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Mineralogy of Crystallized Melt Inclusions from Gardiner and Kovdor Ultramafic Alkaline Complexes: Implications for Carbonatite Genesis

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Cumulus olivine, clinopyroxene, melilite and perovskite from silicate rocks and carbonatites of the Gardiner (East Greenland) and Kovdor (Kola Peninsula) ultramafic alkaline complexes contain primary melt inclusions crystallized into aggregates of daughter minerals. The petrography and homogenization temperatures of the inclusions constrain the fractionation paths and the formation of carbonatites in the complexes. Carbonated melanephelinite was parental to both complexes and early cumulates (dunite, olivinite, peridotite and melteigite) are comparable. The common occurrence of phlogopite and amphibole in the inclusions and in the host rocks indicates that these were important liquidus phases. In both complexes the fractionation of phlogopite and amphibole drove the melts towards Ca-rich (larnite-normative) compositions. At the ijolite stage the evolutionary trends are believed to separate and the evolved larnitenormative melt produced calcite-bearing ijolite in Kovdor and melilitolite in Gardiner. The two assemblages are related by decarbonation reactions. A fractional crystallization origin is suggested for the Kovdor carbonatite, whereas the Gardiner carbonatite formed by liquid immiscibility in the course of melilite fractionation. Na-K-Ca and Na-Mg carbonates are common daughter phases and especially abundant in late-stage inclusions. Thus, all carbonatite melts in the two complexes are alkaline. Calcite carbonatites appear to be cumulates.

KEY WORDS: carbonatites; Gardiner; Kovdor; melilitolites; melt inclusions

INTRODUCTION

Carbonatite-bearing ultramafic alkaline complexes generally exhibit chaotic field relations because of explosive magmatism, metasomatic alteration and high activity of volatiles. In these complexes the primary characteristics of the parental melts and the primary liquidus assemblages may be obscured by post-magmatic reactions, and volatile components are easily lost during crystallization together with components soluble in fluids. Melt and fluid inclusions in liquidus minerals constitute microscopic natural autoclaves and their study is especially powerful in volatile-rich systems. The petrography and composition of inclusions constrain petrogenetic models for ultramafic alkaline complexes and carbonatite formation. Carbonatites and related silicate rocks have been the subject of melt and fluid inclusion studies for several decades (e.g. Roedder, 1984, pp. 406-411), and such studies have revealed traces of strongly alkaline carbonatite melt associated with alkali-poor plutonic carbonatite (Aspden, 1981; Le Bas & Aspden, 1981; Kogarko et al., 1991).

Here we present results of an investigation of crystallized melt inclusions in rock-forming minerals from two ultramafic alkaline complexes: the Gardiner complex, East Greenland (Frisch & Keusen, 1977; Nielsen, 1980) and the Kovdor complex, Kola Peninsula, Russia (Kukharenko *et al.*, 1965). Both complexes were formed from

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volatile-rich mantle-derived ultramafic alkaline melt and they both include late-stage melilitolite and carbonatite. The main objective of the paper is to describe the crystallization path for the whole sequence of cumulates from early, high-temperature, olivine-rich ones to latestage carbonatites using a combination of petrography, microprobe techniques, homogenization experiments and published phase equilibria studies.

Melt inclusions are rarely preserved as quenched glasses in plutonic rocks. They are commonly represented by characteristic assemblages of crystalline daughter phases inside the host mineral, and are throughout this paper referred to as 'crystallized melt inclusions'.

THE GARDINER AND KOVDOR COMPLEXES

The two complexes are well studied (see references below) and show many similarities, but differ in relative proportions of exposed rock types. Crystallized melt inclusions are abundant in rock-forming minerals of both complexes and we have studied: (1) olivine in dunites, olivinites, peridotites, phoscorites and carbonatites; (2) clinopyroxene in peridotites, pyroxenites, ijolites and melilitolites; and (3) melilite in melilitolites and turjaites. In addition, apatite in Kovdor carbonatites contains abundant melt and fluid inclusions. The studied samples cover the range of rock types observed and illustrate the entire crystallization sequence in the two intrusions.

The Gardiner complex

The Gardiner complex (68°N, 32°W, East Greenland) formed ~50 my ago during the Early Tertiary break-up in the North Atlantic (Noble et al., 1988; Gleadow & Brooks, 1979). Gardiner was intruded at shallow crustal level into the centre of a regional dyke swarm parallel to the 'failed arm' of the Kangerlussuag triple junction on the East Greenland continental margin. The complex is ~5 km in diameter and is dominated by early ultramafic cumulates (Nielsen, 1981) including dunites (olivine and chromite with minor clinopyroxene, phlogopite and amphibole), peridotites (clinopyroxene, olivine and magnetite with minor amphibole) and pyroxenite (clinopyroxene and magnetite with subordinate amphibole and biotite). The ultramafic cumulates form an onion structure and become younger towards the centre of the complex. They are interpreted as in situ cumulates formed on the walls of an open, shallow level (0.5-1 kbar) subvolcanic magma chamber of a highly alkaline carbonatite-bearing volcano (Nielsen, 1981, 1994; Nielsen et al., 1997).

The ultramafic cumulates are intruded by radial and ring dyke systems of increasingly alkaline composition (Nielsen, 1979, 1980, 1994). Ring dykes are from a few centimetres to several hundred metres wide, whereas radial dykes generally are <1 m wide. Two major ring dykes, >100 m in width, are emplaced in the centre of the complex. The older dyke is composed of meliliteand perovskite-bearing melteigites and ijolites, and the younger is of melilitolite (plutonic melilite rocks) with associated dykes and veins of calcite carbonatite and peralkaline nephelinites (Nielsen, 1980). Melilite from the melilitolite ring dyke contains coexisting inclusions of melilitite melt and immiscible alkali carbonatite melt in addition to separate inclusions of natrocarbonatite melt. The natrocarbonatite melt is interpreted to have formed by degassing of supercritical CO₂-rich, alkaline brines (Nielsen et al., 1997).

Isotopic studies suggest all units of the intrusion to be comagmatic (Nielsen & Buchardt, 1985; Nielsen & Holm, 1993).

The Kovdor complex

The Kovdor complex ($67^{\circ}35'N$, $30^{\circ}20'E$, Kola Peninsula, Russia) of ultramafic alkaline silicate rocks and carbonatites is ~370 my old (Kramm *et al.*, 1993; Zaitsev & Bell, 1995). The complex was emplaced into Archaean granites and gneisses and is, together with Sokli and Turyi–Mys intrusions, related to the Yuov–Kandalaksha fracture zone (Bulakh & Ivanikov, 1984; Kogarko *et al.*, 1995; Bell *et al.*, 1996).

Kovdor is a concentrically zoned subvolcanic plutonic body surrounded by fenites. The geology, mineralogy and petrography were summarized by Kukharenko *et al.* (1965) and Kapustin (1980; see also Kogarko *et al.*, 1995). The earliest rocks, olivinites, occupy the central part of the intrusion and are surrounded by irregular zones of peridotite, pyroxenites, melilitolites and rocks of the jacupirangite–ijolite series. Melilitolite and turjaite (plutonic clinopyroxene–nepheline–melilite rock), are located between the inner zones of mafic and ultramafic rocks and the outer ring of alkaline rocks. Phlogopite-rich peridotites and garnet–amphibole–monticellite-bearing rocks are related to the melilitolites.

