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The Ilímaussaq alkaline complex, South Greenland: status of mineralogical research with new results

Edited by
Henning Sørensen

Contributions to the mineralogy of Ilímaussaq, no. 100
Anniversary volume with list of minerals

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Cover
Igneous layering in kakortokites in the southern part of the Ilímaussaq alkaline complex, South Greenland. The central part of the photograph shows the uppermost part of the layered kakortokite series and the overlying transitional kakortokites and aegirine lujavrite on Laksefjeld (680 m), the dark mountain in the left middle ground of the photograph. The cliff facing the lake in the right middle ground shows the kakortokite layers + 4 to + 9. The kakortokite in the cliff on the opposite side of the lake is rich in xenoliths of roof rocks of augite syenite and naujaite making the layering less distinct. On the skyline is the mountain ridge Killavaat ('the comb'), the highest peak 1216 m, which is made up of Proterozoic granite which was baked and hardened at the contact to the intrusive complex. The lake (987 m) in the foreground is intensely blue and clear because it is practically devoid of life. The whole area is devoid of vegetation, with crumbly rocks typical of the nepheline syenites of the complex.

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Contents

Preface
H. Sørensen 5

Brief introduction to the geology of the Ilímaussaq alkaline complex, South Greenland, and its exploration history
H. Sørensen 7

List of all minerals identified in the Ilímaussaq alkaline complex, South Greenland
O.V. Petersen 25

Geochemical overview of the Ilímaussaq alkaline complex, South Greenland
J.C. Bailey, R. Gwozdz, J. Rose-Hansen and H. Sørensen 35

Distribution of germanium in rocks and minerals of the Ilímaussaq alkaline complex, South Greenland
J.C. Bailey 55

The eudialyte group: a review
O. Johnsen, J.D. Grice and R.A. Gault 65

The distribution of minerals in hyper-agpaitic rocks in terms of symmetry: evolution of views on the number and symmetry of minerals
A.P. Khomyakov 73

The hyper-agpaitic stage in the evolution of the Ilímaussaq alkaline complex, South Greenland
H. Sørensen and L.M. Larsen 83

Naujakasite from the Ilímaussaq alkaline complex, South Greenland, and the Lovozero alkaline complex, Kola Peninsula, Russia: a comparison
A.P. Khomyakov, H. Sørensen, O.V. Petersen and J.C. Bailey 95

Zoning in steenstrupine-(Ce) from the Ilímaussaq alkaline complex, South Greenland: a review and discussion
A.P. Khomyakov and H. Sørensen 109

Notes on leucophanite from the Ilímaussaq alkaline complex, South Greenland
H. Bohse, O.V. Petersen and G. Niedermayr 119

Notes on ephesite, terskite, Na-komarovite, ceriopyrochlore-(Ce), joaquinite-(Ce) and other minerals from the Ilímaussaq alkaline complex, South Greenland
E.I. Semenov 123

Thalcusite from Nakkaalaaq, the Ilímaussaq alkaline complex, South Greenland
S. Karup-Møller and E. Makovicky 127

Hiortdahlite II from the Ilímaussaq alkaline complex, South Greenland, the Tamazeght complex, Morocco, and the Iles de Los, Guinea
E.R. Robles, F. Fontan, P. Monchoux, H. Sørensen and P. de Parseval 131

Natrophosphate from the Ilímaussaq alkaline complex, South Greenland
O.V. Petersen, A.P. Khomyakov and H. Sørensen 139

Two new rare-earth-rich mineral associations in the Ilímaussaq alkaline complex, South Greenland
I.V. Pekov and I.A. Ekimenkova 143

Stability of Na–Be minerals in late-magmatic fluids of the Ilímaussaq alkaline complex, South Greenland
G. Markl 145

A review of the composition and evolution of hydrocarbon gases during solidification of the Ilímaussaq alkaline complex, South Greenland
J. Konnerup-Madsen 159

A note on the occurrence of gold in the Ilímaussaq alkaline complex, South Greenland
H. Bohse and J. Frederiksen 167

Preface

The Mesoproterozoic Ilímaussaq alkaline complex located near the town of Narsaq in South Greenland is the type locality for agpaitic nepheline syenites and represents an enormous concentration of a number of rare elements, particularly Li, Be, Nb, Zr, REE, Y, U and Th. This explains the presence of about 220 minerals, 27 of these discovered in and first described from the complex, and nine only found there.

In 1965 it was decided to collate papers on the mineralogy (in a broad sense) of the complex published in various scientific journals into a consecutively numbered series: *Contributions to the mineralogy of Ilímaussaq*. The first issue appeared in 1965, no. 102 in 1999, and the series has now reached no. 113. Issue no. 100 was reserved for the anniversary volume presented here. This volume contains a brief account of the geology of the complex and the history of exploration, a list of the minerals identified so far in the complex, and papers which review selected topics and present new information on the mineralogy and geochemistry of Ilímaussaq. A companion report, *Danmarks og Grønlands Geologiske Undersøgelse Rapport* **2001/102**, compiled by J. Rose-Hansen, H. Sørensen and W.S. Watt, presents an inventory of the literature of the complex, collated from an unusually wide variety of sources and containing about 750 entries, together with a list of the series *Contributions to the mineralogy of Ilímaussaq*. The report brings these both in print and on a CD-ROM, accessible for electronic searching.

We hope that this collection of papers on Ilímaussaq will be received in the same positive way as was its predecessor, 'The Ilímaussaq intrusion, South Greenland. A progress report on geology, mineralogy, geochemistry and economic geology', published as Contribution to the mineralogy of Ilímaussaq no. 63 in *Rapport Grønlands Geologiske Undersøgelse* **103** edited by J.C. Bailey, L.M. Larsen & H. Sørensen in 1981.

Contribution no. 63 was compiled after more than ten years of intensive field activity and presented new information on the geology and geochemistry of the Ilímaussaq complex together with papers on mineralogy, fluid inclusions and economic geology. Since then there has only been limited field activity in the complex. Contribution no. 100 (this volume) therefore presents results of the continued laboratory investigations of material collected during the earlier field work and drilling programmes together with discussions of a few selected topics in the light of new developments in the study of agpaitic rocks and their minerals.

The paper by J.C. Bailey, R. Gwozdz, J. Rose-Hansen and H. Sørensen contains the first general discussion of the geochemistry of the complex since V.I. Gerasimovsky's 1969 memoir on this subject. This overview of the geochemistry is based on the on-going detailed analysis of 120 large samples of the major rock types collected by blasting in order to obtain fresh material. Mineral separates have been prepared of many of the samples with the aim of analysing the rock-forming and accessory minerals, together with the bulk rocks, for more than 50 elements. The ultimate purpose is to evaluate the composition of the agpaitic melts and the distribution of a number of elements between minerals and the melt and fluid phases in order to better understand the conditions of formation of agpaitic mineral associations. The following paper by J.C. Bailey illustrates this by describing the distribution of germanium in the rocks and minerals of the complex.

Eudialyte may be called the typomorphic mineral of agpaitic rocks *sensu stricto* and is one of the minerals first found and described from Ilímaussaq. The nomenclature of the mineral has, however, been rather confusing. Based on the optical properties three varieties, eudialyte, mesodialyte and eucolite, have been distinguished, but it has been impossible to relate these differences to chemical properties. In recent years it has been demonstrated that eudialyte comprises a group of minerals. It was therefore felt timely to include a review of this mineral group in the anniversary volume (the paper by O. Johnsen, J.D. Grice and R.A. Gault).

The most highly evolved agpaitic rocks and mineral associations have been called hyper-agpaitic by Russian colleagues working in the Khibina and Lovozero complexes of the Kola Peninsula. Hyper-agpaitic rocks are extremely rich in rare minerals, a result of crystallisation of peralkaline, volatile-rich, low-viscosity melts over a broad temperature interval, ending at low temperatures. This results in long-range ordering of the crystal structures and the predominance of triclinic minerals (paper by A.P. Khomyakov). In Ilí-

maussaq, hyper-agpaitic mineral associations are found not only in pegmatites and hydrothermal mineralisations as in the Kola complexes but also in the most evolved lujavrites; a review is presented in the paper by H. Sørensen and L.M. Larsen.

The mineral naujakasite presents an enigmatic problem. It is composed of the most common elements, Na, Al, Fe, Mn and Si, but has nevertheless until now only been known from the Ilímaussaq complex, where it is sometimes a rock-forming mineral which may constitute more than 75 vol.% of some lujavrites. The recent discovery of a Mn-rich naujakasite, manganonaujakasite, in a pegmatite from the Lovozero complex of the Kola Peninsula is reported in the paper by A.P. Khomyakov, H. Sørensen, O.V. Petersen and J.C. Bailey. This paper also reviews the occurrence of naujakasite in hyper-agpaitic lujavrites of the Ilímaussaq complex and examines why this mineral is common in Ilímaussaq, very rare in Lovozero and absent in the Khibina complex of the Kola Peninsula.

Steenstrupine is a very important rock-forming mineral in the hyper-agpaitic mineral associations of Ilímaussaq and is the main radioactive mineral in the Kvanefjeld uranium deposit. The mineral is generally metamict. Varieties with marginal anisotropic zones have, however, been known for a long time, but their origin was not well understood. New microprobe analyses of zoned steenstrupine crystals have demonstrated chemical differences which can explain the coexistence of metamict and crystalline steenstrupine (paper by A.P. Khomyakov and H. Sørensen).

Some rare minerals, as for instance steenstrupine, rinkite, epistolite and ussingite, are found in considerable quantities throughout the Ilímaussaq complex. Others like semenovite and chalcothallite have only been found in a few places as isolated grains. Until recently, leucophanite was considered to belong to the last-named group but is now known to occur in a number of localities within the complex (paper by H. Bohse, O.V. Petersen and G. Niedermayr).

In E.I. Semenov's pre-microprobe 1969 memoir on the mineralogy of Ilímaussaq, a number of minerals were described under preliminary names. E.I. Semenov's paper in the present volume reports the status of some of these minerals, including the occurrence of a new mineral, Na-komarovite.

In spite of a low average content of 1.9 ppm thallium in the complex, four minerals having Tl as a major component have been found. The paper by S. Karup-Møller and E. Makovicky reports the discovery of a new occurrence of thalcusite and discusses the tarnishing of polished sections of this mineral.

Brown prismatic crystals of rinkite are of widespread occurrence in Ilímaussaq. It was therefore a surprise that rinkite-looking crystals in a naujaite pegmatite were found to be hiortdahlite (the paper by E.R. Robles, F. Fontan, P. Monchoux, H. Sørensen and P. de Parseval). This brings important information about a stage of reduced alkalinity, in conformity with the occurrence of fayalite and hedenbergite in the adjacent naujaite.

More than 80 water-soluble minerals are known from the Khibina and Lovozero complexes. Until recently only three such minerals were known from Ilímaussaq: villiaumite, trona and thermonatrite. Water-soluble minerals have been looked for in drill cores and the material from the Kvanefjeld adit, but unfortunately not immediately after drilling and blasting. Therefore only two additional water-soluble minerals have been found: the discovery of natrophosphate is reported in the paper by O.V. Petersen, A.P. Khomyakov and H. Sørensen.

Nacareniobsite-(Ce) and vitusite are additional examples of minerals considered to be rare at Ilímaussaq. The paper by I.V. Pekov and I.A. Ekimenkova shows that these minerals are of more widespread occurrence, and provides examples of new types of rare-earth mineralisation in the complex.

Agpaitic and hyper-agpaitic nepheline syenites contain a number of rare Na–Be-minerals such as chkalovite and tugtupite, whereas common Be minerals such as beryl, euclase and chrysoberyl are absent. The paper by G. Markl examines the stability relations of the various Be minerals and explains why the agpaitic rocks contain Na–Be minerals and the order of formation of the minerals.

The fluid phase of agpaitic nepheline syenites is rich in hydrocarbons, especially methane. The paper by J. Konnerup-Madsen reviews the evolution of the fluids and brings new isotopic evidence in support of the non-biogenic origin of these hydrocarbons.

Henning Sørensen

Brief introduction to the geology of the Ilímaussaq alkaline complex, South Greenland, and its exploration history

Henning Sørensen

The Ilímaussaq alkaline complex, the type locality of agpaitic nepheline syenites, is made up of three intrusive phases, (1) augite syenite, (2) alkali acid rocks and (3) agpaitic nepheline syenites which occupy the major part of the complex. The agpaitic phase comprises a roof series, a floor series and an intermediate sequence of rocks. The roof series crystallised from the roof downwards beginning with non-agpaitic pulaskite and ending with distinctly agpaitic naujaite. The exposed part of the floor series is made up of the layered agpaitic nepheline syenite kakortokite. The intermediate sequence consists of several types of distinctly agpaitic lujavrites which are accompanied by occurrences of uranium and other rare elements.

The complex was first visited by K.L. Giesecke in 1806 and 1809. The first detailed mapping of the complex was carried out by N.V. Ussing in 1900 and 1908. He presented a precise description of the major rock types and an illuminating discussion of the petrology of the complex in his 1912 memoir. In the period 1912–1955 there was very limited activity in the complex. Exploration for radioactive minerals in Ilímaussaq was initiated in 1955 and in subsequent years followed by geological mapping carried out by the Geological Survey of Greenland. This led to a series of detailed studies of the occurrences of not only U, but also Be, Nb, REE and Zr, and to mineralogical, geochemical and petrological studies as well as commercial evaluation and drilling.

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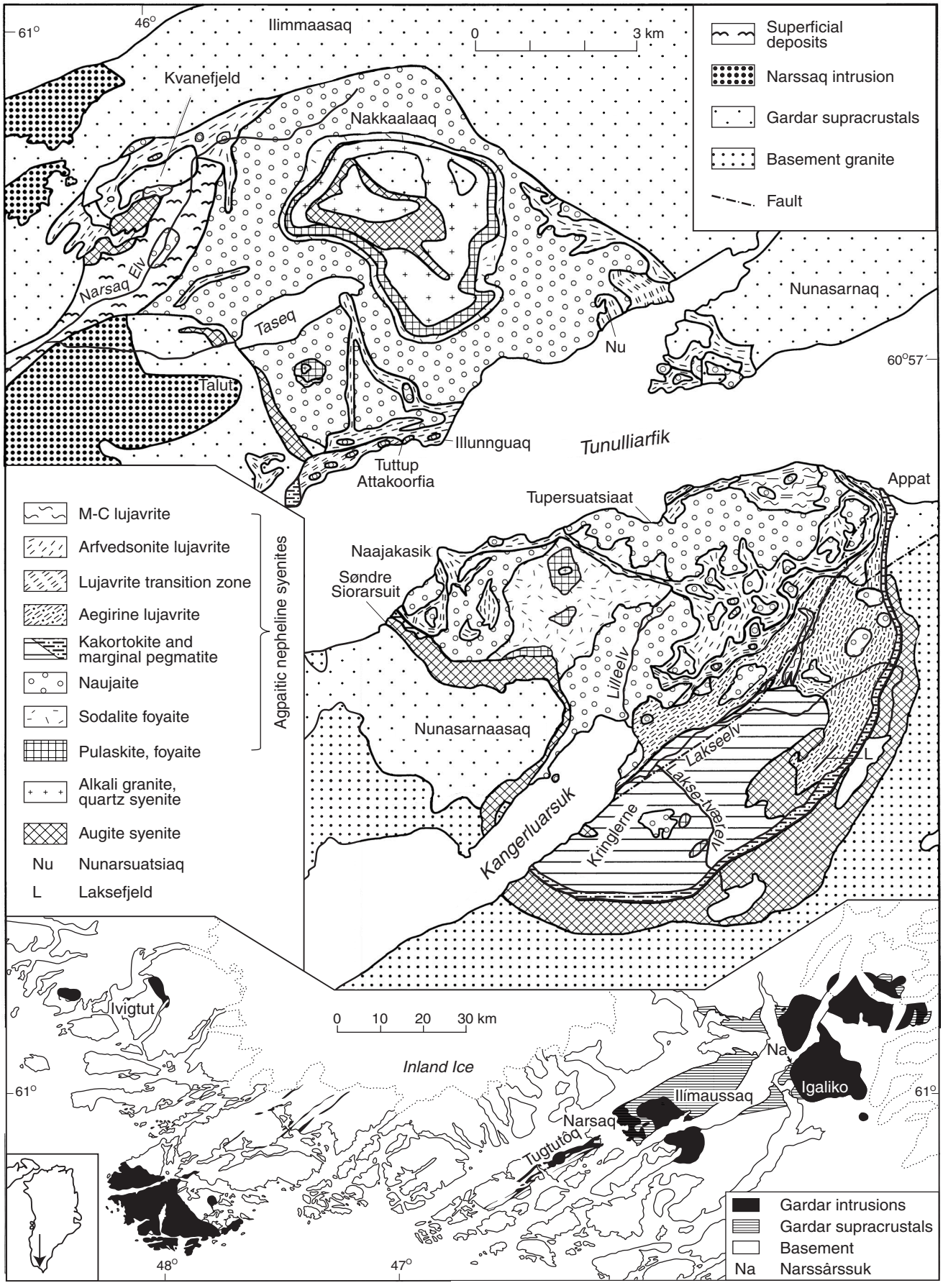
Keywords: agpaite, alkaline complex, Ilímaussaq, nepheline syenites, South Greenland, uranium deposit

The Ilímaussaq alkaline complex (Fig. 1) is one of a number of intrusive complexes in the Gardar igneous province, a mid-Proterozoic rift zone in South Greenland (Allaart 1973; Upton & Emeleus 1987; Kalsbeek *et al.* 1990; Macdonald & Upton 1993). The first detailed description, with a geological map and a discussion of the petrogenesis of the complex, was presented by Ussing (1912), who introduced the term agpaitic nepheline syenite. According to the recommendations of the IUGS Subcommission on the Nomenclature and Classification of Igneous Rocks (Le Maitre 1989), the term agpaitic should be restricted to peralkaline nepheline syenites having complex Zr-Ti silicate minerals such as eudialyte and rinkite instead of the more common minerals zircon, titanite and ilmenite. Since the appearance of Ussing's memoir numerous papers on the geology, mineralogy, petrology, geochemistry and economic geology of the complex have been published as is apparent from the bibliography presented in a companion report (Rose-Hansen *et al.* 2001). The most recent presentations of the general geology and petrology of the complex are those of Larsen & Sørensen (1987) and Sørensen & Larsen (1987).

The complex has been dated at 1143 ± 21 Ma (recalculated from Blaxland *et al.* 1976), 1130 ± 50 Ma (Paslick *et al.* 1993), 1160 ± 5 Ma (U–Pb, G. Markl, Tübingen University, personal communication 2000), 1160.7 ± 3.4 Ma and 1161.8 ± 3.4 Ma (Rb–Sr, T. Waight, Danish Lithosphere Centre, personal communication 2000).

The complex measures 17 × 8 km, and the exposed

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61°
46°
Ilimmaasaq
0
3 km
Kvanefjeld
Nakkaalaaq
Narsaq Elv
Taseq
Talut
Nu
Nunasarnaq
60°57′
Illunnguaq
Tunulliarfik
Tuttup Attakoorfia
Appat
Tupersuatsiaat
Naajakasik
Søndre Siorarsuit
Lilleelv
Nunasarnaasaq
Lakseelv
Laksefjeld
Kangerluarsuk
Kringlerne
Laksetværelv
Superficial deposits
Narssaq intrusion
Gardar supracrustals
Basement granite
Fault
M-C lujavrite
Arfvedsonite lujavrite
Lujavrite transition zone
Aegirine lujavrite
Kakortokite and marginal pegmatite
Naujaite
Sodalite foyaite
Pulaskite, foyaite
Alkali granite, quartz syenite
Augite syenite
Nu Nunarsuatsiaq
L Laksefjeld
Agpaitic nepheline syenites
Ivigtut
0 10 20 30 km
Inland Ice
Na
Igaliko
61°
Ilímaussaq
Narsaq
Tugtutôq
48°
47°
Gardar intrusions
Gardar supracrustals
Basement
Na Narssârssuk

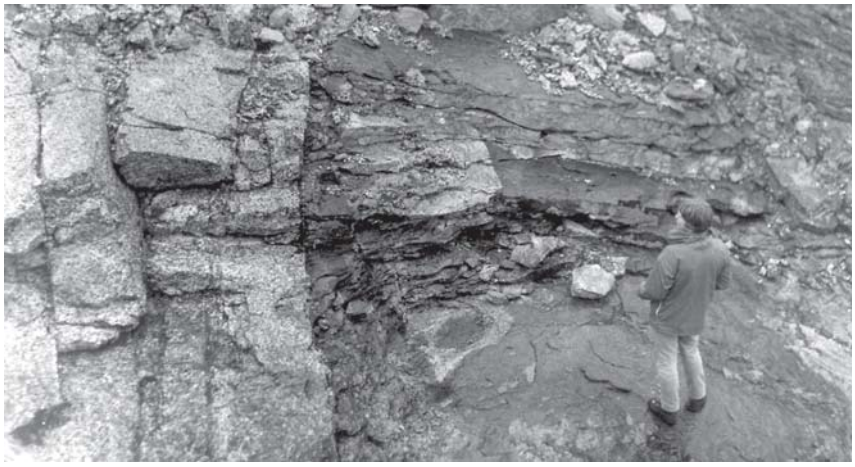


Fig. 2. The contact between the agpaitic rocks (on the right) and the augite syenite (on the left). The augite syenite is penetrated by fractures parallel to the contact, and rafts of augite syenite are enclosed in the agpaitic rock. Lakse-tværelv in the southernmost part of the complex.

vertical thickness is about 1700 m. It is estimated that the complex was emplaced 3–4 km below the contemporary surface at the discontinuity between the Ketilidian crystalline basement (*c.*1800 Ma, e.g. Chadwick & Garde 1996) and the overlying Eriksfjord Formation made up of continental sandstones and lavas of mainly basaltic composition. The basement and the overlying sandstones and lavas are intruded by numerous mainly basaltic dykes. The Eriksfjord Formation is the surface expression of Gardar activity and is preserved only in down-faulted blocks. Gardar activities embrace the period 1350 to *c.* 1120 Ma (Paslick *et al.* 1993); the Ilímaussaq complex is thus an expression of young Gardar activity.

Three intrusive phases may be distinguished in the formation of the Ilímaussaq complex (Fig. 1). The first phase is made up of augite syenite which is preserved only as a partial marginal shell and in the roof (Fig. 2). The second phase consists of alkali granite and quartz syenite which are found in the roof and as blocks engulfed by rocks of the third intrusive phase (Steenfelt 1981). The third intrusive phase occupies the major part of the complex. It is made up of a roof series, a floor series, and an intermediate sequence (Fig. 3).

The major rock types of the complex are presented in Table 1.

The roof series crystallised from the top downwards, forming the succession pulaskite, foyaite, sodalite foyaite and naujaite (Figs 3, 4). The contacts of these rocks grade into each other, but blocks of the uppermost rocks were loosened from the temporary roof of the magma chamber and engulfed by the underlying crystallising rocks. Larsen (1976) demonstrated that there is a gradual evolution in mineralogy from pulaskite to naujaite. The primary mineral association alkali feldspar, nepheline, fayalite, hedenbergite, apatite and titanomagnetite is substituted downwards by sodalite, nepheline, alkali feldspar, aegirine, arfvedsonite, eudialyte and aenigmatite. Sodalite is an interstitial mineral in the early stages of formation of the sodalite foyaite, but gradually becomes a liquidus phase and is a flotation cumulus phase in the naujaite. This rock is poikilitic and made up of crystals of sodalite, up to 1 cm across, enclosed in grains of alkali feldspar, aegirine, arfvedsonite and eudialyte, which may measure 10 cm or more. The sodalite foyaite and naujaite are agpaitic nepheline syenites.

The floor series is made up of a layered and laminated series of kakortokite, that is an agpaitic nepheline syenite with the major minerals alkali feldspar, nepheline, aegirine, arfvedsonite and eudialyte. The bottom of the series is unknown. The lowermost visible part is made up of centimetre-thick layers with varying contents of mafic minerals, feldspar and eudialyte. It displays trough structures and cross-bedding and is overlain by a series made up of 29 three-layer units, each about 10 m thick and made up of a lower black layer rich in arfvedsonite and an upper much thicker white layer rich in alkali feldspar (Fig. 5). Between these layers, there is often a thin red layer rich in eudialyte (Bohse *et al.* 1971). The black, red and white layers pass gradually into each other, whereas the black layers are separated from the underlying

Fig. 1. Simplified geological map of the Ilímaussaq alkaline complex. The area to the north of Tunulliarfik is based on Ferguson (1964), the area to the south of this fjord on Andersen *et al.* (1988), with minor modifications. Index map with names of Gardar complexes mentioned in the text. **M-C** lujavrite: medium- to coarse-grained. For further explanation see Table 1.

Table 1. The major rock types of the Ilímaussaq alkaline complex

Rock type	Texture	Essential minerals*	Minor minerals
Augite syenite	hypidiomorphic to xenomorphic granular, massive or layered, medium to coarse	alkali feldspar, hedenbergite, titanomagnetite, ferropargasite, olivine, biotite	ternary feldspar, apatite, pyrrhotite, nepheline
Pulaskite and foyaite	massive, medium to coarse, platy feldspars	alkali feldspar, nepheline, hedenbergite, fayalite, aegirine-augite to aegirine, katophorite	titanomagnetite, apatite, aenigmatite, biotite, fluorite, eudialyte
Sodalite foyaite	foyaitic, coarse	alkali feldspar, nepheline, sodalite, aegirine-augite to aegirine, katophorite, arfvedsonite	fayalite, hedenbergite, apatite, aenigmatite, titanomagnetite, eudialyte, rinkite, fluorite, biotite
Naujaite	poikilitic, coarse to pegmatitic	sodalite, alkali feldspar, nepheline, aegirine, arfvedsonite, eudialyte	aenigmatite, hedenbergite, aegirine-augite, fayalite, apatite, katophorite, rinkite, polylithionite, biotite, sphalerite, pectolite, villiaumite, fluorite, titanomagnetite
Kakortokite	laminated, layered, medium to coarse	alkali feldspar, nepheline, aegirine, arfvedsonite, eudialyte	sodalite, aenigmatite, magnetite, rinkite, fluorite, löllingite, sphalerite, galena
Lujavrite†	laminated, fine-grained; sometimes layered or massive, medium to coarse	microcline, albite, nepheline, sodalite, analcime, naujakasite, aegirine, arfvedsonite,eudialyte,	monazite, britholite, villiaumite, sphalerite, pectolite, steenstrupine, lovozerite, vitusite, polylithionite, ussingite, lueshite, neptunite
Alkali granite, quartz syenite	hypidiomorphic granular, medium to coarse	alkali feldspar, quartz, aegirine, arfvedsonite	aenigmatite, elpidite, zircon, ilmenite, pyrochlore, neptunite, fluorite, sphalerite

* Analcime and natrolite are secondary minerals in most rocks.

† There are several types of lujavrites. Three major groups may be distinguished: *aegirine or green lujavrite* with aegirine being the dominant mafic mineral; *arfvedsonite or black lujavrite,* fine-grained, often laminated with arfvedsonite as the dominant mafic mineral; *medium- to coarse-grained lujavrite (M-C lujavrite)* with arfvedsonite as the dominant mafic mineral and generally showing foyaitic textures. *Naujakasite lujavrite* is a variety of arfvedsonite lujavrite containing naujakasite instead of nepheline and with steenstrupine instead of eudialyte.

white layers by sharp contacts. Bohse *et al.* (1971) have numbered the layered units, the lower part from unit no. –11 to unit 0, the upper part from units 0 to +17. The most recent discussions of the origin of the layering are given by Larsen & Sørensen (1987) and Bailey (1995); see also Upton *et al.* (1996).

The lowermost part of the naujaite and the lowermost sodalite-bearing part of the kakortokite may be contemporaneous (Sørensen & Larsen 1987), but the floor sequence which formed simultaneously with the greater part of the roof zone is unexposed.

The kakortokite and in places the naujaite are separated from the augite syenite rim by a marginal pegmatite zone (cf. Bohse *et al.* 1971; Bohse & Andersen 1981).

The layered series of kakortokite passes gradually upwards into a thin unit of transitional layered kakortokite which again passes gradually into the intermediate sequence of lujavrites. These are agpaitic meso- to melanocratic nepheline syenites which are generally fine-grained, laminated and occasionally layered (Sørensen & Larsen 1987).

The lowermost part of the lujavrite sequence is made up of green rocks rich in aegirine and in places also in eudialyte. Bohse & Andersen (1981) distinguish a

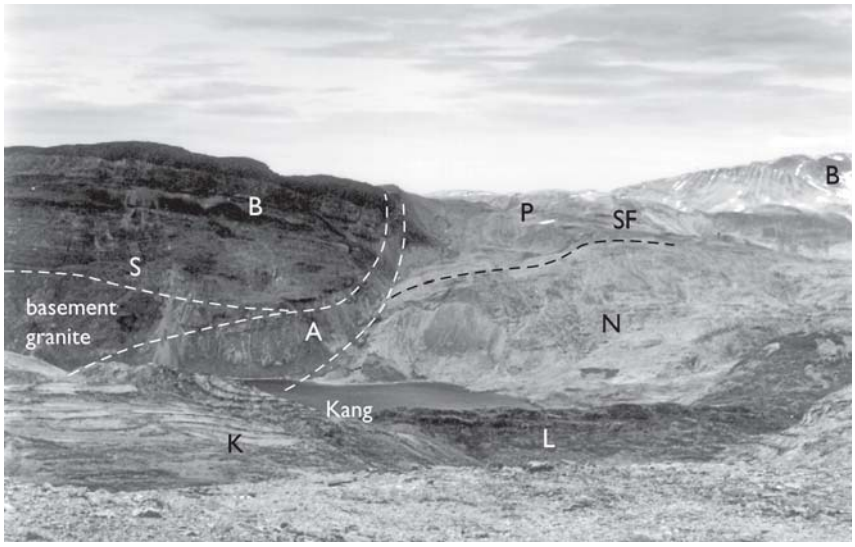


Fig. 3. A section through the complex viewed from Kringlerne plateau towards the north. Foreground layered kakortokites (**K**), the dark rocks in the middle ground belong to the intermediate sequence of lujavrites (**L**). The light grey rocks in the wall facing south towards the fjord Kangerluarsuk (**Kang**) are made up of the roof series with pulaskite-foyaite (**P**) and sodalite foyaite (**SF**) in the upper part, naujaite (**N**) in the lower part bordering the augite syenite shell (**A**). The contact between the roof zone and the basement granite and its overlying sandstone (**S**) with intercalated basalt (**B**) on the mountain Nunasarnaasaq (1442 m, on the left) is very sharp. The high mountains in the far distance (to the north of Tunulliarfik, see Fig. 1) have remnants of the volcanic roof (**B**) on top of the roof series (cf. Fig. 4). The distance to Kangerluarsuk is about 2 km.

lower aegirine lujavrite I zone which gradually passes into the overlying aegirine lujavrite II. The upper part of the intermediate sequence is made up of black arfvedsonite-rich, fine-grained laminated rocks. Dykes and sheets of lujavrite intersect the rocks of the roof zone; in places the naujaite in the immediately overlying roof is brecciated and strongly altered by the lujavrite. On the Kvanefjeld plateau in the northernmost part of the complex (Fig. 6), lujavrites are in contact with the volcanic roof of the complex, which is strongly fenitised adjacent to the lujavrites (Sørensen *et al.* 1969, 1974). There are several generations of lujavrite. One of the latest phases consists of naujakasite lujavrite rich in steenstrupine (Sørensen *et al.* 1974; Sørensen 1997a). It is an important feature that steenstrupine substitutes for eudialyte in the most evolved lujavrites. This represents the hyper-agpaitic stage of development characterised by naujakasite, steenstrupine, ussingite, vitusite and other minerals (Sørensen & Larsen 2001, this volume). The youngest lujavrites are the so-called medium- to coarse-grained lujavrites (M-C lujavrites); they are accompanied by pegmatites and hydrothermal veins containing steenstrupine, pyrochlore, Be and Cu minerals, and by fenitisation of the volcanic roof. The Kvanefjeld uranium deposit is made up of steenstrupine lujavrites and fenitised roof rocks rich in steenstrupine.

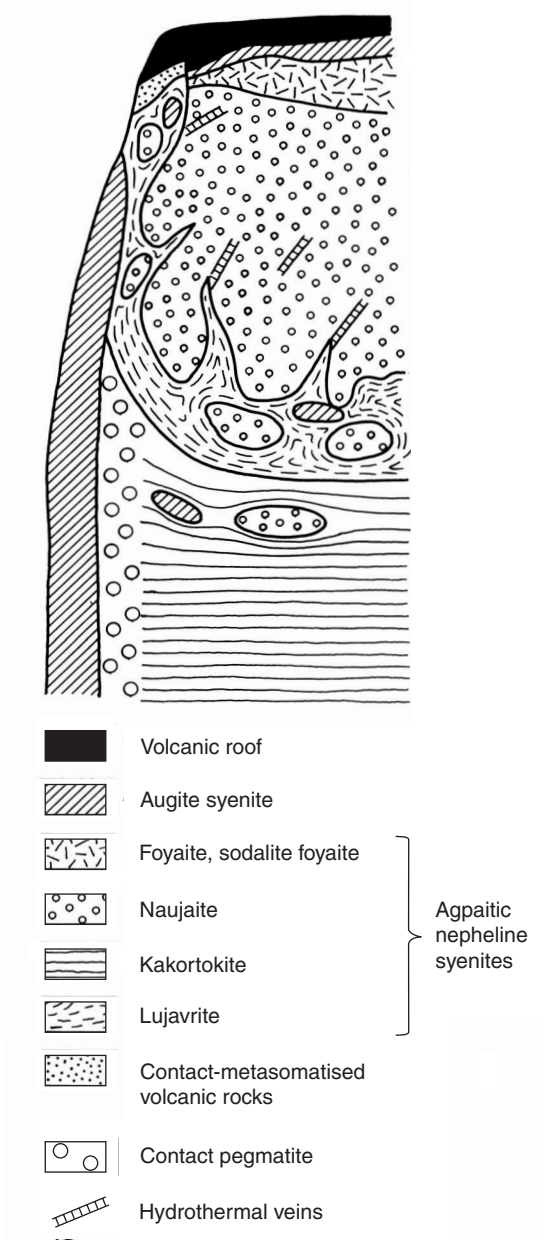


Fig. 4. Schematic section through the *c.* 1700 m of exposed stratigraphy of the Ilímaussaq alkaline complex.



Fig. 5. The lowermost exposed part of the complex, made up of thin layers of kakortokite with trough layering displaced by a minor fault (arrow, lower left). In the background the main series of kakortokite made up of a repetition of three-layer units, in which the black and white layers can be distinguished. The faulted white trough band is approximately 5 m wide and 15 cm thick.

The arfvedsonite lujavrites and the M-C lujavrites have the highest contents of Li, Rb, Be, REE, Zn, U, Th, etc. of all the rocks of the complex, whereas the kakortokites have the highest contents of Nb, Ta, Zr, Hf and Y (Gerasimovsky 1969; Kunzendorf *et al.* 1982; Sørensen 1992; Bailey *et al.* 2001, this volume).

Fluid inclusions in the minerals of the agpaitic rocks of the complex are rich in methane and other hydrocarbons (cf. Konnerup-Madsen 2001, this volume).

The basalts in the part of the Gardar rift zone which contains the Ilímaussaq and Tugtutôq igneous complexes (Fig. 1) are richer in alkalis, P, Ba, Sr, Nb and LREE than the basic rocks in other parts of the Gardar province. This indicates an origin in a mantle source enriched in incompatible elements, perhaps because of metasomatism (Macdonald & Upton 1993, Upton 1996). The agpaitic nepheline syenites of the Ilímaussaq complex are considered to be products of extended fractionation of transitional to alkali basaltic melts in deep magma chambers combined with some crustal contamination (Larsen & Sørensen 1987; Stevenson *et al.* 1997; Bailey *et al.* 2001, this volume). The Tugtutôq–Ilímaussaq zone is underlain by a gravity high which may represent cumulates of olivine and other mafic minerals accumulated during the fractionation processes (Blundell 1978). In this connection it is of interest to note that the Ilímaussaq complex is marked as a magnetic low on the aeromagnetic map of the region (Thorning & Stemp 1997).

The eudialyte-rich parts of the naujaites, kakor-



Fig. 6. The Narsaq Elv valley. The mountain on the left is Kvanefjeld (685 m) made up of volcanic rocks in the upper part and lujavrites, naujaites, etc. in the lower part. The Ilimmaasaq mountain (1390 m, centre) is made up of basaltic rocks underlain by lujavrites. The mountain on the right is Nakkaalaaq 1334 m) made up of the roof series; the slope below, the Taseq slope, is made up of naujaite. The distance between Kvanefjeld and Ilimmaasaq is approximately 4 km.

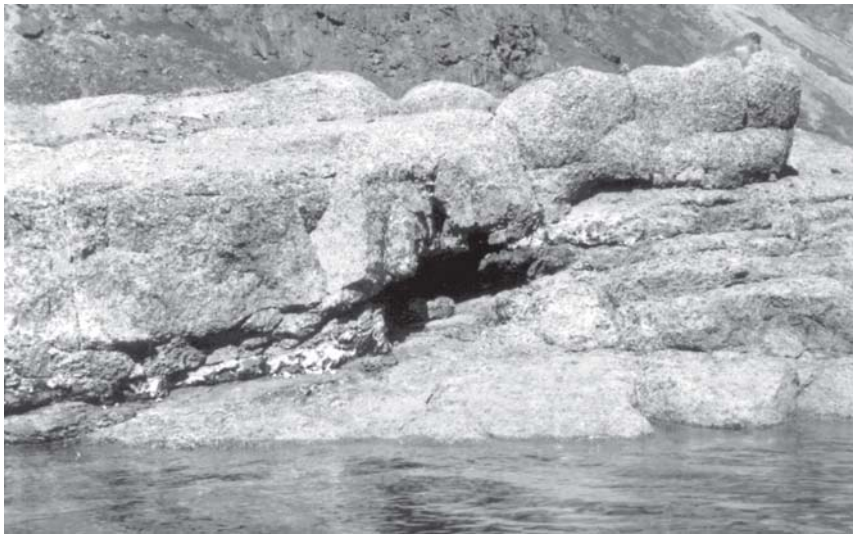


Fig. 7. Layered pegmatite, 0.8 m thick, in naujaite located on the small island in the inner part of Kangerluarsuk. The cave was made by Steenstrup when he collected large samples of eudialyte for the Cryolite Company in 1888. The cave, about 1 m high at the time of photographing in 1964, has since been considerably enlarged by mineral collectors. An attempt is being made to protect the island.

tokites and lujavrites represent an enormous resource of Zr, Nb and REE, especially HREE (Bohse *et al*. 1971; Sørensen 1992). These rock types are accompanied by pegmatites and hydrothermal mineralisations. Examples are ussingite veins rich in chkalovite and other Be minerals (Semenov 1969; Engell *et al*. 1971), occurrences of pyrochlore and other Nb minerals (Hansen 1968), and the above-mentioned Kvanefjeld uranium deposit (Sørensen *et al*. 1974).

History of exploration

Various aspects of the history of exploration of the Ilímaussaq complex have been presented by Sørensen (1967) who considered the history up to 1966, by Nielsen (1981) who described the exploration history of the Kvanefjeld uranium deposit, and by Bondam (1995) who compiled an overview of exploratory activities and environmental studies based on the archives of the Geological Survey of Greenland. In the following a survey of the history of exploration will be presented with emphasis on the period after 1964.

The period 1806–1912

The first scientific study of the complex was carried out by K.L. Giesecke (1761–1833) who made extensive collections of minerals in 1806 and 1809 resulting in the discovery of the minerals arfvedsonite, eudialyte and sodalite.

K.J.V. Steenstrup (1842–1913) visited the complex several times on behalf of the Commission for the Direction of Geological and Geographical Investigations in Greenland and Kryolith-Mine- og Handels-Selskabet (hereafter referred to as the Cryolite Company) and collected numerous mineral and rock samples (Fig. 7). The minerals were examined by J. Lorenzen (1855–1884) who described the new minerals polylithionite, rinkite and steenstrupine.

G. Flink (1849–1932) visited the complex in 1883. His mineral collections from Ilímaussaq were studied by O.B. Bøggild (1872–1956) and C. Winther (1873–1968), who established the new minerals britholite, epistolite and naujakasite, the last-named mineral as late as 1933.

The first thorough geological mapping and petrological investigation of the complex was by N.V. Ussing (1864–1911) in 1900 and 1908 (Fig. 8). His memoir on the geology and petrology of the complex and neighbouring areas was published in 1912 after his untimely death. The memoir gives a detailed interpretation of the petrology of the complex, which by and large still stands today. It introduced the term agpaitic and discussed processes such as overhead stoping, magmatic differentiation, igneous layering, assimilation and feldspar solid solution series. The memoir is one of the corner stones of igneous petrology. Bøggild (1913), who assisted Ussing in the field work, discovered and named the mineral ussingite.

The period 1912–1955

Research activities in the Ilímaussaq complex were very limited from the time of Ussing's memoir in 1912



Fig. 8. N.V. Ussing (left) and O.B. Bøggild (right) and their Greenlandic assistants at the cryolite mine at Ivittuut (Ivigtut), Greenland 1900. Photo: Geological Museum archive, Copenhagen.

until mineral exploration commenced in 1955. The main events are mentioned below:

S.M. Gordon visited the complex in 1923 and published three papers about his examination of mineral localities in South Greenland (Gordon 1924).

C.E. Wegmann (1938) studied the geological chronology of South Greenland and introduced the term Gardar period. He interpreted the rocks of the Ilímaussaq complex as the results of metasomatic processes.

The Cryolite Company (Kryolitselskabet Øresund A/S) undertook investigation of eudialyte-rich naujaite and kakortokite in 1939 and 1946 (Bøgvad 1950a, b), but concluded that exploitation of the eudialyte was not feasible at that time.

The Geological Survey of Greenland (GGU), which was established in 1946, made reconnaissance visits to the complex in 1946 and 1951.

The period 1955–1964

In 1955 the Danish government, on the recommendations of Professor Niels Bohr, the President of the Danish Atomic Energy Commission (AEK), initiated prospecting for uranium deposits in Greenland (Fig.



Fig. 9. Professor Niels Bohr expressing his thanks for the honorary citizenship of Narsaq in 1957.



Fig. 10. The team from the University of Copenhagen which in 1964 initiated the university-directed Ilímaussaq project, and its Russian partners. From left to right: B. Leth Nielsen, J. Rose-Hansen, O.V. Petersen, H. Sørensen, E. Frantzen, V.I. Gerasimovsky, T. Østergaard, E.I. Semenov, K. Hansen and behind her E. Bondesen and S. Andersen. In the background from left to right Kvanefjeld, Ilimmaasaq, Narsaq Bræ, Nakkaalaaq with the Taseq plateau and slope, and the mountain Talut.

9). GGU recommended that prospecting for uranium should begin in the Ilímaussaq complex, the only known occurrence of radioactive minerals in Greenland at that time, apart from allanite in pegmatites. A primitive Geiger counter survey was carried out by military personnel. The southern half of the complex was covered in 1955, the northern half in 1956, in which year the Kvanefjeld deposit was discovered (Nielsen 1981; Sørensen 1981; Bondam 1995). In 1957 additional detailed studies of the Kvanefjeld deposit were made with chemical assays of the uranium ore and the first attempts at developing a method of extracting the uranium from the ore. The ore was found to be refractory and impossible to treat with conventional acid or carbonate leaching methods.

The first drilling programme was carried out in 1958 resulting in 36 holes and a total core length of 3728 m. The extraction experiments were continued in the following years and a method of sulphatising roasting of the ore was designed. In 1962 180 t of ore were taken out in a 20 m long adit in the most radioactive part of the deposit for testing the method of sulphatising roasting. In the same year two of the Kvanefjeld drill holes were deepened with an additional core length of 270 m and seven holes with a total core length of 1400 m were drilled in lujavrites in other parts of the complex.

AEK constructed a base camp at Dyrnæs in connection with the drilling operations in 1958. Dyrnæs is the site of a former Norse settlement located about 5 km to the north of the town Narsaq. This camp was transferred to GGU and served as the base for the geological mapping of the whole complex and for the regional geological mapping of South Greenland. The regional mapping programme was concluded in 1963 after which most of the camp was moved to the site for the next regional mapping programme further to the north. Some of the houses, however, remained in Dyrnæs to serve as the base camp for the follow-up geological investigations of the Ilímaussaq complex, which were entrusted to staff and students from the Geological Institute and Museum of the University of Copenhagen, in co-operation with and with logistic and economic support from GGU and AEK.

A geological map of the Ilímaussaq complex at 1:20 000 was published in 1964 (Ferguson 1964). Hamilton (1964) presented the first geochemical investigation of the northern part of the complex and Ferguson (1970) presented a detailed examination of the geochemistry of the kakortokites.

A number of mineralogical papers were published in the period 1955–1964. Examples are: notes about several minerals (Danø & Sørensen 1959), the discovery of the beryllium minerals chkalovite and tugtupite (Sørensen 1960, 1963), the first description of villiaumite from the complex (Bondam & Ferguson 1962), a detailed examination of the occurrence of steenstrupine (Buchwald & Sørensen 1961; Sørensen 1962) and the discovery of a number of opaque minerals (Oen & Sørensen 1964).



Fig. 11. Diamond drilling on the Kvanefjeld plateau in 1969. A fine view of the upper part of Narsaq Elv valley with the Narsaq Bræ in centre. The thin zone of light-coloured rock above the glacier is naujaite intruding the roof of volcanic rocks in the upper part of Nakkaalaaq mountain.

The period 1964–1977

Staff and students from the University of Copenhagen were, as mentioned above, entrusted with the detailed follow-up investigations in the Ilímaussaq complex. This activity was directed by H. Sørensen, J. Rose-Hansen and in the last phase of the project by B.L. Nielsen (Fig. 10). Field teams worked every summer from 1964 to 1977. About 25 persons took part in the field work and were supported by about 15 more in the follow-up laboratory studies and publication of results. A large number of field assistants and technicians took part in this work. Hydrogeologists, ecologists and geochemists were involved in the accompanying environmental studies.

From the early stages of this activity it was clear that much could be gained if Russian scientists became involved in the work. The Ilímaussaq complex bears a close resemblance to the Khibina and Lovozero complexes of the Kola Peninsula, two complexes which have been examined in great detail by Russian scientists resulting, among other things, in the discovery of a number of new minerals. Two Russian mineralogists, Professors V.I. Gerasimovsky and E.I. Semenov, who had made impressive contributions to the study of the mineralogy and geochemistry of the two Kola complexes, were therefore invited to take part in the Greenland field work in 1964. This gave a significant impetus to the new research programme. Gerasimovsky (1969) produced chemical analyses for major and trace elements of 23 rock samples representing the main rock types of the complex and Semenov (1969) described 120 minerals from the complex, among them five new minerals: chalcothallite, cuprostibite, ilimaussite, tundrite-(Nd) and sorensenite.

Major activities in the research programme of the university geologists were:

1. Geological mapping of the Kvanefjeld area (Sørensen *et al.* 1969, 1974). In connection with this work six exploratory holes totalling 1621 m were drilled in 1969 (Fig. 11), two of these in the lujavrites in the northern part of the plateau which had not been investigated in the earlier phases of uranium exploration. The reasonably assured uranium reserves were estimated to be 5800 metric t U, average grade 310 ppm U; additional reasonably assured ore with a grade of 292 ppm U was estimated to 8700 metric t U. In order to facilitate the geological supervision of the drilling programme and as a general support of the geological investigations in the Kvanefjeld area, a hut was set up in 1968.

2. Mapping of the kakortokites in the southern part of the complex with unravelling of the layered sequence. The resources of Zr and Nb were estimated to 51.6×10^6 metric t ZrO_2 and 5.4×10^6 metric t Nb_2O_5 in the examined part of the complex (Bohse *et al.* 1971).

3. Geological mapping and detailed examination of veins containing beryllium minerals in the north-

ern part of the complex (Semenov 1969; Engell *et al.* 1971).

4. Examination of the occurrences of U, Zr, Nb and Be minerals was carried out in close co-operation with scientists from the Danish Atomic Energy Commission Research Establishment Risø (now Risø National Laboratory) and resulted in development of apparatus to be used in the field and in the laboratory. Examples are: portable beryllium prospecting instruments (Løvborg *et al.* 1968a; Engell *et al.* 1971), portable X-ray fluorescence equipment for quantitative determination of Zr and Nb in the field (Bohse *et al.* 1971; Kunzendorf 1971, 1973), and gamma-spectrometers for use in the field, for assaying drill holes and drill cores and for laboratory determination of contents of U, Th and K in minerals and rocks (e.g. Løvborg *et al.* 1968b, 1972, 1980).

5. From 1968 to 1976, the Danish company Superfos A/S explored the eudialyte-rich kakortokites and naujaites in the southern half of the complex and developed methods to extract Zr, Nb, REE and Y from eudialyte concentrates, but found no markets for the products. To support the bulk sampling undertaken in 1968, a house was constructed at the mouth of Lakseelv in Kangerluarsuk. In subsequent years this house served as the base for many field teams working in this part of the complex.

6. A new geological map over the southern half of the complex in the scale of 1:20 000 (Andersen *et al.* 1988).

7. Collection of 120 samples for detailed geochemical analysis of contents of about 50 elements in whole rocks and separated mineral fractions (work still in progress, see Bailey *et al.* 2001, this volume).

8. Many studies of minerals and rocks collected in the series *Contributions to the mineralogy of Ilímaussaq* (updated in Rose-Hansen *et al.* 2001). The following new minerals were described in the period 1964–1977: sorensenite, chalcothallite, ilimaussite, tetranatrolite (described under the name tetragonal natrolite), tundrite-(Nd), semenovite, skinnerite, cuprostibite and rohaite (see list of minerals in Petersen 2001, this volume).

9. A study of fluid inclusions in the minerals of the complex initiated in co-operation with Russian colleagues (Petersilie & Sørensen 1970; Sobolev *et al.* 1970) demonstrated that fluid inclusions of the agpaitic rocks, like the rocks of the Khibina and Lovozero complexes of the Kola Peninsula, are rich in hydrocarbons. This discovery was followed by detailed studies of the rocks of the complex, e.g. Konnerup-Madsen *et al.* (1979, 1988), Konnerup-Madsen & Rose-Hansen (1982), Konnerup-Madsen (2001, this volume).

10. An investigation of the water balance in the Narsaq Elv valley, which intersects the northern part of the complex, was carried out as one of the Danish contributions to the International Hydrological Decade (Hansen & Pulawski 1966; Larsen 1972, 1973).

11. An ecological and environmental geochemical programme, the *Narsaq Project*, supported by the Danish Natural Science Research Council was carried out 1974–1977 (Larsen 1977; Rose-Hansen & Sørensen 1977; Rose-Hansen *et al.* 1977; Nielsen 1979). The project was initiated at a time when exploitation of the Kvanefjeld uranium deposit was considered possible within a few years. The purpose of the project was to describe the natural state of the environment around the Ilímaussaq complex before the opening of a uranium mine. The project also had the aim to study the distribution of rare elements, including uranium, around the complex, which may be considered a marked geochemical anomaly (Rose-Hansen *et al.* 1986). As described in a later paragraph, uranium mining in the area was given up for political reasons, which meant that the *Narsaq Project* was also discontinued.

1977 to the present

The 1977 field season marked the termination of the field activities in Ilímaussaq by staff and students from the University of Copenhagen. The Dyrnæs base camp was thereafter used to support other activities such as the *Kvanefjeld Uranium Project* and the *Syduran Project* (see below). The base was abandoned in 1983 with the termination of the *Kvanefjeld Uranium Project*. This reduced the logistic support of field work in the complex, but minor operations have nevertheless con-

tinued. One example is mineralogical studies including examination of material from the tunnelling and drilling of the Kvanefjeld uranium deposit mentioned below. This resulted in the discovery of the new minerals vitusite, kvanefjeldite and tuperssuatsiaite. A progress report bringing results of field and laboratory studies up to 1980 was published in 1981 (Bailey *et al.* 1981).

The *Kvanefjeld Uranium Project* was carried out from 1978 to 1983 with the aim of examining the economic potential of the Kvanefjeld uranium deposit. In 1977, this project was preceded by a drilling programme comprising 27 holes with a total core length of 5103 m in the lujavrites in the northern part of the Kvanefjeld plateau and to the east of Kvanefjeld (Nyegaard *et al.* 1977). It was found that the method of sulphatising roasting applied to the steenstrupine-bearing lujavrites in the northern part of the Kvanefjeld plateau gave a low recovery of uranium, whereas pressurised carbonate leaching gave a satisfactory recovery. In order to test this method in a pilot plant established at Risø National Laboratory, 20 000 metric t of ore were extracted from a 960 m long horizontal adit driven through the deposit (Nyegaard 1980). The opening of the adit was in the slope above the Narsaq Elv valley 100–150 m below the surface of the plateau (Nyegaard 1979). In total 4700 metric t of ore were shipped to Risø and treated in the pilot plant. It was found that the method gave a recovery of more than 80% of the uranium content of the different varieties of ore (Forsøgsanlæg Risø 1984; Sørensen & Jensen 1985; Sørensen *et al.* 1990). The reasonably assured resources were estimated to 20 440 metric t U in ore with an average concentration of 365 ppm U (Forsøgsanlæg Risø 1984). Detailed mineralogical studies of the uranium ore were carried out in connection with this project (Makovicky *et al.* 1980).

The *Kvanefjeld Uranium Project* also presented proposals for the planning of the mine and the ore dressing facilities and energy supply, as well as studies of radiation exposure and the environmental impact of the mining activity, including the effects of leaching of tailing products (Pilegaard 1990). Overviews of the many internal reports of this project are found in the report on the project (Forsøgsanlæg Risø 1984) and in Bondam (1995).

In the years 1979–1982, the *Syduran Project* carried out a regional exploration for uranium in South Greenland by means of airborne radiometric surveying and stream sediment geochemistry. This work confirmed the anomalous character of the complex and its surroundings (Armour-Brown *et al.* 1983, 1984; Thorning *et al.* 1994; Schjøth *et al.* 2000).

Exploration of the zirconium-rich kakortokites continued in 1985, when the Danish company A/S Carl Nielsen obtained an exclusive licence to carry out exploration centred around the exposed kakortokites and the adjacent marginal pegmatite in the southern part of the complex. The thickest layer of red kakortokite, layer +16, was examined in two drill holes in 1986. During 1987, potentially economic eudialyte-rich parts of the marginal pegmatite, kakortokites and naujaites within the concession area were mapped and sampled, and samples of the marginal pegmatite were metallurgically tested.

In 1987, the Canadian company Highwood Resources Ltd. obtained permission to explore areas between the fjords Tunulliarfik and Kangerluarsuk and carried out bulk sampling and drilling in order to test the feasibility of exploitation of eudialyte-rich rocks. This company was joined by Platinova Resources Ltd. and Aber Resources Ltd. In 1988 this group and A/S Carl Nielsen formed a joint venture, combining their mineral licences. The main target was the exposed kakortokites, minor targets were the marginal pegmatites in the southern part of the complex. The joint venture co-operation was continued in 1990 with an extensive drilling programme and metallurgical testing of potential ores from the southern part of the complex. At the end of this activity the Canadian partners and the Danish participants went through a period of restructuring resulting in Highwood Resources taking over all interests in the prospect at the end of 1992.

In 1992 the Danish company Mineral Development International A/S (MDI) obtained the exclusive right to explore the sodalite-rich naujaites in the northern part of the complex. The aim was to investigate the possibilities of using sodalite as raw material for the production of synthetic zeolites.

None of the above-mentioned activities have so far been able to demonstrate with certainty that beneficiation of eudialyte and sodalite can be economically viable.

A number of research projects involving colleagues from other countries have been supported by various foundations. The Danish Natural Science Research Council supported a Canadian–Danish project aiming at a comparison of the mineralogy of Mont Saint-Hilaire, Quebec, with the Narssârssuk mineral occurrence associated with the Igaliko Complex, South Greenland, and the Ilímaussaq complex.



Fig. 12. Destruction of one of the tugtupite localities by mineral collectors' excessive use of blasting. The Kvanefjeld plateau July 1974. Scale: Professor Brian Mason, Washington DC, USA, one of the many scientists who have visited the Ilímaussaq complex. Since the photograph was taken this site has been transformed into a veritable crater, about 20 m in diameter and a few metres deep, as a result of the hunt for deeper-lying tugtupite veins.

The Danish company First Development International A/S in 1993 supported a Danish–Russian project consisting of an examination of the drill cores from the 1977 drilling programme kept at the Risø National Laboratory. The aim was to find some of the water soluble minerals discovered in the Khibina and Lovozero complexes (Khomyakov 1995). The drill cores are rich in villiaumite, but holes in the samples indicate that other water soluble minerals have been dissolved during and after drilling. Only one of the Kola minerals was discovered, natrophosphate (Petersen *et al.* 2001, this volume).

In 1994–1997 INTAS (International Association for the Promotion of Co-operation with Scientists from the Independent States of the Former Soviet Union) supported a Danish–French–Russian–Spanish research co-operation with the purpose of promoting comparative studies of the mineralogy of agpaitic nepheline syenites in Ilímaussaq, the Khibina and Lovozero complexes of the Kola Peninsula, and the Tamazeght complex, Morocco. Field work was carried out in Ilímaussaq in 1994, in Khibina and Lovozero in 1997 and in Tamazeght in 1999. One of the outcomes of this work is the paper on hiortdahlite in this volume (Robles *et al.* 2001).

The Danish Natural Science Research Council in 1997 supported an Austrian–Danish research project with the purpose of studying pegmatites and hydrothermal veins and the relations to their country rocks in the Ilímaussaq complex and at the Narssârssuk mineral locality associated with the Igaliko Complex in South Greenland.

A number of excursions, workshops and summer schools have taken place in the Ilímaussaq complex since 1981:

1981, excursion arranged for the directors of the European geological surveys.
1982, excursion for Société Minéralogique de la France.
1984, summer school on environmental geology sponsored by the Nordic Council of Ministers (Nordisk Ministerråd 1984).
1986, NATO Advanced Research Workshop on Igneous Layering (Parsons 1987).
1989, excursion for colleagues from Naturhistorisches Museum and Österreichisches Mineralogische Gesellschaft.
1990, Nordic summer school on igneous petrology.
1992, ABC Mines from École des Mines, Paris, an excursion to Iceland and the Igaliko and Ilímaussaq complexes.

A number of mineral collectors and societies of mineral collectors have visited the complex resulting in the discovery of the minerals bavenite, dorfmannite, fersmite, nacareniobsite-(Ce) and turkestanite. This activity has put heavy pressure on many of the mineral localities in the complex resulting in transformation of many of them into heaps of boulders (Fig. 12).

A significant part of the research carried out in the complex has resulted in the awarding of academic degrees in mineralogy and geology by universities in Denmark and abroad. The Danish awards comprise: three degrees of dr.scient., six lic.scient. and Ph.D. degrees, 18 cand.scient. degrees in geology, five cand.

scient. and four Ph.D. degrees in biology and ecology as a spin-off of the *Narsaq Project*; three scientific papers have been awarded the gold medal of the University of Copenhagen. The number of degrees awarded in other countries is not known with certainty.

Concluding remarks

An impressive number of papers have been published on the geology, mineralogy, petrology and geochemistry of the Ilímaussaq alkaline complex (Rose-Hansen *et al.* 2001). Major exploration programmes have investigated the economic potential of rocks rich in uranium, zirconium, niobium and beryllium and the technical use of sodalite. Much remains, however, to be investigated and published.

The southern half of the complex has been mapped in the scale of 1:20 000; the northern half should be mapped in the same detail.

In order to gain a fuller understanding of the petrogenesis of the complex a number of drill holes are required, first of all in the deepest part of the kakortokites to explore the hidden layered floor series, and through the roof series to give access to the sheets of augite syenite, alkali granite, etc. occurring in a topography which makes access difficult. Many aspects of the geology of the complex have not yet been studied in detail, this applies for instance to the spectacular layering of some of the arfvedsonite lujavrites. Future drilling programmes and quarrying activities should take special measures to safeguard the water-soluble minerals because these must be collected immediately on exposure to the atmosphere.

The agpaitic nepheline syenites are among the most evolved igneous rocks known. Petrological studies of the rocks of the complex can therefore bring important knowledge about many natural petrological processes.

The Ilímaussaq complex contains a treasure of rare elements and minerals. Future developments in material sciences and the need for rare elements in new applications should therefore be followed closely in order to be ready when new opportunities become apparent for use of elements abundant in the complex.

The Ilímaussaq complex is vulnerable if exposed to invasions of mineral collectors, local as well as foreign visitors (Fig. 12). Some mineral occurrences have already been exhausted, others destroyed; an example is the tugtupite occurrence in the south-western part of the Kvanefjeld plateau (Sørensen 1997b). It may be necessary to regulate the collection of minerals in the complex. On the other hand, the complex elucidates many geological processes in a very clear and informative way and should therefore be open for excursions, summer schools, etc. and be a show window for the geological sciences.

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List of all minerals identified in the Ilímaussaq alkaline complex, South Greenland

Ole V. Petersen

About 220 minerals have been described from the Ilímaussaq alkaline complex. A list of all minerals, for which proper documentation exists, is presented with formulae and references to original publications. The Ilímaussaq alkaline complex is the type locality for 27 minerals including important rock-forming minerals such as aenigmatite, arfvedsonite, eudialyte, polylithionite, rinkite and sodalite. Nine minerals, chalcothallite, karupmøllerite-Ca, kvanefjeldite, nabesite, nacareniobsite-(Ce), naujakasite, rohaite, semenovite and sorensenite appear to be unique to the Ilímaussaq complex.

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The agpaitic complexes Ilímaussaq (South Greenland), Khibina and Lovozero (Kola Peninsula, Russia), and Mont Saint-Hilaire (Quebec, Canada) are among the areas in the world which are richest in rare minerals. About 700 minerals have been found in these complexes which hold the type localities for about 200 minerals.

About 220 minerals have been found in the Ilímaussaq complex of which 27 have their type localities within the complex. In comparison Khibina and Lovozero hold the type localities for 127 minerals (Pekov 1998) and Mont Saint-Hilaire holds the type localities for 38 minerals (R.A. Gault, personal communication 1999).

The existence of a locality in South Greenland rich in rare minerals has been known since the beginning of the 19th century when K.L. Giesecke in 1806 and 1809 visited the Kangerluarsuk and Tunulliarfik fjords in the area now known as the Ilímaussaq alkaline complex (Giesecke 1910). Minerals collected by him were examined by European mineralogists resulting in the discovery of the then new minerals sodalite (1810), eudialyte (1819) and arfvedsonite (1823). Since then the complex has been visited by many mineralogists and mineral collectors. This has resulted in the discovery of additional new minerals and a number of minerals known from very few other localities in the world. Most of the minerals for which Ilímaussaq is the type locality have later been found in other complexes of agpaitic rocks.

Two minerals were described simultaneously from Ilímaussaq and the Kola Peninsula, tugtupite and vitusite. Tugtupite was published from the Lovozero complex by Semenov & Bykova (1960) under the name beryllosodalite and from Ilímaussaq by Sørensen (1960) under the preliminary name beryllium sodalite which was changed to tugtupite in later publications (Sørensen 1962, 1963). Vitusite from the Ilímaussaq and Lovozero complexes was described in a joint Danish–Russian publication (Rønsbo *et al.* 1979). A tetragonal form of natrolite was described from Ilímaussaq (Andersen *et al.* 1969) and later found at Mont Saint-Hilaire and given the name tetranatrolite (Chen & Chao 1980). This name has since been discredited by I.M.A. The approved name is gonnardite (Grice 2001).

Nine minerals to our knowledge have not been identified at other localities: chalcothallite, karupmøllerite-Ca, kvanefjeldite, nabesite, nacareniobsite-(Ce), naujakasite, rohaite, semenovite and sorensenite. There is, however, a specimen in the collections of the Geological Museum, University of Copenhagen, labelled chalcothallite from Kazakhstan but the provenance of this specimen is dubious.

