

A review of the composition and evolution of hydrocarbon gases during solidification of the Ilímaussaq alkaline complex, South Greenland

Jens Konnerup-Madsen

Fluid inclusions in minerals from agpaitic nepheline syenites and hydrothermal veins in the Ilímaussaq complex and in similar agpaitic complexes on the Kola Peninsula, Russia, are dominated by hydrocarbon gases (predominantly methane) and hydrogen. Such volatile compositions differ considerably from those of most other igneous rocks and their formation and entrapment in minerals reflects low oxygen fugacities and a wide range of crystallisation temperatures extending to a low-temperature solidus. Their composition reflects initial low carbon contents and high water contents of the magma resulting in the exsolution of a water-rich CO₂-H₂O dominated vapour phase. Fractionation of chlorides into the vapour phase results in high salinities and the subsequent development of a heterogeneous vapour phase with a highly saline aqueous-rich fraction and a methane-dominated fraction, with preferential entrapment of the latter, possibly due to different wetting characteristics. The light stable isotope compositions support an abiogenic origin for the hydrocarbons in agpaitic nepheline syenite complexes.

Geological Institute, University of Copenhagen, Øster Voldgade 10, DK-1350 Copenhagen K, Denmark. E-mail: jenskm@geo.geol.ku.dk

Keywords: alkali syenite, fluid inclusions, Gardar, Greenland, hydrocarbons, Ilímaussaq, stable isotopes

The importance of volatile components in the generation and solidification of alkaline rocks in general and agpaitic nepheline syenites in particular has been emphasised by a number of authors (e.g. Larsen & Sørensen 1987). The highly reduced nature of carbonic fluids associated with silica-undersaturated alkalic complexes has been documented (e.g. Kogarko & Romanchev 1983; Sørensen 1997), and the presence of similar hydrocarbon-rich fluids has also been described from peralkaline granitic complexes (e.g. Salvi & Williams-Jones 1992). Since alkaline magmatic activity typically occurs in intraplate locations and presents geochemical and isotopic characteristics consistent with an important contribution from upper-mantle-derived magmas, studies of associated gas compositions potentially provide information on the characteristics of mantle degassing in extensional-type settings.

One method of obtaining information on the gases is to study the volatiles trapped and preserved as fluid inclusions in minerals during solidification of the melts. This paper is a review of available data on the com-

positional characteristics of the hydrocarbon-rich fluid inclusions in the Ilímaussaq alkaline complex.

The Ilímaussaq complex

The Ilímaussaq alkaline complex belongs to the Mesoproterozoic Gardar continental magmatic rift province in South Greenland. It was emplaced at a high level in the crust and cuts both a Proterozoic basement granite and the overlying Gardar lavas and continental sandstones (Fig. 1). The geological setting and petrologic evolution of the Ilímaussaq complex has been summarised by Sørensen (2001, this volume).

An initial temperature of about 900°C, a pressure of 1–2 kbars and contents of H₂O around 4 wt% at emplacement and initial cooling of the main Ilímaussaq magma were suggested by Larsen & Sørensen (1987), indicating initial volatile undersaturation. During solidification of the magma, oxygen fugacities were well below the synthetic QFM buffer (Larsen 1976)

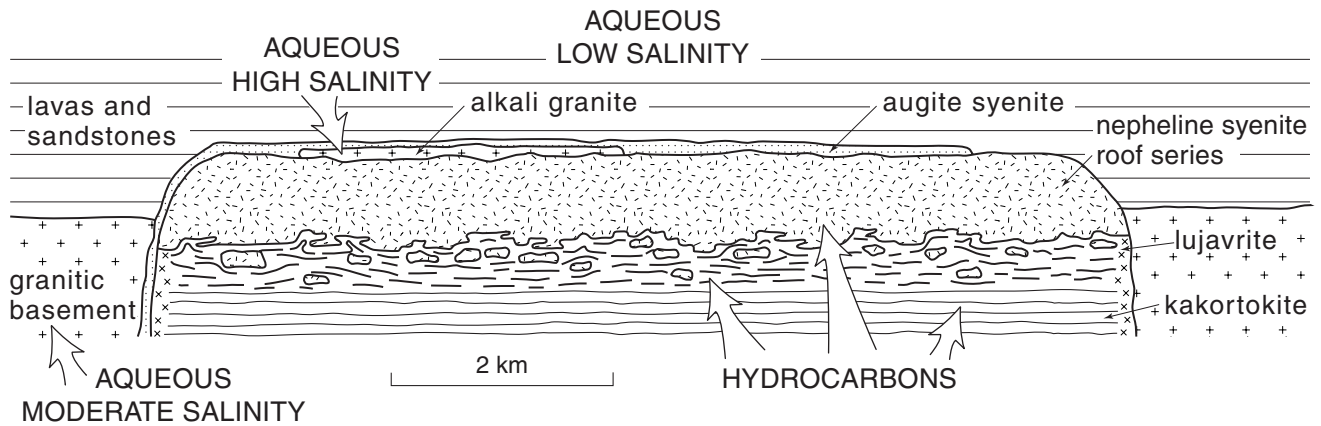


Fig. 1. Simplified E-W cross-section through the Ilímaussaq alkaline complex. Fluid types trapped in minerals in the various rock types are indicated. Same horizontal and vertical scale. From Konnerup-Madsen (1980).

