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

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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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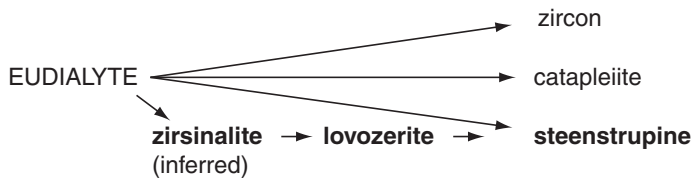
Russian mineralogists and petrologists studying the Lovozero and Khibina complexes of the Kola Peninsula introduced the term hyper- or ultra-agpaitic mineral associations and rocks in order to characterise special types of pegmatites and hydrothermal mineralisations rich in rare minerals (cf. Khomyakov 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.
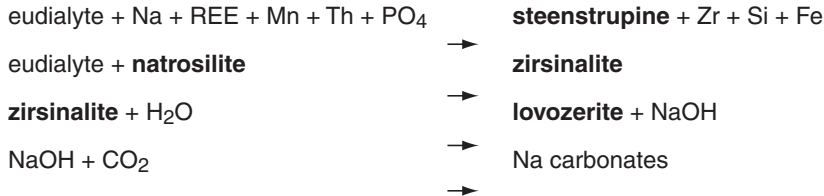
Khomyakov (1995) demonstrated that stages of increasing and decreasing alkalinity are involved in the evolution of hyper-agpaitic rocks. Three stages may be distinguished: increasing, maximum and decreasing alkalinity. This is illustrated by the succession: eudialyte in an agpaitic rock is altered into 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
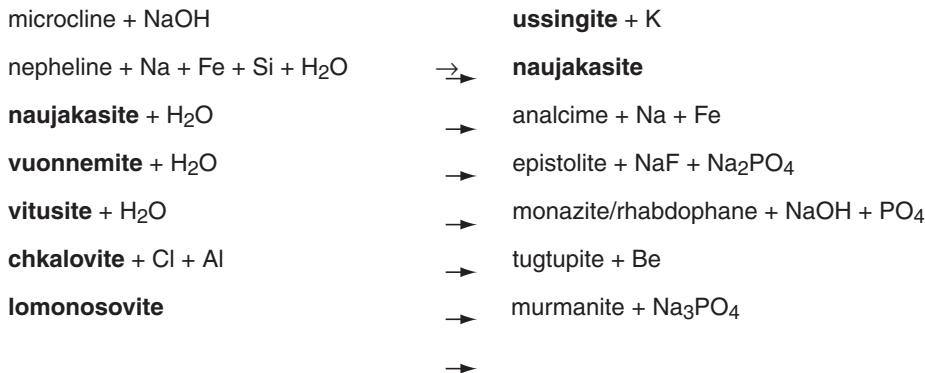
**a** *Reactions involving eudialyte*

zircon

EUDIALYTE ———————→ catapleiite

zirsinalite → lovozerite → steenstrupine
(inferred)

*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 lomonoso-vite. 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 in-creasing, maximum, and decreasing stages of alkalin-ity.

## Hyper-agpaitic mineral associations of the Ilímaussaq complex

The agpaitic nepheline syenites of the Ilímaussaq com-plex are, in order of formation: sodalite foyaite, naujaite, kakortokite and lujavrites (Ussing 1912; Sø-rensen 2001, this volume). The earliest mineral as-semblage to crystallise from the main magma was fayalitic olivine, hedenbergitic pyroxene, titanomag-netite, 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 ac-companied by an increase in alkalinity, which is seen from a series of continuous and discontinuous min-eral reactions. Fayalite, hedenbergite and titanomag-netite 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 steen-strupine. These late lujavrites are hyper-agpaitic and contain minerals such as ussingite, lovozerite, nauja-kasite, 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 petro-graphically. A number of mineral reactions are shown schematically in Fig. 1.

Three groups of hyper-agpaitic rocks may be dis-tinguished in the Ilímaussaq complex: (1) steenstru-pine 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 lovo-zerite (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 com-mon elements (Na, Fe, Al, Si) as seen from its formula (Fig. 1b). It is therefore surprising that a second oc-currence has not been found until recently. Naujakasite is a rare constituent of lovozerite-lomonosovite luja-vrites 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 nauja-kasite 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 mi-crocline and sodalite.

