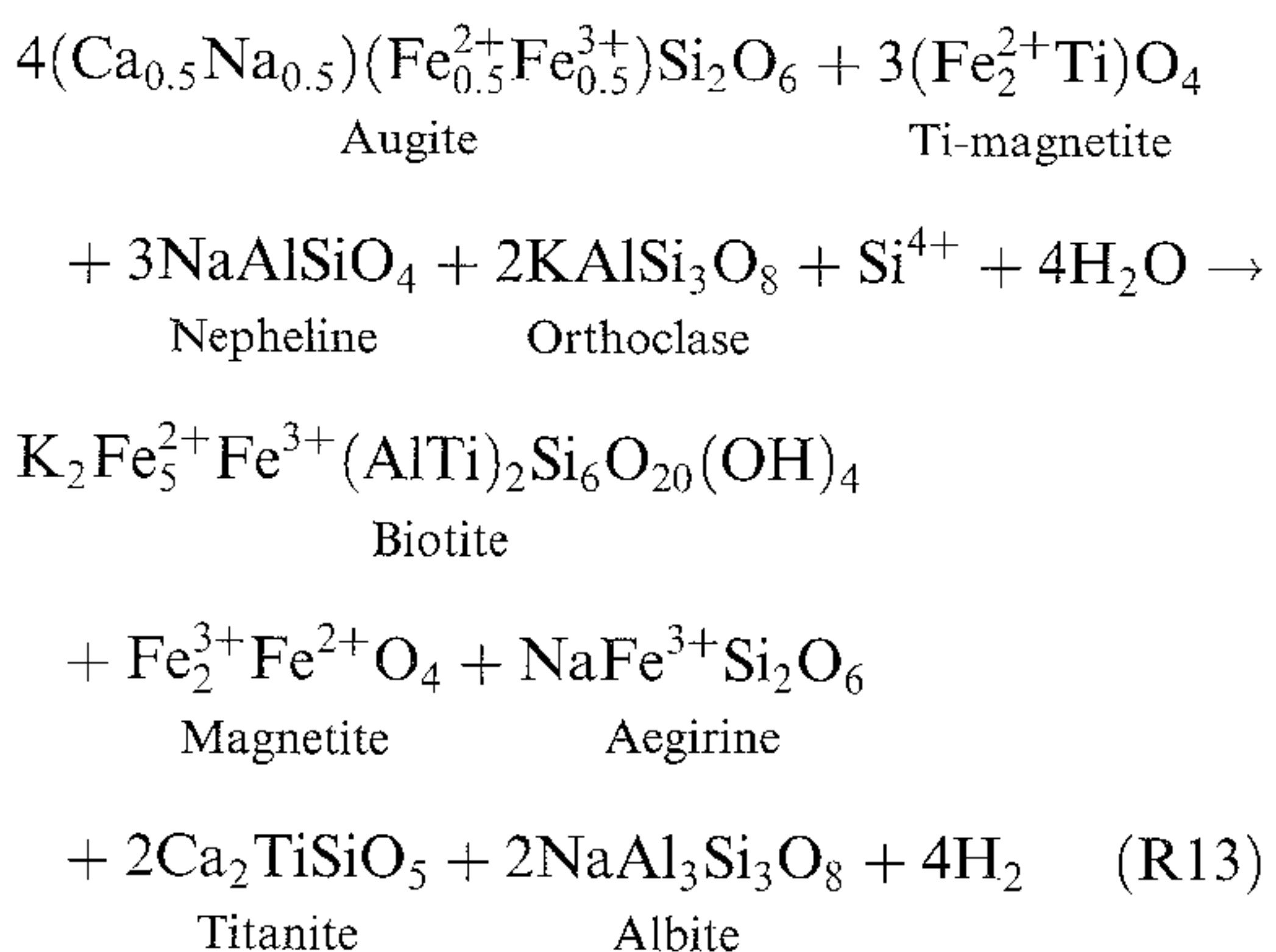
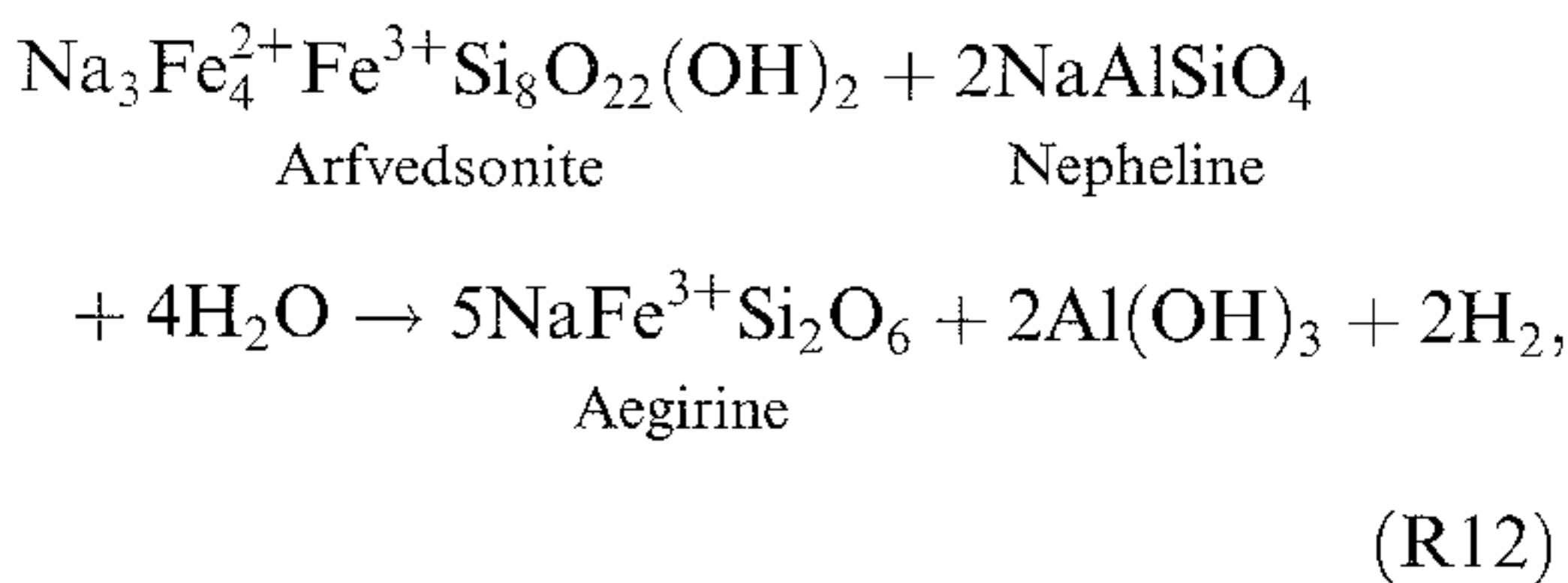
Sherwood-Lollar *et al.* 1993).