Bøggild (1905, 1953) described all the then known

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Table 1. All minerals identified in the Ilímaussaq alkaline complex

Mineral	Formula	Reference
Aegirine	$NaFe^{3+}Si_2O_6$	1806 (Giesecke)‡‡; Allan (1813)
Aegirine-augite	$(Na,Ca,Mg,Fe^{2+},Fe^{3+})_2(Si,Al)_2O_6$	Ussing (1894)
Aenigmatite	$Na_2(Fe^{2+})_5TiSi_6O_{20}$	Breithaupt (1865), Lorenzen (1881)
Albite	$NaAlSi_3O_8$	Ussing (1894)
Alkali feldspar	$(K,Na)AlSi_3O_8$	Ussing (1894)
Allanite	$Ca(Ce,La)(Al,Fe,Cr,V)_3(Si_2O_7)(SiO_4)(O,OH)_2$	Semenov & Sørensen (1966)
Allargentum	Ag_6Sb	López-Soler *et al.* (1975)
Alumino-ferro-hornblende (barkevikite)	$Ca_2Fe_4Al(Si_7Al)O_{22}(OH)_2$	Ussing (1894)
Analcime	$Na(AlSi_2)O_6{\cdot}H_2O$	Lorenzen (1881)
Ancylite-(La)	$Sr(La,Ce)(CO_3)_2(OH){\cdot}H_2O$	Petersen *et al.* (in press a)
Antimony	Sb	Karup-Møller (1974)
Apatite	$Ca_5(PO_4)_3(F,OH,Cl)$	Ussing (1894)
Apophyllite	$KCa_4Si_8O_{20}(F,OH){\cdot}8H_2O$	Bøggild (1953)
Arfvedsonite	$Na_3(Fe^{2+},Mg)_4Fe^{3+}Si_8O_{22}(OH)_2$	Brooke (1823)
Argentite	Ag_2S	Semenov (1969)
Arsenopyrite	FeAsS	Bøggild (1953)
Astrophyllite	$(K,Na)_3(Fe,Mn)_7Ti_2Si_8(O,OH)_{31}$	Lorenzen (1884b)
Augite	$(Ca,Mg,Fe)_2(Si,Al)_2O_6$	Ussing (1912)
Avicennite *	Tl_2O_3	Semenov *et al.* (1967b)
Azurite *	$Cu_3(CO_3)_2(OH)_2$	Karup-Møller *et al.* (1978)
Baddeleyite	ZrO_2	Markl & Marks (1999)
Barkevikite, *see* alumino-ferro-hornblende		
Barylite	$BaBe_2Si_2O_7$	Petersen *et al.* (1991)
Bastnäsite	$(Ce,La)CO_3F$	Hansen (1968)
Bavenite	$Ca_4(Al,Be)_4Si_9O_{26}(OH)_2$	Petersen *et al.* (1995)
Bertrandite	$Be_4Si_2O_7(OH)_2$	Andersen (1967)
Beryllite	$Be_3SiO_4(OH)_2{\cdot}H_2O$	Andersen (1967)
Beudantite	$PbFe_3(AsO_4,SO_4)_2(OH)_6$	Karup-Møller & Makovicky (1977)
Biotite	$K(Mg,Fe)_3(Si_3Al)O_{10}(OH,F)_2$	Ussing (1894)
Birnessite	$(Na,Ca,K)_{0.6}(Mn^{4+},Mn^{3+})_2O_4{\cdot}1.5H_2O$	Semenov (1969)
Bornite	Cu_5FeS_4	Bøggild (1905)
Breithauptite	(Ni,Pd)Sb	Oen & Sørensen (1964)
Britholite	$(Ce,Ca,Sr)_2(Ce,Ca)_3(SiO_4,PO_4)_3(O,OH,F)$	Winther (1899)
Brochantite	$Cu_4SO_4(OH)_6$	Karup-Møller *et al.* (1978)
Burpalite†	$Na_2CaZrSi_2O_7F_2$	F. Fontan, personal commun. 2000
Calcioancylite-(Ce)	$(Ce,Ca,Sr)CO_3(OH,H_2O)$	Pekov *et al.* (1997b)
Calcite	$CaCO_3$	1806 (Giesecke)‡‡
Cancrinite	$(Na,Ca)_8(Si_6Al_6)O_{24}(CO_3)_2{\cdot}2H_2O$	Ussing (1894)
Carbonate-fluorapatite (staffelite)	$Ca_5(PO_4,CO_3)_3F$	Semenov (1969)
Carbonate-hydroxylapatite (dahllite)	$Ca_{10}(PO_4)_3(CO_3)_3(OH)_2$	Bøggild (1915)
Catapleiite	$Na_2ZrSi_3O_9{\cdot}2H_2O$	Ussing (1894)
Ceriopyrochlore-(Ce)	$(Ce,Ca,Y,\square)_2(Nb,Ta)_2(O,OH,F)_7$	Semenov (1969)
Cerussite	$PbCO_3$	Semenov (1969)
Chabazite	$Ca(Al_2Si_4)O_{12}{\cdot}6H_2O$	Bøggild (1953)
Chalcocite	Cu_2S	Bøggild (1905)
Chalcopyrite	$CuFeS_2$	Semenov (1969)
Chalcostibite	$CuSbS_2$	Karup-Møller (1974)
Chalcothallite	$(Cu,Fe,Ag)_{6.3}(Tl,K)_2SbS_4$	Semenov *et al.* (1967b)
Chkalovite	$Na_2BeSi_2O_6$	Sørensen (1960)
Chlorite	$(Mg,Al)_6(Si,Al)_4O_{10}(OH)_8$	Flink (1898)
Chrysocolla	$(Cu,Al)_2H_2Si_2O_5(OH)_4{\cdot}nH_2O$	Karup-Møller *et al.* (1978)
Connellite	$Cu_{19}Cl_4SO_4(OH)_{32}{\cdot}3H_2O$	Karup-Møller *et al.* (1978)
Copper	Cu	Semenov (1969)
Corundum	Al_2O_3	Ussing (1912)
Covellite	CuS	Karup-Møller (1974)
Crocidolite, *see* riebeckite *var.* crocidolite		
Cryptomelane	KMn_8O_{16}	Semenov (1969)

Table 1 (*continued*)

Mineral	Formula	Reference
Cuprite	Cu_2O	López-Soler *et al.* (1975)
Cuprostibite	$Cu_2(Sb,Tl)$	Sørensen *et al.* (1969)
Dahllite, *see* carbonate-hydroxylapatite		
Diaspore	$AlO(OH)$	Ussing (1894)
Digenite	$Cu_{1.8}S$	López-Soler *et al.* (1975)
Djerfisherite	$K_6(Na,Li)(Fe,Cu,Ni)_{24}S_{26}Cl$	Karup-Møller (1978b)
Djurleite *	$Cu_{1.96}S$	Karup-Møller *et al.* (1978)
Dorfmanite	$Na_2(PO_3OH)\cdot 2H_2O$	Petersen *et al.* (1993)
Dyscrasite	Ag_3Sb	López-Soler *et al.* (1975)
Elpidite	$Na_2ZrSi_6O_{15}\cdot 3H_2O$	Ussing (1912)
Ephesite	$NaLiAl_2(Si_2Al_2)O_{10}(OH)_2$	Semenov (2001)
Epididymite	$NaBeSi_3O_7(OH)$	Hamilton (1964)
Epidote	$Ca_2FeAl_2(Si_2O_7)(SiO_4)(O,OH)_2$	Flink (1898)
Epistolite	$Na_5TiNb_2(Si_2O_7)_2(O,F)_4\cdot 5H_2O$	Bøggild (1899)
Erikite ‡		Bøggild (1903), Pekov *et al.* (1997a)
Eudialyte	$Na_{15}Ca_6Fe_3Zr_3Si(Si_{25}O_{73})(O,OH,H_2O)_3(Cl,OH)_2$	Stromeyer (1819)
Eudidymite	$Na_2Be_2Si_6O_{15}\cdot H_2O$	Semenov & Sørensen (1966)
Evenkite * †	$C_{24}H_5$	
Famatinite	Cu_3SbS_4	Karup-Møller (1974)
Fayalite	Fe_2SiO_4	Ussing (1912)
Ferrosalite	$Ca_3Fe_2Mg(Si_2O_6)_3$	Larsen (1976)
Ferropargasite	$NaCa_2(Fe,Mg,Al)_5(Si_6Al_2)O_{22}(OH)_2$	Larsen (1976)
Fersmite	$(Ca,Ce,Na)(Nb,Ta,Ti)_2(O,OH,F)_6$	Petersen *et al.* (1998)
Fluorite	CaF_2	1809 (Giesecke)‡‡
Galena	PbS	1809 (Giesecke)‡‡
Garnet (group)		Flink (1898)
Gelbertrandite * ‡		Semenov (1969)
Genthelvite	$Be_3Zn_4(SiO_4)_3S$	Bollingberg & Petersen (1967)
Gerasimovskite	$(Mn,Ca)(Nb,Ti)_5O_{12}\cdot 9H_2O(?)$	Semenov *et al.* (1967a)
Gmelinite	$Na_4(Al_4Si_8)O_{24}\cdot 11H_2O$	Karup-Møller (1976)
Goethite (limonite)	$FeO(OH)$	1806 (Giesecke)‡‡
Gold	Au	Davison (1989), Bohse & Frederiksen (2001)
Gonnardite (*formerly* tetranatrolite)	$(Na,K)_2(Si,Al)_5O_{10}\cdot 2H_2O$	Grice (2001)
Gudmundite	$FeSbS$	Oen & Sørensen (1964)
Halite	$NaCl$	Sobolev *et al.* (1970)
Halloysite	$Al_2Si_2O_5(OH)_4$	Semenov (1969)
Hastingsite	$NaCa_2(Fe,Mg)_5(Si_6Al_2)O_{22}(OH,Cl)_2$	Larsen (1976)
Hedenbergite	$Ca(Fe,Mg)Si_2O_6$	Semenov (1969)
Helvite	$Be_3Mn_4(SiO_4)_3S$	Johnsen & Bohse (1981)
Hematite	Fe_2O_3	Ussing (1894)
Hemimorphite	$Zn_4Si_2O_7(OH)_2\cdot H_2O$	Sørensen (1962)
Herschelite	$(Na,Ca,K)(AlSi_2)O_6\cdot 3H_2O$	Karup-Møller (1976)
Hisingerite	$Fe_2Si_2O_5(OH)_4\cdot 2H_2O$	Semenov (1969)
Hiortdahlite	$Na_4Ca_6Zr_2(Nb,Mn,Ti,Fe,Mg,Al)_2(Si_2O_7)_4O_3F_5$	Larsen & Steenfelt (1974), Robles *et al.* (2001)
Hydrargillite (gibbsite)	$Al(OH)_3$	Semenov (1969)
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	Karup-Møller (1975)
Hydronephelite ‡		Ussing (1894)
Ilimaussite	$Na_4Ba_2CeFeNb_2Si_8O_{28}\cdot 5H_2O$	Semenov *et al.* (1968)
Ilmenite	$FeTiO_3$	Ussing (1912)
Ilvaite	$CaFe^{3+}(Fe^{2+})_2O(Si_2O_7)(OH)$	Lorenzen (1881)
Joaquinite-(Ce)	$NaBa_2FeTi_2Ce_2(SiO_3)_8O_2(OH)\cdot H_2O$	Semenov (1969)
Katophorite	$(Na,Ca)_3(Mg,Fe,Al)_5(Si_7Al)O_{22}(F,OH)_2$	Ussing (1912)
Karupmøllerite-Ca †		Name accepted by IMA 2001
Kvanefjeldite	$Na_4(Ca,Mn)Si_6O_{14}(OH)_2$	Johnsen *et al.* (1983), Petersen *et al.* (1984)

Table 1 (*continued*)

Mineral	Formula	Reference
Lead	Pb	Karup-Møller (1975)
Leifite	$Na_6Be_2Al_2Si_{16}O_{39}(OH)_2 \cdot 1.5H_2O$	Petersen *et al.* (1994)
Leucophanite	$NaCaBeSi_2O_6F$	Bøggild (1905)
Limonite, *see* goethite		
Linarite	$CuPbSO_4(OH)_2$	Karup-Møller *et al.* (1978)
Litharge	PbO	Karup-Møller (1975)
Löllingite	$FeAs_2$	Flink (1898)
Lomonosovite	$Na_5Ti_2O_2(Si_2O_7)(PO_4)$	Karup-Møller (1983)
Lomonosovite-β ‡	$(Na,Ca)_2(Ti,Nb)_2(Si_2O_7)O(OH,F) \cdot NaPO_2(OH)_2$	Semenov (1969)
Lorenzenite	$Na_2Ti_2O_3(Si_2O_6)$	Karup-Møller (1986)
Lovdarite	$K_4Na_{12}Be_8Si_{28}O_{72} \cdot 18H_2O$	Petersen *et al.* (in press b)
Lovozerite	$(Na,Ca)_3(Zr,Ti)Si_6(O,OH)_{18}$	Danø & Sørensen (1959)
Lueshite	$NaNbO_3$	Danø & Sørensen (1959)
Magnetite	Fe_3O_4	Ussing (1894)
Malachite	$Cu_2CO_3(OH)_2$	López-Soler *et al.* (1975)
Mangan-neptunite	$KNaLi(Mn,Fe)_2Ti_2Si_8O_{24}$	Semenov (1969)
Marcasite	FeS_2	Karup-Møller (1978b)
Microcline	$KAlSi_3O_8$	Breithaupt (1858), Ussing (1894)
Molybdenite	MoS_2	Ussing (1912)
Monazite	$(Ce,La,Nd,Th)PO_4$	Ussing (1912)
Montmorillonite	$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot nH_2O$	Semenov (1969)
Murmanite	$Na_3(Ti,Nb)_4O_4(Si_2O_7)_2 \cdot 4H_2O$	Buchwald & Sørensen (1961)
Muscovite	$KAl_2(Si,Al)_4O_{10}(OH,F)_2$	Ussing (1894)
Nabesite †	$Na_2BeSi_4O_{10} \cdot 4H_2O$	Name accepted by IMA 2000
Nacareniobsite-(Ce)	$Na_3Ca_3(Ce,La)Nb(Si_2O_7)_2OF_3$	Petersen *et al.* (1989)
Nahcolite †	$NaHCO_3$	
Na-komarovite §	$(Na,Ca,H)_2Nb_2Si_2O_{10}(OH,F)_2 \cdot H_2O$	Krivokoneva *et al.* (1979), Semenov (1969)
Nahpoite * †	$Na_2(PO_3OH)$	
Narsarsukite	$Na_2(Ti,Fe,Zr)Si_4(O,F)_{11}$	Semenov & Sørensen (1966)
Natrolite	$Na_2(Si_3Al_2)O_{10} \cdot 2H_2O$	Kobell (1838)
Natrophosphate	$Na_7(PO_4)_2F \cdot 19H_2O$	Petersen *et al.* (2001b)
Naujakasite	$Na_6(Fe,Mn)Al_4Si_8O_{26}$	Bøggild (1933)
Nenadkevichite	$Na(Nb,Ti)Si_2O_6(O,OH) \cdot 2H_2O$	Semenov *et al.* (1967a)
Nepheline	$(Na,K)AlSiO_4$	Steenstrup (1881)
Neptunite	$KNa_2Li(Fe,Mg,Mn)_2Ti_2Si_8O_{24}$	Bøggild (1905)
Nickeline	NiAs	Oen & Sørensen (1964)
Niobophyllite	$(K,Na)_3(Fe,Mn)_6(Nb,Ti)_2Si_8(O,OH)_{31}$	Hansen (1968), Semenov (1969)
Nontronite	$Na_{0.3}(Fe^{3+})_2(Si,Al)_4O_{10}(OH)_2 \cdot nH_2O$	Semenov (1969)
Odintsovite	$K_2Na_4Ca_3Ti_2Be_4Si_{12}O_{36}$	Petersen *et al.* (2001a)
Orthoclase	$KAlSi_3O_8$	1888 (Steenstrup)‡‡, Ussing (1894)
Palygorskite	$(Mg,Al)_2Si_4O_{10}(OH) \cdot 4H_2O$	Semenov (1969)
Pearceite *	$(Ag,Cu)_{16}As_2S_{11}$	Oen & Sørensen (1964)
Pectolite	$NaCa_2Si_3O_8(OH)$	Semenov (1969)
Pectolite (manganoan)	$Na(Mn,Ca)_2Si_3O_8(OH)$	Winther (1899)
Plagioclase	$(Na,Ca)(Si,Al)_3O_8$	Ussing (1912)
Plattnerite	PbO_2	Semenov (1969)
Polybasite	$(Ag,Cu)_{16}Sb_2S_{11}$	Oen & Sørensen (1964)
Polylithionite	$KLi_2AlSi_4O_{10}(F,OH)_2$	Lorenzen (1881)
Prehnite	$Ca_2Al(Si,Al)_4O_{10}(OH)_2$	Metcalf-Johansen (1983)
Pyrite	FeS_2	Ferguson (1964)
Pyrochlore	$(Na,Ca)_2Nb_2(O,OH,F)_7$	Ussing (1912)
Pyrolusite	MnO_2	Bøggild (1953)
Pyrophanite	$MnTiO_3$	Semenov (1969)
Pyrrhotite	$Fe_{1-x}S$	Ferguson (1964)
Quartz	SiO_2	Ussing (1894)
Rhabdophane	$(Ce,La,Ca)PO_4 \cdot H_2O$	Semenov (1969)

Table 1 (*continued*)

Mineral	Formula	Reference
Riebeckite	$Na_2(Fe^{2+},Mg)_3(Fe^{3+})_2Si_8O_{22}(OH,F)_2$	Ussing (1894)
Riebeckite *var.* crocidolite (crocidolite)	$Na_2(Fe^{2+},Mg)_3(Fe^{3+})_2Si_8O_{22}(OH,F)_2$	1809 (Giesecke)‡‡
Rinkite	$(Na,Ca)_3(Ca,Ce)_4(Ti,Nb)(Si_2O_7)_2(O,F)_4$	Lorenzen (1884a)
Rinkolite ‡		Semenov (1969)
Rohaite	$(Tl,Pb,K)_2Cu_{8.7}Sb_2S_4$	Karup-Møller (1978a)
Rosenbuschite	$(Ca,Na)_5(Zr,Ca)_2(Ti,Mn)(Si_2O_7)_2(F,OH)_4$	Ussing (1912)
Rutile	TiO_2	Semenov (1969)
Sauconite	$Na_{0.3}Zn_3(Si,Al)_4O_{10}(OH)_2{\cdot}4H_2O$	Semenov (1969)
Schizolite *see* pectolite (manganoan)		
Seinäjokite	$(Fe,Ni)(Sb,As)_2$	Karup-Møller (1978b)
Semenovite	$(Na,Ca)_9Fe(Ce,La)_2(Si,Be)_2(O,OH)_{48}$	Petersen & Rønsbo (1972)
Senarmontite	Sb_2O_3	Karup-Møller (1974)
Sepiolite	$Mg_4Si_6O_{15}(OH)_2{\cdot}6H_2O$	Semenov (1969)
Siderite	$FeCO_3$	1806 (Giesecke)‡‡
Silver	Ag	Semenov *et al.* (1967b)
Skinnerite	Cu_3SbS_3	Karup-Møller & Makovicky (1974)
Skutterudite	$(Co,Fe,Ni)As_{3-x}$	Oen & Sørensen (1964)
Sodalite	$Na_4(Si_3Al_3)O_{12}Cl$	Thomson (1811)
Sodium-acetate-tri-hydrate	$CH_3COONa{\cdot}3H_2O$	Sørensen *et al.* (1970)
Sorensenite	$Na_4Be_2Sn(Si_3O_9)_2{\cdot}2H_2O$	Semenov *et al.* (1965)
Sphaerobertrandite ‡		Semenov & Sørensen (1966)
Sphalerite	ZnS	Flink (1898)
Staffelite, *see* carbonate-fluorapatite		
Stannite *	Cu_2FeSnS_4	Oen & Sørensen (1964)
Steenstrupine	$Na_{14}Ce_6Mn_2Fe_2Zr(PO_4)_7Si_{12}O_{36}(OH)_2{\cdot}3H_2O$	Lorenzen (1881)
Stilbite	$NaCa_4(Al_9Si_{27})O_{72}{\cdot}30H_2O$	Ferguson (1964)
Stillwellite	$(Ce,La,Ca)BSiO_5$	Karup-Møller (1975)
Strontianite †	$SrCO_3$	
Synchysite †	$Ca(Ce,La)(CO_3)_2F$	
Talc †	$Mg_3Si_4O_{10}(OH)_2$	
Tenorite	CuO	Karup-Møller & Makovicky (2001)
Terskite	$Na_4Zr(H_4Si_6O_{18})$	Khomyakov *et al.* (1983)
Tetrahedrite	$(Cu,Fe)_{12}Sb_4S_{13}$	Karup-Møller (1974)
Tetranatrolite ¶ *see* Gonnardite		Chen & Chao (1980), Grice (2001)
		Andersen *et al.* (1969)
Thalcusite	$Cu_3FeTl_2S_4$	Makovicky *et al.* (1980)
Thermonatrite	$Na_2CO_3{\cdot}H_2O$	Sørensen *et al.* (1970)
Thorianite	ThO_2	Bondam & Sørensen (1958)
Thorite	$ThSiO_4$	Buchwald & Sørensen (1961)
Tin *	Sn	Karup-Møller (1978b)
Titanite	$(Ca,Na)(Ti,Ta,Al,Nb,Sb)SiO_4(O,F)$	Hamilton (1964)
Titanomagnetite		Larsen (1976)
Todorokite	$(Na,Ca,K,Ba,Sr)_{1-x}(Mn,Mg,Al)_6O_{12}{\cdot}3{-}4H_2O$	Semenov (1969)
Troilite	FeS	Karup-Møller (1978b)
Trona	$Na_3(HCO_3)(CO_3){\cdot}2H_2O$	Sørensen *et al.* (1970)
Tugtupite	$Na_4BeAlSi_4O_{12}Cl$	Sørensen (1962)
Tundrite	$Na_2Ce_2TiO_2SiO_4(CO_3)_2$	Semenov *et al.* (1967a)
Tundrite (Nd) **	$Na_2NdTiO_2SiO_4(CO_3)$	Semenov *et al.* (1967a)
Tuperssuatsiaite	$NaFe_3Si_8O_2(OH)_2{\cdot}5H_2O$	Karup-Møller & Petersen (1984)
Turkestanite	$Th(Ca,Na)_2(K_{1-x}\square_x)Si_8O_{20}{\cdot}nH_2O$	Petersen *et al.* (1999)
Ulvöspinel	Fe_2TiO_4	Karup-Møller (1978b)
Uranothorite	$(Th,U)SiO_4$	Makovicky *et al.* (1980)
Ussingite	$Na_2AlSi_3O_8(OH)$	Bøggild (1913)
Valentinite	Sb_2O_3	Karup-Møller (1974)
Vesuvianite †	$(Ca,Na)_{19}(Al,Mg,Fe)_{13}(SiO_4)_{10}(Si_2O_7)_4(OH,F,O)_{10}$	
Villiaumite	NaF	Bondam & Ferguson (1962)
Vinogradovite	$(Na,Ca)_4Ti_4Si_8O_{26}{\cdot}(H_2O,K_3)$	Rønsbo *et al.* (1990)

Table 1 (*continued*)

Mineral	Formula	Reference
Vitusite ††	$Na_3(Ce,La,Nd)(PO_4)_2$	Rønsbo *et al.* (1979)
Vrbaite *	$Hg_3Tl_4As_8Sb_2S_2$	Semenov *et al.* (1967b)
Vuonnemite	$Na_5TiNb_2(Si_2O_7)_2O_2F_2{\cdot}2Na_3PO_4$	Rønsbo *et al.* (1983)
Westerveldite	(Fe,Ni,Co)As	Karup-Møller & Makovicky (1977)
Whewellite †	$CaC_2O_4{\cdot}H_2O$	
Willemite	Zn_2SiO_4	Metcalf-Johansen (1977)
Yofortierite	$(Mn,Mg)_5Si_8O_{20}(OH)_2{\cdot}8–9H_2O$	Semenov (1969)
Zircon	$ZrSiO_4$	Ussing (1894)

* Identity/location uncertain.
† Unpublished.
‡ Dubious species.
§ The mineral or name has never been appraised by the Commission on New Minerals and Mineral Names of IMA.
¶ First presented from Ilímaussaq as 'a tetragonal natrolite'.
** First published analysis of a tundrite with Nd as the dominant REE.
†† Described simultaneously from the Ilímaussaq alkaline complex and the Lovozero alkaline complex.
‡‡ First collected, year and collector.
Mineral names and formulae, with a few exceptions, are drawn from The MINERAL Database – © Aleph/CSIRO-1997.

Species for which the Ilímaussaq alkaline complex is the type locality are marked in bold.

The following minerals, listed in Sørensen *et al.* (1981), for various reasons are omitted in the present list: graphite, acmite (now aegirine), antigorite, cookeite (now ephesite), ferrohortonolite (now fayalite), guarinite (now hiortdahlite), lepidolite (now polylithionite), leucosphenite, mosandrite (now rinkite), potash feldspar (now orthoclase, microcline), serandite, mineral A and chalcedony.

minerals from the complex. Lists of the minerals found in the complex have been compiled by Sørensen (1967), Semenov (1969), Sørensen *et al.* (1981) and Petersen & Secher (1993).

Table 1, compiled for this anniversary volume, contains all the Ilímaussaq minerals for which sufficient documentation exists. Those first described from the Ilímaussaq complex are indicated in bold type.

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Geochemical overview of the Ilímaussaq alkaline complex, South Greenland

John C. Bailey, Raymond Gwozdz, John Rose-Hansen and Henning Sørensen

The Ilímaussaq alkaline complex is one of the latest members of the Mesoproterozoic Gardar igneous province. It was emplaced in three phases, (1) augite syenite, (2) alkali acid rocks and (3) the dominant agpaitic nepheline syenites. The immediate parent for the nepheline syenites is the augite syenite whose geochemical features, such as the low Zr/Nb ratio (3.7), match benmoreites from a nearby alkali basalt series.

The agpaitic nepheline syenites are characterised by exceptionally high contents of Zr, Hf, Nb, Ta, REE, Th, U, Sn, Li, Be, Rb, Zn, Pb, Sb, W, Mo, As and Ga, and the volatile elements F, Cl, Br, I and S but exceptionally low levels of Ba, Sr, Co, Cu, Ni, Sc, V and Cr. Fractionation of cumulus phases with a distinctive geochemistry, such as sodalite (rich in Cl, Br, I, B), eudialyte (Zr, Hf, Nb, Ta, W, As) and arfvedsonite (Co, Sc, V, Cr), caused exhaustion of these elements in the residual magmas. The agpaitic magmas underwent extreme fractionation with the final lujavrite forming after 99% crystallisation of the augite syenite. Zirconium was apparently soluble in Ilímaussaq melts up to a concentration of *c.* 9000 ppm. Whole-rock analyses define a number of discrete Zr–U arrays which are restricted to certain intervals of the cumulate stratigraphy and are taken as evidence for liquid layering in the Ilímaussaq magma chamber. The distribution of the less common trace elements (Bi, Cd, Co, Ge, In, I, Hg, Sc, Se, V, W) and of the more abundant trace elements which failed to form minerals (Br, Cs, Ga, Hf, Rb, Sr) is summarised.

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Keywords: agpaite, alkaline rocks, cumulates, geochemistry, Greenland, Ilímaussaq, liquid layering, solubility, trace elements, zirconium

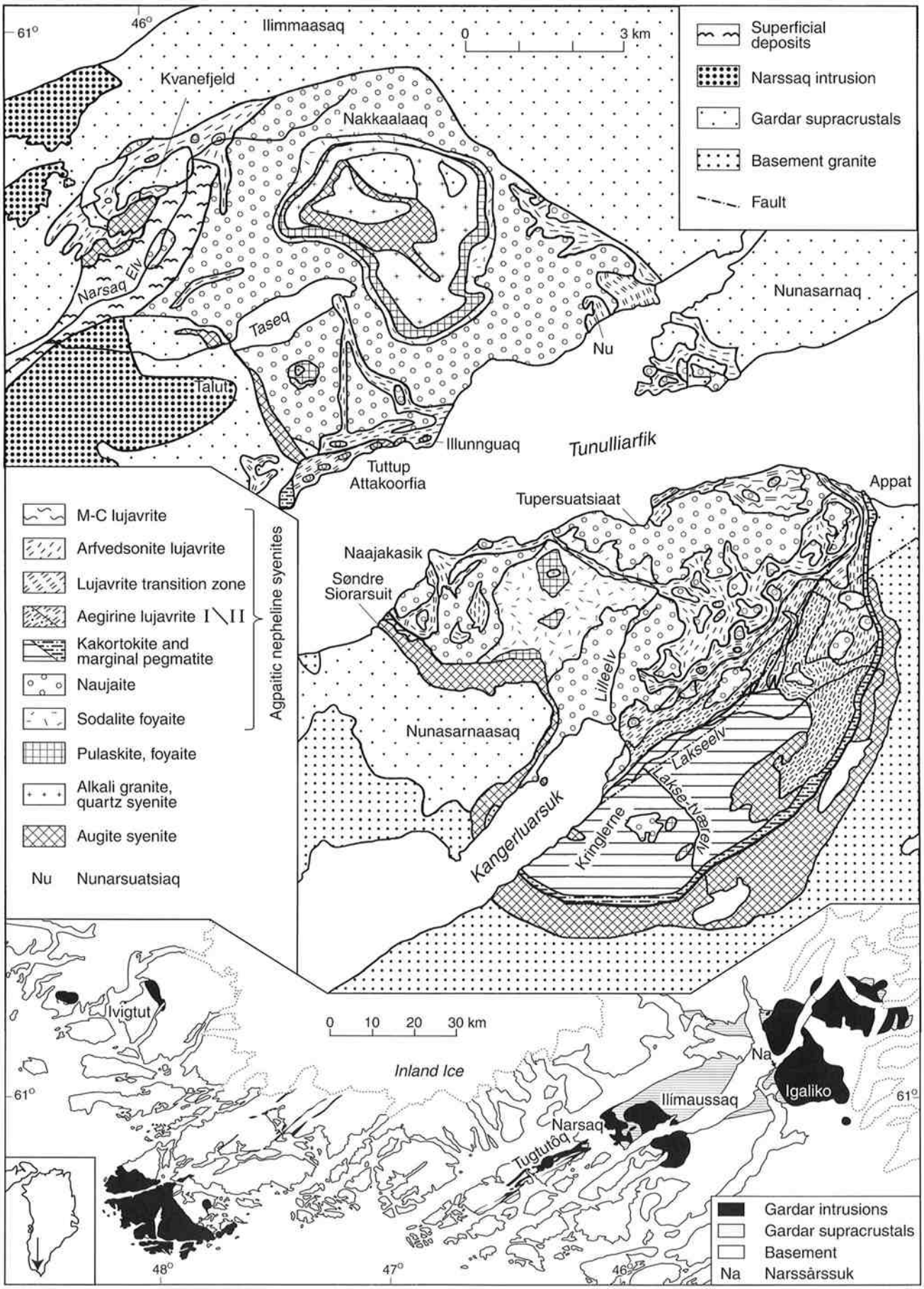
The aim of this paper is to review the main geochemical features of the Ilímaussaq complex. We emphasise studies on the dominant agpaitic rock types of the complex rather than the less voluminous pegmatites and veins. The influences of petrological processes such as extreme fractionation, crystallisation of cumulus versus intercumulus materials, and possible layering of the Ilímaussaq magma chamber are considered. This geochemical overview is largely based on work in progress and preliminary interpretations by the authors but also includes published work by a number of investigators.

Petrology of the Ilímaussaq complex

A summary of the geological setting and rock types of the Ilímaussaq complex is presented by Sørensen (2001, this volume) and only a brief overview of the setting and petrological evolution is given here.

The Ilímaussaq complex is one of the youngest members of the Mesoproterozoic Gardar province of South Greenland which comprises a suite of extrusive and intrusive igneous rocks produced in an extensional continental environment (Upton & Emeleus 1987). The complex was intruded into basement granitoids and the unconformably overlying sandstones and largely basaltic lavas of the Eriksfjord Formation, part of the Gardar supracrustals (Fig. 1).

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61°
46°
Ilimmaasaq
0
3 km
Kvanefjeld
Nakkaalaaq
Narsaq Elv
Taseq
Talut
Nunasarnaq
Nu
Illunnguaq
Tunulliarfik
Tuttup Attakoorfia
Appat
Tupersuatsiaat
Naajakasik
Søndre Siorarsuit
Lilleelv
Nunasarnaasaq
Lakseelv
Lakseværelv
Kangerluarsuk
Kringlerne
Superficial deposits
Narssaq intrusion
Gardar supracrustals
Basement granite
Fault
M-C lujavrite
Arfvedsonite lujavrite
Lujavrite transition zone
Aegirine lujavrite I \ II
Kakortokite and marginal pegmatite
Naujaite
Sodalite foyaite
Agpaitic nepheline syenites
Pulaskite, foyaite
Alkali granite, quartz syenite
Augite syenite
Nu Nunarsuatsiaq
Ivigtut
0 10 20 30 km
Inland Ice
61°
Ilímaussaq
Narsaq
Tugtutôq
Na
Igaliko
61°
48°
47°
46°
Gardar intrusions
Gardar supracrustals
Basement
Na Narssârssuk

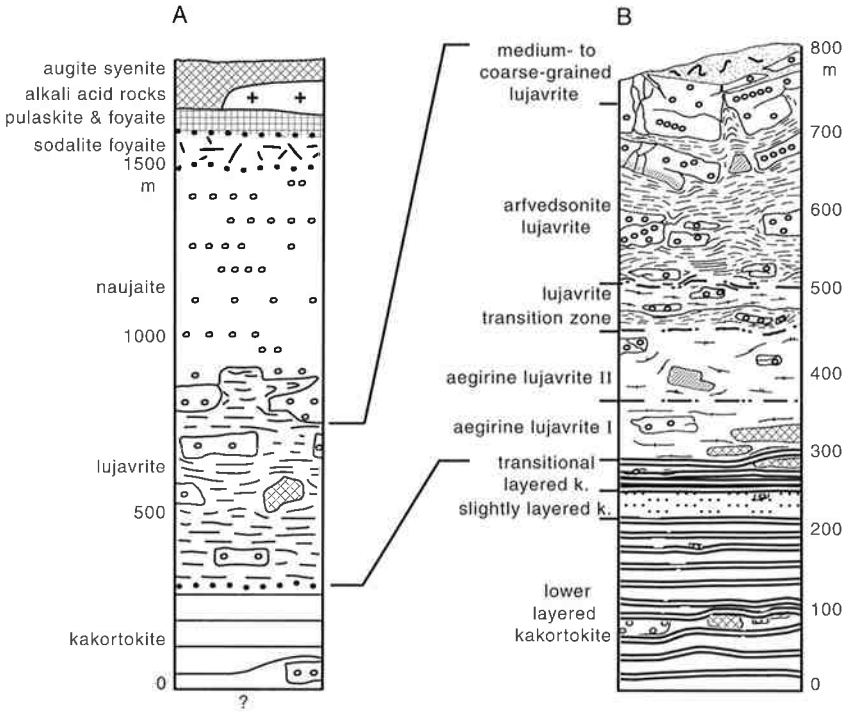


Fig. 2. **A**: Schematic section through the Ilímaussaq alkaline complex. **B**: The lowermost 800 m of the complex showing the detailed igneous stratigraphy of the kakortokites and lujavrites. Modified from Andersen *et al.* (1981).

The Ilímaussaq complex was emplaced in three main phases. Phase 1 is composed of a mildly alkaline augite syenite while phase 2 consists of peralkaline quartz syenite and alkali granite. Phase 3 starts with slightly peralkaline Si-undersaturated rocks which evolve into the areally dominant, agpaitic nepheline syenites of the complex (Fig. 2; Table 1). The agpaitic rocks at Ilímaussaq are characterised by an agpaitic index (molar $(Na_2O + K_2O)/Al_2O_3) > 1.2$ and by complex Zr–Ti silicates such as eudialyte and rinkite.

Phase 3 consists of a series of roof cumulates, and a series of floor cumulates which are overlain by an intermediate sequence of rocks whose cumulate character decreases upwards so that the later rock types are intrusive into the earlier materials. The roof rocks crystallised from the top downwards, forming the succession pulaskite, foyaite, sodalite foyaite and naujaite. Floor cumulates contemporaneous with the greater part of the roof cumulates are thought to occur below the deepest exposed levels.

The earliest exposed floor cumulates are the lower layered kakortokites which exhibit a striking macrorhythmic layering. Each of the 29 three-layer units starts with a black arfvedsonite-rich layer; this is followed with a few exceptions by a red eudialyte-rich layer and then a thicker white layer rich in alkali feldspar. The 29 units are numbered from –11 upwards through 0 to +17 (Bohse *et al.* 1971). Based on analyses of individual layers, we have computed a bulk kakortokite composed of 12.7% black, 11.5% red and 75.8% white layers. The lower layered kakortokites are overlain by slightly layered kakortokite and then by transitional layered kakortokite where the black, red and white layers are labelled F to A upwards (Bohse & Andersen 1981).

There is a gradual and concordant contact to the overlying aegirine lujavrite I where detailed studies have established weakly developed macrorhythmic layering (Bailey 1995). Additional stratified and more evolved lujavrites at higher levels are termed aegirine lujavrite II, lujavrite transition zone and arfvedsonite lujavrite. The final medium- to coarse-grained lujavrite (M-C lujavrite), which occurs as intrusive sheets, approaches pegmatites in its grain size and texture. These late lujavrites are associated with a uranium deposit in the roof zone at Kvanefjeld (Sørensen *et al.* 1974).

Most of the Ilímaussaq rocks are cumulates but rare chilled margins, dykes and sills thought to be close to magmatic compositions of the evolving Ilímaussaq system are now starting to be recognised and are discussed below.

Fig. 1. Simplified geological map of the Ilímaussaq complex. Modified from Ferguson (1964) and Andersen *et al.* (1988). **M-C** lujavrite: medium- to coarse-grained.

Table 1. The major rock types of the Ilímaussaq alkaline complex

Rock type	Texture	Cumulus minerals	Other minerals
Phase 1			
augite syenite	hypidiomorphic to xenomorphic granular, massive or layered, medium to coarse	alkali feldspar, hedenbergite, olivine, titano-magnetite, apatite, plagioclase, pyrrhotite, chalcopyrite	ferropargasite, biotite, nepheline
Phase 2			
alkali granite, quartz syenite	hypidiomorphic granular, medium to coarse		alkali feldspar, quartz, arfvedsonite, aegirine, aenigmatite, ilmenite, sphalerite, galena, pyrochlore, fluorite, zircon
Phase 3			
pulaskite and foyaite	massive, medium to coarse, platy feldspars	alkali feldspar, hedenbergite, fayalite, titanomagnetite, apatite	katophorite-arfvedsonite, aegirine-augite to aegirine, nepheline, aenigmatite, biotite, eudialyte, fluorite, analcime, natrolite
Agpaitic nepheline syenites			
sodalite foyaite	foyaitic, coarse	alkali feldspar, sodalite, nepheline, hedenbergite, fayalite, titanomagnetite, apatite	katophorite-arfvedsonite, aegirine, eudialyte, aenigmatite, analcime, natrolite
naujaite	poikilitic, coarse to pegmatitic	sodalite, alkali feldspar, nepheline, hedenbergite, fayalite, titanomagnetite,	katophorite-arfvedsonite, aegirine, eudialyte, aenigmatite, analcime, apatite, natrolite, fluorite, villiaumite, rinkite, sphalerite
kakortokite	laminated, layered, medium to coarse	alkali feldspar, nepheline, arfvedsonite, aegirine, eudialyte, sodalite, fluorite, aenigmatite	analcime, natrolite, rinkite, sphalerite, galena, löllingite
lujavrite †	laminated, fine-grained; sometimes layered or massive, medium to coarse	aegirine, arfvedsonite, microcline, albite, nepheline, eudialyte	analcime, natrolite, sodalite, naujakasite, steenstrupine, vitusite, monazite, villiaumite, sphalerite, galena

† See Sørensen (2001, Table 1) for further information.

Analytical methods

Most of the data presented here were obtained by X-ray fluorescence analysis on glass discs (major elements) or powder tablets (trace elements), and by instrumental neutron activation analysis. These methods were supplemented by optical emission spectrometry for B, delayed neutron counting for U, Cerenkov counting for Li, photometry for F, and atomic absorption spectrometry for Li, Be and Cd. Minerals were separated by conventional methods of magnetic separation and heavy liquids.

Agpaitic geochemistry

Representative analyses for the main rock types in the Ilímaussaq complex are given in Table 2, and analyses of rare dykes and sills thought to be close to Ilímaussaq magma compositions are given in Table 3.

The agpaitic magmas and derivative rocks possess a number of unique geochemical features. Outstanding among these is their peralkaline, highly sodic character. In the Ilímaussaq complex, this led to the appearance of a long series of Na-bearing minerals (formulae are given by Petersen 2001, this volume). They include minerals of Na–Fe (arfvedsonite, aegirine, aenigmatite), Na–Zr (eudialyte, catapleiite), Na–Nb (pyrochlore, lueshite), Na–Ti–Nb (rinkite, neptunite, astrophyllite-niobophyllite), Na–REE (steenstrupine, tundrite, joaquinite), Na–Be (chkalovite, sorensenite, leucophane) and Na–P (vitusite, vuonnemite, Na-rich apatite). Na was linked with volatile components in minerals of Na–Cl (sodalite), Na–F (villiaumite) and Na–CO_2 (trona and thermonatrite). K–Na even enter the sulphide djerfisherite. Many of these minerals have limited occurrences in late pegmatites, veins and pockets but sodalite, arfvedsonite, aegirine and eudialyte are important rock-forming minerals (Table 1).

In terms of trace elements, the Ilímaussaq rocks are characterised by exceptionally high levels of the normally incompatible elements Zr, Hf, Nb, Ta, REE, Th, U, Sn, Li, Be, Rb, Zn, Pb, Sb, W, Mo, As and Ga, as well as the volatile elements F, Cl, Br, I and S. Less well documented, because of analytical difficulties, are the exceptionally low levels attained by compatible trace elements such as Sc and Co (< 0.1 ppm), V, Cr and Ni (< 0.5 ppm), Cu (< 1 ppm), Ba (< 5 ppm) and Sr (< 10 ppm).

Elements which are usually coherent geochemically can exhibit bizarre relations. Thus during evolution of the complex K/Rb falls from 460 to 35, Zr/Hf rises from 45 to 97, and Cl/Br rises from 170 to 1500. Average Mg/Li ratios of basalts (*c.* 2700) and granites (*c.* 40) can be compared with averages for nepheline syenites from Lovozero (110) and Ilímaussaq (4.5). The average Mg/Li ratio for arfvedsonite can be compared at Lovozero (19) and Ilímaussaq (1.9, with individual ratios down to 0.13). In the final arfvedsonites at Ilímaussaq, Li is a minor element whereas Mg is a trace element (Bailey *et al.* 1993). It should be emphasised that these features apply to rocks and minerals occurring in outcrops over hundreds or even thousands of metres and not to pockets of exotic pegmatite.

The extraction of a series of cumulus phases characteristic of agpaitic nepheline syenites (Table 1) has imposed distinctive element associations on the succession of cumulate rocks. In several of these cumulus phases, elements which are normally considered incompatible, e.g. during basalt fractionation, are strongly compatible and this leads to a sharp decrease in their contents in the succeeding residual magmas.

Thus the build-up of Cl, which occurs in residual phonolitic magmas at many localities, reaches a climax at Ilímaussaq with the voluminous formation of flotation cumulates of sodalite. These flotation cumulates form naujaite, the final rock type of the roof series. Chlorine contents of naujaite typically are in the range 2–3.5 wt% with an extreme value of 4.6 wt%. The earliest sodalites are particularly rich in Br, I and B and this leads to decreasing levels in subsequent rocks.

In the earliest exposed floor cumulates, the kakortokites, the Na–Zr silicate eudialyte is an important cumulus phase, particularly in the eudialyte-rich red kakortokite layers. Eudialyte not only strongly partitions Zr but also Hf, Nb, Ta, W and As so that all these elements show decreasing contents in the subsequent rocks. Moderate partitioning of Ca, Sr and Ba, and of Cl and Br, accelerates the already dwindling amounts of these elements. Even the rising levels of REE and Pb in the Ilímaussaq system receive a short-lived setback as a result of their significant incorporation in the abundant eudialyte of the kakortokites.

Also at the kakortokite stage, cumulus arfvedsonite and aegirine scavenge large amounts of the rare transition metals Co, Sc, V and Cr. Levels of Sc, for example, fall to < 0.1 ppm in the subsequent rocks.

Fluorite is a cumulus phase in the kakortokites and its fractionation leads to a reduction in F levels so that contents only recover to > 1000 ppm in the final lujavrites with the crystallisation of villiaumite.

Clearly, a number of elements which are normally incompatible in alkaline magma series (Cl, Zr, Hf, W) pass through maxima in the Ilímaussaq agpaitic system and may then evolve to significantly lower levels. Thus in the final medium- to coarse-grained lujavrite, Zr may fall to 328 ppm and Hf to 2.6 ppm. This allows new associations of minerals and elements to be established: instead of Th and U substituting in eudialyte, they concentrate in the Th-REE silicophosphate steenstrupine.

Agpaitic cumulate rocks, and presumably their parental melts, solidify at remarkably low magmatic temperatures, probably < 500°C (Sood & Edgar 1970). They may even exhibit a continuous transition through hyper-agpaitic melts to hydrothermal solutions (Khomyakov 1995). Such behaviour suggests that fractionation proceeds to an extremely high degree. The recognition of a rare suite of dykes and sills corresponding to Ilímaussaq liquids (Table 3) has allowed us to quantify this fractionation. During most though not all of the evolution, Th, U, La, Cs, Li, Be and Pb behaved as

Table 2. Representative analyses of Ilímaussaq rock types

	Phase 1		Phase 2		Phase 3		
	fine augite syenite	coarse augite syenite	quartz syenite	alkali granite	pulaskite	foyaite	sodalite foyaite
GGU no.	154361	154334	152118	152116	154387	154384	154351
SiO_2 (wt%)	50.78	56.97	70.17	71.01	62.54	58.50	48.24
TiO_2	2.76	1.27	0.26	0.23	0.10	0.32	0.33
ZrO_2	0.02	0.06	0.19	0.46	0.21	0.27	0.51
Al_2O_3	13.69	16.82	10.03	8.65	16.97	16.21	18.99
Fe_2O_3	2.78	1.47	3.03	4.33	2.02	3.03	4.16
FeO	11.69	6.68	4.67	3.79	1.48	3.80	3.08
MnO	0.35	0.22	0.18	0.21	0.12	0.19	0.20
MgO	2.32	0.76	0.11	0.18	0.15	0.11	0.12
CaO	5.12	3.47	0.38	0.24	1.53	1.76	1.67
Na_2O	3.84	5.65	5.28	4.67	8.19	7.56	14.87
K_2O	4.16	5.16	4.25	3.91	4.69	5.64	3.47
P_2O_5	1.22	0.34	0.02	0.07	0.05	0.04	0.06
H_2O^+	0.36	0.56	0.34	0.28	0.83	1.26	1.24
H_2O^-	0.24	0.19	0.16	0.26	0.20	0.21	0.22
CO_2	0.07	0.05	0.10	0.09	0.06	0.04	0.10
S	0.16	0.07	0.00	0.00	0.01	0.02	0.07
Cl	0.02	0.04	0.02	0.01	0.02	0.12	2.34
F	0.16	0.14	0.35	0.27	0.20	0.20	0.17
others	0.05	0.06	0.19	0.47	0.18	0.17	0.40
	99.79	99.98	99.35	99.12	99.55	99.45	100.24
– O	0.16	0.10	0.15	0.12	0.09	0.12	0.66
	99.63	99.88	99.20	99.00	99.46	99.33	99.58
A.I.	0.80	0.88	1.32	1.38	1.09	1.14	1.49
Cs (ppm)	< 0.1	1.2	0.35	1.2	2.3	5.3	6.3
Rb	66	68	438	557	234	315	348
Tl	< 0.5	< 0.5	2.3	0.5	1.0	1.3	1.7
Ba	2580	2320	16	48	30	42	10
Pb	12	15	69	163	36	45	89
Sr	281	395	15	54	16	27	11
La	73	77	252	537	223	244	619
Ce	163	163	510	1110	445	512	1420
Nd	83	76	205	423	185	219	572
Sm	15.0	13.9	31.2	65.6	36.3	38.2	95.9
Eu	5.08	4.53	2.13	4.16	3.08	3.60	10.1
Tb	2.06	1.88	5.73	12.1	5.89	5.82	16.6
Yb	5.21	5.30	18.5	36.8	24.7	17.9	50.9
Lu	0.68	0.80	2.80	5.38	3.69	2.43	6.42
Y	50	45	187	356	240	184	488
Th	3.4	7.9	48.5	123	23.5	27.8	54.0
U	0.55	1.9	15.6	44.1	8.9	9.8	15.5
Zr	208	272	1790	4560	2790	2070	4110
Hf	5.8	11.4	38.0	108	52.6	42.5	98.9
Sn	7.3	12	38	88	25	27	62
Nb	55	93	312	912	386	325	777
Ta	3.9	6.0	18.7	56.6	21.3	19.2	48.4
Li	16	80	182	156	91	132	161
Zn	148	117	402	1260	182	276	534
Cu	26	16	5	6	5	10	8
Co	10	3.8	1.1	-	1.1	3.6	0.32
Ni	< 0.5	< 0.5	< 0.5	< 0.5	3.1	0.5	< 0.5
Sc	40	18	1.9	1.2	0.21	0.52	0.09
V	< 0.5	< 0.5	2.1	1.6	1.5	< 0.5	< 0.5
Cr	8.2	1.8	3.5	3.9	1.1	1.8	1.9
Ga	23	29	41	37	56	58	66
Ge	1.9	1.9	1.8	2.1	1.3	1.4	1.6
B	< 3	8	13	13	7	5	3
Be	1.5	3.5	24	59	15	16	32
Sb	< 0.1	< 0.1	0.2	0.9	0.2	0.1	< 0.5
Mo	4.1	4.4	2	8.4	< 0.5	< 0.5	10
As	0.7	3.3	2.8	14	4.3	2.8	9.9
F	1560	1350	3550	2740	2040	1960	1730
Cl	210	450	190	120	160	1200	23400
Br	< 0.5	1.5	0.5	< 0.5	0.8	2.9	117
I	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	1.8
S	1570	690	45	40	105	160	730

Analysts: J.C. Bailey, J. Kystol, R. Gwozdz, B. Damgaard, H. Bollingberg and R. Fuge.

Table 2 (*continued*)

	Phase 3						
	naujaite	black kakortokite	red kakortokite	white kakortokite	aegirine lujavrite	arfvedsonite lujavrite	medium- to coarse-grained lujavrite
GGU no.	154346	154335	154326	154314	57033	154358	154399
SiO_2 (wt%)	48.25	48.06	52.20	53.30	53.24	53.06	53.87
TiO_2	0.32	0.57	0.68	0.16	0.17	0.15	0.43
ZrO_2	0.49	0.51	2.37	1.30	0.96	0.74	0.10
Al_2O_3	19.30	8.16	10.51	13.40	15.08	14.29	12.94
Fe_2O_3	4.07	7.17	6.04	7.90	8.83	2.89	3.48
FeO	3.08	17.08	6.90	3.42	2.20	7.75	8.29
MnO	0.21	0.48	0.41	0.31	0.21	0.44	0.61
MgO	0.10	0.58	0.28	0.23	0.19	0.14	0.10
CaO	1.68	4.39	3.58	2.10	0.79	0.38	0.29
Na_2O	14.37	6.95	9.26	8.84	11.52	9.84	7.91
K_2O	3.41	2.79	3.39	4.04	3.32	3.42	5.34
P_2O_5	0.06	0.01	0.04	0.04	0.03	0.54	0.47
H_2O^+	1.25	1.66	2.18	2.81	1.98	4.26	3.01
H_2O^-	0.17	0.15	0.21	0.41	0.15	0.13	0.12
CO_2	0.11	0.05	0.06	0.09	0.09	0.06	0.04
S	0.08	0.00	0.01	0.01	0.04	0.15	0.14
Cl	2.34	0.04	0.30	0.04	0.05	0.02	0.00
F	0.16	2.07	0.38	1.05	0.04	0.15	0.12
others	0.10	0.18	0.78	0.48	0.52	1.35	2.06
	99.55	100.90	99.58	99.93	99.41	99.76	99.32
- O	0.65	0.88	0.23	0.46	0.05	0.14	0.13
	98.90	100.02	99.35	99.47	99.36	99.62	99.19
A.I.	1.42	1.77	1.80	1.41	1.51	1.39	1.45
Cs (ppm)	6.2	4.4	3.9	5.5	5.1	7.4	82
Rb	334	186	314	542	665	551	1280
Tl	2.3	1.1	1.3	1.6	2.4	3.0	1.3
Ba	11	112	187	163	68	47	58
Pb	94	17	115	139	111	663	391
Sr	10	177	193	108	51	61	45
La	594	415	1330	743	844	3690	2830
Ce	1180	429	2640	1460	1760	5040	3960
Nd	540	246	717	573	684	1570	1150
Sm	96.1	72.1	199	105	107	176	98.8
Eu	9.63	2.95	18.3	7.18	11.6	17.3	8.63
Tb	16.1	4.91	34.2	21.0	17.9	23.1	10.7
Yb	38.3	19.8	129	65.2	56.7	40.1	17.3
Lu	5.24	2.68	17.4	9.26	6.79	5.32	2.41
Y	461	162	1100	759	607	642	297
Th	41.0	5.6	59.4	67.4	72.1	63.5	329
U	19.5	2.3	20.6	23.4	21.7	124	187
Zr	4360	4230	20100	12200	6620	5270	709
Hf	76.2	123	594	248	121	60.6	7.7
Sn	63	61	79	88	180	197	307
Nb	742	419	1890	894	595	499	892
Ta	51.8	23.0	157	63.9	32.5	39.0	21.5
Li	161	159	155	217	153	650	1000
Zn	505	577	377	619	846	2570	3070
Cu	9	3	3	3	13	3	< 1
Co	0.29	4.1	1.7	-	0.34	-	-
Ni	0.8	< 0.5	< 0.5	< 0.5	3.0	< 0.5	1.3
Sc	< 0.01	8.0	2.4	1.5	0.26	0.01	0.05
V	< 0.5	15	5.5	1.8	1.0	4.0	5.4
Cr	0.9	35	11	7.8	11	11	11
Ga	73	54	47	70	85	101	159
Ge	2.0	3.4	1.7	1.2	1.2	1.5	1.6
B	10	6	3	11	7	5	5
Be	22	8	20	23	25	21	44
Sb	0.4	1.1	< 1.5	0.6	1.2	< 0.5	2.9
Mo	9	3	8	8	5	< 0.5	< 0.5
As	11	7.0	21	16	22	17	2.0
F	1580	20700	3830	10500	373	1470	1220
Cl	23400	400	3010	410	460	180	15
Br	119	1.2	2.1	1.1	< 0.5	< 0.5	< 0.5
I	1.8	< 0.5	< 0.5	0.8	< 0.5	< 0.5	1.8
S	770	35	65	65	420	1500	1430

A.I.: Agpaitic index, $(Na_2O+K_2O)/Al_2O_3$ mol. -: not analysed.

Table 3. Analyses of rocks representing Ilímaussaq liquids

	1 augite syenite, chilled margin	2 evolved augite syenite, av. of 3	3 Cl-poor sodalite foyaite, av. of 3	4 Fe-rich phonolite dyke	5 Fe-rich phonolite dyke	6 aegirine lujavrite av. of 3	7 arfvedsonite lujavrite av. of 2	8 medium- to coarse-grained lujavrite weighted av.
SiO_2 (wt%)	53.24	62.33	51.01	51.83	52.27	52.38	52.25	52.71
TiO_2	2.44	0.50	0.34	0.55	0.46	0.22	0.23	0.35
ZrO_2	0.04	0.11	0.36	0.55	0.78	0.95	0.25	0.13
Al_2O_3	14.79	15.65	17.38	14.57	14.09	13.20	12.23	13.29
Fe_2O_3	2.64	2.12	4.73	7.56	11.03	10.90	6.06	4.04
FeO	8.66	3.54	4.62	4.61	1.15	1.96	8.72	8.21
MnO	0.24	0.16	0.25	0.48	0.30	0.37	0.64	0.60
MgO	1.60	0.31	0.13	0.14	0.07	0.10	0.12	0.12
CaO	4.94	1.69	1.97	2.54	2.06	1.20	0.27	0.30
Na_2O	4.68	6.74	10.08	8.81	9.27	10.72	9.25	9.20
K_2O	4.26	5.53	3.93	4.87	4.12	2.82	3.23	4.69
P_2O_5	0.74	0.08	0.05	0.08	0.09	0.18	0.54	0.41
H_2O^+	0.29†	0.68	4.19	1.56†	1.18†	3.44	3.65	3.70
H_2O^-	0.19	0.20	0.16	0.47	0.36	0.28	0.24	0.13
CO_2		0.23	0.07			0.09	0.19	0.07
S	0.15	0.00	0.02	0.12	0.03	0.06	0.06	0.14
Cl	0.03	0.01	0.09	0.33	0.08	0.05	0.03	0.05
F	0.10	0.15	0.41	0.84	1.80	0.08	0.14	0.16
others	0.46	0.08	0.31	0.42	0.71	0.89	1.64	1.47
	98.99	100.11	100.10	100.33	99.85	99.89	99.74	99.77
- O	0.12	0.07	0.20	0.49	0.79	0.07	0.10	0.15
	98.87	100.04	99.90	99.84	99.06	99.82	99.64	99.62
A.I.	0.83	1.09	1.20	1.36	1.40	1.57	1.53	1.52
FeO*	11.04	5.45	8.88	11.41	11.08	11.77	14.17	11.85
Zr (ppm)	284	836	2690	4040	5740	7010	1860	939

Analysts: J. Kystol, J.C. Bailey and R. Fuge.
† Loss on ignition corrected for other volatiles where known.
A.I.: Agpaitic index, $(Na_2O+K_2O)/Al_2O_3$ mol.
FeO*: Total Fe as FeO.

1: GGU 153394 (new analysis of sample U-106 from Ussing's collection in the Geological Museum, Copenhagen).
2: Average of GGU 152122, 152130, 154378.
3: Average of GGU 57070, 154303, 154347.
4: Sample GGU 42475 (Larsen & Steenfelt 1974), new analysis.
5: Sample ARM 62/8010 (Martin 1985). New analysis.
6: Average of GGU 152128, 154302, 66143.
7: Average of GGU 152127, 154363.
8: 1:1 average of (a) 3 large surface samples (GGU 154397, 154399, 154724) and (b) 21 smaller samples from drill cores.
GGU prefixed to sample numbers: samples in the collections of the Geological Survey of Denmark and Greenland.

almost perfectly incompatible elements. Based on their increasing contents, it was calculated that the final rock type, medium- to coarse-grained lujavrite, was formed after 99% crystallisation of the augite syenite.

Agpaitic melts are relatively depolymerised with a high ratio of non-bridging oxygens to tetrahedrally coordinated cations (Larsen & Sørensen 1987; Ewart & Griffin 1994), and possess enhanced solubility for high-field-strength elements such as Zr (Watson 1979; Farges *et al.* 1991; Hess 1991). Worldwide, contents of Zr in nepheline syenites (and phonolites) increase from around 50 (250) ppm to 1400 (1750) ppm as their agpaitic index increases from 0.8 to 1.1 (Fig. 3). Only two phonolitic series are known to us with significantly higher agpaitic indices. Firstly, agpaitic phonolites in the Igaliko dyke swarm (Pearce 1988), 25 km NE of the Ilímaussaq complex, range up to 6250 ppm Zr with a somewhat aberrant dyke possibly extending the trend to 7600 ppm. Secondly, the rare phonolitic dykes and sills in and around the Ilímaussaq complex show Zr contents rising to 8700 ppm (Fig. 3).

In the foyaite at Ilímaussaq, combining the maximum Zr content in the (001) sector of interstitial aegirine (1.33%, Larsen 1976) with the Zr partition coefficient appropriate to this sector (*c.* 1.33, Wolff & Toney 1993) suggests a saturation level of *c.* 1.0% Zr. The same calculation method yields saturation levels of 0.89% Zr in sodalite foyaite and 0.85% Zr in naujaite. While such Zr contents may only reflect metastable crystallisation in anomalous interstitial micropockets, they are in broad agreement with the highest value so far reported from dykes and sills.

Zirconium contents around 9000 ppm are probably close to the solubility limit for Zr at Ilímaussaq since higher Zr whole-rock contents are only found in cumulates rich in eudialyte. Fractionation of eudialyte produced late lujavritic liquids at Ilímaussaq with Zr contents falling to < 500 ppm. The rise and fall of Zr contents at Ilímaussaq is confirmed by analyses of both cumulus and intercumulus pyroxenes (Larsen 1976).

Enhanced solubility is also evident for (1) F prior to the crystallisation of fluorite, e.g. contents of 0.84% and 1.80% F in two phonolite dykes; (2) P in late lujavrites, e.g. up to 0.39% in arfvedsonite lujavrite and up to 0.40% in medium- to coarse-grained lujavrite; (3) REE + Y in late lujavrites, e.g. up to 1.1% in arfvedsonite lujavrite and up to 1.5% in medium- to coarse-grained lujavrite.

Components which are normally volatile or prone to escape in hydrothermal solutions from many magmas were soluble to a high degree and were largely

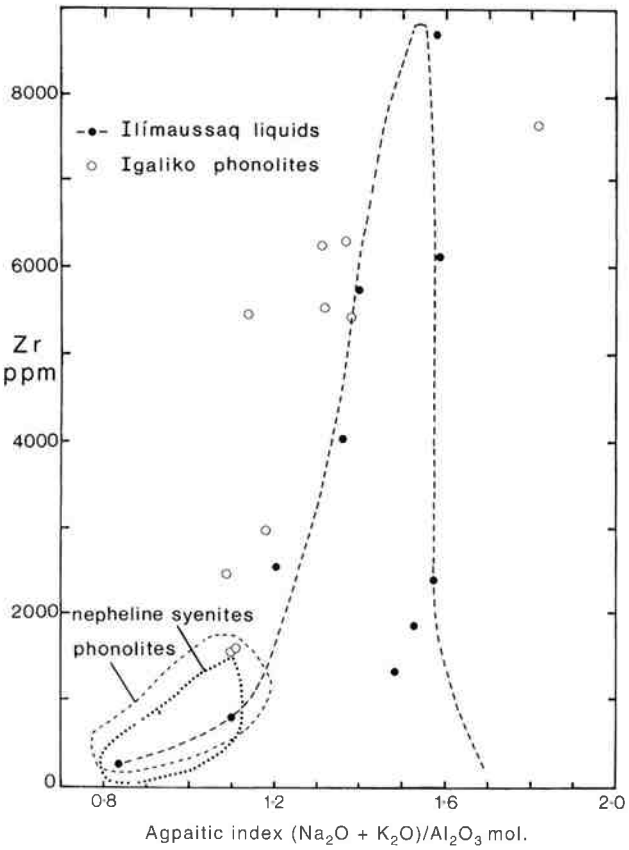


Fig. 3. Zr contents versus agpaitic index showing the main fields for nepheline syenites and phonolites (authors' compilation of 210 localities), the agpaitic phonolite series in the Igaliko dyke swarm (Pearce 1988; new analyses by the authors), and the proposed trend for Ilímaussaq liquids (Table 3).

retained by the agpaitic magmas at Ilímaussaq, e.g. H_2O, Cl, Br, I, S, Mo, As, Tl, B and Cs (cf. Kogarko 1974). Fugacities of oxygen, water and sulphur are inferred to be low, even though their contents are high (Larsen 1976; Karup-Møller 1978; Konnerup-Madsen & Rose-Hansen 1982; Larsen & Sørensen 1987).

The geochemistry of the proposed magma compositions at Ilímaussaq has enabled us to estimate bulk partition coefficients for all studied elements during the main fractionation stages of the complex and to integrate these coefficients with the geochemistry of the various cumulus phases. Some distortion, however, results from the fact that these phases have often modified their chemistry during continued growth at the intercumulus stage.

Such modelling has allowed us, for example, to recognise that, during the early stages at Ilímaussaq, P behaved as a compatible element and was fractionated in apatite. However, after crystallisation of the earliest

agpaitic nepheline syenite, the sodalite foyaite, bulk partition coefficients for P fell to < 0.03 and the build-up of P contents in the late lujavrites, which led to the appearance of the phosphates and silico-phosphates vitusite, monazite, steenstrupine and vuonnemite, can be explained solely by fractional crystallisation.

It is widely recognised that fractionation of magmas is attended by a number of characteristic geochemical trends. Thus K/Rb ratios normally decrease and this trend is also present in the Ilímaussaq rocks with ratios falling from around 500 to 35. Other well-established trends, however, such as the fall in Ba/Rb ratios show reversals at Ilímaussaq. Thus the Ba/Rb ratio sharply rises in the kakortokitic rocks; this can be attributed to the high Ba/Rb ratio of cumulus eudialyte (*c.* 10) compared to Ilímaussaq magmas at this stage (*c.* 0.1). In general, as noted by Gerasimovsky (1969) and Ferguson (1970), there is a good correlation between fractionation trends and the chronology inferred from field relations. In addition, the reversals in the trends of trace element ratios noted by Ferguson (1970) can now be explained on the basis of cumulus processes and mineral geochemistry.

Comparing averages for agpaitic nepheline syenites from various localities, it is found that the Ilímaussaq rocks have lower K/Rb, K/Cs and Sr/Ca but higher Li/Mg, Zn/Fe and Ga/Al ratios than similar materials from Lovozero (Kola Peninsula) and Pilanesberg (South Africa) (Bailey *et al.* 1978). It can thus be inferred that the Ilímaussaq rocks arose from a more extreme fractionation history. This is also reflected in the fact that hyper-agpaitic conditions are not restricted to pegmatites and veins, as at Lovozero and Khibina (Khomyakov 1995), but are already present in the late lujavrites at Ilímaussaq (Sørensen 1997; Sørensen & Larsen 2001, this volume).

Other geochemical ratios, however, are more indicative of the differing parent magmas at these localities. It is characteristic for the more Si-undersaturated basalts that they possess lower Zr/Nb ratios but higher ratios of LREE/HREE (light/heavy REE), e.g. La/Lu. In the Gardar province, early- and mid-Gardar basalts have Zr/Nb ratios around 18 (Upton & Emeleus 1987) whereas among the late-Gardar Tugtutôq–Ilímaussaq dykes two populations of basalt with Zr/Nb ratios of *c.* 6.4 and 3.9 have been distinguished (Pearce 1988). Transitional basalts with Zr/Nb of *c.* 6.4 evolve to Si-oversaturated compositions. In contrast, the more Si-undersaturated suite has Zr/Nb ratios which are relatively constant in basanite/tephrite (3.6), basalt (2.9), benmoreite (3.8) and phonolite (3.5). These can be matched by Zr/Nb ratios from Ilímaussaq in the chilled margin to the Ilímaussaq augite syenite (3.7) which is equivalent to a benmoreite.

Among the agpaitic nepheline syenites from different localities, one can compare lujavrites with a similar degree of differentiation (Bailey *et al.* 1978). Zr/Nb ratios for lujavrites at Ilímaussaq (16) are higher than for lujavrites from Lovozero (10) and Pilanesberg (11) whereas La/Lu ratios in lujavrites at Ilímaussaq (170) are lower than for lujavrites from Lovozero (270) and Pilanesberg (280). These features suggest that the nepheline syenites at Lovozero and Pilanesberg were derived from more Si-undersaturated parental magmas than those from Ilímaussaq. Kogarko (1979) reached the same conclusion on the basis of lower Sr/Ca ratios and more pronounced negative Eu anomalies in the REE patterns at Ilímaussaq compared to those at Lovozero. She concluded that the Ilímaussaq nepheline syenites were derived from nepheline-normative alkali basalts whereas the Lovozero and Khibina nepheline syenites were derived from melilite nephelinites. At Pilanesberg, the high Sr/Ca ratios, subdued Eu anomalies, and association with kimberlite and carbonatite (Ferguson 1973), suggest that the nepheline syenites there were also derived from highly Si-undersaturated magmas.

Rare-earth elements

The main features of REE geochemistry at Ilímaussaq were presented in earlier work by Gerasimovsky (1969), Semenov (1969), Fryer & Edgar (1977), Bailey *et al.* (1978) and Sørensen (1992). Contents of REE are high, reaching maxima in the eudialyte-rich red kakortokites and in the final lujavrites where a number of REE minerals including steenstrupine and vitusite have crystallised. With evolution in the Ilímaussaq system, REE spectra reveal (1) a general increase in total REE, (2) high LREE/HREE (light/heavy REE) ratios which increase sharply in the lujavrites and (3) a more or less uniformly negative Eu anomaly. The only rocks lacking a negative Eu anomaly are some of the earliest augite syenites which still preserve plagioclase cores within their alkali feldspars.

In the earlier agpaitic rocks – sodalite foyaite, naujaite and kakortokites – REE contents correlate with Zr, and REE are mainly located in eudialyte. Total contents of RE_2O_3 (including Y_2O_3) in eudialyte increase fairly regularly from about 1.7 wt% in the early roof rocks (sodalite foyaite) to 8.7 wt% in the late, more evolved aegirine

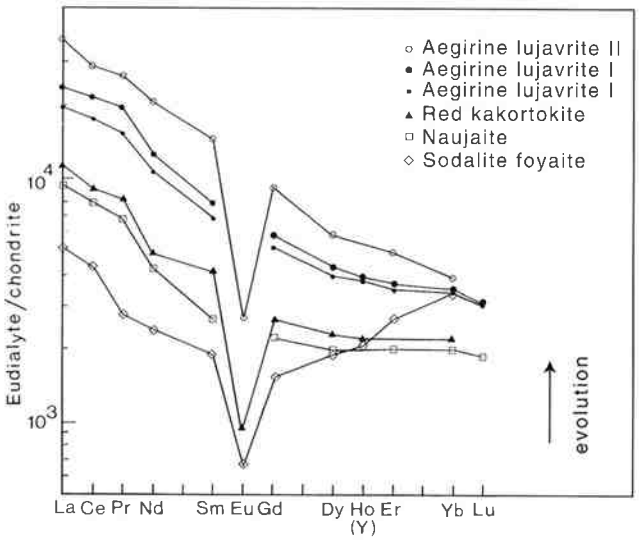


Fig. 4. REE patterns for eudialytes from the Ilímaussaq complex. Sources of data: Aegirine lujavrite II, GGU 77018 (Gerasimovsky 1969); Aegirine lujavrite I, drill core VII (GGU 108107) at 96 m (larger point) and at 146 m (smaller point) (Bailey 1995); Red kakortokite, GGU 77045 (Gerasimovsky 1969); Naujaite, drill core VII (GGU 108107) at 34 m (Bailey 1995); Sodalite foyaite, GGU 138761 (Fryer & Edgar 1977).

lujavrite (Fig. 4). In this sequence, $(La/Yb)_N$ (chondrite normalised) ratios also increase from about 1.5 to 9.4; this is largely due to an increase in $(Gd/Yb)_N$ ratios from 0.45 to 2.3 since $(La/Sm)_N$ ratios show no clearly defined trend. The REE patterns of eudialyte tend to show an increasing slope for HREE in the early rocks but a decreasing slope in the later rocks. Europium anomalies, as measured by Eu/Eu^* ratios, typically scatter around 0.2–0.4 but show no clear trend with evolution. The Ilímaussaq eudialytes cover most, though not all, of the REE range of the eudialyte group (Johnsen & Gault 1997). The huge tonnages, and relatively high contents of HREE compared to presently exploited REE sources, bastnaesite and monazite, mean that Ilímaussaq eudialyte has the potential to be an important future resource of REE (Sørensen 1992).

The distribution of REE between co-existing minerals can be illustrated by a sample of aegirine lujavrite I (Fig. 5). Eudialyte dominates the REE budget. The REE patterns of all minerals are characterised by LREE enrichment and a negative Eu anomaly. Compared to the bulk rock, the eudialyte REE pattern is slightly enriched in MREE (middle REE) and Eu indicating the preferential entry of Ca-Sr-Eu into this phase. Relative to the bulk rock, REE patterns of the remaining minerals are slightly depleted in MREE and the negative Eu anomaly is more pronounced; the La/Yb_N ratio is similar in aegirine, higher in microcline + nepheline and analcime + natrolite, but lower in arfvedsonite. These features are broadly consistent with preferential entry of LREE into an optimal site of about 1.10 Å in feldspars, and of HREE into an optimal site of about 0.70 Å in pyroxenes and amphiboles (Jensen 1973 but with revised ionic radii from Shannon 1976).