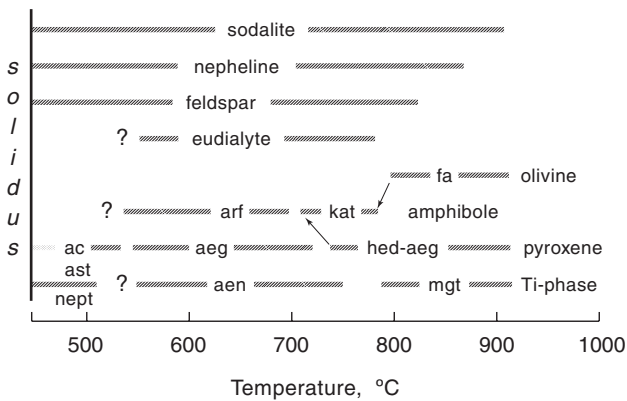


Fig. 2. Sequence of crystallisation of minerals in Ilímaussaq roof cumulates. Modified from Konnerup-Madsen *et al.* (1981). Abbreviations: **ac**: acmite, **aen**: aenigmatite, **arf**: arfvedsonite, **ast**: astrophyllite, **fa**: fayalite, **hed-aeg**: hedenbergite-aegirine, **kat**: kataphorite, **mgt**: magnetite, **nept**: neptunite.

and activities of water thus well below unity (Curtis & Currie 1981). The solidus temperature is around 450°C according to melting experiments (e.g. Edgar & Parker 1974). The sequence of crystallisation during solidification of a typical roof cumulate is summarised in Fig. 2.

Types of fluid inclusions

The types of fluid inclusions observed in the various rock types in the Ilímaussaq complex and immediately adjacent host rocks are indicated in Fig. 1 and illustrated in Fig. 3.

Hydrocarbon-rich gaseous inclusions predominate in all examined minerals from the Ilímaussaq neph-

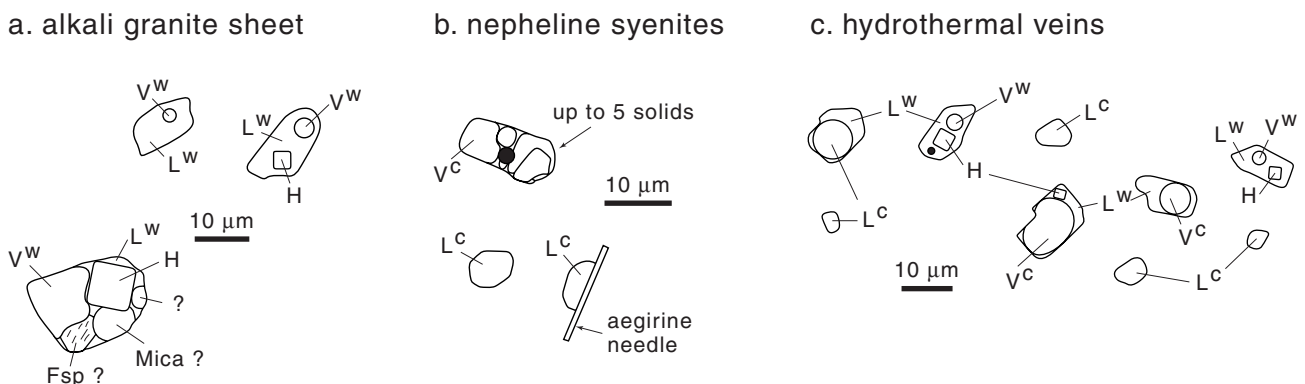


Fig. 3. Sketches of the main types of fluid inclusions in minerals from the Ilímaussaq rocks. **a**: alkali granite sheet, **b**: nepheline syenites, and **c**: late hydrothermal veins. Length of bar is 0.01 mm. Abbreviations: **L^w** and **V^w**: liquid and vapour H₂O, respectively; **H**: halite; **L^c** and **V^c**: liquid and vapour hydrocarbons, respectively; **Fsp**: feldspar. Modified from Konnerup-Madsen & Rose-Hansen (1982).

line syenites and late hydrothermal veins formed from fluids expelled from the late nepheline syenites (Fig. 3b, c); aqueous inclusions are only rarely observed. Mixed hydrocarbon–aqueous inclusions are only very rarely seen in minerals from the nepheline syenites. The isolated occurrence of a few aqueous high-salinity inclusions in minerals from the nepheline syenites suggests that they were entrapped prior to the hydrocarbon inclusions which are largely confined to more or less effectively healed fractures. The vapour phase in some of these highly saline inclusions is composed predominantly of CO_2 (Sobolev *et al.* 1970). A minor number of the hydrocarbon inclusions, however, also occur isolated or associated with aegirine microlites in nepheline from naujaite.