Reports on abiogenic CH₄ generation at mid-ocean ridges, hydrothermal vents, seamounts and in ophiolites, plausible due to Fischer-Tropsch synthesis during serpentinization, are becoming increasingly more common (Welhan & Craig 1983; Abrajano *et al.* 1990; Charlou *et al.* 1991, 1998; Kiyosu *et al.* 1992; Kelley 1996; Sakata *et al.* 1997).

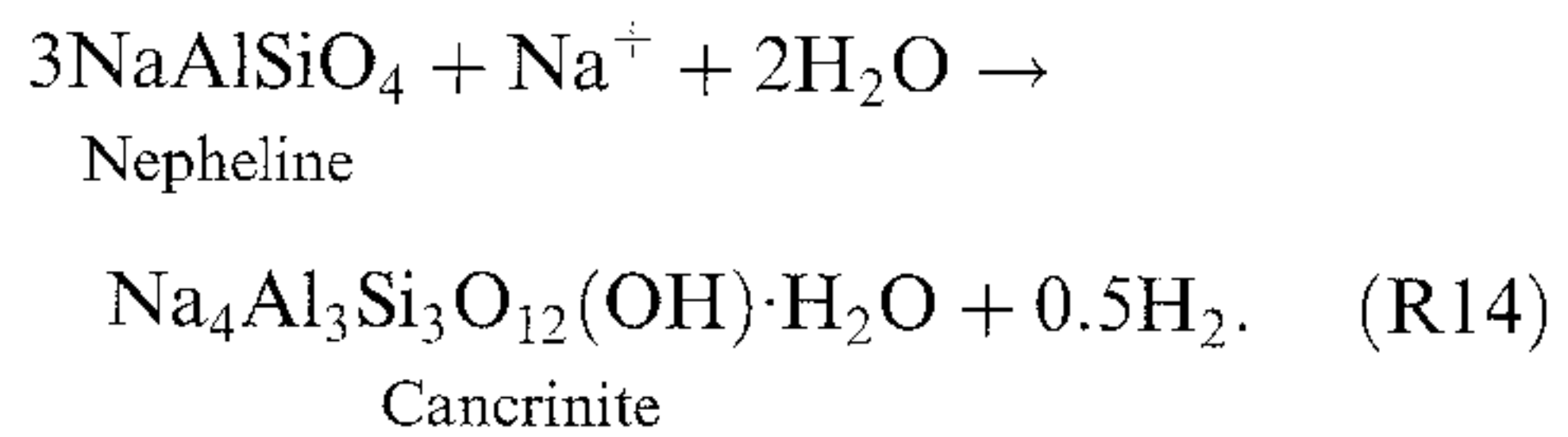
The association between post-magmatic alteration involving Fe oxidation, Fischer-Tropsch synthesis and hydrocarbon generation in igneous rocks can also be extended to include alkaline rocks (Salvi & Williams-Jones 1997; Potter *et al.* 1998, 1999). Hydrocarbon generation in the Khibina, Lovozero and Strange Lake complexes has been related to the alteration of the primary mineral assemblages (nepheline, augite, arfvedsonite, Ti-magnetite) to late biotite, cancrinite, aegerine, magnetite and natrolite via reactions such as:



(Salvi & Williams-Jones 1997)



and



Therefore, this model can be readily applied to abiogenic hydrocarbon generation in a wide variety of igneous rock types and has become increasingly popular in recent years.

Overview and discussion of the models for the origin of hydrocarbons in igneous rocks

The generally secondary nature of the hydrocarbon-dominated inclusions in hitherto studied igneous rocks and the estimated low pressures and temperatures of their entrapment preclude a direct mantle origin as suggested by Gold (1979). Whether the hydrocarbon fluids in the silica-undersaturated alkaline rocks evolved in a late-magmatic setting through re-equilibration of a C–O–H fluid, or formed during post-magmatic mineral–fluid reactions, is still questionable (Gerlach 1980; Konnerup-Madsen 1988; Potter *et al.* 1998). However, it is generally accepted that the presence of hydrocarbons (and H₂) in basic rocks is due to the reduction of an early CO₂-rich fluid during post-magmatic serpentinization processes (e.g. Neal & Stanger 1983; Abrajano *et al.* 1990; Sherwood-Lollar *et al.* 1993).

The magmatic re-equilibration model suggested by Gerlach (1980) and Konnerup-Madsen *et al.* (1981) involving the evolution of a CH₄-rich fluid at low temperatures in a closed magmatic system is theoretically feasible for some particular alkaline melt compositions. Previous studies have indicated that the fulfilment of the most critical melt properties for the formation of a hydrocarbon-rich volatile phase is to be found in hyper-alkalic nepheline syenites such as those at Ilímaussaq, Khibina and Lovozero. The formation of a hydrocarbon-rich volatile phase at the late-magmatic stage in this setting appears related to: (1) a wide temperature range of crystallization to very low solidus temperatures, enabling the buffering of any exsolved volatiles by the magma and minerals to temperatures as low as 450 °C; (2) low oxygen fugacities, with values roughly corresponding to those of the synthetic graphite–CH₄ curve during final solidification. Initial H₂O and C contents in the Ilímaussaq melt of about 4 wt% and 250 ppm, respectively, would at 2 kbars result in vapour saturation at

