

Ilímaussaq ‘en miniature’: closed-system fractionation in an agpaitic dyke rock from the Gardar Province, South Greenland (contribution to the mineralogy of Ilímaussaq no. 117)

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ABSTRACT

Based on petrography, mineral chemistry, and petrology, the physico-chemical evolution of an agpaitic dyke was found to be very similar to that of the neighbouring Ilímaussaq complex. Various mineral assemblages were used to reconstruct the crystallization conditions of the dyke rock for different stages during cooling. The early magmatic phenocryst assemblage is alkali feldspar + nepheline + augite + olivine + magnetite and indicates liquidus temperatures of ~850°C, silica activities of ~0.5, and oxygen fugacities of FMQ –1.5 to –3. The groundmass assemblage albite + microcline + nepheline + sodalite + arfvedsonite + aegirine + aenigmatite + astrophyllite indicates lower temperatures of between 600 and 450°C, at silica activities of 0.25, and oxygen fugacities around the FMQ buffer. Amphibole composition strongly responds to fluorite saturation and proves crystallization occurred in a system closed to oxygen. Late-stage hydrothermal conditions are indicated by the conversion of nepheline and sodalite to analcime and the growth of aegirine on arfvedsonite. These late-stage reactions are constrained to temperatures of <300°C, water activities of between 0.5 and unity, and oxygen fugacities above MH. The dyke has to be regarded as a small equivalent of the larger Ilímaussaq complex, in which identical differentiation processes proceeded at a scale very different in terms of magma volume and cooling times.

KEYWORDS: peralkaline, agpaitic, closed-system fractionation, Ilímaussaq, Greenland.

Introduction

BASED on their molar (Na+K)/Al ratio, alkaline igneous rocks are subdivided into peralkaline (>1.0) and agpaitic (>1.2) rocks (Ussing, 1912). The term agpaitic is restricted to nepheline syenites, which are additionally characterized by the occurrence of complex Zr- and Ti-silicate minerals, such as eudialyte (Sørensen, 1997). Based on the type of rare-metal silicates and accessory minerals present, a further subdivision into miaskitic, low agpaitic, medium agpaitic, highly agpaitic and hyperagpaitic rocks has been introduced by Khomyakov (1995).

Geochemically, agpaitic rocks are characterized by high contents of alkali metals, halogens,

and rare elements such as Li, Be, Rb, Ga, Zr, Zn, REE and by the presence of aegirine and sodium di-silicate in the norm (Sørensen, 1997). They have small contents of compatible elements like Mg, Ca, Cr, Sc, Co, Ni. Whole-rock and mineral ratios of Mg/Fe, Mg/Li, K/Na and Ca/(Na+K) approach zero, whereas others like Zr/Hf or Cl/Br increase to exceptionally high levels. Based on all these characteristics, agpaitic rocks represent the most differentiated plutonic rocks known.

The genesis of agpaitic rocks is generally explained by prolonged fractional crystallization of alkali basaltic or nephelinitic mantle-derived magmas (Larsen and Sørensen, 1987; Kramm and Kogarko, 1994; Stevenson *et al.*, 1997; Frisch and Abdel-Rahman, 1999). Contamination with crustal material during emplacement has been shown to play a significant role, mainly in the genesis of silica-oversaturated peralkaline rocks

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(Davies and Macdonald, 1987; Heaman and Machado, 1992; Harris, 1995; Mingram *et al.*, 2000; Schmitt *et al.*, 2000; Späth *et al.*, 2001; Marks *et al.*, 2003), whereas closed-system fractionation without significant contamination has been postulated for the evolution of the agpaitic Ilímaussaq intrusion (Markl *et al.*, 2001a,b).

Experimental results have demonstrated that agpaitic rocks have an unusually long crystallization interval, down to temperatures of <400°C (Piotrowski and Edgar, 1970; Sood and Edgar, 1970; Edgar and Parker, 1974; Kogarko and Romanchev, 1977, 1982; Scaillet and MacDonald, 2001). This long crystallization interval is mainly explained by the retention of volatiles and alkali metals in the melt by prohibiting their exsolution into a residual fluid phase. Therefore, a continuous transition from peralkaline volatile-rich silicate melts to hydrothermal Na-oversaturated solutions is assumed (Kogarko, 1974; Khomyakov, 1995; Sørensen, 1997). The late separation of a Na-rich fluid phase causes late- to post-magmatic alteration of the primary mineral assemblage (e.g. Salvi and Williams-Jones, 1990; Boily and Williams-Jones, 1994; Markl, 2001; Markl *et al.*, 2001a; Chakhmouradian and Mitchell, 2002; Markl and Baumgartner, 2002). At some localities, these residual fluids give rise to the formation of ore deposits of high economic potential (Sørensen, 1992).

The effects of retained and circulating fluids have been studied in some peralkaline intrusions of the alkaline Gardar Province of South Greenland (Parsons *et al.*, 1991; Finch *et al.*, 1995; Coulson, 1997; Markl, 2001; Markl *et al.*, 2001a; and Marks *et al.*, 2003). Probably the best-known and most extensively studied of these intrusions is the Ilímaussaq intrusion. Field geology, geochemistry, systematic mineralogy and the economic potential of the intrusion have been extensively discussed, and are reviewed in Sørensen (2001). Based on mineral chemistry and phase petrology it has been shown that the extreme fractionation trend found in the Ilímaussaq complex is governed by low water activity, low SiO₂ activity, low oxygen fugacity and a principally closed-system evolution (Larsen, 1976, 1977, 1981; Markl *et al.*, 2001a,b; Marks and Markl, 2001).

The agpaitic dyke rock, which is the focus of this work, was first described by Allaart (1969). It was found to be the youngest member of a dyke

swarm southeast of the Ilímaussaq intrusion. Based on petrographic similarities to some of the layered nepheline syenites (kakortokites) of the Ilímaussaq complex, he termed the dyke a micro-kakortokite (MiKa) and proposed it to represent a hypabyssal extension of the main Ilímaussaq kakortokites. We will show that this hypothesis is not in full agreement with our detailed petrographic and isotopic data. Larsen and Steenfelt (1974) presented some mineral and whole-rock geochemical data on the dyke, based on which, they also concluded that the dyke formed from the Ilímaussaq magmas. Furthermore they suggested that high temperatures in the country rocks due to the vicinity of the Ilímaussaq intrusion, led to a loss of alkalis, water and halogens, in some parts of the dyke. The present study investigates the fractionation mechanisms in this volumetrically small dyke as compared to its larger neighbour (the Ilímaussaq magma chamber) and tries to delimit the time of separation of the two.

Geology

South Greenland is characterized by extensive mid-Proterozoic rift-related alkaline magmatism (e.g. Upton *et al.*, 2003). Interlayered lavas and sedimentary rocks (Eriksfjord Formation; Poulsen, 1964), numerous dyke rocks of variable composition, and about ten alkaline plutonic centres intruded the Ketilidian basement, which consists of Early-Proterozoic granites and gneisses (Emeleus and Upton, 1976). It is believed that magmatism during the Gardar Period (1.30 to 1.12 Ga) involved three principal cycles of activity (Early, Mid and Late; Upton and Blundell, 1978). Each extensional phase commenced with the uprise of olivine basaltic to hawaiitic magmas and terminated with the emplacement of highly fractionated alkaline plutonic centres (Upton and Blundell, 1978).

During the late-Gardar period (~1.20–1.12 Ga), two WSW–ENE to SW–NE trending dyke swarms intruded in two main areas, which are separated by a zone in which Gardar-aged dykes are rare (Upton and Emeléus, 1987). The southerly swarm, of which the micro-kakortokite is a part, occurs on the Tugtutôq islands and the Narsaq peninsula and can be traced northeastwards to Mellemlandet and the G.F. Holm Nunataq, where it disappears under the ice cover. The dyke compositions of the swarm range from primitive olivine basalt through

hawaiitic and benmoreitic to phonolitic, trachytic and alkali rhyolitic compositions. Lamprophyres and carbonatitic dykes are less abundant (e.g. Scharbert, 1967; Allaart, 1969; Macdonald, 1966; Upton and Fitton, 1985). Some basaltic dykes of the swarm ("Big Feldspar Dykes") contain plagioclase megacrysts, which are interpreted to stem from anorthosite xenoliths (Bridgwater, 1967; Bridgwater and Harry, 1968; Watt, 1968; Halama *et al.*, 2002). The dykes are remarkable in their size and lateral extension: widths of 5–20 m are common and many of them can be traced over several tens of kilometres. The plutonic complexes of Tugtutoq, Ilímaussaq and Igaliko are situated within this dyke swarm, which is >100 km long and has a track ~15 km wide. Fluid inclusion data from the Ilímaussaq complex (Konnerup-Madsen and Rose Hansen, 1984; Markl *et al.*, 2001a), and estimates of the overburden sedimentary rocks and lavas (Poulsen, 1964) indicate that the plutonic complexes, and by analogy the dykes, intruded at a high crustal level (3–5 km) and probably had surface expression (Emeleus and Upton, 1976; Upton *et al.*, 2003).

Field observations and petrography

The MiKa dyke has a total length of ~18 km and a variable width of between 10 and 30 m. The contacts with the basement granite are always sharp. Towards its western termination, it appears to cut the marginal augite syenite of the Ilímaussaq intrusion (Larsen and Steenfelt, 1974). However, at outcrop evidence, is inconclusive as to whether there is a connection between the dyke sections on either side of the intrusion. (Fig. 1). On the basis of petrography and whole-rock geochemistry, Larsen and Steenfelt (1974) distinguished two different facies of the dyke: a high-alkali facies and a low-alkali facies, the latter being explained by loss of alkalis, water and halogens, which they attributed to the thermal effect of the Ilímaussaq intrusion. The low-alkali facies of the dyke is restricted to its westernmost part, in the vicinity of the Ilímaussaq intrusion, and will not be discussed further here. All samples of this study are taken from the high-alkali facies and sample localities are shown in Fig. 1. At each locality, a sampling profile from the margin towards the centre of the dyke (e.g. approximately

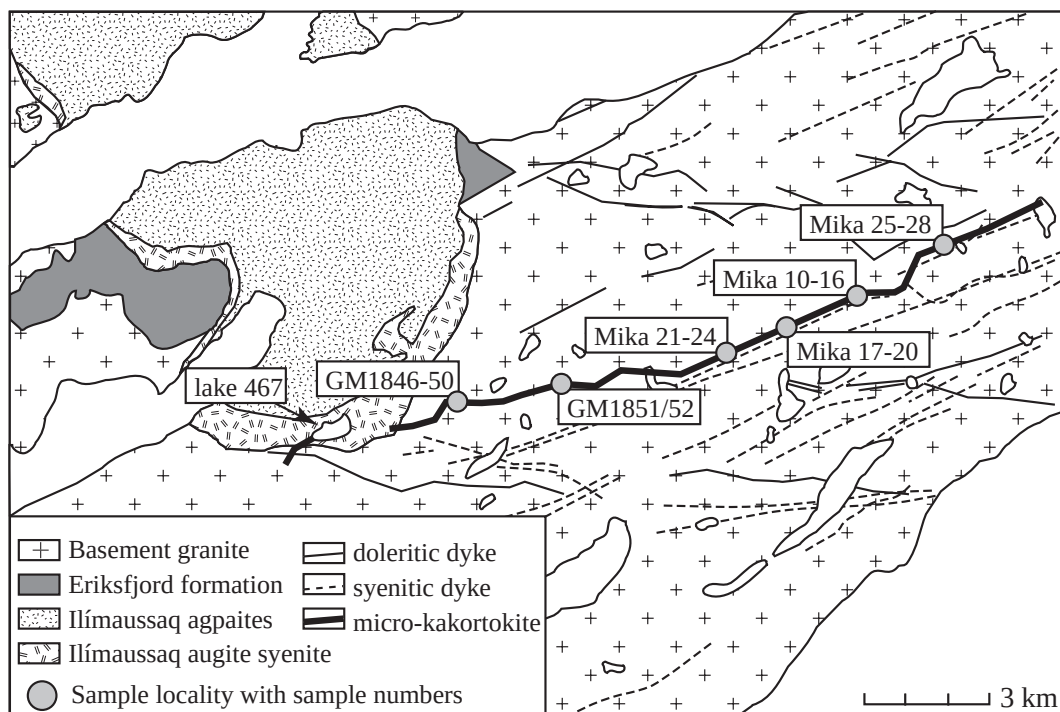


FIG. 1. Sketch map of part of the Igaliko Peninsula showing the apgaitic Ilímaussaq intrusion and the investigated micro-kakortokite dyke (MiKa) with sample localities indicated. Map is redrawn from Larsen and Steenfelt (1974)

parallel to the assumed direction of crystallization) was collected. Most samples were taken from approximately the same stratigraphic height of between 600 and 800 m above sea level. The dyke rock is dark green to dark grey and cm-scale feldspar and nepheline phenocrysts, in a fine-grained matrix (Fig. 2a), are abundant throughout. The feldspar phenocrysts are aligned parallel to the contacts of the dyke. At some localities, the dyke is marginally 'chilled' with no phenocrysts in the outer 15–30 cm. Some samples contain additional phenocrysts of olivine, augite and magnetite up to some mm in size. The major groundmass minerals are albite, microcline, nepheline, sodalite, aegirine, arfvedsonite and aenigmatite. Minor and accessory minerals are eudialyte, astrophyllite, zircon, hjordahlite, monazite, titanite, apatite, fluorite and various sulphides. Late-stage or secondary minerals include analcime, natrolite and Fe-hydroxides. Table 1 shows the mineral abbreviations used in the text and figures; Table 2 summarizes the mineral assemblages found in the samples studied.