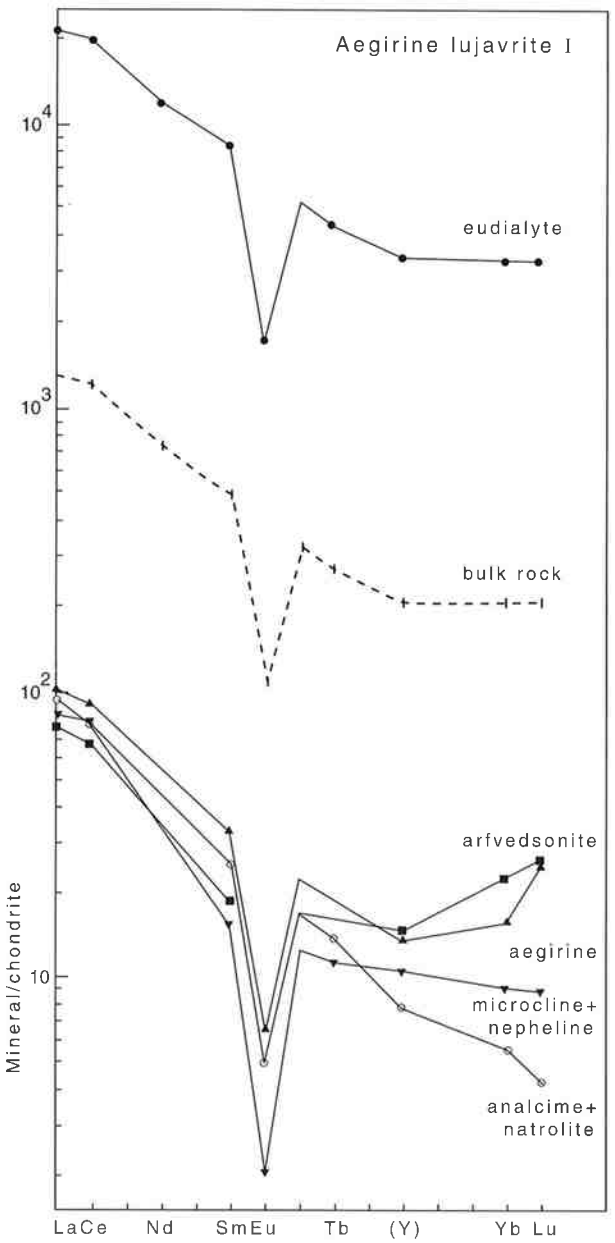


Fig. 5. REE patterns for bulk rock and separated minerals from aegirine lujavrite I, drill core VII (GGU 108107) at 191 m (Bailey 1995).

Cumulate rocks and processes

Ever since the memoir of Ussing (1912), it has been realised that the cumulitic character of many Ilímaussaq rock types has a profound effect on their geochemistry. This is most obviously seen in the exceptionally high contents of Cl in sodalite cumulates (up to 4.6% in naujaite), Zr, Hf and Nb in eudialyte cumulates (up to 3.4%, 0.11% and 0.33%, respectively, in red kakortokite), Fe and Zn in arfvedsonite cumulates (up to 20.3% and 0.082%, respectively, in black kakortokite) and F in fluorite cumulates (up to 2.1% in black kakortokite).

Varying amounts of intercumulus material, i.e. trapped liquid, and varying amounts of additional growth on the cumulus minerals are also significant. For example, in aegirine lujavrite I – which is considered an orthocumulate with virtually no adcumulus growth – Li is dominantly concentrated in the intercumulus material which varies from 25 to 48 wt% (or roughly 30 to 55 vol.%) leading to a variation in Li contents from 80 to 260 ppm (Bailey & Gwozdz 1994).

Because eudialyte more readily accepts U than Th, it has a lower Th/U ratio (*c.* 0.3–0.6) than the magmas from which it crystallises (*c.* 3). Accordingly, in cumulate rocks where additional growth of eudialyte from trapped intercumulus liquid occurs, there appears to be a build-up of Th/U ratios in the shrinking volume of intercumulus liquid. Some of this material is thought to crystallise at a late stage as autometasomatic alteration products on eudialyte and other phases. This non-isomorphous Th and U rarely seems to escape from whole-rock samples even though it is weakly bound in mineral lattices; in consequence it can be leached out of rock powders by a weak leaching agent, a 2% ammonium oxalate solution (Bailey *et al.* 1983).

In the lower layered kakortokites, each white layer accumulated after the underlying, more densely packed, black and red layers and thus has a higher proportion of intercumulus liquid. This has led to relatively high contents of U despite only moderate levels of the main U carrier (eudialyte; Bailey *et al.* 1981), and relatively high levels of Li and Zn despite low contents of the main Li and Zn carrier (arfvedsonite). Clearly, the intercumulus liquid had high contents of U, Li and Zn. In these kakortokites, the percentage of Zn leachable in dilute hydrochloric acid, i.e. the Zn held by sphalerite rather than silicates, increases from 7% in black to 32% in red and 45% in white kakortokite. This suggests that increasing amounts of Zn crystallised as sphalerite from the enhanced amounts of intercumulus liquid in the weakly packed white layers. This is in agreement with the greater amounts of sphalerite separated from white kakortokite (Karup-Møller 1978).

A layered magma chamber

Geochemical evidence is accumulating that the exposed Ilímaussaq rocks of phase 3 crystallised from a layered magma chamber. A number of geochemical parameters shift in a step-like pattern with the steps occur-

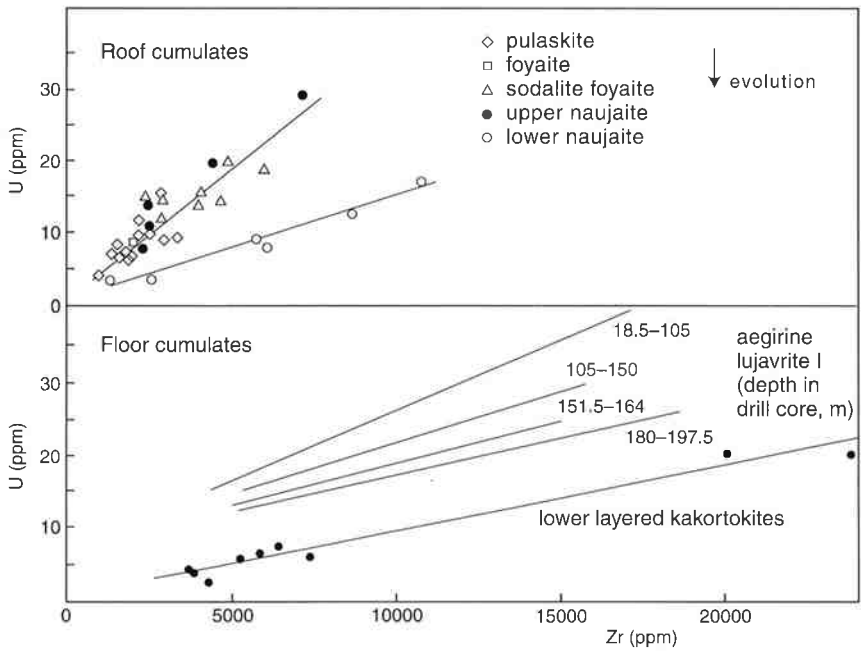


Fig. 6. Zr versus U contents for selected samples of roof and floor cumulates in the Ilímaussaq complex. Data for aegirine lujavrite I in drill core VII (GGU 108107) are from Bailey (1995) but the 200 data points are not shown. The compositional arrays are largely independent of the macrorhythmic layering and are considered to indicate the presence of liquid layering in the Ilímaussaq magma chamber (see text).

ring independently of the boundaries between the various rock types. Thus in the roof cumulates of phase 3, the pulaskite, foyaite, sodalite foyaite and upper layers of naujaite fall along a single array on a Zr–U diagram (Fig. 6). The lower and younger layers of naujaite, however, plot along a different array which has lower U contents – around three times lower – for a given Zr content.

In the floor cumulates which crystallised later, the black and red kakortokites plot along an array with even lower U contents though intercumulus liquids which are concentrated in white layers (see above) are more uraniferous. Floor cumulates from a higher, more evolved stratigraphic level – aegirine lujavrite I – are characterised by higher U contents and by several Zr–U compositional arrays at well-defined stratigraphic intervals. All samples on a given array must be controlled by a chemically uniform eudialyte – the dominant carrier of Zr and U – and the shift to the next line is attributed to the onset of crystallisation in the next chemically distinct double-diffusive liquid layer (Bailey 1995). The shifts occur independently of the macrorhythmic layering in aegirine lujavrite I.

Later lujavrites at higher stratigraphic levels are richer in U and culminate in the Kvanefjeld uranium deposit lying immediately beneath the roof of the complex (Sørensen *et al.* 1974; Kunzendorf *et al.* 1982).

Work is in progress to confirm and to establish more precisely the nature of liquid layering in the Ilímaussaq complex.

The conclusion from these Zr–U relations at Ilímaussaq is that U-rich magmas were restricted to the early uppermost layers of the roof cumulates and the late uppermost layers of the floor cumulates (Fig. 6). This is consistent with heat-flow measurements suggesting that the highly radioactive part of the complex is thin (*c.* 1 km) and the underlying rocks contain very little K, U and Th (Sass *et al.* 1972).

Geochemical notes on selected elements

This geochemical overview would not be complete without summarising new information on the less common trace elements (Bi, Cd, Co, Ge, In, I, Hg, Sc, Se, V, W). In addition, given the mineralogical emphasis of the present work, we outline the geochemistry of elements whose contents exceed 100 ppm in certain rocks but which nevertheless failed to form minerals in the Ilímaussaq complex (Br, Cs, Ga, Hf, Rb, Sr).

Bismuth. Both chalcophile and lithophile tendencies are apparent at Ilímaussaq. Among sulphides, galena from a vein contained 235 ppm Bi; sphalerite from medium- to coarse-grained lujavrite contained 15 ppm and two vein sphalerites contained 15 and 20 ppm. In cuprostibite, we found 34 ppm Bi. In silicates, Bi was located in the REE–Th mineral steenstrupine where it is in the range 7–14 ppm in pegmatites and 6–17 ppm in veins. We failed to detect Bi in minerals of Nb–REE (pyrochlore < 3 ppm, rinkite < 4 ppm), Nb (nenadkevichite < 1 ppm) and Zr (eudialyte < 1 ppm). These few results suggest that Bi accumulates in the sulphides and steenstrupine of late pegmatites and veins where it may locally amount to 1–2 ppm.

Bromine. Median Br contents increase from around 0.5 ppm in augite syenite through 0.6 ppm in pulaskite + foyaite and 17 ppm in sodalite foyaite to 57 ppm in naujaite. Thereafter contents fall in bulk kakortokite (1.1 ppm) through aegirine lujavrite (0.5 ppm) to < 0.5 ppm in arfvedsonite lujavrite and medium- to coarse-grained lujavrite. Cl/Br ratios are around 340 in the early stages at Ilímaussaq but fall to around 170 when crystallisation of cumulus sodalite (Cl/Br 170) starts in sodalite foyaite and naujaite. Fractionation of sodalite causes a rapid depletion in Br so that the final naujaites and all subsequent rock types have higher ratios of roughly 400–1500.

Whole-rock trends are repeated in eudialytes with Cl (and Br) contents increasing from 1.1% (12 ppm) to 1.7% (40 ppm) and then decreasing to 0.6% (3 ppm). Br contents of sodalite fall from around 340 ppm to 100 ppm.

Cadmium. Preliminary analyses by atomic absorption on Ilímaussaq rocks suggest they contain around 0.15 ppm Cd rising to 2 ppm in the most Zn-rich samples. Sphalerite from aegirine lujavrite and medium- to coarse-grained lujavrite contains 20 and 50 ppm Cd, respectively (Karup-Møller 1978).

Caesium. Median Cs contents increase from 0.9 ppm in augite syenite through 6.0 ppm in pulaskite + foyaite, 5.0 ppm in sodalite foyaite + naujaite, 6.6 ppm in bulk kakortokite, 7.9 ppm in aegirine lujavrite and 8.7 ppm in arfvedsonite lujavrite to 72 ppm in medium- to coarse-grained lujavrite.

In aegirine lujavrite I, a sample from drill core VII (GGU 108107) at 191 m depth contained Cs in analcime + natrolite (42 ppm), microcline + nepheline (1.8 ppm) and arfvedsonite (1.7 ppm) but Cs was undetected in

aegirine and eudialyte. Contributions from these minerals sum to 9.3 ppm and indicate that *c.* 90% of the Cs is held in the interstitial zeolites (Bailey 1995). Separates of analcime + natrolite from 11 different depths in this drill core showed a wide range of Cs contents from 2.2 to 44 ppm. Enhanced contents of Cs (6.1–16 ppm) were found in zeolite-rich hydrothermal coatings scraped from fracture planes.

Contents of Cs in 10 samples of medium- to coarse-grained lujavrite from Kvanefjeld drill cores increased at shallow depths. Averages for Cs (and Rb/Cs) changed from 8.3 ppm (154) at 100–150 m depth to 72 ppm (17) at 50–100 m depth and 231 ppm (4.0) at < 50 m depth. Thus samples at 100–150 m depth have Rb/Cs ratios above typical magmatic values at Ilímaussaq and appear to have lost Cs. At shallow depths, Rb/Cs ratios fall below these magmatic values and contents of H_2O^+, Th and U (but not K and Rb) increase. This suggests that medium- to coarse-grained lujavrite has undergone Cs-rich zeolitisation in the Kvanefjeld roof zone.

Many veins are likely to be rich in Cs since samples of the widespread phase analcime contain 200–250 ppm Cs. Lesser amounts of Cs occur in pyrochlore (42 ppm), lueshite (13 ppm), neptunite (8.1 ppm), natrolite (< 0.2–7.3 ppm), tetranatrolite (4.7 ppm), tugtupite (1.3 ppm), quartz (1.0 ppm) and ussingite (0.7 ppm) but not chkalovite (< 0.5 ppm) or epistolite (< 1 ppm)

Cobalt. Median Co contents decrease from augite syenite (6.0 ppm) through pulaskite + foyaite (0.47 ppm) to sodalite foyaite + naujaite (0.36 ppm). Co levels rise in the bulk kakortokite (1.3 ppm) but fall again in aegirine lujavrite (0.25 ppm), arfvedsonite lujavrite (< 0.05 ppm) and medium- to coarse-grained lujavrite (0.20 ppm).

The Fe/Co ratio for the average nepheline syenite at Ilímaussaq (137 000) is higher than all values in our survey of nepheline syenites and phonolites. Significantly, low Co contents and high Fe/Co ratios were already present in the earliest rock type at Ilímaussaq – the augite syenite.

In kakortokites, median Co contents decrease from black (3.3 ppm) through red (1.5 ppm) to white layers (0.93 ppm) reflecting the fact that Co is mainly hosted by arfvedsonite. Arfvedsonite here occurs as a cumulus phase and contains higher Co (4.2–4.8 ppm) than in the preceding interstitial arfvedsonite from the roof-zone naujaite. Co is notably present, substituting for Fe, in accessory löllingite (0.92%) and westerveldite (0.38%) from a white kakortokite (GGU 154327; Karup-Møller 1978). The Fe/Co ratios for löllingite (29) and westerveldite (110) are much lower than in the host rock (85 000) and emphasise the chalcophile behaviour of Co in these phases.

Scavenging of Co by arfvedsonite from the magma co-existing with the kakortokites led to a fall in Co contents. Thus arfvedsonites from early black layers -9 (4.7 ppm) and 0 (4.8 ppm) contain more Co than arfvedsonites from black layer +16 (4.2 ppm) and layer A (2.6 ppm) in the later, transitional layered kakortokites. In kakortokites, Co was also found in fluorite (0.01 ppm) but not in eudialyte (< 1 ppm) or microcline + nepheline (< 0.5 ppm).

Gallium. Ga contents reach exceptionally high levels in Ilímaussaq rocks, averages increasing from 27 ppm in augite syenite through 59 ppm in pulaskite + foyaite, 69 ppm in sodalite foyaite + naujaite, 60 ppm in bulk kakortokites and 102 ppm in aegirine lujavrite to 113 ppm in arfvedsonite lujavrite and 106 ppm in medium- to coarse-grained lujavrite.

Analyses of minerals from agpaitic nepheline syenites reveal around 180 ppm Ga in analcime and 270 ppm in natrolite. Lower contents are found in microcline (142–144 ppm), arfvedsonite (57–62 ppm), nepheline (28 ppm) and sphalerite (15 ppm).

Within the katophorite–arfvedsonite series, during crystallisation from pulaskite to aegirine lujavrite, Ga contents decrease from around 54 to 37 ppm along with Al contents from around 1.9 to 0.75%. In late arfvedsonites, however, from arfvedsonite lujavrite to medium- to coarse-grained lujavrite and derivative pegmatites, Al contents continue to fall from around 0.75 to 0.4% whereas Ga contents increase from around 37 to 62 ppm.

For any given rock type, Ga/Al ratios increase in the sequence aluminosilicate < arfvedsonite < aegirine < magnetite, i.e. ratios increase along with rising Fe^{3+} contents of minerals. Thus Ga, rather than Al, preferentially enters minerals rich in Fe^{3+} reflecting the similar ionic radii of Ga^{3+} (0.620 Å VI) and Fe^{3+} (0.645 Å VI).

Germanium. Median Ge contents decrease slightly through the Ilímaussaq rocks from around 1.8 to 1.5 ppm. The outstanding feature of Ge geochemistry at Ilímaussaq is the exceptionally low and falling contents in feldspars during magmatic evolution, from about 0.8 to 0.2 ppm. This trend is discussed elsewhere in this volume (Bailey 2001, this volume).

Hafnium. Median Hf contents rise from 9 ppm in augite syenite through 40 ppm in pulaskite + foyaite and 67.5

ppm in sodalite foyaite + naujaite to 219 ppm in bulk kakortokite and then fall through 101 ppm in aegirine lujavrite and 47 ppm in arfvedsonite lujavrite to 7.7 ppm in medium- to coarse-grained lujavrite. Individual samples emphasise the extremes of concentration and depletion, from 5.0 ppm in a primitive augite syenite to 1070 ppm in a red kakortokite and down to 2.6 ppm in a medium- to coarse-grained lujavrite.

Median Zr/Hf ratios are relatively constant from augite syenite (45) through pulaskite + foyaite (49) and sodalite foyaite + naujaite (45) to bulk kakortokite (44). But in the later rocks, there is a steady increase from aegirine lujavrite (73) and arfvedsonite lujavrite (86) to medium- to coarse-grained lujavrite (97). These are some of the highest Zr/Hf ratios recorded in igneous rocks.

In aegirine lujavrite I, about 97% of all Hf is held in eudialyte which shows contents decreasing overall from 1580 to 1320 ppm at higher stratigraphic levels and Zr/Hf ratios rising from 63 to 70. Hf contents of aegirine decrease from 59 to 38 ppm with Zr/Hf rising from 37 to 41.

Eudialytes studied to date from early sodalite foyaite to late aegirine lujavrite I show decreasing Hf contents from *c.* 2000 to 1320 ppm with Zr/Hf ratios rising from *c.* 50 to 70. The same overall trend is shown by arfvedsonite (Hf from *c.* 60 to 6 ppm, Zr/Hf from *c.* 37 to 86). Rising Zr/Hf trends in rocks and minerals reflect the preferential partitioning of Hf^{4+} (0.71 Å) rather than Zr^{4+} (0.72 Å) into eudialyte where the site dominated by Zr^{4+} has an optimum size for cations close to 0.67 Å (Johnsen & Grice 1999).

Following its extensive fractionation in the kakortokites and aegirine lujavrite I, eudialyte is absent from the final lujavrite (medium- to coarse-grained lujavrite) and from the late pegmatites and veins. The reduced amounts of Zr and Hf substitute for REE–Th (steenstrupine), Nb–Ti (neptunite, epistolite, pyrochlore, lueshite) and perhaps Fe (aegirine, arfvedsonite). Zr/Hf ratios are exceptionally high in some of these late minerals rising to 200 or more in epistolite and lueshite.

Indium. Sphalerite separates from aegirine lujavrite and medium- to coarse-grained lujavrite contain 8 and 10 ppm In, respectively (Karup-Møller 1978).

Iodine. Median iodine contents at Ilímaussaq rise from augite syenite (< 0.5 ppm) and pulaskite + foyaite (< 0.5 ppm) to sodalite foyaite + naujaite (0.6 ppm). In the floor cumulates, iodine was undetected in bulk kakortokite (< 0.5 ppm) and aegirine lujavrite (< 0.5 ppm) but contents rise through arfvedsonite lujavrite (0.8 ppm) to medium- to coarse-grained lujavrite (1.8 ppm).

In naujaite, there are clear stratigraphic trends with iodine contents decreasing from around 1.7 ppm in the earliest, uppermost samples to 0.5 ppm in the deepest samples. This reflects the pronounced removal of iodine in the earliest cumulus crystals of sodalite.

Mercury. Contents of Hg range from 0.62 ppb in alkali granite to 11.7 ppb in naujaite (Stakheev *et al.* 1975).

Rubidium. Median Rb contents increase from 83 ppm in augite syenite through 312 ppm in pulaskite + foyaite, 364 ppm in sodalite foyaite + naujaite, 459 ppm in bulk kakortokite and 674 ppm in aegirine lujavrite + arfvedsonite lujavrite to 1280 ppm in medium- to coarse-grained lujavrite. Median K/Rb ratios decrease from 463 in augite syenite through 134 in pulaskite + foyaite, 83 in sodalite foyaite + naujaite, 79 in bulk kakortokite and 40 in aegirine lujavrite + arfvedsonite lujavrite to 35 in medium- to coarse-grained lujavrite.

In aegirine lujavrite I, Rb contents parallel K showing maxima in layers rich in microcline. These maxima have Rb contents of 775–1130 ppm whereas layers with background levels of K-feldspar only contain about 400 ppm. Preferred Rb contents in minerals are: microcline + nepheline (2570–3110 ppm Rb, K/Rb 42–49), arfvedsonite (79–104 ppm, K/Rb 215–272), eudialyte (47–116 ppm, K/Rb 47–74), analcime + natrolite (6.5–128 ppm, K/Rb 38–132) and aegirine (3–4 ppm, K/Rb 218–366) (Bailey 1995). Hydrothermal coatings scraped from fracture planes contain 93–450 ppm Rb.

The evolution of Rb contents in the rock-forming minerals at Ilímaussaq has not been systematically studied but we note that Rb contents in microcline increase from 125 ppm in augite syenite to 3100 ppm in aegirine lujavrite I. Rb contents in arfvedsonite increase from 57 ppm in naujaite to 142 ppm in medium- to coarse-grained lujavrite, and in eudialyte from 20 ppm in foyaite to 81 ppm in aegirine lujavrite I.

Scandium. Median Sc contents fall from 30 ppm in augite syenite through 0.52 ppm in pulaskite + foyaite to 0.16 ppm in sodalite foyaite + naujaite. The succeeding kakortokites have a bulk content of 2.0 ppm but there is a further fall to 0.018 ppm in aegirine lujavrite and arfvedsonite lujavrite with only a slight recovery in medium- to coarse-grained lujavrite (0.075 ppm).

In augite syenite, Sc decreases from 39 ppm to 3.5 ppm as total Fe falls from 10.5 to 2.4 wt%. Sc is dominantly held in hedenbergite (226 ppm) with lesser amounts in magnetite (*c.* 4 ppm), apatite (1.1 ppm), olivine (< 1 ppm) and microcline (0.04 ppm).

In the lower layered kakortokites, there is a clear Sc–Fe correlation with median contents of Sc decreasing from black (5.1 ppm) through red (1.9 ppm) to white (1.5 ppm) kakortokite. In the black layers of the lower layered kakortokites, Sc ranges from 9.8 to 2.4 ppm as total Fe falls from 19.5 to 9.1 wt%. The dominant mafic phase, arfvedsonite, contains 5.8–13 ppm Sc and Sc is also present in cumulus aegirine (4.7 ppm), eudialyte (0.6–2.1 ppm) and fluorite (0.004–1.3 ppm) but not in aenigmatite or microcline + nepheline (both < 0.3 ppm).

By the time the following aegirine lujavrites crystallised, Sc appears to have been almost totally removed from the system; contents average 0.1 ppm and even fall to 0.0*x* ppm. A succeeding modest recovery in median Sc contents is seen in values for arfvedsonite lujavrite (0.05 ppm) and medium- to coarse-grained lujavrites (0.1 ppm).

The Fe–Sc relationship is absent in a group of Fe-poor, complex oxides and silicates with high contents of quadri- and pentavalent ions. These minerals – pyrochlore, astrophyllite, rinkite, epistolite and catapleiite – occur in pegmatites and veins and contain up to 9.3 ppm Sc. The association arises from the similarity in ionic radii between Sc^{3+} (0.745 Å) and Ti^{4+} (0.605 Å), Zr^{4+} (0.72 Å), Nb^{5+} (0.64 Å) and Sn^{4+} (0.690 Å).

Selenium. Se was reported on or just above the detection limit (0.01%) during microprobe analysis of Ilímaussaq sulphides as follows: chalcothallite 0.02%, rohaite and cuprostibite – both 0.01% but thalcusite < 0.01% (Makovicky *et al.* 1980). However, we were unable to detect 1 ppm Se in cuprostibite. Instead, Se was found in a vein galena (850 ppm) and in sphalerites from medium- to coarse-grained lujavrite (33 ppm), a pegmatite (23 ppm) and two veins (28 and 47 ppm). The sulphur-bearing silicates sodalite and helvine contain < 1 ppm Se emphasising the chalcophile character of Se.

Strontium. Median Sr contents decrease from augite syenite (284 ppm) through pulaskite + foyaite (25 ppm) to sodalite foyaite + naujaite (11 ppm) but there is a significant increase in bulk kakortokite (87 ppm) followed by a further decrease in aegirine lujavrite (74 ppm), arfvedsonite lujavrite (61 ppm) and medium- to coarse-grained lujavrite (45 ppm).

Thus, Sr contents appear to increase from the agpaitic roof rocks to the eudialyte-rich floor cumulates – the kakortokites. This reflects the fact that, in the kakortokites, eudialyte and fluorite with high Ca and Sr contents became cumulus phases. Their extraction led to CaO contents falling from about 2.0 to 0.2%, and Sr falling from about 100 to 40 ppm in the subsequent lujavrites. As a result, the final lujavrites move to a unique position in Ca–Sr space finishing with a very low Ca/Sr ratio of *c.* 30.

Tungsten. Median W contents increase from 1–2 ppm in augite syenite to 3 ppm in pulaskite + foyaite and 6 ppm in sodalite foyaite + naujaite to 15 ppm in bulk kakortokite. Thereafter W contents decrease to 10 ppm in aegirine lujavrite, 4 ppm in arfvedsonite lujavrite and 5 ppm in medium- to coarse-grained lujavrite.

At Ilímaussaq, W contents correlate strongly with Zr rising to a value of 75 ppm W in a red kakortokite with a particularly high content of eudialyte. Analyses of eudialytes reveal wide variations in their W contents. An interstitial eudialyte from pulaskite contains a high level of 244 ppm W. There is a remarkable increase in W contents of eudialytes from 4 ppm at the sodalite foyaite + naujaite contact through 61 ppm, 129 ppm and 146 ppm at progressively deeper, later stages. This reflects the build-up of W in residual magmas at the naujaite stage.

With the arrival of eudialyte on the liquidus in the lower layered kakortokites, the earliest available eudialyte (from layer –10) contains 295 ppm W. Contents fall progressively through 248 ppm (layer –9), 200 ppm (layer –4), 184 ppm (layer 0) and 143 ppm (layer +3) to 101 ppm in layer A of the later transitional layered kakortokites. It seems clear that eudialyte preferentially extracts W from the kakortokite magmas so that later stages have lower contents.

Vanadium. The Ilímaussaq rocks contain exceptionally low V contents. Overall, median values decrease from 3.4 ppm in augite syenite to 1.1 ppm in pulaskite + foyaite and 0.7 ppm in sodalite foyaite + naujaite; in the subsequent floor cumulates V concentrates in arfvedsonite-rich materials – bulk kakortokite (4.0 ppm), arfvedsonite lujavrite (5.6 ppm) and medium- to coarse-grained lujavrite (4.2 ppm) – rather than in aegirine lujavrite (1.3 ppm). The increased V contents in the floor sequence of agpaitic rocks coincide with increasing levels of Fe, one of the characteristic features of agpaitic crystallisation.

The unusual geochemistry of V in the Ilímaussaq

complex has its origins in the augite syenite, the immediate parent magma for the complex. The augite syenite contains 1.7–9.9 ppm V which is mainly held in titanomagnetite (156 ppm) and hedenbergite (6 ppm) but not in olivine (< 1 ppm) or microcline (< 0.5 ppm). The conclusion seems inescapable that the augite syenite parental magma at Ilímaussaq had experienced considerable fractionation of V before it was emplaced; this presumably occurred in a deeper magma chamber (cf. Larsen & Sørensen 1987).

In pegmatites, V ranges widely from 54–59 ppm in rinkite to 24–25 ppm in aenigmatite, 17–23 ppm in steenstrupine, 0.9–18 ppm in arfvedsonite, 0.7–6.0 ppm in polylithionite, 2.1 ppm in aegirine and < 0.5 ppm in microcline and catapleiite.

In veins, V ranges even more widely from 0.5–479 ppm in epistolite, 233 ppm in astrophyllite, 112 ppm in neptunite, 64 ppm in lueshite, 6.4–12 ppm in steenstrupine, < 0.5–8.2 ppm in pyrochlore, 4.4–4.7 ppm in sphalerite, 2.6 ppm in calcite, 1.5–1.6 ppm in arfvedsonite, 0.9 ppm in pectolite, < 0.5–0.6 ppm in aegirine, < 0.5–0.5 ppm in natrolite and < 0.5 ppm in eudialyte, sodalite, sorensenite, ussingite, tugtupite, tetranatrolite, chkalovite, analcime and albite.

Concluding remarks. Overall then, for the dominant agpaitic nepheline syenites of the Ilímaussaq complex, Co, Sc and V can be safely grouped with the ferromagnesian elements. The chalcophile character of Bi, Cd, In and Se is already discernible, though a quantitative assessment must await whole-rock analyses. Hafnium and W follow other high field-strength elements into eudialyte and both elements are impoverished in late pegmatites and veins. Iodine and Br closely follow their fellow halogen Cl being largely held by the sodalites of sodalite foyaite and naujaite. Gallium, Rb and Sr are well-known examples of camouflaged elements which substitute in Al, K and Ca minerals, respectively; they maintain this behaviour in the Ilímaussaq complex.

Summary

1. The agpaitic nepheline syenites of the Ilímaussaq complex are characterised by a great variety of sodic minerals, and by high contents of Zr, Hf, Nb, Ta, REE, Th, U, Sn, Li, Be, Rb, Zn, Pb, Sb, W, Mo, As, Ga, F, Cl, Br, I and S but low levels of Ba, Sr, Co, Cu, Ni, Sc, V and Cr.

2. The agpaitic nature of Ilímaussaq magmas led to the appearance of Na-rich rock-forming minerals (sodalite, albite, arfvedsonite, aegirine, eudialyte) and combinations of Na with rare elements, e.g. Na–Nb (pyrochlore), Na–REE (steenstrupine), Na–Be (chkalovite) and Na–P (vitusite).

3. During fractionation of the agpaitic magmas, separation of cumulus phases with a distinctive geochemistry, such as sodalite (rich in Cl, Br, I, B), eudialyte (Zr, Hf, Nb, Ta, W, As) and arfvedsonite (Co, Sc, V, Cr), was responsible for exhaustion of these elements in the residual magmas.

4. The agpaitic magmas were capable of dissolving high contents of Zr (*c.* 9000 ppm), REE, Y and P, as well as normally volatile or mobile elements such as H_2O, Cl, Br, I, S, Mo, As, Tl and Cs.

5. The agpaitic magmas underwent more than 99% fractional crystallisation from the parental augite syenite. This fractionation, along with the cumulate character of most rocks, was responsible for the extreme concentration and impoverishment of the different elements.

6. Whole-rock analyses define a number of discrete Zr–U arrays which are restricted to certain intervals of the cumulate stratigraphy and are taken as evidence for liquid layering in the Ilímaussaq magma chamber.

7. The distribution of the less common trace elements (Bi, Cd, Co, Ge, In, I, Hg, Sc, Se, V, W) and of the more abundant trace elements which failed to form minerals (Br, Cs, Ga, Hf, Rb, Sr) is summarised.

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Distribution of germanium in rocks and minerals of the Ilímaussaq alkaline complex, South Greenland

John C. Bailey

In the agpaitic nepheline syenites of the Ilímaussaq complex, analyses by X-ray fluorescence spectrometry reveal that Ge is largely held in arfvedsonite (2.4–4.3 ppm) and aegirine (2.5–4.3 ppm) and has abnormally low contents (down to < 0.2 ppm) in microcline. This distribution is discussed in relation to three controls: (1) increased ratios of octahedral to tetrahedral Ge in Na-rich, Ge-bearing melts and in high-pressure melts, (2) increased ratios of bivalent to quadrivalent Ge in highly reduced melts and (3) reduced admittance of Ge into the structurally ordered low microcline which crystallised in the low-temperature agpaitic magmas.

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As part of an on-going geochemical study, the distribution of germanium has been investigated in the rocks and minerals of the Ilímaussaq alkaline complex.

General properties of germanium

The igneous geochemistry of Ge is characterised by its occurrence at the level of 1–2 ppm, and by its entry into silicates as a result of the similarity in properties between Ge and the vastly more abundant Si (Hörmann 1970; Bernstein 1985).

With its high ionic potential, Ge readily forms tetrahedral complexes of $(GeO_4)^{4-}$ with mixed covalent–ionic bonding. These complexes are thought to replace $(SiO_4)^{4-}$ in silicate melts and minerals reflecting the fact that quadrivalent Ge and Si have similar covalent radii (Ge 1.22 Å, Si 1.17 Å; Cotton & Wilkinson 1966) and ionic radii (Ge 0.390 Å, Si 0.26 Å; Shannon 1976). In agreement with this, crystallographers have long recognised that germanates are isostructural with many silicates and many of these analogues have been synthesised experimentally.

Geochemists have generally assumed that Ge^{4+}, at trace element levels, follows Si^{4+} into silicate minerals and is thus tetrahedrally co-ordinated. The various anionic silicate groups found in minerals are demonstrably present in the local co-ordination of silicate glasses and melts (e.g. Hess 1980). It can thus be inferred that Ge, like Si, behaves as a network-forming cation in silicate melts.

In detail, when magmatic silicates crystallise it is found that Ge contents are higher in pyroxenes, amphiboles and olivines than in the tectosilicates feldspar or quartz where the three-dimensional silicate network is less amenable to distortion by the larger $(GeO_4)^{4-}$ tetrahedra.

Germanates with purely octahedral surroundings have also been reported, e.g. the perovskite-like $La_2Mg\,Ge^{VI}O_6$. Germanium dioxide has two polymorphs with differing anion co-ordination about the central cation: α-quartz-type GeO_2 with GeO_4 units, and rutile-type GeO_2 with GeO_6 units. Zeolitic germanates have GeO_4 tetrahedra and GeO_6 octahedra, e.g. $Na_3H(Ge^{VI}_4Ge^{IV}_3O_{16})\cdot nH_2O$ (Wittmann 1970).

The octahedral ionic radius of Ge^{4+} (0.53 Å), unlike the smaller radius of Si^{4+} (0.400 Å), should allow Ge^{4+} to follow Al^{3+} (0.535 Å), Ti^{4+} (0.605 Å), Fe^{3+} (0.645 Å) and Zr^{4+} (0.72 Å) into, e.g. Ti-rich minerals or the octahedral sites of mafic silicates. However, since optimal octahedral sites in the mafic silicates of igneous rocks are around 0.66–0.71 Å and significantly larger than

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the germanium ion, the tendency to enter these sites will be reduced.

The electronegativity of Ge (2.01) is higher than those of Sn (1.96) and Si (1.90) and leads to the chalcophile character of Ge. Entry of Ge into sulphides, however, is more evident at low temperatures than in magmatic sulphides.

Compounds of divalent Ge are generally restricted to low-temperature reducing conditions and are not reliably established under natural conditions. Nevertheless, the possibility of high Ge^{2+}/Ge^{4+} ratios in the low-fo_2 agpaitic melts at Ilímaussaq is considered below.

During magmatic fractionation, early removal of olivine with a partition coefficient for Ge around 0.7 should lead to a slight increase in Ge contents (Capobianco & Watson 1982). However, with the subsequent fractionation of combinations of mafic silicates and feldspars, most magmatic series tend to maintain roughly constant Ge contents – around 1.4 ppm in basic rocks and 1.5 ppm in acid rocks (Bernstein 1985). Relatively high contents of Ge (x0–x00 ppm) in pegmatitic phases such as topaz, muscovite, spodumene, perthite and plagioclase suggest that Ge, at least locally, concentrates in highly fractionated Si-oversaturated magmas (Goldschmidt 1954; Bernstein 1985).

Germanium in alkaline rocks

No systematic studies have been made on the Ge contents of alkaline rocks. A compilation of recent data by the author suggests averages of around 1.3 ppm in nepheline syenites and 1.5 ppm in phonolites, i.e. levels close to those in other magmatic rocks. Similar values for alkaline rocks were reported by Novokhatskiy *et al.* (1968) and Schrön (1968).

In the Lovozero complex, Kola Peninsula, Russia, whole-rock analyses of Ge have not been reported but Ge has been detected by optical emission spectrometry in titanite, beryllite, sphalerite, lorenzenite and aenigmatite (Gerasimovsky *et al.* 1966).

In the Tezhsar complex of Armenia, Ge is present at around 1.6 ppm in nepheline syenites; it is concentrated in magnetite (5 ppm), titanite (10 ppm) and melanite (20 ppm), in accessory allanite (10–30 ppm), other REE minerals (30 ppm) and Ti-Nb minerals (30–100 ppm), and in secondary sodalite (30 ppm) (Meliksetyan 1971).

In the nepheline syenite pegmatites of Langesundsfjord in south Norway, optical emission spectrometric analyses revealed Ge in biotite (8.8 ppm), aegirine (10.4–12.3 ppm), oligoclase + nepheline (10.6 ppm) and perthite (22.7 ppm) (Hörmann 1963). From the same locality, older analyses indicate that orangite, a variety of zircon, contains 60 ppm Ge (Noddack & Noddack 1931) while the hydrothermal phases datolite with about 7 ppm and diaspore with about 70 ppm Ge (Goldschmidt 1954) also have relatively high contents of Ge.

Analytical method

Although Ge is rarely determined by X-ray fluorescence spectrometry, it is well within the capabilities of modern equipment. The following machine conditions were used: Philips PW1400 spectrometer, Mo tube, 80 kV, 30 mA, fine collimator, flow plus scintillation counter, LiF (200) crystal. The analysis was made for 400 seconds at the Ge$K\alpha$ peak and 400 seconds at the background at -0.46° 2θ, and was repeated four times for each sample. For many rock types there are no significantly interfering X-ray lines unless a tungsten carbide pot is used for grinding. However, in many Ilímaussaq rocks and minerals, interferences from Ta$L\beta_2$, W$L\beta_2$, W$L\beta_3$ and Zn$K\beta$ on Ge$K\alpha$ can be significant. They were monitored by determining interference factors on three synthetic mixtures made from pure SiO_2 and 100 ppm Ta, 100 ppm W and 1000 ppm Zn relative to Ta$L\beta_2$, W$L\beta_1$ and Zn$K\beta_1$, respectively, all with 100 seconds analytical time. Interference from the second-order tube line Mo$K\beta$ is potentially troublesome because it is matrix dependent. However, following the removal of Ta, W and Zn interferences, it was eliminated by computing Ge ppm values directly from peak/background ratios. Calibration was made against (1) a series of synthetic standards made from ultra-pure SiO_2, Fe_2O_3 and GeO_2 and (2) the international reference materials G-2 (1.14 ppm), W-1 (1.65 ppm) and Mica-Fe (3.2 ppm). Agreement between the two sets of standards was good. Under the above conditions, precision was close to ± 0.1 ppm and the detection limit was around 0.2 ppm. Accuracy can be judged from the following Ge ppm values on other reference materials (the values in brackets, where available, are from Govindaraju (1994), except for NIM-L which is from Halicz (1990)): GSP-1 1.2 (1.36), STM-1 1.35 (1.4), SY-2 1.3 (1.3), SY-3 1.35 (1.4), NIM-L 0.9 (0.89), NIM-S 0.5 (–), NIM-G 1.6 (–), ASK-1 1.5 (2), Mica-Mg 0.7 (0.55), FK-N 2.4 (2.5), MA-N 3.4 (3.5), AL-1 1.5 (1.4), ZGI-GNA 8.0 (–).

Minerals were separated by conventional methods

Table 1. Ge contents in rocks of the Ilímaussaq alkaline complex

	Rock type	Number of samples	Ge (ppm) median	Ge (ppm) range
Augite syenite	Fine augite syenite	5	1.9	1.7–1.9
	Coarse augite syenite	4	1.7	1.6–2.3
Oversaturated rocks	Quartz syenite	7	1.8	1.1–2.0
	Alkali granite	8	1.7	1.4–2.1
Nepheline syenites	Pulaskite	8	1.8	1.3–2.0
	Foyaite	5	1.4	1.2–2.0
Agpaitic rock types	Sodalite foyaite	10	1.6	1.3–2.4
	Naujaite	12	1.7	1.2–2.0
	Black kakortokite	11	3.1	2.0–3.7
	Red kakortokite	5	1.5	0.3–1.7
	White kakortokite	11	1.5	1.2–2.0
	Aegirine lujavrite	8	0.9	0.6–1.2
	Arfvedsonite lujavrite	12	1.6	1.4–2.5
	Medium- to coarse-grained lujavrite	3	1.6	1.5–2.4

The rock types are listed in the approximate succession in which they crystallised.

of magnetic separation and heavy liquids. Corrections were made for impurities but proved to be insignificant in the present work.

Germanium in the Ilímaussaq complex

Ge contents in a number of Ilímaussaq rocks were reported in a preliminary study by Bailey *et al.* (1978), and these results have been confirmed and extended in the present work (Table 1). An outline of the geology and rock types at Ilímaussaq, together with localities referred to here, is given by Sørensen (2001, this volume) and can be supplemented by the references therein.

Overall, median Ge contents decrease slightly through the sequence of rocks in the Ilímaussaq complex (Table 1) from around 1.8 ppm in augite syenite to 1.6 ppm in pulaskite + foyaite, 1.65 ppm in sodalite foyaite + naujaite and 1.7 ppm in bulk kakortokite to 0.9 ppm in aegirine lujavrite; there is a partial recovery in arfvedsonite lujavrite (1.6 ppm) and medium- to coarse-grained lujavrite (1.6 ppm). However, in a wider survey of 21 smaller samples of medium- to coarse-grained lujavrite from drill cores, Ge contents were generally lower, ranging from 0.2 to 2.2 ppm with a median of 1.4 ppm. Among the Si-oversaturated rocks, levels in quartz syenite (1.8 ppm) and alkali granite (1.7 ppm) are close to those in augite syenite.

Samples of dykes and sills that are thought to represent Ilímaussaq liquids (Bailey *et al.* 2001, this volume), although few in number, also show a decreasing trend, from 1.9 to 1.6 ppm Ge.

The gentle trends found through the sequence of rock types in the complex can hide significant variations: from 1.3 to 2.4 ppm in sodalite foyaite, and from 1.2 ppm in a white kakortokite to 3.7 ppm in a black kakortokite. Given that Ge is one of the most geochemically monotonous elements in igneous rocks, its wide range of contents at Ilímaussaq is particularly striking.

There is a clear correlation with Fe in many rock types, particularly the kakortokites where, as total Fe decreases from 29 to 4 wt%, Ge decreases from 3.7 to 1.2 ppm. This reflects a trend from cumulates rich in arfvedsonite and aegirine (black kakortokites) to cumulates rich in feldspar, nepheline and zeolites (white kakortokites).

Along with the marked Ge–Fe correlation in individual rock types at Ilímaussaq, there is a trend towards decreasing Ge contents at any given Fe content. Thus, at 9% Fe, contents of Ge decrease from around 1.9 ppm in augite syenite through 1.7 ppm in sodalite foyaite + naujaite to 1.6 ppm in kakortokites and the following lujavrites.

The distribution of Ge among minerals co-existing in individual samples is given in Table 2, and can be supplemented by data on minerals scattered through the various rock types.

The main carriers of Ge at Ilímaussaq are the amphiboles: katophorite in pulaskite (4.5–5.3 ppm), and arfvedsonite in sodalite foyaite (4.1–5.2 ppm), naujaite

Table 2. Ge contents in co-existing minerals of the Ilímaussaq alkaline complex

Rock type GGU number	Minerals ppm				
augite syenite	microcline*	hedenbergite	olivine	magnetite	
154722	1.4	3.6	2.7	2.3	
sodalite foyaite	microcline*,†	arfvedsonite	aegirine	nepheline	sodalite
154351	0.4	5.2	4.1	0.4	0.3
naujaite	microcline*	arfvedsonite	aegirine	eudialyte	sodalite
154345	0.5	4.3	3.7	1.4	0.4
naujaite	microcline*	arfvedsonite	eudialyte	nepheline	sodalite
57041	0.8	5.3	1.5	0.9	0.2
border pegmatite‡	microcline*	arfvedsonite	polylithionite		
107654	0.8	4.6	8.1		
border pegmatite§	microcline*	arfvedsonite			
109617	0.7	4.3			
aegirine lujavrite	microcline†	arfvedsonite	aegirine	eudialyte	A + N
108107-004	0.3	4.3	2.6	1.4	< 0.2
M-C lujavrite	microcline†	arfvedsonite	nepheline	A + N	
154724	0.2	3.9	1.3	< 0.2	

Structure of microcline: * microcline microperthite, † low microcline.
Border pegmatite: ‡ adjacent to kakortokite, Kangerluarsuk, § Kvanefjeld.
A + N: Analcime plus natrolite.
M-C lujavrite: Medium- to coarse-grained lujavrite.

(4.3–6.0 ppm), kakortokite (3.7–4.4 ppm), aegirine lujavrite I (3.7–4.7 ppm), aegirine lujavrite II (2.4 ppm), arfvedsonite lujavrite (6.2–6.3 ppm), medium- to coarse-grained lujavrite (3.9–4.5 ppm), pegmatites (3.7–5.0 ppm) and veins (4.4–6.2 ppm).

Slightly lower levels occur in pyroxenes: hedenbergite in augite syenite (3.6 ppm), aegirine-augite in pulaskite (3.7–4.0 ppm), and aegirines in sodalite foyaite (3.8–4.1 ppm), naujaite (3.7–4.3 ppm), kakortokite (3.7 ppm), aegirine lujavrite I (2.5–3.4 ppm), aegirine lujavrite II (2.9–3.6 ppm), pegmatites (2.9–3.3 ppm) and veins (3.2–4.3 ppm).

There are no well-defined trends in Ge contents for these two minerals as the Ilímaussaq system evolves, not even at the stage of pegmatites and veins. Cumulus and intercumulus varieties also show no clear differences.

In contrast, Ge contents in microcline show an irregular decrease from augite syenite (1.4 ppm) through sodalite foyaite (0.4 ppm), naujaite (0.5–0.8 ppm), kakortokite (0.8 ppm), aegirine lujavrite I (0.3–0.4 ppm), aegirine lujavrite II (< 0.2 ppm) and medium- to coarse-grained lujavrite (0.2–0.3 ppm). Among pegmatites, the Ge content of microcline decreases from a naujaite pegmatite (1.6 ppm) to the border pegmatites adjacent to the kakortokites (0.6 ppm) and on Kvanefjeld (0.7 ppm). The decreasing contents of Ge appear to be linked to the degree of structural order in the microcline, from microcline microperthite in the augite syenite and early nepheline syenites to low microcline in the late nepheline syenites (Table 2). This relationship is considered more fully in the discussion below.

At the magmatic stage, other leucosilicates also generally have low contents of Ge: nepheline (< 0.2–1.3 ppm), sodalite (0.3–0.5 ppm) and the zeolites analcime and natrolite (< 0.2–0.3 ppm). In veins, Ge contents are even lower in sodalite (< 0.2 ppm) and albite (< 0.2 ppm), and are barely higher in analcime (< 0.2–0.2 ppm), tugtupite (0.2 ppm), natrolite (< 0.2–0.5 ppm), ussingite (0.2–0.5 ppm) and chkalovite (0.5 ppm). In the magmatic rocks, the crystallisation sequence for leucocratic phases both within and between the vari-

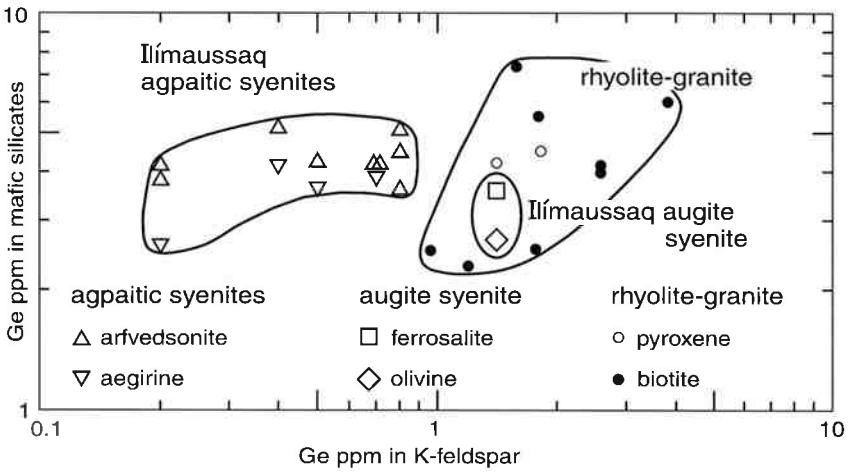


Fig. 1. Distribution of Ge in co-existing mafic silicates and K-feldspars in the Ilímaussaq complex and other igneous rocks. The character of the mafic silicate is distinguished by different symbols. Data for pyroxene-sanidine pairs in rhyolites from Ewart & Griffin (1994) and for biotite–K-feldspar pairs in granites from Hörmann (1963) and Schrön (1968). Note the low Ge contents in microclines from the Ilímaussaq agpaitic nepheline syenites.

ous rock types is early microcline and nepheline ± sodalite but late analcime and natrolite, and it is clear that this sequence is characterised by generally decreasing contents of Ge.

Of the remaining rock-forming minerals, Ge contents in eudialyte (1.3–1.9 ppm) and steenstrupine (0.7–0.9 ppm) were determined with great difficulty because of large interferences but seem unremarkable.

To date, Ge contents greater than 10 ppm have been detected only in two minerals. Aenigmatite from naujaite pegmatites contains 10.2–10.7 ppm Ge, recalling the high Ge level of 22.1 ppm reported in phenocrystal aenigmatite from a peralkaline rhyolite at Mayor Island, New Zealand (Ewart & Griffin 1994). Around 50 ppm Ge was reported for aenigmatite from alkali pegmatites (Vlasov 1966), presumably from Lovozero, Russia.

Sphalerite from an albite-steenstrupine vein at Ilímaussaq contains 42 ppm Ge but a second sphalerite from a different vein only contains 7.8 ppm Ge, and the rare antimonide cuprostibite has 5.0 ppm. Thus the chalcophile tendencies of Ge appear subdued in the Ilímaussaq complex.

Judged from mineral analyses, especially the relatively low levels in sphalerite which is only of local occurrence, it seems likely that the decreasing trend of Ge contents in the Ilímaussaq magmas continues into late pegmatites and veins.

Overall, the outstanding feature of the geochemistry of Ge at Ilímaussaq is the change in the mineralogical distribution of Ge between the augite syenite and the agpaitic nepheline syenites. The distribution of Ge in augite syenite is consistent with that established at other igneous localities: pyroxene > olivine > feldspar (Harris 1954) and the minerals show comparable absolute contents. In the agpaitic nepheline syenites, the mineralogical preference is generally: aenigmatite > arfvedsonite > aegirine > eudialyte > microcline = nepheline > sodalite > zeolites. Partition coefficients for Ge between minerals and magma, though only roughly estimated, are highest in aenigmatite (6), arfvedsonite (3) and aegirine (2) and distinctly lower in K-feldspar (0.5 falling to 0.1) and other tectosilicates.

Most significantly, the Ge contents of K-feldspars in the agpaitic nepheline syenites of Ilímaussaq are exceptionally low and fall from about 0.8 to 0.2 ppm during magmatic evolution (Fig. 1). These levels contrast sharply with contents in K-feldspars in the augite syenite at Ilímaussaq (1.4 ppm), and in granites (0.9–3.8 ppm) and granitic pegmatites (2.1–29.2 ppm) from various localities (Hörmann 1963; Novokhatskiy *et al.* 1968; Schrön 1968; Bernstein 1985; author's unpublished data). Contents in other Ilímaussaq tectosilicates (nepheline, sodalite, analcime and natrolite) can also fall to < 0.2 ppm.

In terms of partitioning between co-existing minerals, the ratio of Ge in mafic silicate to K-feldspar is *c.* 1–5 in normal igneous rocks but 5–20 in the Ilímaussaq agpaitic rocks (Fig. 1).

Discussion

The paucity of Ge in Ilímaussaq tectosilicates and consequently its unusual distribution between co-existing silicates can be explained by several mechanisms.

Co-ordination of Ge

Firstly, studies on sodium germanate glasses indicate that the co-ordination of Ge changes with increasing

contents of sodium and with increasing pressure. The similarity in behaviour of Ge and Si in glasses is far from perfect, since alkali germanate glasses show maxima and minima in physical properties such as density, viscosity and heat of solution at around 20 mol.% Na_2O and this behaviour is absent in alkali silicate glasses. Liquid and vitreous GeO_2 forms a disordered three-dimensional network made up of GeO_4 tetrahedra joined at their corners. It has been argued that, with addition of Na_2O, the tetrahedral units are converted into octahedral GeO_6 units. For each oxygen added to GeO_2 as Na_2O, one octahedron is produced without, however, formation of non-bridging oxygens. Studies by X-ray diffraction (Kamiya & Sakka 1979), extended X-ray absorption spectroscopy (Lapeyre *et al.* 1983) and neutron scattering (Ueno *et al.* 1983) suggest that the fraction of octahedral Ge atoms increases linearly with increasing Na_2O content and reaches a maximum in the vicinity of mol. fraction Na_2O (x) = 0.20. During the conversion of GeO_4 to complex $(GeO_6)^{2-}$ ions, charge neutrality would be maintained by addition of $2Na^+$. The increased packing efficiency of the GeO_6 units could explain the observed maximum in density around x = 0.20.

High-temperature X-ray diffraction suggests that at x = 0.20, glasses and melts have a structure similar to $Na_2Ge_4O_9$ crystals which can crystallise in metastable form and which contain both GeO_6 octahedra and GeO_4 tetrahedra (Kamiya *et al.* 1988).

However, Henderson & Fleet (1991) consider that these various spectral studies have been misinterpreted and that the evidence simply indicates that a lengthening of the Ge–O bonds occurs as Na_2O is added to the glass. They propose that bond lengthening is not due to GeO_6 formation but to distortions of the tetrahedra which occur when small three-membered GeO_4 rings are formed.

Hussin *et al.* (1998) admit that the correct structural model for alkali germanate glasses is still unknown, and that both the above models may prove to have some validity. Their own nuclear magnetic resonance structural analysis revealed different chemical shifts for oxygen in GeO_4 and GeO_6 units in quartz-type and rutile-type GeO_2, respectively. Furthermore, they found that in sodium germanate glasses at 10 mol.% Na_2O some fraction of the germanium is in sixfold co-ordination whereas at 18.2 mol.% Na_2O the co-ordination is predominantly fourfold.

Pressure is potentially an additional factor, since there is a gradual change from fourfold to sixfold Ge co-ordination in GeO_2 and Na_2O–GeO_2 glasses (Itié *et al.* 1989) and in $MgGeO_3$ enstatite and $CaGeO_3$ wollastonite (Andrault *et al.* 1992) with increasing pressure. Raman spectra on high-temperature glasses and liquids of $Na_2Ge_2O_5{\cdot}H_2O$ composition indicate that the proportion of Ge^{VI} relative to Ge^{IV} increases several fold with pressure up to 22 kbar, from near 0% to > 50% (Farber & Williams 1992). This suggests that the change from ambient pressure to 1 kbar, the pressure inferred for the Ilímaussaq system 3–4 km below the contemporary surface (see Sørensen 2001, this volume), would only increase the proportion of Ge^{VI} by a few percent relative. Such a small increase is not consistent with the pronounced changes in Ge distribution at Ilímaussaq, e.g. Ge contents of K-feldspar varying from 1.4 to < 0.2 ppm. Furthermore, it fails to explain why the minerals of other shallow-level intrusions reveal a markedly different Ge distribution from those in the Ilímaussaq complex.

There is, of course, a considerable step from simple sodium germanate glasses to natural and highly complex silicate melts where Ge occurs at the 1–2 ppm level. We can only speculate, therefore, that if the high Ge^{VI}/Ge^{IV} ratios of Na-bearing glasses, i.e. melts, persist during the transition to the crystalline state, then minerals favouring Ge^{VI} will tend to have higher Ge contents than normal whereas minerals favouring Ge^{IV} will tend to have lower. This appears consistent with the low contents of Ge in Ilímaussaq tectosilicates where only Ge^{IV} is able to enter.

The question then arises whether there is evidence to show that Ge^{VI} concentrates in minerals along with octahedrally co-ordinated Al, Ti, Fe^{3+} and Zr. Larsen (1976) has demonstrated that, as the Ilímaussaq system becomes more agpaitic, these elements increasingly enter octahedral sites in pyroxenes, occurring as the components $NaFe^{3+}Si_2O_6$, $NaAlSi_2O_6$ and $Na(Ti,Zr)AlSiO_6$. However, only Fe^{3+} has a size close to optimum for the M1 site in pyroxenes and it can be estimated that partition coefficients between pyroxene and melt decrease rapidly from roughly 5 (Fe^{3+}) to 2 (Zr), 1 (Ti) and 0.1 (Al). Ignoring their different valencies, octahedral Ge^{4+} (0.53 Å) with a similar size to octahedral Al^{3+} (0.535 Å) would also be expected to show only minor partitioning into the M1 sites of pyroxenes.

Among the Ilímaussaq silicates, the Ti mineral aenigmatite has the highest content of Ge – slightly above 10 ppm. Significantly, one of the octahedral sites in aenigmatite is distinctly smaller than the remaining six (nearest neighbour distance of 1.98 Å versus 2.10–2.17 Å) (Cannillo *et al.* 1971). This single site favours entry of a cation with an ionic radius of 0.60 Å explaining

the high occupancy of Ti^{4+} (0.605 Å) and presumably of Ge^{4+} (0.53 Å). Aenigmatite, however, is never more than a minor to accessory phase at Ilímaussaq and is unlikely to influence the entry of Ge into the rock-forming minerals.

Valency of Ge

The occurrence at Ilímaussaq of melts with low oxygen fugacities (see below) may have converted some of the Ge from a quadrivalent to bivalent state. Among the rock-forming minerals, Ge shows preferential entry into Fe^{2+}-rich arfvedsonite rather than Fe^{3+}-rich aegirine. This might be explained by the details of the two silicate structures, but it may also point to the presence of Ge in bivalent rather than quadrivalent form. In octahedral co-ordination, Ge^{2+} has a formal ionic radius of 0.73 Å, distinctly higher than the ionic radius for Ge^{4+} (0.53 Å), and might be expected to substitute for Fe^{2+} (0.78 Å). Furthermore, a magma with a high Ge^{2+}/Ge^{4+} ratio will contain fewer $(GeO_4)^{4-}$ ions and this will lead to reduced substitution of Si in tetrahedral sites. This reduced substitution would be most visible among the leucosilicates where tetrahedral sites are the only possible point of entry for Ge.

The highly reduced character of the agpaitic melts at Ilímaussaq has been repeatedly emphasised. At the magmatic stage, it is seen by the displacement of the FMQ buffer curve to low values of oxygen fugacity, by the presence of ferri-aenigmatite, arfvedsonite (Larsen 1977) and native lead (Karup-Møller 1978), and by the presence of CH_4 or H_2 or both in fluid inclusions (Konnerup-Madsen *et al.* 1981).

Experimental work on the valency of Ge in reduced magmas should throw light on these ideas. Here, one can only note that the chemically similar element below Ge in Group IVA is Sn and recent work has demonstrated that Sn^{2+}/Sn^{4+} ratios in haplogranitic melts rise sharply under more reducing conditions (Linnen *et al.* 1996). However, Sn shows a much greater tendency to occur in the bivalent state than Ge, and the quadrivalent compounds of Ge are more stable than its bivalent compounds (Rochow & Abel 1975). Furthermore, Ge^{2+} is a distinctly lone-electron-pair element and requires an irregular co-ordination polyhedron (E. Makovicky, personal communication 1999).

It also seems likely that, if Ge^{2+} were actually to substitute for Fe^{2+} in octahedral sites of arfvedsonite, more substitution would be expected than is observed. Ge contents in arfvedsonite are similar to those in inosilicates at many localities and are not dramatically higher than those in Fe^{2+}-poor aegirine.

Feldspar structure

Variations in the structure of the Ilímaussaq K-feldspars may have played a role in the partitioning of Ge. As a broad generalisation, the ability of crystals to take in non-stoichiometric cations increases under rapid, structurally disordered or high-temperature crystallisation.

Feldspars show particularly complex relations. Most igneous feldspars crystallise with disordered Al and Si atoms but, on cooling or during direct crystallisation at lower temperatures, the Si and Al ordering increases. In high sanidine, all T–O distances between the tetrahedral cation and the oxygen anion statistically lie around 1.642 Å; in intermediate microcline, on average, two T–O distances are relatively large (1.694 and 1.642 Å) and two are small (1.618 and 1.616 Å); in low microcline, on average, a single T–O distance is large (1.741 Å) and the other three are small (around 1.613 Å) (Smith 1977; Blasi *et al.* 1984). Using a radius of 1.38 Å for fourfold O^{2-} (Shannon 1976), the optimal ionic radii for the tetrahedral cations are 0.26 Å in high sanidine; 0.31, 0.26 and 0.24 Å in intermediate microcline; and 0.36 and 0.23 Å in low microcline. Si^{4+} (0.26 Å) will tend to prefer the smaller sites whereas Al^{3+} (0.39 Å) will tend to prefer the largest site in low microcline. Hence the increased ordering.

It is expected that during partitioning into these different types of K-feldspar, the Ge^{4+} ion will be introduced randomly into all four tetrahedral sites in high sanidine, but will have more difficulty in entering tetrahedral sites in high microcline and even greater difficulty in entering any tetrahedral sites in low microcline. This is because Ge^{4+} (0.39 Å) cannot easily follow Si^{4+} into the three smaller sites of low microcline as a result of its much larger size and cannot easily follow Al^{3+} into the largest site as a result of charge balancing problems. The content of Al in these three feldspars will be constant because of stoichiometric requirements but the content of Ge should decrease towards low microcline because of the reduced number of suitable tetrahedral sites.

Low microcline is rare in nature but is known from low-temperature agpaitic nepheline syenites where it shows characteristic 'chessboard' or 'tiled' twinning. At Ilímaussaq, it occurs as euhedral to subhedral tablets or laths, and these may have crystallised directly with high or maximum triclinicity from the magma at

< 400°C (Brøgger 1890; Ussing 1898; Vlasov *et al.* 1959; Sørensen 1962; Borutskii & Semenov 1969; Ferguson 1970; Smith & McLaren 1983). These studies also demonstrated that the earlier, higher temperature K-feldspars at Ilímaussaq are microcline microperthites, moderately ordered in augite syenite but highly ordered in the nepheline syenites.

Based solely on microscope observations, the two types of feldspar at Ilímaussaq are indicated in Table 2. The microcline perthites from the agpaitic nepheline syenites which, according to the detailed studies noted above, are highly ordered have lower Ge contents than K-feldspars from 'normal' granitic and rhyolitic rocks. Microclines with even lower Ge contents (0.3 ppm or less) are judged to be low microclines where none of the tetrahedral sites is suitable for Ge.

On present evidence, the low Ge contents in the Ilímaussaq microclines, and perhaps in the other leucosilicates, appear to be linked to the high degree of ordering attained during crystallisation under exceptionally low-temperature conditions. The unusual distribution of Ge may thus be yet another expression of crystallisation in an agpaitic system.

Conclusions

1. Germanium contents in Ilímaussaq rocks and magmas (dykes, sills) decrease from about 1.8 to 1.5 ppm, and probably fall to even lower levels in late pegmatites and veins. In the agpaitic rocks, the bulk of Ge is held in arfvedsonite (2.4–6.3 ppm) and aegirine (2.5–4.3 ppm) with lower contents in eudialyte (1.3–1.9 ppm), microcline (< 0.2–0.8 ppm), nepheline (< 0.2–1.3 ppm), sodalite (0.3–0.5 ppm), analcime and natrolite (< 0.2–0.3 ppm). The highest contents are reported from aenigmatite (10.2–10.7 ppm) in pegmatites and sphalerite (7.8–42 ppm) in veins.

2. It is significant that mafic silicates have normal contents of Ge, whereas microcline has low and decreasing contents – from 0.8 to < 0.2 ppm.

3. Conversion of some Ge from fourfold to sixfold co-ordination is likely in Na-rich melts, but the size of Ge^{4+} ions in sixfold co-ordination is too small to significantly promote entry into the octahedral sites of Ilímaussaq mafic silicates.

4. Reduction of some Ge^{4+} to Ge^{2+} is conceivable in the low-fo_2 magmas at Ilímaussaq. It should promote the entry of Ge^{2+} into Fe^{2+}-rich minerals such as arfvedsonite but this is not observed.

5. The decreasing Ge contents in microclines appear to be linked to crystallisation over a wide temperature range. Early microcline microperthites are moderately ordered but give way to highly ordered microcline microperthites and then to low microclines which crystallised at exceptionally low magmatic temperatures. It is argued that, in these low microclines, Ge^{4+} has difficulty in entering any of the highly ordered tetrahedral sites.

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The eudialyte group: a review

Ole Johnsen, Joel D. Grice and Robert A. Gault

The eudialyte group of complex Na, Ca, Zr silicates encompasses a wide range of compositions in which all the main elements Si, Zr, Ca, Fe and Na vary, and many relatively minor elements such as Mn, REE, Sr Nb, K, Y and Ti are present. For most members of the group the empirical formula is $Na_{15}[M(1)]_6[M(2)]_3Zr_3[M(3)](Si_{25}O_{73})(O,OH,H_2O)_3(Cl,F,OH)_2$ and the best method of formula calculation is on the basis of 29 (Si, Al, Zr Ti, Hf, Nb, W, Ta) *apfu* ($Z = 3$), which are the elements assigned to the *Zr*, *M*(3) and all *Si* sites in the structure. The commonest substitutions are found with the solid solution series eudialyte *sensu stricto* (enriched in Si, Ca, Fe and Cl) and kentbrooksite (enriched in Nb, REE, Mn and F), but recent studies show that the series extends beyond kentbrooksite to an exceptionally Ca-deficient eudialyte now named oneillite. Most eudialytes are trigonal $R\bar{3}m$ or $R3m$ but oneillite is $R3$. Additional members of the group are khomyakovite and manganokhomyakovite.

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Eudialyte (Fig. 1), a Na-rich zirconosilicate with varying amounts of Ca, Fe, Mn, rare-earth elements (REE), Sr, Nb, K, Y and Ti, was first described from the Kangerluarsuk area within the Ilímaussaq alkaline complex (Stromeyer 1819). There, it is widespread as a major constituent of the nepheline syenites and their pegmatites; locally in Kangerluarsuk up to 1 m thick continuous layers of almost pure eudialyte are found (Ussing 1912; Bøggild 1953). A particularly impressive occurrence of eudialyte in Kangerluarsuk is a rhythmic sequence of layered rocks (kakortokites) with black, red and white layers in which the varying concentrations of the main constituents arfvedsonite, eudialyte and alkali feldspar result in the banded appearance of the rocks (Fig. 2; Bohse *et al.* 1971; see Sørensen 2001, this volume).

Since the first analysis of eudialyte by Stromeyer (1819) many more from other localities have been published which display a wide range of compositions, much of which is real, but at least some variation was due to errors inherent in the analytical methods in use at the time. The result is considerable doubt about the formula of eudialyte, and even after the basic structural features of eudialyte became known (Giuseppetti *et al.* 1971; Golyshev *et al.* 1971), ambiguity has remained with regard to the number and types of atomic sites in the mineral.

This paper reviews the recent literature on this complex mineral with special emphasis on the relationship between chemical and physical properties and crystal structure. Eudialyte has now developed into a group of several distinct mineral species including kentbrooksite from the Amdrup Fjord, Kangerdlugssuaq intrusion in East Greenland.