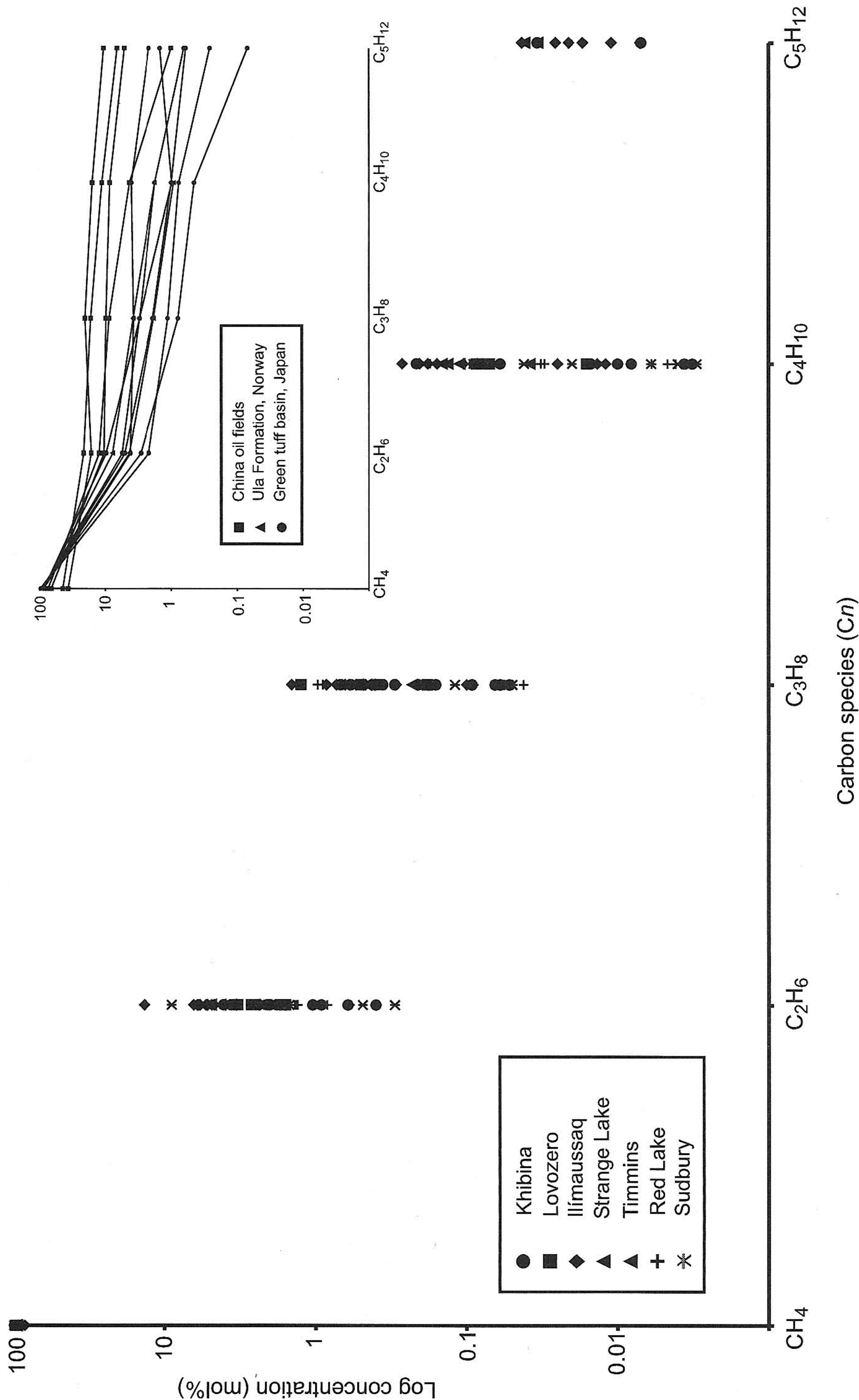


Fig. 3. A plot of log normalized hydrocarbon abundances (mol%) against increasing carbon number (C_n) for abiogenic hydrocarbon gases at Khibina and Lovozero, Russia (Petersilie *et al.* 1961; Petersilie & Sørensen 1962; Petersilie & Sørensen 1970; Voytov 1992), Ilímaussaq, Greenland (Petersilie & Sørensen 1970; Konnerup-Madsen *et al.* 1979; Konnerup-Madsen & Rose-Hansen 1982), Strange Lake, Canada (Salvi & Williams-Jones 1997) and Sudbury, Timmins and Red Lake, Canada (Sherwood-Lollar *et al.* 1993). For comparison, hydrocarbon abundances are also shown for biogenic hydrocarbon gases in the China Oil fields (average mol%) (Chen *et al.*

close to 700 °C and the exsolution of a CO₂-H₂O rich fluid with X_{H₂O} about 0.7. As oxygen fugacities about 2–3 log units below the synthetic QFM buffer curve are indicated from mineral equilibria studies, respeciation of the exsolved fluid to very CH₄-rich compositions would result (Konnerup-Madsen 2001). The additional presence of about 0.5 wt% Cl in the melt furthermore would result in high salinities of the exsolved aqueous fluid and the subsequent formation of two non-miscible fluid phases, one rich in CH₄, the other rich in H₂O plus chlorides. This evolution is in agreement with the fluid inclusion arrays observed in the Ilímaussaq intrusion (Konnerup-Madsen *et al.* 1985).

However, for a large range of H₂O/CO₂ ratios of any exsolved fluid, re-equilibration to low oxygen fugacities would result in the precipitation of graphite (Fig. 2a), albeit in very small amounts. No graphite has been found in the fluid inclusions in the Khibina and Lovozero complexes and little has been found in Ilímaussaq (Konnerup-Madsen *et al.* 1981). Therefore this simple magmatic re-equilibration model is not considered to explain adequately all fluid inclusion features observed in alkaline (and other) igneous intrusions in general; also the model does not explain the significant concentrations of higher hydrocarbons.

The generation of hydrocarbons through Fischer-Tropsch synthesis during post-magmatic alteration may provide an additional mechanism for the formation of CH₄ and higher hydrocarbons in these silica-undersaturated alkaline complexes and also other igneous rocks. Evidence for this type of process may be found in the bulk gas, stable isotope data and from textural observations.

Using the published bulk gas data shown in Table 2, the distribution of hydrocarbons in the alkaline intrusions of Khibina, Lovozero, Ilímaussaq and Strange Lake, plus those found in the Canadian Shield, show a clear log-linear trend from C₂ to C₅ decreasing in concentration from 10¹ to 10⁻² (Fig. 3). It is apparent that Khibina, Lovozero and Ilímaussaq have very low ethane/methane ratios (0.01 to 0.08) (Table 5). The ratios for the higher hydrocarbons either remain at the same low figures, indicating the dominance of lighter hydrocarbons, or increase, then level out at around 0.18 to 0.25 (Table 5). This is consistent with a Schulz-Flory distribution (Anderson 1984), with production of a hydrocarbon mixture dominated by light hydrocarbons with a C_{n+1}/C_n ratio of less than 0.6 and a clear indication that the hydrocarbons are being generated by Fischer-Tropsch reactions (Anderson 1984; Szatmari 1989). The hydrocarbon-bearing

fluids at Strange Lake have ratios that level out at slightly higher values (~0.34), indicating a slightly higher proportion of higher hydrocarbons than the fluids in the Khibina, Lovozero and Ilímaussaq complexes. The ratios of the hydrocarbon fluids found in the Canadian and Fennoscandian shield rocks are also below 0.6 (with the exception of Elliot Lake). They have generally very low ratios, but tend to be more variable between sites. Comparing the Schulz-Flory distribution of these abiogenic hydrocarbons with the distribution of abundances of biogenic hydrocarbons (Fig. 3) in oil fields and geothermal (thermogenic) springs, the two are clearly different. The biogenic hydrocarbons have a flatter distribution (particularly for the oil fields). This clearly indicates that these hydrocarbons are of an abiogenic nature probably generated by Fischer-Tropsch reactions.