The youngest suite of rocks in Kovdor includes carbonatite and phoscorite. The latter term is used in Kovdor for a group of forsterite-, calcite- and phlogopite-bearing apatite-magnetite rocks of cumulative origin. Carbonatites and phoscorites form a vertical stock on the contact between pyroxenites and ijolites in the SW part of the complex. The stock is currently mined for magnetite, apatite and baddeleyite, and has been mapped and studied in great detail (Krasnova & Kopylova, 1988). Several types of carbonatite are recorded and include early diopside-, nepheline- and forsterite-bearing calcite carbonatite and late-stage dolomite carbonatite. Melt inclusion studies (Sokolov, 1983, 1994) and Sr and Nd isotope studies (Zaitsev & Bell, 1995) suggest a close genetic relationship between carbonatites and phoscorites. Wide variations in Sr and Nd isotopic composition in some early carbonatites indicate, however, that the evolution of the carbonatites and phoscorites cannot be explained by a simple magmatic differentiation under closed-system conditions alone.

SAMPLE PREPARATION AND ANALYTICAL METHODS

The common occurrence of water-soluble phases in the inclusions of carbonatitic composition requires special sample preparation techniques. Water cannot be used, and mineral oils and organic solvents (acetone) were used for grinding, washing and polishing of mineral fragments. The contrast in hardness between silicates and carbonates often results in the loss of the softer carbonate phases.

The Gardiner samples were analysed using the Jeol 733 Superprobe at the Department of Geology, University of Copenhagen, as described by Nielsen et al. (1997) and as described for the Kovdor samples below. Short counting times and a defocused beam (dependent on the size of the target) were used for carbonates and other easily volatilized phases. The electron microprobe (EMP) study of Kovdor samples and X-ray mapping were carried out with a Cameca SX-100 microprobe (wavelength dispersive) at the American Museum of Natural History (New York). Different analytical procedures were used for the quantitative analyses of silicates (15 kV, 20 nA and 20 s counting time) and carbonates (15 kV, 4 nA and 40 s). A defocused beam was used wherever possible, but the daughter phases in the inclusions are usually too small to allow a beam size of more than $5-10 \mu m$. Despite all these precautions, sodium volatilization occurred during analysis of the most sodium-rich carbonates.

PETROGRAPHY OF MELT INCLUSIONS

All inclusions are products of unique chemical and physical conditions. The inclusions (Fig. 1) may also have undergone chemical modification after entrapment and they may not represent the bulk composition of a parental melt, e.g. because of heterogeneous trapping and local disequilibrium (Roedder, 1984). The host minerals are important constituents of the inclusion assemblages. Hosts are in most cases not inert containers, and may have reacted with the trapped melt and daughter minerals of the inclusions. This is especially true for inclusions of the



Fig. 1. A group of secondary inclusions and a larger primary melt inclusion in clinopyroxene from Kovdor ijolite. The primary inclusion is \sim 40 µm across.

volatile-rich silica-undersaturated composition. In the descriptions below we accordingly present the petrography and composition of crystallized melt inclusions by comparing inclusions in the same host minerals (olivine, clinopyroxene, perovskite, etc.) of equivalent rock types (dunite and olivinite, peridotite, pyroxenite, etc.) from the two complexes.

The assemblages of daughter minerals in crystallized melt inclusions from Gardiner and Kovdor are summarized in Tables 1 and 2, and representative EMP analyses of host minerals and daughter phases are listed in Tables 3–7.

Melt inclusions in olivine

In the Gardiner complex the occurrence of olivine is restricted to dunite and peridotite; it is rarely found in the pyroxenite, where phlogopite becomes the liquidus phase in the place of olivine. Olivine remained a major rock-forming mineral (often together with phlogopite) throughout the petrogenetic development of Kovdor, with clinopyroxene in peridotite, with melilite in olivine melilitolite, and with calcite, magnetite, phlogopite and apatite in phoscorite and forsterite carbonatite.

Crystallized melt inclusions are abundant in olivine phenocrysts of all olivine-bearing rock types in both

| Rock: | Dunite | Perido | tite | Pyroxenite | Melteigite | Cpx-me | lilitolite | Melilito | lite | |
|---------------------|--------|--------|------|------------|------------|--------|------------|----------|------|-----|
| Host mineral: | ol | ol | срх | срх | срх | срх | mel | срх | mel | prv |
| Silicates | | | | | | | | | | |
| Fe-monticellite | | | | | | | | | х | |
| Cuspidine(?) | | | | | | | | | Х | |
| Clinohumite | | х | | | | | | | | |
| Melilite | | | | | | х | Х | Х | Х | |
| Clinopyroxene | х | Х | Х | х | Х | х | Х | Х | | х |
| Wollastonite | | | | | | | | | x | х |
| Hydrogrossular | | | | | | | | | х | Х |
| Cebollite(?) | | | | | | | | | Х | |
| Pectolite | | | | | | | | х | х | Х |
| Nepheline | | | | | | | | | | Х |
| Sodalite | | Х | | | | | | | | |
| Nosean | | | | | | | | Х | | |
| Cancrinite | | | | Х | | | | | | Х |
| Amphibole | Х | х | Х | | | | | | | |
| Phlogopite | Х | х | Х | Х | Х | Х | Х | | Х | Х |
| Sphene | | | | x | | | | | х | |
| Carbonates | | | | | | | | | | |
| Calcite | х | | | x | | х | | Х | Х | х |
| Na–Ca carbonate | x | х | х | х | Х | х | | Х | Х | х |
| Other non-silicates | ; | | | | | | | | | |
| Apatite | | x | х | x | | х | х | | x | х |
| Magnetite | х | Х | х | х | Х | х | Х | Х | Х | х |
| Perovskite | | | | x | | x | | | x | х |
| Sulphides | x | х | | | | x | | х | x | |
| Scheelite | | | | x | | | | | | |

Table 1: Daughter minerals of crystallized melt inclusions in the Gardiner complex

Major and minor phases are marked by large and small crosses, respectively. Abbreviations for mineral names are listed in the Appendix.

complexes. The inclusions often have the shape of negative crystals and they are suggested to be primary melt inclusions because of (1) a random distribution of inclusions and (2) the lack of obvious relationships to secondary features such as healed fractures. The primary nature and closed-system behaviour of the inclusions are supported by the presence of low-temperature daughter phases and unstable minerals that are absent from the bulk rocks. This is demonstrated, for example, by the occurrence of shortite, Na₂Ca₂(CO₃)₃, in Gardiner (Nielsen *et al.*, 1997). Shortite is not stable above 400°C (Cooper *et al.*, 1975) and could not be trapped as a solid in association with high-temperature silicate daughter phases.

The olivine hosts of the inclusions contain abundant solid, oriented, magnetite micro-inclusions. They seem to be a result of oxidation of Fe^{2+} in olivine. The early olivine phenocrysts also contain oriented exsolutions of monticellite. In Kovdor olivine compositions do not follow a trend towards Fe enrichment with progressive fractionation, and the occurrence of forsteritic olivine in Kovdor and other ultramafic alkaline complexes is not necessarily indicative of early high-temperature crystallization. Compositions of Mg-Fe silicates, e.g. phlogopite (Brigatti et al., 1996), suggest that the ferrous-ferric ratio decreases in the residual melts of ultramafic alkaline magmatic systems and the composition of olivine in late-stage carbonatite approaches that of pure forsterite (Kapustin, 1980). Thus, narrow rims of Fe-depleted, but Mn-enriched host olivine are often observed around the crystallized melt inclusions (see back-scattered electron images and X-ray maps, Figs 2 and 3). These rims are,