Feldspar phenocrysts are cryptoperthitic alkali feldspar (Fig. 2b). In one sample from the margin of the dyke (GM1846), μm -sized Ba-rich patches occur within one perthitic feldspar phenocryst (Fig. 2c,d). Groundmass feldspars are discrete

grains of albite and microcline. In some samples, microcline forms small euhedral laths and albite occurs as anhedral grains (Fig. 2e). In other samples, the opposite is the case. Albite is partly altered to analcime.

Nepheline phenocrysts are present in most samples (Fig. 2a). In some samples, nepheline is found as euhedral to subhedral inclusions in feldspar phenocrysts (Fig. 2b). These crystals have slightly corroded margins and are associated with aegirine aggregates occurring at the margins of the nepheline. In the groundmass, small nepheline crystals are rarely euhedral but mostly subhedral, interstitial grains (Fig. 2f), which are partly altered to analcime.

Sodalite forms anhedral crystals in the groundmass. In some places, euhedral microcline laths occur as inclusions in sodalite (Fig. 2e). At the rims, along cracks and, locally, at the contact with microcline, sodalite has been replaced by analcime.

Olivine phenocrysts are in most cases rimmed by arfvedsonite or aegirine (Fig. 3a). In samples GM1846–GM1852, olivine is replaced by orange to red Fe hydroxides ('iddingsite'), whereas in most other samples, relics of olivine are still present. Rarely, olivine was found as an inclusion in alkali feldspar phenocrysts.

TABLE 1. Mineral abbreviations used in text, figures, and tables.

Abbreviation	Mineral	Abbreviation	Mineral
Ab	albite	Jd	jadeite
Aeg	aegirine	Ks	kalsilite
Aen	aenigmatite	La	larnite
Alkfsp	alkali feldspar	Mt	magnetite
Am	amphibole	Mz	monazite
An	anorthite	Ne	nepheline
Anl	analcime	Ntr	natrolite
Ap	apatite	Ol	olivine
Arf	arfvedsonite	Or	K-feldspar
Astr	astrophyllite	Qtz	quartz
Aug	augite	Rh�	rh�nite
Cs	celsian	Sod	sodalite
Di	diopside	Sp	spinel
Eud	eudialyte	Sph	sphalerite
Fa	fayalite	Tit	titanite
Fl	fluorite	Tp	tephroite
Fo	forsterite	Usp	ulv�spinel
Hed	hedenbergite	Wilk	wilkinsonite
Hj	hjordahlite	Zrn	zircon

TABLE 2. Mineral assemblages in micro-kakortokite dyke rock samples.

Sample	Approximate distance from dyke margin	Phenocrystals	Major groundmass minerals	Accessories	Secondary minerals
GM 1846	0.1 m	Alkfsp	Ab, Or, Ne, Sod, Aeg	Eud, Fl, Astr, Hj, Ap, Sp, FeS	Anl, Ntr
GM 1847	1.0 m	–	Ab, Or, Ne, Sod, Aeg, Aen, Arf	Eud, Fl, Astr, Hj, Ap, FeS	Anl, Ntr
GM 1848	4.5 m	Alkfsp, Ne	Ab, Or, Ne, Sod, Aeg, Aen, Arf	Eud, Fl, Astr, Ap, FeS, Tit	Anl, Ntr
GM 1849	7.5 m	Alkfsp, Ne, Hed	Ab, Or, Ne, Sod, eg, Aen, Arf	Eud, Fl, Astr, FeS, Tit	Anl, Ntr, FeOOH _x
GM 1850	0.2 m	–	Ab, Or, Ne, Sod, Aeg, Aen, Arf	Eud, Fl, Astr, Sp, FeS, Tit	Anl
GM 1851	0.1 m	Alkfsp, Ne	Ab, Or, Mt, Aeg, Arf	Fl, Ap, Sp, Zrn, Mz	Anl, FeOOH _x
GM 1852	6.5 m	Akfsp, Ne, Hed, Mt	Ab, Or, Ne, Sod, Aeg, Aen	Astr, Hj, Ap, Sp, FeS, Zrn, Mz	Anl, FeOOH _x
Mika 13	1.5 m	Alkfsp, Ne, Hed, Ol, Mt	Ab, Or, Ne, Sod, Aeg, Aen, Arf	Fl, Ap, Sp, FeS, Zrn, Mz	Anl, FeOOH _x
Mika 14	5.5 m	Alkfsp, Ne, Hed, Ol, Mt	Ab, Or, Ne, Sod, Aeg, Aen, Arf	Fl, Ap, Sp, FeS, Zrn, Mz	Anl, FeOOH _x
Mika 24	8.0 m	Alkfsp, Ne, Hed, Ol, Mt	Ab, Or, Ne, Sod, Aeg, Aen, Arf	Fl, Ap, Sp, FeS, Zrn, Mz	Anl, FeOOH _x
Mika 28	4.0 m	Alkfsp, Ne, Hed, Ol, Mt	Ab, Or, Ne, Sod, Aeg, Aen, Arf	Fl, Ap, Sp, FeS, Zrn, Mz	Anl, FeOOH _x

Magnetite occurs as anhedral inclusions in augite (Fig. 3a) or as subhedral to anhedral phenocrysts rimmed by arfvedsonite, astrophyllite, aegirine, aenigmatite or an intergrowth of these phases (Fig. 3b).

Augite forms subhedral phenocrysts, which are commonly associated with olivine and magnetite (Fig. 3a). It is strongly zoned with colourless to grey cores and grass green poikilitic aegirine-rich rims. Along cracks, augite has typically been converted to aegirine (Fig. 3c).

Aegirine, arfvedsonite and aenigmatite occur as mafic groundmass minerals in different modal proportions. Texturally, they are clearly later than olivine, augite and magnetite. Samples from the margin of the dyke are dominated by aegirine. Towards the centre of the dyke, the modal contents of arfvedsonite and aenigmatite increase (Fig. 3d). In most samples, aegirine, arfvedsonite, and aenigmatite appear to coexist (Fig. 3e). However, each can be observed to overgrow or replace the others, often within the same sample (Fig. 3f). Where arfvedsonite is replaced by aegirine, secondary fluorite and Fe-hydroxides occur. Additional interstitial (i.e. magmatic)

fluorite occurs only in samples GM1846–GM1851. Eudialyte occurs as an interstitial groundmass phase; more rarely it is included in aegirine. Hjordahlite, zircon, apatite, titanite, monazite and various sulphides occur as inclusions in groundmass feldspar, aegirine, amphibole and aenigmatite.

Mineral chemistry

Analytical methods

Some mineral data have been presented by [Larsen and Steenfelt \(1974\)](#). Here we augment these analyses with detailed microprobe data on a variety of mineral phases from the dyke.

Electron microprobe measurements of minerals were performed using a JEOL 8900 electron microprobe at the Institut für Geowissenschaften at the Universität Tübingen, Germany. The emission current was 15 nA and acceleration voltage, 15 kV. Peak counting times were 16 s for major and 30–60 s for minor elements. Background counting times were half of the peak counting times. Natural (albite, baryte, sanidine, diopside, hematite, rhodochrosite,

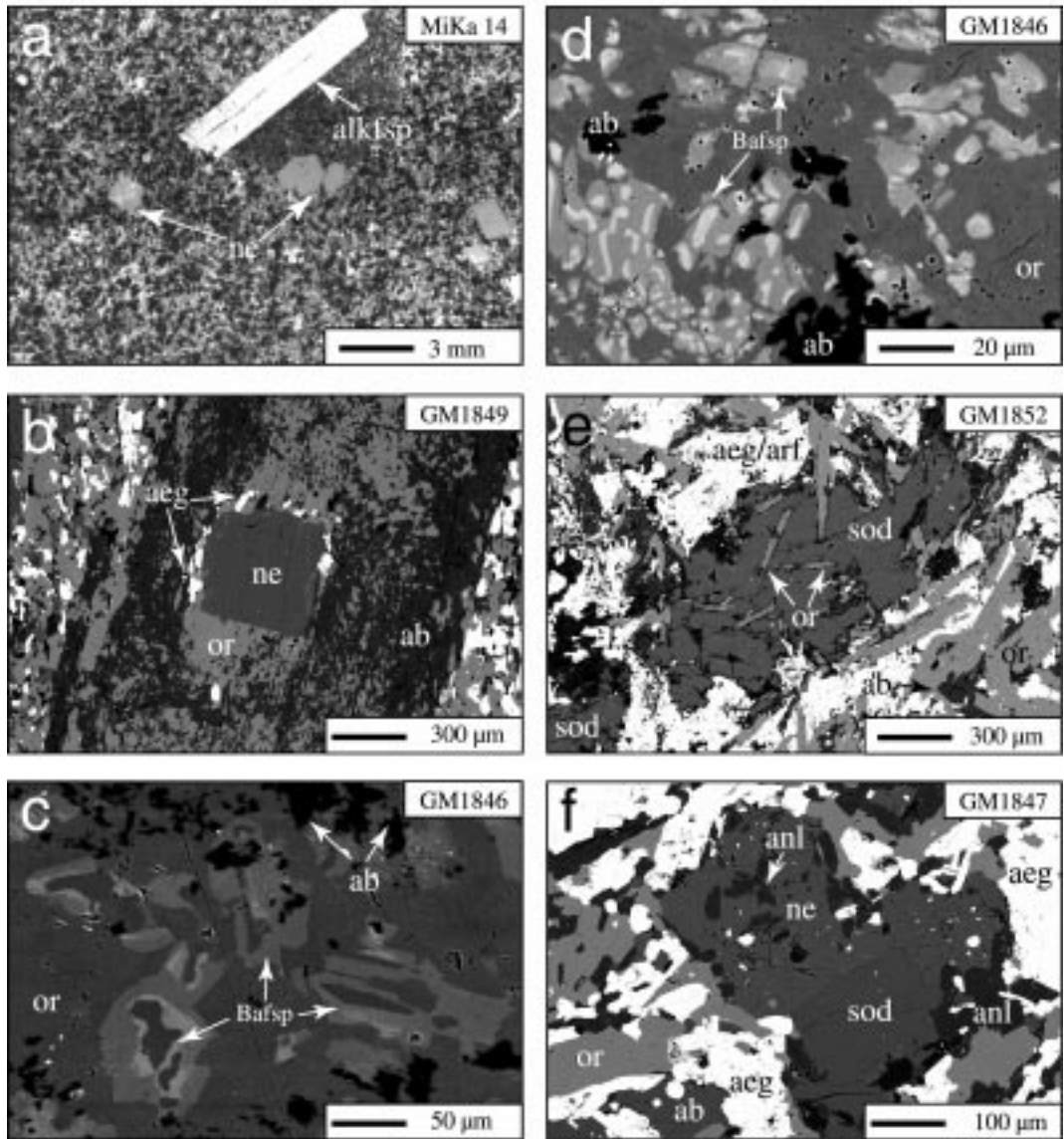


FIG. 2. Photomicrograph (plane-polarized light) and back-scattered electron (BSE) images of textures among the felsic minerals. (a) Photomicrograph of sample MiKa 14 with phenocrysts of alkali feldspar and nepheline in a fine-grained groundmass. (b) Euhedral inclusion of nepheline in an alkali feldspar phenocryst. Note the small aegirine crystals aligned along the margin of nepheline. (c and d) BSE images of Ba-rich areas in an alkali feldspar phenocryst of sample GM1846. (e) Euhedral laths of microcline partly as inclusions in anhedral sodalite. (f) Nepheline and sodalite partly replaced by later analcime.