The fractionation of δ¹³C isotope signatures during Fischer-Tropsch synthesis in a relatively closed system can vary. Initial conversion of a primary magmatic CO₂ fluid to CH₄ with subsequent partitioning will fractionate the CH₄ to lighter δ¹³C signatures. Later CH₄ associated with the total conversion of the CO₂ fluid will produce δ¹³C signatures closer to the initial magmatic value. Therefore, a wide range of δ¹³C_{CH₄} values, as observed in Table 4 (-10‰ to -30‰), can be produced during CH₄ generation (Voytov 1992). The majority of CH₄ found in igneous rocks show signatures between -20‰ and -28‰ (Table 4), indicating fractionation from the initial magmatic fluid at temperatures between 300 °C and 400 °C (Bottinga 1969). Plotting δ¹³C values for CH₄ to C₃H₈ from hydrocarbon-bearing fluids at Khibina (Fig. 4), it is apparent that the δ¹³C values become depleted with increasing carbon number (C_n). Comparing these values with published δ¹³C values for hydrocarbon gases in oil fields and geothermal (thermogenic) springs, it is clear that these fluids were not derived from biogenic processes (i.e. they have been generated by polymerization from simple hydrocarbon species with preferential enrichment of ¹²C to ¹³C with increasing C_n rather than thermal cracking of complex organic species giving an inverse δ¹³C distribution). This is also strong evidence for an abiogenic origin. The hydrogen isotope signatures observed in these hydrocarbon-bearing rocks are also in accordance with the theory that hydrocarbons were produced by Fischer-Tropsch synthesis. The signatures of these hydrocarbons commonly show depleted δD_{CH₄} values of around -135‰ and a δD_{H₂} values of -600‰ (Devirts *et al.* 1993; Sherwood-Lollar *et al.* 1993).

Table 5. Carbon number ratios

Rock type	C ₂ /C ₁	C ₃ /C ₂	C ₄ /C ₃	C ₅ /C ₄
Khibina				
Nepheline Syenite	0.01	0.22	0.21	—
Rischorrite	0.08	0.24	0.41	—
Ijolite	0.04	0.26	0.27	0.55
Kukisvumchorr Mine	0.07	0.25	0.18	0.28
Rasvumchorr Mine	0.05	0.13	0.24	0.18
Rasvumchorr Mine	0.07	0.08	0.1	—
Khibinite	0.03	0.05	0.01	—
Rischorrite	0.04	0.05	0.05	—
Lovozero				
Juvite	0.07	0.08	0.59	—
Syenite	0.05	0.21	0.06	—
Foyaite	0.03	0.47	0.19	—
Ilímaussaq				
Syenite	0.03	0.09	0.18	—
Naujaite	0.12	0.18	0.28	—
Foyaite	0.1	0.18	0.28	—
Lujavrite	0.13	0.07	0.05	—
Sodalite & nepheline	0.12	0.15	0.31	0.13
Arfvedsonite	0.09	0.13	0.38	0.03
Sodalite	0.12	0.21	0.32	—
Sodalite	0.1	0.15	0.25	0.25
Arfvedsonite	0.1	0.13	0.24	0.11
Nepheline	0.11	0.13	0.24	0.12
Eudialyte	0.3	0.15	0.25	0.12
Strange Lake				
fresh pegmatite	0.08	0.18	0.34	0.34
altered pegmatite	0.1	0.14	0.41	0.34
Canadian Shield				
Sudbury N	0.006	0.29	—	—
Sudbury CCS	0.06	0.07	0.42	—
Elliot Lake	0.002	0.18	1.5	—
Timmins	0.06	0.15	0.32	—
Red Lake – Dickenson	0.03	0.56	0.08	—
Red Lake – Campbell	0.03	0.45	—	—
Fennoscandian Shield				
Juuka	0.01	0.01	—	—

The carbon ratios are calculated from the bulk gas analyses shown in Table 2 (vol%) from Khibina and Lovozero (Russia), Ilímaussaq (Greenland), Strange Lake (Quebec) and the Canadian and Fennoscandian shield rocks.

Textural observations provide further evidence that most of the hydrocarbons in alkaline and basic rocks have been generated by Fischer–Tropsch type reactions. Catalysts for the Fischer–Tropsch synthesis in industry include magnetite, Fe-silicates and zeolites. The often-observed close relationship between the hydrocarbon-bearing fluids and the magnetite, Fe-silicates and hydrated Na/K silicates (i.e. zeolites) in the rock assemblages suggests this is also occurring in nature (Salvi & Williams-Jones 1997; Potter *et al.* 1999).

Implications for the generation of abiogenic hydrocarbons in igneous rocks

The occurrence of hydrocarbons in igneous rocks may not be as rare as previously thought. Over the last 20 years there has been a proliferation of reports on the presence of hydrocarbons in igneous rocks found in ultrabasic, basic, per-alkaline granites and silica-undersaturated igneous rocks from plutonic to hypabyssal and volcanic levels. Most of these occurrences have a biogenic or thermogenic origin, but many