| Rock: | Olivinite | Perid | lotite | Pyro- | Ol-m | elilitolite | Turjai | te | ljolite | | Phoscorite | Calcite | carbonatite |
|---------------------|-----------|-------|--------|-------|------|-------------|--------|-----|---------|----|------------|---------|-------------|
| Host mineral: | ol | ol | срх | cpx | ol | mel | срх | mel | срх | ne | ol | срх | ol |
| Silicates | | | | | | | | | | | | | |
| Fe-monticellite | Х | | х | | Х | | | | | | | | |
| Clinopyroxene | Х | Х | Х | Х | | Х | Х | Х | Х | Х | | | |
| Wollastonite | | | | | | | х | | | | | | |
| Cebollite(?) | | | | | | | х | | | | | | |
| Amphibole | | | Х | Х | | | | | Х | | | Х | |
| Phlogopite | Х | Х | Х | Х | Х | Х | Х | Х | Х | х | х | Х | Х |
| Cancrinite | | | | | | | х | | Х | х | | | |
| Clinohumite | х | | | | | | | | | | | | |
| Cuspidine | | | | | | | х | х | | | | | |
| Carbonates | | | | | | | | | | | | | |
| Calcite | х | х | Х | х | Х | | х | х | х | х | x | Х | х |
| Dolomite | | | | | | | | | | | х | | Х |
| Na–Ca carbonates | x | Х | х | | Х | | х | | | | Х | | х |
| Na–Mg carbonates | | | | | | | | | | | Х | | Х |
| Sr–Ba carbonates | | | | | | | | | | | х | | х |
| Other non-silica | ites | | | | | | | | | | | | |
| Magnetite | х | Х | Х | х | Х | Х | x | Х | Х | x | x | | Х |
| Apatite | x | x | х | х | | x | х | | x | х | | х | х |
| Perovskite | | | | | | | х | x | х | | | | |
| Sulphides | | | х | | | | х | | | | х | | |
| Scheelite | | | | | | | х | | | | | х | |

Table 2: Daughter minerals of crystallized melt inclusions in the Kovdor complex

Major and minor phases are marked by large and small crosses, respectively. Abbreviations for mineral names are listed in the Appendix.

as noted above, part of the assemblage of the crystallized melt inclusions. The mineralogy of olivine-hosted inclusions is summarized in Tables 1 and 2, and below we concentrate on mineral reactions and the carbonate assemblages within the inclusions.

Monticellite-diopside relationships

Monticellite and diopsidic clinopyroxene are common in the olivine-hosted inclusions (Tables 1 and 2), but these two daughter phases are never found together. Diopside, monticellite, forsterite and calcite may be related to each other at crustal pressures by the following carbonation reaction:

$$3CaMgSiO_4 + 2CO_2 = CaMgSi_2O_6 + Mg_2SiO_4 + 2CaCO_3$$
 (1)
monticellite fluid diopside forsterite calcite

which was experimentally constrained by Walter (1965)

and Zharikov *et al.* (1977). The mineral equilibria depend on P, T and CO_2 fugacity, and these may account for monticellite–diopside incompatibility in the Kovdor inclusions.

Neither clinopyroxene nor monticellite are present in the inclusions in olivine from Kovdor phoscorite and carbonatite (Table 2 and Fig. 3). Apart from the host forsterite, the only silicate stable in the carbonatite associations is phlogopite with a composition close to that of the Al-free tetraferriphlogopite end-member (Table 5). Tetraferriphlogopite is a common mineral in carbonatites (Kapustin, 1980; McCormick & Le Bas, 1996).

Carbonate daughter minerals

The most striking feature of olivine-hosted inclusions in in both complexes is the strong development in the proportion and the compositions of the carbonates

| Rock: | Dunite | Peridotite | | Pyroxenite | Melteigite | Cpx-melilit | olite | Melilitolite |
|------------------|--------|------------|-------|------------|------------|-------------|-------|--------------|
| Mineral: | ol | ol | срх | срх | срх | срх | mel | mel |
| SiO ₂ | 40.58 | 39.95 | 52.58 | 53.06 | 53.15 | 50.79 | 44.84 | 44-48 |
| TiO ₂ | _ | _ | 0.90 | 0.49 | 1.00 | 1.14 | 0.05 | n.d. |
| AI_2O_3 | _ | _ | 1.18 | 1.24 | 1.75 | 2.22 | 5.91 | 5.50 |
| Cr_2O_3 | _ | _ | 0.57 | 0.05 | 0.01 | n.d. | 0.03 | n.d. |
| FeOt | 12.57 | 14.76 | 3.93 | 3.29 | 4.06 | 4.81 | 2.99 | 2.17 |
| MnO | 0.11 | 0.15 | n.d. | 0.09 | 0.01 | n.d. | 0.03 | 0.17 |
| NiO | 0.22 | 0.26 | n.d. | 0.05 | n.d. | n.d. | 0.01 | 0.01 |
| MgO | 46-69 | 44.63 | 16.42 | 16-42 | 14.62 | 15.28 | 8.83 | 9.23 |
| CaO | 0.09 | 0.07 | 24.23 | 25.48 | 24.75 | 24.54 | 33.57 | 35.11 |
| Na₂O | _ | _ | n.d. | 0.35 | 0.46 | 0.58 | 3.57 | 3.61 |
| K₂O | _ | _ | _ | 0.02 | 0.05 | 0.03 | 0.08 | n.d. |
| P_2O_5 | _ | _ | _ | 0.03 | 0.08 | 0.32 | 0.03 | n.d. |
| Total | 100.26 | 99.82 | 99.81 | 100.03 | 100.03 | 99.71 | 99.94 | 100-28 |

Table 3: Compositions of host minerals from the Gardiner complex in wt % of oxides

n.d., not determined.

Table 4: Compositions of host minerals from the Kovdor complex in wt % oxides

| Rock: | Olivinite | Peridotit | e | Pyroxe- | Ol-melil | itolite | Turjaite | | | ljolite | Carbona | tites |
|------------------|-----------|-----------|-------|---------|----------|---------|----------|-------|--------|---------|---------|--------|
| Host: | ol | ol | срх | cpx | ol | mel | cpx* | cpx* | mel | срх | ol | срх |
| SiO ₂ | 40.57 | 40.37 | 53.35 | 51.84 | 40.80 | 43.60 | 52.09 | 54.24 | 43.71 | 50.79 | 41.48 | 54.24 |
| TiO ₂ | n.d. | n.d. | 0.54 | 0.71 | 0.09 | 0.01 | 0.85 | 0.07 | 0.07 | 0.97 | 0.02 | 0.49 |
| AI_2O_3 | n.d. | n.d. | 1.14 | 2.80 | 0.01 | 3.27 | 1.91 | 0.18 | 3.35 | 2.09 | n.d. | 0.18 |
| Cr_2O_3 | _ | n.d. | _ | 0.01 | 0.04 | _ | _ | _ | _ | _ | _ | _ |
| FeOt | 9.05 | 12.11 | 2.91 | 4.17 | 7.78 | 2.91 | 4.53 | 2.41 | 3.05 | 5.85 | 7.82 | 4.25 |
| MnO | 0.31 | 0.55 | 0.11 | 0.22 | 0.32 | 0.04 | 0.13 | 0.12 | 0.12 | 0.13 | 0.43 | 0.11 |
| NiO | 0.12 | 0.17 | 0.03 | _ | _ | _ | n.d. | n.d. | n.d. | n.d. | _ | n.d. |
| MgO | 50.26 | 47.39 | 16.37 | 15.02 | 50.20 | 9.32 | 15.45 | 16.95 | 10.45 | 14.54 | 50.92 | 16.42 |
| CaO | 0.36 | 0.30 | 24.76 | 24.99 | 0.34 | 36.62 | 24.56 | 25.56 | 36.86 | 24.44 | 0.06 | 24.12 |
| Na₂O | n.d. | 0.01 | 0.22 | 0.36 | 0.03 | 2.35 | 0.54 | 0.13 | 2.26 | 0.57 | 0.01 | 0.64 |
| K₂O | 0.01 | n.d. | n.d. | 0.01 | 0.01 | 0.05 | n.d. | n.d. | 0.05 | 0.01 | 0.01 | 0.01 |
| P_2O_5 | n.d. | 0.02 | _ | 0.01 | 0.01 | n.d. | 0.03 | 0.02 | 0.09 | n.d. | 0.27 | n.d. |
| Total | 100.69 | 100.92 | 99.43 | 100.14 | 99.65 | 98·17 | 100.08 | 99.67 | 100.00 | 99.45 | 101.04 | 100.49 |

*Zones in the same crystal.

n.d., not determined.