Structure overview

Eudialyte-group minerals are trigonal with $a \sim 14$ Å and $c \sim 30$ Å, crystallising in space groups $R\bar{3}m$, $R3m$ or $R3$. The most characteristic property of the eudialyte structure is the unique combination of three- and nine-membered rings of $[SiO_4]$ tetrahedra (Golyshev *et al.* 1971; Giuseppetti *et al.* 1971). These $[Si_3O_9]^{6-}$ and

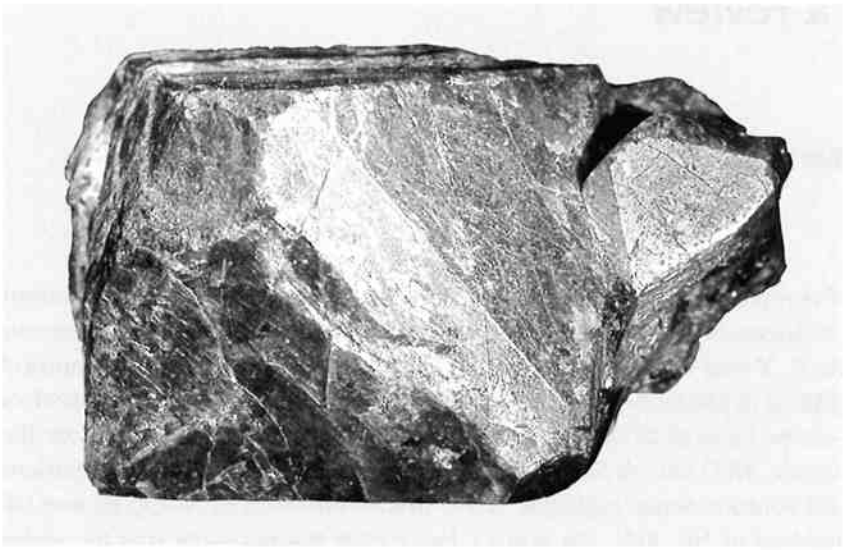


Fig. 1. Eudialyte from Kangerluarsuk, the Ilímaussaq complex. Crystals are dominated by {10$\bar{1}$1} and {0001}. Edge of large crystal 35 mm. Sample GM 1912,274 (Geological Museum, Copenhagen).

$[Si_9O_{27}]^{18-}$ rings are arranged in layers perpendicular to [001] with the configuration shown in Fig. 3. Two such layers, related by a centre or a pseudo-centre of symmetry, embrace a layer of discrete rings of six $[M(1)O_6]$ octahedra linked together by $[M(2)O_n]$ polyhedra forming a 2:1 composite layer. The site notation adopted here is taken from Johnsen & Grice (1999). The 2:1 composite layers are cross-linked by Zr in octahedral co-ordination and related to one another in accordance with the rhombohedral symmetry. This open structure is filled with $[Na\phi_n]$ polyhedra having various coordinations (where ϕ indicates ligands of O, OH, and F).

In the stacking sequence of the 2:1 layers and the layers with $[ZrO_6]$ octahedra, twelve levels can be recognised within the repeat distance of the *c* cell dimension. Figure 4 gives a simplified representation of these levels from one sixfold ring of $[M(1)O_6]$ octahedra to the next ring. Oblong cages exist along the triad axes reaching from one constriction made by a $[Si_3O_9]^{6-}$ ring up through the layer sequence to the next $[Si_3O_9]^{6-}$ ring constriction including nine of the twelve levels. In these cages the central level comprises a region surrounded by six $[ZrO_6]$ octahedra (only four of them are shown in Fig. 4) and on either side followed by (1) an intra-$[Si_9O_{27}]^{18-}$ ring level, (2) a level with a region surrounded by $[M(1)O_6]$ and $[M(2)O_n]$ polyhedra, (3) an inter-$[Si_9O_{27}]^{18-}$ ring level and (4) a level with a region surrounded by three $[ZrO_6]$ octahedra.

Na dominates the $[ZrO_6]$ octahedra levels and other



Fig. 2. View of Kringlerne, Kangerluarsuk, the Ilímaussaq complex. Kringlerne is a rhythmic sequence of black, red and white layers of kakortokite in which the varying concentrations of the main constituents arfvedsonite, eudialyte and alkali feldspar result in the banded appearance of the rocks. The plateau above the rhythmic layering is about 400 m above the fjord. Photo: Henning Bohse.

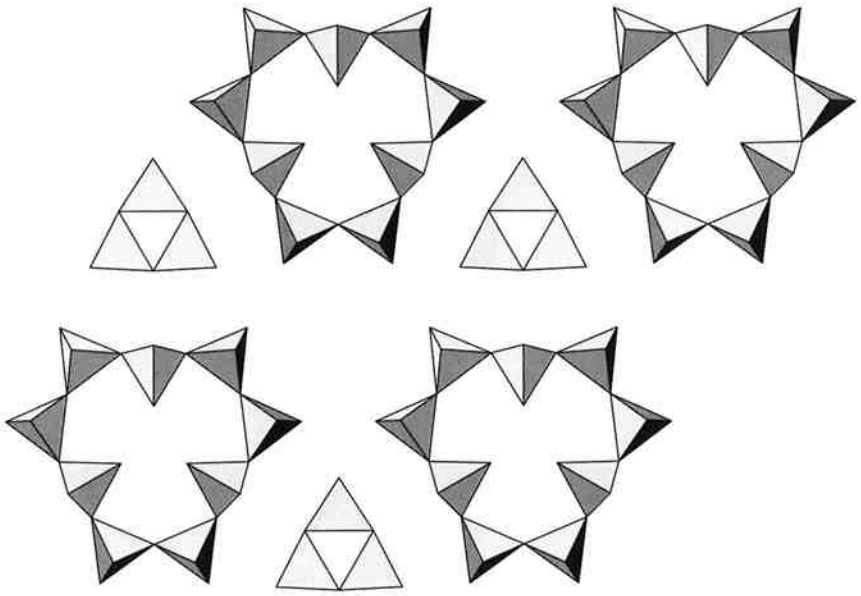


Fig. 3. The nets of threefold and ninefold silicate rings in eudialyte seen along [001]. From Johnsen & Grice (1999).

cavities in or at the border of other levels. Cl, F, OH and H_2O are accommodated in the inter-$[Si_9O_{27}]^{18-}$ ring levels while the central parts of the $[Si_9O_{27}]^{18-}$ rings offer space for a cation in tetrahedral (*Si*(7)) or octahedral (*M*(3)) co-ordination pending the occupation or not of the *O*(19) site. *M*(2) is either fourfold co-ordinated in an almost planar arrangement or fivefold co-ordinated in a distorted square pyramid when *O*(19) is involved. Finally, *O*(19) is also ligand to the *Na*(4) site, which adds to the capability of this site to carry stronger bonding atoms such as REE or Sr. Table 1 gives a full list of cation sites in eudialyte structures.

The eudialyte structure is more or less centrosymmetric depending on the degree of disorder and the chemical content of certain sites. Eudialyte *sensu stricto* rich in Si, Fe and Ca, such as eudialyte from Ilímaussaq, represents the most centrosymmetric structures and as substitutions of the type Si → (Nb,W), Fe → Mn, (Ca,Na) → (REE,Sr) take place, the structures become progressively less centrosymmetric as in the case of kentbrooksite (Johnsen & Grice 1999).

Chemistry

A comprehensive survey of all published analyses of eudialyte minerals is outside the scope of this paper. References to a large number of eudialyte papers containing information on chemistry and paragenesis are found in Deer *et al.* (1986) and Sørensen (1974), and a number of more recent papers are quoted by Johnsen & Gault (1997).

Johnsen & Gault (1997) focus on chemical variation by investigating a large suite of eudialyte minerals of different provenance by microprobe analysis performed under uniform conditions. The differences in chemical composition observed in this study reflect most of what has been noted previously in the literature and the following discussion is principally based on this work and subsequent studies based on single-crystal structure data (Johnsen & Grice 1999).

Practically all the main elements, Si, Zr, Ca, Fe and Na vary in concentration and a large number of the relatively minor elements such as Mn, REE, Sr, Nb, K, Y and Ti can enter the eudialyte structure in different quantities. The anions Cl and F, determined by microprobe analysis, also show variations, and indications that the total number of anions do vary in eudialyte minerals are confirmed by single-crystal data. In spite of this Johnsen & Gault (1997) found that the most reliable procedure was to calculate the atoms per formula unit (*apfu*) on the basis of 78 anions and $Z = 3$ for all analyses.

Al is rarely found in significant amounts in eudialyte. This fact, combined with the absence of other tetrahedrally co-ordinated elements like Be that could substitute for Si, suggests that the variation of Si is a very special chemical property of eudialyte. The Si contents are consistently above 24 *apfu*, i.e., more than required to build the ring network. Regression analysis of the Si *apfu* versus other elements show a strong negative correlation with Nb *apfu*. Nb varies from zero up to ~ 1 *apfu*; the highest Nb content hitherto reported is from the Pilanesberg complex, South Africa

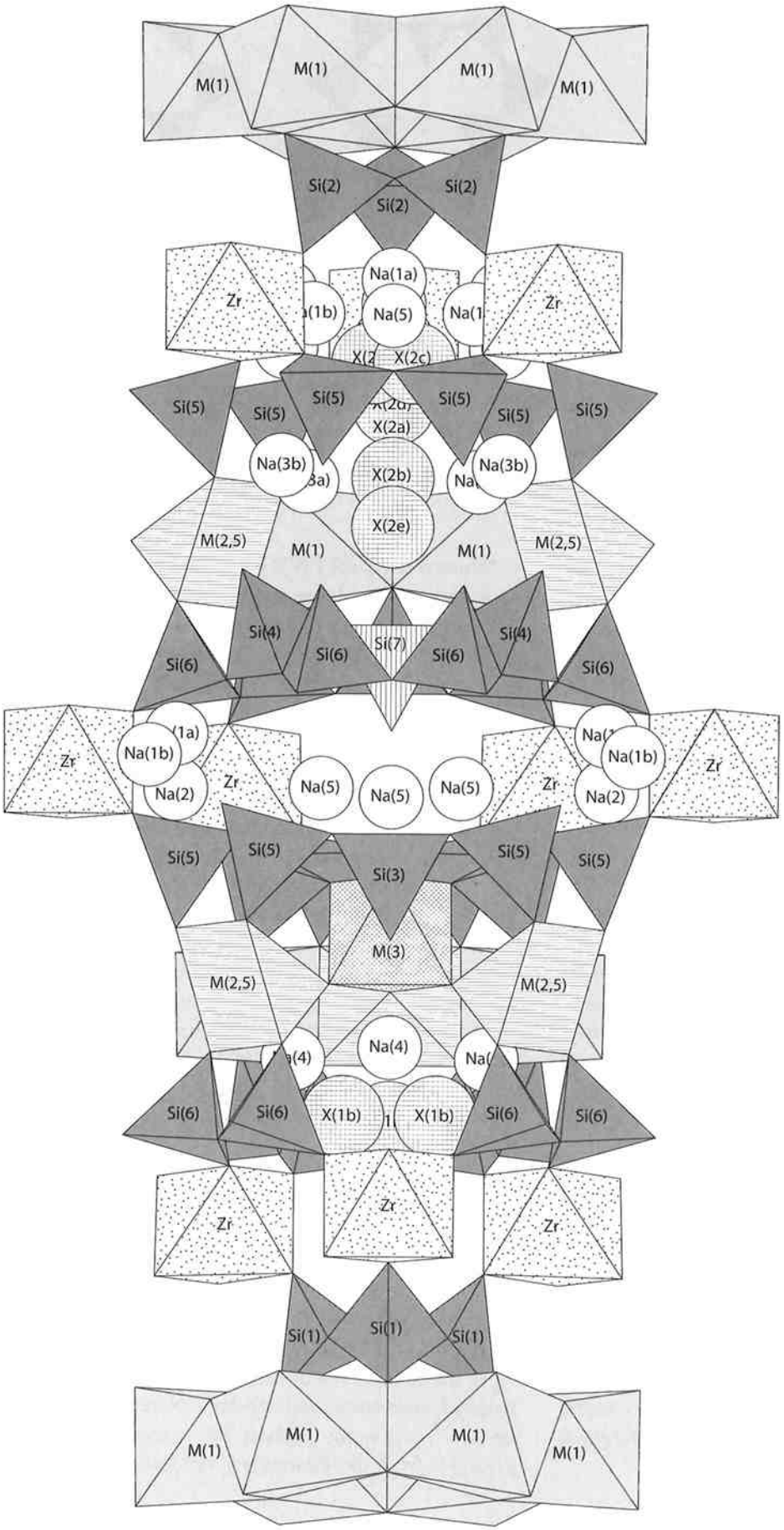


Fig. 4. A simplified polyhedral model of a non-centrosymmetric eudialyte (*sensu lato*) viewed approximately along [010]. From Johnsen & Grice (1999).

Table 1. Assignment of cations to sites in eudialyte-group minerals

	N	Av.$M-\phi$	Si	Al	Zr	Ti	Nb	W	Fe	Mn	REE	Y	Ca	Sr	K	Na
M(1)	6	2.35			(x)				(x)	x	X	x	X			
M(1a)*	3	2.23								X						
M(1b)*	3	2.43									X		X			x
M(2,5)	3	2.15		x	(x)	x			X	X						
M(2,4)		2.10							X	X						
M(3)†	1	1.87			x	x	X	X								
Si(7)†	1	1.58	X	X												
Si(7a)†		1.60	X	X												
Na(1)‡	3	2.65–2.61														X
Na(2)§	3	2.63											x			X
Na(3)‡	3	2.68–2.71									x		x	x		X
Na(4)§	3	2.63									X	(x)	x	X	X	X
Na(5)	3	2.77														X
Zr	3	2.068			X	X	x									
Si(1)‡	3	1.617	X	X												
Si(2)§	3	1.619	X	X												
Si(3)‡	3	1.618	X	X												
Si(4)§	3	1.618	X	X												
Si(5)‡	6	1.620	X	X												
Si(6)§	6	1.615	X	X												

* sites found in *R*3 eudialyte only
† distinct sites in *R*3*m* eudialyte only
‡ related by centre of symmetry to § in *R*3*m* eudialyte
X preferred site(s)
x additional site(s)

N: Number of sites in the formula unit.
M–ϕ: Cation–anion distance, Å.

(Olivo & William-Jones 1999). The crystallochemical explanation for the strong Si–Nb correlation can be expressed by the substitution $M^{VI}(3) + Si^{IV}(7) \leftrightarrow 2Si^{IV}(7)$ where *M*(3) and *Si*(7) are the two central sites of the two crystallographically distinct nine-membered silicate rings.

The amount of Zr is generally close to the ideal value of 3 *apfu*. Nb plays a subordinate role in this site and Ti is the only element that substitutes for Zr to any significant degree; usually only up to ~ 0.5 *apfu*. Recently, a eudialyte with about one-half of Zr substituted by Ti has been found in Lovozero, Kola Peninsula (A.P. Khomyakov, personal communication 1999). This eudialyte is thus halfway towards the Ti end-member alluaivite (Khomyakov *et al.* 1990).

Ca is the dominant element in the general site *M*(1) which amounts to 6 *apfu*. Mn is the most important substitutional element in this site followed by REE and Y. About half of Ca can be replaced until an ordering of the elements into two distinct sites, *M*(1a) and *M*(1b), occurs. Ca is also found in the *Na* sites but only in limited amounts, and the Ca ↔ Na substitution often reported (e.g. Deer *et al.* 1986) is insignificant in comparison with other substitutions in eudialyte.

Fe is accommodated in *M*(2). The main replacing element in this site is Mn and in most cases the substitution is of the type $Fe^{IV} \leftrightarrow Mn^{V}$. Full occupation of *M*(2) gives 3 *apfu*, but most often this site is only partly occupied, typically in the range of 2–3 *apfu*. Fe and Mn are generally present as Fe^{2+} and Mn^{2+} (Pol'shin *et al.* 1991; Johnsen & Grice 1999). In rare cases Al or Ti are accommodated in *M*(2).

All five *Na* sites are special sites and add up to 15 *apfu*. The *Na* sites can to some degree accommodate other elements such as Ca, K, REE, Sr, Y, H_2O or even H_3O^+ (Rastsvetaeva *et al.* 1990). In a few remarkable cases, a *Na* site – primarily the *Na*(4) site – is dominated by one of the replacing elements such as in khomyakovite and manganokhomyakovite (Johnsen *et al.* 1999a) where Sr constitutes ~ 2.6 out of 3 *apfu*.

Based on a number of simple correlations between individual elements or small groups of elements, Johnsen & Gault (1997) suggested a solid solution series between eudialyte *sensu stricto* rich in Si, Ca, Fe and Cl, and kentbrooksite (Johnsen *et al.* 1998) rich in Nb, REE, Mn and F. Single-crystal studies (Johnsen & Grice 1999) largely confirmed this series with minor modifications, one of them being that the anion part is of insignificant importance in this context, another is that Nb in the kentbrooksite component may be sub-

stituted by other elements such as W, and finally, that the series extends beyond kentbrooksite up to an exceptionally Ca-deficient eudialyte crystallising in *R*3, now established as an independent mineral species by the name of oneillite (Johnsen *et al.* 1999b).

Johnsen & Grice (1999) present a detailed crystallochemical discussion of the substitutions and their interactions in the eudialyte group. A summary of elements assigned to the various sites in eudialyte-group minerals is shown in Table 1.

Formula calculation

In the general case where single-crystal structure data are not available, a formula must be calculated from the chemical analysis alone. As most chemical information is based on microprobe analysis, a H_2O determination is generally not available which is a serious disadvantage when calculating a formula based on the number of anions. The use of this method without further corrections results in *apfu* values of cations systematically too high; by way of example, in a typical eudialyte the *apfu* of Si will drop from 25.90 to 25.30 by the incorporation of 1 wt% H_2O.

An alternative method of formula calculation is proposed by Johnsen & Grice (1999). This method is based on the number of cations accommodated in the framework composed of the silicate rings and the Zr octahedra supplemented with the two sites (*M*(3) and *Si*(7)) in the centres of the nine-membered rings, i.e. Si + Al + Zr + Ti + Hf + Nb + W + Ta, ideally adding up to 29 *apfu* (Z = 3). This method is fully applicable without the determination of hydrogen or other cations. The main disadvantage of this method is that some of the elements involved (Al, Ti and Zr) occasionally also occur in other parts of the structure. However, these cases are exceptions and in the majority of cases the method works well. For the majority of the eudialyte-group minerals the empirical formula will be of the type: $Na_{15}[M(1)]_6[M(2)]_3Zr_3[M(3)](Si_{25}O_{73})(O,OH,H_2O)_3X_2$ where X represents (Cl,F,OH).The following procedure is recommended when constructing the empirical formula for eudialyte based on a chemical analysis only:

1. Calculate the *apfu* based on 29 (sum of Si, Al, Zr, Ti, Hf, Nb, W, Ta) and with all Fe and Mn as divalent.
2. Assign all Si + Al to the 25 Si *apfu*. Any excess Si should be added to *M*(3).
3. Assign all Zr to the *Zr* site and if deficient make up the total to 3 atoms with Ti.
4. Assign all Nb and W to *M*(3).
5. Assign all Fe and Mn to *M*(2). Any excess Mn should be assigned to *M*(1).
6. Assign all Ca to *M*(1) and any remaining Mn then Y and REE to bring the total to 6 atoms. Any excess Ca should go into the *Na* sites.
7. Assign all Na, K, Sr and remaining Ca and REE to the *Na* sites.
8. Assign 73 of the O atoms to the silicate rings with the remaining anions partitioned into a O fraction and a halogen fraction.
9. The number of H atoms is based on charge balance.

Rare cases where Ca *apfu* is below 50% of the *M*(1) site or Na is below 50% in the *Na*(4) site will become evident during the course of formula calculation. In such cases crystal structure refinement data will be required in order to calculate a reliable formula.

Optical and physical properties

Johnsen *et al.* (1997) investigated the optical properties of a selection of eudialyte samples. The refractive indices measured are in the range of 1.60–1.64 thus covering the range previously reported in the literature, as do the birefringences. Most samples are optically negative showing great variation in refractive indices as well as in birefringences, whereas the few optically positive samples all have low refractive indices and both refractive indices and birefringences fall within narrow fields. Only a few samples are truly uniaxial; most samples show axial angles up to ~ 25°. The colour varies from brown through reddish-pink and yellow to colourless; pleochroism is, if at all present, insignificant. In a few samples a poor (001) cleavage has been observed.

Johnsen *et al.* (1997) examined the mean refractive indices and birefringencies and their correlation with the chemical composition and concluded that an isomorphous series between Na- and Ca-rich end-members, if it exists, is of no importance as a controlling factor in the variation of optical properties as suggested by, e.g. Deer *et al.* (1986). The overriding influence on the mean refractive indices comes from substitutions such as Si ↔ (Nb,W) and (Ca,Na) ↔ (REE,Sr) and as expected the mean refractive index increases as these substitutions go to the right. The birefringence shows the best correlation to the Si ↔ (Nb,W) substitution. However, as this substitution is an integral part of the

complex substitution between the two end-members eudialyte and kentbrooksite, it cannot be asserted as the only controlling factor in the birefringence. It is concluded that the term eucolite, which has been used for an optically negative and Ca-rich eudialyte, is meaningless and in some respects misleading, so the use of this term should be discontinued. Also, mesodialyte as a name for an optically isotropic intermediate member of an inferior, if existing, series should be abolished.

The density varies in the range 2.85–3.25 g/cm^3. With eudialyte *sensu stricto* rich in Na, Ca, Fe and Si as a starting point, all major substitutions, except the Fe ↔ Mn substitution, go from a relatively light element towards a heavier element. Thus, the density increases as the series goes from eudialyte towards kentbrooksite and oneillite.

Members of the eudialyte group

Within the eudialyte group the following species can be recognised:

eudialyte (Stromeyer 1819):
$Na_{15}Ca_6Fe_3Zr_3Si(Si_{25}O_{73})(O,OH,H_2O)_3(Cl,OH)_2$

kentbrooksite (Johnsen *et al.* 1998):
$Na_{15}Ca_6Mn_3Zr_3Nb(Si_{25}O_{73})$ $(O,OH,H_2O)_3(F,Cl)_2$

khomyakovite (Johnsen *et al.* 1999a, b):
$Na_{12}Sr_3Ca_6Fe_3Zr_3W(Si_{25}O_{73})$ $(O,OH,H_2O)_3(Cl,OH)_2$

manganokhomyakovite (Johnsen *et al.* 1999a, b):
$Na_{12}Sr_3Ca_6Mn_3Zr_3W(Si_{25}O_{73})$ $(O,OH,H_2O)_3(Cl,OH)_2$

oneillite (Johnsen *et al.* 1999a, b):
$Na_{15}Ca_3Mn_3Fe_3Zr_3Nb(Si_{25}O_{73})$ $(O,OH,H_2O)_3(OH,Cl)_2$

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The distribution of minerals in hyper-agpaitic rocks in terms of symmetry: evolution of views on the number and symmetry of minerals

Alexander P. Khomyakov

Among the unique mineral localities of the Earth the complexes of nepheline syenites with hyper-agpaitic differentiates are of special interest due to their extreme diversity of mineral species. The four best studied complexes of this type – Khibina, Lovozero, Ilímaussaq and Mont Saint-Hilaire – have yielded more than 700 mineral species of which about 200 are new. The great mineral diversity is due to the combination of several factors, the most important of which is the extremely high alkalinity of agpaitic magmas, causing about half of the elements of the periodic table to be concentrated together. Minerals from hyper-agpaitic rocks are characterised by the predominance of highly ordered, low-symmetry crystal structures resulting, in particular, from the markedly extended temperature range of crystallisation. Generalisation of available data for unique mineral localities underpins the hypothesis that there is no natural limit to the number of mineral species. It is predicted that by the middle of the 21st century, the overall number of minerals recorded in nature will exceed 10 000, with the proportion of triclinic species increasing from the present 9% to 14.5%, and that of cubic species decreasing from 10% to 5%.

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The development of mineralogy in the latter half of the 20th century has been marked by an accelerating pace of new mineral discoveries. The number of minerals discovered worldwide since 1970 is roughly equal to that recorded throughout the preceding historic time. This dramatic acceleration has radically changed our views on the chemical and structural diversity of minerals and on the distribution patterns of various elements in rocks and mineral deposits. It also provides a powerful stimulus for further advancement of mineralogy and allied sciences and challenges long-held theories of the mineral system, its limits, symmetry features, and prospects for further mineralogical discoveries.

The main sources of new mineral discoveries during the last few decades were unique deposits, in particular the mineral-rich complexes of agpaitic nepheline syenites. The best known of these are Ilímaussaq in South Greenland, Khibina and Lovozero on the Kola Peninsula in Russia and Mont Saint-Hilaire, Quebec in Canada. Between 1970 and 2000, more than 150 IMA-approved minerals were discovered in these four complexes. The overall list of new mineral species described from these complexes includes approximately 200 entries (Semenov 1972, 1997; Kostyleva-Labunstova *et al.* 1978; Khomyakov 1980, 1990, 1995; Sørensen *et al.* 1981; Horváth & Gault 1990; Petersen & Secher 1993; Sørensen 1997). In all, more than 700 mineral species have been identified in these complexes.

About two-thirds of the aforementioned 150 IMA-approved minerals were described from the Khibina and Lovozero complexes (94 species), which have been the main target of the author's research over the last 30 years and presented in a monograph (Khomyakov 1990, 1995). The vast majority of these minerals were discovered in a special type of silicate-salt pegmatoid, supersaturated in alkaline, volatile and rare elements.

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Rocks of this type, distinguished as hyper-agpaitic (Khomyakov 1977, 1995; Sokolova 1986, see also Sørensen & Larsen 2001, this volume), contain accumulations of maximally alkaline minerals; an indication of the extreme peralkalinity which is the principal factor controlling the extraordinary mineral diversity of nepheline syenite complexes with hyper-agpaitic rocks.

The mineral discoveries in the Khibina and Lovozero complexes are briefly reviewed in the first section of this paper. The data, supplemented by new facts and ideas, provide the basis for subsequent generalisations which are summarised in the second and third sections of the paper.

The Khibina and Lovozero complexes and their new minerals

The Khibina and Lovozero complexes are the world's largest localities of agpaitic alkaline rocks outside the Ilímaussaq complex where they were originally described (Ussing 1912; see Sørensen 2001, this volume). Situated in the centre of the Kola Peninsula, these adjacent complexes occupy about 2000 km^2 in area. They are the type localities of 126 minerals whose discovery began with the expeditions of the Finnish geologist W. Ramsay in the 1890s.

A vast array of compositionally unusual minerals were discovered by members of A.E. Fersman's expeditions conducted under the auspices of the Academy of Sciences of the USSR before World War II. Fersman demonstrated the significance of the two complexes as a unique ore-bearing and mineralogical province. They hold the world's largest deposits of apatite and rare metals in which an unprecedented number of new minerals has been identified.

Fersman (1937) listed 111 mineral species and varieties that were then known in Khibina and Lovozero. In the postwar years, Fersman's students and followers successfully continued and expanded the achievements of their predecessors, considerably increasing the number of new minerals described from the complexes. The overall list of mineral species has now reached about 500 entries, far surpassing any other complex or deposit in the world, including such famous ones as the Ilmen and Vishnevye mountains in the Urals, Ilímaussaq in Greenland, Mont Saint-Hilaire in Canada, Franklin in the United States, Långban in Sweden and Tsumeb in Namibia (each with 200 to 350 species).

The history of discovery of new minerals in the Khibina and Lovozero complexes may be divided into three major periods.

1. 1890–1941: 11 new minerals were discovered.
2. 1950–1969: 21 new minerals were discovered.
3. 1970–1999: 94 minerals were identified.

Table 1 brings a list of the rare minerals mentioned in this paper.

The enormous increase in the number of new minerals was brought about by the discovery (Khomyakov 1977, 1980, 1990, 1993, 1995) that the deep zones of the complexes (below the zone of weathering) are very rich in hyper-agpaitic rocks. These are enriched in half the elements of the periodic table and contain previously unknown persodic minerals which are readily soluble in water and are therefore not encountered under near-surface conditions. These minerals tend to occur near phosphate (apatite) and rare-element (loparite and eudialyte) deposits.

In particular, these rocks contain water-soluble Na carbonates, making them candidates for commercial extraction of soda (Khomyakov 1985). The most important clue to the origin of Na carbonate mineralisa-

Table 1. Selected new minerals discovered in the Khibina and Lovozero complexes in 1970–1999

Mineral	Formula
Arctite	$Na_5BaCa_7(PO_4)_6F_3$
Bornemanite	$Na_7BaTi_2NbPSi_4O_{21}F$
Crawfordite	$Na_3Sr(CO_3)(PO_4)$
Deloneite-(Ce)	$NaCa_2SrCe(PO_4)_3F$
Fluorcaphite	$(Ca,Sr,REE,Na)_5(PO_4)_3F$
Kalborsite	$K_6Al_4Si_6O_{20}B(OH)_4Cl$
Khibinskite	$K_2ZrSi_2O_7$
Laplandite-(Ce)	$Na_4CeTiSi_7PO_{22}\cdot 5H_2O$
Lintisite	$Na_3LiTi_2Si_4O_{14}\cdot 2H_2O$
Lithosite	$K_3HAl_2Si_4O_{13}$
Lovdarite	$Na_3KBe_2Si_7O_{18}\cdot 4H_2O$
Megacyclite	$Na_8KSi_9O_{18}(OH)_9\cdot 19H_2O$
Nacaphite	Na_2CaPO_4F
Nafertisite	$Na_3(Fe^{2+},Fe^{3+})_6Ti_2Si_{12}O_{34}(O,OH)_7\cdot 2H_2O$
Nastrophite	$Na(Sr,Ba)PO_4\cdot 9H_2O$
Natisite	Na_2TiSiO_5
Natrite	Na_2CO_3
Natrosilite	$Na_2Si_2O_5$
Olgite	$Na(Sr,Ba)PO_4$
Olympite	$Na_5Li(PO_4)_2$
Phosinaite-(Ce)	$Na_3(Ca,Ce)SiPO_7$
Sazhinite-(Ce)	$Na_3CeSi_6O_{15}\cdot 6H_2O$
Shafranovskite	$Na_2H_2(Mn,Fe)Si_3O_9\cdot H_2O$
Sobolevite	$Na_{14}CaMgTi_4Si_4P_4O_{34}F_2$
Umbite	$K_2ZrSi_3O_9\cdot H_2O$

tion of this highly unusual type was provided by the discovery, deep within the complexes, of the new mineral natrite which is an anhydrous Na carbonate, a natural analogue of soda ash, which is produced industrially by fusing limestone and common salt. In addition to natrite, hyper-agpaitic rocks contain more than 20 minerals that are sodium salts, including the most alkaline silicate (natrosilite) and phosphate (olympite) encountered in nature (Khomyakov 1987). Silicate melts and supercritical aqueous solutions saturated with these salts show an exceedingly high reactivity which is used, in particular, in the hydrothermal synthesis of many insoluble compounds (Litvin 1975). Prior to their discovery, the very possibility of these salts separating as crystalline phases of rocks was difficult to predict on the basis of traditional theories. Now, the existence of natrite, natrosilite, and olympite as magma-related minerals is beyond question.

It is quite possible that further research on hyper-agpaitic rocks will reveal even more highly alkaline salt minerals, e.g. hydroxides such as NaOH and KOH. This possibility is indirectly confirmed by the fact that these hydroxides constitute the 'side chain' (according to V.I. Vernadsky) in the formulas of some minerals that are peculiar to hyper-agpaitic rocks, such as ussingite $NaAlSi_3O_8 \cdot NaOH$ (albite + NaOH) and lithosite $2KAlSi_2O_6 \cdot KOH$ (leucite + KOH), which have the highest known agpaicity in sodic and potassic phases (Na/Al = 2, K/Al = 1.5). Another indication is provided by experiments in which crystals of Na_2TiSiO_5 (the composition of the mineral natisite which is a characteristic mineral of hyper-agpaitic rocks) were synthesised in titanosilicate systems (Litvin 1975) only at NaOH concentrations ranging from 38 to 100%, whereas lower NaOH concentrations produced lorenzenite $Na_2Ti_2Si_2O_9$ which contains relatively less Na than natisite. Similarly, the synthesis of steenstrupine, a characteristic mineral of hyper-agpaitic rocks, only takes place in a system oversaturated in Na (Sørensen *et al.* 1985).

The new minerals of the Kola Peninsula are dominated by highly alkaline compounds of P (e.g. arctite and nacaphite) and rare elements: Li (lintisite, olympite), Be (lovdarite), Sr (crawfordite, olgite), REE (laplandite, sazhinite), Zr (khibinskite, umbite), and Nb (bornemanite, sobolevite), see Table 1. Some of these minerals have turned out to be the first representatives of new compound types. An example is provided by hydrous zirconosilicates of K (e.g. umbite) which are particularly remarkable because all attempts to synthesise them in laboratories had long been unsuccessful. Lithosite and kalborsite contain more K than all other known alkaline aluminosilicates. The list of compositional groups was supplemented by silicatophosphates (phosinaite), hydrophosphates (nastrophite) and manganoferrosilicates (shafranovskite). New members were added to the mineral groups of apatite, bradleyite, cancrinite, eudialyte, hilairite, keldyshite, labuntsovite–nenadkevichite, lomonosovite and lovozerite.

The discovery of this vast array of new minerals and the concomitant investigation of their crystal structures have furthered the development of structural mineralogy. Khibina and Lovozero minerals have been used to elucidate some 80 crystal structures. These studies have extended the list of structure types with a wide variety of ring, chain, layer and framework radicals, such as the framework formed by three-membered rings of Be and Si tetrahedra in lovdarite, the huge 18-membered cycloradical in megacyclite, and the multirow (six Si tetrahedra wide) branched amphibole band in nafertisite. The structure determinations also led to the prediction or explanation of pronounced ion-exchange, molecular-sieve, and other technologically important properties in many minerals, stimulating research aimed at synthesising the equivalents of naturally occurring phases and using the latter (e.g. lovdarite) as prototypes for creating new materials with desired properties.

The mineralogical investigations in Khibina and Lovozero greatly influenced work in analogous complexes elsewhere, in particular in the Gardar and Monteregian alkaline provinces. In the latter, in addition to the main site of alkaline rocks at Mont Saint-Hilaire, a whole series of nepheline syenite sills with peralkaline mineral associations have been studied. One of them, the Saint-Amable Sill, yielded more than 100 minerals, including a large group of species characteristic of Khibina–Lovozero hyper-agpaitic suites (Horváth *et al.* 1998). An important contribution to the investigation of agpaitic rocks of pronounced potassic character was made in recent years by investigators of the Murun alkaline complex, situated in Yakutia within the Aldan Shield (Konev *et al.* 1996).

Symmetry of minerals from hyper-agpaitic rocks and symmetry trend in the mineral world

The statistical distribution of mineral species over crystal systems, symmetry classes, space groups and other symmetry ranks shows certain consistent regularities (Povarennykh 1966b; Shafranovsky & Feklichev 1982;

Yushkin 1982, 1993). Shafranovsky (1967, 1983) generalised these regularities in his 'law of the constancy of symmetry statistics of minerals' and introduced the concept of 'mineralogical-crystallographic clarkes' representing the average symmetry characteristics of all known mineral species. He suggested that, by comparing the symmetry data for specific provinces and types of deposits with the clarkes, it is possible to obtain valuable genetic information.

Yushkin (1982) and Dolivo-Dobrovolsky (1984) have, for instance, detected a gradual transformation of a 'cubic' or 'cubic-orthorhombic' mineral world into a 'monoclinic' one from the early to the late evolutionary stages of the Earth, and a progressive decrease in the symmetry of material in the Earth's layers from the interior to the surface of our planet. Marin (1973) demonstrated a distinct lowering of the symmetry of accessory minerals in granitoids (at various hierarchical levels from rock series to individual complexes) from early to late stages in their evolution. One line of research is to use the average characteristics of the symmetry of the mineral world in the analysis of the symmetry features of minerals from specific complexes that formed under unusual physicochemical conditions. This is demonstrated below for the four best studied complexes of hyper-agpaitic rocks: Khibina, Lovozero, Ilímaussaq and Mont Saint-Hilaire.

Statistical analysis was performed on the symmetry data for 250 characteristic minerals which included the following: all minerals with known crystal systems that were first described as new species within these complexes; major rock- and ore-forming minerals; water-soluble (saline) minerals typical of hyper-agpaitic rocks that occur below the zone of weathering; and a group of highly alkaline minerals of various classes that were found, as a rule, in more than one of the four complexes. For minerals recorded in only one complex, the main consideration was whether they are characteristic of highly alkaline complexes in general. Other minor and accessory minerals that occur widely outside alkaline complexes were ignored. Calculations were also performed on a smaller data set of 173 minerals that were first described from the four complexes. The minerals were compared with updated mineralogical-crystallographic clarkes, calculated by the author for 3534 minerals with known crystal systems listed in the *Glossary of Mineral Species* by Fleischer & Mandarino (1995).

The results are presented in Table 2. Minerals of hyper-agpaitic suites show a relative deficiency in high-symmetry cubic species and an excess of low-symmetry species, especially triclinic minerals. The mineral world as a whole is characterised by the predominance of cubic minerals over triclinic ones, whereas hyper-agpaitic rocks show a roughly threefold predominance of triclinic species over cubic ones. Such a strong prevalence of highly ordered, low symmetry structures can be attributed to the specific properties of alkali- and volatile-supersaturated, low-viscosity melts and solutions which lower the temperature and markedly extend the range of crystallisation in terms of both temperature and time.

Another conspicuous feature is the marked predominance of silicates in the list of characteristic minerals (170 species out of 250 in the full set, or 122 species out of 173 in the smaller data set). Silicates differ from most other minerals by having more complex compositions and, hence, lower symmetry (according to the

Table 2. Distribution of hyper-agpaitic rock minerals in terms of symmetry categories and systems

Category	System	All minerals* No. of species		%		Hyper-agpaitic rock minerals† No. of species		%	
High	Cubic	353		10.0		13 (9)		5.2 (5.2)	
Medium	Hexagonal	316	892	8.9	25.2	22 (14)	59 (43)	8.8 (8.1)	23.6 (24.9)
	Tetragonal	269		7.6		16 (10)		6.4 (5.8)	
	Trigonal	307		8.7		21 (19)		8.4 (11.0)	
Low	Orthorhombic	796	2289	22.5	64.7	60 (42)	178 (121)	24.0 (24.3)	71.2 (70.0)
	Monoclinic	1170		33.1		79 (55)		31.6 (31.8)	
	Triclinic	323		9.1		39 (24)		15.6 (13.9)	
	Sum	3534		99.9		250 (173)		100.0 (100.1)	

* Fleischer & Mandarino (1995).

† The first number relates to the data set of 250 characteristic minerals; the second (in parentheses) relates to the data set of 173 minerals whose type localities are at Khibina, Lovozero, Ilímaussaq and Mont Saint-Hilaire.

Table 3. Distribution of hyper-agpaitic rock silicates in terms of symmetry categories and systems

Category	System	All silicates* No. of species		%		Hyper-agpaitic rock silicates† No. of species		%	
High	Cubic	36		3.9		2 (1)		1.2 (0.8)	
Medium	Hexagonal	87		9.5		11 (6)		6.5 (4.9)	
	Tetragonal	48	195	5.3	21.4	10 (8)	35 (27)	5.9 (6.6)	20.6 (22.2)
	Trigonal	60		6.6		14 (13)		8.2 (10.7)	
Low	Orthorhombic	190		20.9		43 (33)		25.3 (27.0)	
	Monoclinic	379	680	41.6	74.7	59 (42)	133 (94)	34.7 (34.4)	78.2 (77.0)
	Triclinic	111		12.2		31 (19)		18.2 (15.6)	
	Sum	911		100.0		170 (122)		100.0 (100.0)	

* Fleischer & Mandarino (1995).

† The first number relates to the data set of 250 characteristic minerals; the second (in parentheses) relates to the data set of 173 minerals whose type localities are at Khibina, Lovozero, Ilímaussaq and Mont Saint-Hilaire.

Fedorov–Groth law). In order to assess the importance of this factor, Table 3 presents data similar to those in Table 2, but relating solely to silicates (911 out of the 3534 species). It can be seen that, in terms of their symmetry distinctions, silicates of hyper-agpaitic rocks resemble minerals of all classes. The monoclinic anomaly that is typical of silicates as a whole (41.6%) is due to the very high proportion of amphiboles, pyroxenes, and micas (about 120 species out of 911 in the data set), the vast majority of which belong to the monoclinic system. The triclinic minerals show a nearly 20-fold predominance over cubic ones in the data set of 122 new silicates described from the four complexes (Table 3). This data set contains only one cubic mineral, sodalite.

The effect of a highly alkaline environment on the lowering of the symmetry of crystallising minerals can be illustrated by the apatite group. The most characteristic representatives of this group in the Khibina complex form the following evolutionary sequence: REE,Sr-bearing fluorapatite, $(Ca,REE,Sr)_5(PO_4)_3F$ – fluorcaphite, $Ca(Sr,Na,Ca)(Ca,Sr,REE)_3(PO_4)_3F$ – belovite-(Ce), $NaSr_3Ce(PO_4)_3F$ – deloneite-(Ce), $NaCa_2SrCe(PO_4)_3F$, with the corresponding sequential lowering of the space group symmetries: $P6_3/m$–$P6_3$–P3–P$\bar{3}$ (Khomyakov *et al.* 1996, 1997). The highest symmetry mineral of this series – fluorapatite – is characteristic of the moderately alkaline rocks of the principal intrusive phases and their closely associated apatite deposits, whereas the remaining members of the series are found only in bodies of hyper-agpaitic pegmatites and their hydrothermal equivalents, in which fluorapatite is not stable.

Phosphates with the compositions of belovite and deloneite synthesised under laboratory conditions share the high-symmetry space group $P6_3/m$ with fluorapatite. This can be attributed to the much higher temperatures (1100°C; Mayer *et al.* 1974) and shorter duration of the processes in experiments than the temperature range 150–300°C within which deloneite and belovite are assumed to have formed in nature. This sequence of apatite-group phosphates is an example of early higher symmetry members being successively transformed into lower symmetry members, a sequence already demonstrated by Fersman (1940, p. 336) for minerals in granite pegmatites.

There is no doubt that the differentiated complexes of nepheline syenites will continue to make a contribution to the overall mineral system, thereby reducing the average symmetry of the mineral world as a whole. The change in the triclinic to cubic ratio over the last 100 years speaks for itself: in 1891, it equaled 0.3; in 1966, 0.6; in 1991, 0.9; and now it is steadily approaching 1.0. According to the predictions of Khomyakov (1998a, b) based on correlation diagrams (the number of species versus time), the total number of known minerals will approach 11 000 by the year 2050, with the proportion of triclinic minerals increasing from the present 9.1 to 14.5%, and that of cubic minerals decreasing from 10 to 5%. The cubic–triclinic 'inversion' of the mineral world is expected to occur near the year 2005.

Recent mineralogical discoveries and the number of mineral species

At present the number of naturally occurring minerals is in the order of 4000 whereas the number of artificial compounds amounts to many millions. According to Fersman (1938), the limited number of mineral species existing in the Earth's crust, despite the astronomical number of theoretically possible combinations of chemical elements, is due mainly to the pattern of geochemical distribution of elements and the relatively narrow range of physicochemical parameters realised during the mineral-forming processes. Because of these and other limiting factors it has been suggested (Povarennykh 1966c; Urusov 1983) that the discovery of new minerals would soon be a very rare event. The last few decades, however, have witnessed an unprecedented expansion of the number of minerals, with 50–100 new minerals annually approved by the International Mineralogical Association.

What are the limits to the mineral world as a whole? Analysis of the long-held theory that there is a natural limit to the number of mineral species (Fersman 1938; Saukov 1946; Povarennykh 1966c; Kostov 1968; Yushkin 1977; Urusov 1983) shows that this theory is mainly valid for ordinary types of rocks and mineral deposits. The principal source of new mineral discoveries is in unusual deposits formed in anomalous geotectonic and geochemical environments. The conditions of formation of these deposits encompass virtually the entire range of physicochemical parameters (*T, P, X,* pH, Eh, etc.) accessible to modern experimental mineralogy and also involve geological time and other factors unattainable in experiments. This serves to remove barriers to the diversity of natural crystalline phases and allows the presentation of a hypothesis of an infinite diversity of mineral species in the mineral world (Khomyakov 1986, 1990, 1994, 1995, 1996, 1998b).

According to general theories of physical chemistry, one peculiar property of peralkaline aluminosilicate melts and solutions is that all dissolved electropositive elements less basic than Na are made to behave as amphoteric elements, stimulating their transition from the cationic part to the much more capacious anionic part of the melt structure. Furthermore, a rise in the alkalinity of these melts causes a substantial increase in the solubility of H_2O and other volatile components such as F, Cl, S, and CO_2 (Kogarko 1977). Therefore, agpaitic magmas can be regarded as universal solvents, capable of concentrating, in addition to alkalis and volatiles, virtually all other chemical elements. This may explain the unique ability of these magmas to extract diverse elements, including those that form mineral deposits of P, Nb, Ta, Zr, Hf, Ti, REE, Sr, etc. from sources such as deep transmagmatic fluids. Hence, economically important deposits of the alkaline series tend to occur near ultra-deep faults which were figuratively described by Ovchinnikov (1985) as 'punctures' in the Earth's hot spots.

Data for the four best-studied complexes of this type – Khibina, Lovozero, Ilímaussaq and Mont Saint-Hilaire – indicate that, in addition to the petrogenetically important elements O, Si, Al, Na, K, Ca, Fe, Mg, Mn and Ti, there are approximately 30 other elements that form their own minerals: Li, Be, Sr, Ba, B, Ce, La, Nd, Y, Zr, Nb, P, Th, U, Ag, Au, Tl, Cu, Zn, Sn, Pb, As, Sb, Mo, W, Co, Ni, as well as F, S, Cl, C and H. A large number of the minerals have very complex compositions with as many as 10 elements occupying separate structural sites.

Table 4 shows the calculated number of theoretically possible combinations (C_n^m) of a known number of chemical elements (n) in a system and the actual

Table 4. The number of theoretical combinations (C) of a known number (n) of chemical elements in a system; m is the actual number of significant elements in a mineral

Variant 1	*m*	2	3	4	5	Total
n = 30, m = 2 to 5	*C*	435	4060	27 405	142 506	174 406

Variant 2	*m*	2	3	4	5	6	7	8	Total
n = 17, m = 2 to 8	*C*	136	680	2380	6188	12 376	19 448	24 310	65 518

See text for discussion.

number of significant elements in each individual mineral (m) according to the formula $(C_n^m) = n!/m!(n-m)!$. Two sets of calculations were carried out. One set included approximately one-third of the elements in the periodic table ($n = 30$) that form relatively simple compounds ($m \leq 5$); the other set involved a narrow range of the most characteristic elements of alkaline rocks ($n = 17$) that form more complex compounds ($m \leq 8$). The calculations show that, when $n = 30$ and m ranges from 2 to 5, the number of combinations equals 174 406; when $n = 17$ and m ranges from 2 to 8, the result is 65 518. Even though this approach is fairly arbitrary, the number of possible minerals of alkaline rocks can nevertheless be estimated to be of the order of 10^4–10^5 species.

The diversity of the crystal structures of alkaline minerals can be illustrated by compounds of the type $Na_xM_ySi_pO_q$, where M = Ti, Zr, Be, and other amphoteric elements. The special features of the atomic arrangements of these compounds and their more complex analogues have been examined in detail elsewhere (Belov 1961, 1976; Povarennykh 1966a; Sandomirsky & Belov 1984; Voronkov *et al.* 1975, 1978; Pyatenko *et al.* 1976; Egorov-Tismenko & Sokolova 1990; Ferraris, 1997; Ferraris *et al.* 1997; Merlino & Pasero 1997). In the crystal structures, Ti and other high-charge elements together with Si form mixed radicals whose negative charge is compensated by alkali cations. The presence of Na is important because, as a large cation, it performs the function of a 'rigid fragment' relative to the more flexible MSiO radicals and, as a strong base, it helps amphoteric elements play their anion-forming role (Belov 1961, 1976). Na is characterised by a unique range in co-ordination numbers (from 4 to 12) and shapes of the corresponding polyhedra. Na atoms are capable of off-centre displacements within co-ordination polyhedra and of forming highly unequal Na–O bond lengths, thus ensuring complete charge balance for the Na-linked anions. Na polyhedra are able to link by corner-, edge-, or face-sharing with each other, producing diverse structural units, including one-dimensional (chains and columns) and two-dimensional (sheet and net) structures, and each type of association can have several different topologies.

In these structural arrangements, the variety of M–O and Si–O fragments is complex and varied. For example, Ti polyhedra characteristically form (in addition to single and coupled octahedra) geometrically diverse rings, chains, bands, one- and multilevel layers, and intricate frameworks. An additional factor controlling the diversity of Ti–O structural units is the ability of Ti to lower its co-ordination number from six to five.

The polymorphism of Si–O fragments is well known: for example, the same metasilicate formula $[SiO_3]_n$, with $n = \infty$, may represent the pyroxene chain Si_2O_6 or any of more than ten topologically different bands; the dimetasilicate formula $[Si_2O_5]_n$ may represent a variety of cyclogroups, bands, sheets and frameworks. Along with homogeneous Si–O structural units, some structures involve heterogeneous Si–O fragments, such as three- and nine-membered rings in eudialyte or chains and bands in vinogradovite.

The mutual combinations of Na–, M–, and Si–O structural units in $Na_xM_ySi_pO_q$ compounds are no less diverse than the structural units themselves, and the diversity of MSiO combinations markedly increases with the degree of polymerisation. According to Sandomirsky & Belov (1984), among mixed radicals, only one finite radical is known; there are 10-odd known band (or chain) radicals and about 50 layer radicals, whereas framework radicals run into the hundreds. The great variety of cationic and anionic motifs and their combinations explain the abundance of distinct structure types of alkaline amphosilicates (silicates with amphoteric elements) and, in particular, the existence of vast families of Ti, Nb, Zr and Be silicates that have similar compositions but differ in stoichiometry or structural features (or both). The majority of titanosilicates and their analogues recently discovered in differentiated nepheline syenite complexes represent hitherto unknown structure types. A large number of new structure types have also been identified in other silicates (Bokii 1996), as well as in phosphates (Yakubovich & Urusov 1996), carbonates (Pobedimskaya & Trinh 1985), and complex sulphides (Makovicky 1997). These facts, which fully agree with Yushkin's (1977) observation that the structural diversity of minerals steadily increases as the mineral system expands, highlight the role of the structural factor as a determinant of the hypothesised infinite diversity of mineral species. This hypothesis is in agreement with the conclusions of Skinner & Skinner (1980), based on their analysis of other factors, that there are no predictable limits to the number of minerals.

It stands to reason that most of the minerals that form large crystals and grains – more than 10 cm across – have already been discovered. The majority of species yet undiscovered can be broadly divided according to size into objects of the binocular level (0.1–1 mm), microscopic level (0.001–0.1 mm), and nanolevel (< 0.001 mm). The number of minerals of the binocular level alone appears to exceed that of the currently

known minerals by at least one order of magnitude. Although the great majority of these will be mineralogical rarities, the identification and study of the yet undescribed natural phases is not only of interest from a purely scientific point of view, but also has practical implications. Among the future minerals, there will undoubtedly be various types of commercial ores and compounds with unique structures and technologically useful properties.

Conclusions

The deep zones of Khibina and Lovozero contain abundant hyper-agpaitic rocks – essentially a new type of silicate-salt pegmatoid, supersaturated in alkaline, volatile and rare elements. Rocks of this type contain very large amounts of the most alkaline minerals of various classes ever recorded in nature. These rocks and minerals are indicators of special physicochemical conditions of agpaitic magma differentiation, which promote the accumulation of most of the less common elements and the crystallisation of an enormous number of minerals.

The unusual physicochemical conditions under which hyper-agpaitic rocks form predetermine the prevalence of complexly built minerals with highly ordered low-symmetry structures, characterised by a substantial predominance of triclinic species over cubic ones. In the future, the number of minerals from hyper-agpaitic rocks will undoubtedly continue to grow and, in turn, will serve to reduce the average symmetry of the mineral world. It is also clear that, regardless of the source of new species, they will be increasingly dominated by micro- and nanominerals, most of which crystallise after macrominerals at lower temperatures, thus being generally of lower symmetry. It can be predicted that, in the near future, the proportion of triclinic minerals in the mineral world will become equal to, and subsequently exceed, that of cubic minerals.

The long-held thesis that there is a limit to the number of mineral species is valid only for ordinary types of rocks and mineral deposits. The principal sources of new mineral discoveries are deposits formed in anomalous geotectonic and geochemical environments under conditions that encompass virtually the entire range of physicochemical parameters (*T, P, X,* pH, Eh, etc.) accessible to modern experimental mineralogy and, moreover, include geological time and other factors unattainable experimentally in the laboratory. All this serves to remove any barriers that limit the number of mineral species.

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The hyper-agpaitic stage in the evolution of the Ilímaussaq alkaline complex, South Greenland

Henning Sørensen and Lotte Melchior Larsen

The term hyper-agpaitic covers mineral associations characterised by a wealth of Na-rich minerals such as natrosilite, zirsinalite, ussingite, vuonnemite, vitusite and lomonosovite. This mineral association clearly indicates a higher degree of alkalinity than for agpaitic rocks in general. In the Ilímaussaq complex hyper-agpaitic mineral associations occur not only in pegmatites and hydrothermal veins as in the Kola complexes, Khibina and Lovozero, but also in highly evolved lujavrites and in the fenitised volcanic rocks in the roof of the complex. This paper reviews the occurrences of hyper-agpaitic mineral associations in the Ilímaussaq complex. The mineral assemblages are determined by an interplay of temperature, pressure, oxygen fugacity, alkalinity, especially the concentration of Na, and contents of elements such as Zr, Ti, Nb, REE, Fe, Mn, U, Th, P, F, Cl and H_2O. Increasing and decreasing stages of alkalinity may be distinguished. At increasing alkalinity nepheline is for instance substituted by naujakasite, while at decreasing alkalinity and temperature naujakasite is substituted by analcime.

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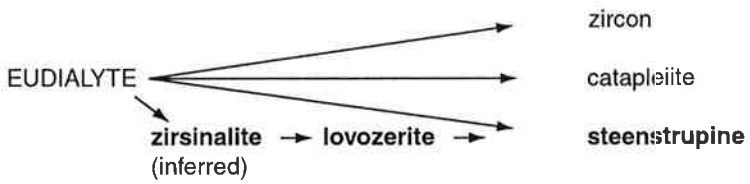
Russian mineralogists and petrologists studying the Lovozero and Khibina complexes of the Kola Peninsula introduced the term hyper- or ultra-agpaitic mineral associations and rocks in order to characterise special types of pegmatites and hydrothermal mineralisations rich in rare minerals (cf. Khomyakov 1995, 2001, this volume). These mineral associations formed from melts and fluids oversaturated in alkalis, volatiles and rare elements and represent a more highly evolved stage than agpaitic rocks in general. Hyper-agpaitic rocks are distinguished by an extraordinary variety of sodium-rich minerals, many of which are readily soluble in water and break down under atmospheric conditions. Examples of hyper-agpaitic minerals from Khibina and Lovozero are: zirsinalite, vuonnemite, lomonosovite, steenstrupine, vitusite, chkalovite, ussingite, natrosilite and villiaumite (Fig. 1). A characteristic feature of some of the minerals of hyper-agpaitic rocks is that they can be gradually transformed into hydrogen-bearing analogues with preservation of crystal morphology and parts of the crystal structure. Minerals formed by this mechanism are termed transformation mineral species (Khomyakov 1995). Examples are lovozerite formed after zirsinalite, and epistolite formed after vuonnemite.

Khomyakov (1995) demonstrated that stages of increasing and decreasing alkalinity are involved in the evolution of hyper-agpaitic rocks. Three stages may be distinguished: increasing, maximum and decreasing alkalinity. This is illustrated by the succession: eudialyte in an agpaitic rock is altered into zirsinalite which with decreasing alkalinity is transformed into lovozerite (Fig. 1a).

In the Khibina and Lovozero complexes the hyper-agpaitic mineral associations are found in pegmatites and hydrothermal veins but not in the major rock types. Khomyakov (1995) pointed out, however, that the porphyritic lovozerite-murmanite lujavrites of Lovozero may mark the former presence of hyper-agpaitic lujavrites, because lovozerite and murmanite are known

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a *Reactions involving eudialyte*



Schematic reactions

eudialyte + Na + REE + Mn + Th + PO_4 → **steenstrupine** + Zr + Si + Fe

eudialyte + **natrosilite** → **zirsinalite**

zirsinalite + H_2O → **lovozerite** + NaOH

NaOH + CO_2 → Na carbonates

b *Reactions involving other minerals*

Schematic reactions

microcline + NaOH → **ussingite** + K

nepheline + Na + Fe + Si + H_2O → **naujakasite**

naujakasite + H_2O → analcime + Na + Fe

vuonnemite + H_2O → epistolite + NaF + Na_2PO_4

vitusite + H_2O → monazite/rhabdophane + NaOH + PO_4

chkalovite + Cl + Al → tugtupite + Be

lomonosovite → murmanite + Na_3PO_4

Mineral formulae

analcime: $NaAlSi_2O_6 \cdot H_2O$
catapleiite: $Na_2ZrSi_3O_9 \cdot 2H_2O$
chkalovite: $Na_2BeSi_2O_6$
epistolite: $Na_2(Nb,Ti)_2Si_2O_9 \cdot nH_2O$
eudialyte: $Na_4(Ca,Ce)_2Fe,Mn,Y)ZrSi_8O_{22}(OH,Cl)_2$
gerasimovskite: $(Mn,Ca)(Nb,Ti)_5O_{12} \cdot 9H_2O)(?)$
lomonosovite: $Na_5Ti_2O_2(Si_2O_7)_2(PO_4)_2$
lorenzenite: $Na_2Ti_2O_3(Si_2O_6)$
lovozerite: $Na_2Ca(Zr,Ti)Si_6(O,OH)_{18}$
microcline: $KAlSi_3O_8$
monazite: $(Ce,La,Nd,Th)PO_4$
murmanite: $Na_3(Ti,Nb)_4O_4(Si_2O_7)_2 \cdot 4H_2O$
natrosilite: $Na_2Si_2O_5$
naujakasite: $Na_6(Fe,Mn)Al_4Si_8O_{26}$
nenadkevichite: $Na(Nb,Ti)Si_2O_6(O,OH) \cdot 2H_2O$
nepheline: $(Na,K)AlSiO_4$
rhabdophane: $(Ce,La,Ca)PO_4 \cdot H_2O$
sodalite: $(NaAlSiO_4)_6 \cdot 2NaCl$
sorensenite: $Na_4Be_2Sn(Si_3O_9)_2 \cdot 2H_2O$
steenstrupine-(Ce): $Na_{14}Ce_6Mn_2Fe_2(Zr,Th)(Si_6O_{18})_2(PO_4)_7 \cdot 3H_2O$
tugtupite: $Na_4AlBeSi_4O_{12}Cl$
ussingite: $NaAlSi_3O_8 \cdot NaOH$
villiaumite: NaF
vinogradovite: $(Na,Ca)_4Ti_4Si_8O_{26} \cdot (H_2O,K_3)$
vitusite-(Ce): $Na_3Ce(PO_4)_2$
vuonnemite: $Na_5Nb_3Ti(Si_2O_7)_3O_2F_2 \cdot 2Na_3PO_4$
zircon: $ZrSiO_4$
zirsinalite: $Na_6CaZrSi_6O_{18}$

Fig. 1. Mineral formulae and reactions in hyper-agpaitic rocks. The hyper-agpaitic minerals are indicated with **bold typeface**. **a**: Examples of reactions involving eudialyte. Eudialyte may be substituted by zircon under non-alkaline conditions (Ussing 1898), by catapleiite during late-magmatic alteration under agpaitic conditions and zirsinalite and steenstrupine under hyper-agpaitic conditions. The transformation of zirsinalite into lovozerite releases NaOH which may react with CO_2 to form Na carbonates. **b**: Examples of reactions involving other minerals. The transformation of vuonnemite into epistolite releases NaF and Na phosphate.

to be alteration products of zirsinalite and lomonosovite. This is corroborated by the recent discovery of naujakasite in these rocks (Khomyakov *et al.* 2001, this volume). In contrast, hyper-agpaitic lujavrites are well preserved in the Ilímaussaq complex in addition to hyper-agpaitic pegmatites and hydrothermal veins.

It is the purpose of the present paper to review the occurrence of hyper-agpaitic mineral associations and rocks in the Ilímaussaq complex with emphasis on the succession of minerals which can be linked to the increasing, maximum, and decreasing stages of alkalinity.

Hyper-agpaitic mineral associations of the Ilímaussaq complex

The agpaitic nepheline syenites of the Ilímaussaq complex are, in order of formation: sodalite foyaite, naujaite, kakortokite and lujavrites (Ussing 1912; Sørensen 2001, this volume). The earliest mineral assemblage to crystallise from the main magma was fayalitic olivine, hedenbergitic pyroxene, titanomagnetite, apatite, nepheline, sodalite and alkali feldspar. The Na-free minerals, fayalite, hedenbergite, apatite and titanomagnetite, are only found in the sodalite foyaite and as scarce constituents in the naujaite. Eudialyte, which may be termed the typomorphic mineral of agpaitic nepheline syenites, first appears in the sodalite foyaite and becomes a major constituent in the naujaite, kakortokite and some of the lujavrites.

The crystallisation of the agpaitic magma was accompanied by an increase in alkalinity, which is seen from a series of continuous and discontinuous mineral reactions. Fayalite, hedenbergite and titanomagnetite are substituted by respectively katophorite, aegirine-augite and aenigmatite (Larsen 1976, 1977). In the naujaite, hiortdahlite appears to be the first formed Zr phase and is earlier than eudialyte (Robles *et al.* 2001, this volume). The lujavrites represent the latest magmatic stage and the major minerals are microcline, albite, nepheline, arfvedsonite, aegirine and eudialyte; minor components are britholite, sodalite and neptunite. In the latest formed lujavrites, eudialyte is missing and its place is taken by steenstrupine. These late lujavrites are hyper-agpaitic and contain minerals such as ussingite, lovozerite, naujakasite, vitusite, vuonnemite and villiaumite. They were clearly formed from melts richer in Na, F, a number of rare elements and water than the melts responsible for the formation of the major part of the lujavrites of the complex (Bondam & Sørensen 1958; Buchwald & Sørensen 1961; Sørensen 1962; Larsen & Sørensen 1987). The most evolved parts of the pegmatites and hydrothermal veins of the complex similarly contain hyper-agpaitic minerals such as ussingite, chkalovite and steenstrupine.

The fields of stability of most of the hyper-agpaitic minerals appear to be narrow; their break-down and replacement by other phases can be followed petrographically. A number of mineral reactions are shown schematically in Fig. 1.

Three groups of hyper-agpaitic rocks may be distinguished in the Ilímaussaq complex: (1) steenstrupine and naujakasite lujavrites, (2) pegmatites and hydrothermal veins, and (3) fenitised volcanic rocks in the roof of the complex.

Steenstrupine and naujakasite lujavrites

In the hyper-agpaitic lujavrites steenstrupine takes the place of eudialyte, the former presence of which is indicated by pseudomorphs of the size and form of eudialyte crystals and consisting mainly of ill-defined pigmentary material. There are also grains of lovozerite (Danø & Sørensen 1959; Sørensen 1962) which may be taken as evidence for the presence of zirsinalite at an earlier stage (Fig. 1a, 2).

Naujakasite takes the place of nepheline (Petersen & Andersen 1975; Sørensen 1997; Khomyakov *et al.* 2001, this volume) and is an important rock-forming mineral which may make up more than 75% of the volume of the naujakasite lujavrites. It consists of common elements (Na, Fe, Al, Si) as seen from its formula (Fig. 1b). It is therefore surprising that a second occurrence has not been found until recently. Naujakasite is a rare constituent of lovozerite-lomonosovite lujavrites in the eudialyte lujavrite complex at Lovozero (Khomyakov *et al.* 2001, this volume). This shows that the high levels of alkalinity and special conditions of formation responsible for the formation of the naujakasite lujavrites in Ilímaussaq were only attained in Lovozero under exceptional conditions.

Vitusite (Rønsbo *et al.* 1979; Pekov *et al.* 1997), vuonnemite (Rønsbo *et al.* 1983) and villiaumite have most probably formed at an early stage of hyper-agpaicity; there is no petrographic evidence of any predecessors of these minerals. Ussingite replaces microcline and sodalite.

The hyper-agpaitic minerals contain inclusions of the earlier formed rock-forming minerals, arfvedsonite, aegirine, microcline, analcime (often lath-shaped indi-

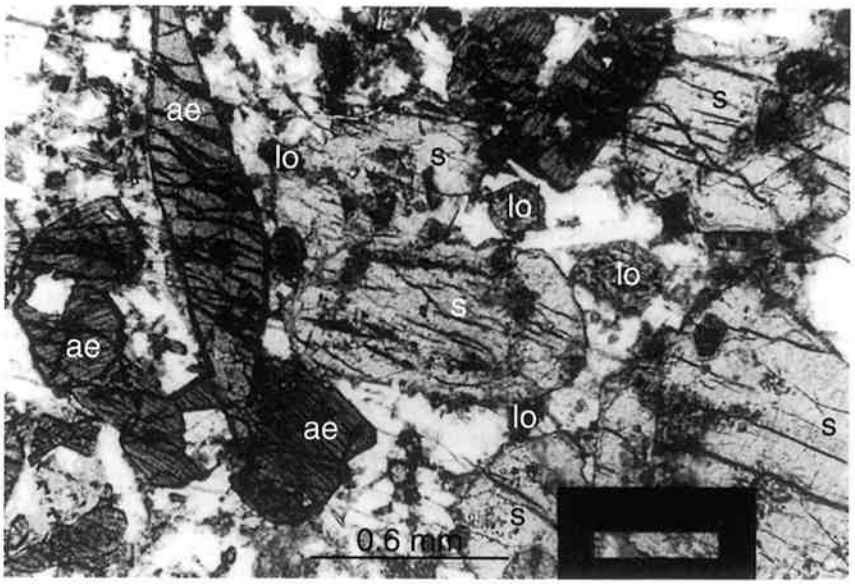


Fig. 2. Steenstrupine crystals (**s**), the one in the centre with minute inclusions of altered lovozerite outlining the original centre of the crystal. The matrix consists of microcline and ussingite (**both white**), aegirine (**ae**) and altered grains of lovozerite (**lo**), which are larger than the lovozerite enclosed in steenstrupine. Vein in naujaite, the head of Kangerluarsuk. GGU 18468a, plane polarised light, scale bar 0.6 mm.

cating replacement of microcline or albite) and pseudomorphs after eudialyte. The enclosed minerals occur in smaller grains than in the surrounding rock and with the same orientation as in the latter (Figs 2, 3). This indicates that the hyper-agpaitic minerals began to grow when a sufficient level of alkalinity was reached during consolidation of the melt. Steenstrupine occurs as perfectly developed crystals and as poikilitic grains with irregular forms (Fig. 4), evidence of a long period of formation of this mineral.

Steenstrupine breaks down to aggregates of ill-defined pigmentary materials, a brown micaceous mineral, monazite, neptunite, thorite, thorianite, etc. (Buchwald & Sørensen 1961; Makovicky *et al.* 1980). Buchwald & Sørensen (1961) noted that the freshest steenstrupine is found in albite–ussingite-rich lujavrites, whereas steenstrupine is generally more strongly altered in lujavrites in which analcime makes up the groundmass.