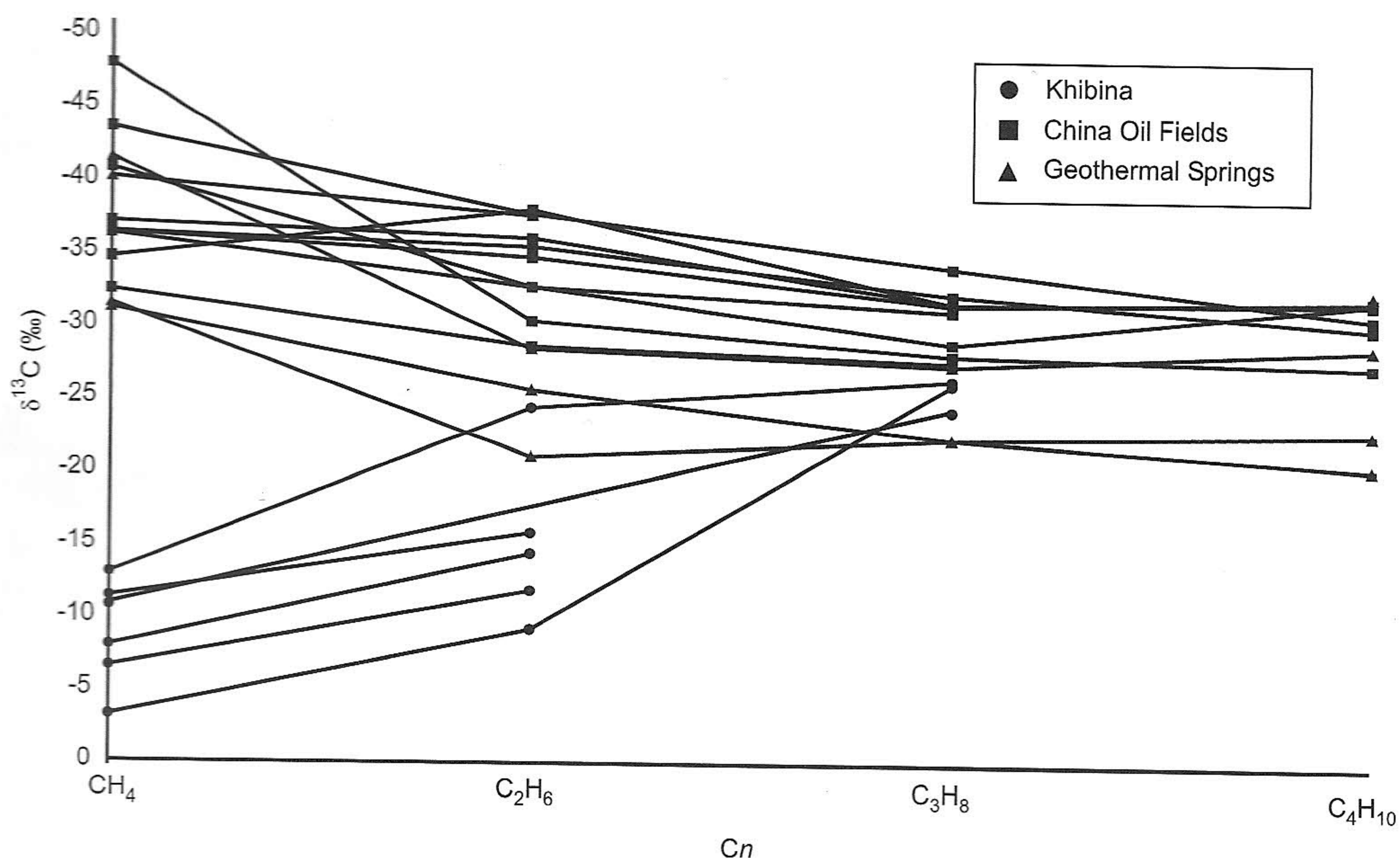


Fig. 4. A plot showing the distribution of $\delta^{13}\text{C}$ values with increasing carbon number (C_n) for the abiogenic hydrocarbon gases at Khibina (Voytov 1992) and for comparison, biogenic gases from the China oil fields (Dai *et al.* 1996; Chen *et al.* 2000) and various geothermal springs, USA (Des Marais *et al.* 1981).

have an abiogenic origin. A large proportion of these reports relates the hydrocarbons to post-magmatic alteration of the assemblage, in particular, serpentinization of ultrabasic and basic rocks.

Although a model involving near-solidus re-equilibration at low oxygen fugacities of an initially exsolved $\text{CO}_2\text{-H}_2\text{O}$ fluid can explain the generation of hydrocarbon-dominated fluid compositions, the melt compositional requirements are such that they are only met with in very rare situations, such as in some hyper-alkalic nepheline syenite intrusions. Alternatively, the model for Fischer-Tropsch synthesis of hydrocarbons in igneous rocks, as proposed by Salvi & Williams-Jones (1997), Potter *et al.* (1998) and Potter (2000), is considered to be more generally applicable to predict the presence of hydrocarbons in a variety of igneous rocks. The operation of this process may become important in searching for future natural gas resources in these rocks. Fischer-Tropsch synthesis not only produces abundant CH_4 , but, depending on the temperature at which the reactions take place, various other complex higher hydrocarbons. One obvious example of a potential reservoir for hydrocarbons formed by this process is the CH_4 -clathrates trapped at the sea floor. Serpentinization of ocean floor basalts by circulating seawater and hydrothermal fluids has the potential to produce large volumes

of CH_4 and higher hydrocarbons via Fischer-Tropsch reactions from magmatic CO_2 fluids. The continuing advances in ocean floor exploration may make these hydrocarbons an economically viable resource.

The Fischer-Tropsch model for hydrocarbon generation in igneous rocks can theoretically be applied to many magmatic bodies of all compositional types. Hydrothermally altered Fe-rich assemblages are common features in many intrusive bodies. Therefore, this model might suggest that hydrocarbons should be found in most igneous bodies. This is clearly not the case. It has been observed in industry that the Fe catalysts for Fischer-Tropsch reactions can be poisoned by the presence of sulphur (Anderson *et al.* 1965; Szatmari 1989). A comparative study of fluids present in the serpentinized carbonatitic intrusion, Sokli in Finland (Potter 2000) revealed the presence of little or no hydrocarbons in the samples. The majority of Sokli samples contain abundant sulphides which may have inhibited any Fischer-Tropsch type reaction from occurring. The extensive serpentinization (and phlogopitization) of the assemblage also suggests that large volumes of H_2O infiltrated the complex, potentially washing out any hydrocarbons generated. Therefore, in order for Fischer-Tropsch synthesis to occur, sulphur should not be present and, for the hydrocarbons to be retained within the assemblage,

hydrothermal alteration should not be pervasive with large volumes of H₂O migrating through the complex.

Conclusions

Awareness among scientists of the presence of hydrocarbons in igneous rocks has been steadily on the increase over the past 20 years. Although in most cases, the hydrocarbons have been derived from biogenic sources, there has been a recent proliferation of reports on the presence of hydrocarbons formed by abiogenic processes. These are commonly found in basic and SiO₂-undersaturated alkaline igneous rocks and in hydrothermal plumes associated with basic rocks. From where these hydrocarbons were derived and how they were generated still remains debatable. In the 1970s it was proposed that these hydrocarbons were derived directly from the mantle and that large abiogenic hydrocarbon reservoirs might be stored in the deep crust, having flowed up from the mantle. However, more recent studies have determined that this is unlikely and that these hydrocarbons were generated during late or post-magmatic processes. Two models have been proposed: a late-magmatic equilibrium model and a post-magmatic disequilibrium model. It has been shown that a CH₄-rich fluid can evolve from a magmatic CO₂-rich fluid in a closed system at late-magmatic conditions (below 500 °C). This model can only be applied to igneous rocks with extreme compositions with low solidus temperatures and wide crystallization ranges (i.e. SiO₂-undersaturated alkaline rocks). A post-magmatic model has also been suggested, where hydrocarbons are generated during post-magmatic hydrothermal alteration of the mineral assemblages. This involved Fischer–Tropsch type reactions between an early CO₂-rich fluid and H₂ generated from the hydrothermal reactions. The Fischer–Tropsch reactions are catalysed in the presence of Fe-rich minerals abundant in the basic and alkaline igneous complexes (e.g. magnetite, aegirine). Textural, fluid inclusion, isotopic and bulk gas data from a variety of complexes support this model. Therefore, although the late-magmatic model may still be valid for generation of hydrocarbons in the SiO₂-undersaturated alkaline complexes, the Fischer–Tropsch model is favoured and can be applied to a wide variety of igneous environments. This model suggests that abiogenic hydrocarbons may be more common than previously anticipated, with possible implications for natural gas resources in the future.