fluorite, tugtupite) and synthetic (SrTiO_3 , MgO , Al_2O_3 , Zr) standards were used for calibration. To avoid Na migration under the electron beam, feldspar, nepheline, analcime and sodalite were analysed using a defocused beam of 15 μm

diameter. The peak overlap between the Fe- $L\beta$ and F- $K\alpha$ lines and the Ba- $L\alpha_{1(3)}$ and Al- $K\alpha$ lines has been corrected. Data reduction was performed using internal $\phi\rho Z$ procedures of JEOL (Armstrong, 1991).

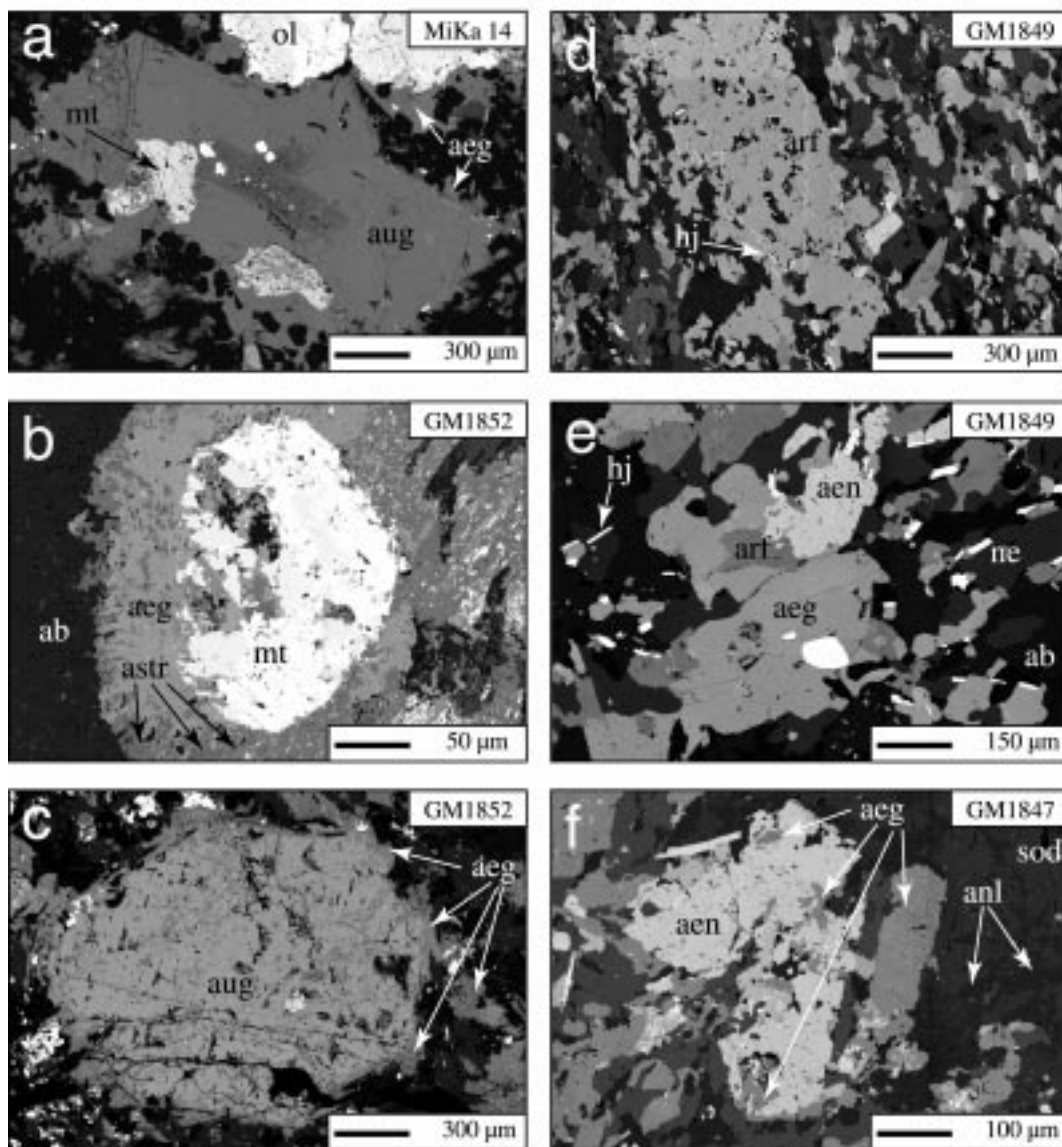


FIG. 3. BSE images of textures among the mafic minerals. (a) Augite phenocryst with Mg-rich core, inclusions of magnetite and associated olivine, which is rimmed by aegirine. (b) Primary magnetite rimmed by aegirine and astrophyllite. (c) Augite phenocryst with poikilitic margins consisting of aegirine-rich pyroxene. Along cracks, augite is converted to aegirine as well. (d) Aggregate of arfvedsonite with small inclusions of euhedral hjordahlite. (e) Stable mafic groundmass assemblage of aegirine, arfvedsonite and aenigmatite. (f) Aenigmatite partly rimmed and resorbed by aegirine.

Bulk compositions of perthitic feldspars were recalculated by combining image processing (NIH Image software) of BSE images of the perthitic minerals with point analyses of the exsolved phases

(see Marks and Markl, 2001, for a detailed description of the technique). Bulk feldspar compositions in each sample were calculated from the average of 3 to 5 different reintegrated grains.

Feldspar

Euhedral alkali feldspar phenocrysts in sample GM1846 are exsolved into pure albite and K-feldspar. One phenocryst contains small Ba-rich areas within the exsolved K-feldspar phase (Fig. 2*c,d*). In this phenocryst, the exsolved K-feldspar varies in composition between $\text{Or}_{93}\text{Ab}_7$ and $\text{Or}_{99}\text{Ab}_1$, and the exsolved albite phase has almost end-member composition ($\text{Ab}_{98}\text{Or}_2\text{—Ab}_{100}$). Both phases are essentially Ba- and Ca-free (<0.05 wt.% BaO and CaO, respectively). Among the two Ba-bearing feldspar phases, which show sharp borderlines against each other, two compositional ranges occur: $\text{Ab}_{20}\text{Or}_{96}\text{Cs}_2\text{—Ab}_{10}\text{Or}_{85}\text{Cs}_5$ and $\text{Ab}_{10}\text{Or}_{70}\text{Cs}_{20}\text{—Ab}_9\text{Or}_{49}\text{Cs}_{42}$. Tiny grains of extremely celsian-rich feldspar have compositions of about $\text{Ab}_{10}\text{Or}_{17}\text{Cs}_{73}$ (Fig. 4).

The recalculated magmatic composition of feldspar in all other samples varies between $\text{Ab}_{41}\text{Or}_{59}$ and $\text{Ab}_{60}\text{Or}_{40}$ and is invariably Ca-free (Fig. 4). Ba contents are <0.1 wt.%. The feldspar in the groundmass consists of separate grains of end-member albite and end-member microcline with no measurable amounts of Ca and Ba. The Sr contents in all types of feldspar reach ~ 0.6 wt.% SrO, but show no systematic behaviour with any of the other elements. Representative analyses are shown in Table 3.

Nepheline

Nepheline phenocrysts show a wide range of compositions between $\text{Ne}_{67}\text{Ks}_{12}\text{Qtz}_{21}$ and $\text{Ne}_{75}\text{Ks}_{21}\text{Qtz}_4$. Some phenocrysts are chemically zoned with increasing Ks component and

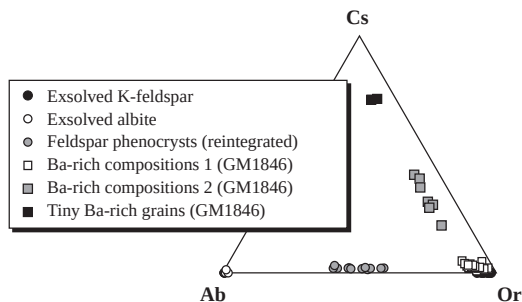


FIG. 4. Feldspar compositions observed in MiKa samples in the ternary system Ab-Or-Cs. Ba-rich compositions only occur in alkali feldspar phenocryst of sample GM1846.

decreasing Qtz component towards the rim. The composition of groundmass nepheline overlaps with that of phenocrysts but shows a clear tendency to more Ks-rich and Qtz-poor compositions (Fig. 5, Table 4). CaO is <0.5 wt.% in all cases.

Sodalite

Sodalite approaches an end-member composition, with SO_3 contents of <1.5 wt.% (Table 5). In some chemically zoned crystals, SO_3 contents decrease from core to rim.

Olivine

Olivine ranges in composition from $\text{Fo}_{12}\text{Fa}_{81}\text{Tp}_5\text{La}_2$ to $\text{Fo}_1\text{Fa}_{92}\text{Tp}_6\text{La}_1$ (Table 6). It is not zoned and there is only a small

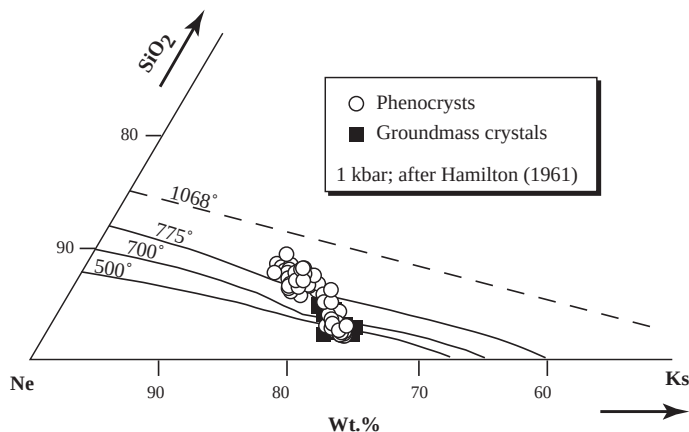


FIG. 5. Ne-Ks- SiO_2 triangle (wt.%) showing the compositions of nepheline phenocrysts and groundmass nepheline. Isotherms are after Hamilton (1961).

TABLE 3. Representative microprobe analyses and reintegrated compositions (reint.) of feldspar.