Naujakasite is altered into analcime with brown pigmentation (Petersen 1967; Makovicky *et al.* 1980; Khomyakov *et al.* 2001, this volume), vuonnemite into

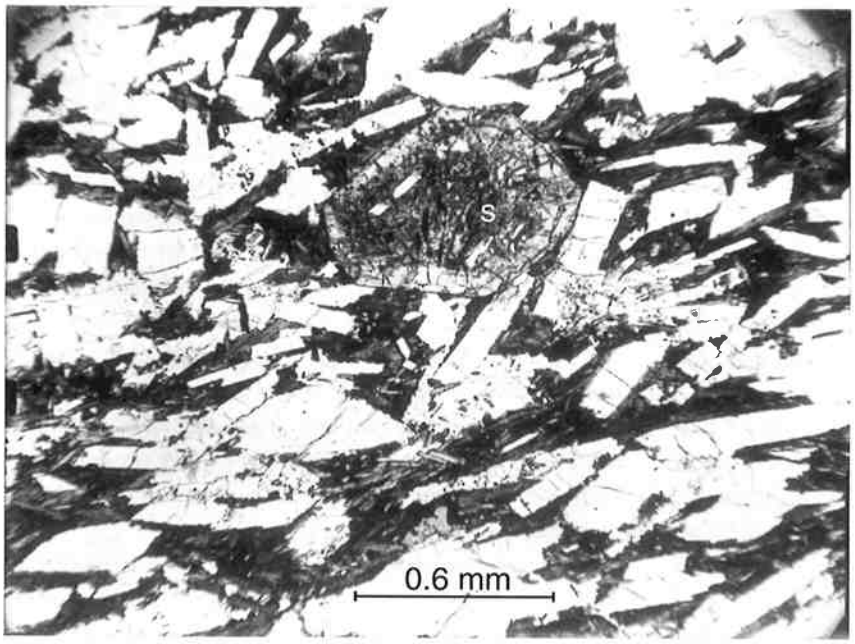


Fig. 3. Steenstrupine crystal (**s**) in lujavrite dyke made up of microcline (**light**) and arfvedsonite (**dark**). The central part of the steenstrupine crystal contains minute inclusions of microcline and arfvedsonite, much smaller than the grains of the matrix. The microcline inclusions in the marginal part of the crystal are intermediate in size. GGU 21154, head of Kangerluarsuk, plane polarised light.

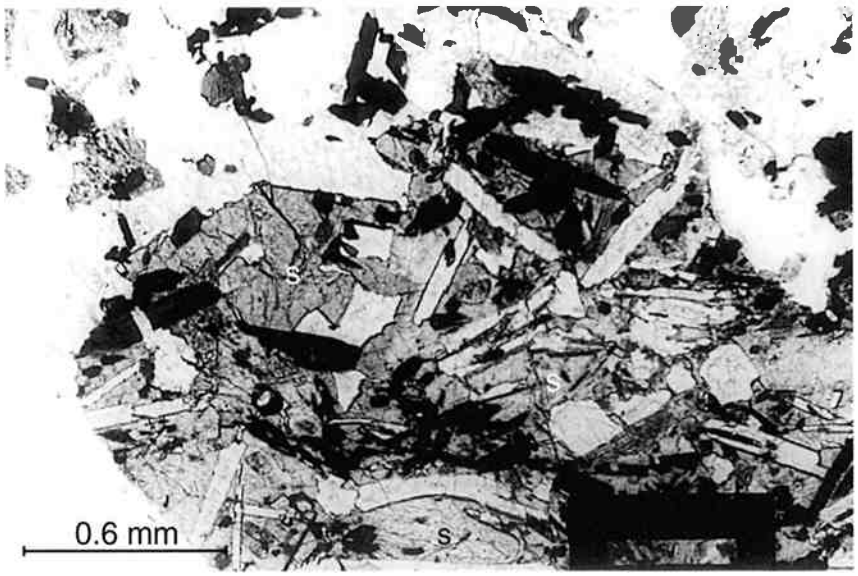


Fig. 4. Large poikilitic crystals of steenstrupine (**s**) in matrix of arfvedsonite (dark prisms), ussingite, analcime and natrolite (**all white**) and enclosing these minerals. The **white laths** are pseudomorphs after alkali feldspar. Arfvedsonite lujavrite, Tuttup Attakoorfia, GGU 21111, plane polarised light, scale bar 0.6 mm.

epistolite (Rønsbo *et al.* 1983) and vitusite into monazite–rhabdophane–analcime (Pekov *et al.* 1997). Ussingite appears to be substituted by natrolite and analcime, and villiaumite to be dissolved out in the late- and post-magmatic stages, leaving holes in the rocks.

Pegmatites and hydrothermal veins

These rocks contain the hyper-agpaitic minerals ussingite, steenstrupine, chkalovite and sorensenite (Sørensen 1962; Sørensen *et al.* 1971). Steenstrupine in places overgrows crystals of pegmatitic eudialyte (Fig. 5) and may be associated with villiaumite in interstices between sodalite, microcline and other vein minerals (Fig. 6). Epistolite (Karup-Møller 1986b), lovozerite and clusters of monazite–rhabdophane (Fig. 7) are very probably secondary after the hyper-agpaitic minerals vuonnemite, zirsinalite and vitusite.

Chkalovite and sorensenite react with late fluids under the formation of tugtupite, beryllite, and other Be minerals (Sørensen *et al.* 1971; Markl 2001, this volume). Epistolite is altered into nenadkevichite and gerasimovskite (Semenov *et al.* 1967; Karup-Møller 1986c). Epistolite is also replaced by aggregates of lues-

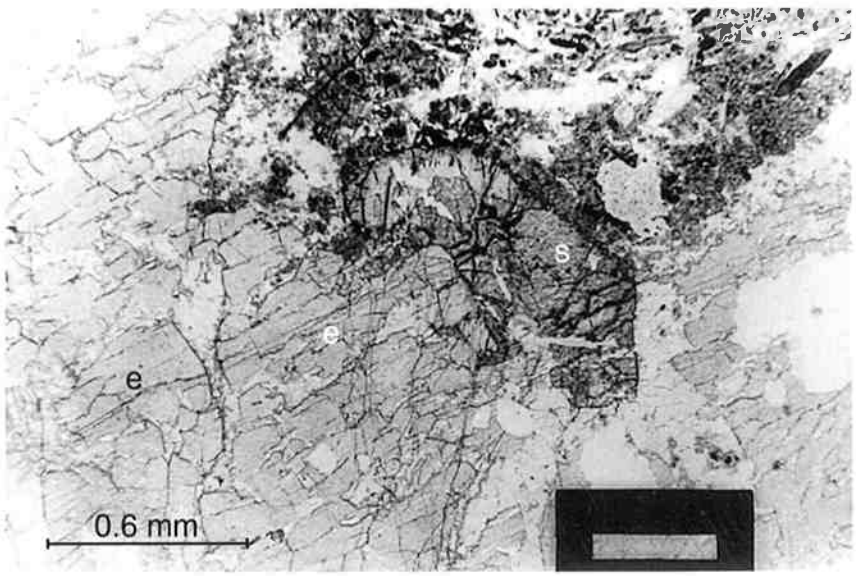


Fig. 5. Crystal of steenstrupine (**s**) overgrowing a large crystal of eudialyte (**e**, lower left) in a fine-grained matrix (upper part of photograph) of albite, microcline, aegirine, lovozerite, ussingite, analcime and natrolite. The steenstrupine is surrounded by an accumulation of small grains of altered lovozerite (**dark rim**) giving the impression that they have been pushed aside by the growing steenstrupine. Pegmatite in naujaite, the head of Kangerluarsuk, GGU 21148, plane polarised light, scale bar 0.6 mm.

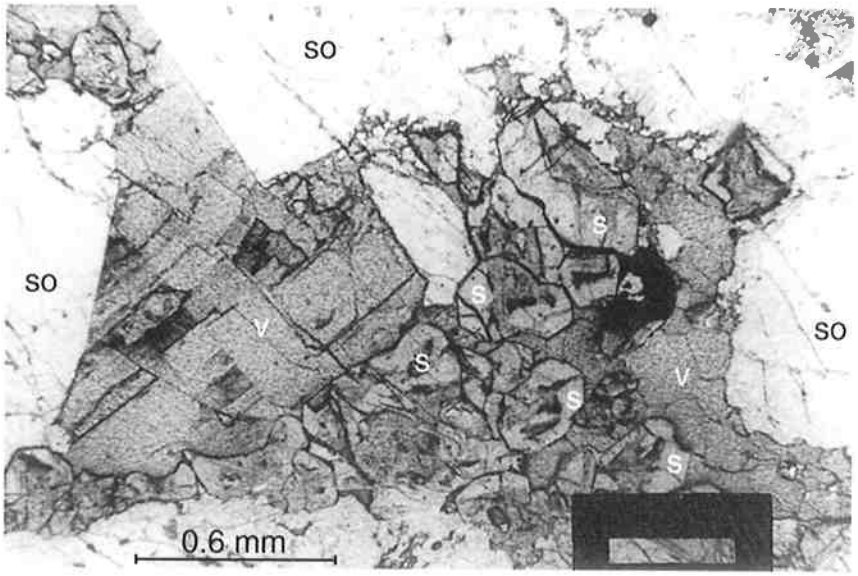


Fig. 6. Aggregate of small steenstrupine crystals (**s**) enclosed in villiaumite (**v**) filling the interstices between large grains of sodalite (**so**) which are partially replaced by analcime and natrolite. Vein in lujavrite, Kvanefjeld. Drill core 53 at 207.90 m, plane polarised light, scale bar 0.6 mm.

hite, pyrochlore and neptunite (Semenov *et al.* 1965). Steenstrupine, lovozerite and ussingite behave as described under steenstrupine and naujakasite lujavrites.

Fenitised rocks

The volcanic roof overlying lujavrites in the Kvanefjeld area in the northern part of the complex is strongly fenitised and contains steenstrupine, lomonosovite and murmanite (Semenov 1969; Sørensen *et al.* 1974; Karup-Møller 1983, 1986a). The cores of the lomonosovite grains are rich in minute inclusions of albite, nepheline, arfvedsonite, aegirine and lorenzenite (Fig. 8). Lomonosovite alters into murmanite, which again alters into lorenzenite (Karup-Møller 1986a) and vinogradovite (Rønsbo *et al.* 1990). Lomonosovite and murmanite have not been found in the hyper-agpaitic lujavrites, which can be explained by the very low contents of TiO_2, about 0.2 wt%, in the latter (Sørensen 1997). Lorenzenite has, however, been found in arfvedsonite lujavrite (Karup-Møller 1986a). A Nb analogue of β-lomonosovite may, according to Rønsbo *et al.* (1983), occur in the vitusite-bearing lujavrites examined by Rønsbo *et al.* (1979).

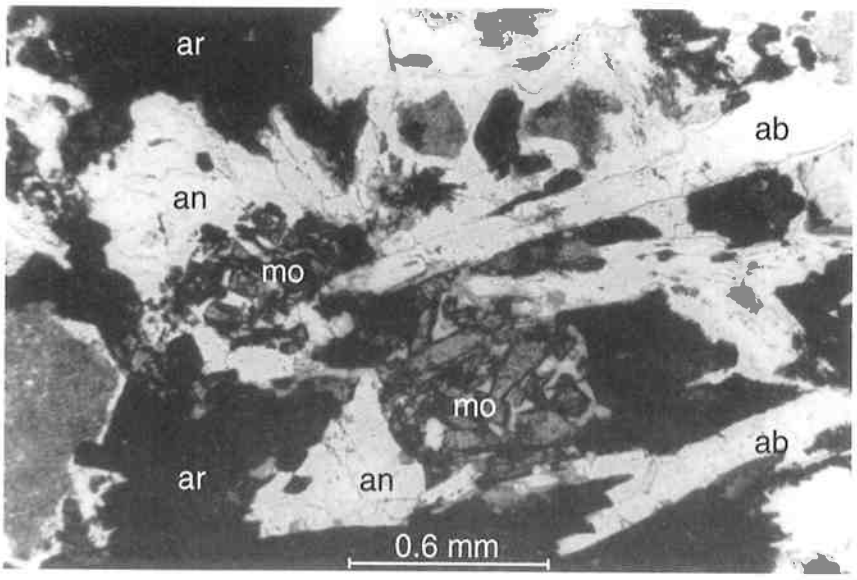


Fig. 7. Clusters of monazite crystals (**mo**) in lujavrite made up of albite (**ab**), arfvedsonite (**ar**) and analcime (**an**). Sample Geox 18, Kangerluarsuk, plane polarised light, lower right cluster measures 0.6 mm across.

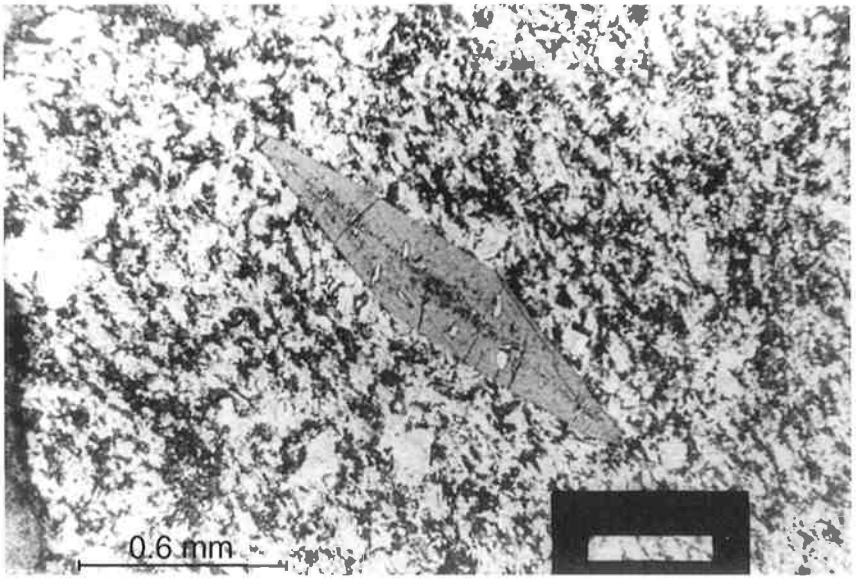


Fig. 8. Large crystal of lomonosovite in fine-grained, fenitised basalt made up of microcline (**light**) and arfvedsonite (**dark**). The core of the lomonosovite crystal is rich in minute crystals of the matrix minerals. Kvanefjeld, drill core 49 at 91.15 m, plane polarised light, scale bar 0.6 mm.

Conditions of formation

It is unfortunately not possible to define the fields of stability of the hyper-agpaitic minerals because very little experimental data exist on systems oversaturated in sodium. It is well known from the studies of Christophe-Michel-Lévy (1961) and others that eudialyte is formed in alkaline, and zircon in less alkaline systems. Piotrowski & Edgar (1970) and Sood & Edgar (1970) demonstrated, based on melting experiments on some of the Ilímaussaq rocks, that agpaitic rocks have a range of crystallisation of several hundred degrees centigrade with solidus temperatures as low as 430°C. The eudialyte of an aegirine lujavrite was at p_{H_2O} = 1030 bars found to begin crystallisation at 750°C, 150°C below the liquidus.

Kogarko *et al.* (1982) and Kogarko & Romanchev (1983) undertook melting experiments on eudialyte-bearing rocks of the Lovozero complex and also made heating experiments on crystallised melt inclusions in the eudialyte crystals of these rocks. They found that crystalline inclusions in the central parts of eudialyte crystals homogenise at 860–820°C, whereas inclusions in the marginal parts of the crystals are made up of crystals and fluids and homogenise at 770–720°C. This implies that eudialyte crystallises over an interval of more than 100°C.

Kogarko & Krigman (1970) examined the system nepheline–NaF, a system oversaturated in Na, and demonstrated a field of liquid immiscibility. There are two liquids over a wide range of temperatures, an ionic melt of almost pure NaF and a polymeric aluminosilicate melt. Kogarko & Romanchev (1983) similarly found liquid immiscibility in melting experiments on villiaumite-bearing foyaite from Lovozero. Two immiscible liquids occurred in the foyaite at 725°C, a silicate melt and a fluoride-rich melt. With further melting the fluoride melt was gradually dissolved in the silicate melt and disappeared at about 900°C. Heating experiments on villiaumite-bearing inclusions in microcline from Lovozero foyaite also produced immiscible silicate and fluoride liquids at low temperatures.

Fluid inclusions in tugtupite and sorensenite homogenise at 400–460°C, when the aqueous phase contains 21 wt% salt, mainly NaCl. Secondary fluid inclusions in tugtupite homogenise at 350–100°C (Sobolev *et al.* 1970). These authors report homogenisation of three-phase fluid inclusions in chkalovite at 860–980°C and a salinity of 40–44 wt% in the aqueous phase. Such a high homogenisation temperature is clearly not realistic and suggests modification of the inclusions after entrapment.

In fluid inclusions in Ilímaussaq minerals, Konnerup-Madsen & Rose-Hansen (1982) and Konnerup-Madsen (2001, this volume) have observed immiscibility between aqueous saline fluids and a vapour phase dominated by methane. The predominance of hydrocarbons in the gas phase is an indication of oxygen fugacities as low as the synthetic graphite/CH_4 buffer curve. The entrapment of the fluids took place at 700–400°C and 1–2 kbar.

Markl (2001, this volume) has calculated the stability conditions of the Na–Be minerals of the late- and post-magmatic mineralisations of Ilímaussaq based on

thermodynamic data. It is estimated that chkalovite formed at 600°C and 1 kbar and that it is replaced by tugtupite at 400–200°C. Tugtupite co-exists at 400°C with a very Na-rich fluid or a fluid characterised by low silica activity and elevated pH. The pH seems to be more important than the concentration of Be and Na. The late-stage ussingite was formed at 350°C and very low silica activity. Hyper-agpaitic conditions are characterised by low oxygen fugacity, elevated pH and high Na/K ratios. The fluids of the early phases are highly saline, the late phases show relatively low salinities.

A study of fluid inclusions in minerals of hyper-agpaitic pegmatites in Lovozero (Shchegoleva *et al.* 1988) indicates that ussingite is formed in the temperature range 305–165°C.

The importance of peralkaline conditions for the formation of hyper-agpaitic minerals is demonstrated by an experimental examination of the stability of steenstrupine (Sørensen *et al.* 1985). At p_{H_2O} = 1000 atm., steenstrupine is stable over the whole temperature range examined, 400–700°C, as long as the starting material is oversaturated in Na, and, in the case of synthetic compositions, that Zr is also present.

The experimentally demonstrated wide interval of crystallisation of agpaitic melts at low temperatures and the probable existence of immiscible NaF-rich melts at late stages of crystallisation of the melts provide a favourable environment for late-magmatic reactions and for the crystallisation of hyper-agpaitic minerals. These reactions most probably take place at temperatures lower than the above-mentioned temperature of about 700°C at which crystallised melt inclusions in eudialyte homogenise (Kogarko *et al.* 1982). It may then be inferred that hyper-agpaitic mineral reactions take place from the cessation of formation of eudialyte to the silicate melt solidus at about 450°C and even at lower temperatures as indicated by the above-mentioned homogenisation temperatures of 350–100°C measured in fluid inclusions in tugtupite (Sobolev *et al.* 1970). In extremely Na-rich systems there may be a gradual transition from melt to hydrothermal fluids (cf. Kogarko 1977, p. 111; Khomyakov 1995, p. 30).

According to Kogarko (1977) the solubility of water in silicate and aluminosilicate melts increases with increasing molar amounts of alkali ions. Melting experiments on melanocratic foyaite and eudialyte-bearing pegmatite from Lovozero revealed solubilities of 4.3–4.5 wt% H_2O at 1 kbar and 6.9–7.3 wt% H_2O at 2 kbar, the highest contents in the strongly peralkaline pegmatite, the agpaitic coefficient of which is 1.77. This corresponds to mol contents higher than 50%. The transition of melts into hydrothermal fluids depends on the pressure of the system; transition is only possible at pressures higher than the maximum of the three-phase curve of liquid + crystals + vapour in *T–P* diagrams of relevant systems. At lower pressures a vapour phase may separate from the silicate melt with subsequent transition into liquid water. A considerable part of the consolidation of the agpaitic melts in the Ilímaussaq complex took place beneath an impermeable roof, i.e., under closed system conditions at pressures favouring the retention of H_2O in the melts (Larsen & Sørensen 1987). Pressure relief allowed fluids to escape to form hydrothermal veins and to fenitise the roof.

Discussion

The textural relations of the hyper-agpaitic minerals, especially the abundance of inclusions of minerals of the adjacent rocks in the central parts of the grains (Fig. 2), indicate that the oversaturation in alkalis was acquired during consolidation of the melts. It is also evident that the hyper-agpaitic minerals have different fields of stability which are determined not only by temperature, pressure, oxygen fugacity and alkalinity, especially the Na content, high Na/K ratios (Khomyakov *et al.* 2001, this volume), but also by contents of a number of elements, especially Zr, Nb, Ti, REE, Mn, Fe, U, Th, P, F, Cl and H_2O. It is therefore difficult to illustrate the mineralogical expression of the stages of alkalinity in simple diagrams.

Under hyper-agpaitic conditions, eudialyte reacts out and is substituted by zirsinalite at an early stage which is characterised by high alkalinity and low contents of REE and P. Zirsinalite has, so far, not been found in Ilímaussaq; one reason may be that it is easily transformed into lovozerite, or that it readily reacts with water and the atmosphere and can only be collected under ideal preservation conditions.

Steenstrupine appears to have formed later than zirsinalite because it contains inclusions of lovozerite (and altered eudialyte) irrespective of the host rock (Fig. 2). At the time of its formation, the magma was depleted in Zr and enriched in Na, Mn, REE, Th and P_2O_5. The stability field of steenstrupine is rather wide (cf. the above-mentioned experimental data; Sørensen *et al.* 1985). One reason for this may be that H^+ readily substitutes for Na^+ without destruction of the crystal structure (Makovicky & Karup-Møller 1981). The con-

tent of Na_2O in steenstrupine varies from practically 0 to more than 14 wt%, and in zoned crystals of steenstrupine anisotropic rims have higher contents of Na than the metamict cores. This may indicate that alkalinity was increasing during crystallisation of steenstrupine, but it may also be a result of secondary processes (cf. Khomyakov & Sørensen 2001, this volume). Steenstrupine co-exists with ussingite, sodalite, analcime and villiaumite.

Naujakasite co-exists with steenstrupine and also contains inclusions of this mineral. It appears to have been formed simultaneously with and later than steenstrupine at the expense of nepheline at a stage of elevated contents of Na, Fe and water and high Na/K ratios (Khomyakov *et al.* 2001, this volume).

Vitusite, vuonnemite and lomonosovite may be primary, formed at elevated concentrations of Na, REE, Nb and P. Their fields of stability appear to be very narrow; they are readily substituted by monazite–rhabdophane, epistolite and murmanite, respectively.

Beryllium minerals are restricted to pegmatites and veins. Chkalovite appears to be a primary mineral co-existing with sodalite under hyper-agpaitic conditions (Fig. 9). Decreasing alkalinity results in its substitution by tugtupite and other Be minerals (Sørensen *et al.* 1971; Markl 2001, this volume). With decreasing temperature ussingite is replaced by analcime and natrolite.

The transformation of zirsinalite into lovozerite and vitusite into monazite releases NaOH, whereas the transformation of vuonnemite and lomonosovite into epistolite and murmanite releases Na_3PO_4 (Fig. 1a). These additions to the melts may be responsible for some of the reactions observed to have taken place in the rocks, as for instance the formation of ussingite, and may have contributed to the hyper-agpaitic conditions in the fluids expelled from the lujavritic magma. There may even, as mentioned above, be a gradual transition from melt to hydrothermal fluids in extremely Na-rich systems. Na-rich fluids were responsible for the formation of hydrothermal veins and fenitisation of the roof rocks. The released material may, however, also have resulted in the formation of the many water-soluble minerals associated with the hyper-agpaitic rocks. In the Khibina and Lovozero complexes about 80 water-soluble minerals have been found; examples are natrosilite, $Na_2Si_2O_5$, natrophosphate, $Na_7(PO_4)_2F \cdot 19H_2O$ and dorfmanite, $Na_2HPO_4 \cdot 2H_2O$ (Khomyakov 1995). From the Ilímaussaq complex only villiaumite

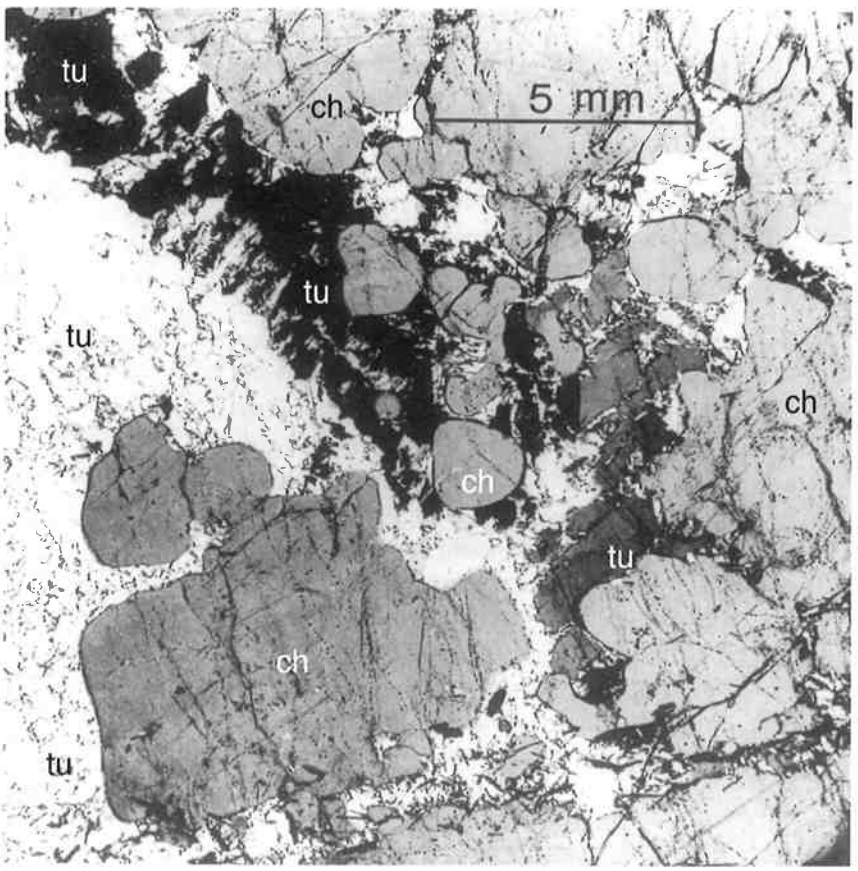


Fig. 9. Corroded grains of chkalovite (**ch**) under replacement by tugtupite (**tu**) showing penetration twinning (one set of individuals light, the other set near extinction). GGU 77450.3, Kvanefjeld, crossed polars. From Sørensen *et al.* (1971). Photo: Harry Micheelsen.

(Bondam & Ferguson 1962), sodium carbonate minerals (Sørensen *et al.* 1970), natrophosphate (Petersen *et al.* 2001, this volume) and dorfmanite (Petersen *et al.* 1993) are known. There is no reason to doubt that many more water-soluble minerals are present, but these minerals, with the exception of villiaumite, react spontaneously with surface water and the atmosphere and must be collected immediately after blasting. In Ilímaussaq there is, contrary to Khibina and Lovozero, no mining activity. The presence of natrosilite may, however, be inferred, because the dissolved matter in the water seepage from the exploration adit in the Kvanefjeld uranium deposit has been shown to be a mixture of NaF and $Na_2Si_2O_5$ (Sørensen 1982).

Conclusions

Further studies are evidently needed in order to unravel the chain of reactions and mineral formation which takes place during the evolution of the hyperagpaitic rocks. On the basis of the available information the following evolution may be envisaged, taking into account that this evolution took place in different environments: crystallising magmas and pegmatitic and hydrothermal systems including metasomatised roof rocks.

With increasing alkalinity (and decreasing temperature) eudialyte was substituted by zirsinalite, and minerals such as vitusite, vuonnemite and lomonosovite were formed. These minerals most probably mark the stage of maximum alkalinity. With decreasing alkalinity zirsinalite was transformed into lovozerite, vuonnemite into epistolite and lomonosovite into murmanite. At this stage steenstrupine was formed and vitusite broke down into monazite–rhabdophane. The formation of naujakasite at the expense of nepheline took place simultaneously with the formation of steenstrupine, but overlapping this mineral, since naujakasite often contains inclusions of steenstrupine. Ussingite and villiaumite were formed more or less simultaneous with and later than steenstrupine. In the latest phases of crystallisation, steenstrupine took up H^+ instead of Na^+ and eventually broke down into pseudomorphs made up of pigmentary material etc. At this stage analcime and natrolite replaced naujakasite, microcline and ussingite, epistolite was replaced by nenadkevichite and murmanite by vinogradovite.

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Naujakasite from the Ilímaussaq alkaline complex, South Greenland, and the Lovozero alkaline complex, Kola Peninsula, Russia: a comparison

Alexander P. Khomyakov, Henning Sørensen, Ole V. Petersen and John C. Bailey

Naujakasite, $Na_6(Fe,Mn)Al_4Si_8O_{26}$, long known from the Ilímaussaq alkaline complex, South Greenland, was not reported until 1999 from other occurrences of alkaline rocks in spite of the fact that the mineral is composed of common elements. In 1999, a variety of naujakasite rich in Mn was found in the Lovozero alkaline complex in the Kola Peninsula, Russia. This variety has been approved by the IMA as a new mineral, manganonaujakasite, $Na_6(Mn_{0.53}Fe^{2+}_{0.47})Al_4Si_8O_{26}$. At Ilímaussaq naujakasite is a rock-forming mineral in the highly evolved rock naujakasite lujavrite in which it may make up more than 75 vol.%; at Lovozero manganonaujakasite is a very rare constituent in mineralised lovozerite–lomonosovite lujavrite. Naujakasite appears to take the place of nepheline in hyper-agpaitic nepheline syenites characterised by exceptionally high Na/K ratios. The nepheline syenites at Ilímaussaq have an average Na/K (atomic) ratio of 3.08, and the naujakasite lujavrites have the extreme ratio 4.56. The nepheline syenites of the Khibina and Lovozero complexes are characterised by lower Na/K ratios, 1.27 for Khibina and 1.67 for Lovozero, and thus nepheline is stable in the hyper-agpaitic rocks and naujakasite occurs only in pegmatites.

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Keywords: agpaite, hyper-agpaite, Ilímaussaq, Lovozero, lujavrite, manganonaujakasite, naujakasite, nepheline syenite

The Ilímaussaq alkaline complex is the type locality for naujakasite, $Na_6(Fe,Mn)Al_4Si_8O_{26}$. For half a century, the only known specimen of this mineral was a boulder weighing 350 gram, collected in 1897 by the Swedish mineralogist G. Flink at the small peninsula Naajakasik (then Naujakasik) on the south coast of the Tunulliarfik fjord, well within the complex (see Sørensen 2001, this volume for a map of the localities mentioned in the text and a brief description of the complex). Flink's original label tentatively identified the silvery white mica-like mineral that constituted 75% of the boulder as 'chlorite?'. Bøggild (1933) established this phase as a new mineral and named it after the place where it was found, and Gossner & Krauss (1933) presented the first set of unit cell parameters. Naujakasite was first found in outcrop in 1955 (Danø & Sørensen 1959). Based on the new material a complete redescription, including a redetermination of the unit cell parameters, was given by Petersen (1967), and the structure was worked out by Basso *et al.* (1975).

Naujakasite is now known to be of widespread occurrence in the Ilímaussaq alkaline complex in the rock called naujakasite lujavrite (see further below) and may constitute more than 75 vol.% of that rock. Because naujakasite is composed of the common elements Na, Fe, Mn, Al and Si, it is surprising that for 100 years naujakasite was a single locality mineral. In 1998, the first discovery of the mineral outside Ilímaussaq was

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Table 1. Crystallography of naujakasite from the Ilímaussaq and Lovozero alkaline complexes

Properties	Ilímaussaq	Lovozero
System	Monoclinic	Monoclinic
Class	2/m	2/m
Space group	C2/m	C2/m
a:b:c	1.8802:1:1.3122	1.8789:1:1.3096
a, Å	15.025	15.033
b, Å	7.991	8.001
c, Å	10.486	10.478
β	113.67°	113.51°
V, Å^3	1153.1	1156
Z	2	2
Hardness, Mohs	2½–3	3–4
Cleavage	{001} mica like {010} and {$\bar{4}$01}, distinct but irregular, cleavage plates brittle	{001} mica like
Density, g/cm^3	2.622 (meas.) 2.714 (calc.)	2.67 (meas.)
Crystal properties	Biaxial (–)	Biaxial (–)
α	1.537	1.539
β	1.551–1.549	1.551
γ	1.556	1.554
2V	52–71° (meas.) 61–74° (calc.) Distinct axial dispersion Y = *b*, Z ^ ⊥ (001) = 45° (in obtuse angle)	54° (meas.)
Transparency	Semitransparent	Transparent
Lustre on {001}	Strongly pearly, to a certain degree metallic	Adamantine to pearly
General appearance	Euhedral and subhedral silvery white to blue, platy crystals, up to 20 mm showing the forms {001}, {110} and {$\bar{1}\bar{1}$1}; the crystals are rhomb-shaped and pronouncedly platy on {001}	Irregular shaped, bright blue grains, 0.5 to 1.0 mm in size, occasionally aggregates up to 5 mm. The only form observed is {001}.

made by one of the authors (A.P.K.) in the Lovozero alkaline complex, Kola Peninsula, Russia.

The present paper describes the mineralogy and occurrence of naujakasite in the two complexes and discusses the stability relations of the mineral.

Mineralogy

The mineralogical properties of naujakasite from the Ilímaussaq alkaline complex and naujakasite from the Lovozero alkaline complex are compared in Table 1.

X-ray powder diffraction patterns of naujakasites from Ilímaussaq and Lovozero obtained under identical conditions show practically identical sets of lines and relative intensities. The unit cell parameters of naujakasite from Lovozero are almost identical to the parameters determined by Basso *et al.* (1975) for Ilímaussaq (Table 1); see also Khalilov *et al.* 1977).

The chemical analyses of the Ilímaussaq naujakasite published by Bøggild (1933), Petersen (1967) and Semenov (1969) show that it has a very high Fe/Mn ratio: around $Fe_{0.90}Mn_{0.10}$ in the structural formula. The Lovozero mineral, on the other hand, is dominated by Mn. Recalculated on the basis of 26 oxygen atoms, the empirical formula of the naujakasite from Lovozero has $Fe_{0.49}Mn_{0.53}$ (Table 2). The Lovozero mineral is thus the Mn-dominant analogue of the Ilímaussaq naujaka-

Table 2. Chemical analyses of naujakasite

	Ilímaussaq†	Lovozero‡
SiO_2	52.11	50.76
TiO_2	0.03	0.01
Al_2O_3	21.24	21.18
FeO	5.70	3.68
MnO	1.13	3.94
CaO	0.31	0.04
SrO		0.01
Na_2O	18.90	19.44
K_2O	0.51	0.02
P_2O_5	0.07	
	100.00*	99.08

* Recalculated to 100% assuming all iron present as FeO, and disregarding the results of the thermogravimetric analysis.

† From Petersen (1967).

‡ Analyst: G.N. Nechelyustov. Electron microbe analysis, Superprobe 733.

Empirical formulae

Ilímaussaq:

$(Na_{5.72}K_{0.10})_{\Sigma 5.82}(Fe_{0.74}Mn_{0.15}Ca_{0.05})_{\Sigma 0.94}(Al_{3.91}Si_{8.13})_{\Sigma 12.04}O_{26}$

Lovozero: $Na_{5.96}(Mn_{0.53}Fe_{0.49}Ca_{0.01})_{\Sigma 1.03}Al_{3.95}Si_{8.03})_{\Sigma 11.98}O_{26}$

site, and manganonaujakasite has been approved as a new mineral by the Commission of New Minerals and Mineral Names of the International Mineralogical Association (Khomyakov *et al.* 2000).

The occurrence of naujakasite in the Ilímaussaq alkaline complex

The first outcrop of naujakasite-bearing rocks was found by one of the authors (H.S.) in the bay of Tupersuatsiaat and described by Danø & Sørensen (1959). Shiny rhomb-shaped flakes of naujakasite, up to 0.2 cm across, are scattered throughout a thin dyke of fine-grained arfvedsonite lujavrite intersecting a lenticular body of naujaite.

Bondam & Sørensen (1958) and Buchwald & Sørensen (1961) described an occurrence of naujakasite lujavrite from an altitude of 400 m in the mountains south of Tupersuatsiaat. Ferguson (1964) reported that naujakasite lujavrite is quite common on Kvanefjeld where it forms minor horizons rarely wider than 50 m and usually only 5–10 m wide. Petersen (1967) presented the first detailed mineralogical description of naujakasite from Tupersuatsiaat and Kvanefjeld.

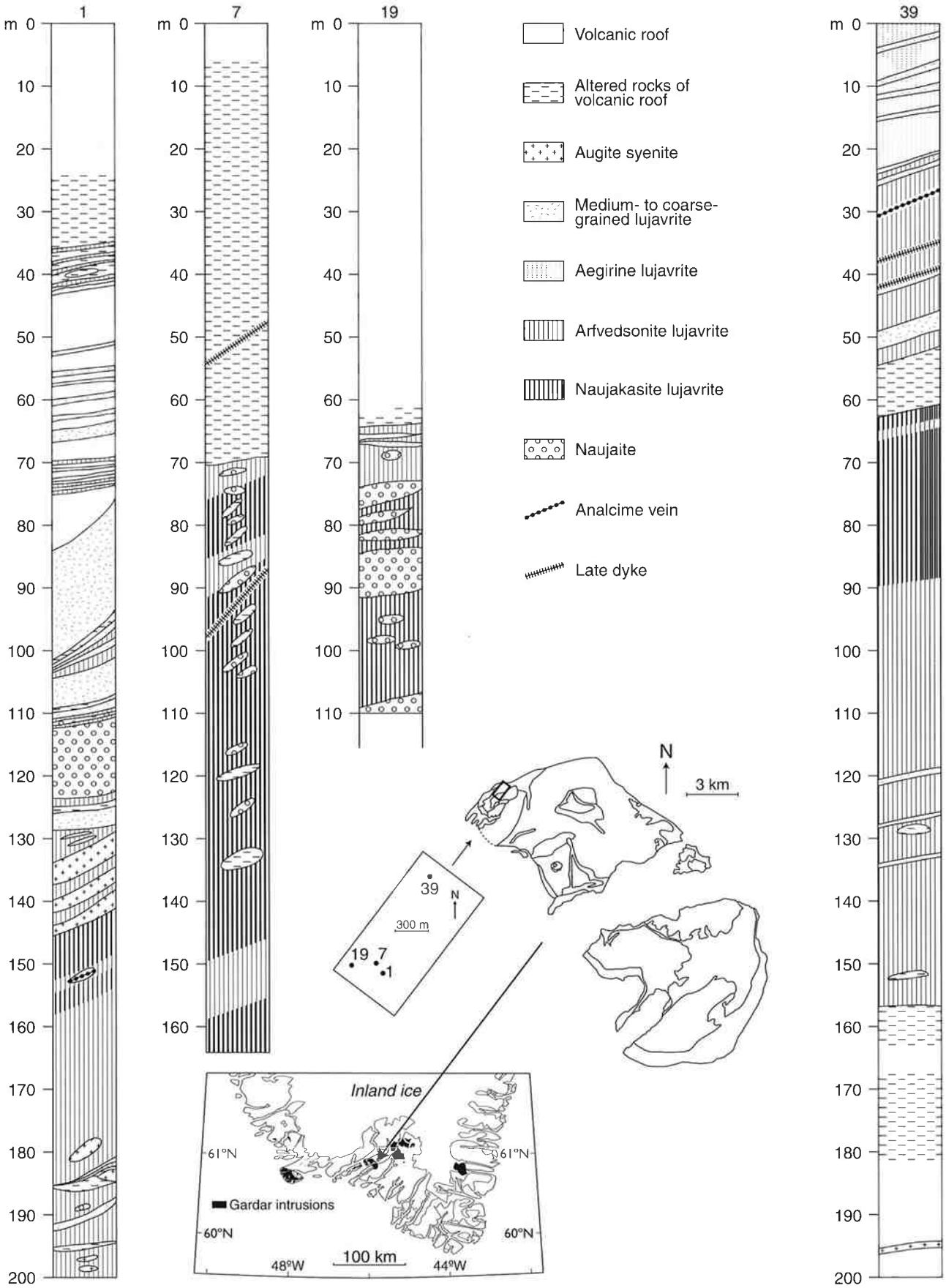
Sørensen *et al.* (1969, 1971, 1974) described the geology of the Kvanefjeld area based on surface mapping and the examination of 42 drill cores from drilling programmes in 1958 and 1969. Several varieties of lujavrites are distinguished (Fig. 1). Naujakasite-bearing lujavrite outcrops in the northernmost part of the Kvanefjeld plateau and at its southern edge in the upper part of the slope facing the Narsaq Elv valley. In the first-named area, there is a succession of lujavrites which form zones running parallel to the contact against the volcanic country rocks to the north. Naujakasite lujavrite occurs as a zone of crumbling, brownish-black lujavrite which is separated from a fine-grained, fissile arfvedsonite lujavrite to the north by a mixed zone made up of alternating bands of these two rock types. The naujakasite lujavrite is ten or more metres wide and can be followed for over a hundred metres. It is intersected by rare veins of green medium- to coarse-grained lujavrite and contains xenoliths of augite syenite, foyaite, naujaite and contact metasomatised volcanic rocks from the roof of the complex. The naujakasite lujavrite in the southern part of the Kvanefjeld plateau occurs mainly as thin sheets intruding naujaite and augite syenite with sharp, but not chilled contacts.

At Tupersuatsiaat and the Taseq slope in the Narsaq Elv valley, naujakasite lujavrite forms minor intrusions in naujaite (Engell 1973).

Petersen & Andersen (1975) described an occurrence of naujakasite located about 1 km south-east of Tupersuatsiaat. They distinguish three modes of occurrence: (1) as an accessory mineral in arfvedsonite lujavrite, that is naujakasite-arfvedsonite lujavrite; (2) as a naujakasite-rich contact facies of lujavrite against a large xenolith of naujaite, containing plates of naujakasite up to 2 cm in size and constituting up to about 75 vol.% of the rock; (3) composite flakes of naujakasite in recrystallised naujaite enclosed in naujakasite lujavrite. The last-named type of naujakasite contains inclusions of nepheline which are arranged in a hexagonal pattern.

The only observation of naujakasite in a hydrothermal vein is reported by Metcalf-Johansen (1977) who found the mineral in an albitite vein in the roof basalt to the east of Kvanefjeld. The vein consists of albite, microcline, aegirine, arfvedsonite, analcime, natrolite, apatite, chkalovite, sphalerite, hemimorphite, willemite, monazite, neptunite and Li-mica. Rhomb-shaped crystals of naujakasite occur in miarolitic cavities in the albitite. These crystals measure 2 × 3 × 0.4 mm.

Nyegaard (1979), Makovicky *et al.* (1980) and Kunzendorf *et al.* (1982) report results of mineralogical and chemical studies of naujakasite lujavrite in cores


1
7
19
39
m 0
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
Volcanic roof
Altered rocks of volcanic roof
Augite syenite
Medium- to coarse-grained lujavrite
Aegirine lujavrite
Arfvedsonite lujavrite
Naujakasite lujavrite
Naujaite
Analcime vein
Late dyke
N
3 km
39
300 m
19
7
1
Inland ice
61°N
60°N
48°W
44°W
100 km
Gardar intrusions

from a drilling programme in 1977 in the northernmost part of the Kvanefjeld area.

A re-examination of the drill core logs presented by Sørensen *et al.* (1971) and Nyegaard (1979) shows that naujakasite lujavrite is of widespread occurrence on the Kvanefjeld plateau where lujavrites are in contact with the volcanic roof of the complex (Fig. 1). Almost half of the drill cores contain horizons of naujakasite lujavrite which vary in thickness from a few centimetres to more than 30 m. It is not possible to correlate from core to core as is evident from fig. 8 in Sørensen *et al.* (1974). Naujakasite lujavrite occurs especially in the uppermost part of sheets of arfvedsonite lujavrite, often in contact with overlying naujaite xenoliths and rafts of augite syenite and volcanic rocks from the roof (Fig. 1, cores 1, 39) and may dominate the lujavrite sheets (Fig. 1, core 7). In addition, it forms sheets intersecting xenoliths of naujaite and augite syenite (Fig. 1, core 9). Sheets of naujakasite lujavrite have been observed to depths of 345 m below the present surface.

The Kvanefjeld adit (Nyegaard 1980) intersects large masses of naujakasite lujavrite. The 960 m long adit is nearly horizontal, its opening on the slope facing the Narsaq Elv valley is located at 470 m and its innermost wall at 512 m above sea level, that is 100–150 m below the surface of the Kvanefjeld plateau. According to Nyegaard (1980) the adit intersects naujakasite lujavrite at the intervals 220–450 m, 585–650 m, 690–730 m and 755–880 m, measured from the opening of the adit. A 50 m long side branch at 230 m also intersects naujakasite lujavrite. The naujakasite lujavrite in the adit contains disseminated villiaumite. It also contains xenoliths of naujaite, sodalite foyaite, alkali syenite, augite syenite and sheared and metasomatised lava and gabbro from the volcanic roof, i.e. the same xenolith association as in the surface exposures. The naujakasite lujavrite is seen to intrude into augite syenite, naujaite and large masses of volcanic rocks from the roof, and it is intersected by sheets of medium- to coarse-grained lujavrite.

Whereas the drill cores from the Kvanefjeld plateau are rich in villiaumite and naujakasite lujavrite, six drill cores through lujavrites in the southern part of the complex are without villaumite and naujakasite lujavrite (J. Rose-Hansen & H. Sørensen, unpublished data 2000). Naujakasite lujavrite has, however, as mentioned above, been observed in surface outcrops at Tupersuatsiaat and on the Taseq slope in the Narsaq Elv valley. It therefore appears that in general naujakasite lujavrite occurs in the upper part of the lujavritic sequence of the complex (Sørensen 2001, this volume).

Fig. 1. Logs of selected drill cores from the Kvanefjeld plateau in the northern part of the Ilímaussaq complex (slightly modified from Sørensen *et al.* 1971). The cores illustrate the mode of occurrence of naujakasite lujavrite. **1**: Drill core 1. Development of naujakasite lujavrite at *c.* 145–160 m in the uppermost *c.* 15 m of a thick sheet of arfvedsonite lujavrite which contains xenoliths of augite syenite and altered volcanic rocks from the roof of the complex and is cut by dykes of medium- to coarse-grained lujavrite. Naujaite and augite syenite immediately above the naujakasite lujavrite are cut by arfvedsonite lujavrite without naujakasite. **7**: Drill core 7. Thick sheet of arfvedsonite lujavrite under roof of volcanic rocks contains naujakasite over more than 95 m (below *c.* 75 m depth). There are xenoliths of naujaite and volcanic rocks. **19**: Drill core 19. Sheets of naujakasite lujavrite at *c.* 75–110 m, intersecting naujaite and with xenoliths of that rock. In this core, the arfvedsonite lujavrite in direct contact with the volcanic roof is without naujakasite. **39**: Drill core 39. Thick sheet of arfvedsonite lujavrite in volcanic rocks with naujakasite in the uppermost *c.* 27 m (at *c.* 63–90 m depth) and with xenoliths of volcanic rocks and intersecting veins of medium- to coarse-grained lujavrite. The arfvedsonite lujavrite in the upper part of the drill core is without naujakasite. The cartoon of the intrusion indicates the positions of the drill cores used in the illustration.

Petrography of naujakasite lujavrite from the Ilímaussaq alkaline complex

The unaltered naujakasite lujavrite may be described as a variety of fine- to medium-grained arfvedsonite lujavrite that contains naujakasite and steenstrupine and is poor in or without nepheline and eudialyte. The rock contains separate laths of microcline and albite and acicular grains of arfvedsonite and more rarely aegirine in parallel orientation, resulting in a more or less pronounced igneous lamination. Nepheline, when present, occurs as corroded grains, often in larger grains than the feldspars and mafic minerals and wrapped by these forming a sub-porphyritic texture.

The content of naujakasite varies from a few to more than 75 vol.%. When present as a minor component, the plates of naujakasite are interstitial to the feldspars and arfvedsonite and generally show irregular outlines in thin section (Fig. 2a, b). When present at 10–50 vol.% the plates of naujakasite normally occur as perfectly developed lozenges with well-defined margins. They are of larger size than the other minerals, forming a sub-porphyritic texture recalling the above-mentioned setting of nepheline (Fig. 2c, d). The naujakasite-rich lujavrites have the appearance of cumulates

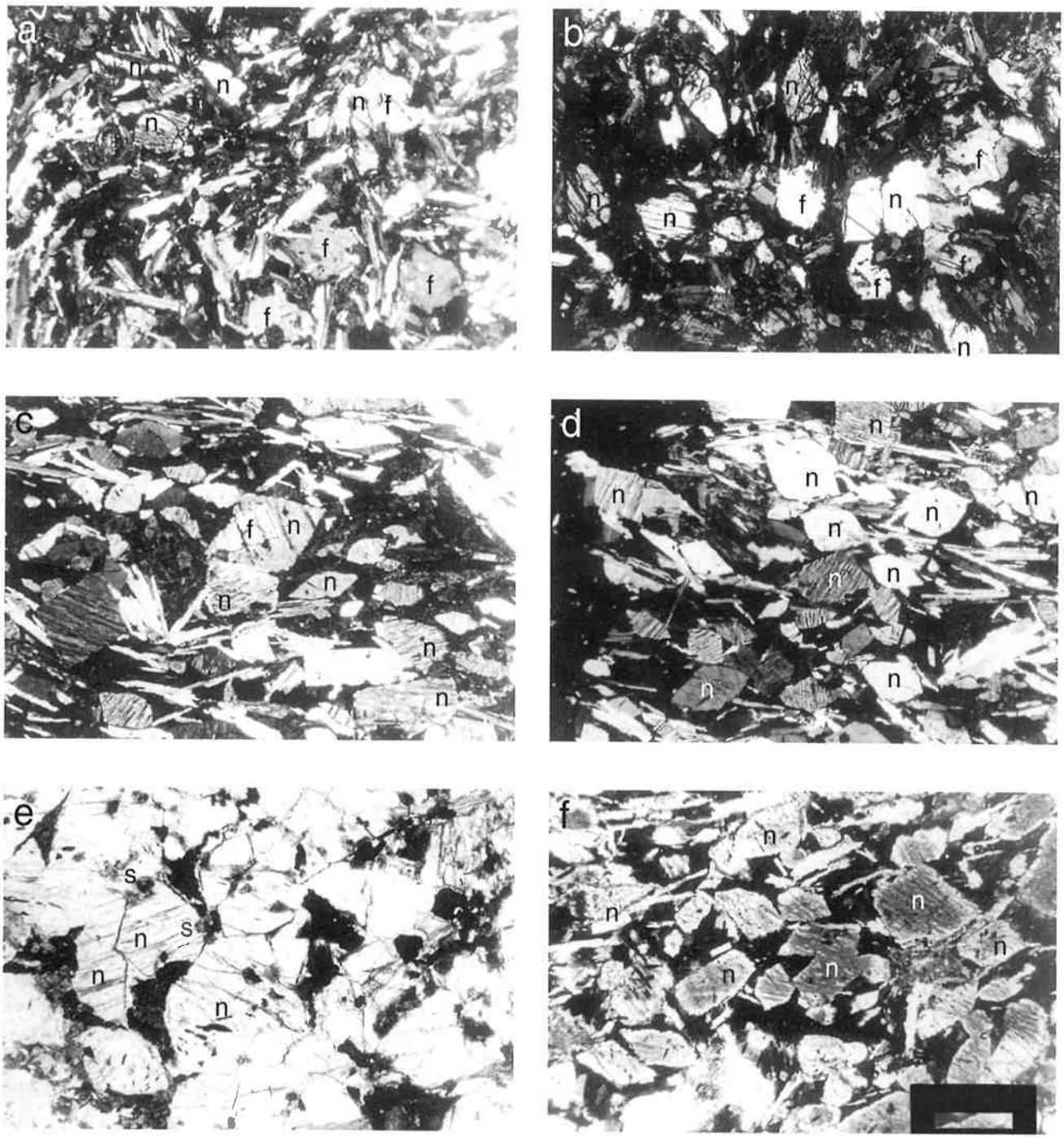


Fig. 2. Photomicrographs showing stages in the formation of naujakasite in arfvedsonite lujavrite; **n**: naujakasite, **f**: nepheline, **s**: steenstrupine. All with crossed polars and scale bar in **f** 0.6 mm. **a**: Small irregularly shaped grains of naujakasite (upper left) in arfvedsonite lujavrite with corroded crystals of nepheline (especially lower right). Drill core 11, Kvanefjeld, at 167.05 m. **b**: Corroded grains of nepheline (centre and centre right) and irregularly shaped grains of naujakasite in matrix of feldspar, arfvedsonite and analcime. Centre right: naujakasite growing on nepheline. Drill core 7, Kvanefjeld, at 112.20 m. **c**: Well-shaped crystals of naujakasite in matrix of dark arfvedsonite and light albite and microcline. Naujakasite crystal in centre overgrows nepheline. Drill core 7, Kvanefjeld, at 110.90 m. **d**: Naujakasite lujavrite with crystals of naujakasite in matrix of dark arfvedsonite, and light albite and minor analcime. Drill core 11, Kvanefjeld, at 130.22 m. **e**: Aggregate of naujakasite crystals with interstitial dark arfvedsonite. The naujakasite encloses tiny grains of arfvedsonite and small crystals of steenstrupine, the latter especially in the marginal parts of the grains. Sample GGU 154364, naujakasite-rich lujavrite in contact with naujaite xenolith, Tupersuatsiaat. **f**: Naujakasite-rich rock in which naujakasite is partially altered into stripes of black pigmentation and analcime. Drill core 7, Kvanefjeld, at 149.95 m.

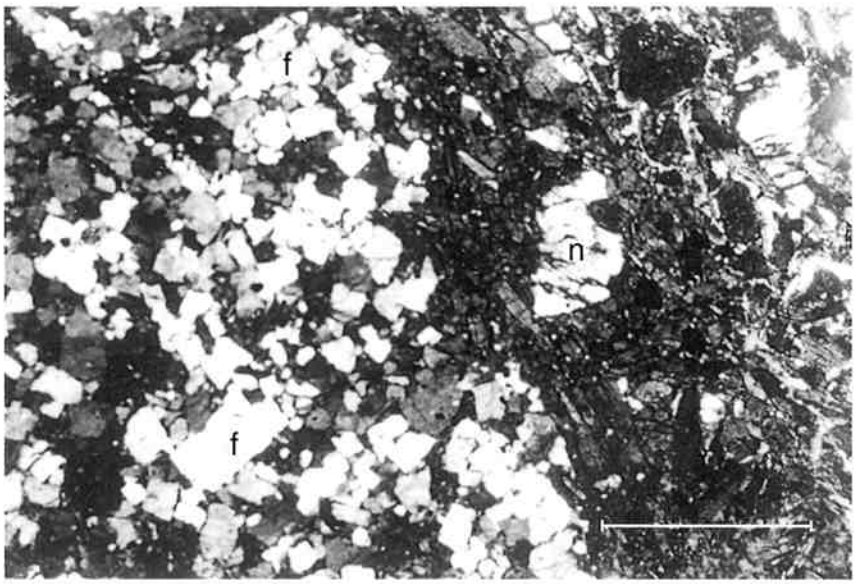


Fig. 3. Fine-grained cumulate of nepheline crystals (**f**) in naujakasite lujavrite with large grains of naujakasite (**n**) in matrix of arfvedsonite, feldspar and analcime. Drill core 11, Kvanefjeld, at 130.22 m. Crossed polars and scale bar 0.6 mm.

made up of closely packed plates of naujakasite with interstitial feldspars and arfvedsonite.

The naujakasite plates may have inclusions of arfvedsonite and zoned small crystals of steenstrupine (Fig. 2e), sometimes also of feldspars and aegirine, generally in smaller grains than in the enclosing rock. The steenstrupine crystals are found particularly in the marginal parts of the naujakasite plates (Fig. 2e).

In some drill cores, the naujakasite lujavrite includes cumulate clusters made up of small crystals of nepheline (Fig. 3). The 3 cm diameter of the drill core makes it impossible to decide whether these cumulates form layers or xenoliths in the lujavrite.

The lack of nepheline in the naujakasite lujavrite examined by Danø & Sørensen (1959) and Engell (1973) and the above-mentioned textural similarity between nepheline and naujakasite made these authors propose that naujakasite may have taken the place of nepheline in the naujakasite lujavrite. Early-formed crystals of eudialyte are very rarely seen in the naujakasite-bearing lujavrite, but eudialyte is generally represented by grains which have preserved the outlines of the eudialyte crystals but are made up of ill-defined pigmentary material. In the rocks with pseudomorphs after eudialyte there are small crystals of steenstrupine which, as discussed further below, appear to occur instead of eudialyte. The steenstrupine crystals show concentric yellow and brown zones and may constitute up to 10 vol.% of the rocks. The steenstrupine in some rocks is altered into dark brown or dusted grains. These rocks generally have more than 300 ppm U and are a part of the Kvanefjeld uranium deposit.

Makovicky *et al.* (1980, table 7) list the mineral associations of many lujavritic rocks from the northernmost part of Kvanefjeld examined by them with special emphasis on the steenstrupine in these rocks. In a number of cases, nepheline, naujakasite, eudialyte and steenstrupine are reported to co-exist. There are, however, no descriptions of the textural relationship between these minerals.

Sørensen (1997) examined thin sections of naujakasite lujavrite from the 1958 drill cores. He found that some of these contain strongly corroded grains of nepheline which may be overgrown by naujakasite. Some plates of naujakasite have inclusions of nepheline. The naujakasite is shown to belong to the hyperagpaitic stage of formation of the Ilímaussaq complex, as is steenstrupine. This is supported by the observation that ussingite in some of the naujakasite lujavrites replaces microcline and that villiaumite, lovozerite and vitusite are minor minerals in some of the rocks. Other accessories are sodalite, sphalerite, pectolite, Li-mica, monazite and neptunite.

The naujakasite lujavrite is generally altered – arfvedsonite is replaced by brown aegirine (acmite in the earlier literature), the feldspars by analcime and perhaps natrolite, and naujakasite by analcime and very fine-grained black pigmentation (Fig. 2f). The end product is a crumbling brown aegirine-rich rock devoid of naujakasite but with textural ghosts of analcime with lines of black pigmentation indicating the former presence of naujakasite.

Table 3. Chemical analyses of naujakasite lujavrites from the Ilímaussaq complex

	Tupersuatsiaat		Kvanefjeld						
	1	2	3	4	5	6	7	8	9
No.	154364	149421C	BH19	BH28	BH35	BH5	BH7	BH38	BH43
depth, m			100.85	88.5	34.2	105.7	85.1	156.2	110.25
SiO_2 (wt%)	50.33	51.49	51.51	53.51	51.04	52.22	51.90	52.30	50.29
TiO_2	0.22	0.16	0.20	0.26	0.12	0.20	0.19	0.19	0.15
Al_2O_3	13.39	15.32	12.86	11.26	15.97	12.78	12.83	13.28	13.02
Fe_2O_3	4.17	5.54	3.81	6.11	3.75	9.02	7.01	6.89	3.06
FeO	10.53	5.23	8.94	8.81	5.45	4.19	5.64	6.14	7.45
MnO	1.06	0.93	0.87	0.76	0.88	0.83	0.91	0.89	0.80
MgO	0.15	0.10	0.00	0.00	0.00	0.00	0.01	0.00	0.00
CaO	0.31	0.26	0.24	0.28	0.19	0.24	0.38	0.35	0.20
Na_2O	12.61	13.16	12.46	10.67	15.03	11.06	10.49	10.26	13.75
K_2O	1.82	2.33	2.53	2.47	2.13	2.59	2.44	2.82	2.92
P_2O_5	0.26	0.29	0.56	0.36	0.67	0.49	0.57	0.73	0.98
volatiles	3.64	2.42	1.73	1.35	1.67	3.59	4.32	3.14	1.99
others	1.87	2.31	3.19	3.23	2.75	2.53	3.21	2.54	3.00
Sum	100.36	99.54	98.90	99.07	99.65	99.74	99.90	99.53	97.61
A.I.	1.70	1.58	1.81	1.80	1.69	1.64	1.55	1.50	1.98
Cs (ppm)	3.8	-	5.5	1.5	7.9	15.9	15.1	16.2	7.3
Rb	401	595	743	623	756	742	703	756	833
Pb	276	352	305	298	269	275	437	318	299
Sr	37	10	41	70	32	32	28	84	19
La	2180	3150	3780	4690	2980	2940	5190	4550	3820
Ce	2840	4040	6880	7460	5400	5250	7840	6250	6970
Nd	830	1120	2240	2210	1790	1880	2220	1710	2340
Sm	99.0	-	238	213	188	235	177	47.	217
Eu	10.5	-	25.0	19.7	20.4	22.8	17.5	9.1	26.8
Tb	18.7	-	29.5	20.4	25.7	29.7	27.1	12.4	35.6
Yb	45.8	-	52.7	31.2	45.6	50.1	63.2	34.9	62.2
Lu	5.9	-	6.3	3.6	5.8	5.1	6.6	2.5	6.7
Y	636	677	943	595	817	943	1060	568	1040
Th	256	673	603	302	446	545	1370	819	633
U	388	287	374	378	336	271	483	282	421
Zr	2770	2720	770	593	884	718	1270	848	777
Hf	25.1	-	10.6	7.8	13.1	9.9	18.1	10.2	11.9
Nb	288	246	355	255	254	248	198	211	253
Ta	31.5	-	14.4	8.3	7.9	7.6	6.8	4.1	7.3
Li	730	440	640	660	290	530	570	620	510
Zn	2110	2290	3000	3700	2180	2390	1690	2920	1610
Co	0.38	-	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	1.3	< 0.3
Sc	< 0.05	-	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.04	< 0.05
Ga	131	136	132	122	141	126	121	128	109
Be	36	20	48	19	40	36	40	33	32
Sb	25	-	46	72	5.4	63	24	31	9.0
S	1080	710	1770	2130	1010	1130	510	1450	1330
Cl	35	140	1050	430	120	820	590	990	1630
F	1000	640	1040	760	4280	760	840	1560	8400

Analysts: J.C. Bailey, R. Gwozdz, B. Damgaard and J. Kystol.
A.I.: Agpaitic index, $(Na_2O + K_2O)/Al_2O_3$ mol.
-: not analysed.

1–5: Naujakasite lujavrite, 6–8: Zeolitized naujakasite lujavrite, 9: Villiaumite-naujakasite lujavrite.
6 digit samples are from the collections of the Geological Survey of Denmark and Greenland.
BH is bore hole no. with depth in metres.

Petrochemistry

Chemical analyses of naujakasite lujavrite have been reported by Gerasimovsky (1969), Engell (1973), Kunzendorf *et al.* (1982) and Sørensen (1997). Some new analyses are presented in Table 3. The rock is characterised by very high contents of Na_2O, up to 15 wt% and even higher in villiaumite-bearing naujakasite lujavrite (Kunzendorf *et al.* 1982). This gives normative values of *ne* 10–20% and of *ac c.* 10%, but as much as 28% in the altered rocks rich in brown aegirine. Normative *ns* is *c.* 10%, but *c.* 14% in villiaumite-bearing rocks and as low as 3% in the altered rocks in which naujakasite is replaced by analcime.

Gerasimovsky (1969), Andersen *et al.* (1981) and Kunzendorf *et al.* (1982) reported trace element analyses of naujakasite lujavrite. Additional data are presented in Table 3. Naujakasite lujavrite shares the highly fractionated character of trace element patterns found in all lujavrites at Ilímaussaq: high contents of Cs, Rb, Pb, REE (especially LREE), Th, U, Li, Zn, Ga, Be, Sn and Sb, and low contents of Sr, Co and Sc (cf. Bailey *et al.* 2001, this volume). Other elements which have been extensively removed at earlier agpaitic stages of the Ilímaussaq evolution by fractionation of sodalite (Cl) and eudialyte (Zr, Hf, Nb and Ta) only occur in moderate concentrations in naujakasite lujavrite. The naujakasite lujavrites differ from the arfvedsonite lujavrites in higher contents of Na, Mn, Fe, Th, U, Zn and P, and in lower contents of K, Sr, Zr, Hf and Nb. There appears to be a continuous transition from agpaitic to hyper-agpaitic rocks without any sharp change in physico-chemical conditions.

Naujakasite lujavrite and medium- to coarse-grained lujavrite are the two latest and most evolved types of lujavrite (see Sørensen 2001, this volume). Their hyper-agpaitic character is seen geochemically in (1) the high agpaitic index (1.5–2.0), (2) the replacement of eudialyte indicators (high Ca, Sr, Zr and Hf) by steenstrupine indicators (high P, REE, Y, Th and U) and (3) the medium- to coarse-grained lujavrite, when compared with the naujakasite lujavrite, shows higher contents of K, Cs, Rb, Li, Be, Ti and Nb and lower contents of Na, Mn, REE, Y, Zr, Hf, Th, U and Pb (unpublished data). The ratio LREE/HREE is markedly lower in the naujakasite lujavrite. Naujakasite lujavrite seems more evolved in its lower Zr/U and Zr/Y ratios (Andersen *et al.* 1981), whereas medium- to coarse-grained lujavrite seems more evolved in its lower K/Rb and Y/U ratios. This difference in behaviour of trace elements in the two most evolved types of lujavrite most probably reflects a difference in composition of the volatile phase in strongly sodic and potassic-sodic systems.

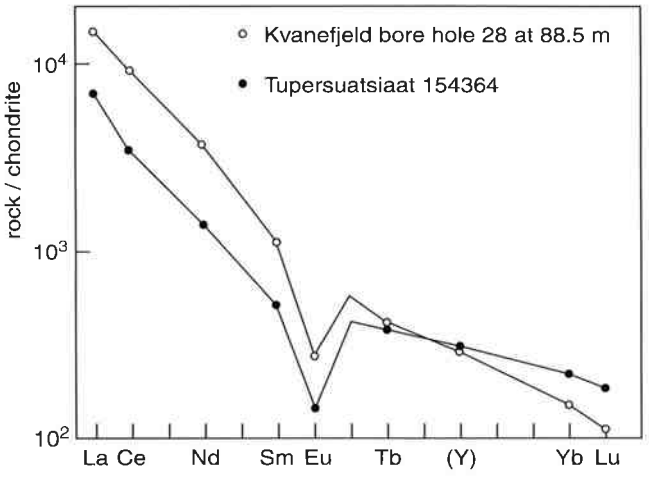


Fig. 4. Chondrite-normalised (Masuda *et al.* 1973) REE diagram of the new analyses of naujakasite lujavrite. The pronounced Eu anomaly is common to all agpaitic rocks of the Ilímaussaq complex.

Naujakasite lujavrite from both Tupersuatsiaat and Kvanefjeld is most readily distinguished from all other lujavrites at Ilímaussaq by the high levels of Na, Na/K, Fe^T (total iron) and Mn, i.e. features which can be attributed to the chemistry of naujakasite itself. Compared to the naujakasite lujavrite from Tupersuatsiaat, those from Kvanefjeld have a more evolved geochemistry with higher levels of P, Cs, Rb, REE, Y and La/Lu but lower levels of Mg, Zr, Hf, Ta, Co and K/Rb. It is worth noticing that Th, U, Nb, Li and Be contents are comparable at the two localities. At Tupersuatsiaat, the REE pattern shows a considerable change in slope between the steep LREE and the less steep HREE (Fig. 4). At Kvanefjeld, the slope is steep throughout the pattern. At Tupersuatsiaat, slightly higher levels of Mn and Mn/Fe^T and lower K and K/Na probably reflect the greater abundance of naujakasite in the two analysed samples from this locality.

Zeolitized samples of naujakasite lujavrite from Kvanefjeld are distinguished by a fall in the agpaitic index but a rise in levels of volatiles, K/Na, Fe^{3+}/Fe^{2+}, Cs, Th/U and Th/P.