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References

- ABRAJANO, T. A., STURCHIO, N. C., BOHLKE, J. K., LYON, G. L., POREDA, R. J. & STEVENS, C. M. 1988. Methane hydrogen gas seeps, Zambales ophiolite, Philippines—deep or shallow origin. *Chemical Geology*, **71**(1-3), 211–222.
- ABRAJANO, T. A., STURCHIO, N. C., KENNEDY, B. M., LYON, G. L., MUEHLENBACHS, K. & BOHLKE, J. K. 1991. Geochemistry of reduced gas related to serpentinization of the Zambales ophiolite, Philippines. *Applied Geochemistry*, **5**, 625–630.
- ANDERSEN, T. 1986. Magmatic fluids in the Fen Carbonatite Complex, S.E. Norway: Evidence of mid-crustal fractionation from solid and fluid inclusions in apatite. *Contributions to Mineralogy and Petrology*, **93**, 491–503.
- ANDERSEN, T. & BURKE, E. A. J. 1996. Methane inclusions in shocked quartz from the Gardnos breccia, South Norway. *European Journal of Mineralogy*, **8**, 927–936.
- ANDERSON, R. B. 1984. *The Fischer–Tropsch synthesis*. Academic Press, New York.
- ANDERSON, R. B., KARN, F. S., KELLY, R. E. & SCHULTZ, J. F. 1965. *Sulfur poisoning of fixed beds of iron catalysts in the Fischer–Tropsch synthesis*. U.S. Dept. of the Interior, Bureau of Mines, Bulletin, **628**.
- BELOKON, T. V., FRIK, M. G., KOBLOVA, A. Z. & KUCHINA, YE. L. 1995. Biomarker distributions in oil and rock organic matter in Russian petroliferous regions. *Geochemistry International*, **32**(9), 126–141.
- BOTTINGA, Y. 1969. Calculated fractionation factors for carbon and hydrogen isotope exchange in the system calcite–carbon dioxide–graphite–methane–hydrogen–water vapour. *Geochimica et Cosmochimica Acta*, **33**, 49–64.
- BOTZ, R., STÜBEN, D., WINCKLER, G., BAYER, R., SCHMITT, M. & FABER, E. 1996. Hydrothermal gases offshore Milos Island, Greece. *Chemical Geology*, **130**, 161–173.
- CESARE, B. 1995. Graphite precipitation in C–O–H fluid inclusions: Closed system compositional and density changes and thermobarometric implications. *Contributions to Mineralogy and Petrology*, **122**, 25–33.
- CHARLOU, J. L., BOUGALT, H., APPRIOU, P., NELSEN, T. & RONA, P. 1991. Different TDM/CH₄ hydrothermal plume signatures: TAG site at 26°N and serpentinized ultrabasic diapir at 15°05'N on the Mid-Atlantic Ridge. *Geochimica et Cosmochimica Acta*, **55**, 3209–3222.
- CHARLOU, J. L., FOUQUET, Y., BOUGALT, H., DONVAL, J. P., ETOUBLEAU, J., JEAN-BAPTISTE, P.,