(Tables 1–3). Na–Ca carbonate, compositionally similar to nyerereite (Na₂Ca(CO₃)₂), is subordinate to calcite, but is present in the olivine-hosted crystallized melt inclusions from early dunite and olivinite, whereas Na–Ca carbonates in general dominate over calcite in the carbonate assemblages in the olivine-hosted inclusions from peridotite. In peridotite, EMP analyses (Table 5) and X-ray maps (Fig. 2) show two Ca–Na carbonate minerals with different Na and K contents in the latter inclusions. The compositions correspond to K-bearing shortite solid solutions and nyerereite. The analyses do not recalculate to the stoichiometric compositions of nyerereite and include minor MgO and SiO₂, probably because of contamination by the host olivine. The atomic Na/Ca values in the nyerereite EMP analyses are <2, which indicates loss of some Na under the electron beam, but

| Comple | x: Gardin | er | | Kovdor | | | | | | | | | | | |
|--------------------------------|-----------|---------------|-------|----------|-----------|-------|--------|------------|-------|-------|------------------------------|-------|-------|-------|--|
| Rock: | Dunite | | | Olivinit | Olivinite | | | Peridotite | | | Phoscorites and carbonatites | | | | |
| | phl | срх | amph | mont | phl | nye | срх | sht | nye* | f-phl | dol | eit | brad | nor | |
| SiO ₂ | 38.39 | 51.77 | 44·13 | 36.95 | 39.27 | 0.01 | 54.70 | 0.05 | 3.52 | 40.54 | 0.00 | 0.32 | 0.08 | 0.07 | |
| TiO₂ | 3.25 | 0.44 | 1.33 | 0.01 | 0.54 | 0.02 | 0.02 | 0.01 | 0.02 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | |
| Al ₂ O ₃ | 13.41 | 0.89 | 8.13 | 0.00 | 15.31 | 0.00 | 0.07 | 0.00 | 0.00 | 0.05 | 0.00 | 0.02 | 0.05 | 0.01 | |
| MgO | 22.77 | 15.61 | 18.92 | 20.12 | 25.17 | 0.01 | 17.40 | 0.06 | 2.51 | 26.18 | 20.54 | 25.18 | 15.07 | 18.77 | |
| FeOt | 4.70 | 3.48 | 5.99 | 9.54 | 4.13 | 0.28 | 2.14 | 0.46 | 0.45 | 16.90 | 0.95 | 0.26 | 0.36 | 0.42 | |
| MnO | 0.06 | 0.07 | 0.01 | 0.35 | 0.02 | 0.01 | 0.07 | 0.02 | 0.02 | 0.13 | 0.35 | 0.95 | 1.52 | 0.63 | |
| NiO | 0.18 | 0.09 | 0.09 | 0.06 | 0.02 | 0.00 | _ | _ | _ | _ | _ | _ | _ | _ | |
| CaO | 0.10 | 24.93 | 11.50 | 33.76 | 0.04 | 29.90 | 25.96 | 36.06 | 35.83 | 0.07 | 29.85 | 0.04 | 0.03 | 0.40 | |
| Na₂O | 2.16 | 1.32 | 3.86 | 0.03 | 1.97 | 28.75 | 0.13 | 17.44 | 23.22 | 0.18 | 0.03 | 27.71 | 26.43 | 31.71 | |
| K₂O | 6.62 | 0.03 | 0.58 | 0.01 | 7.56 | 0.22 | 0.02 | 5.50 | 0.76 | 9.99 | 0.01 | 0.02 | 0.03 | 0.04 | |
| P_2O_5 | 0.16 | 0.40 | 0.05 | 0.03 | 0.01 | 0.00 | 0.01 | 0.12 | 0.04 | 0.01 | 0.01 | 0.00 | 30.83 | 0.03 | |
| SO ₂ | 0.09 | 0.15 | 0.05 | 0.01 | 0.06 | 0.17 | 0.01 | 0.05 | 0.06 | 0.34 | 0.00 | 0.06 | 0.01 | 0.07 | |
| F | _ | _ | _ | 0.02 | 0.08 | 0.00 | _ | 0.00 | 0.02 | 0.02 | 0.03 | 0.04 | 0.01 | 0.07 | |
| CI | _ | _ | _ | _ | _ | _ | _ | 0.00 | 0.02 | _ | 0.00 | 0.02 | 0.00 | 13.91 | |
| SrO | _ | _ | _ | _ | _ | _ | _ | 2.16 | 0.26 | _ | 0.35 | 0.05 | 0.06 | 0.02 | |
| Total | 91.89 | 99 .18 | 94.64 | 100.86 | 94.15 | 59.37 | 100.53 | 61.93 | 66.73 | 94.41 | 52.12 | 54.67 | 74.48 | 66.15 | |

Table 5: Chemical compositions of daughter minerals typical for inclusions in olivine

*Possibly contaminated by the host; some Na may be lost during the analyses.

The concentrations are mean values of 3-5 probe analyses in wt % oxides. Abbreviations for mineral names are listed in the Appendix.

no other phase agrees with the observed element ratios and totals. Kovdor olivine melilitolite is more evolved than peridotites (see homogenization temperatures, Table 8). Nyerereite, alone, is the dominant Na–Ca daughter carbonate in the inclusions in melilite. It is thus observed that through the cumulate sequence the proportion of carbonates increases, the proportion of Na–Ca carbonates increases and the proportion of the most Na-rich carbonate (nyerereite) increases.

The most evolved olivine-bearing rocks in Kovdor are phoscorites and forsterite-calcite carbonatites. Calcite is almost absent as daughter mineral in olivine-hosted inclusions from phoscorites and carbonatites, even though the host rocks are totally dominated by calcite. Nyerereite and shortite in these inclusions are joined by dolomite and complex Na–Mg carbonates and mixed salts (Table 5 Fig. 3), such as $Na_2Mg(CO_3)_2$ (eitelite), and $Na_3Mg(CO_3)(PO_4)$ (bradleyite) and $Na_3Mg(CO_3)_2Cl$ (northupite). Apatite, a very common mineral in Kovdor and Gardiner rocks and melt inclusions, is not found in association with bradleyite, which is the only host for P in the crystallized inclusions of the most evolved melts. Tiny bright spots in back-scattered electron images of several inclusions represent heterogeneous aggregates of very fine-grained Sr- and Ba-rich phases (~14 wt % SrO). The size of the grains prohibits reliable quantitative analyses, but low totals suggest that the phases are Sr and Ba carbonates. The presence of Na–Mg carbonates, the high Mn content of the Mg phases and the enrichment of the trapped melt in trace elements (e.g. Ba and Sr) and volatiles (e.g. CO_2 and Cl) confirm the extremely evolved and residual nature of the melts of phoscorite and calcite–forsterite carbonatite.