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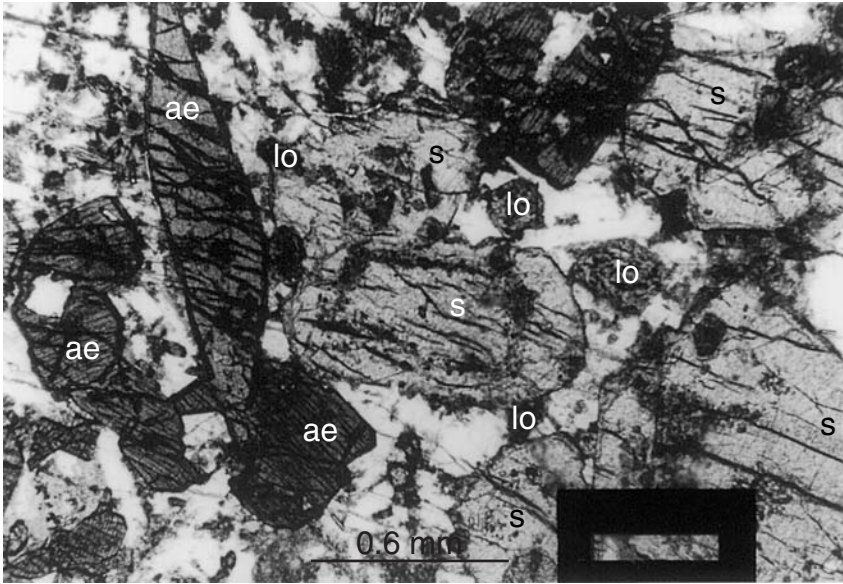
Fig. 2. Steenstrupine crystals (**s**), the one in the centre with minute inclusions of altered lovozerite outlining the original centre of the crystal. The matrix consists of microcline and ussingite (**both white**), aegirine (**ae**) and altered grains of lovozerite (**lo**), which are larger than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

aegirine, microcline, analcime (often lath-shaped indicating 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; Kho-
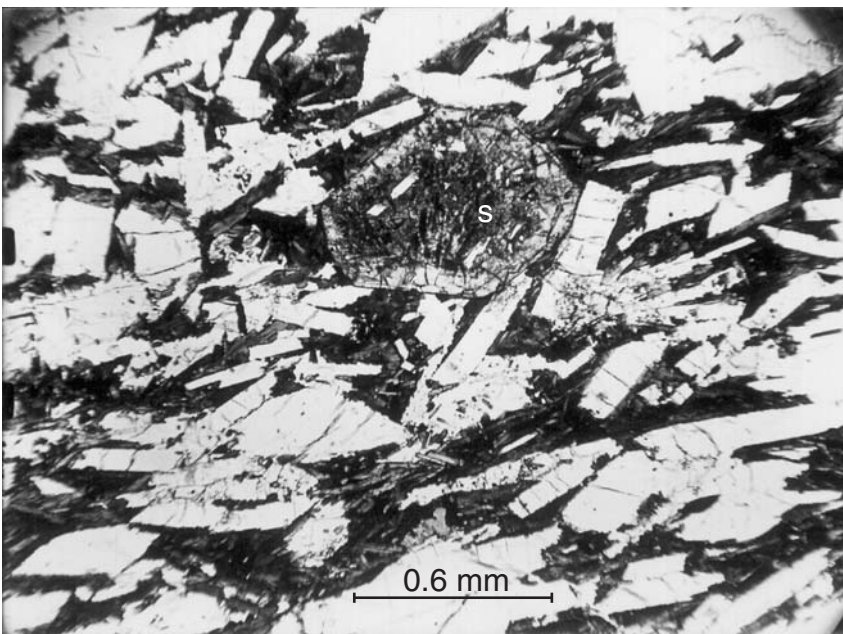