In the hydrothermal vein minerals the generally observed association of highly saline aqueous inclusions and hydrocarbon-rich inclusions (Fig. 3), however, clearly indicate the existence and entrapment of non-miscible fluids at this stage (Konnerup-Madsen & Rose-Hansen 1982).

In quartz from the alkali granite sheet, which is considered to represent a small second magma pulse prior to the main agpaiteic magma, only moderate- to high-salinity aqueous inclusions were observed.

The surrounding country rocks (altered lavas) contain only purely aqueous, low- to moderate-salinity inclusions.

The distribution of fluid inclusion types summarised above – and in particular the lack of hydrocarbon-bearing inclusions outside the nepheline syenites and their associated hydrothermal veins (Fig. 1) – strongly supports an interpretation where the hydrocarbons represent the remains of an associated magmatic volatile phase produced during the cooling and solidification of the alkaline magma, rather than a

phase introduced from outside the complex. Similar observations have been made on hydrocarbon gases in minerals from the Khibina and Lovozero complexes on the Kola Peninsula, Russia, and a similar origin was proposed by Kogarko (1977), Petersil'ye & Pripachkin (1979) and more recently by Potter *et al.* (1997).

Chemical characteristics of the Ilímaussaq gases

Previous studies of the gases in fluid inclusions in Ilímaussaq whole rocks and minerals, by microthermometry, gas chromatography, mass spectrometry and Raman microprobe spectrometry, show them to be composed predominantly of hydrocarbons (especially CH_4 with smaller amounts of higher alkanes), He, CO_2 , N_2 and Ar (Petersilie & Sørensen 1970; Konnerup-Madsen *et al.* 1979; Konnerup-Madsen & Rose-Hansen 1982; Konnerup-Madsen *et al.* 1985). CH_4 , H_2 and C_2H_6 were found to be the dominant species followed in abundance by N_2 and higher alkanes. Raman microprobe spectrometry on individual gaseous inclusions, however, only verified the presence of H_2 , CH_4 , C_2H_6 and occasionally traces of C_3H_8 . When recast into atomic COH proportions most analyses closely approximate to the composition of CH_4 although variations in the C/H ratio are seen (Fig. 4). This suggests that methane was probably the dominant carbon-bearing species at the time of entrapment (Konnerup-Madsen & Rose-Hansen 1982). Also included in Fig. 4 are the compositions obtained on the vapour phase in individual primary inclusions in nepheline from naujaite (Sobolev *et al.* 1970). In contrast to the hydrocarbon-dominated compositions obtained during bulk crushing of Ilímaussaq rocks and minerals, these

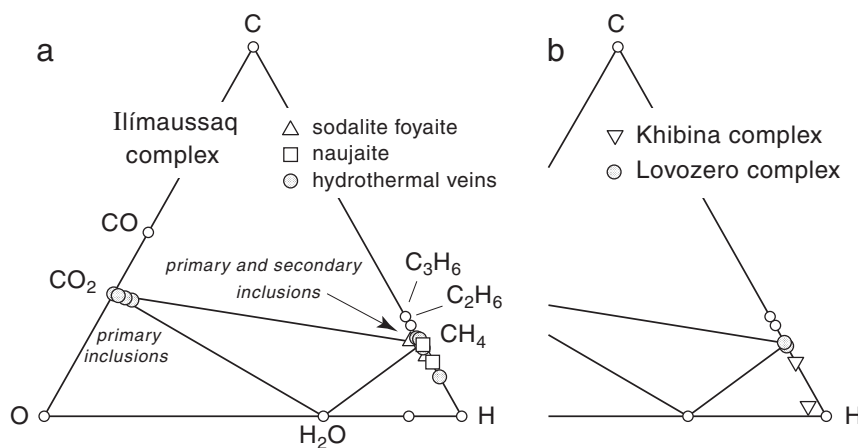


Fig. 4. C–O–H molecular relations for gases released by crushing of minerals and agpaiteic rock types from **a**: Ilímaussaq, and **b**: Khibina and Lovozero complexes. Recalculated on a water-free basis. Data from Petersilie & Sørensen (1970), Sobolev *et al.* (1970) and Konnerup-Madsen *et al.* (1981).