Inclusions in clinopyroxene

High-Ca clinopyroxene is an important rock-forming mineral in peridotite, pyroxenite and ijolite in both complexes. It is also present in some melilitolites and in the early Kovdor carbonatite. Melt inclusions are common in clinopyroxene, and some crystals 1 mm in length may contain dozens or even hundreds of inclusions of different size (5–80 μ m). Smaller inclusions are often observed as 'chains' along healed cracks and were discarded as secondary inclusions (Fig. 1). Large inclusions (60–80 μ m) have tabular, elongated shapes controlled by the crystal structure of the host and are accepted as

| Comple | x: Gardine | er | | | | | | Kovdo | r | | | | | | |
|------------------|------------|------------|----------|--------|-------------|-------|-------|--------|-------|---------|-------|---------|-------|--------|--------|
| Rock: | Peridot | ite and py | roxenite | Cpx-me | elilitolite | 9 | | Pyroxe | enite | ljolite | | Turjait | е | Carbor | natite |
| | amph | phl | canc | mel | phl | pct | nos | сс | phl | phl | canc | phl | nye | amph | phl |
| SiO ₂ | 55.75 | 38.92 | 41.60 | 45·21 | 38.33 | 51.24 | 39.65 | 0.18 | 37.83 | 37.03 | 44.69 | 38.23 | 0.57 | 56.69 | 36.77 |
| TiO ₂ | 0.39 | 0.95 | 0.60 | 0.00 | 1.75 | 0.00 | 0.00 | 0.01 | 0.94 | 1.17 | 0.01 | 0.54 | 0.01 | 0.56 | 0.73 |
| AI_2O_3 | 0.27 | 14.15 | 33.73 | 6.35 | 15.75 | 0.83 | 33.04 | 0.04 | 14.42 | 14.78 | 29.81 | 14.67 | 0.03 | 0.42 | 9.80 |
| MgO | 23.77 | 23.88 | 0.00 | 9.20 | 23.50 | 0.00 | 0.16 | 0.10 | 22.15 | 19.87 | 0.04 | 22.40 | 0.11 | 21.65 | 23.97 |
| FeO _t | 1.92 | 6.15 | 0.29 | 3.04 | 5.22 | 0.28 | 0.37 | 0.18 | 6.95 | 10.88 | 0.19 | 7.59 | 0.19 | 4.44 | 8.82 |
| MnO | 0.06 | 0.20 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.01 | 0.12 | 0.00 | 0.13 | 0.17 | 0.00 | 0.17 | _ |
| NiO | 0.07 | 0.03 | 0.03 | 0.00 | 0.00 | 0.03 | 0.02 | _ | _ | 0.01 | 0.01 | 0.02 | 0.01 | 0.00 | n.a. |
| CaO | 7.22 | 0.09 | 0.81 | 33.59 | 0.00 | 34.83 | 0.30 | 56.56 | 0.80 | 0.06 | 3.69 | 0.30 | 35.75 | 6.59 | 0.48 |
| Na₂O | 5.88 | 1.89 | 20.66 | 3.25 | 1.48 | 8.74 | 24.16 | 0.04 | 0.73 | 0.72 | 12.01 | 0.57 | 31.09 | 5.69 | 0.67 |
| K₂O | 0.42 | 7.58 | 0.05 | 0.03 | 7.90 | 0.00 | 0.18 | 0.02 | 9.27 | 9.00 | 0.03 | 9.72 | 0.04 | 1.65 | 9.11 |
| P_2O_5 | 0.04 | 0.00 | 0.00 | 0.09 | 0.19 | 0.10 | 0.00 | 0.06 | 0.08 | 0.00 | 0.02 | 0.01 | 0.03 | 0.00 | 0.00 |
| SO₃ | 0.07 | 0.00 | 0.19 | 0.00 | 0.00 | 0.50 | 1.28 | _ | _ | 0.01 | 0.01 | 0.04 | 0.03 | 0.04 | 0.03 |
| F | _ | _ | _ | _ | _ | _ | _ | _ | _ | 0.04 | 0.04 | 0.13 | 0.00 | 0.28 | _ |
| Total | 95.86 | 93.84 | 97.96 | 100.8 | 94.12 | 96.55 | 99.16 | 57.20 | 93-29 | 93.57 | 90.68 | 94.39 | 67.85 | 98.19 | 90.38 |

Table 6: Chemical compositions of daughter minerals of the inclusions in clinopyroxene

The concentrations are mean values of several probe analyses in wt % oxides. Abbreviations for mineral names are listed in the Appendix. n.a., not analysed.

| Complex: | Gardine | er | | | | | | Kovdor | | | | | |
|--------------------------------|---------|------------|----------|--------------|--------|-------|-------|--------|-------|-----------------|--------|-------|-------|
| Rock: | Cpx-me | lilitolite | Melilito | Melilitolite | | | | | | Ol-melilitolite | | | |
| | срх | phl | mont | cusp | ceb(?) | pec | phl | срх | phl | sht+?* | срх | phl | pst |
| SiO ₂ | 54.09 | 38.00 | 35.86 | 32.03 | 41.67 | 51.94 | 38.83 | 54.62 | 40.78 | 1.04 | 51.40 | 40.14 | 0.51 |
| TiO₂ | 0.09 | 0.11 | 0.01 | 0.01 | 0.01 | 0.01 | 0.57 | 0.23 | 0.76 | 0.00 | 1.01 | 2.82 | 56.45 |
| Al ₂ O ₃ | 0.73 | 13.83 | 0.01 | 0.01 | 7.37 | 0.66 | 14.40 | 0.16 | 11.98 | 0.02 | 2.73 | 12.98 | 0.14 |
| MgO | 16.53 | 23.73 | 15.02 | 0.01 | 0.01 | 0.10 | 24.97 | 16.94 | 24.16 | 0.26 | 14.97 | 24.14 | 0.01 |
| FeOt | 3.41 | 5.33 | 14.95 | 0.31 | 0.55 | 0.68 | 4.10 | 2.86 | 5.65 | 0.20 | 4.74 | 5.02 | 1.44 |
| MnO | 0.00 | 0.11 | 0.39 | 0.01 | 0.23 | 0.01 | 0.01 | 0.05 | 0.03 | _ | 0.14 | 0.01 | 0.01 |
| NiO | 0.00 | 0.03 | _ | _ | _ | _ | 0.00 | 0.02 | 0.13 | _ | _ | _ | _ |
| CaO | 25.77 | 0.22 | 33.65 | 59.96 | 35.18 | 31.75 | 0.49 | 25.49 | 1.04 | 36.01 | 24.58 | 0.01 | 39.71 |
| Na₂O | 0.16 | 0.21 | 0.08 | 0.11 | 0.23 | 7.24 | 1.77 | 0.18 | 0.08 | 11.72 | 0.48 | 1.18 | 0.32 |
| K₂O | 0.00 | 9.73 | 0.01 | 0.01 | 0.13 | 0.01 | 7.42 | 0.03 | 10.20 | 7.83 | 0.01 | 9.05 | 0.10 |
| P_2O_5 | 0.00 | 0.15 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 0.01 | 5.19 | 0.01 | 0.01 | 0.01 |
| SO3 | 0.07 | 0.00 | _ | _ | _ | _ | _ | 0.01 | 0.01 | 0.19 | _ | _ | _ |
| F | _ | _ | _ | _ | _ | _ | _ | 0.02 | 0.23 | 0.01 | _ | _ | _ |
| Total | 100.85 | 91.45 | 99.94 | 92.61 | 85.66 | 92.43 | 92.57 | 100.61 | 95.02 | 62.54 | 100.15 | 95.78 | 98.70 |

Table 7: Chemical compositions of daughter minerals of the inclusions in melilite

*Average composition of small tabular inclusions. (See the text for the details.)