A comparison of Ca–Na–K relations (atomic) in various lujavrites at Ilímaussaq is seen in Fig. 5. The low Ca proportions of the arfvedsonite lujavrite and the medium- to coarse-grained and naujakasite lujavrites are due to extensive fractionation of eudialyte. The more or less steady advance of Na/K ratios throughout the Ilímaussaq liquids, which reflects prolonged ex-

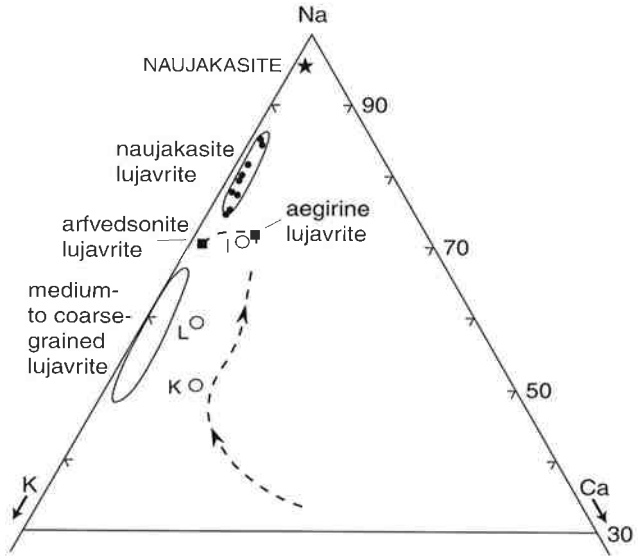


Fig. 5. Na–K–Ca (atomic) diagram showing plots of the various types of lujavrite from the Ilímaussaq alkaline complex and average values for the nepheline syenites of the Ilímaussaq (**I**), Khibina (**K**) and Lovozero (**L**) complexes (authors' compilation). The dashed curve with arrows is the liquid line of descent for the Ilímaussaq complex (based on data in Bailey *et al.* 2001, this volume).

traction of microcline, comes to an end in the lujavrites where the arfvedsonite lujavrites and aegirine lujavrites have approximately similar Na/K ratios. The naujakasite lujavrites typically plot between arfvedsonite lujavrite and the composition of naujakasite in Fig. 5. Some scatter of analyses reflects (1) varying amounts of naujakasite, (2) variable proportions of albite and microcline in the matrix and (3) subsequent alteration to analcime. The final agpaitic rock type at Ilímaussaq, the microcline-rich medium- to coarse-grained lujavrite, is characterised by a sharp decrease in Na/K ratios.

Naujakasite lujavrite marks the culmination of Mn contents (av. 0.70 wt%) and Mn/Fe^T ratios (0.08) at Ilímaussaq. These features can be attributed to the high level of Mn (0.85 wt%) and Mn/Fe^T (0.17) in naujakasite and constitute a subdued reflection of the manganiferous naujakasite at Lovozero.

The new occurrence of naujakasite in the Lovozero alkaline complex

Naujakasite was found by one of the authors (A.P.K.) on Mount Alluaiv in the Lovozero complex in a *c.* 1 m thick zone of intensely mineralised medium-grained lovozerite-lomonosovite lujavrite, which occurs in the eudialyte lujavrite of intrusive phase III of the complex (cf. Gerasimovsky *et al.* 1974). These rocks were encountered in a drill core sample recovered from a depth of about 250 m below the surface. Although the rocks contain readily hydrolysable and water-soluble minerals and the core boxes have been stored in the open air for more than ten years, the cores are still well preserved, although covered by a crust of white opal-like material up to 2 mm thick. Freshly fractured lovozerite-lomonosovite lujavrite consists of vuggy, irregularly shaped aggregates with an irregular lamellar structure, composed mainly of alkali feldspar laths. Interstices between the feldspar laths contain smaller segregations of partially dissolved villiaumite and grains of sodalite, nepheline, analcime, aegirine (fibrous and acicular), lovozerite, and a whole series of other less common minerals, such as tisinalite, lamprophyllite, manaksite, nordite, umbozerite, sphalerite, and molybdenite. Lomonosovite occurs as oikocrysts up to 1 cm across which poikilitically enclose the aforementioned minerals.

The naujakasite is scattered among the interstitial minerals as irregularly shaped grains 0.5 to 1 mm in size, occasionally with a well-defined pinacoid {001}. Less commonly, it occurs as oikocrysts up to 5 mm across pierced by alkali feldspar laths and aegirine needles. It also contains inclusions of euhedral tabular vuonnemite crystals. Against the light grey background of the rocks, naujakasite stands out markedly owing to its bright blue colour and its typical mirror-like or pearly lustre along the plane of perfect mica-like cleavage (001).

Discussion

The new data on the Lovozero naujakasite and published and new data on the Ilímaussaq naujakasite indicate that many minerals associated with naujakasite in the two complexes are characteristic of the special type of alkaline rock distinguished as hyper-agpaitic (Khomyakov 1990, 1995, 2001, this volume; Sørensen 1997; Sørensen & Larsen 2001, this volume). Eudialyte, which is a typical mineral of moderately alkaline agpaitic rocks, has not been found in association with the Lovozero naujakasite and is rarely present in the naujakasite lujavrite of Ilímaussaq. Under conditions of ultra-high alkalinity, eudialyte becomes unstable and is substituted by zirconium minerals with higher contents of alkali metals such as zirsinalite or by steenstrupine. Zirsinalite is substituted by lovozerite with

decreasing alkalinity and hydration (Khomyakov 1990, 1995). In view of this, naujakasite may, as proposed by Sørensen (1997), be regarded as one of the most characteristic minerals of hyper-agpaitic rocks.

The agpaitic index of naujakasite (Na/Al = 1.5) is only slightly lower than that of the most agpaitic sodium aluminosilicate ussingite (Na/Al = 2). Naujakasite accumulations tend to occur in rocks of the main intrusive phases, whereas ussingite is largely confined to post-magmatic and hydrothermal rocks and to late stages of formation of the naujakasite lujavrite. An examination of primary gas–liquid inclusions in minerals of hyper-agpaitic pegmatites in the Lovozero complex indicates that ussingite crystallised over the temperature range 305–165°C (Shchegoleva *et al.* 1988).

Nepheline–naujakasite relations

The relationship between nepheline and naujakasite presents a special problem. At Ilímaussaq, nepheline is evidently unstable under the hyper-agpaitic conditions reigning during the formation of the naujakasite lujavrite. The occurrence in some naujakasite lujavrite samples of corroded grains of nepheline and platy crystals of naujakasite, and the co-occurrence of pseudomorphs after eudialyte and crystals of steenstrupine, indicate that hyper-agpaitic conditions developed gradually during the consolidation of the rock and that there was a short period of co-existence of nepheline and naujakasite but with nepheline rapidly becoming unstable and naujakasite taking over. The subsequent replacement of naujakasite by analcime shows declining hyper-agpaitic conditions. This rise and fall in alkalinity is a characteristic feature of hyper-agpaitic rocks (Khomyakov 1995).

The nepheline grains in the naujakasite lujavrite are sometimes overgrown by naujakasite or may be enclosed in naujakasite plates (Fig. 2c). Petersen & Andersen (1975) have, for instance, shown that plates of naujakasite in a naujaite xenolith enclosed in naujakasite lujavrite have inclusions of nepheline arranged in such a way that the original hexagonal shape of the nepheline grains may be traced. This last observation made A. Finch suggest (personal communication 2000) that there is a topotactic relationship between nepheline and naujakasite, the latter being formed by adaptation of the structure of the former as a result of exchange of elements via a fluid phase. Finch furthermore points out that the crystal structure of naujakasite determined by Basso *et al.* (1975) may be derived from the crystal structure of nepheline: "In the *a-c* plane, the nepheline structure consists of rings of six tetrahedra with apices pointing up and down alternately, a feature common to the same plane in naujakasite. However, in nepheline, the rings are interconnected on all sides to other hexagonal rings forming a flat sheet of rings perpendicular to (0001). In naujakasite, the hexagonal layers are joined to each other by bridging rings of four tetrahedra, forming a chain rather than a sheet. The structure of naujakasite may be derived from that of nepheline by considering the structure first perpendicular to (0001) for the hexagonal rings, and then perpendicular to (1000) for the four-membered rings. The structure of naujakasite therefore represents a zig-zag slice through that of nepheline. The planes, along which disconnection of the 'naujakasite' part of the structure must take place, are parallel to the directions {0001} and {1122}. These are interestingly the two possible cleavages in the nepheline structure, and indicate that metasomatic 'fracturing' of the nepheline structure would provide a naujakasite-type 'framework'" (A. Finch, written communication 2000). A topotactic relationship between nepheline and naujakasite is a possible background for the above-mentioned observation of inclusions of nepheline in naujakasite in metasomatically altered naujaite in contact with naujakasite lujavrite, as will be discussed further below. But the overgrowths of naujakasite on nepheline described by Sørensen (1997) and reported in the present paper (Fig. 2b, c) would rather indicate a reconstructive type of relationship between naujakasite and nepheline, i.e. formation of a new crystal structure.

The role of potassium

The fact that naujakasite is an important rock-forming mineral in the Ilímaussaq complex and very rare or non-existent in the Lovozero and Khibina complexes cannot be ascribed solely to differences in alkalinity during the formation of the three complexes. In Lovozero and Khibina, there are rocks that formed at similar or even more hyper-agpaitic conditions than the Ilímaussaq naujakasite lujavrites, but without naujakasite. Some Khibina rocks, e.g. the rischorrites (nepheline syenites in which nepheline is poikilitically enclosed in microcline perthite and with biotite, aegirine augite and opaque minerals) contain natisite, Na_2TiSiO_5. The synthetic analogue of this mineral crystallises only from melts with a NaOH concentration of 38 to 100%, i.e.

under extremely high alkalinity. These same rocks contain delhayelite, $Na_2K_3Ca_2AlSiO_{19}(F,Cl)_2$, and altisite, $Na_3K_6Ti_2Al_2Si_8O_{26}Cl_3$, with agpaitic indices, respectively, of 5 and 4.5, and other highly alkaline minerals, but naujakasite is absent.

The Khibina–Lovozero rocks contain a whole series of peralkaline minerals that are absent in Ilímaussaq. Such an endemic mineral, which is virtually unknown outside Khibina, is fenaksite, $NaKFeSi_4O_{10}$. This mineral is of interest in that its hypothetical Na analogue, $Na_2FeSi_4O_{10}$, is a key component which, when combined with the nepheline composition, would yield naujakasite:

$$Na_2FeSi_4O_{10} + 4NaAlSiO_4 = Na_6FeAl_4Si_8O_{26}$$

A reaction between the hypothetical pure Na manaksite, $Na_2MnSi_4O_{10}$ and the nepheline composition would yield manganonaujakasite, $Na_6MnAl_4Si_8O_{26}$. Fenaksite and manaksite may accordingly be regarded as the 'antipodes' of naujakasite and managanonaujakasite. All these four minerals are indicators of hyper-agpaitic conditions.

A fundamental difference between the hyper-agpaitic rocks of Ilímaussaq and Khibina is that the former are predominantly sodic and the latter are sodic-potassic. The importance of a high content of Na for the formation of naujakasite is corroborated by the extreme Na/K (atomic) ratio of 3.08 for the average composition of the nepheline syenites of Ilímaussaq, whereas the Na/K ratio for 136 bodies of nepheline syenites generally varies between 0.3 and 2.5 (authors' compilation). Averages for Khibina (1.27) and Lovozero (1.67) fall within this range. The average Na/K ratio of the naujakasite lujavrite is 4.56. K-deficient conditions seem to be favourable for the formation of naujakasite, whereas under K-rich conditions, Fe is bound in $NaKFeSi_4O_{10}$ preventing the formation of naujakasite. Lovozero represents an intermediate case which may explain the co-existence of manganonaujakasite and manaksite in the same rock. Potassium appears to be an inhibitor not only for the formation of naujakasite but also for ussingite which is almost entirely absent in the hyper-agpaitic rocks of Khibina.

Nepheline, which is stable in hyper-agpaitic rocks of Na-K composition in Khibina and Lovozero, is unstable in a hyper-sodic environment. This fact, coupled with the aforementioned relationships, explains why nepheline is readily substituted by naujakasite in large volumes of rocks, and why naujakasite is endemic to Ilímaussaq.

Metasomatic relations

The preceding discussion has only considered naujakasite as a rock-forming mineral formed during crystallisation of hyper-agpaitic lujavritic melts. It should, however, be pointed out that naujakasite has also been observed as a metasomatically formed mineral in naujaite xenoliths in naujakasite lujavrite (Petersen & Andersen 1975), where it appears to replace nepheline in a topotactic way, and as a hydrothermally formed mineral in albitite veins in the roof of the Ilímaussaq complex (Metcalf-Johansen 1977). This most probably reflects that there is a gradual transition from magmatic to hydrothermal conditions in hyper-agpaitic systems.

Petrology

There appears to be a gradual transition from arfvedsonite lujavrite to naujakasite lujavrite. Small flakes of naujakasite with irregular outlines begin to appear in arfvedsonite lujavrite containing corroded grains of nepheline and almost unaltered crystals of eudialyte. With increasing contents, naujakasite may overgrow the nepheline grains. At this stage, eudialyte is altered into brown to black pigmentary material, and zoned steenstrupine crystals become an important constituent. With still further evolution nepheline disappears and well-developed crystals of naujakasite become the dominant mineral. At the most evolved stage, the rocks are made up of densely packed crystals of naujakasite in a cumulate-like manner. It thus appears that naujakasite may be formed partly by a continuous process during which nepheline is dissolved and naujakasite is formed interstitially, and partly as a liquidus phase in highly evolved lujavritic melts when contents of Na and Fe have reached levels which inhibit crystallisation of nepheline and favour the formation of naujakasite.

The fact that the naujakasite lujavrite occurs in the uppermost part of the lujavrite sequence of the complex and is concentrated in the upper part of thick sheets of nepheline-rich arfvedsonite lujavrite below larger masses of naujaite, augite syenite and volcanic rocks is indicative of upwards migration in the magma of volatiles rich in Na, Th, U, etc. and a concentration of volatiles in the uppermost part of the magma beneath the impermeable roof. This results in conditions favouring the crystallisation of naujakasite as a liquidus mineral. In view of the very evolved character of the

melts it may be imagined that naujakasite is formed at relatively low temperatures (cf. Sørensen & Larsen 2001, this volume). Fe^{2+} and Mn^{2+} are important components of the naujakasite structure suggesting that redox conditions may also be of significance for the formation of naujakasite.

The rare occurrence of naujakasite in metasomatically altered naujaite and in albitite veins indicates that naujakasite is also stable in high-temperature hydrothermal fluids which have escaped from the Na-rich lujavrite magma.

Conclusions

Naujakasite is an important rock-forming mineral in a type of lujavrite in the Ilímaussaq alkaline complex, the so-called naujakasite lujavrite which may contain more than 75 vol.% of this mineral. Naujakasite has not been found in the intensively studied Khibina complex and is a very rare mineral in the Lovozero complex where the variety manganonaujakasite has been found. The reason for the practical non-existence of naujakasite in the two Kola complexes and the abundance in the Ilímaussaq complex may be the extremely sodic composition of the hyper-agpaitic rocks of Ilímaussaq, whereas the Kola hyper-agpaitic rocks are sodic-potassic. K-deficient conditions are favourable for the formation of naujakasite, whereas under K-rich conditions surplus Fe is bound in fenaksite, $NaKFeSi_4O_{10}$. The Na analogue of fenaksite, $Na_2FeSi_4O_{10}$, combined with the nepheline composition yields the composition of naujakasite.

The frequent occurrence of naujakasite lujavrite in the upper parts of arfvedsonite lujavrite sheets, where these are overlain by impermeable xenoliths of naujaite, augite syenite and volcanic rocks from the roof, indicates that volatile transfer processes may have played an important role in concentrating Na, Fe, Mn, Th, U, P, etc. in the uppermost parts of the magma masses, thus creating the hyper-agpaitic conditions favouring the formation of naujakasite and steenstrupine. There appears to be a gradual transition from nepheline-bearing arfvedsonite lujavrite to nepheline-free naujakasite lujavrite, an indication of a continuous process of building-up hyper-agpaitic conditions of crystallisation.

In conclusion, the reason for the virtual restriction of naujakasite, a mineral composed of common elements, to the Ilímaussaq alkaline complex is the attainment at late stages of agpaitic crystallisation of hyper-agpaitic conditions characterised by exceptionally high Na/K ratios and high contents of Fe and Mn which make naujakasite stable at the expense of nepheline. Naujakasite has a narrow field of stability and is substituted by analcime with declining alkalinity and temperature.

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Zoning in steenstrupine-(Ce) from the Ilímaussaq alkaline complex, South Greenland: a review and discussion

Alexander P. Khomyakov and Henning Sørensen

Most crystals of steenstrupine are metamict, but some are crystalline throughout or in thin marginal zones parallel to the crystal faces of metamict crystals. The anisotropic parts of the crystals have lower contents of U and Th than the interior isotropic parts. Some features, such as high contents of Na in the anisotropic steenstrupine, favour formation of the zonation as a result of crystallisation in a medium in which decreasing amounts of U and Th were available during the last stages of growth of the crystals. One reason for this could be the fixation of U and Th in interstitial pigmentary material. Another feature, the fact that steenstrupine adjacent to fractures penetrating the crystals from the surface is anisotropic, indicates that leaching and recrystallisation may also play a role in the transformation of parts of metamict steenstrupine into an anisotropic phase.

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Keywords: agpaite, Ilímaussaq, mineral zonation, nepheline syenites, steenstrupine

Steenstrupine-(Ce), with the formula
$Na_{14}Ce_6Mn_2Fe_2(Zr,Th)(Si_6O_{18})_2(PO_4)_7\ 3H_2O$,
is an important rock-forming mineral in the hyper-agpaitic lujavrites of the Ilímaussaq complex, South Greenland (Sørensen & Larsen 2001, this volume). It is the main radioactive mineral in the Kvanefjeld uranium deposit in the northern part of the complex. In the hyper-agpaitic lujavrites it takes the place of eudialyte, the main rare-element mineral in the agpaitic rocks of the complex: naujaite, kakortokite, and aegirine and arfvedsonite lujavrites. Steenstrupine is also common in the hyper-agpaitic pegmatites and hydrothermal mineralisations and in the fenitised volcanic roof of the Kvanefjeld plateau (see Sørensen (1991) for a review of the literature on the occurrence of steenstrupine in the Ilímaussaq complex).

In the Lovozero complex of the Kola Peninsula, Russia, steenstrupine-(Ce) is common in the zeolite-rich cores of pegmatites and in hydrothermal veinlets composed of ussingite, natrolite, analcime, etc. (Khomyakov 1995; Semenov 1997).

Steenstrupine is a complex silico-phosphate mineral composed of more than 20 elements. It often occurs as well-developed trigonal crystals. Most grains are metamict and X-ray amorphous. There are, however, also non-metamict crystals which give distinct X-ray patterns. Makovicky & Karup-Møller (1981) and Moore & Shen (1983) described the crystal structure of steenstrupine based on the examination of an occurrence of crystalline steenstrupine.

The mineral is often altered, which is demonstrated by the great variation in the contents of Na_2O from more than 10 wt% to less than 1 wt%. In the crystal structure Na^+ is easily substituted by H^+ (Makovicky & Karup-Møller 1981; Moore & Shen 1983).

The aim of this paper is to describe and discuss the occurrence of anisotropic rims on metamict crystals of steenstrupine.

Zoned crystals of steenstrupine-(Ce)

Zoning in steenstrupine has been described by a number of authors.

Bøggild (in Bøggild & Winther 1899) distinguished three main morphological types of the mineral based on samples from pegmatites and veins. Types I and II are metamict and type III is non-metamict. The type III

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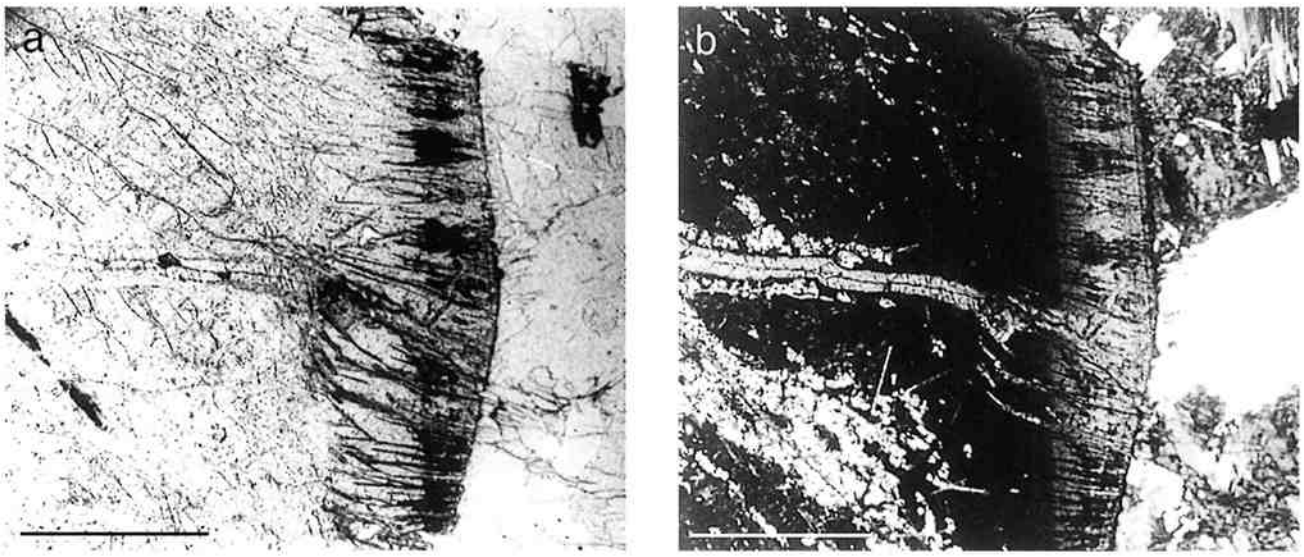


Fig. 1. Crystal of steenstrupine with anisotropic marginal zone penetrated by a dense system of short fractures perpendicular to the surface of the crystal and with crusts of opaque material. Steenstrupine is anisotropic along a fracture penetrating deeper into the crystal (central part of photo). The matrix is made up of microcline (lower right corner) and a sheaf of white Li mica, centre right. **a**: plane polarised light, **b**: crossed polarised light. Narsaq Elv valley, drill core I at 46.26 m; scale bar 0.6 mm.

crystals may be anisotropic throughout, but some crystals have an isotropic or weakly anisotropic central part. All three types may have thin marginal zones which are often anisotropic. There may be a gradual decrease in the degree of metamictisation from centre to rim; more commonly there is a sharp transition to the thin anisotropic rims. In thin section the unaltered steenstrupine crystals are generally clear yellow in the central isotropic parts. The marginal parts are often dark brown and may be isotropic or anisotropic. The dark-coloured marginal parts may send tongues along fissures into the interior of the crystals. The part of the crystals adjacent to the tongues are generally anisotropic (Fig. 1). This means that the anisotropic zones penetrate into the interior of the crystals. These observations have been confirmed by the subsequent authors quoted below.

Buchwald & Sørensen (1961) described steenstrupine from lujavrites, pegmatites and hydrothermal veins coupled with an autoradiographic examination of the distribution of radioactive elements in the crystals. They especially noted the occurrence of several thin zones parallel to the crystal faces (Fig. 2). In some cases there is a gradual increase in anisotropy from centre to margin.

Sørensen (1962) described the paragenesis of steenstrupine in the various rock types and paid special attention to the relationship between eudialyte and steenstrupine. Steenstrupine may form overgrowths on eudialyte in pegmatites, and poikilitic grains of steenstrupine in lujavrites and recrystallised naujaites contain inclusions of fresh and altered crystals of eudialyte and in some rocks also of lovozerite. The small steenstrupine crystals in the lujavrites are primary magmatic minerals, whereas the poikilitic grains are late magmatic and may be associated with ussingite and analcime replacing the primary nepheline and feldspars of the rocks. The metamict grains of steenstrupine are surrounded by radiating fractures in the adjacent minerals (Fig. 3).

Semenov (1969) presented new chemical analyses of steenstrupine and described an altered variety, hydrosteenstrupine, poor in Na_2O, SiO_2 and P_2O_5 and enriched in REE_2O_3, Fe_2O_3, CaO and water.

Wollenberg (1971) undertook a fission track examination of steenstrupine crystals and determined the distribution of U and Th in zoned crystals of this mineral. He found that U is evenly distributed in the crystals, whereas Th is distributed in an irregular way with the highest contents in the centres of the grains.

Makovicky *et al.* (1980) examined a number of occurrences of steenstrupine, with emphasis on the radioactive lujavrites in the northern part of the Kvanefjeld plateau, by autoradiography, fission track studies and electron microprobe analyses. They determined the distribution of U and Th in zoned crystals of steenstrupine and also examined the behaviour of U and Th during alteration of the steenstrupine.

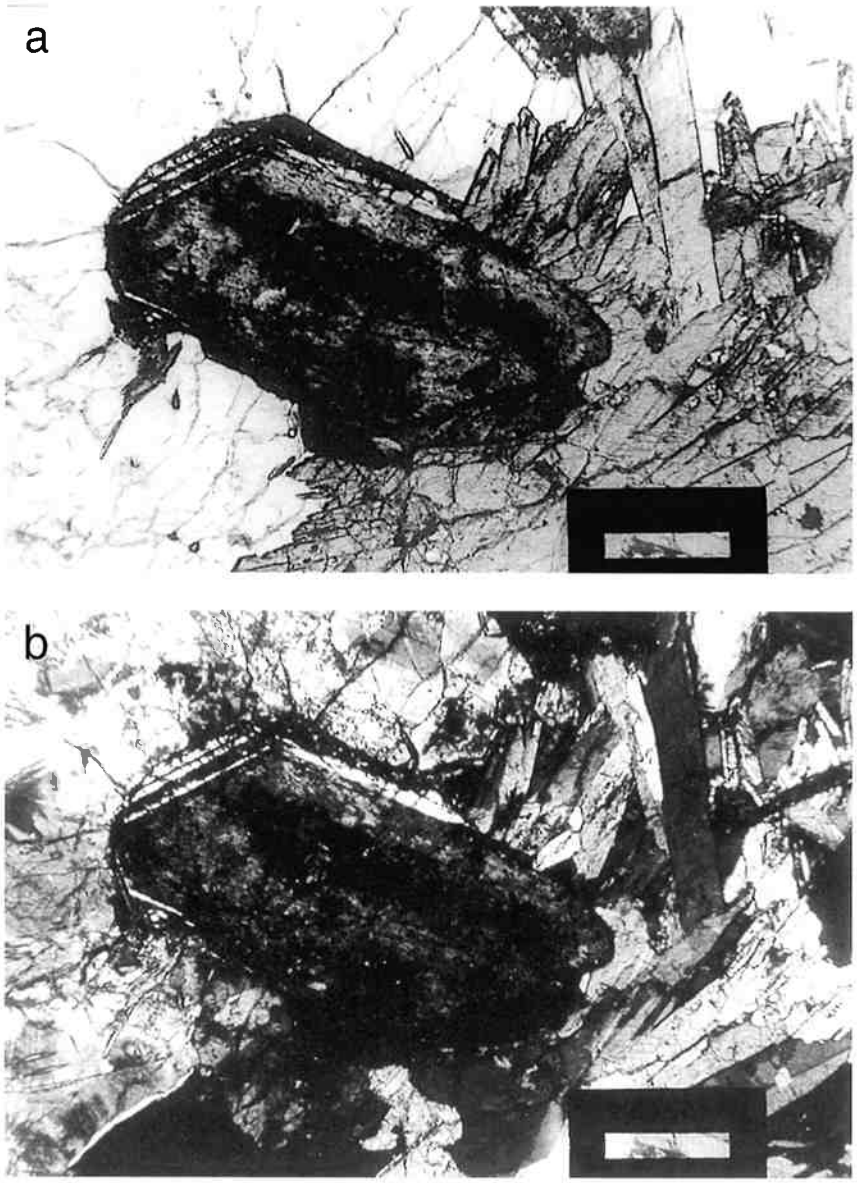


Fig. 2. Steenstrupine crystal associated with an aggregate of aegirine crystals (right) and large grain of analcime (left). The crystal has a turbid, weakly anisotropic interior and three marginal anisotropic zones, each composed of an inner clear part and an outer rust-coloured part. The marginal zones stop against aegirine and only occur in contact with analcime. From vein in lujavrite. **a**: plane polarised light, **b**: crossed polarised light. Kvanefjeld, drill core 50 at 150.50 m; scale bar 0.6 mm.

Makovicky & Karup-Møller (1981) described a crystalline steenstrupine from a vein and noted that partial metamictisation decreases from the centres through the finely zoned parts and surface replacement portions to the distinctly anisotropic rims of the crystals. The centres have a lower birefringence than the marginal zones.

We have examined zoned crystals of steenstrupine from drill core 50, 149.7 to 150.6 m below the surface. These crystals occur in hydrothermal veins in arfvedsonite lujavrite. According to gamma-spectrometric analyses of the drill core, the veins have 350 ppm U and 2000 ppm Th (Nyegaard *et al.* 1977). The steenstrupine crystals measure a few millimetres across. The interior parts of some crystals are turbid (Fig. 2), other crystals have clear, sometimes darker-coloured isotropic centres (Fig. 4), but there are also crystals which are anisotropic throughout but with very low birefringence. There are thin marginal anisotropic zones parallel to crystal faces. The anisotropic zones are often clear, but sometimes dark coloured in their exterior parts (Fig. 2). In a number of cases, zoned crystals of steenstrupine have nucleated on grains of aegirine (Figs 2, 4, 5). In these cases there is no zonation in contact with aegirine, whereas crystal faces and marginal zonation are found in contact with felsic minerals, primarily analcime, natrolite, ussingite and villiaumite. There is no zonation against primary grains of sodalite (Fig. 3).

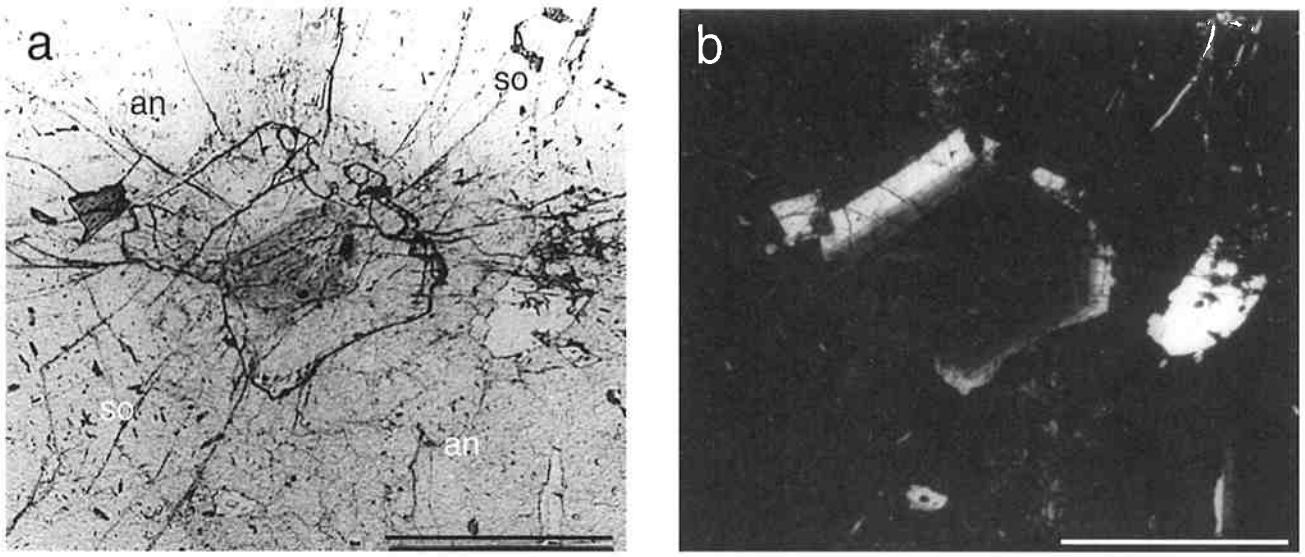


Fig. 3. Steenstrupine crystal in sodalite (**so**) and analcime (**an**), with radiating fractures. The crystal is clear, but with a slightly turbid isotropic interior. The marginal anisotropic zone shows zonation parallel to the crystal faces. The marginal zone has a few fractures perpendicular to the crystal faces. The steenstrupine crystal is situated between two large crystals of sodalite (lower left and upper right) against which there are no crystal faces. Crystal faces and zonation are only developed in contact with analcime. **a**: plane polarised light, **b**: crossed polarised light. Kvanefjeld, drill core 53 at 145.20 m; scale bar 0.6 mm.

Chemical composition of the zoned steenstrupine

The zoned grains of steenstrupine from drill core 50 have been analysed by electron microprobe. Crystal fragments were hand picked from crushed rocks and were analysed by G.N. Nechelyustov with a Superprobe-733 microanalyser. Standards were: chkalovite (Na, Si), microcline (K), diopside (Ca), strontium-apatite (Sr), $BaSO_4$ (Ba), rhodonite (Mn), almandine (Fe), $LaPO_4$ (La), $CePO_4$ (Ce, P), $PrPO_4$ (Pr), $NdPO_4$ (Nd), $SmPO_4$ (Sm), YPO_4 (Y), ThO_2 (Th), Li_2NbO_4 (Nb) and anatase (Ti). The results are presented in Table 1. The centres have 3.95–4.13 wt% ThO_2, the rims 0.42–1.40 wt% ThO_2 and from centre to rim there is an increase in Nb_2O_5, MnO, SrO, Na_2O (in one sample), REE_2O_3 and P_2O_5, and a decrease in TiO_2, FeO, CaO and Y_2O_3. U has not been analysed. From centre to rim there are sharp increases in the ratios Mn/Fe, La/Nd, REE/Th and Nb/Ti (Table 1). The anisotropic rims have distinctly lower contents of Th than the interior parts of the crystals.

Buchwald & Sørensen (1961) presented partial chemical analyses of some crystals of steenstrupine. The contents of U and Th vary from 0.21 wt% U and 1.66 wt% Th in the anisotropic type III crystals to 0.78 wt% U and 5.65 wt% Th in metamict vein steenstrupine. The autoradiographic examination showed that the metamict centres of steenstrupine crystals have α-track densities of 5000–13 600 α/cm²/hour, the anisotropic rims 1000–7000 α/cm²/hour. The altered grains of steenstrupine may have more than 35 000 α/cm²/hour.

Semenov (1969) reported 0.39 wt% U_3O_8 and 2.42 wt% ThO_2 in steenstrupine from a vein, and up to 3.86 wt% ThO_2 in altered steenstrupine (no data for U).

The fission-track study carried out by Wollenberg (1971) gave the following results: metamict centres of crystals have 0.42–0.72 wt% U and 3.3 wt% Th, while the rims have 0.20–0.27 wt% U and 1.39 wt% Th. The anisotropic type III steenstrupine contains 0.05–0.37 wt% U.

Hansen (1977) reported U and Th contents in steenstrupine in the ranges 0.1–1.4 wt% U and 0.2–7.4 wt% Th. For the anisotropic type III steenstrupine he found 0.13 wt% U and 0.73 wt% Th. His electron microprobe studies revealed that there is a great variation in the chemical composition of steenstrupine, even between grains in the same thin section, especially in the contents of Na, Ca, Fe and Mn.

Makovicky *et al.* (1980) presented a wealth of information about the chemical composition of steenstrupine from lujavrite with special emphasis on the alteration of the mineral. The fission track studies revealed up to 1 wt% U_3O_8 in the altered centres and 0.2–0.5 wt% U_3O_8 in the light-coloured parts of the

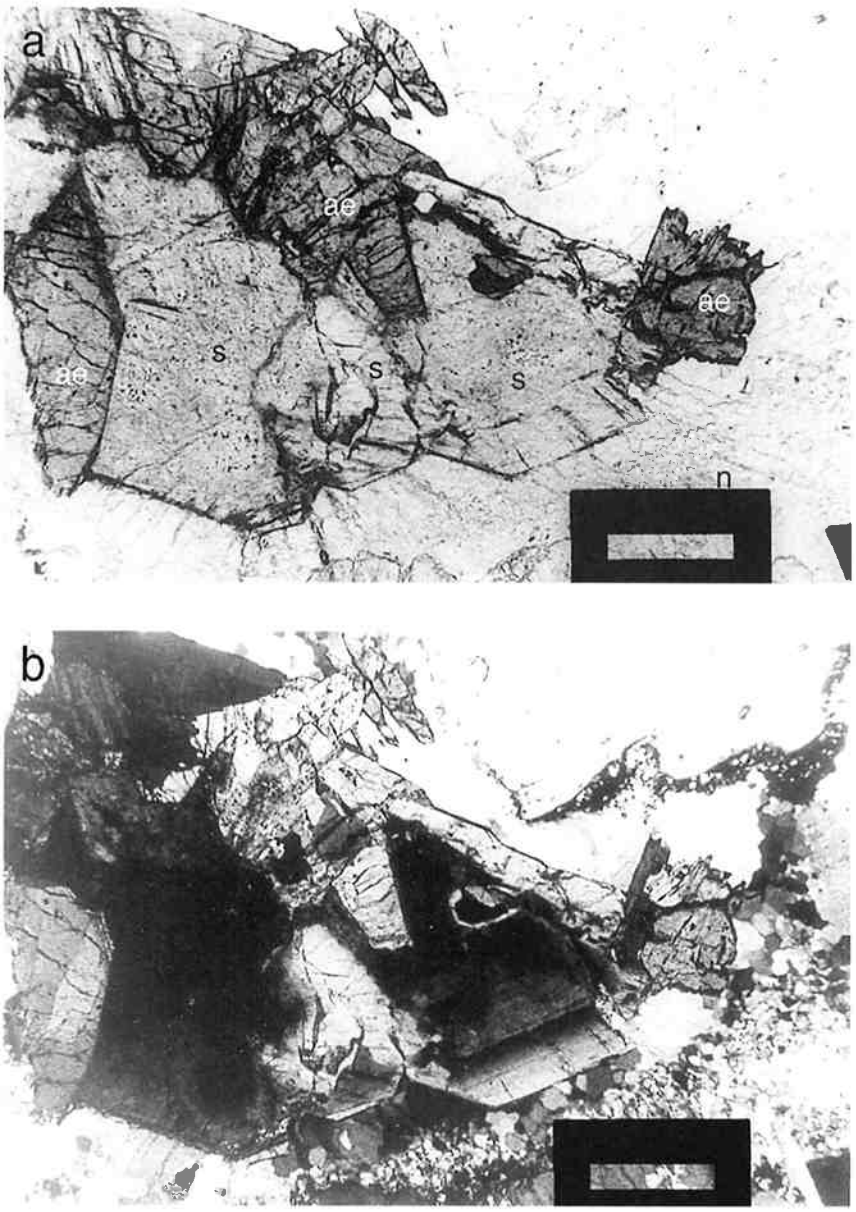


Fig. 4. Group of steenstrupine (**s**) crystals intergrown with aegirine (**ae**) and enclosed in a matrix of nepheline (**n**) penetrated by natrolite and analcime. The steenstrupine to the left is isotropic throughout, apart from a thin marginal zone (bottom right) against natrolite. The right crystal has an isotropic centre and an anisotropic rim in contact with natrolite but not in contact with aegirine. Zonation stops against aegirine (centre right). There are very few fractures in these steenstrupine crystals. Vein in lujavrite. **a**: plane polarised light, **b**: crossed polarised light. Kvanefjeld, drill core 50 at 149.70 m; scale bar 0,6 mm.

crystals. The microprobe analyses showed a variation in the Th content from 0.27 to 5.69 wt% Th, with some zoned crystals from 3.11–3.74 wt% Th in the centres to 1.03–2.05 wt% Th in the rims.

Makovicky & Karup-Møller (1981) reported an average content of 0.46 wt% U in zoned partly anisotropic vein steenstrupine crystals. According to the fission-track data of Makovicky *et al.* (1980), the centres have 0.6–0.8 wt% U_3O_8, the marginal parts 0.3–0.4 wt% U_3O_8. The microprobe analyses reported by Makovicky & Karup-Møller (1981) have been recalculated from element to oxide form and are presented in Table 1. ThO_2 varies from 5.04 to 1.83 wt% from centre to rim; Y_2O_3 also decreases from centre to rim, whereas there is an increase in ZrO_2, MnO, Na_2O and P_2O_5 from centre to rim. The contents of the other elements are similar in centre and rim.

The information available on the chemical composition of zoned steenstrupine crystals from pegmatites and veins consistently shows a marked difference in the contents of U and Th in the central, often metamict parts of the crystals and the thin, often anisotropic rims. In addition the rims are enriched in Na, Mn, P, Zr, Nb and in some examples also REE, and impoverished in Y.

Table 1. Microprobe analyses of zoned crystals of steenstrupine from the Ilímaussaq alkaline complex

Sample No.	50-149.7 centre (5)	50-149.7 rim (6)	50-150.6 centre (2)	50-150.6 rim (1)	199104 centre (4)	199104 rim (1)
SiO_2	26.94	27.75	27.54	25.98	27.40	27.06
TiO_2	0.16	0.07	0.28	0.18	0.25	0.20
ZrO_2	n.a.	n.a.	n.a.	n.a.	1.41	2.33
ThO_2	3.95	0.42	4.13	1.40	5.04	1.83
Al_2O_3	n.a.	n.a.	n.a.	n.a.	0.28	0.04
La_2O_3	8.78	12.85	8.94	14.22	11.49	11.79
Ce_2O_3	14.57	15.53	13.80	13.76	15.74	16.49
Pr_2O_3	1.29	1.04	1.28	1.54	2.39	2.08
Nd_2O_3	3.72	2.80	3.50	2.78	4.01	4.22
Sm_2O_3	0.31	0.19	0.19	0.15	n.a.	n.a.
Y_2O_3	1.47	1.05	1.56	0.31	1.05	0.10
FeO	4.34	2.50	3.96	1.85	3.87	3.42
MnO	3.61	6.22	3.42	5.69	4.42	5.00
CaO	2.18	1.58	2.00	1.65	1.88	1.95
SrO	0.10	0.14	0.07	0.11	n.a.	n.a.
Na_2O	8.41	12.98	7.88	13.65	2.75	6.59
K_2O	0.05	0.02	0.20	0.31	n.a.	n.a.
P_2O_5	9.36	11.26	8.50	9.35	11.31	12.30
Nb_2O_5	0.10	0.24	0.13	0.67	n.a.	n.a.
U_3O_8	n.a.	n.a.	n.a.	n.a.	0.70	0.35
	89.34	96.64	87.38	93.60	93.89	95.75
ΣRE_2O_3	28.67	32.41	27.71	32.45	33.63	34.58
La_2O_3/Nd_2O_3	2.36	4.59	2.55	5.12	2.86	2.79

Analyses in oxide wt%. H_2O and F have not been analysed which explains the low totals.
Figures in brackets: number of analyses.
n.a. = not analysed.
Samples 50-149.7 and 50-150.6 are from drill core 50 at 149.7 and 150.6 m, respectively. Analyst: G.N. Nechelyustov.
199104 is a GGU sample from Makovicky & Karup-Møller (1981), recalculated from element wt% to oxide wt%.

Discussion

The well-developed crystal forms of the metamict grains of steenstrupine and the surrounding radiating fractures in the adjacent minerals, an indication of volume increase during metamictisation, show that steenstrupine was originally crystalline. It may therefore be assumed that the crystal structure allows only a limited content of U and Th without breaking down into the metamict state in accordance with the fact that crystalline anisotropic steenstrupine shows the lowest measured contents of U and Th. The anisotropic type III steenstrupine has the highest contents of Na_2O of all analysed steenstrupine grains, 11.23 wt% (Bøggild & Winther 1899), 14.2 wt% (Hansen 1977), which indicates that secondary leaching must have been very weak. It should be remembered that Na^+ is easily substituted by H^+ during alteration of the crystals (Makovicky & Karup-Møller 1981). Crystals with higher contents of U and Th have been transformed into the metamict state and in many cases altered into aggregates of secondary minerals as described by Buchwald & Sørensen (1961), Sørensen (1962), Semenov (1969) and Makovicky *et al.* (1980). In the strongly altered grains, U and Th are retained in thorianite, thorite and unidentified pigmentary material, which have the highest recorded contents of U and Th.

Buchwald & Sørensen (1961) considered two explanations for these phenomena: either the anisotropic rims are primary, formed in a medium poor in U and Th, or alternatively, the anisotropic rims have been formed by secondary processes.

Anisotropic rims as primary crystallisation products

A decrease in the contents of U and Th in the media in which the crystals grew could be a result of the onset

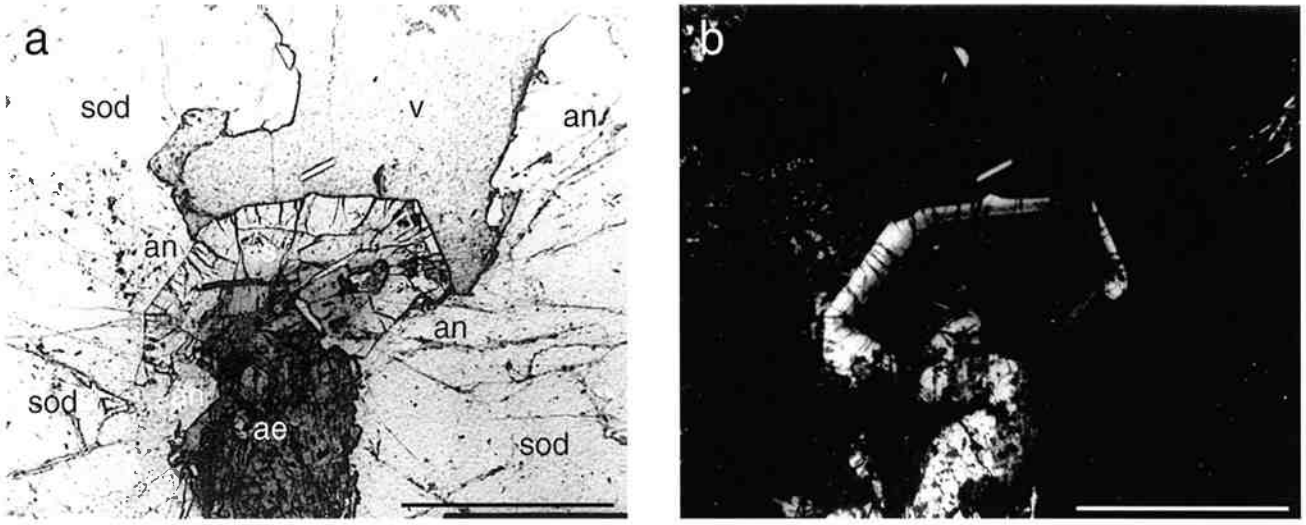


Fig. 5. Crystal of steenstrupine (**s**, centre) growing on aggregate of small aegirine crystals (**ae**) and showing crystal faces against villiaumite (**v**). The matrix consists of large grains of sodalite (**sod**), partly altered into analcime (**an**). Steenstrupine is separated from sodalite by a thin zone of analcime. The core of the steenstrupine crystal is brown, isotropic, and the marginal rim against villiaumite and analcime is clear, anisotropic and intersected by fractures perpendicular to the crystal faces. Zonation is only seen in contact with villiaumite and analcime. From vein in lujavrite. **a**: plane polarised light, **b**: crossed polarised light. Kvanefjeld, drill core 53 at 145.20 m; scale bar 0.6 mm.

of crystallisation of other minerals rich in U and Th. Such minerals are, however, not associated with the steenstrupine. Steenstrupine itself may have such a high capacity to extract U and Th from melts and hydrothermal solutions that the supply of these elements was exhausted during the late stages of crystallisation. The studies of Hansen (1977) and Bailey *et al.* (1983), however, demonstrate that a considerable part of the U and Th in the agpaitic rocks of the Ilímaussaq complex is easily leached out. Therefore, it cannot be bound in silicate minerals but was most probably retained in the residual liquids and subsequently deposited as intercumulus pigmentary material (or in some examples retained in the alteration products of steenstrupine formed by means of reaction between the crystals and late interstitial liquids). These mechanisms may explain why decreasing contents of U and Th were available for the latest stages of growth of the steenstrupine crystals.

Steenstrupine in pegmatites and hydrothermal veins frequently nucleates on aegirine as demonstrated in Figs 2, 4 and 5. In these examples there is no zonation in contact with aegirine, whereas crystal faces and marginal rims are developed against analcime, natrolite, ussingite and villiaumite, but not against earlier-formed sodalite. The zonation abuts against aegirine (Figs 2, 4). These observations strongly support the view that the zonation is a growth phenomenon coupled with a general increase in alkalinity of the residual melts and fluids, resulting in an enrichment in Na, Mn, Nb, REE and P in the marginal zones of the crystals (Table 1).

The formation of zonation may thus have taken place before the metamictisation of the inner parts of the crystals.

It is possible that the physical conditions changed so that U and Th were taken up in a fluid phase and removed from the melt. U-Th mineralisations in the fenitised volcanic rocks of the roof of the complex are indications of fluid transport of U and Th into the country rocks (Sørensen *et al.* 1974). The possibility that a high oxygen fugacity was the cause of the mobilisation of U as $(UO_2)^{2+}$ is not likely since the vapour phase of the agpaitic melts was rich in hydrocarbons (Petersilie & Sørensen 1970; Konnerup-Madsen 2001, this volume).

Anisotropic rims formed by secondary processes

Alternatively, the anisotropic marginal zones may have been formed by secondary processes. This could be due to an early leaching of U and Th from the marginal parts of the crystals before metamictisation or to leaching of U and Th from metamict crystals of steenstrupine combined with recrystallisation of the thin rim

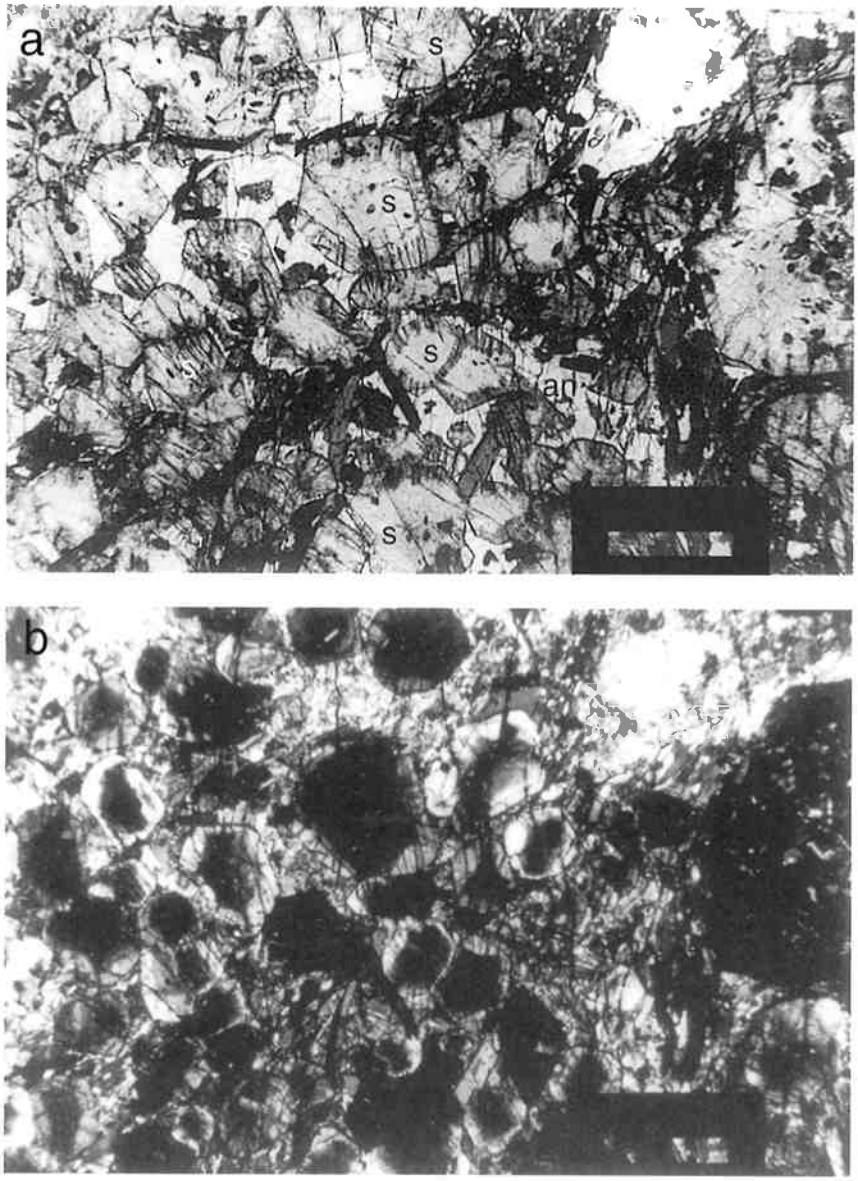


Fig. 6. Aggregate of crystals of steenstrupine (**s**), arfvedsonite and aegirine (dark prisms and needles) in matrix of analcime (**an**). The steenstrupine crystals have dark anisotropic marginal zones rich in fractures and clear isotropic cores poor in fractures. **a**: plane polarised light, **b**: crossed polarised light. GGU 18467b-2, vein from the head of Kangerluarsuk; scale bar 0.6 mm.

of the leached crystals. Makovicky & Karup-Møller (1981) emphasise the importance of exchange of Na^+ and H^+ in the crystal structure of steenstrupine and mention the possibility that the crystal structure of leached steenstrupine may have the ability to accept substantial amounts of Na^+ back into the structure. One may however doubt that such processes would result in a repetition of perfectly parallel marginal zones; some aggregate structure would be more likely (Makovicky & Karup-Møller 1981, p. 302). Leaching is a more straightforward explanation of the presence of anisotropic steenstrupine adjacent to fractures penetrating from the crystal surface into the crystals (Fig. 1) and of the presence of anisotropic steenstrupine in the marginal parts of the crystals with the densest systems of fractures (Fig. 6). But the fact that the anisotropic rims have higher contents of Na than the metamict centres of the crystals contradicts leaching as the main cause of formation of the anisotropic rims. It should also be remembered that anisotropic marginal zones occur in crystals which are practically free from fractures.

Makovicky *et al.* (1980, p. 25) observed zoning only in partly to fully altered grains and did not observe zoning in metamict grains and extremely altered grains. They presumed that primary compositional zoning becomes visible only after the process of alteration and only develops in the compositionally suitable grain portions. In the material studied by us, anisotropic zoning is found in metamict grains which in thin section have clear, unaltered centres.

It is of interest to note that steenstrupine crystals with zonation similar to that described here have so far not been found in the Lovozero complex. This may be caused by a lower degree of alkalinity in Lovozero, as indicated by the absence of rock-forming naujakasite (cf. Khomyakov *et al.* 2001, this volume; Sørensen & Larsen 2001, this volume). Most steenstrupine at Lovozero appears to have crystallised during later stages than at Ilímaussaq, that is at declining alkalinity. Under these conditions the activity of Na was insufficient for the recrystallisation of metamict steenstrupine.

Conclusions

The fact that the marginal zones of the steenstrupine crystals are thin and perfectly parallel and enriched in Na is most easily understood as a growth phenomenon and is less likely to be the result of leaching and recrystallisation. The lobes of anisotropic steenstrupine that penetrate from the crystal surfaces along fractures into the interior of the crystals are, however, best understood as a leaching phenomenon. Such examples have, however, not been included in the present examination of zoned steenstrupine crystals.

The type of marginal zonation of steenstrupine crystals studied in this paper can best be explained as a result of primary growth of the crystals in a medium relatively depleted in U and Th and enriched in Na and REE.

Acknowledgments

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Notes on leucophanite from the Ilímaussaq alkaline complex, South Greenland

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Leucophanite from the Ilímaussaq alkaline complex was first described in 1905. For nearly 60 years it was believed to be rare and of very limited distribution in Ilímaussaq, but it has lately proved to be of relatively widespread occurrence. Detailed descriptions of the various occurrences are given. The crystals show the forms {001}, {110}, {101}, {102}, {111} and {113}; all the crystals are twinned either along (110) or (010). Optically the Ilímaussaq leucophanite is biaxial with $2V_{\alpha}$ (measured) = 40°; α = 1.575, $\beta = \gamma$ = 1.597. The empirical formula, calculated on the basis of Si + Al = 4, is:
$(Ca_{1.97}Mg_{0.05}REE_{0.06})_{\Sigma 2.08}(Na_{2.13}K_{0.01})_{\Sigma 2.14}Be_{1.92}(Si_{3.88}Al_{0.12})_{\Sigma 4.00}O_{12.01}(F_{1.87}OH_{0.19})_{\Sigma 2.06}$.
Unit cell parameters determined on the newly found material are a = 7.38–7.40, b = 7.40–7.41, c = 9.96–9.95, all ± 0.01 Å (Kangerluarsuk) and a = 7.43, b = 7.43, c = 9.90, all ± 0.01 Å (Nakkaalaaq). Thus, a full set of data for the Ilímaussaq leucophanite is now available.

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Leucophanite ($NaCaBeSi_2O_6F$) from the Kangerluarsuk area of the Ilímaussaq alkaline complex, was first collected by K.J.V. Steenstrup in 1899 and described by Bøggild (1905).

For nearly 60 years leucophanite was believed to be a rare mineral of very limited distribution in Ilímaussaq, but it has lately proved to be of more widespread occurrence. In the early 1960s leucophanite was found in albitite veins, which also contain eudidymite and epididymite, in the naujaite on the Taseq slope of the complex, and was briefly mentioned by Semenov & Sørensen (1966). Leucophanite from Kvanefjeld in the northern part of the complex was noticed by Semenov (1969). See Sørensen (2001, this volume) for a map of the localities mentioned in the text and a brief description of the complex.

In the early 1970s leucophanite was re-located in the Kangerluarsuk area and described in detail by Semenov *et al.* (1987). This leucophanite was found in pegmatites in white kakortokite in the upper part of the first major tributary upstream from the estuary of the Lakseelv. According to Semenov *et al.* (1987) these pegmatites are rich in microcline, carry some arfvedsonite and eudialyte, and in the central part are enriched in aegirine, helvite, astrophyllite, rinkite and leucophanite; others carry natrolite both as violet masses and colourless crystals.

During the 1997 field season, leucophanite was found at two additional localities, one in the Kangerluarsuk area and another at the diagonally opposite end of the complex, on the summit of Nakkaalaaq in the northern part of the complex.

In the Kangerluarsuk area leucophanite was found in a pegmatite in augite syenite, near the contact of the complex on the southern side of the fjord, at an altitude of about 100 m. The up to 50 cm wide pegmatite consists of albite, natrolite, fluorite, a profusion of orange, platy crystals of monazite, and leucophanite. The order of crystallisation is: albite → natrolite → fluorite → monazite → leucophanite. The leucophanite is of an unusual appearance; it forms 0.2 mm crusts of pearly white aggregates of bladed crystals on colourless fluorite and corroded albite crystals, as well as millimetre-large aggregates of white to mauve, bladed

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crystals with pearly lustre, between the albite and fluorite crystals.

On the summit of Nakkaalaaq the augite syenite, which constitutes the roof of the Ilímaussaq alkaline complex, is cut by a set of parallel veins, a major one several metres wide and several others down to a width of about half a metre. Though the entire Nakkaalaaq summit is covered by scree, the veins are traceable over several hundred metres. The veins consist mainly of massive or coarsely crystalline flesh-coloured, pinkish or whitish microcline, and are locally rich in druses lined with well-developed crystals of microcline. Leucophanite has been found both in the major vein and in one of the smaller veins; in the former it occurs as millimetre-large aggregates of snow-white bladed crystals with pearly lustre, interstitial to the microcline crystals; in the smaller vein it occurs as very small, transparent, colourless, apparently tetragonal crystals partly lining the walls of a few cavities. Associated minerals, nearly all well-developed crystals in the numerous cavities, include aegirine, calcite, galena, hematite, hemimorphite, and a profusion of Be minerals including bavenite, bertrandite, epididymite, genthelvite and helvite. Fersmite, recently described by Petersen *et al.* (1998), is a rare member of this highly interesting paragenesis. Microcline followed by aegirine were the first minerals, leucophanite among the last of the Be minerals, and calcite probably the very last mineral to crystallise.

Morphology

The surviving material from Bøggild's investigations consists of less than 10 small crystals (1–5 mm), picked out of sodalite syenite. The crystals show the forms {001}, {110}, {101}–({201}), {102}–({101}), {111}–({221}) and {113}–({223}); the indices given are derived from the presently accepted unit cell parameters (The MINERAL Database 1997); indices in parentheses are those of Bøggild (1905) and are only given when different. All the crystals are twinned either along (110) or (010). The former can only be observed in thin sections, the optic axial planes being orientated at right angles to each other in the two individuals; the latter, on the other hand, are visible by means of their re-entrant angles. The properties of this leucophanite are in all essentials like those of the leucophanite from the type locality at Låven, Langesundsfjorden, Norway (e.g., Brøgger 1890).

Table 1. Chemical composition of leucophanite from the Ilímaussaq alkaline complex at Kangerluarsuk

	wt%
SiO_2	46.57
TiO_2	0.02
Al_2O_3	1.22
Fe_2O_3	0.21
RE_2O_3	1.84
MgO	0.44
MnO	0.06
CaO	22.06
BeO	9.56
Na_2O	13.19
K_2O	0.05
H_2O	0.35
F	7.09
–O for F_2	2.97
	99.69

From Semenov *et al.* (1987).

Optical properties

According to Semenov *et al.* (1987) the yellowish green leucophanite forms pseudotetragonal prisms up to 1.5 cm. Optically this leucophanite is biaxial, $2V_\alpha$ (measured) = 40°; the refractive indices are: $\alpha = 1.575$ and $\beta = \gamma = 1.597$, in good agreement with those of leucophanite from elsewhere.

Chemical composition

The only complete chemical analysis of the Ilímaussaq leucophanite is of the material from the locality in the Kangerluarsuk area visited by Semenov in the early 1980s, and is reproduced in Table 1. The REE spectrum (in per cent) is given as:

$La_{11.0}Ce_{33.2}Pr_{5.6}Nd_{24.6}Sm_{5.5}Gd_{6.2}Tb_{2.0}Dy_{2.7}Er_{0.3}Yb_{0.2}Y_{9.0}$.

The SEM energy dispersive (X-ray) spectra of the leucophanite from the two new localities in the Ilímaussaq alkaline complex are both in perfect agreement with that of the leucophanite from Kangerluarsuk for which complete quantitative chemical data are available (Semenov *et al.* 1987).

Unit cell parameters

Leucophanite crystallises orthorhombic (The MINERAL Database 1997), pseudotetragonal. The unit cell pa-

rameters refined from Gandolfi-type powder patterns, Cu$K\alpha$ radiation, λ = 1.54178 Å, were found to be: a = 7.38–7.40, b = 7.40–7.41, c = 9.96–9.95 all ± 0.01 Å and a = 7.43, b = 7.43, c = 9.90, all ± 0.01 Å, from the new localities in Kangerluarsuk and on Nakkaalaaq, respectively. The unit cell parameters of the Ilímaussaq leucophanite are thus in good agreement with those obtained from a Guinier-Hägg type powder pattern, Cu$K\alpha$ radiation with quartz as internal standard, of the leucophanite of Semenov *et al.* (1987) but never published: a = 7.39, b = 7.41 and c = 9.98 Å, and with those given in the literature: a = 7.401, b = 7.412, c = 9.990 Å (The MINERAL Database 1997).

Conclusion

The successive finds of leucophanite in Ilímaussaq have led to more and more detailed knowledge of its properties, and with the determination of the unit cell parameters of the material from the two latest finds a full set of data for the leucophanite from Ilímaussaq is available for the first time.

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The MINERAL Database 1997: Aleph/CSIRO, PO Box 213, Livermore, CA 94557, USA.

Notes on ephesite, terskite, Na-komarovite, ceriopyrochlore-(Ce), joaquinite-(Ce) and other minerals from the Ilímaussaq alkaline complex, South Greenland

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The Semenov (1969) memoir on the mineralogy of the Ilímaussaq alkaline massif mentioned a number of minerals under preliminary names. The present status of these minerals is reported together with new data on ephesite, which was mentioned as white mica in 1969. The mineral described as white Zr-silicate is terskite, the white Nb-silicate is the new mineral Na-komarovite, the red Mn-silicate is Mn-Fe-sepiolite, and the Mn-palygorskite should now be termed yofortierite.

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In the memoir on the mineralogy of the Ilímaussaq alkaline massif (Semenov 1969) a number of minerals were described under preliminary names: Ce-pyrochlore, Si-pyrochlore, hydropyrochlore, Nb-rinkite, Ta-rinkite, avicennite, hydrorinkite, animikite, white Ce-silicate, white Ce-phosphate, white Nb-silicate, red Mn-silicate and white mica mineral. The present status of these minerals is reported below.

Mineralogical notes

Brown Ce-pyrochlore, $Na_{0.5}Ca_{0.5}Ce_{0.5}Nb_2O_6F$, should be named ceriopyrochlore-(Ce) (formerly marignacite). The mineral described as hydropyrochlore is an altered variety of pyrochlore.

Yellow Si-pyrochlore, $(Na,Ca)_2(Nb,Si)_2O_6$, is similar to the endeiolite from the Narssârssuk locality and is considered to be an impure pyrochlore as is chalcolamprite (Hogarth 1977; Clark 1993). The Si content may be a mechanical admixture, but it should be examined whether Nb can substitute for Si in this mineral group.

White Ce-phosphate, $HCaCe(PO_4)_2\ 2H_2O$, is a Ca-bearing rhabdophane.

Rinkite group minerals with low contents of the REE were proposed in the 1969 memoir (Semenov 1969, p. 46) to be called rinkolite or lovchorrite; minerals with similar contents of Nb and Ti were proposed to be called rinkite, and the Nb-rich member was proposed to be named Nb-rinkite, $Na_3Ca_3CeNbSi_4O_{15}F_3$. The last-named mineral has subsequently been described as the new mineral nacareniobsite-(Ce) by Petersen *et al.* (1989), who also recommended that this mineral group is best described under the rinkite group. With regard to the mineral nacareniobsite, it should be pointed out that the altered varieties have low contents of Na, Ca and partly Si. Nb-rinkite would, in my opinion, have been a better name, but this name was not approved by the IMA Commission on New Minerals and Mineral Names.

Some of the chemical analyses of rinkite minerals published in 1969 contained up to 10 wt% Ta_2O_5 (Semenov 1969, p. 48). These samples should be re-examined.

The mineral described as hydrorinkite is an altered form of rinkite.

Joaquinite was originally described as a REE-free Ba mineral (Palache & Foshag 1932), but Semenov *et al.* (1967) discovered the mineral in the Ilímaussaq complex and found that it contains 22.59 wt% REE_2O_3. The pure Ba mineral has later been described by Wise (1982), who established two new minerals in the joaquinite group: strontiojoaquinite and bario-orthojoaquinite and also defined the REE-bearing members joaquinite and orthojoaquinite. The REE-containing mineral from the Ilímaussaq complex should, accord-

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Table 1. Chemical analyses of Na-komarovite and terskite from the Ilímaussaq alkaline complex

	White Nb-silicate Na-komarovite	White Zr-silicate terskite
SiO_2	16.46	54.65
TiO_2	5.27	0.09
ZrO_2	-	23.83
SnO_2	-	1.30
Al_2O_3	1.38	-
Fe_2O_3	0.48	0.59
REE_2O_3	0.46	-
CaO	5.30	-
Na_2O	13.71	5.97
K_2O	-	0.93
Nb_2O_5	50.23	1.63
H_2O	4.64	11.21
F	2.50	-
	100.43	100.20
- O for F_2	1.05	
	99.38	100.20

White Nb-silicate: Semenov (1969, table 22).
White Zr-silicate: Semenov (1969, table 36).
-: not analysed

ing to the now accepted nomenclature for REE minerals, be termed joaquinite-(Ce) (cf. Clark 1993; Fleischer & Mandarino 1995).

The white Zr-silicate in the 1969 memoir (Semenov 1969, p. 75) has been found to be a hydrated Na_2O-poor version of terskite, $Na_4ZrSi_6O_{15}(OH)_2\ H_2O$ (Khomyakov *et al.* 1983). A chemical analysis is presented in Table 1.

The white Nb-silicate (Semenov 1969, p. 55) has been found to be the sodium analogue, $(Na,Ca,H)_2Nb_2Si_2O_{10}(OH,F)_2{\cdot}H_2O$, of komarovite which was first described by Portnov *et al.* (1971) from the Lovozero complex, Kola Peninsula. The Ilímaussaq mineral should consequently be termed Na-komarovite (Krivokoneva *et al.* 1979). A chemical analysis is presented in Table 1.

The white mica of the 1969 memoir (Semenov 1969, p. 96) was originally found to be related to ephesite, though too low in Li and Na to be assigned to this mineral. New chemical analyses of the alkali metals by flame photometry have, however, shown a practically identical composition to the mineral from Postmasburg, South Africa (Table 2; cf. Schaller *et al.* 1967) and it should therefore be termed ephesite, $NaLiAl_2(Al_2Si_2O_{10}(OH)_2$.