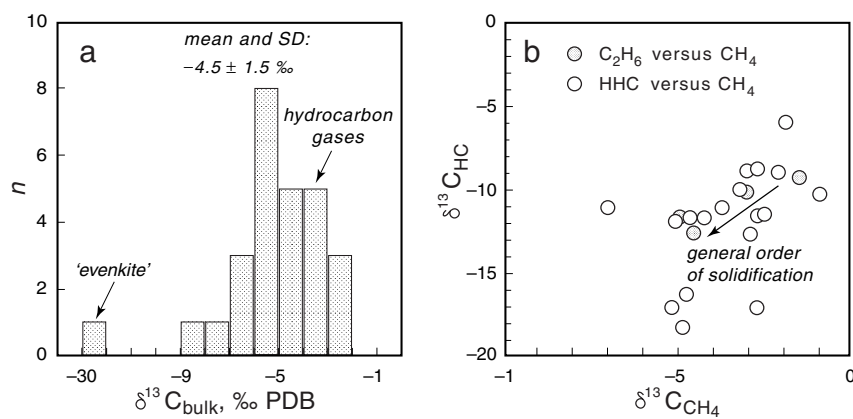


Fig. 5. $\delta^{13}\text{C}$ (in ‰ PDB) of the bulk hydrocarbon gases in fluid inclusions from Ilímaussaq rocks and minerals. **a**: Histogram of $\delta^{13}\text{C}$ values of the bulk hydrocarbon gases in fluid inclusions and of the mineral evenkite from Ilímaussaq. n is number of analyses. Data from Konnerup-Madsen *et al.* (1988). **b**: $\delta^{13}\text{C}$ compositions of C_2H_6 or the sum of higher hydrocarbons (HHC) versus $\delta^{13}\text{C}$ of CH_4 in the same sample. **Arrow** indicates the general order of solidification, derived from stratigraphic position of the individual samples analysed. **HC**: hydrocarbon, as specified in legend.

compositions are CO_2 -dominated (Fig. 4). The compositions of gases extracted from minerals and whole rocks from the Khibina and Lovozero alkaline complexes (Fig. 4b) are very similar to those of the Ilímaussaq complex (Fig. 4a).

Calculations of the PT range for entrapment of the CH_4 -rich fluids give pressures of 1–2 kbar and temperatures from about 700°C down to 400–450°C during final solidification of the nepheline syenites and hydrothermal veins. Calculations of possible equilibrium oxygen fugacity conditions give values approaching those of the synthetic graphite– CH_4 buffer curve (Konnerup-Madsen *et al.* 1981; Larsen 1993). These calculations were based on the assumption of buffering of a COH fluid with graphite even though graphite has not been identified in the Ilímaussaq complex. Therefore, additional calculations were performed on the assumption that the hydrocarbon gas compositions only represent the non-water fraction of a heterogeneous fluid consisting of an aqueous solution and a hydrocarbon-dominated gaseous phase, of which only the latter has been entrapped and preserved in fluid inclusions (Konnerup-Madsen 1988). Although such calculations are encumbered with large uncertainties, they clearly indicate that even under highly reduced conditions H_2O will be the dominant volatile species and constitute around 80–90 mole% of the bulk fluid. CH_4 and H_2 will dominate the non-aqueous fraction of the fluid and will be followed in abundance by N_2 and CO_2 . Similar calculations on entrapped gases from the Lovozero complex (Kogarko *et al.* 1987) gave similar results although higher abundances of N_2 were obtained. The above H_2O -free compositions agree fairly well with those obtained by Raman spectrometry on gaseous inclusions in minerals from these complexes.

An important conclusion of these calculations is that although hydrocarbon-rich fluids form the overwhelming number of fluid inclusions actually observed in minerals, such fluids may have constituted only a small fraction of the bulk fluid originally present.

Stable isotope characteristics of the hydrocarbon gases

The $\delta^{13}\text{C}$ isotope characteristics of hydrocarbon gases in the Ilímaussaq complex are summarised in Fig. 5. The most conspicuous features are the exceptionally high $\delta^{13}\text{C}$ values of bulk C (calculated as the weighted sums of analyses on extracted CH_4 , C_2H_6 and higher hydrocarbons from fluid inclusions) compared to those observed for hydrocarbons in other geological environments, and the systematically higher $\delta^{13}\text{C}$ values for CH_4 compared to those of the higher hydrocarbons in the same fluid sample. Both features are inconsistent with hypotheses only involving formation of CH_4 by thermal cracking of bituminous materials assimilated by the Ilímaussaq magma during emplacement (Des Marais *et al.* 1981). A rough calculation of the $\delta^{13}\text{C}$ value for the total amount of trapped hydrocarbons in the Ilímaussaq complex gives a value around -4.8‰ PDB which is within the range of normal mantle values (Kyser 1986).

The systematically higher $\delta^{13}\text{C}$ values for CH_4 compared to those of the higher hydrocarbons in the same fluid sample (Fig. 5b) is consistent with an inorganic polymerisation process whereby the heavier hydrocarbons are synthesised from methane (Des Marais *et al.* 1981) and provide additional strong support for an abiogenic origin of the hydrocarbons.