Fig. 3. Steenstrupine crystal (**s**) in lujavrite dyke made up of microcline (**light**) and arfvedsonite (**dark**). The central part of the steenstrupine crystal contains minute inclusions of microcline and arfvedsonite, much smaller than the grains of the matrix. The microcline inclusions in the 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.
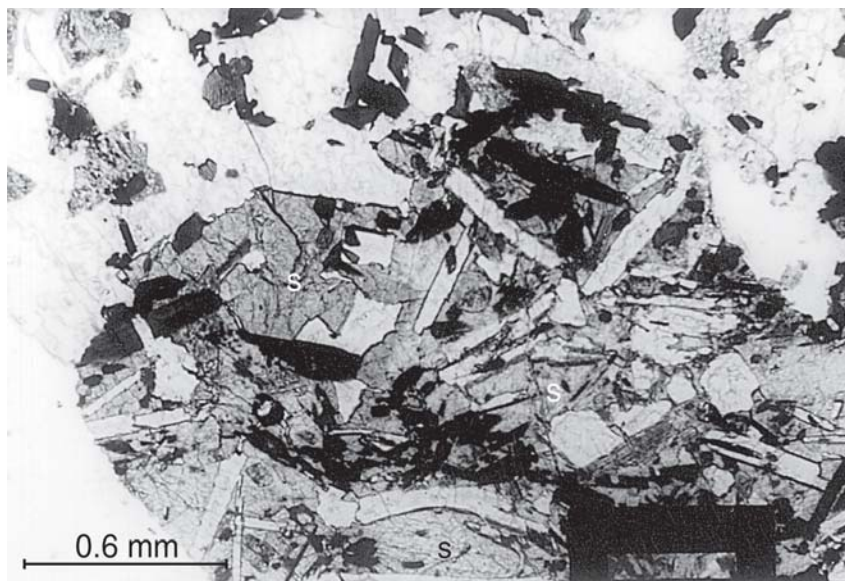
myakov *et al.* 2001, this volume), vuonnemite into epistolite (Rønsbo *et al.* 1983) and vitusite into monazite–rhabdophane–analcime (Pekov *et al.* 1997). Ussingite appears to be substituted by natrolite and analcime, and villiaumite to be dissolved out in the late- and post-magmatic stages, leaving 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



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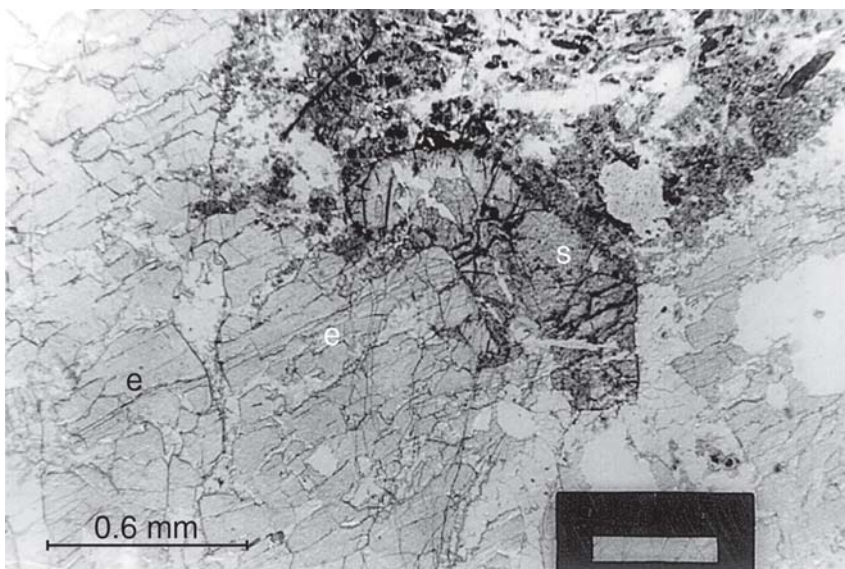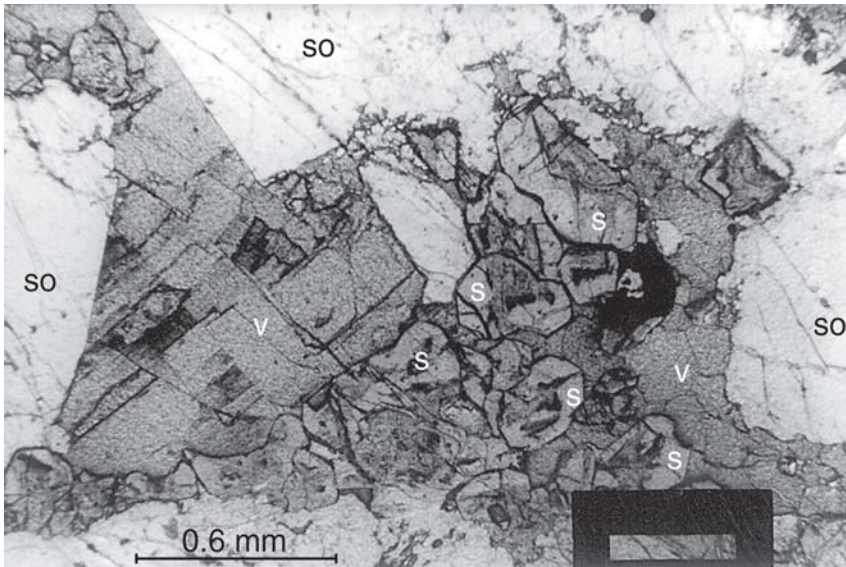
Fig. 6. Aggregate of small steenstrupine crystals (**s**) enclosed in villiaumite (**v**) filling the interstices between large grains of sodalite (**so**) which are partially replaced by analcime and natrolite. Vein in lujavrite, Kvanefjeld. Drill core 53 at 207.90 m, plane polarised light, scale bar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