The concentrations are mean values of several probe analyses in wt % oxides. Abbreviations for mineral names are listed in the Appendix.



Fig. 2. Inclusion in olivine from peridotite, the Kovdor complex. Back-scattered electron image and X-ray maps. Daughter minerals exposed on the surface are diopside, phlogopite, magnetite, shortite and nyerereite. The host crystallized on the walls and in the interstitials of daughter minerals is depleted in fayalite component.

primary inclusions. In clinopyroxene from both Gardiner and Kovdor the primary crystallized melt inclusions contain a variety of minerals (see Fig. 4) and the reader is referred to Tables 1, 2 and 6 for the assemblages. Only the main features will be described here.

In contrast to olivine and melilite, clinopyroxene is saturated in SiO_2 , and any SiO_2 -dependent phase equilibrium in the inclusions trapped by pyroxene would be buffered by the host. It is interesting to compare inclusions trapped by olivine and clinopyroxene from the same rock. Whereas in Gardiner peridotite (olivine–clinopyroxene rock) the mineral associations observed in both hosts are very similar (Table 1), the olivine- and clinopyroxenehosted inclusions from Kovdor peridotite show major differences (Table 2).

Clinopyroxene-hosted inclusions from the Kovdor peridotite contain monticellite and amphibole, but these are not found in inclusions trapped by coexisting olivine hosts. Na–Ca carbonates occur in olivine-hosted inclusions, but are not found in clinopyroxene. Another important observation valid for both Kovdor and Gardiner peridotite is that olivine is not present in the inclusions trapped by pyroxene, whereas clinopyroxene is stable and is a major phase in the inclusions trapped by the



Fig. 3. Inclusion in olivine from phoscorite, the Kovdor complex. Back-scattered electron image and X-ray maps. Daughter phases on the surface are dolomite, Na–Ca carbonates, eitelite, bradleyite and a zoned crystal of tetraferriphlogopite.

coexisting olivine host. It seems likely that olivine in the pyroxene-hosted inclusions is consumed to form mica and amphibole, in accordance with equilibria observed in rocks on a macroscopic scale (Nielsen *et al.*, 1997). The typical negative crystal shape of the inclusions in olivine may result from resorption of the host by the

| Rocks | Host mineral | Homogenization temperature (°C) |
|-----------------------------------|---|---------------------------------|
| Kovdor | | |
| Olivinite | olivine | 1220-1300 |
| Peridotite | clinopyroxene | 1170–1230 |
| Pyroxenite | clinopyroxene | 1130–1210 |
| Turjaite | melilite | 970–1080 |
| | clinopyroxene | 960-1060 |
| | nepheline | 950-1020 |
| ljolite | clinopyroxene | 980-1060 |
| | nepheline | 965-1020 |
| Calcite carbonatite, | clinopyroxene | 880-1020 |
| stage I* | nepheline | 860–920 |
| | apatite | 820-870 |
| Phoscorite, | olivine | 765–900 |
| stage II | apatite | 680–790 |
| Calcite carbonatite, | clinopyroxene | 790–870 |
| stage II | olivine | 740-820 |
| | apatite | 620–750 |
| Dolomite carbonatite stage III | apatite | 640–680 |
| Gardiner | | |
| Cpx-melilitolite | melilite | 950–1100 |
| | clinopyroxene | 1060-1090 |
| Melilitolite† | melilite (I) | 1060 |
| | melilite (II) | 1030-1060 |
| | melilite (III) | 900–1030 |
| Melilitolite† | melilite (I) melilite (II) melilite (III) | 1060 1030–1060 900–1030 |

Table 8: Homogenization temperatures
of
Kovdor and Gardiner melt inclusions
Gardin

*Stages according to Sokolov (1994).

†Types of the inclusions and homogenization temperatures according to Nielsen *et al.* (1997).

trapped melt, whereas daughter clinopyroxene in olivinehosted inclusions remains stable down to near-solidus temperatures.

The following reaction may account for the difference in daughter phase assemblages in the two hosts of Kovdor peridotite:

$$\begin{array}{rrr} Na_{2}CaMg_{5}Si_{8}O_{22}(OH)_{2} + CaMgSiO_{4} + 3CaCO_{3}. \quad (2)\\ richterite & monticellite & calcite \end{array}$$

With excess diopside in clinopyroxene-hosted inclusions nyerereite may be not stable and Na will reside in richterite associated with calcite.

Inclusions in melilite

Three types of crystallized melt inclusions are distinguished in Gardiner melilitolite (Nielsen *et al.*, 1997), and this is also observed in the Kovdor melilitolite. Large primary melt inclusions (30–100 μ m) contain silicate– carbonate solid phase assemblages interpreted as inclusions of melilitic melt. The inclusions are tabular and the daughter phases usually form elaborated intergrowths with the host. This suggests that the bulk melt composition was close to that of the host melilite and that the majority of daughter phases crystallized simultaneously with the host under near-eutectic conditions. Commonly, a significant interstitial volume in the inclusion is occupied by gas.

Two additional types of inclusions are not readily distinguished morphologically, but have different bulk compositions, and they represent coexisting immiscible, alkali carbonatite and natrocarbonatite melts (Table 7). The natrocarbonatite composition was suggested to have developed by degassing from an alkali- and CO_2 -rich brine (Nielsen *et al.*, 1997). These types usually occur in groups of small (<10 µm) tabular inclusions. The inclusions often contain minor, tiny magnetite grains together with Na–K–Ca carbonate and a P-bearing phase (apatite?).

In melilite from Kovdor olivine melilitolite, the larger inclusions (40–60 $\mu m)$ are composed of diopside, phlogopite, apatite and magnetite, and contain gas vesicles. No carbonate phase is observed in them. Diopside, calcite and akermanite (the main component of melilite solid solution) are related to each other by the decarbonation reaction

$$CaMgSi_2O_6 + CaCO_3 = Ca_2MgSi_2O_7 + CO_2$$
 (3)
diopside calcite akermanite fluid

which was studied experimentally by Walter (1965), Yoder (1973) and Zharikov *et al.* (1977). The reaction may account for the absence of daughter carbonate minerals and the presence of gas-filled vesicles in the larger crystallized melt inclusions from Kovdor olivine melilitolites. This requires, however, that clinopyroxene is in excess to calcite in the reaction (3). Stability of the right-hand assemblage is obviously favoured by the decrease in pressure that may result from crystallization within the inclusions.

Inclusions in perovskite

Perovskite from Gardiner melilitolite contains abundant primary crystallized melt inclusions. Dozens of inclusions have been studied, but melilite was never found as a daughter mineral. The daughter minerals include wollastonite, pectolite and hydrogrossular, which are the



Fig. 4. Inclusion in clinopyroxene from pyroxenite, the Gardiner complex. Back-scattered electron image and X-ray maps. Daughter minerals on the surface are Na–Ca carbonates, phlogopite, Na sulphate and scheelite (white grain in the BSE image and the Ca X-ray map).

typical products of low-temperature, fluid-present alteration of melilite. In addition, the inclusions contain clinopyroxene, nepheline, cancrinite and phlogopite (Table 1). Calcite and Na–Ca carbonate are present in minor amounts. Perovskite is a good host for homogenization experiments, because this refractory mineral is mechanically and chemically stable and allows rapid heating and cooling without decrepitation of the inclusions (Nielsen *et al.*, 1997). The disadvantage is its dark brown colour,

which makes optical control during homogenization runs impossible.

Inclusions in nepheline

Nepheline from Kovdor ijolite and early-stage nephelinebearing carbonatites contains small and rare primary crystallized melt inclusions. The main daughter phases of the inclusions from ijolite are phlogopite, cancrinite and clinopyroxene (Table 2).