In summary, the $\delta^{13}\text{C}$ characteristics of the hydro-

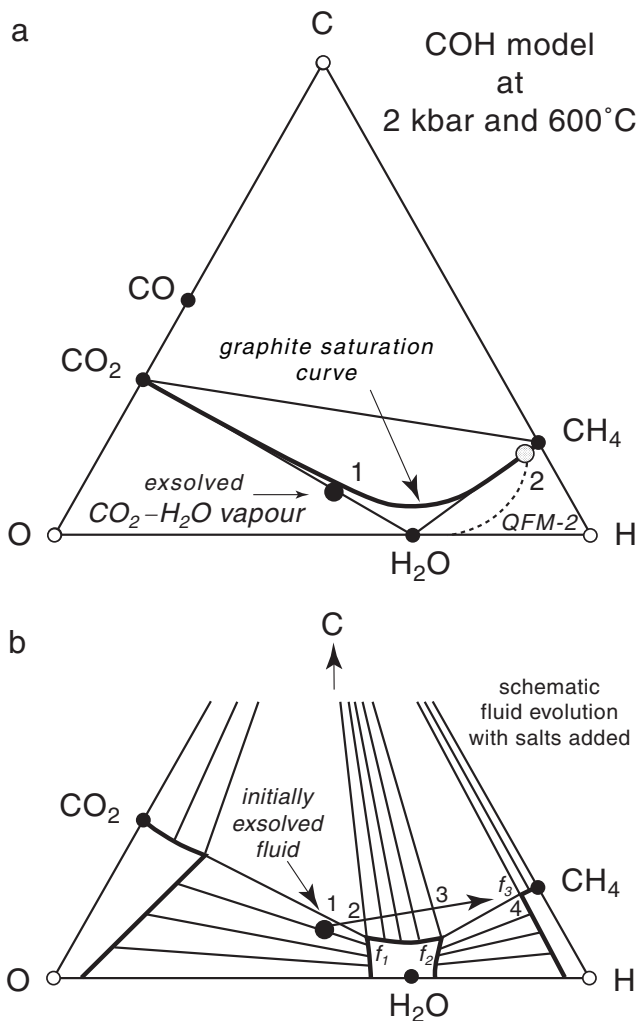


Fig. 6. **a**: Isobaric and isothermal ternary C–O–H diagram at 2 kbar and 600°C. Shown is the graphite saturation curve and the compositional trace (**stippled**) in the graphite-absent part for an oxygen fugacity of QFM –2. The estimated composition of the initially exsolved CO_2 – H_2O fluid from the Ilímaussaq magma is indicated by the **large filled circle**. Upon buffering at oxygen fugacities of QFM –2, this fluid will evolve to point **1** and then follow the graphite saturated curve until point **2**. Data from Huizenga (1995). **b**: Schematic illustration of the evolution of the same fluid as in **a** when salts are added in sufficient amounts to cause fluid immiscibility. The initially exsolved bulk fluid will follow the path indicated by the **arrow** with precipitation of graphite from **1** to **4**. See text for further discussion of the diagram. Based on data from Lamb *et al.* (1996).

carbon gases in the Ilímaussaq complex (and in similar complexes from the Kola Peninsula) support the concept of an abiogenic formation of methane from a COH vapour-saturated, highly reduced melt. Condensation of part of the methane-rich gas phase at relatively low temperatures to higher hydrocarbons during post-entrapment cooling conceivably occurred and

produced the hydrocarbon gas compositions observed. The bulk gas $\delta^{13}\text{C}$ values furthermore indicate a predominantly juvenile origin for the carbon component.

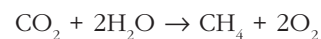
In addition, four samples have been analysed for both the $\delta^{13}\text{C}$ and δD composition of CH_4 ; δD values obtained vary from –132 to –145‰ SMOW, with a decrease in the δD values parallel to a decrease in $\delta^{13}\text{C}$ values from –1 to –5‰ PDB. The possible significance of these data is discussed later.

Volatiles during solidification of the agpaitic Ilímaussaq nepheline syenites

Previous studies have indicated that the most important properties that characterise the formation of a hydrocarbon-rich volatile phase in agpaitic nepheline syenites such as in the Ilímaussaq complex are: (1) a wide temperature range of crystallisation to very low solidus temperatures, enabling buffering of any exsolved volatiles by the magma and minerals to temperatures as low as about 450°C; (2) low oxygen fugacities, with values roughly corresponding to those of the synthetic graphite– CH_4 curve during solidification.

Together, these factors increase the probability for the co-existence of immiscible fluids (a CH_4 -rich gaseous and a saline aqueous liquid phase) and melt during the closing stages of solidification of the nepheline syenites, as schematically modelled for COH-fluids in Fig. 6 for a pressure of 2 kbar and a temperature of 600°C.