Table 2. Chemical analyses of ephesite

	Ilímaussaq	Postmasburg (Schaller *et al.* 1967)
SiO_2	34.12	30.87
Al_2O_3	49.70	51.68
FeO	0.49	0.47
CaO	0.88	0.02
Li_2O	2.61	3.66
Na_2O	8.19	7.69
K_2O	0.21	0.16
H_2O	4.59	4.98
others	-	0.45
	100.79	99.98

The Ilímaussaq ephesite has been found in lujavrite pegmatites in their central hydrothermal zones where it is associated with pink cryptocrystalline albite and spherulitic white natrolite. It forms white shining flakes measuring 3 × 2 × 1 mm. The optical properties are similar to those reported for ephesite: 2V ~ 60°, γ = 1.62, α = 1.60. The unit cell dimensions have been determined as: a = 5.11, b = 8.86 and c = 19.14 Å, β = 95°. There is an endothermic reaction at 900°C. It is a mica polytype 2M, but the major part (70%) of the larger flakes of Ilímaussaq ephesite belong to the unordered modification 1Md: a = 5.11, b = 8.86, c = 9.69 Å, β = 100°, that is with half length of the c axis. The mineral thus displays two or three structural modifications.

Mn and Fe members of sepiolite (X-ray main reflection 12 Å) and palygorskite (10 Å) are of widespread occurrence in the Ilímaussaq as well as the Lovozero complexes. The Mn analogue of palygorskite has been described as yofortierite by Perrault *et al.* (1975). The Na-Mn analogue was described as raite (Merkov *et al.* 1973) and the Fe variety as tuperssuatsiaite (Karup-Møller & Petersen 1984). Of these minerals yofortierite and tuperssuatsiaite occur in the Ilímaussaq complex.

The red Mn silicate of Semenov (1969, p. 103) has been found to be Mn-Fe-sepiolite, $Mn_2Fe_2Si_6O_{15}(OH)_2\ 6H_2O$.

Discarded minerals. Some minerals mentioned by Semenov (1969) have later been discarded from the list of Ilímaussaq minerals. They are animikite (p. 22), vudjavrite (p. 52) and zirfesite (p. 77). According to Clark (1993), animikite is a mixture of silver, galena and nickeline, vudjavrite is an amorphous alteration

product of lovchorrite (altered rinkite), and zirfesite is an alteration product of eudialyte.

The mineral mentioned by Semenov (1969, p. 26) as maucherite has been shown to be westerveldite (Karup-Møller & Makovicky 1977; Oen *et al.* 1977).

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Thalcusite from Nakkaalaaq, the Ilímaussaq alkaline complex, South Greenland

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Thalcusite from a new locality in the Ilímaussaq complex, the Nakkaalaaq mountain, occurs in a coarse ussingite–aegirine vein and is associated with sphalerite and cuprostibite. The empirical composition is $Tl_{1.89}K_{0.08}Cu_{2.86}Fe_{1.34}S_{4.00}$. Secondary tenorite–Sb oxide aggregates are developed along cleavages. Tarnish products are essentially pure Cu^{+} sulphide. All three layered thallium sulphides from the Ilímaussaq complex, thalcusite, chalcothallite and rohaite, contain K substituting for Tl. Varieties with K > Tl were not found in the massif.

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Three primary thallium sulphides have been found in the Ilímaussaq alkaline complex: chalcothallite, rohaite and thalcusite (Semenov *et al.* 1967; Karup-Møller 1978a; Kovalenker *et al.* 1978; Makovicky *et al.* 1980). Chalcothallite and rohaite are only known from the Ilímaussaq complex, whereas thalcusite occurs at four other localities: the type locality Talnakh, Noril'sk region, Polar Siberia, Russia (Kovalenker *et al.* 1976), the Murun massif, Aldan Shield, Yakutia, Russia (Dobrovol'skaya *et al.* 1984; Dobrovol'skaya & Nekrasov 1994), Rajapura-Dariba, Rajasthan, India (Mookherjee *et al.* 1984) and Mont Saint-Hilaire, Quebec, Canada (Mandarino & Anderson, 1989).

At Ilímaussaq chalcothallite has been found in ussingite-bearing hydrothermal veins on the Taseq slope, and rohaite in sodalite–analcime veins on the Kvanefjeld plateau. Cuprostibite and a few common sulphides are present at both localities. See Sørensen (2001, this volume) for a map of the localities mentioned in the text and a brief description of the complex.

Thalcusite, $Tl_2(Cu,Fe)_4S_4$, has been found at three localities within the Ilímaussaq complex: in ussingite veins on the Taseq slope containing chalcothallite and cuprostibite, disseminated in naujaite at the head of the Kangerluarsuk fjord in the southern part of the complex and recently also on the top plateau of the Nakkaalaaq mountain in the northern part of the complex.

Mode of occurrence

The thalcusite-bearing sample from Nakkaalaaq measures seven by five centimetres. It is composed of coarse ussingite containing a few up to several centimetres long aegirine crystals and opaque mineral aggregates. One such aggregate is composed of sphalerite intergrown with thalcusite and partly altered cuprostibite, and another is composed of only thalcusite. In the latter opaque cluster, thalcusite forms a platy aggregate half a centimetre in cross-section and about one



Fig. 1. Polished thalcusite aggregate with tenorite (**dark**) along the open cleavage planes. SEM image; scale division 10 µm. Sample GM 2001,1 (Geological Museum, Copenhagen).

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Table 1. Microprobe analyses of thalcusite

	Thalcusite			Tarnish*	Supergene alteration	
	Av. wt%	St. dev.	Mol. ratio		Av. wt%	St. dev.
Tl	50.10	(138)	18.60	11.2	0.4	(2)
K	0.43	(10)	0.83	0.15	0.02	(2)
Cu	23.49	(38)	28.05	53.3	74.8	(39)
Fe	9.68	(18)	13.15	2.6	0.4	(1)
Sb	0.07	(4)	0.05		5.1	(17)
Cl	0.02	(3)	0.04	1.1–2.7*	0.7	(1)
S	16.60	(36)	39.28	11. –13*	0.03	(3)
	100.38		100.00		81.4	

* Limiting values for the tarnishing product of thalcusite after exposure to air for three years.
Numbers in parentheses are standard deviations in terms of the last digit.
All analyses stem from sample GM 2001.1 (Geological Museum, Copenhagen).

millimetre in thickness. The individual grains of the aggregate are split and partly crumpled along the basal cleavage plane (001) (Fig. 1). Alteration of the aggregate has resulted in loss of much of the aegirine and in malachite staining. The sample is assumed to come from nearby unexposed ussingite-bearing hydrothermal veins; such veins are exposed elsewhere on the plateau.

This mode of occurrence appears similar to that of thalcusite from the Taseq slope, as judged from the photographs of Kovalenker *et al.* (1978). On the Taseq slope thalcusite occurs intergrown with cuprostibite and gudmundite. The mode of occurrence also recalls that of chalcothallite (Semenov *et al.* 1967; Makovicky *et al.* 1980).

Experimental

X-ray identification of thalcusite was made with a Gandolfi Camera, using Cu$K\alpha$ radiation. Microprobe analyses were carried out with a JEOL Superprobe 733 using wavelength dispersive mode with an on-line correction program supplied by JEOL. Standards used were synthetic Cu_3SbS_4 for Cu, Sb and S, synthetic FeS for Fe, and natural $TlAsS_2$ and KCl for Tl, K and Cl. Wavelengths used were Cu$K\alpha$, Sb$L\alpha$, S$K\alpha$, Fe$K\alpha$, Tl$L\alpha$, K$K\alpha$ and Cl$K\alpha$. Detection limits for all seven elements were *c.* 0.2 wt%.

Chemical composition of thalcusite

Fifty-four point analyses of the thalcusite aggregate gave consistent results (Table 1). The resulting molar ratios give the empirical formula $Tl_{1.89}K_{0.08}Cu_{2.86}Fe_{1.31}S_{4.00}$. The quality of the analysis is influenced by the condition of the weathered aggregate. Cl and Sb are present only in trace amounts. Thalcusite at Nakkaalaaq is richer in iron and thallium than thalcusite from Taseq which, according to Kovalenker *et al.* (1978), has the formula $Tl_{1.41}K_{0.07}Cu_{3.10}Fe_{1.11}S_{4.00}$. Both differ in composition from thalcusite at the head of Kangerluarsuk which is K-free, $Tl_{1.91}Cu_{3.01}Fe_{1.01}S_{4.00}$ (Makovicky *et al.* 1980). At the last-named locality the mineral is associated with galena, troilite and djerfisherite and is partly altered to covellite and chalcopyrite.

In spite of its crystallisation in Na-rich environments, thalcusite has a Tl- and K-based structure. These cations are eightfold co-ordinated by sulphur. Being a smaller cation, Na^+ does not fit this co-ordination and structure type; it is octahedrally co-ordinated as, e.g., in $NaCu_5S_3$ (Effenberger & Pertlik 1985).

The absence of Sb in the mineral shows lack of any potential interlayers with chalcothallite or rohaite compositions, even for thalcusite associated with cuprostibite and gudmundite at Taseq.

Supergene alteration

Along some contorted cleavage planes thalcusite is interlayered with a fine-grained aggregate (Fig. 1) which under the microprobe beam gave a homogeneous set of 14 analyses (Table 1). These data agree very closely with tenorite (CuO) with an admixture of Sb oxides (or even a Cu-Sb oxide) of unknown composition.

The fairly uniform oxide mixture (Sb varies from 2.6 to 8.0 wt%) with the summary formula $Cu_{9.1.2}Tl_{0.2}Fe_{0.6}Sb_{3.1}Cl_{1.6}S_{0.1}$ cannot be explained as an oxidation prod-

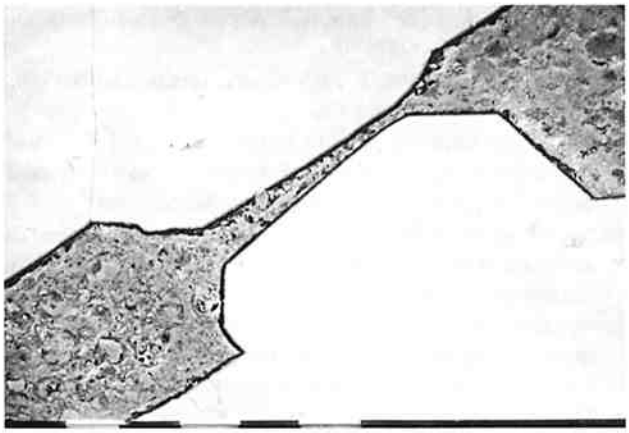


Fig. 2. Euhedral thalcusite growing into a cavity now filled with tenorite (**dark**). SEM image. Scale division 10 µm. Sample GM 2001.1 (Geological Museum, Copenhagen).

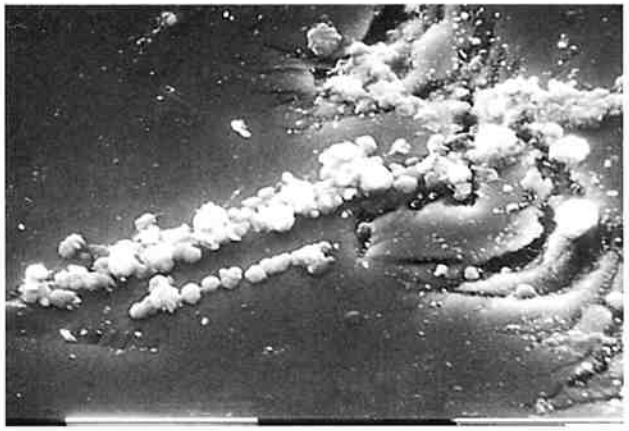


Fig. 3. Secondary Cu_2S growth along polishing scratches and contorted cleavage on the surface of polished thalcusite. Compare with Fig. 1, top centre SEM image. Scale division 10 µm. Sample GM 2001.1 (Geological Museum, Copenhagen).

uct of thalcusite. It undoubtedly originates from the oxidation of a mixture of cuprostibite and chalcosite, originally deposited between the split thalcusite flakes. The textural evidence (Fig. 2) supports this conclusion: surfaces of thalcusite show signs of primary crystal growth.

Tarnishing of thalcusite

Tarnishing of polished sections is a common but little studied phenomenon. Chen *et al.* (1980) examined tarnishing of Ag-bearing chalcopyrite and the chalcopyrite–silver pair. The tarnish is an Ag_2S film encroaching upon chalcopyrite. Their investigation of fast tarnishing tennantite (≤ 0.9 wt% Ag) showed secondary products spreading quickly as rims and dendritic coatings over adjacent silicates and epoxy. Microprobe and X-ray diffraction data indicated digenite in the first-stage coating, and dendritic coatings, gradually replaced by chalcosite with time. Both nodular structures and branched dendritic coatings developed.

Mozgova *et al.* (1994) reported on tarnish products in 10–30 years old sections containing Cu and Ag sulphides and sulphosalts. They found that acantite and Cu sulphides were the principal tarnish product, and they identified the Cu sulphides as chalcosite and djurleite. There was a wide range of starting materials – bornite, Ag, Ag-bearing tetrahedrite, etc. Both Chen *et al.* (1980) and Mozgova *et al.* (1994) emphasise diffusion of Ag and Cu from and over the surface of the primary minerals and their reunion with S into simple sulphides. Finally Mozgova & Tsepin (1983) observed growth of Ag_2S dendrites on the surface of Ag-bearing tetrahedrite (4–5 wt% Ag) during prolonged excitation by the microprobe beam.

Tarnish products were observed on thalcusite after the polished section had been exposed to air for three years. They belong to the nodular type (Fig. 3). Lines of globular secondary products outline either cleavage planes of thalcusite or the polishing scratches across its surface. The multiple microprobe analyses reflect the thinness of the coating by yielding mixtures of the compositions of thalcusite and of the new product in variable proportions. The original 23.5 wt% Cu gradually increases to 53.3 wt%, accompanied by a fall in Tl values from 50.1 wt% down to 11.2 wt%, decrease in Fe from 9.7 wt% to 2.6 wt%, drop in K to values of 0.15 wt% and in S from 16.6 to about 11–13 wt%. The analytical totals change to 80.6–85.0 wt% and chlorine appears, reaching up to 1.1–2.7 wt%. The Cu:S ratio is close to 2:1, indicating that the product is Cu_2S, chalcocite, or very close to it. Calculating the weight deficit as oxygen shows that the investigated phase cannot be a sulphate or a sulphite of copper. Tl apparently is not concentrated; the role of secondary chlorine is unclear. Slight repolishing entirely removes the secondary products.

Mineralogical implications

Potassium contents in sulphides are rare and appear confined to alkaline intrusive massifs and to the late products of the Cu–Ni sulphide magmas in the Noril'sk Intrusion. The presence of potassium in the layered

sulphide and sulphide–antimonide structures (thalcusite, chalcothallite and rohaite) appears to be confined to late veins (ussingite or sodalite–analcime) of the Ilímaussaq complex. Thalcusite enclosed in naujaite at Kangerluarsuk is K-free (Makovicky *et al.* 1980). The potassium analogue of thalcusite, murunite $K_2Cu_3FeS_4$ (Dobrovol'skaya & Nekrasov 1994), has not been found in the Ilímaussaq complex. Djerfisherite is the only other K-bearing sulphide present (Karup-Møller 1978b).

Synthetic selenides related to bukovite, $Tl_2Cu_3FeSe_4$, (Johan & Kvaček 1971), a selenium analogue of thalcusite, $Tl_2Cu_3FeS_4$, stretch over a rich spectrum of Cu-Tl stoichiometries, most of them being richer in Cu than bukovite (Berger 1987). They may be layered structures ($TlCu_2Se_2$, $TlCu_3Se_3$) or tunnel structures ($TlCu_7Se_4$, $TlCu_5Se_3$). Berger (1987) has also established that the mineral sabatierite, $TlCu_6Se_4$, has a layered structure whereas crookesite, $TlCu_7Se_4$, is a tunnel structure. None of these Cu-rich thallium selenides or corresponding sulphides have so far been observed in the Ilímaussaq complex. Instead, their role appears to be taken by chalcothallite, $Tl_2M_{6.35}SbS_4$ (M = Cu, Fe; Cu/Fe ~ 8/1) and rohaite, $Tl_2M_{8.67}Sb_2S_4$ (M = Cu).

Acknowledgements

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Hiortdahlite II from the Ilímaussaq alkaline complex, South Greenland, the Tamazeght complex, Morocco, and the Iles de Los, Guinea

Encarnacion Roda Robles, François Fontan, Pierre Monchoux, Henning Sørensen and Philippe de Parseval

At Ilímaussaq hiortdahlite has only been known from a dyke located immediately to the south-east of the complex. This mineral has now been found in a pegmatite horizon in the sodalite-rich rock naujaite of the complex. It appears to be earlier than eudialyte and is regarded as having been formed at low alkalinity at an early stage of naujaite formation. The optical and X-ray parameters are identical to the data for hiortdahlite from Kipawa, Quebec, and indicate that the Ilímaussaq mineral is type II hiortdahlite.

Minerals from the Iles de Los, Guinea, and the Tamazeght complex, Morocco, have been examined by optical and X-ray methods and chemical analysis, and are shown also to be hiortdahlite II.

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Keywords: agpaite, hiortdahlite, Ilímaussaq, nepheline syenites

Hiortdahlite, $(Ca,Na)_3(Zr,Ti)Si_2O_7(O,F)_2$, is a relatively rare mineral, only known from alkaline rocks. It is a sorosilicate belonging to the cuspidine–låvenite–wöhlerite group. It was first mentioned in a preliminary way by Brögger in 1888 and described in detail by the same author in 1890 from Arø in Langesundsfjord in the south-western part of the Oslo igneous province, Norway, where it occurs in a medium-grained, trachytoid nepheline syenite dyke. Neumann (1985) reports a few other occurrences of hiortdahlite in the Langesundsfjord area and in a granite near Skien to the north of Langesundsfjord.

Hiortdahlite is known from a few other localities. Lacroix (1910) expressed the view that hiortdahlite most probably also occurs in the nepheline syenites of the Iles de Los, Guinea, which has been confirmed by our studies (see below). Di Franco (1942) reported the mineral from Mt. Etna, Sicily, and Kapustin & Bykova (1965) reported it from the Korgeredaba alkaline complex, Sangilen Upland, SE Tuva, Russia. Kempe & Deer (1970) identified the mineral in the Kangerdlugssuaq alkaline complex, East Greenland, and Larsen & Steenfelt (1974) from an iron-rich peralkaline phonolite dyke immediately to the south-east of the Ilímaussaq complex, South Greenland; no chemical analyses or other information about the mineral were reported.

Aarden & Gittins (1974) presented chemical and X-ray data for hiortdahlite from the Kipawa River complex, Quebec, Canada, where it sometimes occurs in almost monomineralic veinlets in pyroxenite and amphibolite belonging to a regionally metamorphosed alkaline complex. Chemical and X-ray data have also been reported for hiortdahlite found in a phonolite dyke from the Jingera Rock syenite complex, New South Wales, Australia (Eggleton *et al.* 1979). The mineral X described by Kadar (1984) from the Tamazeght nepheline syenite complex in the High Atlas Mountains at Midelt, Morocco, has been found to be hiortdahlite (see below).

Merlino & Perchiazzi (1985, 1987) determined the crystal structure of hiortdahlite and distinguished hiortdahlite I and II, which co-exist at Kipawa River. Both

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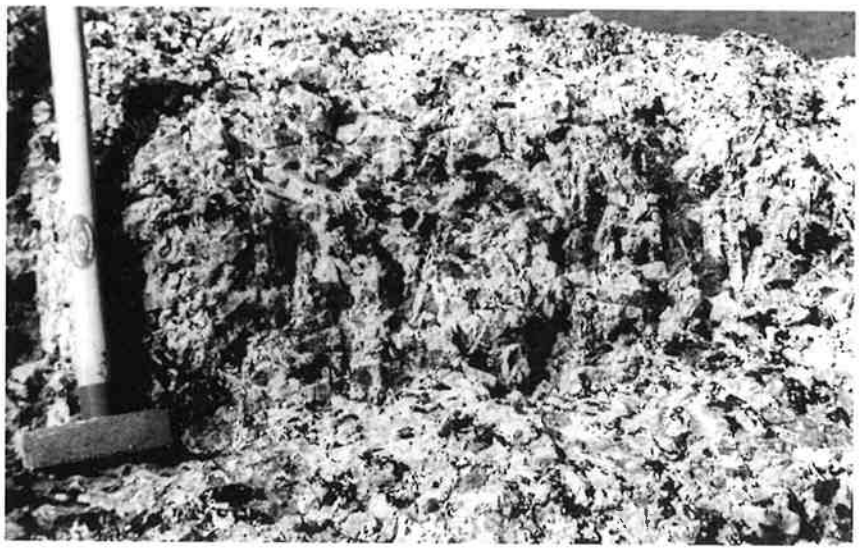


Fig. 1. The pegmatite at Tupersuatsiaat showing prismatic grains of sodalite (**white**) growing downwards from the contact against the overlying naujaite. Hammer head measures 12 cm.

are triclinic, but hiortdahlite II differs from type I in being pseudomonoclinic. They found that the type material from the Langesundsfjord and the Jingera Rock mineral is hiortdahlite I.

Hiortdahlite from the Ilímaussaq complex

Hiortdahlite has recently been found occurring as a subordinate mineral in a horizon of naujaite pegmatite (Fig. 1) in the NW corner of the bay Tupersuatsiaat on the south coast of the fjord Tunulliarfik (see Sørensen 2001, fig. 1, this volume, for the locality names mentioned in the text). These horizons are characterised by up to 10 cm long prismatic crystals of sodalite which have grown downwards from the hanging wall of the pegmatites at right angles to the horizontal contacts against the overlying naujaite (Sørensen & Larsen 1987). The sodalite crystals are partially replaced by analcime with preservation of their crystal forms. Interstitial to the sodalite are plates of microcline, crystals of nepheline, eudialyte and rinkite, and irregular grains of aegirine which often have cores of arfvedsonite in parallel growth, and aenigmatite. Small flakes of biotite and aggregates of natrolite are late minerals. The biotite flakes grow on the faces of the aegirine grains, whereas the natrolite occurs interstitially and as fracture fillings in analcime secondary after the elongated crystals of sodalite.

Hiortdahlite occurs as yellow-brown crystals associated with eudialyte and with aggregates of aegirine (Figs 2, 3). It is separated from the eudialyte by powdery reaction zones which, using the Debye–Scherrer method, have been identified as mixtures of hiortdahlite and catapleiite. There are no reaction zones against the aegirine.

Optical properties. The mineral is weakly pleochroic: γ = amber yellow, α = β = pale yellow or colourless. There is a strong dispersion: r < v, 2V (+) ~ 60°, α =

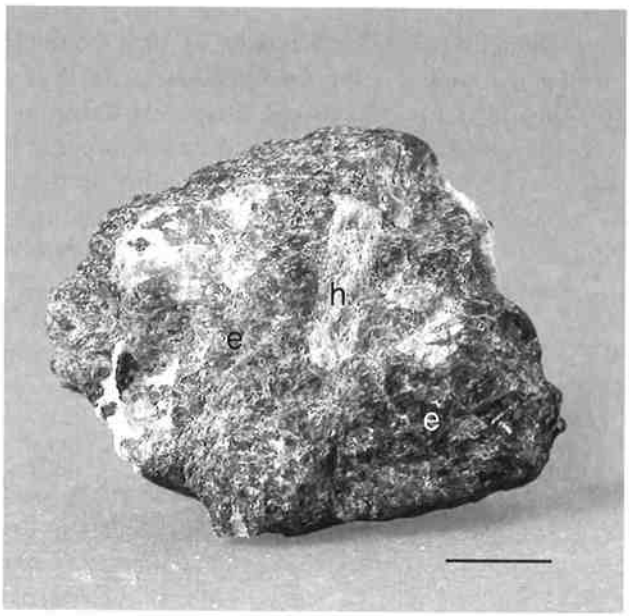


Fig. 2. Hand specimen (sample 104378, Geological Institute, University of Copenhagen) showing crystal of hiortdahlite (**h**) enclosed in eudialyte (**e**), scale = 1 cm. Photo: Ole Bang Berthelsen.

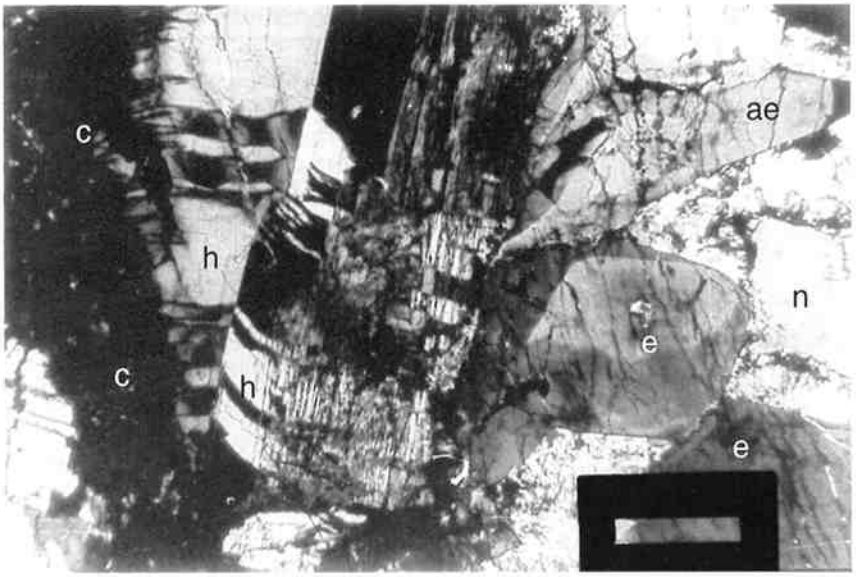


Fig. 3. Crystal of hiortdahlite (**h**) showing complex twinning. It is covered and intergrown by aggregates of fine-grained catapleiite (**c**, black area near left margin of photograph). Right part of photograph: an aegirine crystal (**ae**) and two crystals of eudialyte (**e**) showing zonation; centre right nepheline (**n**). Matrix is made up of fine-grained natrolite. Sample 104378 Geological Institute (same as Fig. 2), crossed polars, scale bar 0.6 mm.

Table 1. X-ray powder diffraction data for hiortdahlite

Ilímaussaq		Tamazeght		Iles de Los	
d	I/I_0	d	I/I_0	d	I/I_0
10.319	5	10.280	30	10.283	30
7.322	2	7.196	15	7.256	5
5.093	12	5.126	10	5.185	30
4.577	3	4.599	10	4.623	5
3.544	10	3.534	5	3.534	20
3.270	46	3.278	100	3.279	70
3.198	3				
3.020	86	2.998	100	2.999	100
2.882	100	2.858	100	2.867	90
2.727	1			2.691	10
2.592	7				
2.515	10	2.508	30	2.522	20
2.445	17	2.442	2	2.449	20
2.306	4	2.338	5	2.312	5
2.258	12	2.259	5	2.254	10
2.113	1				
2.067	9	2.067	30	2.076	10
2.030	33	2.027	30	2.032	40
1.956	11	1.953	10	1.957	5
1.844	15	1.845	20	1.845	30
1.803	27	1.801	20	1.801	20
1.777	17	1.749	10		
1.702	27	1.710	40 vb	1.698	40
1.624	3	1.648	10		
1.595	13	1.595	10 b	1.663	10 vb
1.543	36	1.543	30 b	1.549	20 vb
1.481	5				
1.460	7				
1.418	8				

Ilímaussaq: diffractometer, Geological Inst. (Copenhagen) sample 104040 deposited at Université Paul Sabatier, Toulouse.
Tamazeght: Debye-Scherrer method (Cu$K\alpha$, 360 mm), sample XT 15, Université Paul Sabatier, Toulouse.
Iles de Los: Debye-Scherrer method (Cu$K\alpha$, 360 mm), Lacroix sample MNHN n° 119-115.
b = broad, vb = very broad.

Table 2. Unit cell parameters of hiortdahlite calculated by the least squares method

	Ilímaussaq	Tamazeght	Iles de Los
a	10.979 Å	10.913 Å	11.008 Å
b	10.303 Å	10.427 Å	10.315 Å
c	7.340 Å	7.217 Å	7.335 Å
α	90.01°	90.31°	90.28°
β	109.28°	108.38°	109.36°
γ	90.28°	89.74°	90.11°

Ilímaussaq, Geological Institute (Copenhagen) sample 104040 deposited at Université Paul Sabatier, Toulouse.
Tamazeght, sample XT 15, Université Paul Sabatier, Toulouse.
Iles de Los, Lacroix sample MNHN no. 119-115.

1.643, β = 1.645 and γ = 1.656. The mineral shows polysynthetic twinning (Fig. 3).

Crystallography. The Ilímaussaq hiortdahlite was identified by its X-ray diffractogram (Table 1) which is identical to that of the hiortdahlite from Kipawa River (Aarden & Gittins 1974). The unit cell parameters were calculated by the least squares method (Table 2) and are very similar to the data on the Kipawa River hiortdahlite presented by Aarden & Gittins (1974).

The cell parameters and the refractive indices indicate that the Ilímaussaq hiortdahlite belongs to type II of Merlino & Perchiazzi (1987).

Infra-red spectroscopy and thermogravimetric analysis. The infra-red absorption spectrum recorded on a tablet of hiortdahlite and KBr shows a sharp band at 3430 cm^{-1} corresponding to (OH) in the H_2 vibration field.

The thermogravimetric analysis shows a loss of weight of 0.70% between 200 and 400°C. X-ray diffraction analysis of the powder after heating to 1000°C shows no significant structural change.

Chemical analysis. The hiortdahlites from the Ilímaussaq, Iles de Los and Tamazeght complexes were chemically analysed by electron microprobe (Table 3). The chemical analyses of the hiortdahlite from Ilímaussaq, Iles de Los and Tamazeght show that the Ilímaussaq mineral has the highest contents of Nb and F and that the inverse relation between Nb and F proposed by Mellini & Merlino (1979) for wöhlerite does not exist in any of these samples of hiortdahlite.

Hiortdahlite from Iles de Los and Tamazeght

Iles de Los, Guinea. Lacroix (1910) presented a partial description of a mineral which is abundant in a biotite-eudialyte-låvenite nepheline syenite. It shows various shades of yellow to brown colours and a glassy lustre on the crystal faces, but greasy on fracture surfaces. There is polysynthetic twinning, a weak pleochroism, γ = like yellow wine, β = clear yellow, α = colourless. These properties led Lacroix (1910) to suggest that this mineral may be related to the hiortdahlite described by Brögger (1890). G.C. Parodi and J. Skrok, Muséum d'Histoire Naturelle, Paris, France, kindly made available to us the material examined by Lacroix (MNHN n° 119-115). The X-ray powder diagram (Table 1) clearly indicates that the mineral is hiortdahlite, and the parameters presented in Table 2 show that it is hiortdahlite II. The electron microprobe analysis (Table 3) shows contents of ZrO_2 and F similar to those of the Ilímaussaq hiortdahlite, whereas Nb_2O_5 and REE_2O_3 are absent; their place is taken by MnO and FeO.

The Tamazeght complex, Morocco. Kadar (1984) described a grey-white mineral with conchoidal fracture and greasy appearance from a thin microsyenite dyke near the summit of Bou Tichlilt, where it is associated with nepheline, zircon, alkali feldspar and låvenite. It has γ = 1.652 and α = 1.646 and shows polysynthetic twinning but the data obtained were insufficient for the identification of the mineral, which was mentioned as mineral X. We have managed to obtain an X-ray powder diagram by the Debye–Scherrer method (Table 1) according to which this mineral is hiortdahlite II (Table 2). The electron microprobe analysis (Table 3) shows higher contents of ZrO_2 than in the Ilímaussaq hiortdahlite, and the absence of REE_2O_3 and Nb_2O_5. H_2O was not determined.

Table 3. Electron microprobe analyses of hiortdahlite

	Ilímaussaq		Tamazeght		Iles de Los	
	wt%	atoms*	wt%	atoms*	wt%	atoms*
SiO_2	29.96	1.919	30.08	1.930	30.32	1.945
TiO_2	0.94	0.046	0.36	0.019	0.93	0.046
ZrO_2	15.24	0.475	20.43	0.639	14.93	0.470
La_2O_3	0.11	0.003	n.d.	-	n.d.	-
Ce_2O_3	0.25	0.005	n.d.	-	n.d.	-
Y_2O_3	0.51	0.008	n.d.	-	n.d.	-
FeO	2.64	0.142	0.44	0.023	1.57	0.085
MnO	0.40	0.023	0.65	0.035	2.67	0.146
CaO	32.69	2.244	35.14	2.411	35.72	2.453
Na_2O	6.76	0.839	6.34	0.790	5.41	0.678
K_2O	n.d.	-	0.02	-	0.10	0.008
Nb_2O_5	2.24	0.032	n.d.	-	n.d.	-
H_2O†	0.70	0.231	n.a.	-	n.a.	-
F	11.05	2.233	9.47	1.918	10.41	2.103
	103.49		102.93		102.06	
– O for F_2	4.64		3.98		4.37	
	98.85		98.95		97.69	

Each analysis given is the average of 9 point analyses.
Ilímaussaq, Geological Institute (Copenhagen) sample 104040 deposited at Université Paul Sabaiter, Toulouse.
Tamazeght, sample XT 15, Université Paul Sabatier, Toulouse.
Iles de Los, Lacroix sample MNHN no 119-115.
n.a. = not analysed, n.d. = not detected.
* Calculation of the structural formula for Ilímaussaq material based on (O,OH,F) = 9.000; for Tamazeght and Iles de Los based on (O,F) = 9.000.
† Thermogravimetric analysis.
Camebax SX 50 electron microprobe at the Laboratoire de Minéralogie, Université Poul Sabatier, Toulouse. Standards used: wollastonite (Ca, Si), albite (Na), zircon (Zr), $MnTiO_3$ (Ti), YPO_4 (Y), hematite (Fe), topaz (F), $NbLiO_3$ (Nb), Al_2O_3 (Al). For the REE, the standards of Jarosewich & Boatner (1991) were used.

Paragenesis

In the Ilímaussaq complex, hiortdahlite has so far been identified at only one locality within the complex and in a dyke immediately to the south-east of the complex. In contrast to this, the rinkite group minerals, which are also Na-Ca-Zr-Ti-Nb sorosilicates, are of widespread occurrence in the complex. The rinkite group minerals differ from hiortdahlite in having distinctly higher contents of Na, Ti, Nb, Y and REE, and lower contents of Zr, Ca and F. At Tupersuatsiaat, hiortdahlite occurs in a sodalite-rich naujaite pegmatite which forms a distinct horizon in the naujaite. The naujaite in this horizon contains scattered grains of fayalite, hedenbergite, apatite and titanomagnetite, which were formed at low alkalinity at an early stage of formation of the naujaite (Larsen 1976). The hiortdahlite at this locality is associated with eudialyte (Figs 1, 2) and aegirine and separated from the eudialyte by a fine-grained zone of catapleiite, which is interpreted as a zone of reaction indicating that the hiortdahlite crystallised earlier than the eudialyte. Rinkite is generally formed after eudialyte in the naujaites. The succession hiortdahlite – eudialyte – rinkite may then be interpreted as an expression of increasing alkalinity during the crystallisation of the naujaite.

According to Larsen & Steenfelt (1974), hiortdahlite in the dyke locality to the south of the complex is restricted to alkali-poor parts of the dyke, where it is associated with zircon. This part of the dyke is made up of perthitic alkali feldspar, nepheline, sodalite, aegirine-hedenbergite, biotite, magnetite, apatite, fluorite and pyrrhotite. The alkali-rich parts of the dyke are made up of an agpaitic mineral assemblage corresponding to the early stages of the roof-series of the Ilímaussaq complex (Larsen & Sørensen 1987). Phenocrysts of fayalite, diopside-hedenbergite, nepheline, alkali feldspar and minor magnetite are set in a

matrix of microcline and albite in separate grains, nepheline, sodalite, aegirine, arfvedsonite, eudialyte, aenigmatite, apatite, fluorite, pyrite and late analcime and natrolite. The alkali-poor parts of the dyke are found close to the Ilímaussaq complex and its mineral assemblage is interpreted to have formed as a result of loss of alkalis because of heat from the adjacent intrusion.

This interpretation is in accordance with the description of the Langesundsfjord occurrence of hiortdahlite (Brögger 1890). There, hiortdahlite is restricted to a suite of medium-grained dykes made up of microperthitic alkali feldspar, lepidomelane and nepheline. These dykes are poor in mafic minerals and sodalite and without eucolite (eudialyte), mosandrite (rinkite), astrophyllite, catapleiite and leucophanite, minerals which are important in pegmatites in other parts of this contact zone of the Oslo igneous province. Brögger (1890) mentions that the medium-grained dykes containing the hiortdahlite also contain homilite, erdmannite, löllingite, zircon, fluorite, molybdenite, titanite, Y-garnet, rare wöhlerite, analcime and zeolites. According to this description hiortdahlite is restricted to alkali-poor nepheline syenite dykes.

The Kipawa River hiortdahlite, according to Aarden & Gittins (1974) and Gittins *et al.* (1976), occurs in almost monomineralic veins in alkaline amphibolite and is associated with zircon, britholite, fluorite, albite, nepheline and calcite. It is not clear from the descriptions how these veins are related to the occurrences of eudialyte, wöhlerite, agrellite, miserite, rinkite and vlasovite in this complex.

The Tamazeght hiortdahlite is also associated with zircon.

The Iles de Los hiortdahlite appears from the description of Lacroix (1910) to be associated with nepheline, eudialyte, låvenite and biotite. According to Lazarenkov (1975) hiortdahlite is an accessory mineral in foyaites, which also contain wöhlerite.

The hiortdahlite from Jingera Rock occurs in a metre-wide phonolite dyke made up of aegirine, alkali feldspar and interstitial sodalite and nepheline. The hiortdahlite contains inclusions of magnetite and apophyllite(?) (Eggleton *et al.* 1979).

The description of the occurrences of hiortdahlite at Kangerdlugssuaq, Mt. Etna and Korgeredaba, Tuva referred to above do not supply sufficient information about the paragenetic relations to allow a comparison with the data from Langesundsfjord, Ilímaussaq, Kipawa River, Iles de Los and Tamazeght.

Conclusions

This survey of the mineral associations, in which hiortdahlite is reported to occur, does not lead to a clear picture. An environment relatively poor in alkalis, Ti, REE and Nb and rich in Zr, Ca and F appears to favour the formation of this mineral rather than the rinkite group minerals. The relation to låvenite is uncertain. Hiortdahlite and eudialyte may occur in the same rock, as described from Ilímaussaq and Iles de Los; in Ilímaussaq hiortdahlite appears to be earlier than the eudialyte and not formed in equilibrium with that mineral. The Ilímaussaq occurrence of hiortdahlite is controversial because it occurs in an alkali-rich environment. It appears, however, to have been formed at low alkalinity at an early stage of the evolution of the naujaite. Other chemical parameters may, however, also contribute to the formation of hiortdahlite. It is interesting in this connection to note that hiortdahlite has not been reported from the Khibina and Lovozero alkaline complexes of the Kola peninsula, which are characterised by the occurrence of a wealth of minerals rich in Ti, Nb and REE (cf. Khomyakov 1995; Semenov 1997).

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Natrophosphate from the Ilímaussaq alkaline complex, South Greenland

Ole V. Petersen, Alexander P. Khomyakov and Henning Sørensen

The rare mineral natrophosphate has been identified for the first time in the Ilímaussaq alkaline complex in a drill core from the Kvanefjeld area. It occurs sparsely in zoned veinlets with cores of natrophosphate and borders of fibrous trona. The natrophosphate is more or less smoky, transparent and unaltered. The refractive index n = 1.448 ± 0.005 is low compared to that given for the material from the type locality, Khibina alkaline complex, Kola Peninsula; the unit cell parameter a = 27.76 ± 0.05 Å is in excellent agreement with that given for the material from the type locality. The veins occur in hyper-agpaitic naujakasite lujavrite; villiaumite is an associated mineral. Only a few water-soluble minerals have so far been found in the Ilímaussaq alkaline complex compared to the wealth of such minerals in the Khibina and Lovozero alkaline complexes. This is possibly at least partly due to lack of necessary precautions during sampling.

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Keywords: hyper-agpaite, Ilímaussaq, natrophosphate, water-soluble minerals

Natrophosphate, $Na_7(PO_4)_2F{\cdot}19H_2O$, is a rare mineral, first described by Kapustin *et al.* (1972) from Yukspor Mountain, Khibina alkaline complex, Kola Peninsula, Russia, and subsequently from the nearby Lovozero alkaline complex (Khomyakov & Bykova 1980). The first well-formed crystals were reported from Mont Saint-Hilaire, Quebec, Canada, by Mandarino & Anderson (1989) and Horvath & Gault (1990). Recently, natrophosphate has been described from the Aris phonolites, Windhoek, Namibia (Petersen *et al.* 1997).

In 1993 a search for water-soluble minerals was carried out on some 1000 m of drill core from the Ilímaussaq alkaline complex. Natrophosphate, associated with a carbonate, was optically identified in a small number of very thin parallel veins in drill core 49. The present report is a documentation of the Ilímaussaq occurrence.

Occurrence and general description

The Ilímaussaq natrophosphate occurs in a small number of less than 1 mm wide, fairly regular, parallel veins in drill core 49 at a depth of approximately 71.5 m. The veins are symmetrically zoned, with a core of natrophosphate constituting up to half of the vein, and with borders of fibrous trona, identified from a Gandolfi type X-ray diagram. Trona has previously been described as forming crusts in cavities in ussingite, from drill cores from the same area (Sørensen *et al.* 1970). The natrophosphate is colourless or more often smoky, transparent and, though exposed to air for quite some time, remarkably unaltered. The snow-white trona bordering the veins forms dense fibrous aggregates with the fibres oriented perpendicular to the walls of the veins (Fig. 1). In thin section the parallel fractures containing the natrophosphate veins are closely spaced.

The veins occur in a naujakasite lujavrite containing about 50% naujakasite and a substantial amount of villiaumite (Fig. 1). Parallel arranged laths of microcline and small prismatic grains of arfvedsonite give the rock a distinct igneous lamination. The rock also contains small prismatic grains of aegirine, altered grains of eudialyte, and minor interstitial albite. Sphalerite and an opaque mineral are associated with the albite.

The natrophosphate cores of the veins are associ-

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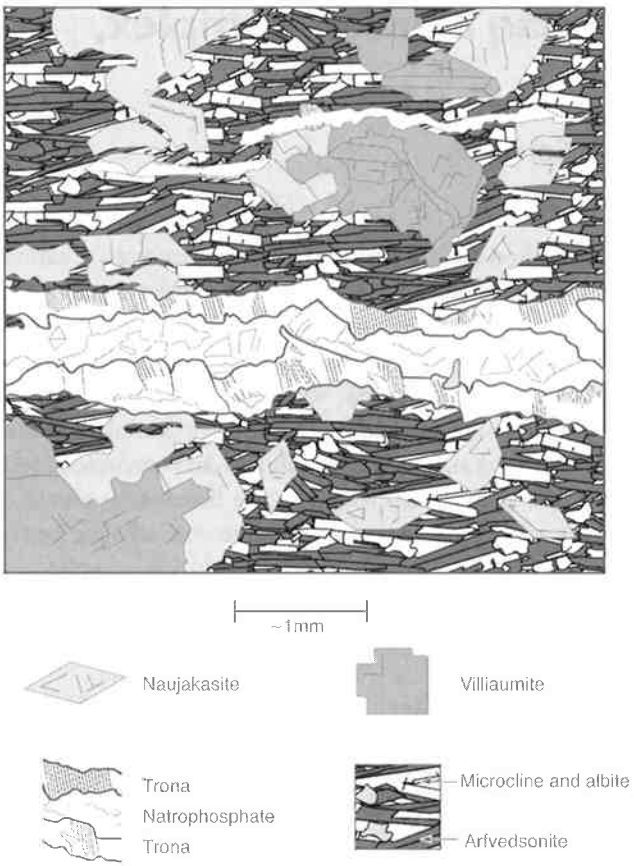


Fig. 1. Sketch showing a typical, symmetrically zoned vein of natrophosphate and trona in naujakasite-bearing arfvedsonite lujavrite. Drill core 49, depth approximately 71.5 m, Kvanefjeld, Ilímaussaq alkaline complex, South Greenland.

ated with a few small irregular grains of villiaumite; the marginal zones consist entirely of fibrous trona. The rusty colour of the trona in thin section in transmitted light is ascribed to scattering of light, probably by micro-inclusions, and the apparently low birefringence to the very fine fibrous nature of the trona.

The veins are discontinuous and branching and can, for instance, penetrate the grains of naujakasite along their cleavage planes. The branches between the rock-forming minerals and along the naujakasite cleavages only consist of trona.

Optical properties, X-ray diffraction and chemistry

The refractive index of the natrophosphate from Ilímaussaq is 1.448 ± 0.005, which is low compared to the values given by Kapustin *et al.* (1972): 1.460–1.462 for the material from the type locality. The low refractive index is believed to be due to the unaltered state of the Ilímaussaq natrophosphate, i.e. the mineral has a high content of H_2O compared to the partly dehydrated natrophosphate from the type locality. The refractive index is close to the value of 1.450 for the natrophosphate from Aris, Namibia (Petersen *et al.* 1997).

The unit cell parameter refined from Gandolfi type powder pattern, Cu$K\alpha$ radiation, λ = 1.54178 Å, of the natrophosphate from Ilímaussaq was found to be a = 27.76 ± 0.05 Å, in excellent agreement with the a = 27.79 Å given by Kapustin *et al.* (1972) for the type material from Yukspor Mountain, Khibina alkaline complex, Kola Peninsula, Russia.

The correct chemical formula of natrophosphate, $Na_7(PO_4)_2F{\cdot}19H_2O$, was first suggested by Khomyakov & Bykova (1980), and finally established by Genkina & Khomyakov (1992) when refining the structure of natural natrophosphate from the Lovozero alkaline complex. The small amount of material available of the Ilímaussaq natrophosphate, together with the extreme amount of H_2O in natrophosphate, precluded a full quantitative analysis.

Discussion

Only a few water-soluble minerals have so far been found in the Ilímaussaq alkaline complex. Villiaumite is of widespread occurrence in drill cores, though only exceptionally at depths less than 50 m below the present surface. Trona and thermonatrite have been found in drill core 6 at 109.74 m (Sørensen *et al.* 1970), and dorfmanite in a single hand specimen from the exploration adit in the Kvanefjeld area (Petersen *et al.* 1993). By comparison with the wealth of water-soluble minerals in the Khibina and Lovozero alkaline complexes (Khomyakov 1995), such minerals should also be expected to be common late-stage minerals in the Ilímaussaq alkaline complex. The presence of such minerals may be inferred from numerous cavities in the rocks of the complex and from chemical analyses of water flowing out of the Kvanefjeld adit. The pH of this water is 11, and the dissolved material consists of 7.7 kg/t NaF, 3.0 kg/t Na_2O and 6.9 kg/t SiO_2, corresponding to a mixture of villiaumite and natrosilite (Sørensen 1982). Furthermore, the walls and roof of the Kvanefjeld adit, and also the drill cores, are covered with white encrustations of thermonatrite and sodium acetate. This encrustation takes place within a few days of exposure to the atmosphere. The source

of the Na must be villiaumite and other water-soluble Na minerals whereas the source of the carbon may be the carbon dioxide of the atmosphere and especially the methane and other hydrocarbons from fluid inclusions in many of the minerals. Natrosilite and other water-soluble minerals must be collected immediately after blasting and fracturing of rocks and drill cores and must be protected from contact with the atmosphere (Khomyakov 1995). This precaution was not taken during the construction of the Kvanefjeld adit and the drilling programmes in the 1960s and 1970s because the possibility of the presence of water-soluble minerals was not appreciated at the time. It is therefore of great satisfaction that natrophosphate has been preserved in drill core 49.

Not surprisingly, the natrophosphate in Ilímaussaq has been found in the hyper-agpaitic naujakasite lujavrite, which is unique to the complex (Sørensen 1997). In the Khibina and Lovozero alkaline complexes of the Kola peninsula, natrophosphate also occurs in hyper-agpaitic pegmatites and veinlets where it is associated with ussingite, natrosilite, analcime, natrolite, villiaumite, thermonatrite, etc. (Khomyakov 1995).

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Two new rare-earth-rich mineral associations in the Ilímaussaq alkaline complex, South Greenland

Igor V. Pekov and Irina A. Ekimenkova

Two new types of REE-rich mineral associations have been discovered at Kvanefjeld in the northern part of the Ilímaussaq alkaline complex. Type 1 consists of ussingite veins intersecting lujavrite and containing 5–7% nacareniobsite-(Ce) and 2–4% steenstrupine-(Ce); the adjacent altered lujavrite contains up to 10–12% nacareniobsite-(Ce). Type 2 consists of cavernous sodalite-rich veinlets and vugs in lujavrite containing 5–8% vitusite-(Ce). The chemical compositions and unit cell parameters of REE minerals are given.

Nacareniobsite-(Ce) and vitusite-(Ce) were considered to be extremely rare minerals in the Ilímaussaq complex. Nacareniobsite-(Ce) is now known to be of more widespread occurrence in some hyper-agpaitic rocks of the Ilímaussaq complex, and vitusite-(Ce) is known to be the precursor of the widespread occurrence of the yellow pseudomorphs termed erikite.

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Keywords: agpaite, Ilímaussaq, nacareniobsite-(Ce), nepheline syenites, vitusite-(Ce)

The agpaitic rocks of the Ilímaussaq alkaline complex and their pegmatites are rich in the rare-earth elements (REE), their average REE content being up to thirty times higher than the average contents in the Earth's crust (Gerasimovsky 1969). The main REE concentrating minerals in the complex are eudialyte and rinkite (in sodalite foyaite, naujaite and kakortokite and their pegmatites, eudialyte also in lujavrites), and steenstrupine-(Ce) (in naujaite and lujavrites and their pegmatites). Steenstrupine-(Ce) is a major mineral in the REE-U deposit at Kvanefjeld in the northern part of the complex (Sørensen 1992; see Sørensen 2001, fig. 1, this volume, for place names mentioned in the text).

Two new types of REE-rich mineral associations have been discovered in material from the adit on the southern slope of Kvanefjeld. Hyper-agpaitic pegmatitic veins and their surrounding rocks contain abundant nacareniobsite-(Ce), $Na_3Ca_3(Ce,Nd)(Nb,Ti)(Si_2O_7)_2OF_3$ (type 1) and vitusite-(Ce), $Na_3(Ce,La)(PO_4)_2$ (type 2).

Two new types of REE mineral associations

Type 1 consists of ussingite veins up to 15 cm wide and the adjacent arfvedsonite lujavrite and medium- to coarse-grained lujavrite. The veins are composed of about 90 vol.% pink to lilac massive ussingite, 5–7 vol.% nacareniobsite-(Ce), 2–4 vol.% steenstrupine-(Ce) and 1–2 vol.% aegirine and sodalite. Light-grey altered lujavrite adjacent to the veins contains up to 10–12 vol.% nacareniobsite-(Ce), whereas steenstrupine is practically absent. Nacareniobsite-(Ce) within and around the veins occurs as lemon-yellow bunches and spherulites up to 7 mm in diameter consisting of curved and split board-like crystals. Nacareniobsite-(Ce), which was first described as an extremely rare mineral from small cavities in lujavrite from the Kvanefjeld adit (Petersen *et al.* 1989), is a minor rock-forming component of these ussingite veins and the adjacent lujavrite and is the main concentrator of REE and Nb here. It is also now known to be of more widespread occurrence in contact modified rocks from the volcanic roof of the complex (H. Sørensen, personal communication 2000).

The chemical composition (Table 1) of this nacareniobsite-(Ce) gives the formula: $Na_{2.98}Ca_{2.62}(Ce_{0.55}Nd_{0.29}La_{0.17}Pr_{0.07}Sm_{0.04}Y_{0.04})_{\Sigma 1.16}(Nb_{0.79}Ti_{0.22})_{\Sigma 1.01}(Si_{4.22}Al_{0.01}O_{14})O(F_{2.86}O_{0.29})_{\Sigma 3.15}$. The unit cell parameters are: a = 18.865±5, b = 5.683±2, c = 7.464±5 Å, β = 101.25±2°, all uncertainties on the last digit.

Na-rich steenstrupine-(Ce) is a minor concentrator of REE (Table 1) in this mineral association.

Type 2 is made up of cavernous veinlets up to 5–7 cm wide and vugs in lujavrite. The veins and vugs consist mainly of sodalite with subordinate amounts of nephe-

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Table 1. Chemical composition of rare-earth minerals from hyper-agpaitic veinlets, Kvanefjeld adit

	1	2	3
SiO_2 (wt%)	29.00	24.6	0.33
TiO_2	2.01	0.0	-
ZrO_2	0.04	0.0	-
ThO_2	0.03	2.8	0.08
UO_2	-	0.8	-
Al_2O_3	0.03	0.2	-
Fe_2O_3	-	1.2	-
La_2O_3	3.19	9.0	16.09
Ce_2O_3	10.34	13.9	18.28
Pr_2O_3	1.35	0.0	1.30
Nd_2O_3	5.57	3.2	3.44
Sm_2O_3	0.83	0.0	0.05
Y_2O_3	0.48	1.1	0.04
MnO	-	3.1	-
CaO	16.88	3.1	1.92
SrO	-	-	0.18
Na_2O	10.57	14.6	23.12
P_2O_5	-	14.6	36.93
Nb_2O_5	12.03	-	-
F	6.22	-	-
– O for F_2	2.62	-	-
	95.95	92.2	101.76

1: nacareniobsite-(Ce) from type 1 association.
2: steenstrupine-(Ce) from type 1 association.
3: vitusite-(Ce), from type 2 association.
Microprobe data, average values of several points; analysts: I.M. Kulikova (1,3), A.N. Nekrasov (2).
Conditions of analysis: analyses 1 and 3 were made with a CAMEBAX micro-beam analyser, 20 kV, 20 nA (10 kV for F and Na, beam diameter 10 μm); analysis 2 was made with a Jeol JXA 850 microprobe, 15 kV, 20 nA. Standards for both machines: $REEPO_4$ for La, Ce, Pr, Nd and Sm, YPO_4 for Y, ThO_2 for Th, UO_2 for U, albite for Na and Al, $SrSO_4$ for Sr, $MnTiO_3$ for Mn and Ti. For CAMEBAX only: diopside for Ca and Si, hornblende for Fe, wadeite for Zr, $LiNbO_3$ for Nb and MgF_2 for F. For Jeol JXA only: andradite for Ca, Fe and Si, zirconium for Zr and niobium for Nb.
-: not analysed.

line, aegirine, potassic feldspar, arfvedsonite, and vitusite-(Ce). The content of vitusite-(Ce) in the veinlets and the bordering sodalite-rich lujavrite is 5–8 vol.%. The mineral forms isometric and tabular grains up to 5 mm across; well-shaped crystals are found in cavities. Their morphology is precisely the same as the erikite crystals described by Bøggild (1903) from Nunarsuatsiaq in the central part of the Ilímaussaq complex. Erikite is a pseudomorph after vitusite made up of common REE phosphates (rhabdophane, monazite) and Na zeolites formed under low-alkaline hydrothermal conditions (Pekov *et al.* 1997).

Vitusite-(Ce) from the Kvanefjeld adit is strongly dichroic: it is greenish brown in daylight and honey coloured when examined in electric light; weak lilac UV fluorescence is observed. The chemical composition (Table 1) corresponds to the formula: $(Na_{2.88}Ca_{0.13})_{\Sigma 3.01}(Ce_{0.43}La_{0.38}Nd_{0.08}Pr_{0.03}Sr_{0.01})_{\Sigma 0.93}(P_{2.00}Si_{0.02})_{\Sigma 2.02}O_8$. The parameters of the orthorhombic cell are: a = 5.342±3, b = 18.661±5, c = 14.061±4 Å.

Concluding remarks

The two types of REE-rich mineral associations described in the present paper demonstrate that the mode of concentration of REE in hyper-agpaitic rocks strongly differs from those in all other natural materials, including the agpaitic rocks proper. In hyper-agpaitic rocks rare minerals such as nacareniobsite-(Ce) and vitusite-(Ce) can become the main concentrators of REE and even occur as rock-forming minerals, as described here.

Acknowledgements

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Stability of Na–Be minerals in late-magmatic fluids of the Ilímaussaq alkaline complex, South Greenland

Gregor Markl

Various Na-bearing Be silicates occur in late-stage veins and in alkaline rocks metasomatised by late-magmatic fluids of the Ilímaussaq alkaline complex in South Greenland. First, chkalovite crystallised with sodalite around 600°C at 1 kbar. Late-magmatic assemblages formed between 400 and 200°C and replaced chkalovite or grew in later veins from an H_2O-rich fluid. This fluid is also recorded in secondary fluid inclusions in most Ilímaussaq nepheline syenites. The late assemblages comprise chkalovite + ussingite, tugtupite + analcime ± albite, epididymite + albite, bertrandite ± beryllite + analcime, and sphaerobertrandite + albite or analcime(?).

Quantitative phase diagrams involving minerals of the Na–Al–Si–O–H–Cl system and various Be minerals show that tugtupite co-exists at 400°C only with very Na-rich or very alkalic fluids [$\log (a_{Na^+}/a_{H^+}) > 6–8$; $\log (a_{Be^{2+}}/(a_{H^+})^2) > -3$]. The abundance of Na-rich minerals and of the NaOH-bearing silicate ussingite indicates the importance of both of these parameters. Water activity and silica activity in these fluids were in the range 0.7–1 and 0.05–0.3, and X_{NaCl} in a binary hydrous fluid was below 0.2 at 400°C. As bertrandite is only stable at < 220°C at 1 kbar, the rare formation of epididymite, eudidymite, bertrandite and sphaerobertrandite by chkalovite-consuming reactions occurred at still lower temperatures and possibly involved fluids of higher silica activity.

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Keywords: agpaite, Be-minerals, Greenland, Ilímaussaq, stability relations

Beryllium minerals occur in small quantities in many magmatic rocks of broadly granitoid composition and in larger quantities in some granitic pegmatites. The earliest Be mineral in most granitic rocks is beryl; later minerals, in many cases replacing beryl, include euclase, bertrandite, phenakite (e.g. Mårtensson 1960; Černý 1963, 1968; Roering & Heckroodt 1966; Burt 1975; Hemingway *et al.* 1986; Markl & Schumacher 1997), herderite (Burt 1975) and many more. The greatest variety and abundance of Be minerals is invariably connected to pegmatitic liquids and late- to postmagmatic fluids. Table 1 provides the chemical formulae of Be minerals mentioned and discussed in the present paper.

In contrast to these 'normal' granitoid Be minerals, Na-rich peralkaline rocks are typically devoid of the Be minerals mentioned above, but contain Na–Be silicates such as chkalovite, tugtupite, epididymite, eudidymite or sorensenite (Semenov *et al.* 1965; Semenov & Sørensen 1966; Andersen 1967; Mandarino & Harris 1969; Sobolev *et al.* 1970; Engell *et al.* 1971 and references therein). Interestingly, no corresponding K-Be silicate assemblages exist in K-rich, peralkaline magmatic rocks. The physico-chemical conditions under which the Na-bearing Be silicates crystallise and the compositional parameters which favour the Na-bearing or the Na-free Be mineral assemblages in the Ilímaussaq alkaline complex in South Greenland are the topic of this contribution. Of special interest is the unique occurrence of large masses of pinkish red tugtupite which is used as a semiprecious gemstone in the Ilímaussaq area.

The Ilímaussaq alkaline complex (Fig. 1) was emplaced in the late Gardar period at about 1.16 Ga (unpublished data by the author, see also Sørensen 2001, this volume) into the Mesoproterozoic Julianehåb granite and earlier Gardar sandstones and basalts. The depth of intrusion is estimated as about 3–4 km, corresponding to about 1 kbar pressure (Konnerup-Madsen & Rose-Hansen 1982, 1984). The intrusive complex was formed by three distinct magma batches which are believed to represent successively more fractionated liquids from an alkali basaltic magma chamber at depth (Larsen & Sørensen 1987; Sørensen & Larsen 1987). It

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Table 1. Chemical formulae of Be minerals discussed or mentioned in this paper

Barylite: $BaBe_2Si_2O_7$
Bavenite: $Ca_4Be_2Al_2Si_9O_{26}(OH)_2$
Bertrandite: $Be_4Si_2O_7(OH)_2$
Beryl: $Be_3Al_2Si_6O_{18}$
Beryllite: $Be_3SiO_4(OH)_2 \cdot H_2O$
Chkalovite: $Na_2BeSi_2O_6$
Chrysoberyl: $BeAl_2O_4$
Epididymite: $NaBeSi_3O_7OH$
Euclase: $BeAlSiO_4OH$
Eudidymite: $NaBeSi_3O_7OH$
Genthelvite: $Zn_8Be_6Si_6O_{24}S_2$
Helvite: $(Mn,Fe,Zn)_8Be_6Si_6O_{24}S_2$
Herderite: $CaBePO_4(F,OH)$
Leifite: $Na_2(Si,Al,Be)_7(O,OH,F)_{14}$
Leucophanite: $(Ca,REE)CaNa_2Be_2Si_4O_{12}(F,O)_2$
Phenakite: Be_2SiO_4
Sorensenite: $Na_4SnBe_3Si_6O_{16}(OH)_4$
Sphaerobertrandite: $Be_4Si_2O_7(OH)_2 \cdot xH_2O$
Tugtupite: $Na_8Be_2Al_2Si_8O_{24}Cl_2$

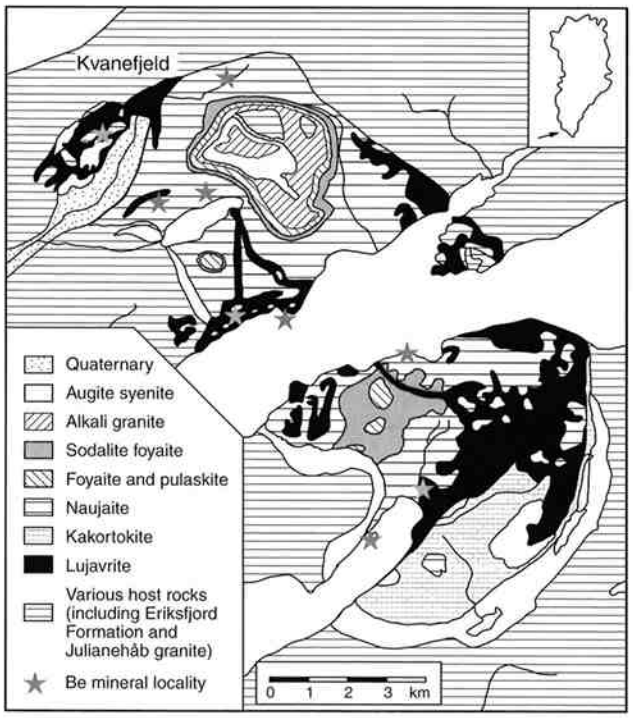


Fig. 1. Geological map of the Ilímaussaq alkaline complex based on Ferguson (1964). The stars denoting the localities where Be minerals have been found are after Engell *et al.* (1971). Note that Be minerals additionally occur at various places in the alkali granite.

consists of a variety of rock types, ranging from early, just silica-saturated or slightly under-saturated augite syenite through agpaitic nepheline syenites (sodalite foyaite, naujaite and kakortokite) to later, extremely silica-undersaturated nepheline syenites (lujavrites) and finally to hyper-agpaitic assemblages which probably crystallised from relatively SiO_2-rich fluids rather than from SiO_2-undersaturated melts. In addition to this fractionation line towards lower silica activities which comprises two out of three different intrusive events at Ilímaussaq (phases 1 and 3), the second intrusive phase is represented by a small sheet of alkali granite. This rock type is interpreted as an augite syenite contaminated with SiO_2-rich crustal rocks or melts, e.g. with Gardar quartzitic sandstones (Stevenson *et al.* 1997), although fluid inclusion studies (Konnerup-Madsen & Rose-Hansen 1984) do not support this hypothesis.

In the course of the 'undisturbed' fractionation process towards lower silica activities, temperature decreased from about 950°C to below 450°C, silica activity dropped from about 0.8 to below 0.2 (Larsen & Sørensen 1987; Markl *et al.* in press; Marks & Markl in press) and water activity continuously increased until saturation with a water-rich fluid was reached at the late lujavrite stage. This fluid was most probably connected to the formation of abundant aegirine-, albite- and analcime-bearing veins cutting through all other Ilímaussaq rocks, which locally contain Be silicates such as chkalovite and tugtupite. Hence, it appears that Be mineralisation is closely connected to late-stage peralkaline magmatic fluids or liquids as was described in great detail by Engell *et al.* (1971).

Be mineral assemblages and textures in the Ilímaussaq complex

Be minerals known to occur at Ilímaussaq include chkalovite, tugtupite, sorensenite, leucophanite, sphaerobertrandite(?), helvite, genthelvite, beryllite, eudidymite, epididymite, bavenite, barylite, bertrandite and Be-bearing leifite (Semenov *et al.* 1965; Semenov & Sørensen 1966; Sobolev *et al.* 1970; Engell *et al.* 1971; Sørensen *et al.* 1971, 1981; Petersen *et al.* 1991, 1994, 1995; Bohse *et al.* 2001, this volume; chemical formulae in Table 1). As far as it can be assessed from the literature and from my own field observations, the first three of these minerals are the only ones occurring in large quantities (tugtupite is even being 'mined' as an important local gemstone); the others appear to be restricted to specific local chemical environments.

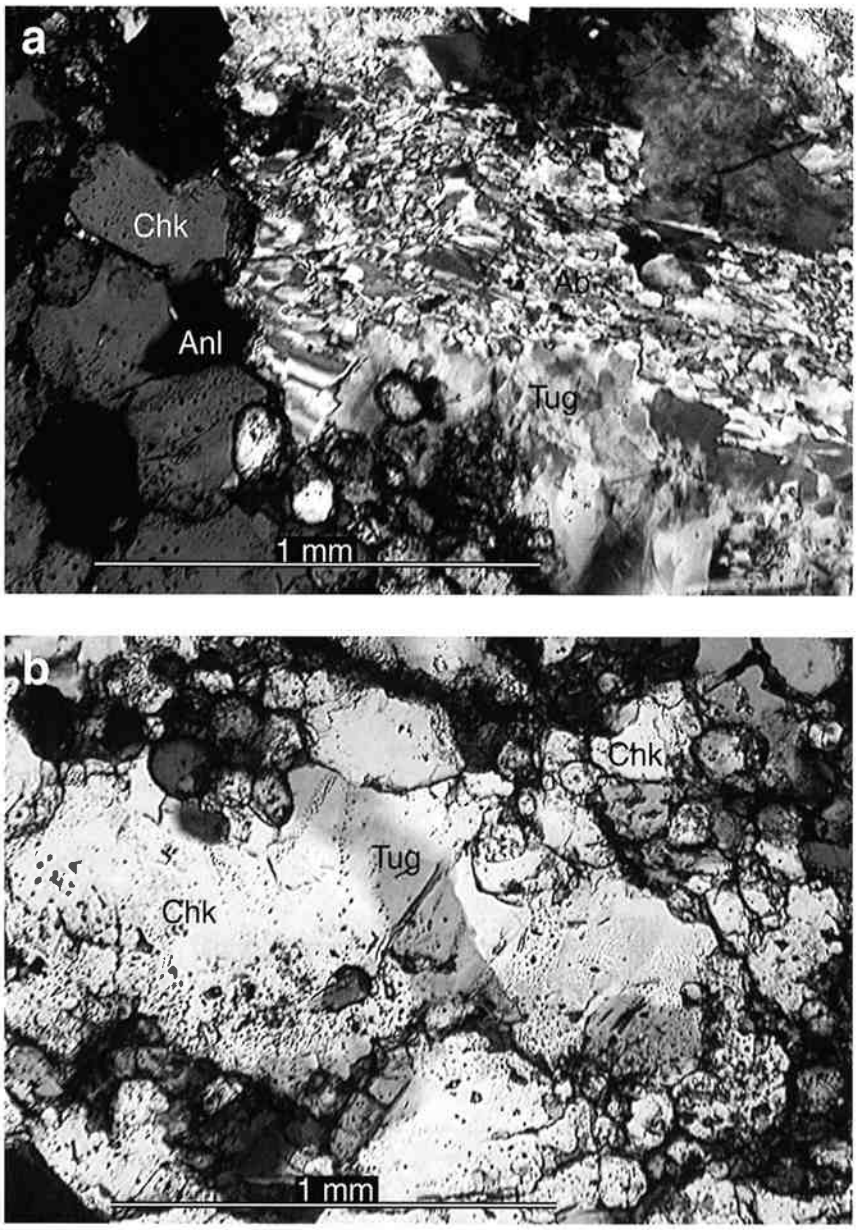


Fig. 2. Photomicrographs of tugtupite replacing chkalovite in a sample from the Kvanefjeld area. **a**: Tugtupite (**Tug**), albite (**Ab**) and analcime (**Anl**) enclosing relics of chkalovite (**Chk**). Crossed nicols. **b**: Tugtupite (**Tug**) replacing coarse chkalovite (**Chk**) in a vein-like manner. Finer grained chkalovite may be a second generation or may be recrystallised during late-magmatic deformation. Author's sample GM 1401.