Inclusions in apatite

Apatite crystals from carbonatites and related silicate rocks often contain numerous well-developed crystallized melt and fluid inclusions. The vast majority of studies of the inclusions in ultramafic alkaline rocks and carbonatites, including those of the Kovdor complex (Sokolov, 1994) were carried out in apatite (Rankin & Le Bas, 1974; Rankin, 1975, 1977; Aspden, 1980, 1981; Le Bas & Aspden, 1981; Andersen, 1986; Samson et al., 1995). The close association of contrasting fluid and crystallized melt inclusions is, however, poorly understood. Coexisting inclusions within the same apatite crystal may differ dramatically in the proportions of solid daughter minerals, aqueous solution and gas bubbles, possibly as the result of necking down, recrystallization and annealing of apatite to low temperature (Roedder, 1984). The inclusions range from essentially crystalline (60-80 vol. % of solids) to low-density gas and liquid-gas inclusions, and cover the entire range from melt to fluid inclusions. The former have a bulk composition (EMP analyses of quenched products of homogenization runs, in wt %) of 20-30 CaO, 12.5-14 Na₂O, 2.3-5.2 K₂O, $6-7\cdot 2$ MgO, $0\cdot 5-1\cdot 6$ SO₂, $4\cdot 5-9\cdot 5$ P₂O₅ and no detectable silica.

HOMOGENIZATION TEMPERATURES OF THE INCLUSIONS

The results of homogenization experiments for the Kovdor and Gardiner melt inclusions are summarized in Table 6. The table includes previously published results (Sokolov, 1983, 1994; Nielsen *et al.*, 1997) and new results of this study. The homogenization temperatures are in good agreement with the evolutionary trend deduced from field relations, liquidus parageneses and mineral compositions, as described by Nielsen (1980, 1981) and Romanchev & Sokolov (1979). The homogenization temperatures gradually decrease from olivinite or dunite, through peridotite, pyroxenite and ijolite, to melilitolites and carbonate-rich assemblages. The homogenization temperatures of the apatite-hosted inclusions in Table 8

were obtained from inclusions dominated by solids and interpreted as melt inclusions.

DISCUSSION

Carbonate-rich crystallized melt inclusions do not quench to homogeneous glasses in homogenization experiments, and the bulk compositions of the quenched run products cannot be determined by conventional microprobe techniques. Scanning EMP techniques and computer image analyses of the original crystallized inclusions may result in close approximations to the bulk compositions of the trapped melts. This is, however, beyond the scope of this study and we focus in this discussion on the qualitative information given by the crystallized melt inclusions. In combination with published experimental studies the inclusion parageneses constrain the fractional crystallization histories and the formation of carbonatite in the Gardiner and Kovdor complexes.

Parental melts and olivine-rich cumulates

The earliest cumulates of the Gardiner complex are dunites composed of olivine and chromite with minor interstitial amphibole, phlogopite and clinopyroxene (Nielsen, 1981). In Kovdor, the most olivine-rich cumulates are olivinites composed of olivine, phlogopite and magnetite. In both complexes the olivine-rich cumulates are followed by increasingly clinopyroxene-rich cumulates including peridotites. The similarity of the petrological development in the two complexes and the similarity between the melt inclusions in the early cumulates of Gardiner and Kovdor (Tables 1 and 2) suggest that the parental melts were comparable. However, a high Cr content in Gardiner dunites (Nielsen, 1981) and low Cr in Kovdor olivinites suggests that the former originated from a more primitive melt and that the earliest cumulates of Kovdor may not be exposed.

All inclusions in early cumulates of both complexes contain hydrous phases such as phlogopite and amphibole. Phlogopite is a primary magmatic phase in all studied inclusions and is not metasomatic (see above). Liquidus phlogopite, and probably also amphibole, breaks thermal barriers between non-larnite-normative and larnite-normative compositions of dry experimental systems (e.g. Yoder, 1986). The stability and fractionation of liquidus phlogopite thus leads to increase in CaO content of the liquid and the parental melanephelinite melts will evolve to larnite-normative (melilititic) compositions, as suggested by Nielsen (1994) and shown experimentally by Fedorchuk & Veksler (1997) and Veksler *et al.* (1998*a*). The crystallized inclusions in early liquidus olivine from both complexes contain calcite and Na–Ca carbonates. This indicates that the parental melt of both complexes was a CO_2 -bearing alkaline ultramafic melt, i.e. carbonated olivine melanephelinite. How much CO_2 was present in the parental melts is not known, and only 0.25% CO_2 was found in a fine-grained, larnitenormative melanephelinite from the Gardiner dyke swarms (MM 20385A; Nielsen, 1994). However, it is noteworthy that all the inclusions trapped in the succession of host minerals (Tables 1 and 2) contain progressively higher amounts of alkali-rich carbonates, which indicates that alkali-bearing *and only alkali-bearing* carbonatite melt can be a genuine product of the magmatic evolution in both complexes.

Pyroxenites, ijolites and melilitolites

In both complexes peridotite is followed by pyroxenite, melteigite and ijolite with increasing amounts of felspathoids. The melt evolution was characterized by increasing alkalis, CaO and volatiles (including CO_2), and decreasing SiO₂. The ijolite paragenesis (ne + cpx) is an important branching point in the evolution of the complexes because the ne + cpx association is related, through a number of reactions, to melilitolites and the residual melts may follow two alternative trends dependent on the stability of melilite solid solutions and calcite crystallization.

In the absence of CO_2 the reaction may be demonstrated by phase equilibria on the NaAlSiO₄– CaMgSi₂O₆ join at atmospheric pressure [Yoder (1973) and references therein], where melilite crystallizes as a reaction product:

$$3\text{CaMgSi}_{2}\text{O}_{6} + 2\text{NaAlSiO}_{4} = (4)$$

diopside nepheline
$$\text{Ca}_{2}\text{MgSi}_{2}\text{O}_{7} + \text{NaCaAlSi}_{2}\text{O}_{7} + \text{Mg}_{2}\text{SiO}_{4} + \text{NaAlSi}_{3}\text{O}_{8}.$$

melilite olivine albite

In CO_2 -bearing systems of ultramafic alkaline complexes, such as Kovdor and Gardiner, ijolites and melilitolites are related to each other by decarbonation reactions as expressed by equation (3) for diopside (see above) and by a similar reaction for nepheline:

$$NaAlSiO_{4} + CaCO_{3} + SiO_{2} = NaCaAlSi_{2}O_{7} + CO_{2}.$$
 (5)
nepheline calcite melt Na-melilite fluid

In effect, these reactions show that the same larnitenormative melilititic melt can crystallize as a carbonatebearing ijolite or as a melilitolite.

Stability of melilite and the formation of carbonatites

In the main body of the Kovdor complex progressively evolved ijolite contains increasing amounts of primary calcite in accordance with the absence of liquidus melilite [reactions (3) and (5)]. Continued fractionation results in the formation of clinopyroxene–nepheline calcite carbonatites, which further evolve (via fractionation of silicates and calcite) to forsterite–magnetite–apatite–phlogopite carbonatites with phoscorite cumulates and to dolomite carbonatites (Kukharenko *et al.*, 1965; Krasnova & Kopylova, 1988).

Melilite is a stable phase in evolved Gardiner ijolite, and ijolite is succeeded by melilitolites. The occurrence of coexisting inclusions of silicate (melilitite) and alkalibearing carbonatite melt in Gardiner melilite (Nielsen *et al.*, 1997) suggests that the melilitolite fractionation path led to the formation of carbonatitic melts by liquid immiscibility. Minor melilitolite occurs in Kovdor and, as in Gardiner melilitolite, Kovdor melilite host contains conjugate silicate and carbonatite melt inclusions. In no other rock types of both intrusions have we found minerals to trap coexisting silicate and carbonatite melts.