Sample	GM1846 ab	GM1846 ab	GM1846 or	GM1846 or	GM1846 Ba-Fsp 1	GM1846 Ba-Fsp 1	GM1846 Ba-Fsp 2	GM1846 Cs	GM1848 (reint.)	MiKa 14 (reint.)
Wt.%										
SiO ₂	64.14	64.25	68.04	68.79	64.04	62.50	57.38	38.32	65.98	66.64
Al ₂ O ₃	18.22	18.02	19.55	19.19	18.66	18.96	20.69	25.41	18.75	19.11
FeO	0.13	0.15	0.00	0.01	0.02	0.03	0.00	0.00	0.05	0.02
MnO	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MgO	0.00	0.00	0.01	0.00	0.00	0.01	0.01	0.00	0.00	0.01
BaO	0.02	0.00	0.05	0.00	0.94	2.53	10.44	32.48	0.02	0.01
SrO	0.17	0.15	0.15	0.13	0.15	0.17	0.14	0.27	0.09	0.10
CaO	0.00	0.00	0.00	0.00	0.01	0.13	0.00	0.01	0.00	0.00
Na ₂ O	0.33	0.62	11.53	11.57	0.27	0.31	1.01	0.82	5.12	6.73
K ₂ O	16.08	16.34	0.14	0.09	15.73	15.20	10.88	2.43	9.07	6.85
Total	99.09	99.54	99.47	99.79	99.81	99.84	100.53	99.73	99.98	99.47
Formulae based on 8 oxygens										
Si	3.00	3.00	2.99	3.01	2.98	2.95	2.81	2.24	3.00	2.99
Al	1.00	0.99	1.01	0.99	1.02	1.05	1.19	1.75	1.00	1.01
Mg	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Fe	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Mn	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ba	0.00	0.00	0.00	0.00	0.02	0.05	0.20	0.75	0.00	0.00
Sr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.00	0.00	0.00
Na	0.03	0.06	0.98	0.98	0.02	0.03	0.10	0.09	0.46	0.59
K	0.96	0.97	0.01	0.01	0.93	0.91	0.68	0.18	0.54	0.39
Sum	5.00	5.02	5.00	4.99	4.98	5.00	4.98	5.02	5.00	4.99
Ab	3.0	5.4	99.1	99.5	2.5	2.9	9.8	9.1	46.2	60.0
Or	96.9	94.6	0.8	0.5	95.7	92.4	69.7	17.8	53.8	40.0
Cs	0.0	0.0	0.1	0.0	1.7	4.7	20.5	73.1	0.0	0.0

compositional range within one specific sample. Mn reaches up to 4.2 wt.% MnO and is positively correlated with Fe content (Fig. 6). CaO varies between 0.6 and 1.6 wt.% and is positively correlated with Fe. An exception is sample MiKa 28, which displays a low Ca content (Fig. 6).

Clinopyroxene

Clinopyroxene phenocrysts range in composition between $\text{Aeg}_9\text{Jd}_0\text{Di}_{35}\text{Hed}_{56}$ and $\text{Aeg}_{82}\text{Jd}_{12}\text{Di}_0\text{Hed}_6$ (Fig. 7, Table 7). They have Ca-rich cores ($\text{Aeg}_9\text{Jd}_0\text{Di}_{35}\text{Hed}_{56}$ to $\text{Aeg}_{14}\text{Jd}_6\text{Di}_7\text{Hed}_{73}$), but show a strong Na-enrichment at the rim of and along cracks within the mineral grains. The compositional range found by Larsen and Steenfelt (1974) displays more Mg-rich compositions of

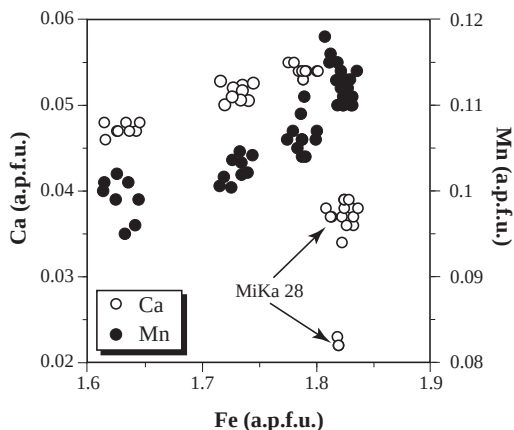


FIG. 6. Correlation diagram of Ca and Mn with Fe content. Both show a positive correlation, except for Ca in sample MiKa 28.

TABLE 4. Representative microprobe analyses of nepheline.

Sample	GM1848 phenocryst	GM1852 phenocryst	GM1847 phenocryst	GM1849 groundmass	GM1849 groundmass
Wt. %					
SiO ₂	42.79	45.68	43.91	45.46	43.32
Al ₂ O ₃	33.15	31.90	32.51	32.26	33.32
FeO	0.38	0.54	0.59	0.62	0.50
MnO	0.00	0.02	0.03	0.01	0.00
MgO	0.00	0.02	0.00	0.00	0.00
CaO	0.00	0.01	0.00	0.01	0.00
Na ₂ O	15.81	16.12	16.02	16.54	16.85
K ₂ O	7.17	5.25	6.46	5.07	6.35
Total	99.30	99.54	99.51	99.97	100.34
Formulae based on 32 oxygens					
Si	8.32	8.73	8.48	8.66	8.32
Al	7.60	7.18	7.40	7.24	7.54
Mg	0.00	0.00	0.00	0.00	0.00
Fe	0.06	0.09	0.09	0.10	0.08
Mn	0.00	0.00	0.00	0.00	0.00
Ca	0.00	0.00	0.00	0.00	0.00
Na	5.96	5.97	6.00	6.11	6.28
K	1.78	1.28	1.59	1.23	1.56
Sum	23.72	23.26	23.57	23.34	23.78

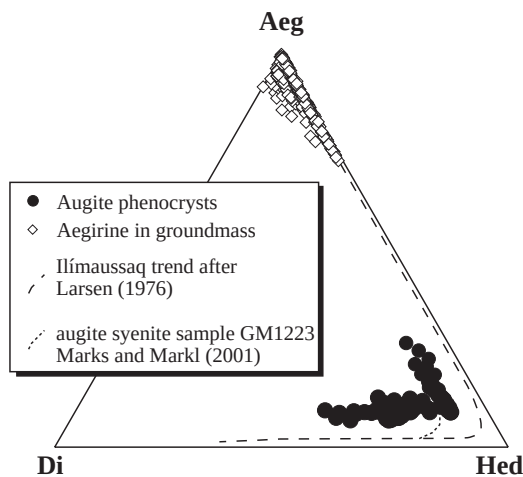


FIG. 7. Clinopyroxene compositional trend in the investigated samples plotted in the ternary system diopside (Di), hedenbergite (Hed) and aegirine (Aeg). Published trends for the Ilímaussaq intrusions are shown for comparison (from Larsen, 1976; Marks and Markl, 2001).

Aeg₆Di₄₈Hed₄₆. Figure 8a shows zoning profiles from the core to the rim of a phenocryst, illustrated in Fig. 3a. Fe³⁺ contents are calculated based on stoichiometry (4 cations and 6 oxygens). After a smooth enrichment of Na and Fe³⁺ towards the rim of the crystal, a sudden increase of Na, Fe³⁺ and ^{VI}Al at the outermost rim can be detected, whereas Ca, Fe²⁺, Mg, ^{IV}Al, Mn, Ti and Zr decrease. At the rim, Na contents exceed Fe³⁺. This indicates the presence of significant amounts of the jadeite molecule (up to 12 mol.%), in addition to aegirine.

In rare cases, hedenbergite phenocrysts with older and partially rounded cores (Fig. 2c) show strong enrichment of Fe²⁺ and Mn and depletion of Mg in the core region (Fig. 8b). Ti and ^{IV}Al are relatively high, whereas ^{VI}Al is low. Ca, Na, Fe³⁺ and Zr are rather constant and have concentrations comparable to the normal phenocrysts.

The groundmass pyroxene in all samples is aegirine with a compositional range of between Aeg₇₃Jd₀Di₂Hed₂₅ and Aeg₈₈Jd₁₂Di₀Hed₀ (Fig. 7, Table 7). Aegirine is essentially unzoned. The most important minor element is Al reaching 3.2 wt.%, resulting in a jadeite component of up to 12 mol.%. In many cases, Na content exceeds

TABLE 5. Representative microprobe analyses of sodalite.

Sample	GM1852	GM1850	GM1849	GM1847	GM1849
Wt.%					
SiO ₂	38.24	37.43	37.80	37.23	37.58
Al ₂ O ₃	30.67	30.61	30.49	30.37	30.54
FeO	0.08	0.21	0.21	0.15	0.18
MnO	0.06	0.00	0.00	0.00	0.24
MgO	0.00	0.00	0.00	0.01	0.00
CaO	0.03	0.07	0.00	0.00	0.02
Na ₂ O	23.52	24.06	23.57	24.69	23.77
K ₂ O	0.03	0.06	0.03	0.03	0.03
SO ₃	0.33	0.61	0.90	1.05	1.07
Cl	6.87	6.98	6.74	6.53	6.67
Total	99.83	100.03	99.74	100.06	100.10
Formulae based on 25 oxygens					
Si	6.19	6.08	6.11	6.02	6.06
Al	5.85	5.86	5.81	5.79	5.80
Fe	0.01	0.03	0.03	0.02	0.02
Mg	0.00	0.00	0.00	0.00	0.00
Mn	0.01	0.00	0.00	0.00	0.03
Ca	0.01	0.01	0.00	0.00	0.00
Na	7.38	7.58	7.39	7.74	7.43
K	0.01	0.01	0.01	0.01	0.01
SO ₃	0.04	0.07	0.11	0.13	0.13
Cl	1.88	1.92	1.85	1.79	1.82
Sum	21.28	21.56	21.31	21.50	21.30

total Fe³⁺ and ^{VI}Al. This indicates the presence of other Na-bearing components such as NaTiAlSiO₆ as proposed by Larsen (1976) for the Ilímaussaq pyroxenes. The CaO content is negatively correlated with aegirine component. CaO is low in samples from the outer parts of the dyke (<2 wt.%), but relatively high (up to 8 wt.%) in samples from central parts. TiO₂, MnO and ZrO₂ are <1.6 wt.%, 0.6 wt.% and 0.2 wt.%, respectively, with the highest Ti and Zr and the lowest Mn contents in aegirine of marginal samples.

Fe-Ti oxides

Magnetite ranges in composition between Mt₄₀Usp₅₇Sp₃ and Mt₂₁Usp₇₈Sp₁. Despite the Ti-rich composition, no signs of later oxy-exsolution have been observed. MgO contents are <0.1 wt.% and ZnO contents <0.6 wt.%. Al₂O₃ reaches ~2 wt.% and MnO ~5.5 wt.%. Representative analyses are shown in Table 8.

Amphibole

Amphibole in all samples is arfvedsonite with $X_{\text{Fe}}(\text{Fe}^{2+}/(\text{Mg} + \text{Fe}^{2+}))$ of between 0.96 and 0.99. Some typical analyses are reported in Table 9. Fe³⁺ contents are calculated based on stoichiometry (16 cations and 23 oxygens). On the basis of F and Ca content, two groups of amphiboles can be distinguished. Group 1 is F- and Ca-rich and comes from the eastern samples MiKa 13, 14, 24 and 28; group 2 is Ca- and F-poor from samples the western samples GM1847–GM1851, which were collected close to the Ilímaussaq intrusion (Figs 1 and 9a). In group 1 amphiboles, F reaches up to 2.2 wt.%. In group 2 amphiboles, the F contents do not exceed 0.2 wt.%. The Cl in all samples is <0.03 wt.%. Si varies between 7.6 a.p.f.u. and 8 a.p.f.u., with the lowest Si contents occurring in amphiboles of group 1. Zoned crystals of group 1 amphiboles show an increase of Si and Fe²⁺ and a decrease of Fe³⁺ from core to rim, whereas the other elements are more or less constant. Group 2 amphiboles are

TABLE 6. Representative microprobe analyses of olivine.