lueshite, 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).
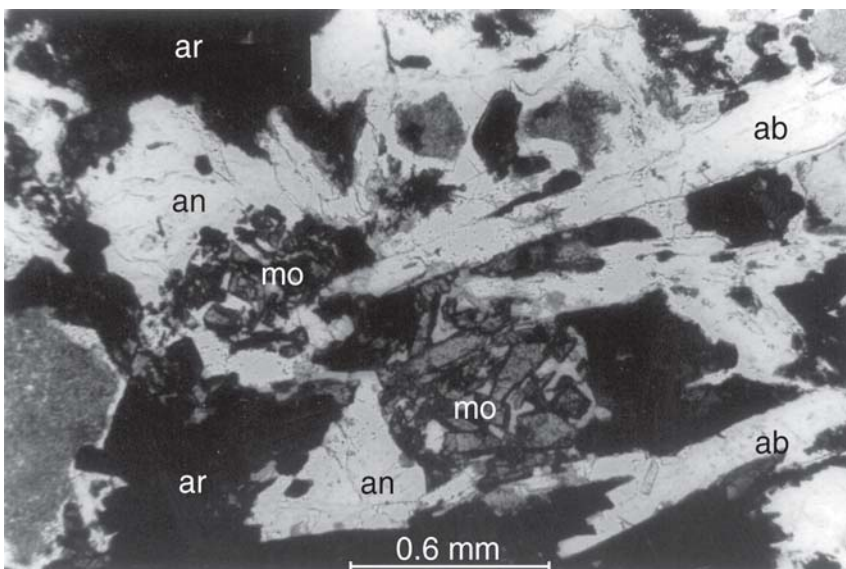


Fig. 7. Clusters of monazite crystals (**mo**) in lujavrite made up of albite (**ab**), arfvedsonite (**ar**) and analcime (**an**). Sample Geox 18, Kangerluarsuk, plane polarised light, lower right cluster measures 0.6 mm across.