The difference between the two evolutionary trends can best be illustrated by phase relationships in simplified synthetic systems. Lee & Wyllie (1997, 1998) used synthetic systems to model crystallization of silicatecarbonate liquids in a wide range of magmatic compositions and they discussed the relationships between two important topological features: (1) the silicatecarbonate miscibility gap and (2) the silicate-carbonate liquidus field boundary. The crystallization sequences documented by homogenization temperatures (Table 8), the parageneses of the cumulates and the crystallized melt inclusions from Kovdor and Gardiner suggest that the silicate-carbonate liquidus field boundary does not intersect the two-liquid surface (e.g. in the Ne₉₀Ab₁₀- $CaCO_3$ join; Lee & Wyllie, 1997). When plotted on the Hamilton projection, the two-liquid field is surrounded by liquidus fields of silicates (Fig. 5a and b).

Melts in equilibrium with melilite solid solutions (e.g. Gardiner) would be expected to fractionate melilite and to evolve towards the miscibility gap (see Fig. 5a). At the two-liquid boundary immiscible carbonatite and silicate melts would form, as is also observed in the inclusions in melilite (Nielsen et al., 1997). The conjugate silicate and carbonatite liquids will continue to crystallize melilite and will evolve along the two-liquid field boundary until melilite reacts out and is replaced by clinopyroxene and nepheline. At this stage the silicate liquid may be consumed or be separated from the carbonatitic liquid. The carbonatitic melt may eventually reach the carbonate liquidus field boundary by fractional crystallization of silicates and oxides and evolve to an alkali-rich eutectic by fractionation of calcite (Lee & Wyllie, 1997). These experimental predictions are well illustrated by the crystallization sequence in the Gardiner melilitolite ring dyke (Nielsen, 1980).



Fig. 5. Two hypothetical trends of the late-stage melt evolution in ultramafic alkaline complexes presented in the Hamilton projection [general topology after Lee & Wyllie (1997) with modifications]. The star denotes the position of the evolved larnite-normative melt; its further evolution is shown by arrows. (a) Melilite is stable and the melt reaches the two-liquid field boundary. (b) Melilite is not stable and the melt evolves towards the calcite liquidus field. (See the text for details.)

If melilite is not stable (Fig. 5b) the crystallization paths may not intersect the two-liquid field, but reach the calcite liquidus field in response to fractionation of the ne + cpx (+ phl) mineral assemblage. Fractionation will continue along the silicate–carbonate field boundary towards the alkali-rich carbonatite eutectic. This is the trend from ijolites to calcite carbonatites observed in Kovdor (Table 8).

Phase equilibria in multi-component natural systems are much more complex and many factors including pressure, CO_2 and H_2O fugacities, and chemical characteristics of the melts [e.g. CaO/MgO, (Na₂O + K₂O)/Al₂O₃ and SiO₂ activity] can influence the stability of

mineral phases and the position of miscibility gap (Lee & Wyllie, 1998). Melilite is not stable at pressures above ~15 kbar (Yoder, 1973) and the melilitolite trend will develop only at middle- to upper-crustal conditions. In natural systems the reactions (3) and (5) may run at low partial pressures of CO_2 (Yoder, 1973) and the replacement of calcite-bearing ijolite by melilitolite could reflect subtle changes in P-T conditions, or bulk melt chemistry. Marginal chemical differences of CO_2 may explain the minor occurrences of melilitolite in Kovdor.

Carbonatites: calcite fractionation and separation of aqueous fluids

Carbonatitic melts, immiscible or residual, are rich in alkalis and evolve to progressively more alkali-rich compositions (Lee & Wyllie, 1997). This is supported by abundant Na-K-Ca and Na-Mg carbonate daughter minerals in forsterite-hosted inclusions from Kovdor carbonatites and phoscorites, and by alkali-rich carbonatitic inclusions in Gardiner melilite (Nielsen et al., 1997). Na-K-Ca and Na-Mg carbonates are extremely rare in the host rocks (Sokolov, 1979, 1981; Khomyakov et al., 1982), and carbonatite rocks in both intrusions are dominated by calcite (excluding late-stage, dolomite-rich carbonatite in Kovdor). The relationship between alkalirich carbonatitic melts and alkali-poor (calcitic and dolomitic) crystallization products has been discussed in many studies (e.g. Le Bas, 1981; Gittins, 1989; Lee & Wyllie, 1997) and the general consensus seems to be that calcite and dolomite carbonatite of ultramafic alkaline complexes represent cumulates of calcite (\pm dolomite). The melt was alkaline, but as suggested also by Nielsen et al. (1997), alkalis were lost from the cumulates to evolved carbonatite melt and/or to alkali-rich aqueous fluids responsible for the common phlogopitization and metasomatic alteration in carbonatite-bearing complexes.

Although the residual and immiscible carbonatitic melts have, as illustrated in Fig. 5a and b, a similar general trend to alkali-rich compositions, the crystallization products may differ in some important aspects. First, the Kovdor trend of the ne + cpx + phl fractionation [Fig. 5b and reaction (3)] appears to result in a higher proportion of calcite-rich cumulates, because calcite starts to crystallize earlier and from more Ca-rich liquids. Second, the residual carbonatitic melts may have higher MgO contents than immiscible ones (supported by abundant magnesium daughter phases in forsterite from Kovdor carbonatites) and thus have higher potential to produce dolomitic cumulates. Third, distribution coefficients for trace elements between coexisting immiscible silicate and carbonatite liquids (Hamilton et al., 1989; Jones et al., 1995; Veksler et al., 1998b) suggest that immiscible carbonatite melts are depleted in Zr, Nb and the other high field strength elements. By contrast, the residual carbonatites generated along the Kovdor trend will retain high concentrations of these trace elements and as a result have the potential to form economic deposits of pyrochlore, baddeleyite, etc. (Romanchev & Sokolov, 1979).

CONCLUSIONS

(1) The mineralogy of the inclusions confirms that the parental magmas of the complexes were silica-undersaturated volatile-rich melts, i.e. CO_2 -bearing melanephelinite.

(2) The broad occurrence of phlogopite and amphibole as daughter minerals in the inclusions and in the host rocks suggests a fractionation trend towards highly larnitenormative melilititic residuals, which accounts for the formation of late-stage melilitolite in both the Gardiner and the Kovdor complexes.

(3) Alkali-rich Na–K–Ca and Na–Mg carbonates are common daughter minerals. In late-stage crystallized melt inclusions they are more abundant than calcite and dolomite and show the high contents of alkalis in residual carbonatite melts.

(4) Carbonatite melt compositions can form by fractional crystallization (Kovdor), or by liquid immiscibility (Gardiner), depending on the stability of melilitite relative to the cpx-ne-cc assemblage.

(5) All potential carbonatite melts of Kovdor and Gardiner would be alkali bearing. Calcite carbonatites in both complexes are regarded as calcite cumulates formed by crystal fractionation parallel to the loss of alkalis to aqueous fluids.

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APPENDIX

Table A1: Abbreviations for mineral names used in the text and tables

| amph brad canc cc | amphibole bradleyite cancrinite calcite cebollite | mont mt ne nor | monticellite magnetite nepheline northupite |
|----------------------------|---|-------------------------|--|
| chr | chromite | nye | nyerereite |
| cpx cusp | clinopyroxene cuspidine | ol pec | olivine pectolite |
| dol eit | dolomite eitelite | phl prv | phlogopite perovskite |
| f-phl mel | tetraferriphlogopite melilite | sht | shortite |