Sample	MiKa 24	MiKa 24	MiKa 14	MiKa 13	MiKa 28
Wt.%					
SiO ₂	30.78	30.41	29.76	29.41	29.80
TiO ₂	0.03	0.06	0.04	0.08	0.07
Al ₂ O ₃	0.01	0.00	0.00	0.00	0.00
FeO	59.25	60.22	63.64	64.67	64.86
MnO	3.67	3.58	3.84	3.97	3.93
MgO	4.70	4.48	1.00	0.65	0.46
CaO	1.33	1.36	1.50	1.09	0.84
Total	99.76	100.10	99.77	99.88	99.96
Formulae based on 4 oxygens					
Si	1.00	0.99	1.00	0.99	1.00
Ti	0.00	0.00	0.00	0.00	0.00
Al	0.00	0.00	0.00	0.00	0.00
Mg	0.23	0.22	0.05	0.03	0.02
Fe	1.62	1.64	1.79	1.82	1.83
Mn	0.10	0.10	0.11	0.11	0.11
Ca	0.05	0.05	0.05	0.04	0.03
Sum	3.00	3.00	3.00	3.00	2.99
Fo	11.5	10.9	2.5	1.6	1.2
Fa	81.1	81.9	89.3	90.8	91.5
Tp	5.1	4.9	5.5	5.6	5.6
La	2.3	2.4	2.7	2.0	1.2

less zoned. At the same Si content, group 1 amphiboles are relatively high in Fe²⁺, Ca and F and low in Fe³⁺, Na, Ti and Mg compared to group 2 amphiboles (Fig. 9b). For Al and Mn, there is no significant difference. In both groups, Si is positively correlated with Fe²⁺ and negatively with Fe³⁺, but on a different level (Fig. 9b). A positive correlation between Si and Ca and a negative one with Na is clear for group 2, but less obvious for group 1 amphiboles (Fig. 9b). Hence, the most important substitution for both groups is $2\text{Fe}^{3+} \rightleftharpoons \text{Fe}^{2+} + \text{Si}$, whereas the substitution $\text{Na}_B + \text{Fe}^{3+} \rightleftharpoons \text{Ca} + \text{Fe}^{2+}$ is significant only in group 2 amphiboles.

Aenigmatite

According to the classification scheme of Kunzmann (1999), aenigmatites in the dyke belong to the aenigmatite subgroup and are dominated by the aenigmatite-wilkinsonite cation exchange ($\text{Fe}^{2+} + \text{Ti}^{4+} \rightleftharpoons 2\text{Fe}^{3+}$). A substitution towards the rhönite subgroup ($\text{Na}^+ + \text{Si}^{4+} \rightleftharpoons \text{Ca}^{2+} + \text{Al}^{3+}$) is of only minor importance (Fig. 10, Table 10). Overall, the observed

compositions vary between Aen₉₅Wilk₅Rh₀ and Aen₅₂Wilk₄₂Rh₆. Minor elements are Mn (up to 3.2 wt.% MnO), Zr (up to 1.1 wt.% ZrO₂), and Mg (up to 0.13 wt.% MgO). Some aenigmatites show distinct chemical zoning with a decrease of rhönite component and an increase of wilkinsonite component from core to rim.

Phase petrology

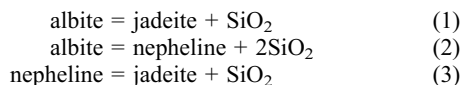
The mineral assemblages observed were used to constrain the conditions of crystallization of the dyke rock and allow the reconstruction of their changes during emplacement and cooling. The early magmatic stage is represented by the phenocryst assemblage alkali feldspar-nepheline-augite-olivine-magnetite. The groundmass assemblage albite-microcline-nepheline-sodalite-arfvedsonite-aegirine-aenigmatite-astrophylite represents a later stage of crystallization. Still later hydrothermal conditions are indicated by the conversion of nepheline and sodalite to analcime. Parameters to be calculated are T , a_{SiO_2} , f_{O_2} , $a_{\text{H}_2\text{O}}$ and a_{NaCl} .

TABLE 7. Representative microprobe analyses of clinopyroxene.

Sample	MiKa 14	MiKa 14	MiKa 28	MiKa 28	GM1852	GM1848	GM1848	GM1846	GM1846	GM1847
	Augite phenocryst				Groundmass					
Wt.%										
SiO ₂	50.15	48.52	49.09	48.96	52.30	50.35	50.70	51.49	51.94	52.25
TiO ₂	0.51	0.84	0.31	0.54	0.10	0.49	0.41	1.11	0.71	0.44
Al ₂ O ₃	1.41	1.80	0.51	0.74	2.49	0.95	1.09	0.33	0.34	2.25
FeO	18.92	20.89	26.27	25.71	27.82	27.74	28.35	28.54	28.93	27.61
MnO	0.82	0.75	0.69	0.93	0.08	0.39	0.29	0.23	0.29	0.41
MgO	5.90	4.37	1.38	1.59	0.02	0.14	0.10	0.36	0.57	0.03
ZrO ₂	0.31	0.22	0.17	0.13	0.05	0.04	0.03	0.05	0.04	0.03
CaO	21.29	20.72	20.37	20.32	12.60	7.65	4.74	2.54	0.87	0.03
Na ₂ O	1.20	1.18	1.15	1.29	0.93	9.65	11.14	12.03	12.90	13.40
Total	100.51	99.29	99.94	100.21	96.85	97.40	96.85	96.68	96.59	96.45
Formulae based on 4 cations and 6 oxygens										
Si	1.95	1.92	1.99	1.97	2.00	1.96	1.97	1.99	2.00	1.99
Al	0.06	0.08	0.02	0.04	0.12	0.04	0.05	0.02	0.02	0.10
Ti	0.01	0.03	0.01	0.02	0.00	0.01	0.01	0.03	0.02	0.01
Fe ³⁺	0.09	0.09	0.07	0.08	0.82	0.73	0.83	0.84	0.91	0.88
Mg	0.34	0.26	0.08	0.10	0.00	0.01	0.01	0.02	0.03	0.00
Fe ²⁺	0.53	0.59	0.82	0.78	0.07	0.18	0.09	0.08	0.01	0.00
Mn	0.03	0.03	0.02	0.03	0.00	0.01	0.01	0.01	0.01	0.01
Zr	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Ca	0.89	0.87	0.88	0.88	0.06	0.32	0.20	0.11	0.04	0.00
Na	0.09	0.09	0.09	0.10	0.02	0.73	0.84	0.90	0.96	0.99
Sum	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Aeg	9.4	10.6	7.1	8.2	82.0	79.3	88.3	84.0	91.0	88.9
Jd	0.0	0.0	2.0	2.0	11.0	0.0	1.1	6.0	5.0	11.1
Di	35.4	29.8	8.1	10.2	0.00	1.1	1.1	2.0	3.0	0.0
Hed	55.2	59.6	82.8	79.6	7.00	19.6	9.5	8.0	1.0	0.0

Early magmatic conditions

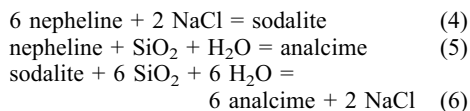
The following equilibria among nepheline, albite and jadeite (components in nepheline, alkali feldspar and clinopyroxene solid solution) were used to constrain T and a_{SiO_2} for the early magmatic conditions:



We used the range of nepheline, clinopyroxene and alkali feldspar compositions observed in phenocrysts. Additionally, equilibria among olivine, clinopyroxene and magnetite were used to calculate T , a_{SiO_2} and f_{O_2} during crystallization of these mafic phenocrysts.

Late magmatic conditions

The crystallization conditions of the groundmass assemblage were calculated based on compositions of the groundmass minerals albite, nepheline and aegirine. With the following equilibria, it is possible to constrain T , a_{SiO_2} , $a_{\text{H}_2\text{O}}$, and a_{NaCl} during late-stage conditions:



The groundmass assemblage aegirine-arfvedsonite-aenigmatite buffers oxygen fugacity by equilibria of the general type (related to observed textures, but not stoichiometrically balanced

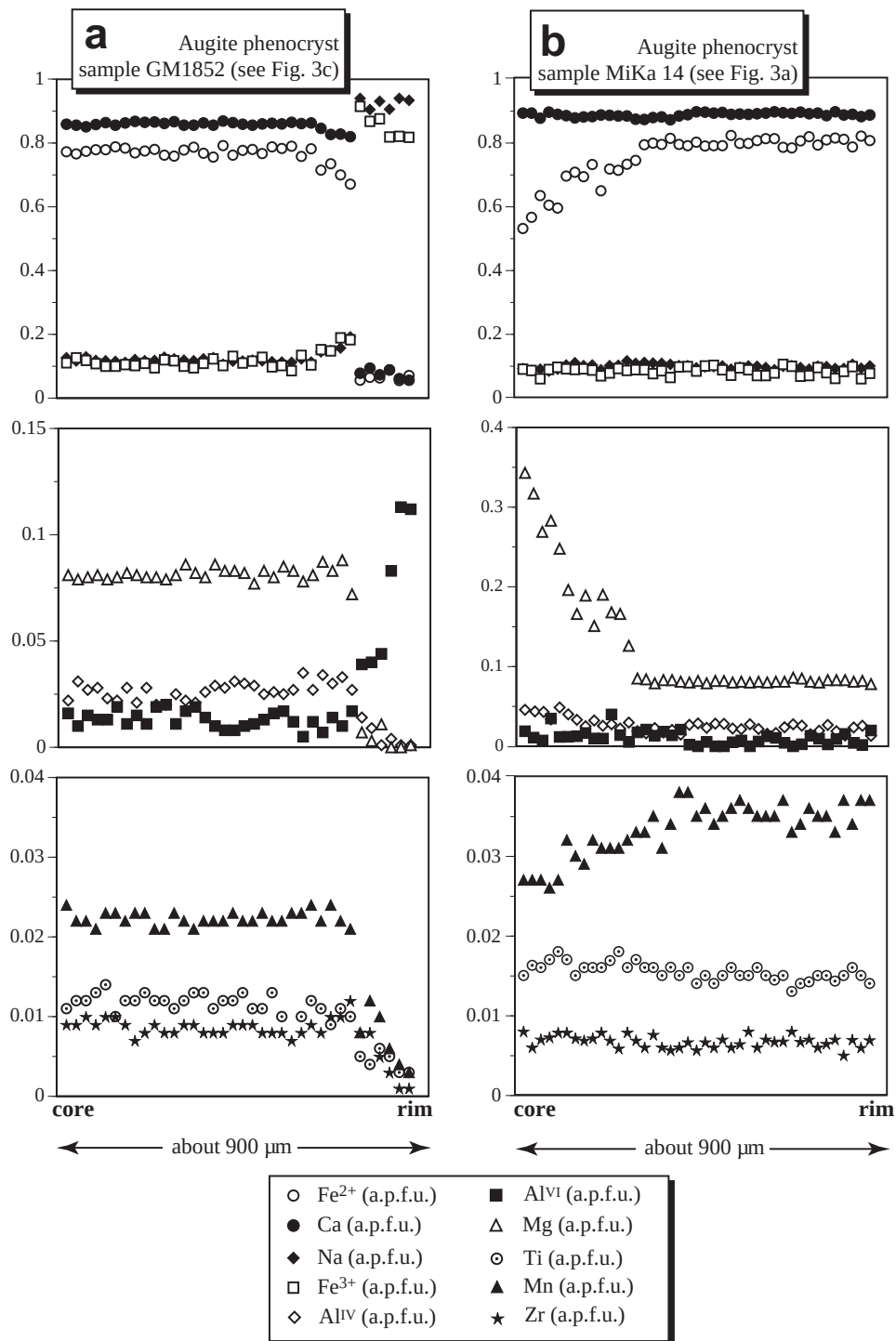
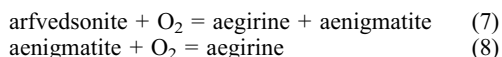


FIG. 8. Zoning profiles through augite grains of two different samples. (a) GM1852 (see also Fig. 3c). (b) MiKa 14 (Fig. 3a).

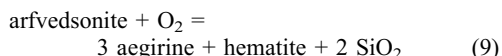
TABLE 8. Representative microprobe analyses of magnetite.