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.
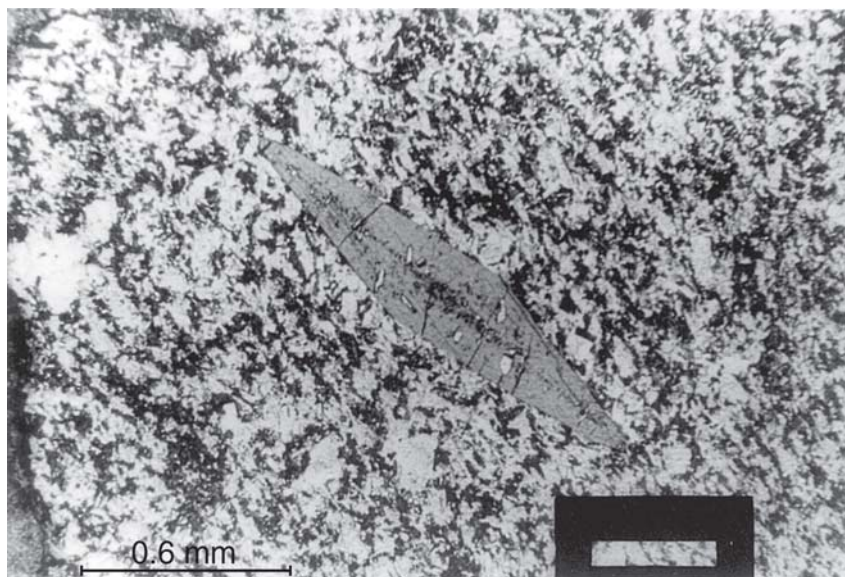
## Conditions of formation

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

content 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 substitu-tion 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, $Na_2HPO_4 \cdot 2H_2O$
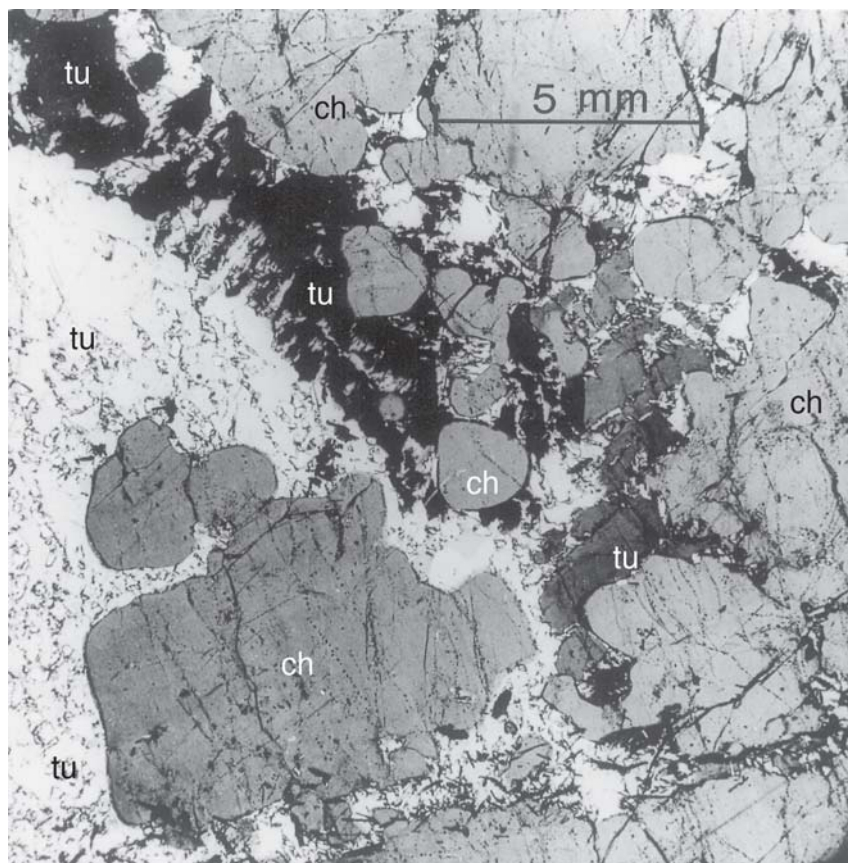


Fig. 9. Corroded grains of chkalovite (**ch**) under replacement by tugtupite (**tu**) showing penetration twinning (one set of individuals light, the other set near extinction). GGU 77450.3, Kvanefjeld, crossed polars. From Sørensen et al. (1971). Photo: Harry Micheelsen.

(Khomyakov 1995). From the Ilímaussaq complex only villiaumite (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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