The agpaitic rocks – an overview*

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Abstract

It is now generally agreed that the term 'agpaitic' should be restricted to peralkaline nepheline syenites (and phonolites) containing minerals such as eudialyte and rinkite, that is complex silicates of Zr, Ti, the rare earth elements (*REE*), and F and other volatiles. There are, however, cases of transition into more common types of nepheline syenites containing zircon, titanite, ilmenite, etc.

The agpaitic rocks are characterized by extremely high contents of rare elements such as Li, Be, Nb, Ta, *REE*, Zr, Th, etc. and of volatiles, first of all F and Cl. This gives rise to a wealth of mineral species, more than 500 in the Lovozero and Khibina complexes of the Kola peninsula, about 250 in Mont Saint-Hilaire, Quebec, Canada, and about 200 in the type locality, the Ilímaussaq complex, South Greenland.

These rocks have very long melting intervals and solidus temperatures as low as 500 to 400°C. They are accompanied by a gas phase rich in methane and other hydrocarbons and most probably also by sodium-rich fluids as indicated by the presence of minerals such as ussingite ($NaAlSi_3O_8{\cdot}NaOH$) and villiaumite (NaF) and of pegmatites and hydrothermal veins rich in sodium and rare and volatile elements.

Agpaitic nepheline syenites are considered to have been formed by consolidation of melts oversaturated in alkalis, especially sodium, under conditions preventing the volatiles from escaping. These melts have been derived by extreme fractionation processes in alkali basaltic or nephelinitic magmas. The main stage of crystallization of the melts is characterized by minerals such as nepheline (sometimes also sodalite), alkali feldspars, arfvedsonite, aegirine and eudialyte, but the most highly developed, hyperagpaitic lujavrites of the Ilímaussaq complex have been formed from melts with extreme concentrations of sodium and volatiles resulting in the formation of naujakasite instead of nepheline, ussingite instead of sodalite and alkali feldspars, and steenstrupine instead of eudialyte. During the late stages of crystallization, sodium-rich fluids are the cause of late- and postmagmatic alteration and of the formation of hydrothermal mineralizations. The late stages are characterized by water-soluble sodium-rich minerals of which more than 80 have been found in the Khibina and Lovozero complexes.

KEYWORDS: agpaitic rocks, nepheline syenite, phonolite, eudialyte, rinkite, Ilímaussaq complex.

Introduction

SOME of the characteristic minerals of agpaitic rocks, such as sodalite, arfvedsonite and eudialyte, have been known for almost 200 years. They were collected in the Ilímaussaq complex by K.L. Giesecke in 1806 and were subsequently examined by European mineralogists. The scientific study of agpaitic rocks was initiated by the expeditions of W. Ramsay to the Khibina and Lovozero complexes, the Kola Peninsula, Russia, from 1887 to 1899 and of N.V. Ussing to South Greenland in 1900 and 1908. The detailed investigation of the Khibina and Lovozero complexes began in the 1920s under the direction of A.E. Fersman and have been carried out ever since. This makes these two complexes the by far best known occurrences of agpaitic rocks.

During the last two decades a considerable amount of new information has been provided about the agpaitic rocks. Their mineralogy has been intensively studied in the Khibina and Lovozero complexes; the Ilímaussaq complex, Greenland; Mont Saint-Hilaire, Quebec, Canada and the Tamazeght complex, Morocco. This has resulted in the discovery of many new minerals bringing the total number of mineral species described from agpaitic rock to well above 500. The discovery of about 80 unstable and in part water-soluble sodium-rich minerals from the Khibina and Lovozero complexes (Khomyakov, 1990, 1995) has laid the foundation for new directions of research, including the establishment of a special group of agpaitic rocks, named ultra-agpaitic (Sokolova, 1986) or hyperagpaitic (Khomyakov, 1995).

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A considerable amount of new geochemical data, including isotopic data, has resulted in a number of papers bringing new ideas about the origin and development of agpaitic magmas. Examples are the discovery of a quenched sample of what may have been an agpaitic melt (Wolff, 1987; Wolff and Toney, 1993); the many papers by Kogarko and coworkers (1977 and later); the Poços de Caldas Project: Natural Analogues of Processes in a Radioactive Waste Repository (Chapman *et al.*, 1992); the study of deformed and metamorphosed agpaitic rocks, e.g. Curtis and Currie (1981) and Currie and van Breemen (1996), etc.

The present paper will review some of these lines of development with special emphasis on the somewhat controversial isotopic data and the special case of the hyperagpaitic stages in the evolution of agpaitic rocks as exemplified by new information about the Ilímaussaq complex.