Sample	MiKa 24	MiKa 24	MiKa 14	MiKa 24	MiKa 28
Wt. %					
SiO ₂	0.08	0.02	0.06	0.06	0.05
TiO ₂	21.42	22.61	24.78	25.98	27.54
Al ₂ O ₃	0.81	1.29	0.52	0.29	0.51
FeO	71.40	72.51	67.60	66.70	67.85
MnO	3.83	1.37	4.94	5.23	2.46
MgO	0.00	0.00	0.00	0.00	0.00
ZnO	0.32	0.24	0.20	0.12	0.14
CaO	0.03	0.06	0.04	0.08	0.06
Total	97.89	98.09	98.14	98.46	98.60
Formulae based on 3 cations and 4 oxygens					
Si	0.00	0.00	0.00	0.00	0.00
Al	0.04	0.06	0.02	0.01	0.02
Ti	0.60	0.63	0.70	0.73	0.77
Fe ³⁺	0.76	0.68	0.58	0.52	0.43
Mg	0.00	0.00	0.00	0.00	0.00
Fe ²⁺	1.47	1.58	1.54	1.56	1.69
Mn	0.12	0.04	0.16	0.17	0.08
Zn	0.01	0.01	0.01	0.00	0.00
Ca	0.00	0.00	0.00	0.00	0.00
Sum	3.00	3.00	3.00	3.00	3.00
Usp	60.3	63.3	69.8	73.1	77.5
Mt	37.9	33.8	29.0	26.2	21.4
Sp	1.8	2.8	1.1	0.6	1.1

except for equation 9):



Late-stage decomposition of arfvedsonite is constrained by the following equilibrium:



In principle, equilibria 7 and 8 would allow calculation of the oxygen fugacity for the assemblage aegirine-arfvedsonite-aenigmatite, if reliable thermodynamic data of arfvedsonite and aenigmatite existed. Unfortunately, this is not the case.

Methods of calculation

Phase diagrams in the system Na-Al-Si-O-Cl-H were calculated using the GEOCALC software of Berman *et al.* (1987) and Lieberman and Petrakakis (1990) with the database of Berman (1988). Thermodynamic data for analcime and

sodalite were taken from Sharp *et al.* (1989) and Johnson *et al.* (1992). End-member component activities from mineral formulae were calculated using the solution model of Fuhrman and Lindsley (1988) for feldspar and the model of Holland (1990) for clinopyroxene. For nepheline, a mixing-on-site model was used; analcime and sodalite were treated as pure phases. Unit activity of SiO₂ was referred to a standard state of a pure SiO₂ modification at *P* and *T*. Equilibria among olivine, clinopyroxene and magnetite were calculated using the QUILF program of Andersen *et al.* (1993). For a discussion of the theoretical background of the QUILF calculations see Frost and Lindsley (1992) and Lindsley and Frost (1992). Markl *et al.* (1998) showed that clinopyroxene tends to become enriched in Mg during later re-equilibration. In order to minimize these effects, the average olivine composition and the most Fe-rich core composition of clinopyroxene were used for these calculations. Details of the procedure are given in Marks and Markl (2001). The uncertainty of these calcula-

TABLE 9. Representative microprobe analyses of amphibole.

Sample	GM1848	GM1847	GM1846	MiKa 13	MiKa 28	MiKa 14
Wt. %						
SiO ₂	49.18	48.87	48.49	47.00	48.70	47.20
TiO ₂	0.42	0.39	0.46	0.17	0.07	0.16
Al ₂ O ₃	2.26	2.23	2.33	2.00	0.93	2.43
FeO	32.50	33.22	33.54	33.81	34.26	34.03
MnO	0.95	1.05	1.06	1.33	1.31	1.06
MgO	0.62	0.48	0.49	0.38	0.33	0.37
CaO	1.70	1.18	1.23	3.17	3.21	2.62
Na ₂ O	6.73	7.09	7.31	6.16	6.05	6.76
K ₂ O	2.77	2.70	2.54	2.19	2.03	1.97
ZrO ₂	0.01	0.03	0.02	0.05	0.01	0.02
Cl	0.00	0.00	0.00	0.01	0.02	0.01
F	0.00	0.03	0.03	1.94	1.83	2.01
Total	97.16	97.26	97.47	98.95	99.54	99.42
Formulae based on 16 cations and 23 oxygens						
Si	7.91	7.85	7.76	7.71	7.96	7.67
Al	0.43	0.42	0.44	0.39	0.18	0.47
Ti	0.05	0.05	0.06	0.02	0.01	0.02
Fe ³⁺	0.32	0.54	0.72	0.58	0.22	0.70
Mg	0.15	0.11	0.12	0.09	0.08	0.09
Fe ²⁺	4.05	3.92	3.77	4.06	4.46	3.92
Mn	0.13	0.14	0.14	0.18	0.18	0.15
Ca	0.29	0.20	0.21	0.56	0.56	0.46
Na	2.10	2.21	2.27	1.96	1.92	2.13
K	0.57	0.55	0.52	0.46	0.42	0.41
Zr	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.00	0.00	0.00	0.00	0.01	0.00
F	0.00	0.02	0.02	1.01	0.95	1.03
Sum	16.00	16.00	16.00	16.00	16.00	16.00

tions are estimated at $\sim\pm 50^\circ\text{C}$ for temperature and ± 0.05 for silica activity.

Evolution of crystallization conditions during cooling *Pressure*

Based on fluid-inclusion data (Konnerup-Madsen and Rose-Hansen, 1984; Markl *et al.*, 2001a) and estimated overburden (Poulsen, 1964), the pressure of emplacement of the Ilímaussaq intrusion was estimated to be ~ 1 kbar. By analogy, all calculations for the MiKa were performed for a fixed pressure of 1 kbar.

Temperature and silica activity

The results of nepheline liquidus thermometry after Hamilton (1961) are illustrated in Fig. 5. Nepheline phenocrysts indicate temperatures

between ~ 900 and $< 500^\circ\text{C}$, whereas groundmass nepheline temperatures are invariably below 775°C .

Equilibration temperatures between 840 and 690°C at silica activities from 0.5 to 0.25 where deduced from the olivine-augite-magnetite assemblage with the QUILF program (Andersen *et al.*, 1993) (Fig. 11). There is a fairly good correlation between degree of fractionation (expressed as X_{Fe} in olivine) and calculated T and a_{SiO_2} .

Equilibria 1–3 among nepheline, albite and jadeite (components in nepheline, alkali feldspar and clinopyroxene solid solution) for the early magmatic phenocrysts indicate liquidus temperatures of between 720 and 780°C and silica activities of between 0.5 and 0.4 (Fig. 12a). The same calculations for groundmass nepheline, albite and aegirine indicate temperatures between 450 and 600°C and lower silica activities

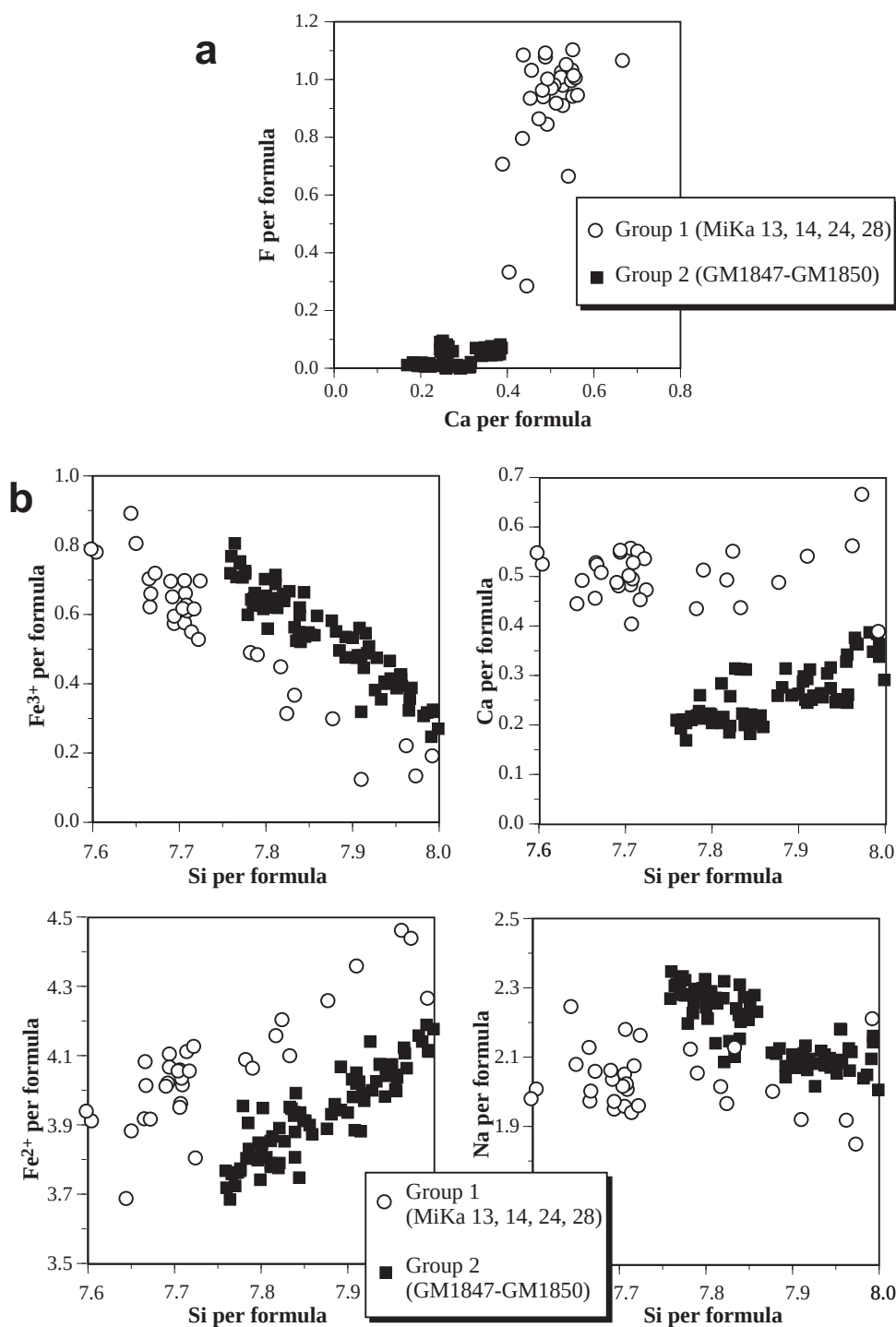


FIG. 9. Amphibole chemistry. (a) Ca vs. F in amphiboles, distinguishing two groups of amphiboles in MiKa samples. (b) Correlation diagrams of several elements with Si atoms per formula for amphibole.

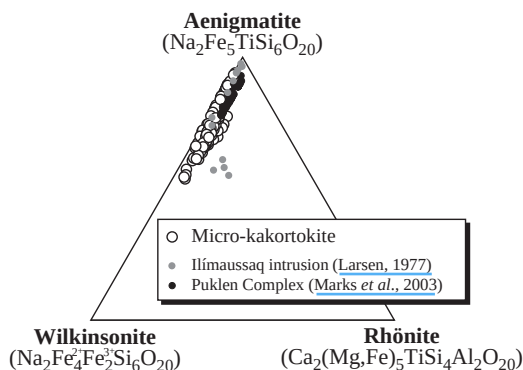


FIG. 10. Composition of measured aenigmatite in the system aenigmatite-wilkinsonite-rhönite. Analyses of aenigmatites from the Ilímaussaq Intrusion (Larsen, 1977) and from the Puklen complex (Marks *et al.*, 2003) are shown for comparison.

of ~ 0.4 to 0.25 (Fig. 12*b*). Sodalite crystallized at temperatures of $<400^{\circ}\text{C}$ (Fig. 13*a*). The late-stage formation of analcime at the expense of nepheline and sodalite was calculated to occur at temperatures of below $\sim 300^{\circ}\text{C}$, assuming a low silica activity of ~ 0.2 (Fig. 13*b*). This low value was assumed because a decrease in silica activity during cooling was shown to occur in similar phase assemblages in the Ilímaussaq intrusion (Markl *et al.*, 2001) and because of the significant decrease in a_{SiO_2} from early to late-magmatic conditions. In summary, the different mineral assemblages in the dyke record the complete history of crystallization from early magmatic conditions at $850\text{--}900^{\circ}\text{C}$ down to late-stage hydrothermal fluid activity, at $<300^{\circ}\text{C}$. During this process, silica activity decreases from ~ 0.5 to at least 0.25 , and possibly, even lower values.