Initial H_2O and C contents of the main Ilímaussaq magma of about 4 wt% H_2O (Larsen & Sørensen 1987) and 250 ppm C (J.C. Bailey, personal communication 1999) would result in vapour saturation at close to 2 kbars and the exsolution of a CO_2 – H_2O rich fluid with $X_{\text{H}_2\text{O}}$ of about 0.7 (Holloway & Blank 1994; Fig. 6a, large filled circle). As oxygen fugacities about 2 log units below the synthetic QFM buffer reaction (QFM –2) are indicated (Larsen 1976), this fluid buffering would result in a change in bulk fluid composition from the initially exsolved through composition 1 to composition 2 of Fig. 6a according to the reaction (1)



until a composition in accordance with the imposed oxygen fugacity is obtained (Fig. 6a point 2 for QFM –2). As this change in bulk fluid composition to 2 occurs along the graphite saturation curve, some graphite should be precipitated. Graphite has not been ob-

served in the Ilímaussaq rocks; however, the amounts precipitated, according to this change in composition, would be trivial and could easily go undetected (total exsolution of 0.9 wt% CO₂ would result in a maximum precipitation of about 10⁻³ vol.% graphite). That these fluids are actually capable of precipitating graphite is indicated by the occasional observation of a thin film of poorly ordered graphite on the inclusion walls by Raman microprobe spectrometry.

The additional presence in the Ilímaussaq magma of at least 0.5 wt% Cl (Larsen & Sørensen 1987) would, however, result in high salinities of the exsolved aqueous fluid (Kilinc & Burnham 1972) and the formation of two immiscible fluid phases, one rich in CH₄, the other rich in H₂O plus chlorides (Lamb *et al.* 1996). The high contents of F (up to about 1 wt%; J.C. Bailey, personal communication 1999) in the Ilímaussaq magma would not affect the composition of the vapour phase as F is strongly partitioned into the melt (Carroll & Webster 1994).

The immiscibility resulting from the addition of chlorides to the vapour would further enrich the salinity of the aqueous fluid fraction to high values in agreement with the fluid inclusion observations. The compositional evolution during buffering of such an exsolved heterogeneous fluid mixture is shown schematically in Fig. 6b. The compositional change of exsolved *bulk* fluid composition is shown by the arrow from 1 to 4 whereas the compositional change of the *aqueous* fluid co-existing with the precipitated graphite follows the path from f_1 to f_2 . Upon final equilibration, the immiscible fluids would have composi-

tions f_2 (aqueous fluid) and f_3 (hydrocarbonic fluid). The minerals may have had a possible catalytic effect and contributed to the formation of some of the higher hydrocarbons and hydrogen from methane at lower temperatures.

The features of Fig. 6 demonstrate that although the fluid which initially exsolved was rich in CO₂ and H₂O, buffering of this fluid to low temperatures at low oxygen fugacities would result in a CH₄-rich fluid co-existing with a highly saline, aqueous fluid. The fluid inclusion observations suggest that preferential entrapment of the CH₄-rich fluid occurred, probably as a result of preferential wetting characteristics or as a result of re-dissolution of the aqueous fraction upon further development of the residual melt. The characteristics of Fig. 6 further indicate that variations in the CO₂/CH₄ ratio can result from variations in the initial CO₂/H₂O ratio of exsolved fluid (that is, initial C and H₂O contents of the melt) and imposed oxygen fugacities. The range in COH compositions shown in Fig. 4 may reflect the interplay between these parameters. Finally, the lack of observed graphite in the Ilímaussaq complex may be due to a high water content relative to carbon in the melt.

Origin of the carbon component

The observed distribution and type of occurrence of the hydrocarbon inclusions and their stable isotope characteristics in the Ilímaussaq rock types point towards a likely abiogenic origin.