- DAPOIGNY, A., APPRIOU, P. & RONA, P. A. 1998. Intense CH₄ plumes generated by serpentinization of ultramafic rocks at the intersection of the 15°20'N fracture zone and the Mid-Atlantic Ridge. *Geochimica et Cosmochimica Acta*, **62**(13), 2323–2333.
- CHEN, J., XU, Y. & HUANG, D. 2000. Geochemical characteristics and origin of natural gas in Tarim Basin, China. *AAPG Bulletin*, **84**(5), 591–606.
- DAI, J., SONG, Y., DAI, C. & WANG, D. 1996. Geochemistry and accumulation of carbon dioxide gases in China. *AAPG Bulletin*, **80**(10), 1615–1626.
- DARLING, W. G. 1998. Hydrothermal hydrocarbon gases: 2, Application in the East African Rift system. *Applied Geochemistry*, **13**(7), 825–840.
- DARLING, W. G., GREISSHABER, E., ANDREWS, J. N., ARMANNON, H. & O'NIONS, R. K. 1995. The origin of hydrothermal and other gases in the Kenyan Rift Valley. *Geochimica et Cosmochimica Acta*, **59**(12), 2501–2512.
- DES MARAIS, D. J., DONCHIN, J. H., NEHRING, N. L. & TRUESDELL, A. H. 1981. Molecular carbon isotopic evidence for the origin of geothermal hydrocarbons. *Nature*, **292**, 826–828.
- DEVIRTS, A. L., GAGAUZ, F. G., GRINENKO, V. A., LAGUTINA, YE.P., PEREVERZOV, V. V. & SHUKOLYUKOV, YU. A. 1993. Origin of hydrogen in Kempirsay-intrusion ultramafites. *Geochemistry International*, **30**(2), 139–144.
- GERLACH, T. M. 1980. Chemical characteristics of the volcanic gases from Nyiragongo Lava Lake and the generation of CH₄-rich fluid inclusions. *Journal of Volcanic and Geothermical Research*, **8**, 177–189.
- GIARDINI, A. A., MELTON, C. E. & MITCHELL, R. S. 1982. The nature of the upper 400 km of the earth and its potential as the source for non-biogenic petroleum. *Journal of Petroleum Geology*, **5**(2), 173–190.
- GIZE, A. & MACDONALD, R. 1993. Generation of compositionally atypical hydrocarbons in CO₂-rich geologic environments. *Geology*, **21**, 129–132.
- GOLD, T. 1979. Terrestrial sources of carbon and earthquake outgassing. *Journal of Petroleum Geology*, **1**(3), 3–19.
- GUNTER, B. D. & MUSGRAVE, B. C. 1971. New evidence on the origin of methane in hydrothermal gases. *Geochimica et Cosmochimica Acta*, **35**, 113–118.
- HOLLOWAY, J. R. 1984. Graphite-CH₄-H₂O-CO₂ equilibria at low grade metamorphic conditions. *Geology*, **12**, 455–458.
- HORITA, J. & BERNDT, M. E. 1999. Abiogenic methane formation and isotopic fractionation under hydrothermal conditions. *Science*, **285**, 1055–1057.
- HUIZENGA, J. M. 1995. *Fluid evolution in shear zones from the late Archean Harare-Shamva-Bindura greenstone belt (NE Zimbabwe)*. PhD thesis, Proefschrift Vrije Universiteit, Amsterdam.
- HUIZENGA, J. M. 2001. Thermodynamic modelling of C-O-H fluids. *Lithos*, **55**, 101–114.
- IKORSKI, S. V. 1991. Hydrocarbon gases in alkali intrusions. *Geochemistry International*, **28**(6), 17–23.
- IKORSKI, S. V., NIVIN, V. A. & PRIPACHKIN, V. A. 1993. New information about natural gases of alkaline massifs. *Isotopenpraxis*, **28**, 289–291.
- JEFFREY, A. W. A. & KAPLAN, I. R. 1988. Hydrocarbons and inorganic gases in the Gravberg-1 well, Siljan ring, Sweden. *Chemical Geology*, **71**, 237–255.
- KARLSEN, D. A., NEDKVITNE, T., LARTER, S. R. & BJØR-LYKKE, K. 1993. Hydrocarbon composition of authigenic inclusions: Application to elucidation of petroleum reservoir filling history. *Geochimica et Cosmochimica Acta*, **57**, 3641–3659.
- KARZHAVIN, V. K. & VENDILLO, V. P. 1970. Thermodynamic equilibrium and conditions for existence of hydrocarbon gases in a magmatic process. *Geochemistry International*, **7**, 797–803.
- KELLEY, D. S. 1996. Methane rich fluids in the oceanic crust. *Journal of Geophysical Research*, **101**(B2), 2943–2962.
- KELLEY, D. S. & FRÜH-GREEN, G. L. 2001. Volatile lines of descent in submarine plume environments: Insights from stable isotope and fluid inclusion analyses. *Geochimica et Cosmochimica Acta*, **65**(19), 3325–3346.
- KERR, R. A. 1990. When a radical experiment goes bust. *Science*, **247**, 1177–1179.
- KHARMALOV, YE. S. *et al.* 1981. Origin of carbonatites of the Kovdor deposit. *International Geology Review*, **23**(8), 865–880.
- KIYOSU, Y., ASADA, N. & YOSHIDA, Y. 1992. Origin of light hydrocarbon gases from the Matsukawa geothermal area in Japan. *Chemical Geology*, **94**, 321–329.
- KOGARKO, L. N., KOSZTOLANYI, CH. & RYABCHIKOV, I. D. 1987. Geochemistry of the reduced fluid in alkali magmas. *Geochemistry International*, **24**(7), 20–27.
- KONNERUP-MADSEN, J. *et al.* 1981.
- KONNERUP-MADSEN, J. 1988. Abiogenic hydrocarbon gases, *In: SANTOSH, M. (ed.) Fluid Inclusions*. Special Memoirs of Geological Society of India, 13–24.
- KONNERUP-MADSEN, J. 2001. Non-biogenic hydrocarbon gases associated with solidification of the Ilímaussaq alkaline complex, South Greenland. *Geology of Greenland Survey Bulletin*, **190**, 163–170.
- KONNERUP-MADSEN, J. & ROSE-HANSEN, J. 1982. Volatiles associated with alkaline igneous rift activity: Fluid inclusions in the Ilímaussaq intrusion and the Gardar granitic complexes (South Greenland). *Chemical Geology*, **37**, 79–93.
- KONNERUP-MADSEN, J., DUBESSY, J. & ROSE-HANSEN, J. 1985. Combined Raman microprobe spectrometry and microthermometry of fluid inclusions in minerals from igneous rocks of the Gardar Province (South Greenland). *Lithos*, **18**, 271–280.
- KONNERUP-MADSEN, J., LARSEN, E. & ROSE-HANSEN, J. 1979. Hydrocarbon-rich fluid inclusions in minerals from the alkaline Ilímaussaq intrusion, South Greenland. *Bulletin de Minéralogie*, **102**, 642–653.
- KONNERUP-MADSEN, J., ROSE-HANSEN, J. & LARSEN, E. 1981. Hydrocarbon gases associated with alkaline igneous activity: evidence from composition of fluid inclusions. *Rapport Grønlands Geologiske Undersøgelse*, **103**, 99–108.