Oxygen fugacity

Relative oxygen fugacities during early magmatic conditions were calculated using the

TABLE 10. Representative microprobe analyses of aenigmatite.

Sample	GM1848	MiKa 13	GM1850	GM1849	MiKa 28	GM1847
Wt. %						
SiO ₂	41.88	40.51	39.76	39.57	39.84	40.10
TiO ₂	8.56	7.81	7.60	6.40	7.87	6.98
Al ₂ O ₃	0.03	0.96	1.33	1.06	1.46	1.56
FeO	40.62	40.46	39.86	42.94	39.66	40.43
MnO	1.63	1.89	3.21	1.57	3.12	1.92
MgO	0.06	0.04	0.12	0.09	0.11	0.05
ZrO ₂	0.00	0.57	0.49	0.16	0.20	0.68
CaO	0.02	0.44	0.49	0.53	0.59	0.71
Na ₂ O	7.28	6.99	7.00	7.01	6.91	6.86
Total	100.09	99.67	99.86	99.32	99.76	99.29
Formulae based on 14 cations and 20 oxygens						
Si	5.99	5.83	5.70	5.70	5.71	5.78
Al	0.00	0.16	0.23	0.18	0.25	0.27
Ti	0.92	0.84	0.82	0.69	0.85	0.76
Fe ³⁺	0.21	0.45	0.68	1.00	0.56	0.59
Mg	0.01	0.01	0.02	0.02	0.02	0.01
Fe ²⁺	4.65	4.42	4.10	4.16	4.20	4.29
Mn	0.20	0.23	0.39	0.19	0.38	0.23
Zr	0.00	0.04	0.03	0.01	0.01	0.05
Ca	0.00	0.07	0.08	0.08	0.09	0.11
Na	2.02	1.95	1.95	1.96	1.92	1.92
Sum	14.00	14.00	14.00	14.00	14.00	14.00
Rhönite	89.8	75.8	67.5	54.6	71.3	66.9
Aenigmatite	10.1	21.0	29.2	42.0	24.7	27.9
Wilkinsonite	0.1	3.1	3.2	3.4	4.0	5.2

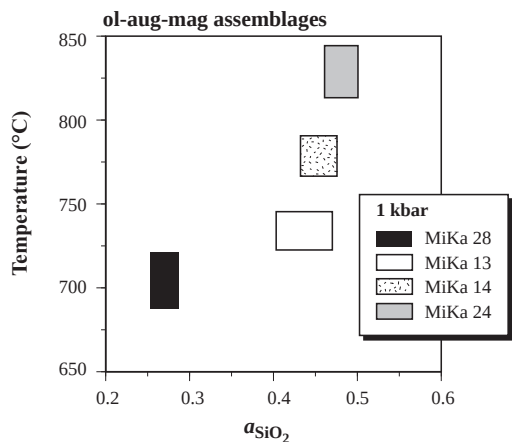


FIG. 11. Temperature-silica activity diagram showing the results of QUILF calculations.

assemblage olivine-augite-magnetite. In the early magmatic stage, relative oxygen fugacity decreases from ~FMQ –1.5 to ~FMQ –3. The stabilization of aenigmatite-aegirine-arfvedsonite assemblages at the expense of the olivine-augite-magnetite assemblage during late magmatic conditions indicates that after evolving along a lower f_{O_2} displaced FMQ buffer, during early magmatic conditions, oxygen fugacity reached and possibly exceeded that of the synthetic FMQ buffer value (Nicholls and Carmichael, 1969; Marsh, 1975; Marks *et al.*, 2003). The destabilization of arfvedsonite and the formation of aegirine (reaction 9) associated with Fe-hydroxides indicates a further rise in oxygen fugacity during hydrothermal activity. The T - f_{O_2} -dependency of this equilibrium was calculated for similar mineral activities by Marks *et al.* (2003). They showed that this reaction occurs at low temperatures of ~300°C and at oxygen fugacities slightly above the HM buffer.

Water and NaCl activity

Equilibrium 5 constrains the formation of analcime at the expense of nepheline at low silica activities of ~0.2 and temperatures between 200 and 300°C, and at water activities of between 0.5 and unity (Fig. 13b). Equilibrium of sodalite with groundmass nepheline buffers NaCl activity and was calculated to occur at temperatures of <~400°C. According to the calculated T - a_{NaCl} dependency of equilibrium 4, higher temperatures would prevent the stable formation of sodalite. Using equilibria 4–6 among nepheline, sodalite

and analcime, the activity of NaCl during late-stage conditions is estimated to range between 0.1 and 0.4 (Fig. 13b).

Discussion

Interpretation of mineral chemistry

The compositional variation of the rock-forming minerals reflect typical fractional crystallization processes. With increasing Fe content (degree of fractionation) olivine becomes more Mn- and Ca-rich. The large Mn contents are comparable to other silica-undersaturated suites (e.g. Stephenson, 1974) and reflect the highly fractionated state of the parent magma. High contents of Ca in a relatively Ca-poor magma are indicative of low silica activities and low pressure, during crystallization (Stormer, 1972; Markl *et al.*, 2001b). Because Ca is known to have fast diffusion rates in olivine (e.g. McKay *et al.*, 1998), the exceptionally low Ca contents in olivine from sample MiKa 28 may be due to post-magmatic diffusional re-equilibration related to lower cooling rates of this sample, which is from the central part of the dyke.

There are two different types of augite phenocrysts present in the dyke (Fig. 8). Augite of sample MiKa 14 (Figs 3a and 8b) reflects an early stage of fractional crystallization with a relatively Mg-rich and Mn-poor core, whereas augite of sample GM1852 (Figs 3c and 8a) crystallized later (but still during the early magmatic stage), since the Fe and Mg content in the core of this crystal is approximately the same as at the rim of the MiKa 14 augite. Further fractional crystallization led to a progressive enrichment of Na and Fe³⁺. The sudden increase of Na, Fe³⁺ and ^{VI}Al at the outermost rim, and along cracks, may be due to the later activity of a Na-rich and oxidizing residual melt or fluid phase. According to equilibrium 1, relatively high contents of ^{VI}Al in pyroxene, at this stage, may be due to low silica activities in this residual melt/fluid. The sudden decrease of minor elements (Mn, Ti, Zr) in augite may be ascribed to precipitation of eudialyte, which acts as a sink for these elements (Larsen, 1976; Markl *et al.*, 2001a).

Amphibole compositions vary along the strike of the dyke: the westernmost samples (GM1847–GM1851) are Ca- and F-poor, the more easterly samples (MiKa 13, 14, 24, 28) are Ca- and F-rich. In view of these chemical differences, it is tempting to look for a relation with fluorite

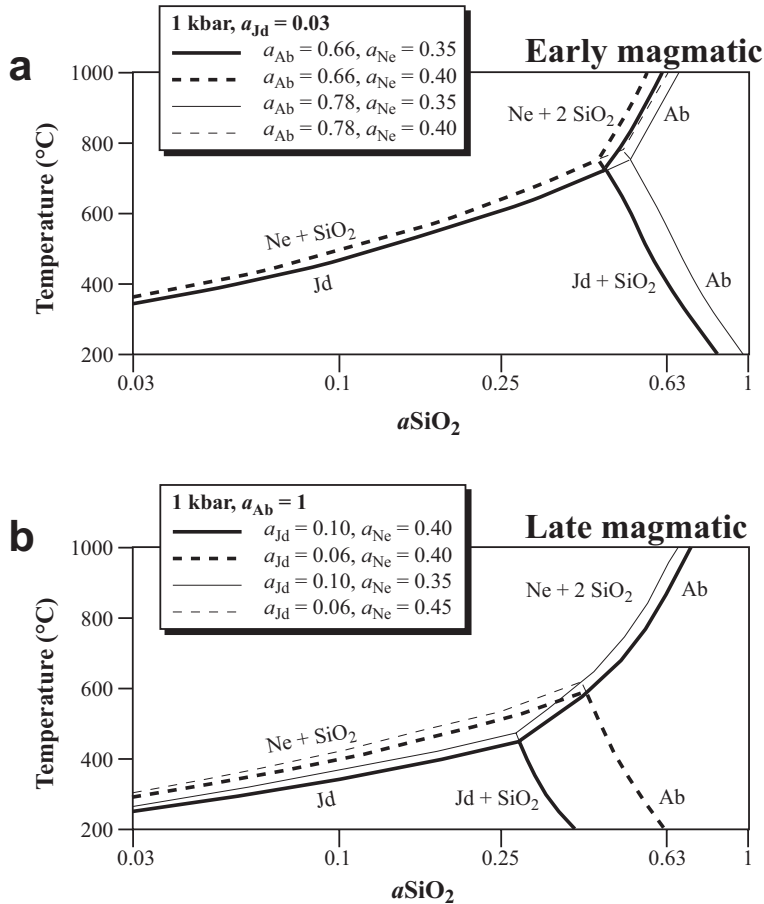


FIG. 12. Temperature-silica activity diagrams showing equilibria among nepheline, albite and jadeite. (a) Phenocryst phases. (b) Groundmass phases. End-member activities were calculated for the range of mineral composition observed.

occurrence. Indeed, detailed petrography showed that interstitial (i.e. magmatic) fluorite occurs only in samples with low-Ca and low-F amphiboles but not in samples with Ca- and F-rich amphiboles. Thus, amphibole chemistry is governed by fluorite saturation in the melt, which obviously was reached only in the westernmost part of the dyke, close to the Ilímaussaq intrusion. This may reflect inhomogeneities in the melt, the thermal effect caused by the hot pluton, or slightly different outcrop levels with respect to original crystallization in the dyke. Since amphibole is, apart from fluorite, the only major F-bearing mineral phase in these rocks, it is an important tracer for such effects.