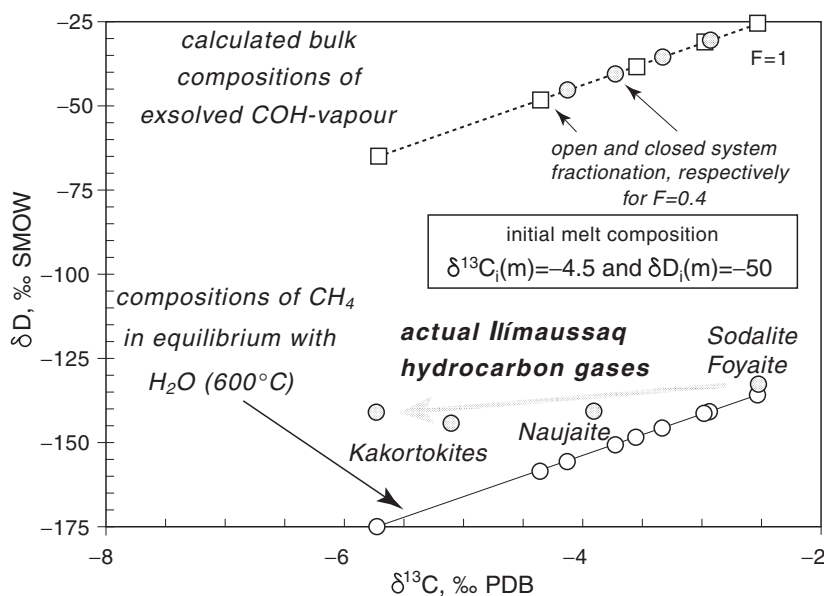


Fig. 7. δD (in ‰ SMOW) versus $\delta^{13}C$ (in ‰ PDB) of hydrocarbon gases released on crushing of various rock types from the Ilímaussaq complex compared to the fluids considered associated with the generation of hydrocarbons in the Ilímaussaq complex. Initial model compositions (m) of δD and $\delta^{13}C$ in the melt are indicated in the inset box. The change in isotopic composition of bulk exsolved COH fluid is shown by the **upper curve** for both closed (**circles**) and open (**squares**) system fractionation (F: fraction remaining in melt; **F = 1** marks the composition of the first exsolved fluid). The **lower curve** indicates the isotopic composition of CH₄ unmixed from the COH bulk fluid at the temperature indicated in the diagram and assuming total conversion of CO₂ to CH₄. Diagram constructed on the basis of data from Taylor (1986).

Based upon the available data for $\delta^{13}\text{C}$ and δD values of hydrocarbons in the Ilímaussaq complex and published fractionation factors for $\delta^{13}\text{C}$ and δD , the composition of an evolved COH-vapour in equilibrium with the melt may be modelled (Fig. 7). For initial melt values of -4.5 $\delta^{13}\text{C}$ and -50‰ δD the composition of the vapour would start at -2.6 $\delta^{13}\text{C}$, -30‰ δD and evolve towards lower values in both, as indicated in Fig. 7 by the upper stippled curve. Upon the onset of immiscibility and the formation of CH_4 -dominated and H_2O -dominated fluid fractions, further fractionation in δD would occur and result in δD values around -150‰ for the CH_4 fluid (Fig. 7, lower curve). The four samples of whole rocks on which analyses of $\delta^{13}\text{C}$ and δD on the hydrocarbons have been performed are included in Fig. 7. Compared to the modelled $\delta^{13}\text{C}$ and δD values (based on the premises indicated in Fig. 7), the overall compositional trend obtained on the Ilímaussaq hydrocarbon gases agrees with a possible signature obtained from isotopic equilibration of an immiscible CH_4 -dominated fluid with the magma.

Conclusions

The hydrocarbon-rich fluid inclusions observed in the Ilímaussaq complex – and in similar alkaline, both silica-undersaturated and silica-oversaturated complexes elsewhere – have characteristics compatible with a magmatic origin. Their formation may reflect buffering to unusually low temperatures during reduced conditions of normal magmatic fluids while variations in the compositional characteristics between different complexes may be due to an interplay between the initial volatile contents of the magmas and small variations in solidification conditions.

Acknowledgements

The author wishes to thank T. Andersen, J.C. Bailey, and L.M. Larsen for critical comments and valuable suggestions to the manuscript and to acknowledge the financial support provided by the Danish Natural Science Research Council and Carlsbergfondet during part of this work.

References

- Carroll, M.R. & Webster, J.D. 1994: Solubilities of sulfur, noble gases, nitrogen, chlorine, and fluorine in magmas. In: Carroll, M.R. & Holloway, J.R. (eds): Volatiles in magmas. *Reviews in Mineralogy* **30**, 231–279.
- Curtis, L.W. & Currie, K.L. 1981: Geology and petrology of the Red Wine alkaline complex, Central Labrador. *Geological Survey of Canada Bulletin* **294**, 61 pp.
- 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.
- Edgar, A.D. & Parker, L.M. 1974: Comparison of melting relationships of some plutonic and volcanic peralkaline undersaturated rocks. *Lithos* **7**, 263–273.
- Holloway, J.R. & Blank, J.G. 1994: Application of experimental results to C–O–H species in natural melts. In: Carroll, M.R. & Holloway, J.R. (eds): Volatiles in magmas. *Reviews in Mineralogy* **30**, 187–230.
- Huizenga, J.M. 1995: Fluid evolution in shear zones from the late Archean Harara–Shamva–Bindura greenstone belt (NE Zimbabwe), 146 pp. Unpublished Ph.D. thesis, Vrije Universiteit, Amsterdam, The Netherlands.
- Kilinc, I.A. & Burnham, C.W. 1972: Partitioning of chloride between a silicate melt and coexisting aqueous phase from 2 to 8 kilobars. *Economic Geology* **67**, 231–235.
- Kogarko, L.N. 1977: Problems of genesis of agpaite magmas, 294 pp. Moscow: Nauka (in Russian).
- Kogarko, L.N. & Romanchev, B.P. 1983: Phase equilibria in alkaline melts. *International Geology Review* **25**, 534–546.
- Kogarko, L.N., Kosztolanyi, C. & Ryabchikov, I.D. 1987: Geochemistry of the reduced fluid in alkaline magmas. *Geochemistry International* **24**, 20–27.
- Konnerup-Madsen, J. 1980: Fluid inclusions in minerals from igneous rocks belonging to the Precambrian continental Gardar rift province, South Greenland: the alkaline Ilímaussaq intrusion and the alkali acidic igneous complexes, 140 pp. Unpublished lic.scient. thesis, Institute of Petrology, University of Copenhagen, Denmark.
- Konnerup-Madsen, J. 1988: Abiogenic hydrocarbon gases associated with alkaline igneous activity. *Geological Society of India Memoir* **11**, 13–24.
- Konnerup-Madsen, J. & Rose-Hansen, J. 1982: Volatiles associated with alkaline igneous activity: fluid inclusions in the Ilímaussaq intrusion and the Gardar granitic complexes (South Greenland). *Chemical Geology* **37**, 79–93.
- 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 compositions of fluid inclusions. In: Bailey, J.C., Larsen, L.M. & Sørensen, H. (eds): The Ilímaussaq intrusion, South Greenland. A progress report on geology, mineralogy, geochemistry and economic geology. *Rapport Grønlands Geologiske Undersøgelse* **103**, 99–108.