- KROT, A. N., POSUKHOVA, T. V., GUSEVA, YE. V., GALIMOV, E. M., BOTKUNOV, A. I., RAMENSKAYA, M. YE. & OGLOBALINA, A. I. 1994. Origin of garnets containing hydrocarbon inclusions in the Mir kimberlite pipe. *Geochemistry International*, **31**(1), 122–128.
- LANCET, M. S. & ANDERS, E. 1970. Carbon isotope fractionation in the Fischer–Tropsch synthesis and in meteorites. *Science*, **170**, 981–983.
- LARSEN, R. B., BROOKS, C. K. & BIRD, D. K. 1992. Methane bearing, aqueous, saline solutions in the Skaergaard intrusion, East Greenland. *Contributions to Mineralogy and Petrology*, **112**, 428–437.
- MATHEZ, E. A. 1987. Carbonaceous matter in mantle xenoliths: Composition and relevance to the isotopes. *Geochimica et Cosmochimica Acta*, **51**, 2339–2347.
- MOROGAN, V. & LINDBLOM, S. 1995. Volatiles associated with the alkaline-carbonatite magmatism at Alnö, Sweden: A study of fluid and solid inclusions in minerals from the Långarsholmen Ring Complex. *Contributions to Mineralogy and Petrology*, **122**, 262–274.
- NEAL, C. & STANGER, G. 1983. Hydrogen generation from mantle source rocks in Oman. *Earth and Planetary Science Letters*, **60**, 315–321.
- NIVIN, V. A., DEVIRTS, A. L. & LAGUTINA, YE. P. 1995. The origin of the gas phase in the Lovozero massif based on hydrogen-isotope data. *Geochemistry International*, **32**(8), 65–71.
- PETERSILIE, I. A. 1962. Origin of hydrocarbon gases and dispersed bitumens of the Khibina alkaline massif. *Geochemistry International*, **1**, 14–29.
- PETERSILIE, I. A. & SØRENSEN, H. 1970. Hydrocarbon gases and bituminous substances in rocks from the Ilímaussaq alkaline intrusion, South Greenland. *Lithos*, **3**, 59–76.
- PETERSILIE, I. A., IKORSKI, S. V., SMIRNOVA, L. I., ROMANIKHIN, A. M. & PROSKURYAKOVA, E. B. 1961. Application of gas logging to the investigation of natural gases and bitumens in the Khibina intrusive massif. *Geochemistry International*, **10**, 945–962.
- POMMIER, B., REYMOND, J. P. & TEICHNER, S. J. 1985. Fischer–Tropsch synthesis on oxidised supported iron catalyst. *Zeitschrift physische chemie Neue Folge*, **144**, 203–222.
- PORFIR'EV, V. B. 1974. Inorganic origin of petroleum. *AAPG Bulletin*, **58**(1), 3–33.
- POTTER, J. 2000. *The characterisation and origin of hydrocarbons in the alkaline igneous complexes in the Kola Alkaline Province*. PhD thesis, Kingston University, London, UK.
- POTTER, J., RANKIN, A. H., TRELOAR, P. J., NIVIN, V. A., TING, W. & NI, P. 1998. 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. *European Journal of Mineralogy*, **10**, 1167–1180.
- POTTER, J., RANKIN, A. H. & TRELOAR, P. J. 1999. The relationship between CH₄ and CO₂ inclusions and Fe–O–S mineralization in intrusions of the Kola Alkaline Province. In: STANLEY, C. J. *et al.* (eds) *Mineral deposits: Processes to processing*, Vol. 1. Balkema, Rotterdam, 87–90.
- ROEDDER, E. 1984. *Fluid Inclusions*. Mineralogical Society of America, Reviews in Mineralogy, **12**.
- SAKATA, S., SANO, Y., MAEKAWA, T. & IGARI, S. I. 1997. Hydrogen and carbon isotopic composition of methane as evidence for biogenic origin of natural gases from the Green Tuff Basin, Japan. *Organic Geochemistry*, **26**(5/6), 399–407.
- SALVI, S. & WILLIAMS-JONES, A. E. 1992. Reduced orthomagmatic C–O–H–N–NaCl fluids in the Strange Lake rare-metal granitic complex, Quebec/Labrador, Canada. *European Journal of Mineralogy*, **4**, 1155–1174.
- SALVI, S. & WILLIAMS-JONES, A. E. 1997. Fischer–Tropsch synthesis of hydrocarbons during subsolidus alteration of the Strange Lake peralkaline granite, Quebec/Labrador, Canada. *Geochimica et Cosmochimica Acta*, **61**(1), 83–99.
- SAMSON, I. M. & WILLIAMS-JONES, A. E. 1991. C–O–H–N–salt fluids associated with contact metamorphism, McGerrigle mountains, Quebec: A Raman spectroscopic study. *Geochimica et Cosmochimica Acta*, **55**, 169–177.
- SAMSON, I. M., LUI, W. & WILLIAMS-JONES, A. E. 1995. The nature of orthomagmatic hydrothermal fluids in the Oka carbonatite, Quebec, Canada: Evidence from fluid inclusions. *Geochimica et Cosmochimica Acta*, **59**(10), 1963–1977.
- SCHIDLÓWSKI, M. 1982. Content and isotopic composition of reduced carbon in sediments. In: HOLLAND, H. D. & SCHIDLÓWSKI, M. (eds) *Mineral deposits and the evolution of the biosphere*. Springer-Verlag, New York, 103–122.
- SCHOELL, M. 1983. Genetic characterisation of natural gases. *AAPG Bulletin*, **67**(12), 2225–2238.
- SCHOELL, M. 1988. Multiple origins of methane in the earth. *Chemical Geology*, **71**(1–3), 1–10.
- SHERWOOD-LOLLAR, B., FRAPE, S. K., WEISE, S. M., FRITZ, P., MACKO, S. A. & WELHAN, W. A. 1993. Abiogenic methanogenesis in crystalline rocks. *Geochimica et Cosmochimica Acta*, **57**, 5087–5097.
- SHERWOOD-LOLLAR, B., WESTGATE, T. D., WARD, J. A., SLATER, G. F. & LACRAMPE-COULOUME, G. 2002. Abiogenic formation of alkanes in the earth's crust as a minor source for global hydrocarbon reservoirs. *Nature*, **416**, 522–524.
- SIMONEIT, B. R. T. 1988. *Organic matter in hydrothermal systems—maturation, migration and biogeochemistry*. Pergamon, Oxford.
- SUGISAKI, R. & MIMURA, K. 1994. Mantle hydrocarbons: Abiotic or biotic. *Geochimica et Cosmochimica Acta*, **58**(11), 2527–2542.
- SZATMARI, P. 1989. Petroleum formation by Fischer–Tropsch synthesis in plate tectonics. *AAPG Bulletin*, **73**(8), 989–998.
- TING, W., BURKE, E. A., RANKIN, A. H. & WOOLLEY, A. R. 1994. Characterisation and petrogenetic significance of CO₂, H₂O and CH₄ fluid inclusions in apatite from the Sukulu Carbonatite, Uganda. *European Journal of Mineralogy*, **6**, 787–803.
- VARD, E. & WILLIAMS-JONES, A. E. 1993. A fluid inclusion study of vug minerals in dawsonite-altered phonolite sills, Montreal, Quebec: Implications for HFSE mobility. *Contributions to Mineralogy and Petrology*, **113**, 410–423.

- VLIERBOOM, F. W., COLLINI, B. & ZUMBERGE, J. E. 1986. The occurrence of petroleum in sedimentary rocks of the meteor impact crater at Lake Siljan, Sweden. *Organic Geochemistry*, **10**, 153–161.
- VOYTOV, G. I. 1992. Chemical and carbon-isotope fluctuations in free gases (gas jets) in the Khibiny. *Geochemistry International*, 14–24.
- WELHAN, J. A. & CRAIG, H. 1983. Methane, hydrogen and helium in hydrothermal fluids at 21°N, East Pacific Rise. In: RONA, P. A., BOSTRÖM, K., LAUBIER, L. & SMITH JNR, K. L. *Hydrothermal processes at seafloor spreading centres*. Plenum, New York, 391–409.
- WELHAN, J. A. & LUPTON, J. E. 1987. Light hydrocarbon gases in Guaymas Basin hydrothermal fluids: Thermogenic versus abiogenic origin. *AAPG Bulletin*, **71**(2), 215–223.
- ZAKRZHEVSKAYA, N. G. 1964. Origin of gases in the Khibiny apatite deposits. *Geochemistry International*, 128–131.
- ZHANG, Y. G. & FRANTZ, J. D. 1992. Hydrothermal reactions involving equilibrium between minerals and mixed volatiles 2. Investigations of fluid properties in the CO₂-CH₄-H₂O system using synthetic fluid inclusions. *Chemical Geology*, **100**, 51–72.