Another important feature to be explained is the increase of Si and the decrease of Fe^{3+} in the

amphiboles with progressive fractionation, which is governed by the substitution mechanism $2Fe^{3+} \rightleftharpoons Fe^{2+} + Si$. This effect can be seen both in amphibole core-rim zoning patterns and in the comparison of samples from the margin and from the centre of the dyke. This compositional evolution results in a decrease of the Fe^{3+}/Fe^{2+} ratio of the amphiboles during fractionation, which may be explained by crystallization in a system closed with respect to oxygen (see Philpotts, 1990, page 210). Once early amphibole crystallized with a high Fe^{3+}/Fe^{2+} ratio, the absolute oxygen fugacity in the system decreases and results in later amphibole having a lower Fe^{3+}/Fe^{2+} ratio. This process works, despite the fact that relative oxygen fugacity increased during cooling of the magma (see later), because

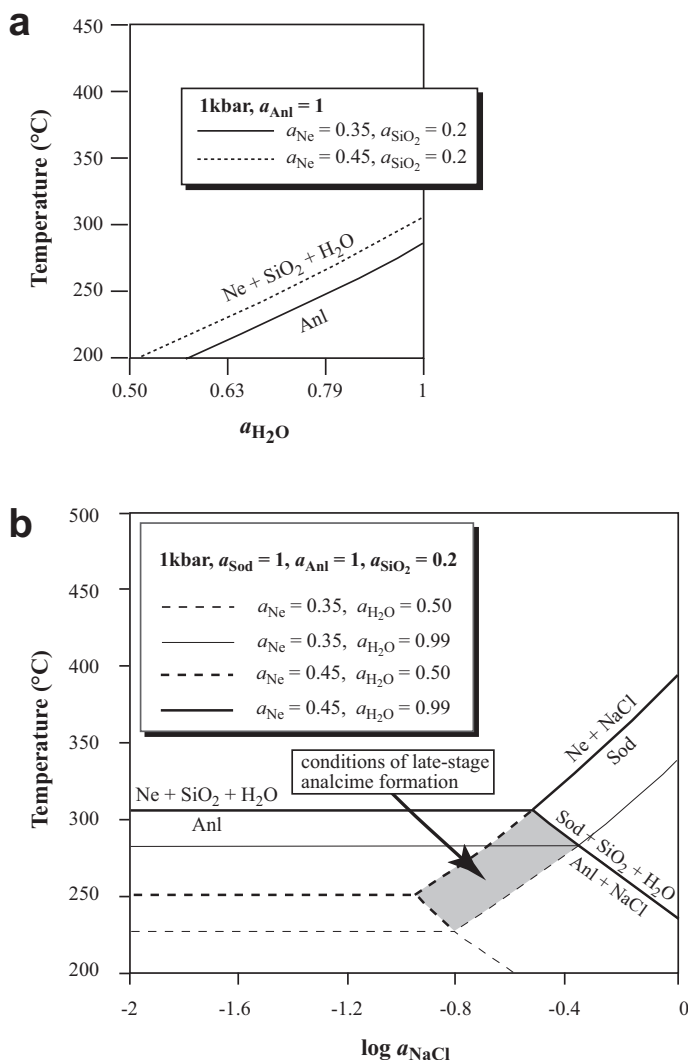


FIG. 13. (a) Temperature- $\log a_{\text{NaCl}}$ diagram showing phase equilibria in the system Na-Al-Si-O-H-Cl. (b) Temperature- $a_{\text{H}_2\text{O}}$ diagram for the equilibrium $\text{Ne} + \text{SiO}_2 + \text{H}_2\text{O} = \text{Anl}$.

amphibole crystallization probably occurred over a relatively small temperature interval.

Comparison with the Ilímaussaq rocks

Aside from their close proximity, the petrographical and mineralogical similarities, specifically their principal mineral assemblages, mineral chemistry and the evolutionary trends, of the intrinsic parameters between the MiKa and the agpaitic nepheline syenites of the Ilímaussaq intrusion, imply a close relationship between the

dyke rock and the intrusive complex (Allaart, 1969; Larsen and Steenfelt, 1974). The most obvious similarities between the investigated MiKa samples and the agpaitic Ilímaussaq complex are as follows:

(1) The early mafic minerals of the MiKa are olivine, Ti-rich magnetite and augite. The same is the case in the early alkaline member of the Ilímaussaq complex, the augite syenite (Larsen, 1976; Marks and Markl, 2001). In both rocks, olivine approaches end-member fayalite and augite, hedenbergite composition, and the latter

shows a pronounced Na-enrichment towards the rim (Fig. 8). Relics of this mineral assemblage are preserved in the early agpaiteic sodalite foyaite of the Ilímaussaq complex (Larsen, 1976; Markl *et al.*, 2001a) and are overgrown or resorbed by aegirine and arfvedsonite. The same can be seen in the MiKa samples.

(2) In the agpaite of the Ilímaussaq intrusion and in the MiKa, aegirine, arfvedsonite, aenigmatite, sodalite and eudialyte are stable phases in the later stages of fractionation.

(3) Feldspar in both the agpaite of the Ilímaussaq complex and the MiKa are invariably Ca-free (Markl *et al.*, 2001a). Early feldspar phenocrysts in the MiKa are albite-K-feldspar solid solutions, which is also the case for all Ilímaussaq agpaite except for the late lujavrites (e.g. Ferguson, 1964; Larsen, 1976). These lujavrites contain two separate feldspars (albite and K-feldspar), which are mirrored by the groundmass feldspars of the MiKa.

(4) The textures resulting from the late-stage replacement of nepheline, albite and sodalite by analcime and natrolite in the MiKa show remarkable similarities to the late-stage assemblages in the Ilímaussaq rocks (Markl *et al.*, 2001a; Markl and Baumgartner, 2002).

(5) Oxygen isotope composition of olivine from the MiKa dyke and the augite syenite of the Ilímaussaq intrusion are remarkably similar (Marks *et al.*, unpublished data).

Similar mineral assemblages and similar mineral compositions reflect similar petrological evolutionary trends: phase equilibria in the MiKa record early magmatic temperatures of ~850°C and hydrothermal fluid activity at temperatures <300°C, a systematic decrease of silica activity from early magmatic to late-stage hydrothermal assemblages, and a change in redox conditions from very reduced, in the early rocks, to oxidized in the later stages. The same can be seen in the Ilímaussaq rocks (Larsen, 1976; Markl *et al.*, 2001a; Marks and Markl, 2001). Ignoring the Ilímaussaq alkali granite, all the different magma batches of the Ilímaussaq intrusion can be correlated to specific phase assemblages of the MiKa. Hence, the fractionation processes known from the Ilímaussaq rocks can be observed in the MiKa in a surprisingly similar way, despite the large difference in size. Obviously, magma volume is not a crucial factor in determining fractionation trends.

However, some differences between the MiKa and the Ilímaussaq rocks should be emphasized:

(1) Sodalite in the Ilímaussaq rocks is, in some agpaite, a primary magmatic phase crystallized at temperatures of ~800°C (Markl *et al.*, 2001a). In contrast, sodalite occurs only as an anhedral groundmass phase in the MiKa. It crystallized at significantly lower temperatures, governed by the lower nepheline activities in the MiKa compared to the Ilímaussaq rocks.

(2) Given the same X_{Fe} , early magmatic olivine in the MiKa is more Mn-rich and hedenbergite phenocrysts are more Na-rich than in the Ilímaussaq augite syenite. Additionally, magnetite is more Mn- and Fe³⁺-rich. (Marks and Markl, 2001). Furthermore, aenigmatite and aegirine clearly dominate in most MiKa samples over Na-amphibole, which is in contrast to most Ilímaussaq agpaite.

(3) Nd isotope data (Marks *et al.*, unpublished data) show the MiKa to be slightly different from the Ilímaussaq rocks. A positive $\epsilon_{Nd(T)}$ value of +0.7 compared to the negative values for the plutonic agpaite of the Ilímaussaq complex ($\epsilon_{Nd(T)}$ between -0.1 and -3.1) implies less contamination with low ϵ_{Nd} material for the MiKa dyke.

The assumption of Allaart (1969) that the MiKa represents a hypabyssal extension of the kakortokites (layered agpaite nepheline syenites) of the Ilímaussaq intrusion is not strictly correct because of the significant neodymium isotopic differences. Two kakortokite samples have $\epsilon_{Nd(T)}$ values of -1.5 and -1.8, respectively (Marks *et al.*, unpublished data), which contrasts the positive $\epsilon_{Nd(T)}$ value of +0.7 for a MiKa sample. Moreover, the plutonic kakortokites lack early magmatic olivine, hedenbergite and Ti-magnetite. The occurrence of these minerals as early magmatic phases in the MiKa dyke implies that a separation of the dyke from the Ilímaussaq magma must have occurred at the latest during the sodalite foyaite stage (or possibly earlier) of the Ilímaussaq intrusion because olivine, hedenbergite and Ti-magnetite are early magmatic phases only in the early Ilímaussaq rocks (augite syenite and sodalite foyaite) and not in the later agpaite (e.g. kakortokites). Furthermore, the differences in the composition of the early mafic minerals (olivine, augite, magnetite) imply, that the MiKa melt was slightly more evolved and more oxidized than the Ilímaussaq melt. The late crystallization of sodalite, may be explained by lower Cl contents and therefore later crystallization of sodalite in the MiKa magma.

It may well be that this, and the other small compositional and petrographic differences between the dyke and the intrusion, are the result of different amounts of contamination after separation of the two magmas. Petrography clearly suggests an early separation of the dyke from the Ilímaussaq magma and an independent, but remarkably similar, evolution after this separation. However, a common melt source can be assumed because of the great petrographic and petrologic similarities and the similar oxygen isotopic composition of early magmatic olivine. Based on Nd isotope data, no major contamination of the dyke took place during intrusion and fast ascent through the granitic upper crust (Julianehåb Batholith). We propose that the small heat capacity, and resultant low potential for assimilation of the dyke, was the reason for this. This indicates that the MiKa dyke rock is a less contaminated equivalent of the Ilímaussaq rocks.

Time constraints on dyke cooling

Using the one-dimensional stationary heat flow equations of Peacock (1989), we modelled the cooling history of the MiKa dyke rock using MATLAB software. Based on the calculations above, we chose a liquidus temperature of 850°C. The average thermal conductivity for syenites of $k = 8 \times 10^{-7} \text{ m}^2 \text{ s}^{-1}$ was taken from Landolt-Börnstein (1982) and the half-thickness of the dyke was fixed at 15 m. Assuming a depth of emplacement of 3–5 km and a typical temperature gradient of ~30°C/km, the temperature of the basement was assumed to be <150°C. With these parameters, we calculated that the dyke cooled from 850 to 250°C in <10 y. If we consider the thermal effect of the nearby Ilímaussaq intrusion and therefore allow the basement to be as hot as 500°C, the final cooling of the dyke occurred within a time span of ~100 y. A further indication for the fast cooling history is provided by the Ba-rich patches within feldspar phenocrysts (Fig. 2c,d). Assuming that the Ba-rich patches in the feldspar phenocryst of sample GM1846 represent primary magmatic and not later metasomatic features, they would have been erased if the dyke had remained at temperatures of ~800°C for between 2000 and 9000 y (Cherniak, 2002). Hence, the dyke cooled faster than the maximum constraints. This simple calculation shows that the observed fractionation trends may occur in extraordinarily short time intervals which

are two to four orders of magnitude shorter than for plutonic rocks (e.g. Brown and Fletcher, 1999; Vazquez and Reid, 2002; Charlier and Zellmer, 2002). Obviously, neither the volume in which the fractionation takes place, nor the time span during which it occurs plays a significant role.

Summary

The various mineral assemblages of the agpaitic micro-kakortokite dyke represent different stages of magma evolution and allow the reconstruction of the evolution of intrinsic parameters (T , a_{SiO_2} , f_{O_2} , a_{NaCl} , $a_{\text{H}_2\text{O}}$) during cooling.

The phenocryst assemblage alkali feldspar + nepheline + olivine + augite + magnetite constrain early magmatic conditions to ~850°C, silica activity to ~0.5 and a relatively reduced condition of $\Delta\text{FMQ} = -1.5$ to -3 . The agpaitic groundmass assemblage indicates lower temperatures (600° to 450°C) and lower silica activity (down to ~0.25) but higher relative oxygen fugacity around or slightly above the FMQ buffer. In some parts of the dyke, magmatic fluorite saturation occurred, which is strongly reflected in the crystallization of Ca- and F-poor amphiboles in contrast to Ca- and F-rich amphiboles in the fluorite-devoid parts of the dyke. The evolution of the amphiboles is indicative of crystallization in a system closed to oxygen. The retention of Cl and water down to low temperatures is indicated by the formation of groundmass sodalite at temperatures of <400°C, at NaCl activities of between 0.1 and 0.4. While the late-stage formation of analcime, at the expense of nepheline and sodalite, occurred at temperatures of <300°C, silica activities of ~0.25 and water activities of between 0.5 and unity. The consumption of arfvedsonite by aegirine indicates oxygen fugacities above the HM buffer, during late-stage conditions.

Mineral assemblages and chemical evolution are very similar to the rocks of the Ilímaussaq intrusion, with specific phase assemblages of the MiKa representing specific rock types of the Ilímaussaq complex. Petrography, mineral chemistry and isotope data indicate a common magma source but an early separation of the MiKa from the Ilímaussaq magma and less contamination with country rocks for the MiKa. The very similar fractionation processes observed in the MiKa occurred in a comparatively small magma volume and within a short time interval. Thus, these two parameters have no influence on the course of fractionation.

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