- 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., Kreulen, R., & Rose-Hansen, J. 1988: Stable isotope characteristics of hydrocarbon gases in the alkaline Ilímaussaq complex, South Greenland. *Bulletin de Minéralogie* **111**, 567–576.
- Kyser, T.K. 1986: Stable isotope variations in the mantle. In: Valley, J.W., Taylor, H.P. & O'Neil, J.R. (eds): Stable isotopes in high temperature geological processes. *Reviews in Mineralogy* **16**, 141–164.
- Lamb, W.M., Popp, R.K. & Boockoff, L.A. 1996: The determination of phase relations in the CH₄-H₂O-NaCl system at 1 kbar, 400 to 600°C using synthetic fluid inclusions. *Geochimica et Cosmochimica Acta* **60**, 1885–1897.
- Larsen, L.M. 1976: Clinopyroxenes and coexisting mafic minerals from the alkaline Ilímaussaq intrusion, South Greenland. *Journal of Petrology* **17**, 258–290.
- Larsen, L.M. & Sørensen, H. 1987: The Ilímaussaq intrusion – progressive crystallization and formation of layering in an agpaitic magma. In: Fitton, J.G. & Upton, B.G.J. (eds): Alkaline igneous rocks. Geological Society Special Publication (London) **30**, 473–488.
- Larsen, R.B. 1993: Geofluid: A FORTRAN 77 program to compute chemical properties of gas species in C–O–H fluids. *Computers and Geosciences* **19**, 1295–1320.
- Petersil'ye, I.A. & Pripachkin, V.A. 1979: Hydrogen, carbon, nitrogen and helium in gases from undersaturated igneous rocks. *Geokhimiya* **1979**(7), 1028–1034 (in Russian). (Translation: *Geochemistry International* **16**(4), 50–55.)
- Petersilie, I.A. & Sørensen, H. 1970: Hydrocarbon gases and bituminous substances in rocks from the Ilímaussaq alkaline intrusion, South Greenland. *Lithos* **3**, 59–76.
- Potter, J., Rankin, A.H., Treloar, P.J., Nivin, V.A., Ting, W. & Ni, P. 1997: 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* **11**, 1167–1180.
- Salvi, S. & Williams-Jones, A.E. 1992: Reduced orthomagmatic C–O–H–NaCl fluids in the Strange Lake rare-metal granitic complex, Quebec/Labrador. *European Journal of Mineralogy* **4**, 1155–1174.
- Sobolev, V.S., Bazarova, T.Y., Shugurova, N.A., Bazarov, L.Sh., Dolgov, Yu.A., & Sørensen, H. 1970: A preliminary examination of fluid inclusions in nepheline, sorensonite, tugtupite and chkalovite from the Ilímaussaq alkaline intrusion, South Greenland. *Bulletin Grønlands Geologiske Undersøgelse* **81**, 32 pp. (also *Meddelelser om Grønland* **181**(11)).
- Sørensen, H. 1997: The agpaitic rocks – an overview. *Mineralogical Magazine* **61**, 485–489.
- Sørensen, H. 2001: Brief introduction to the geology of the Ilímaussaq alkaline complex, South Greenland, and its exploration history. In: Sørensen, H. (ed.): The Ilímaussaq alkaline complex, South Greenland: status of mineralogical research with new results. *Geology of Greenland Survey Bulletin* **190**, 7–23 (this volume).
- Taylor, B.E. 1986: Magmatic volatiles: isotopic variation of C, H, and S. In: Valley, J.W., Taylor, H.P. & O'Neil, J.R. (eds): Stable isotopes in high temperature geological processes. *Reviews in Mineralogy* **16**, 185–225.