Epididymite and eudidymite are polymorphs and they have been assumed to have the same stability fields in the qualitative and semi-quantitative diagrams in this contribution. Helvite, genthelvite and sorensenite contain additional components (Zn, S or Sn) that complicate evaluation of their stability fields, and therefore they will not be discussed further in this contribution.

The most comprehensive accounts of Ilímaussaq Be minerals and their occurrences are given by Engell *et al.* (1971) and Sørensen *et al.* (1971). According to them, chkalovite is the earliest Be mineral in Ilímaussaq. It occurs together with ussingite or sodalite and appears to have formed due to reaction of late-magmatic fluids with nepheline-bearing wall rocks. The assemblage chkalovite + sodalite is replaced by a variety of assemblages during infiltration with later hydrous fluids, the most important of which is the assemblage tugtupite + analcime + albite. This mode of occurrence is identical to that reported from the Kola peninsula (Lovozero complex; Semenov & Bykova 1960). Typical textures of tugtupite in the late-stage veins from Kvanefjeld in the northern part of the Ilímaussaq complex are shown in Fig. 2 and are more extensively documented in Sørensen *et al.* (1971). Tugtupite forms in evident equilibrium with analcime and most probably albite (although corroded grains of albite associated with tugtupite have been reported in some samples) during metasomatic recrystallisation of the

Table 2. Equilibrium assemblages involving Be minerals and observed reaction textures in the Ilímaussaq alkaline complex (Na–Be–Al–Si–O–H–Cl system only)

Assemblages
chkalovite + sodalite
chkalovite + ussingite
chkalovite + albite
chkalovite + natrolite (?)
tugtupite + albite + analcime
tugtupite + sphaerobertrandite + analcime
tugtupite + chkalovite + analcime + albite (?)
eudidymite + epididymite + albite
eudidymite + albite + quartz
epididymite + sphaerobertrandite
bertrandite + analcime
beryllite + analcime
Reaction textures
chkalovite + sodalite → tugtupite + analcime
chkalovite + albite → analcime + tugtupite (?)
chkalovite → epididymite + sphaerobertrandite
chkalovite + ussingite → tugtupite + analcime
chkalovite → beryllite
chkalovite I → chkalovite II
eudidymite + epididymite + albite → tugtupite + analcime
epididymite → bertrandite (?)
epididymite → beryllite
analcime → ussingite

Compiled from Andersen (1966); Semenov & Sørensen (1966); Engell *et al.* (1971); Sørensen *et al.* (1971) and own observations.

complete host rock. As far as one can tell from the outcrops on Kvanefjeld, the most intensely red coloured varieties come from veins cutting through altered augite syenite, whereas veins cutting through altered naujaite or lujavrite appear to show lighter, pinkish or pinkish red colours. All assemblages from Ilímaussaq reported in the literature so far are collected in Table 2. Figure 1 shows the areas of Be mineralisation in the Ilímaussaq intrusion after Engell *et al.* (1971) and own observations.

In the alkali granite, epididymite was reported to form stable, probably rather late assemblages with quartz and albite (Semenov & Sørensen 1966) which are partly altered to bertrandite. In similar textures, epididymite has also been reported from the Puklen intrusion on Nunarsuit in the Gardar province (Pulvertaft 1961). In some Ilímaussaq nepheline syenites and in late-stage analcime-bearing veins, epididymite and eudidymite form by decomposition of chkalovite and are themselves replaced by still later tugtupite.

All in all, the reported and observed textures support the interpretation that chkalovite is the earliest Be mineral in the undersaturated rocks of Ilímaussaq (maybe contemporaneous with epididymite/eudidymite in the alkali granite) and most later Be minerals formed by decomposition of this early chkalovite during infiltration of later hydrous fluids (see also Sørensen *et al.* 1971). The temperature and the most important chemical and physico-chemical characteristics of these fluids may be estimated using various types of phase diagrams.

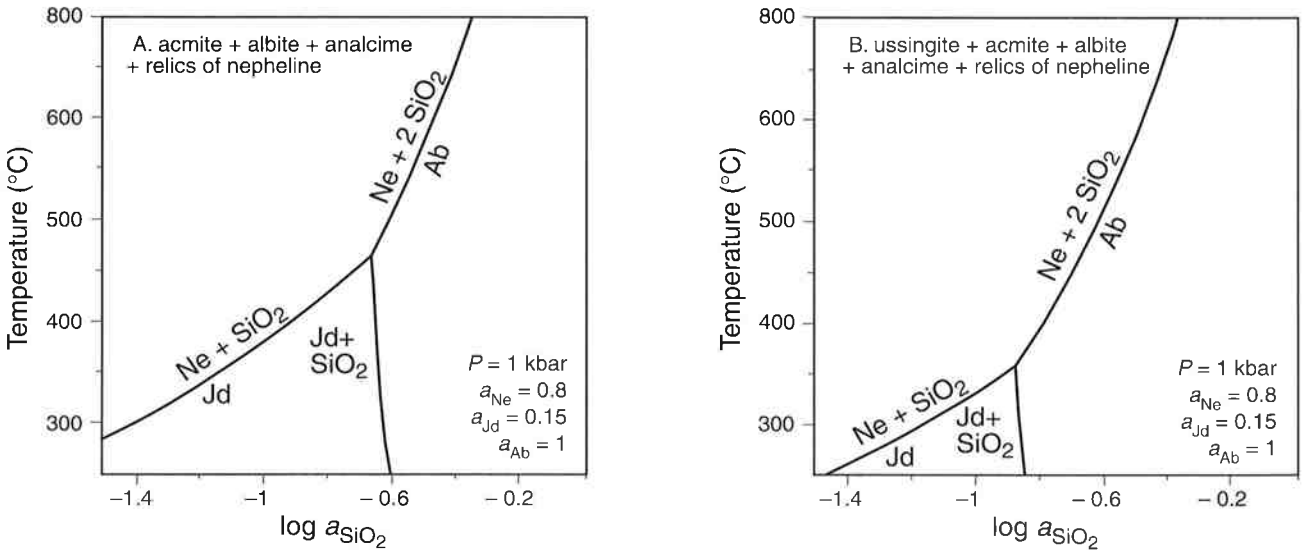


Fig. 3. Temperature–silica activity diagrams for lujavrites from Ilímaussaq (from Sommer 1999). **A**: Ussingite-free, analcime-bearing assemblages, **B**: Ussingite + analcime-bearing assemblages. Nepheline and jadeite activities are calculated from measured mineral compositions reported in Sommer (1999). **Ab**: albite, **Jd**: jadeite, **Ne**: nepheline.

Table 3. Reactions used in the construction of Figures 3 to 7

Fig. 3

albite = jadeite + SiO_2
albite = nepheline + 2 SiO_2
jadeite = nepheline + SiO_2

Fig. 4

sodalite + 6 SiO_2 = 6 jadeite + 2 NaCl
sodalite = 6 nepheline + 2 NaCl
analcime = jadeite + H_2O
analcime = nepheline + H_2O + SiO_2
analcime + SiO_2 = albite + H_2O

Fig. 5

chrysoberyl + 2 Be^{2+} + 6 SiO_2 + 2 H_2O = beryl + 4 H^+
3 chrysoberyl + 2 NaCl + 6 Na^+ + 4 H_2O + 6 SiO_2 = sodalite + 3 Be^{2+}
beryl + 2 NaCl + 6 Na^+ + 2 H2O + 2 SiO_2 = tugtupite + Be^{2+} + 4 H^+
chrysoberyl + 2 NaCl + 6 Na^+ + Be^{2+} + 4 H_2O + 8 SiO_2 = tugtupite + 8 H^+
3 tugtupite = sodalite + 18 SiO_2 + 12 Na^+ + 6 Be^{2+} + 4 NaCl
2 euclase + Be^{2+} + 4 SiO_2 = beryl + 2 H^+
2 euclase + 2 NaCl + 6 Na^+ + 3 H_2O + 6 SiO_2 = tugtupite + 6 H^+
2 euclase + 2 H^+ = chrysoberyl + 2 SiO_2 + Be^{2+} + 2 H_2O
euclase + SiO_2 + Na^+ + H^+ = analcime + Be^{2+}
chrysoberyl + 2 Na^+ + 4 SiO_2 + 3 H_2O = analcime + 2 H^+ + Be^{2+}
tugtupite + 8 H^+ = 2 analcime + 4 Na^+ + 2 Be^{2+} + 4 SiO_2 + 2 NaCl + 2 H_2O
2 Be^{2+} + SiO_2 + 2 H_2O = phenakite + 4 H^+
2 Na^+ + Be^{2+} + 2 SiO_2 + 2 H_2O = chkalovite + 4 H^+
Na^+ + Be^{2+} + 3 SiO_2 + 2 H_2O = epididymite/eudidymite + 3 H^+

Fig. 6

tugtupite + 8 H^+ = 2 albite + 2 NaCl + 4 Na^+ + 2 Be^{2+} + 2 SiO_2 + 4 H_2O
tugtupite + 8 H^+ = 2 jadeite + 2 NaCl + 4 Na^+ + 2 Be^{2+} + 4 SiO_2 + 4 H_2O
tugtupite + 8 H^+ = 2 nepheline + 2 NaCl + 4 Na^+ + 2 Be^{2+} + 6 SiO_2 + 4 H_2O
sodalite + 6 H_2O + 6 SiO_2 = 6 analcime + 2 NaCl

Fig. 7

2 phenakite + 2 Na^+ + 4 H^+ = chkalovite + 3 Be^{2+} + 2 H_2O
2 epididymite/eudidymite + 4 Na^+ + Be^{2+} + 2 H_2O = 3 chkalovite + 6 H^+
3 phenakite + Na^+ + 9 H^+ = epididymite/eudidymite + 5 Be^{2+} + 4 H_2O
phenakite + 4 Na^+ + H_2O + 3 SiO_2 = 2 chkalovite + 4 H^+
phenakite + 2 Na^+ + 2 H_2O + 5 SiO_2 = 2 epididymite/eudidymite + 2 H^+
epididymite/eudidymite + Na^+ = chkalovite + SiO_2 + H^+

Phase diagrams for estimation of Be mineral stabilities

The phase diagrams of this section were calculated using the computer program GEOCALC of Lieberman & Petrakakis (1991) with the thermodynamic database of Berman (1988) for the anhydrous albite–jadeite–nepheline phase diagrams (Figs 3, 4), and the program SUPCRT of Johnson *et al.* (1992) with its thermodynamic database for the rest of the diagrams (Figs 5–7). The latter internally consistent database was augmented with data for sodalite from Sharp *et al.* (1989) and for the beryllium minerals beryl, chrysoberyl, euclase, bertrandite and phenakite from Hemingway *et al.* (1986) and Barton (1986). Although thereby loosing its internal consistency, this method provides the only means of approximately quantifying the chemical parameters responsible for the formation of the Na–Be silicates. The results appear reasonable insofar as they agree with theoretical (Schreinemakers) predictions and observed phase assemblages, but the actual values may be slightly incorrect. Incorrect values may be the reason for the obviously incorrect feature in Fig. 5, that phenakite saturation occurs at too low

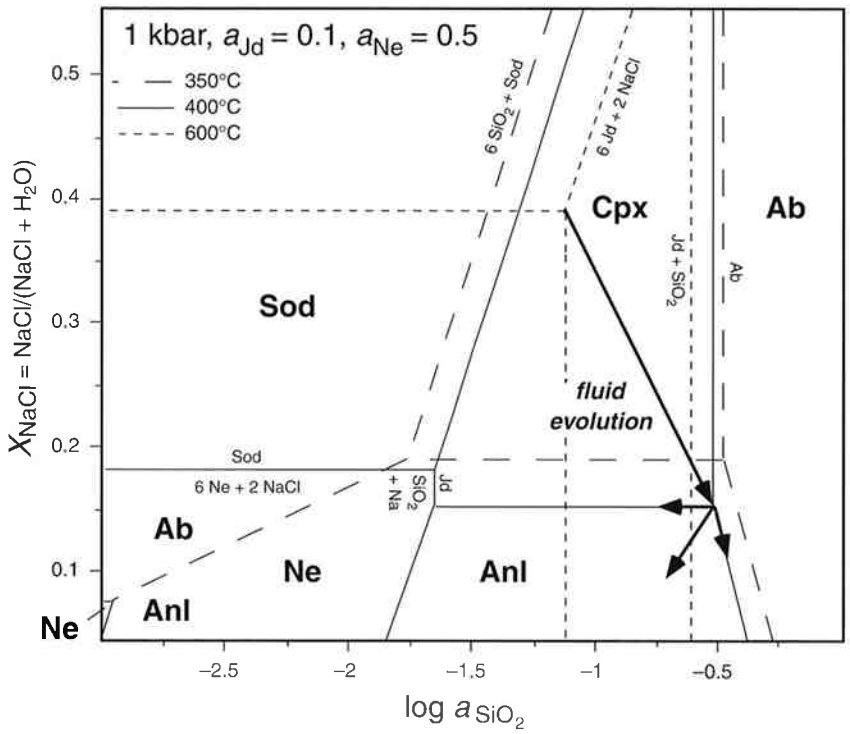


Fig. 4. X_{NaCl}–silica activity diagram for minerals in the Na–Al–Si–O–H–Cl system at various temperatures and 1 kbar. Possible fluid evolution paths during cooling are schematically represented by the thick arrows. **Anl**: analcime, **Ab**: albite, **Cpx**: clinopyroxene, **Jd**: jadeite, **Ne**: nepheline, **Sod**: sodalite.

values to permit stable occurrence of beryl or euclase at 600 and 400°C, respectively. It is assumed that the actual saturation value for phenakite in terms of the $Be^{2+}/(H^+)^2$ activity ratio is about 2 orders of magnitude higher than the calculated value which would be consistent with the rest of the topology on Fig. 5, on which such a possible value is plotted as 'true phenakite saturation?'. The calculated value for phenakite saturation is also plotted on Fig. 5 and the part of the diagram above phenakite and above chkalovite saturation would correctly have to be termed metastable. The interpretation below, however, assumes that phenakite saturation occurs at values permitting beryl and euclase to be stable in Fig. 5A, B, respectively ('true phenakite saturation?').

It was chosen to fix the pressure for all phase diagrams at 1 kbar which is the depth of intrusion of Ilímaussaq based on fluid inclusion studies (Konnerup-Madsen & Rose-Hansen 1984). Variations in the few hundred bars range do not have a major influence on the results of this study. Hence, fixing the pressure and considering the reactions of interest (Table 3), the following major physico-chemical parameters remain to be investigated: temperature, a_{SiO_2}, $a_{Be^{2+}}/(a_{H^+})^2$, a_{Na^+}/a_{H^+}, a_{H_2O} and X_{NaCl}. The latter two are closely connected as it was chosen to treat the fluid, as a first approximation, as a binary H_2O–NaCl mixture with mixing and solution properties calculated according to Aranovich & Newton (1996). In order to constrain as many of the variables as possible, the problem was divided into several steps as follows.

1. Temperature and a_{SiO_2} constraints were estimated as a first step using anhydrous albite–nepheline–jadeite equilibria (Fig. 3) and results from fluid inclusion studies on lujavrites (Sommer 1999; unpublished data). The mineral compositional data for these calculations are reported in Sommer (1999); nepheline and jadeite activities were calculated from the respective solid solutions using the models of Ghiorso (http://melts.geology.washington.edu) and Holland (1990). These phase equilibria showed that very late-stage ussingite-bearing lujavrite (which still contains sodic clinopyroxene, albite and relics of nepheline) formed at temperatures around 350°C and at silica activities around 0.1–0.2 (referring to unit silica activity for pure quartz at the applicable *P* and *T*). In comparison, fluid inclusion studies indicate homogenisation temperatures between 300 and 400°C for primary and some secondary inclusions in various lujavrite minerals and in tugtupite (Sommer 1999; Markl *et al.* in press). Sobolev *et al.* (1970) measured temperatures of 400–460°C for primary inclusions in tugtupite and sorensenite; secondary inclusions record temperatures between 100 and 350°C. Based on their textures, the chkalovite–sodalite assemblages are believed to have formed

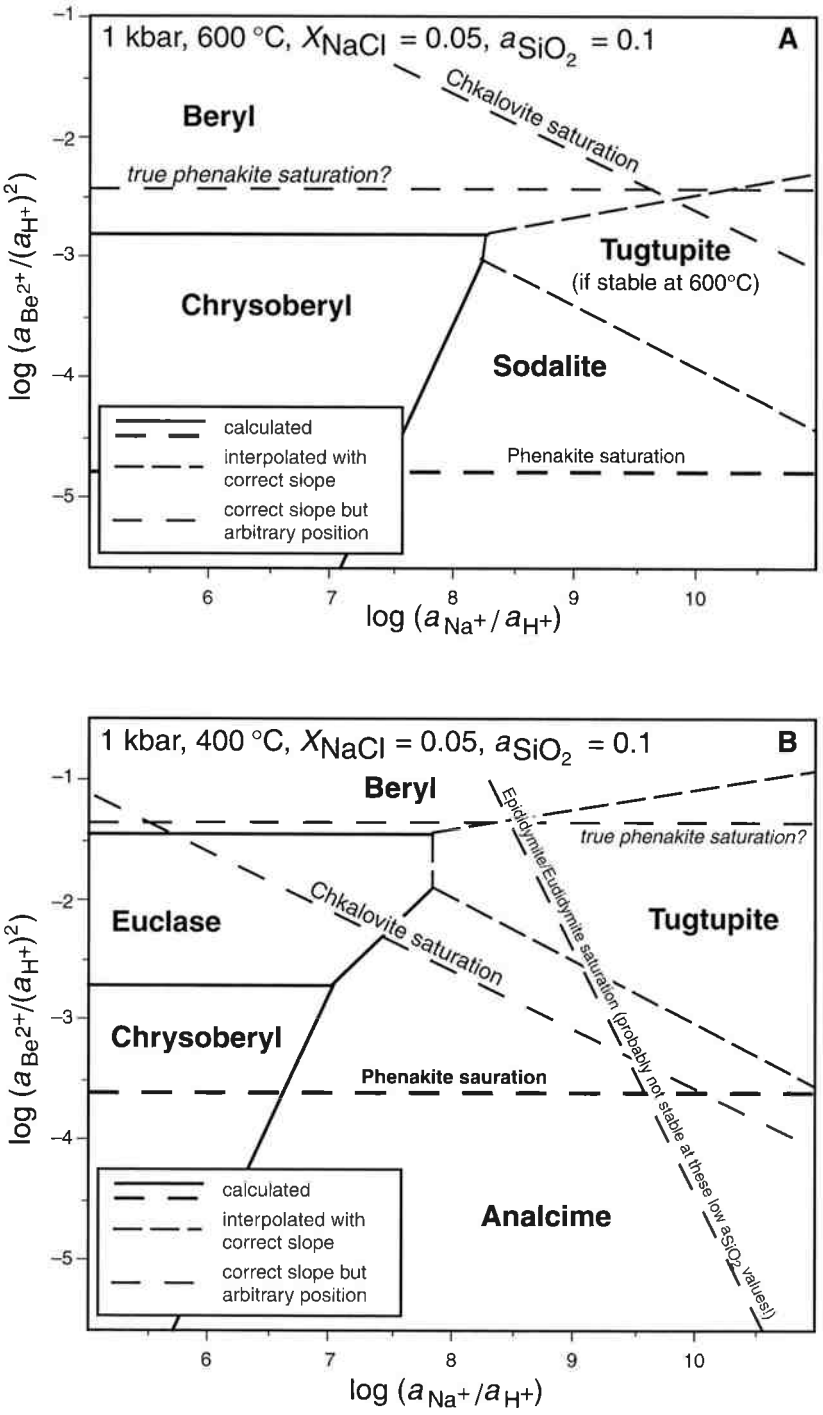


Fig. 5. Activity–activity diagrams involving minerals from the Be–Na–Al–Si–O–H–Cl system at 600°C (**A**) and 400°C (**B**). Field boundaries and saturation lines which were calculated from thermodynamic data (see text) are plotted as thick lines; short dashed lines represent interpolated lines with correct (stoichiometric) slope; and widely dashed lines have the correct slope but are not fitted to any independently constrained invariant point. Note that tugtupite may not be stable at 600°C and that epididymite and eudidymite may not be stable at SiO_2 activities around 0.1. Note also that calculated phenakite saturation occurs at unrealistically low $Be^{2+}/(H^+)^2$ activity ratios and that the part above phenakite and chkalovite saturation in **A** and **B** is actually metastable as plotted here. 'True phenakite saturation?' shows a possible value for phenakite saturation consistent with the rest of the Be mineral topology. See text for discussion.

at some higher temperatures and a temperature of 600°C was arbitrarily chosen for this stage. Studies of Sobolev *et al.* (1970) indicate still higher temperatures in the 860–980°C range, but these results are impossible to reconcile with all other estimates in the Ilímaussaq rocks based on melting experiments and phase equilibria (Sood & Edgar 1970; Markl *et al.* in press; Marks & Markl in press).

2. Based on this framework, limits on a_{H_2O} and X_{NaCl} of a fluid in equilibrium with the observed phases of the Na–Al–Si–O–H–Cl system (e.g., analcime, sodalite, clinopyroxene, albite etc.) were calculated (Fig. 4). Both variables are tied together when considering a binary H_2O–NaCl fluid only. The activity–composition relationships were derived from the formulation of Aranovich & Newton (1996) and activities were referenced to unit activities for pure H_2O

and pure crystalline halite at appropriate P and T. These calculations showed that sodalite-bearing assemblages at 600°C require an X_{NaCl} greater than about 0.39 (Fig. 4), while analcime-bearing assemblages at 400°C or below require hydrous fluids with an X_{NaCl} lower than about 0.15 corresponding to an H_2O activity of 0.7 or higher (Fig. 4). These values are limits for the formation of the two most important Be minerals at Ilímaussaq, chkalovite and tugtupite. The early chkalovite–sodalite assemblage obviously equilibrated with a fluid (or melt?) of relatively high salinity, while later tugtupite, although also Cl-bearing, formed from fluids of lower salinity.

3. These data were then used to place constraints on the fluid chemistry in terms of $Be^{2+}/(H^+)^2$ and Na^+/H^+ activity ratios by considering the typical granite association of the Na-free Be-minerals beryl, phenakite, euclase and chrysoberyl and their stability relations with respect to tugtupite and sodalite. In an Al-balanced activity–activity diagram as shown on Fig. 5, phenakite, chkalovite and epididymite/eudidymite do not have their own stability fields but are only shown by saturation lines because they contain no Al. The stability fields and saturation line for beryl, euclase, chrysoberyl, sodalite and phenakite were calculated quantitatively, while those for tugtupite, chkalovite and epididymite/eudidymite – because of the lack of thermodynamic data – were inserted with correct slopes, but at arbitrary positions constrained by calculated invariant points and by the observed mineral assemblages reported above.

   Figure 5 shows that at 600°C and 1 kbar, euclase is not stable with respect to chrysoberyl and beryl, while at 400°C, all three Be–Al silicates have stability fields on such a diagram. Whether tugtupite is stable with respect to chkalovite and sodalite at 600°C is not clear – it may well be that at these temperatures, tugtupite is only stable at extremely (unrealistically?) high $Be^{2+}/(H^+)^2$ and/or Na^+/H^+ activity ratios, or that it is not stable at all. At 400°C, the best temperature estimate for tugtupite formation, the Be–Al silicates are replaced by sodalite or tugtupite when the Na^+/H^+ activity ratio exceeds about 10^8, while the Be concentration in the fluid appears to be of only marginal importance for this reaction. The diagrams of Fig. 5 also clearly show that phenakite is expected to be a stable phase in the Ilímaussaq Be mineral assemblages both at 600°C and at 400°C – with the exception of extremely high Na^+/H^+ activity ratios. However, this evaluation at 600°C depends critically on the position of the chkalovite saturation line for which no real constraints exist at this temperature. At 400°C, phenakite should be associated with tugtupite (see Fig. 5B) but probably, in the presence of significant amounts of Zn and S in the fluid, genthelvite is stable with respect to phenakite (Burt 1988). However, genthelvite has only rarely been observed at Ilímaussaq.

4. The combined importance of both SiO_2 and $Be^{2+}/(H^+)^2$ activity ratio at fixed Na^+/H^+ activity ratio and fixed fluid composition for the stability of both chkalovite and tugtupite is investigated in Fig. 6 for a temperature of 400°C. This diagram again combines quantitatively calculated stability field boundaries and saturation lines with ones not calculated but fixed at an arbitrary, but reasonable, position and with correct slope. The salinity of the fluid appears to be of surprisingly little importance for the stability of the NaCl-bearing mineral tugtupite. Silica activity, in contrast, is of much greater importance, as is the $Be^{2+}/(H^+)^2$ activity ratio. This diagram indicates that the assemblage of tugtupite and albite should also contain phenakite as a stable Be phase at silica activities above $10^{-0.4}$.

   The diagrams of Fig. 7 show the qualitative phase relations among the Al-free Be silicates. Here, no quantitative constraint can be put on the site of the invariant point, where phenakite, chkalovite and epididymite or eudidymite are stable together. However, the slopes of the corresponding univariant reaction curves can be readily calculated from reaction stoichiometry (see Table 3). Phenakite is stable at the highest $Be^{2+}/(H^+)^2$ activity ratios, chkalovite at the highest Na^+/H^+ activity ratios and epididymite or eudidymite at the highest SiO_2 activities.
5. Bertrandite stability was calculated according to the reaction:

$$\text{bertrandite} = 2\ \text{phenakite} + H_2O$$

   at 1 kbar. At this pressure, this reaction lies at about 220°C (see also Markl & Schumacher 1997). This means that the occurrence of bertrandite is clear proof of the circulation of low-temperature hydrous fluids in the Ilímaussaq rocks. It is assumed that the formation of beryllite and sphaerobertrandite (Semenov & Sørensen 1966; Andersen 1967) is also related to these low-temperature hydrous fluids.

6. The compatibility of the various Be mineral assemblages observed in various granitoid rock types can

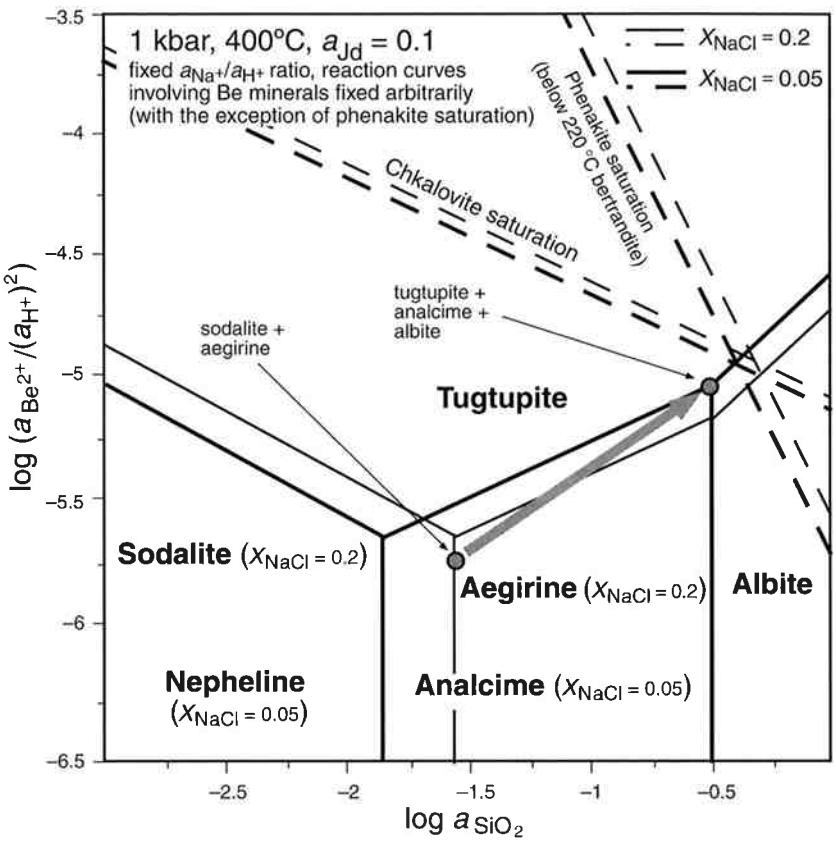


Fig. 6. Activity–activity diagram at 1 kbar and 400°C constraining the stability of various Be minerals with regard to various Be-free minerals in equilibrium with fluids of variable salinity. Note that only phenakite saturation and the vertical field boundaries among the Na–Al silicates are thermodynamically calculated, the other lines are fixed at arbitrarily chosen invariant points. The grey arrow represents a possible fluid evolution path at constant temperature which would lead to tugtupite formation. Note that everything above the saturation lines are only metastable extensions.

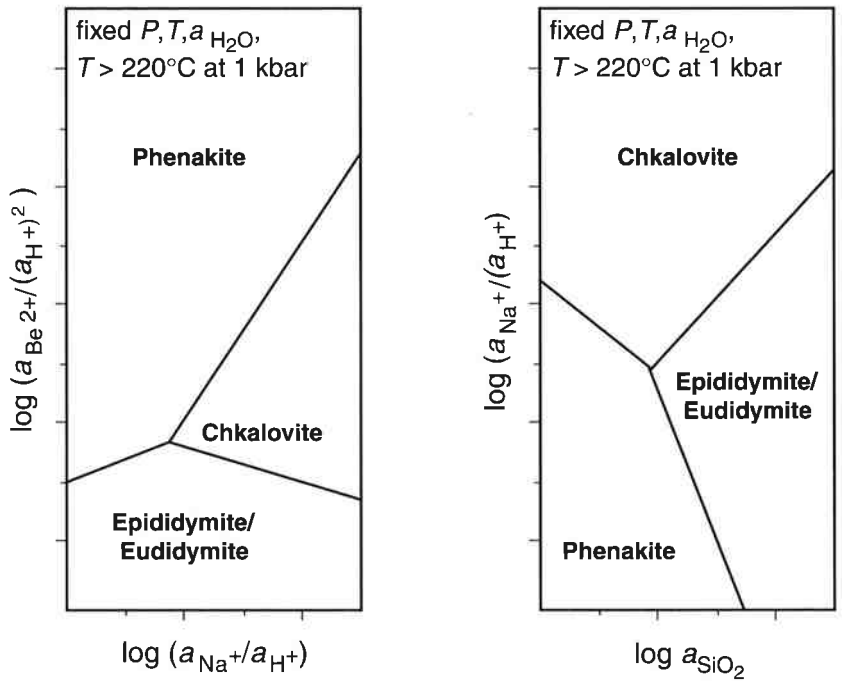


Fig. 7. Qualitative activity–activity diagrams representing the stability relations among various Al-free Be silicates. Note that the slopes are correctly calculated from reaction stoichiometry.

also be illustrated in another way. Figure 8 shows two SiO_2–Na_2O–BeO triangles with the inferred Be mineral associations at 'higher' (e.g. 600°C) and 'lower' (e.g. 200°C) temperature. These diagrams are projections from albite and an H_2O–NaCl fluid, and in this projection euclase and chrysoberyl cannot be plotted. At higher temperatures, chkalovite is stable with sodalite and, possibly, with phenakite. If stable at these high temperatures, the assemblage epididymite or eudidymite with phenakite would effectively render the co-existence of chkalovite with beryl impossible. Beryl, however, should be stable with phenakite and with epididymite/eudidymite. Tugtupite appears not to be stable at these high temperatures. All these constraints appear to agree with natural occurrences. At lower temperatures, phenakite is replaced by bertrandite, and beryl and chkalovite may become unstable depending on the exact details of the chemical environment. Tugtupite as well as epididymite/eudidymite may form by various reactions involving chkalovite, phenakite and sodalite. Under these conditions, tugtupite may form a stable assemblage with epididymite/eudidymite and bertrandite (or, at temperatures above 220°C, with phenakite). Epididymite/eudidymite may be in equilibrium with beryl and bertrandite (or phenakite).

Discussion

Stability of Na-bearing versus Na-free Be silicates

The very pronounced differences in Be mineral assemblages in peralkaline versus calc-alkaline granitoid rocks can be explained in terms of fluid chemistry which is also an approximate monitor of the melt chemistry. Na-bearing Be silicates only appear in peralkaline or alkaline rocks (Fig. 8), whereas calc-alkaline intrusives are characterised by Be- or Be–Al silicates without Na. Chkalovite and tugtupite appear to be restricted to peralkaline rocks (i.e. fluids with extremely high Na^+/H^+ activity ratios, Fig. 5), whereas epididymite and eudidymite are indicative of moderately alkaline rocks or fluids forming a link to beryl-bearing assemblages. Epididymite and eudidymite are especially indicative of higher silica activities than those observed in agpaitic rocks (Fig. 7). Phenakite at high and bertrandite at low temperatures are stable in both alkaline and calc-alkaline environments, unless helvite-group minerals replace them due to the presence of additional components such as Mn, Zn or S (e.g. Burt 1988). Chrysoberyl is principally expected to be stable at low SiO_2 activities and in high Al environments but obviously requires additionally either very high tem-

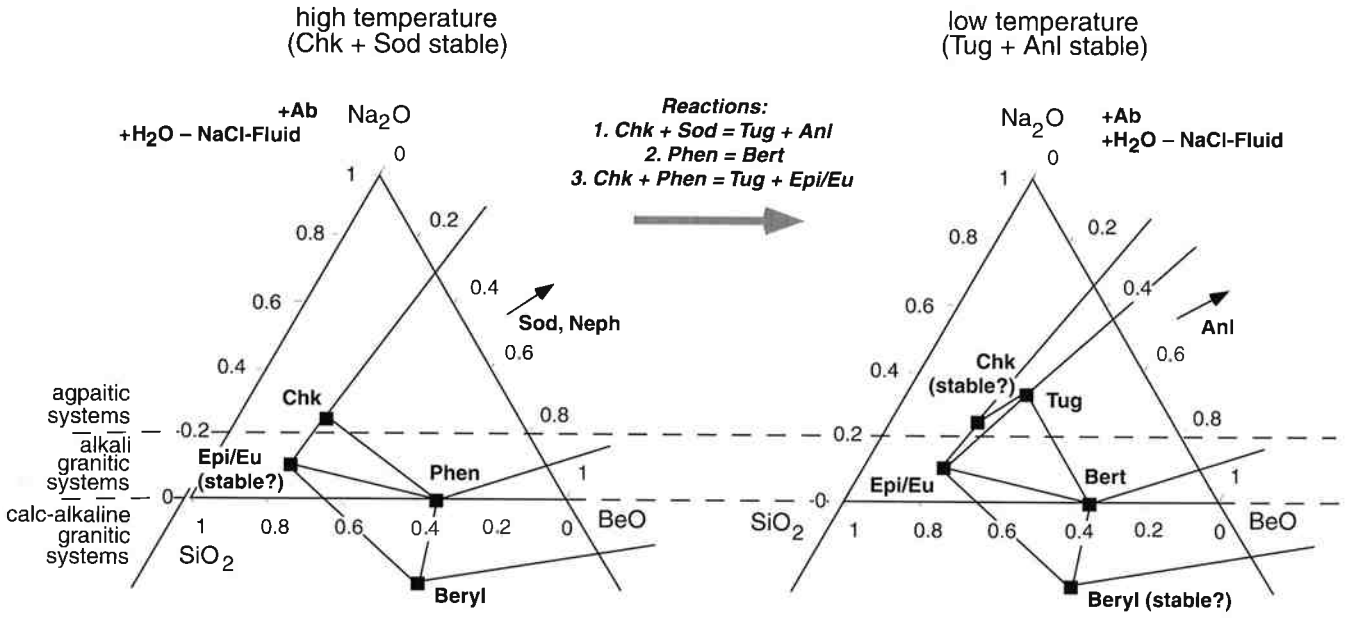


Fig. 8. Phase relations in the Be–Na–Al–Si–O–H–Cl system projected from albite (**Ab**) and a binary NaCl–H_2O fluid (variable salinity has no effect on depicted phase relations). At high temperatures (e.g. 600°C, **left diagram**), chkalovite (**Chk**) + phenakite (**Phen**) + sodalite (**Sod**) or nepheline (**Neph**) form a stable assemblage. Chkalovite + beryl is not stable if epididymite/eudidymite (**Epi/Eu**) is a stable phase at these temperatures. At lower temperature (e.g. 200°C, **right diagram**), chkalovite and beryl may no longer be stable, bertrandite (**Bert**) replaces phenakite, and tugtupite (**Tug**) forms by various reactions. Tugtupite should be stable with both epididymite/eudidymite and bertrandite as well as analcime (**Anl**).

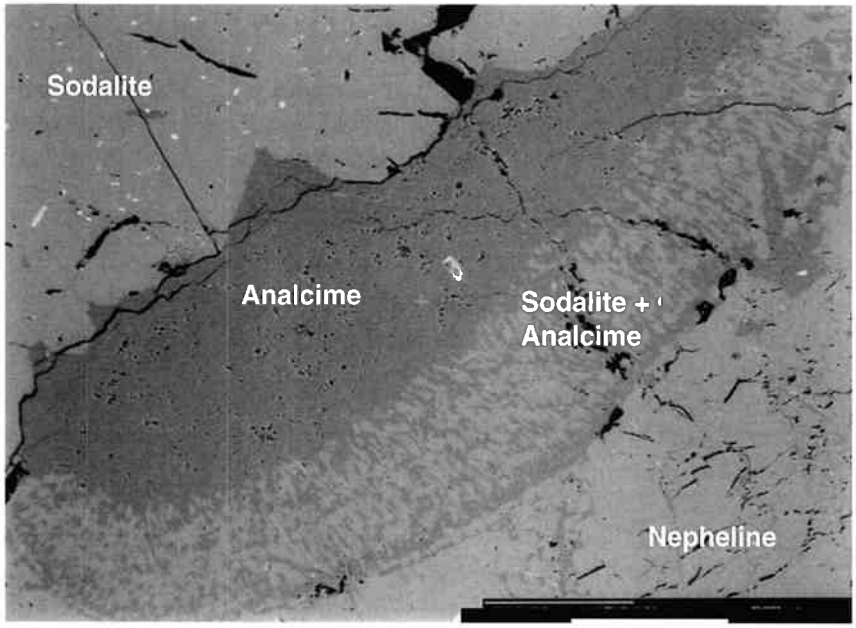


Fig. 9. Reaction textures from an Ilímaussaq sodalite foyaite in which a primary grain boundary between sodalite (upper left) and nepheline (lower right) is replaced by analcime and an analcime + sodalite symplectite. See text for discussion. Scale bar 200 μm. Author's sample GM 1346.

peratures or very low Na^+/H^+ activity ratios, or both, to be stable. Natural occurrences appear to be confined to high-grade metamorphic rocks or metamorphosed pegmatites of low SiO_2 and low Na content (e.g. Franz & Morteani 1984).

Stability of tugtupite versus chkalovite

The above considerations indicate four possible causes for the conversion from chkalovite- to tugtupite-bearing assemblages: decrease of temperature, increase of a_{SiO_2}, increase of $a_{Be^{2+}}/(a_{H^+})^2$, and increase of a_{H_2O} (= decrease of X_{NaCl}).

All available field observations, fluid inclusion studies and phase equilibrium considerations detailed above indicate decreasing temperature during formation of the various Be–silicate assemblages and during conversion from chkalovite to tugtupite-bearing assemblages. Furthermore, fluid inclusions provide evidence for the existence of very water-rich fluids at temperatures in agreement with tugtupite formation estimates. The net reaction connecting the chkalovite and the tugtupite assemblages is:

$$2 \text{ chkalovite} + 2 \text{ sodalite} + 4\ H_2O + 6\ SiO_2 = 1 \text{ tugtupite} + 4 \text{ analcime}.$$

At Ilímaussaq this reaction appears to occur around 400°C at SiO_2 activities around 0.1 (see Figs 3, 4) and with fluids of high H_2O activity. Sobolev *et al.* (1970) reported high salinities of about 21 wt% NaCl equivalent in primary fluid inclusions in tugtupite, while primary as well as secondary hydrous fluid inclusions in various minerals from various lujavrite samples record very low salinities in the 3–5 wt% NaCl equivalent range (Sommer 1999; Markl *et al.* in press). Sobolev *et al.* (1970) also report CO_2 as an important species in the gas phase of these inclusions, but CO_2 has never been reported by anyone else in any fluid inclusion from the entire Ilímaussaq alkaline complex, where methane is generally the most important species in any gaseous inclusion. Hence, the data of Sobolev *et al.* (1970) are considered with some caution – perhaps the fluid inclusions in tugtupite leaked H_2O and were oxidised during later cooling, which would explain both their increased salinity and the CO_2.

However, consideration of the tugtupite-forming reaction above and comparison with a reaction texture from a different Ilímaussaq rock, a sodalite foyaite (Schwinn 1999), offers a possible explanation compatible with the observation of fluid inclusions of both low and high salinity in the late magmatic stages of the Ilímaussaq complex. This texture in the sodalite foyaite is shown in Fig. 9. There, sodalite and nepheline crystals co-existed at high temperatures. At lower temperatures, an obviously H_2O-rich fluid infiltrated the rock along its grain boundaries and converted both sodalite and nepheline to analcime. The reaction zone consists of a zone of pure analcime close to sodalite, and a zone of symplectic intergrowth of analcime and sodalite close to nepheline. This texture is interpreted to reflect changes in salinity during analcime growth:

while the starting fluid was H_2O-rich and therefore formed only analcime, it became progressively more saline due to consumption of H_2O and liberation of NaCl from dissolving sodalite, until the salinity was so high that both analcime and a second generation of sodalite were precipitated in a symplectic intergrowth. This texture in the sodalite foyaite very likely formed during a late-stage auto-metasomatic event similar to the events that led to the formation of the analcime–tugtupite assemblages in the late veins, and hence a similar mechanism may have operated there. In the late veins, sodalite was dissolved along with chkalovite, rendering the fluid successively Be and NaCl rich, while analcime precipitated. At a certain level of Be and NaCl enrichment, tugtupite began to crystallise and enclosed some samples of the more saline fluid which Sobolev *et al.* (1970) found. While this does not explain their report of CO_2, this mechanism shows how the Cl-rich mineral tugtupite could grow during influx of a hydrous, low-salinity fluid into sodalite-bearing rocks. The pre-existence of sodalite may even be a prerequisite for tugtupite formation – the similarity of their crystal structures and chemical formulae (tugtupite = sodalite + $Be_2Si_2Al_{-4}$) may also facilitate the chemical conversion of one into the other (see also Burt 1991).

Nature of the fluids in late-magmatic, agpaitic systems

One type of primary fluid inclusions in lujavrites and most secondary fluid inclusions in lujavrite and all other rock types contain a hydrous fluid with about 3 wt% NaCl equivalent (Schwinn 1999; Sommer 1999; Markl *et al.* in press). In rare examples, hydrous fluid inclusions of higher salinity have been found in these rock types and also in tugtupite and chkalovite (Sobolev *et al.* 1970; Konnerup-Madsen & Rose-Hansen 1982), and these may be fluids whose compositions were modified during interaction with sodalite-bearing rocks as detailed above. The possible existence of late-stage immiscible hydrocarbon-bearing fluids (Konnerup-Madsen 2001, this volume) does not alter the results of the present contribution because the aqueous fluid would still approximately behave as a binary H_2O–NaCl system.

If one considers the low-salinity hydrous fluids to be the typical late-stage fluids of agpaitic rocks (which at least for Ilímaussaq appears to be reasonable), these fluids have one very distinctive feature: they obviously have an anomalously high pH, as indicated by the stability of ussingite ($NaAlSi_3O_8$ NaOH) and as indicated by the extremely high Na^+/H^+ and $Be^{2+}/(H^+)^2$ activity ratios calculated for the stability of the observed assemblages. Interestingly, experimental mixtures of andalusite, paragonite and H_2O develop extremely high pH at temperatures in the 400°C range (L. Baumgartner, personal communication 2000) which is probably caused by the interplay between aluminosilicate dissociation (which consumes H^+ ions) and formation of strong Na-silicate complexes (which replace NaOH-complexes more stable at higher temperatures). These features, however, may only be developed in hydrous fluids with a high Na/(Na+K) ratio and with very low CO_2 contents, such as in agpaitic fluids. The high pH in these fluids creates, at moderate Be and Na ion activities, the extremely high pH-normalised activities which, in turn, give rise to the formation of the observed Be silicates. Neither the absolute Be nor the absolute Na contents in agpaitic fluids have to be very high, if the pH is as high as indicated. In conclusion, the unique mineralisation of agpaitic magmatic rocks and the formation of exotic hyper-agpaitic, water-soluble minerals (e.g. Sørensen & Larsen 2001, this volume) may be an effect of the low oxidation state, low water activity and high Na/(Na+K) ratio of the parental magma which renders formation of a hydrous, CO_2-poor, K-depleted, high-pH fluid phase possible in the very late stages of magmatic evolution.

Conclusions

Na-bearing Be minerals in the peralkaline Ilímaussaq alkaline complex, South Greenland, formed during cooling and chemical evolution of agpaitic, late-magmatic liquids and fluids in the temperature range 600–200°C. The earliest mineral to form was chkalovite which was successively replaced by tugtupite (in large quantities) and some rare Be silicates in small quantities. Qualitative and quantitative estimates of conditions and chemical parameters during formation indicate that the early assemblages crystallised from liquids (or fluids) of high salinity, while the replacement occurred later during influx of a hydrous fluid of low salinity. Neither high Be nor high Na contents are necessary to explain the observed mineral assemblages, but the high pH of late agpaitic fluids, as demonstrated by the occurrence of the NaOH-bearing silicate ussingite, appears to be responsible for high metal ion/H^+ activity ratios in the late stage fluids. High pH and high Na/(Na+K) ratios appear to be responsible for the distinct

differences in Be mineral assemblages between peralkaline, alkaline and calc-alkaline granitoid rocks.

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

Jens Konnerup-Madsen

Fluid inclusions in minerals from agpaitic nepheline syenites and hydrothermal veins in the Ilímaussaq complex and in similar agpaitic complexes on the Kola Peninsula, Russia, are dominated by hydrocarbon gases (predominantly methane) and hydrogen. Such volatile compositions differ considerably from those of most other igneous rocks and their formation and entrapment in minerals reflects low oxygen fugacities and a wide range of crystallisation temperatures extending to a low-temperature solidus. Their composition reflects initial low carbon contents and high water contents of the magma resulting in the exsolution of a water-rich CO_2–H_2O dominated vapour phase. Fractionation of chlorides into the vapour phase results in high salinities and the subsequent development of a heterogeneous vapour phase with a highly saline aqueous-rich fraction and a methane-dominated fraction, with preferential entrapment of the latter, possibly due to different wetting characteristics. The light stable isotope compositions support an abiogenic origin for the hydrocarbons in agpaitic nepheline syenite complexes.

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

One method of obtaining information on the gases is to study the volatiles trapped and preserved as fluid inclusions in minerals during solidification of the melts. This paper is a review of available data on the compositional characteristics of the hydrocarbon-rich fluid inclusions in the Ilímaussaq alkaline complex.

The Ilímaussaq complex

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

An initial temperature of about 900°C, a pressure of 1–2 kbars and contents of H_2O around 4 wt% at emplacement and initial cooling of the main Ilímaussaq magma were suggested by Larsen & Sørensen (1987), indicating initial volatile undersaturation. During solidification of the magma, oxygen fugacities were well below the synthetic QFM buffer (Larsen 1976) and ac-

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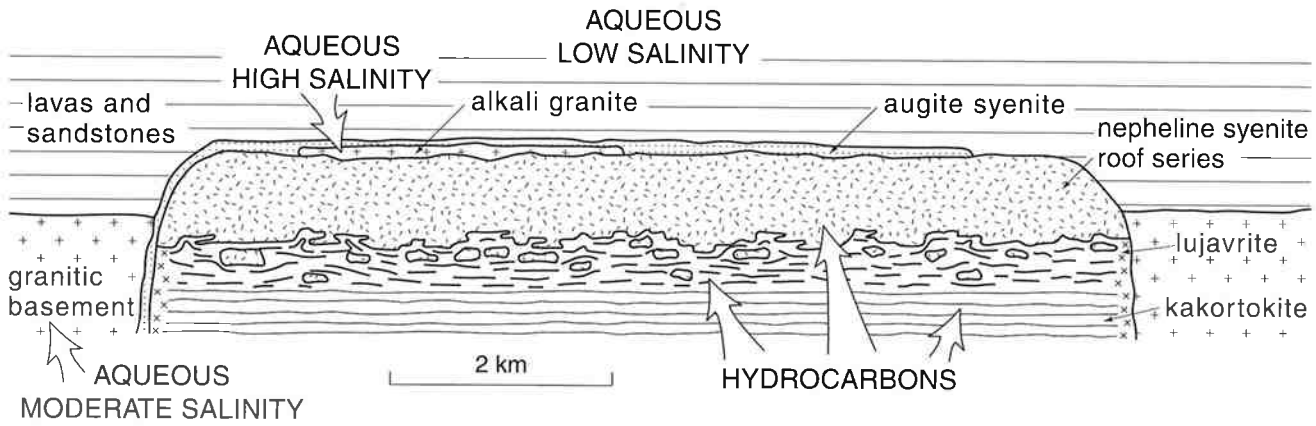


Fig. 1. Simplified E–W cross-section through the Ilímaussaq alkaline complex. Fluid types trapped in minerals in the various rock types are indicated. Same horizontal and vertical scale. From Konnerup-Madsen (1980).

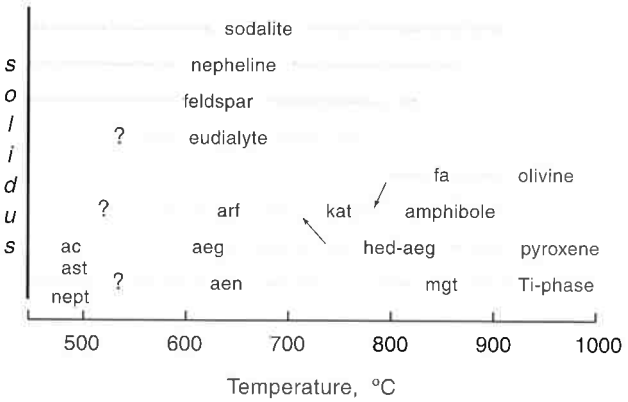


Fig. 2. Sequence of crystallisation of minerals in Ilímaussaq roof cumulates. Modified from Konnerup-Madsen *et al.* (1981). Abbreviations: **ac**: acmite, **aen**: aenigmatite, **arf**: arfvedsonite, **ast**: astrophyllite, **fa**: fayalite, **hed-aeg**: hedenbergite-aegirine, **kat**: katophorite,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

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

Types of fluid inclusions

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

Hydrocarbon-rich gaseous inclusions predominate in all examined minerals from the Ilímaussaq nepheline syenites and late hydrothermal veins formed from

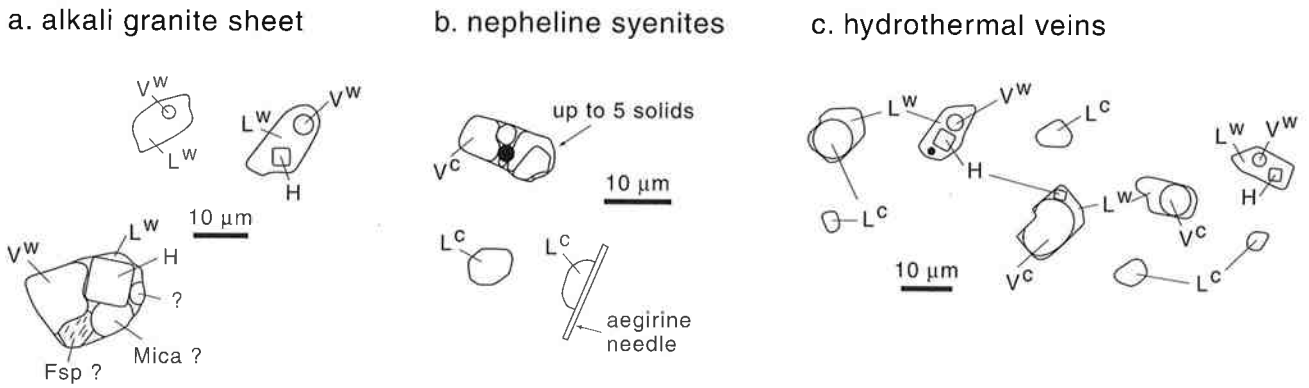


Fig. 3. Sketches of the main types of fluid inclusions in minerals from the Ilímaussaq rocks. **a**: alkali granite sheet, **b**: nepheline syenites, and **c**: late hydrothermal veins. Length of bar is 0.01 mm. Abbreviations: $\mathbf{L^w}$ and $\mathbf{V^w}$: liquid and vapour H_2O, respectively; **H**: halite; $\mathbf{L^c}$ and $\mathbf{V^c}$: liquid and vapour hydrocarbons, respectively; **Fsp**: feldspar. Modified from Konnerup-Madsen & Rose-Hansen (1982).

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

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

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

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

The distribution of fluid inclusion types summarised above – and in particular the lack of hydrocarbon-bearing inclusions outside the nepheline syenites and their associated hydrothermal veins (Fig. 1) – strongly supports an interpretation where the hydrocarbons represent the remains of an associated magmatic volatile phase produced during the cooling and solidification of the alkaline magma, rather than a phase introduced from outside the complex. Similar observations have been made on hydrocarbon gases in minerals from the Khibina and Lovozero complexes on the Kola Peninsula, Russia, and a similar origin was proposed by Kogarko (1977), Petersil'ye & Pripachkin (1979) and more recently by Potter *et al.* (1997).

Chemical characteristics of the Ilímaussaq gases

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

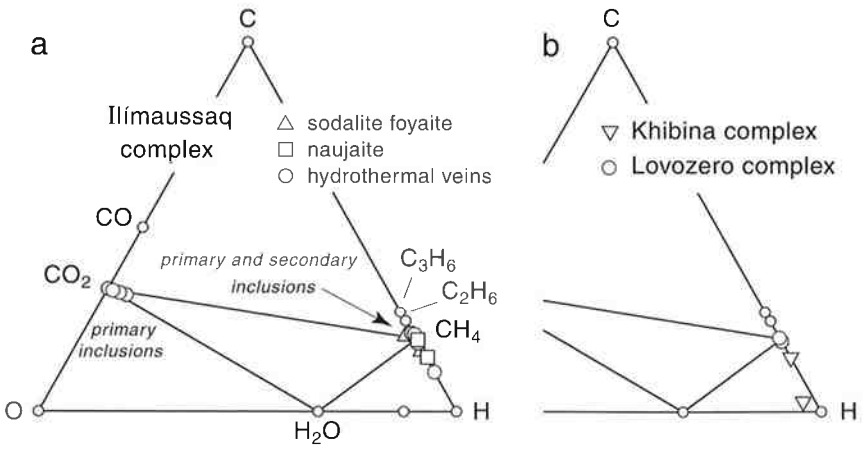


Fig. 4. C–O–H molecular relations for gases released by crushing of minerals and agpaitic rock types from **a**: Ilímaussaq, and **b**: Khibina and Lovozero complexes. Recalculated on a water-free basis. Data from Petersilie & Sørensen (1970), Sobolev *et al.* (1970) and Konnerup-Madsen *et al.* (1981).

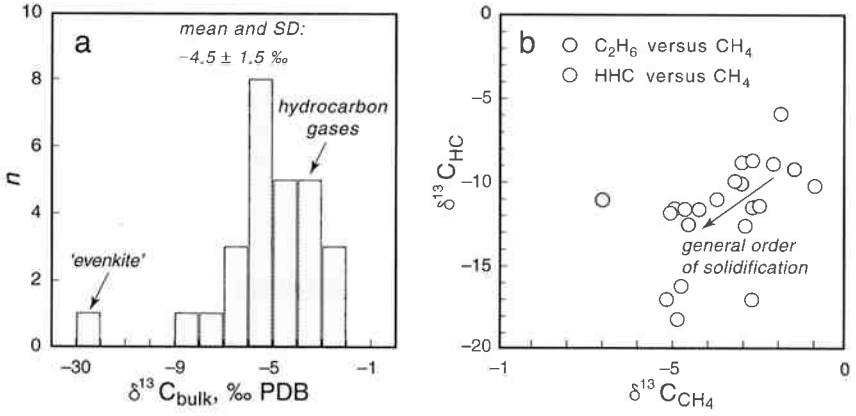


Fig. 5. $\delta^{13}C$ (in ‰ PDB) of the bulk hydrocarbon gases in fluid inclusions from Ilímaussaq rocks and minerals. **a**: Histogram of $\delta^{13}C$ values of the bulk hydrocarbon gases in fluid inclusions and of the mineral evenkite from Ilímaussaq. ***n*** is number of analyses. Data from Konnerup-Madsen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

from minerals and whole rocks from the Khibina and Lovozero alkaline complexes (Fig. 4b) are very similar to those of the Ilímaussaq complex (Fig. 4a).

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

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

Stable isotope characteristics of the hydrocarbon gases

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

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

In summary, the $\delta^{13}C$ characteristics of the hydrocarbon gases in the Ilímaussaq complex (and in similar complexes from the Kola Peninsula) support the concept of an abiogenic formation of methane from a

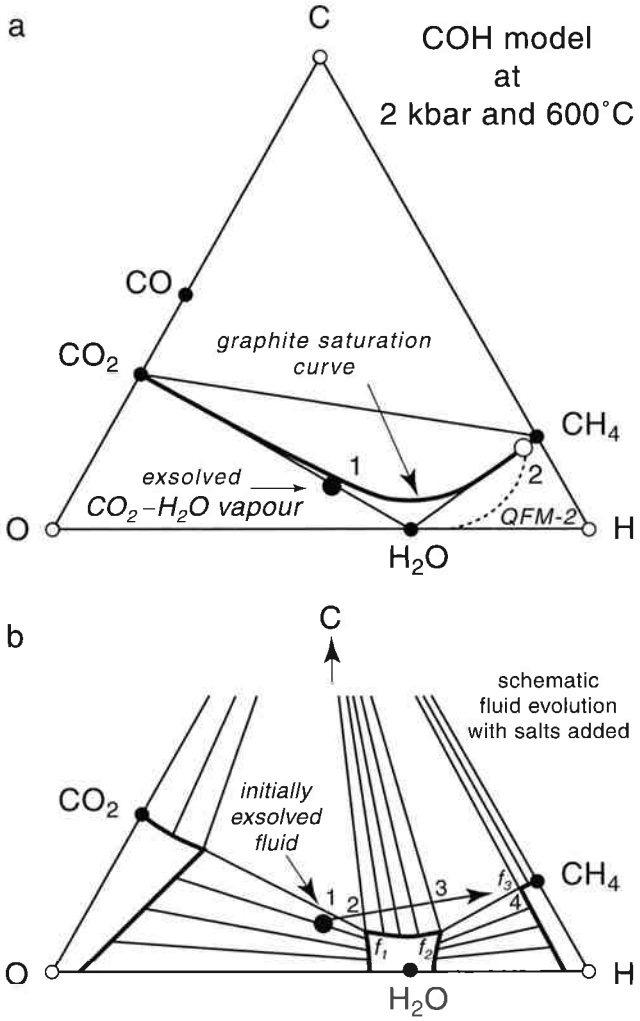


Fig. 6. **a**: Isobaric and isothermal ternary C–O–H diagram at 2 kbar and 600°C. Shown is the graphite saturation curve and the compositional trace (**stippled**) in the graphite-absent part for an oxygen fugacity of QFM –2. The estimated composition of the initially exsolved CO_2–H_2O fluid from the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

COH vapour-saturated, highly reduced melt. Condensation of part of the methane-rich gas phase at relatively low temperatures to higher hydrocarbons during post-entrapment cooling conceivably occurred and produced the hydrocarbon gas compositions observed. The bulk gas $\delta^{13}C$ values furthermore indicate a predominantly juvenile origin for the carbon component.

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

Volatiles during solidification of the agpaitic Ilímaussaq nepheline syenites

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

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

Initial H_2O and C contents of the main Ilímaussaq magma of about 4 wt% H_2O (Larsen & Sørensen 1987) and 250 ppm C (J.C. Bailey, personal communication 1999) would result in vapour saturation at close to 2 kbars and the exsolution of a CO_2–H_2O rich fluid with X_{H2O} of about 0.7 (Holloway & Blank 1994; Fig. 6a, large filled circle). As oxygen fugacities about 2 log units below the synthetic QFM buffer reaction (QFM – 2) are indicated (Larsen 1976), this fluid buffering would result in a change in bulk fluid composition from the initially exsolved through composition 1 to composition 2 of Fig. 6a according to the reaction (1)

$$CO_2 + 2H_2O \rightarrow CH_4 + 2O_2 \qquad (1)$$

until a composition in accordance with the imposed oxygen fugacity is obtained (Fig. 6a point 2 for QFM – 2). As this change in bulk fluid composition to 2 occurs along the graphite saturation curve, some graphite should be precipitated. Graphite has not been observed in the Ilímaussaq rocks; however, the amounts precipitated, according to this change in composition, would be trivial and could easily go undetected (total exsolution of 0.9 wt% CO_2 would result in a maximum

precipitation of about 10^{-3} vol.% graphite). That these fluids are actually capable of precipitating graphite is indicated by the occasional observation of a thin film of poorly ordered graphite on the inclusion walls by Raman microprobe spectrometry.

The additional presence in the Ilímaussaq magma of at least 0.5 wt% Cl (Larsen & Sørensen 1987) would, however, result in high salinities of the exsolved aqueous fluid (Kilinc & Burnham 1972) and the formation of two immiscible fluid phases, one rich in CH_4, the other rich in H_2O plus chlorides (Lamb *et al.* 1996). The high contents of F (up to about 1 wt%; J.C. Bailey, personal communication 1999) in the Ilímaussaq magma would not affect the composition of the vapour phase as F is strongly partitioned into the melt (Carroll & Webster 1994).

The immiscibility resulting from the addition of chlorides to the vapour would further enrich the salinity of the aqueous fluid fraction to high values in agreement with the fluid inclusion observations. The compositional evolution during buffering of such an exsolved heterogeneous fluid mixture is shown schematically in Fig. 6b. The compositional change of exsolved *bulk* fluid composition is shown by the arrow from 1 to 4 whereas the compositional change of the *aqueous* fluid co-existing with the precipitated graphite follows the path from f_1 to f_2. Upon final equilibration, the immiscible fluids would have compositions f_2 (aqueous fluid) and f_3 (hydrocarbonic fluid). The minerals may have had a possible catalytic effect and contributed to the formation of some of the higher hydrocarbons and hydrogen from methane at lower temperatures.

The features of Fig. 6 demonstrate that although the fluid which initially exsolved was rich in CO_2 and H_2O, buffering of this fluid to low temperatures at low oxygen fugacities would result in a CH_4-rich fluid co-existing with a highly saline, aqueous fluid. The fluid inclusion observations suggest that preferential entrapment of the CH_4-rich fluid occurred, probably as a result of preferential wetting characteristics or as a result of re-dissolution of the aqueous fraction upon further development of the residual melt. The characteristics of Fig. 6 further indicate that variations in the CO_2/CH_4 ratio can result from variations in the initial CO_2/H_2O ratio of exsolved fluid (that is, initial C and H_2O contents of the melt) and imposed oxygen fugacities. The range in COH compositions shown in Fig. 4 may reflect the interplay between these parameters. Finally, the lack of observed graphite in the Ilímaussaq complex may be due to a high water content relative to carbon in the melt.

Origin of the carbon component

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

Based upon the available data for $\delta^{13}C$ and äD values of hydrocarbons in the Ilímaussaq complex and published fractionation factors for $\delta^{13}C$ and δD, the composition of an evolved COH-vapour in equilibrium with the melt may be modelled (Fig. 7). For ini-

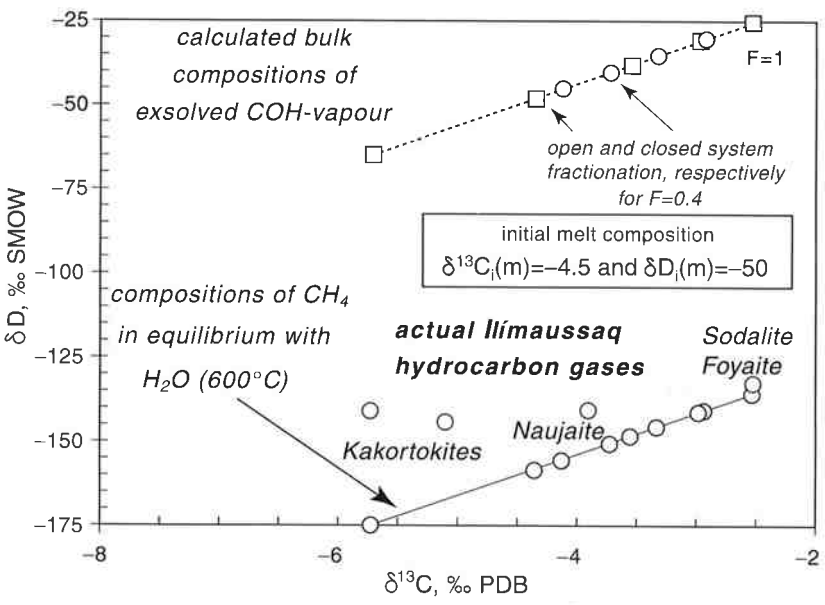


Fig. 7. δD (in ‰ SMOW) versus $\delta^{13}C$ (in ‰ PDB) of hydrocarbon gases released on crushing of various rock types from the Ilímaussaq complex compared to the fluids considered associated with the generation of hydrocarbons in the Ilímaussaq complex. Initial model compositions (m) of δD and $\delta^{13}C$ in the melt are indicated in the inset box. The change in isotopic composition of bulk exsolved COH fluid is shown by the **upper curve** for both closed (**circles**) and open (**squares**) system fractionation (F: fraction remaining in melt; **F = 1** marks the composition of the first exsolved fluid). The **lower curve** indicates the isotopic composition of CH_4 unmixed from the COH bulk fluid at the temperature indicated in the diagram and assuming total conversion of CO_2 to CH_4. Diagram constructed on the basis of data from Taylor (1986).

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

Conclusions

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

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A note on the occurrence of gold in the Ilímaussaq alkaline complex, South Greenland

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Single grains of gold measuring 22 µm have been found in analcime veinlets intersecting concentrations of pyrrhotite, pyrite and marcasite in the lowermost part of layer +16 red of the kakortokite sequence in the southernmost part of the Ilímaussaq alkaline complex (Davison 1989). The kakortokite sequence consists of a repetition of units of lower black layers rich in arfvedsonite, red layers rich in eudialyte and white layers rich in microcline (cf. Sørensen 2001, this volume, for a review of the geology of the Ilímaussaq complex). Layer +16 red is the most prominent eudialyte-rich layer of the complex. The identification of the gold grains was verified by SEM - Energy dispersive X-ray analysis (Fig. 1).

Flotation concentrates of the sulphide minerals show 8.8 g/t gold (Davison 1989). A number of kakortokite samples have been analysed for gold by atomic absorption spectrometry of 5 g samples decomposed in aqua-regia, detection limit 10 ppb gold, most with a negative result (Le Couteur 1990). The samples of layer +16 red all showed < 10 ppb gold. Up to 50 ppb gold was found in layer B red of the transitional layered kakortokite (Bohse & Andersen 1981).

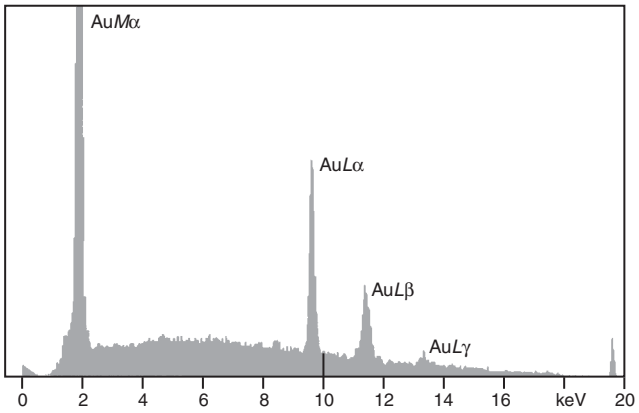


Fig. 1. Energy spectrum of native gold from analcime veinlet in kakortokite layer +16 red. The spectrum was obtained with a scanning electron microscope. From Davison (1989).

Samples of lujavrite from the Kvanefjeld area in the northern part of the complex have been analysed for gold by direct current plasma determination of metal in a fire-assay bead. Fifteen out of 42 samples gave more than 2 ppb, and the highest content found was 10 ppb (Tilsley & Fisher 1983).

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