Definition and classification

The term agpaitic was originally defined by Ussing (1912, p. 341) as follows: "if na, k and al are the relative amounts of Na-. K- and Al-atoms in the rock, the agpaites may be characterized by the equation

$$(na + k)/al \geqslant 1.2,$$

whereas in ordinary nepheline syenites this ratio does not exceed 1.1." Ussing's equation has been known as the agpaitic index, but should more correctly be termed the peralkalinity index. The term agpaitic has been applied in a number of ways and has even been used as a synonym for peralkaline (see review by Sørensen, 1974). The Subcommission on the Systematics of Igneous rocks of the International Union of Geological Sciences now recommends to restrict the term to peralkaline nepheline syenites characterized by complex Zr and Ti minerals, such as eudialyte and mosandrite (rinkite), rather than simple minerals such as zircon and ilmenite (LeMaitre, 1989). The chemical formula of the rare minerals mentioned in the text are presented in Table 1.

An agpaitic index higher than 1 is not sufficient to distinguish agpaitic rocks, as shown by the McGerrigle complex, Quebec (Wallace *et al.*, 1990) where two nepheline syenites both have an agpaitic index of 1.09 and near-identical whole-rock compositions, but the one has the minerals zircon and biotite, that is a miaskitic mineral assemblage, whereas the other contains the agpaitic assemblage: arfvedsonite, aegirine and eudialyte. This is an indication that the formation of agpaitic rocks depends on specific conditions of crystallization of their magmas.

High contents of rare and volatile elements result in a wealth of mineral species, often of complex composition with more than 10 major elements. More than 500 minerals have been identified in the Lovozero and Khibina complexes, the Kola Peninsula (e.g. Semenov, 1972; Kostyleva-Labuntsovca *et al.*, 1978; Khomyakov, 1995), about 250 in Mont Saint-Hilaire, Quebec (Horvath and Gault, 1990), more than 200 in the type locality, the Ilímaussaq complex, South Greenland (Sørensen *et al.*, 1981, Petersen and Secher, 1993), and more than 50 in the Tamazeght complex, Morocco (Kadar, 1984; Khadem Allah, 1993). Mining and quarrying is carried out in Khibina, Lovozero and Mont Saint-Hilaire, which is part of the explanation of the higher numbers of minerals found there than in Ilímaussaq, where only explorative activities have taken place, and at Tamazeght, which is located at an altitude of about 3000 m in the High Atlas Mountains and only accessible with difficulty.

The Ilímaussaq complex is made up mainly of agpaitic rocks *sensu stricto*, that is rocks having a pure agpaitic mineralogy. Other complexes, such as Lovozero and Khibina, have a more mixed mineralogy containing not only eudialyte and other typical agpaitic minerals, but also titanite, ilmenite, apatite, etc. In the Tamazeght complex, Morocco, some rocks show transitional stages, zircon overgrown by eudialyte and in other rocks eudialyte overgrown by zircon, which is evidence of changing alkalinity (Khadem Allah, 1993). These features call for a subdivision of the agpaitic rocks. Semenov (1967, see also Sørensen, 1974) subdivided nepheline syenitic rocks into five subgroups: agpaitic nepheline syenites or the Ilímaussaq type, characterized by F-arfvedsonite, eudialyte, steenstrupine, etc.; three groups of intermediate types characterized respectively by Mg-arfvedsonite (Lovozero type), Al-arfvedsonite (Khibina type) and katophorite (Langesundsfjord type) and containing zircon, titanite and ilmenite in addition to eudialyte, and the miaskitic nepheline syenites having hastingsite, zircon, etc.

Khomyakov (1995) has also divided the nepheline syenitic rocks into five groups, based on the typomorphism of rare-metal and accessory minerals, mainly silicates with the general formula $A_xM_ySi_pO_q$, where A = Na, K and other strong bases, M = Nb, Ti, Zr, Be and other substitutes of Al. The subdivision into five types is based on the alkalinity modulus, $K_{alk} = (x \times 100)/(x + y + p)$, that is the atomic percentage of the most basic cations of the A group in the chemical formula of the minerals:

(1) $K_{alk} > 40$ %: *Hyperagpaitic* rocks with zirsinalite, vuonnemite, vitusite, steenstrupine, chkalovite, etc. together with Li-arfvedsonite, ussingite, natrosilite, villiaumite, etc.

(2) $K_{alk} = 35-40$ %: *Highly agpaitic* rocks with eudialyte, lamprophyllite, astrophyllite, etc. together with Li-arfvedsonite, aenigmatite, nepheline, analcime, sodalite, villiaumite, etc.

TABLE 1. Rare minerals mentioned in the text

Aenigmatite	$Na_2Fe_5^{2+}TiSi_6O_{20}$
Astrophyllite	$(K,Na)_3(Fe^{2+},Mn)_7Ti_2Si_8O_{24}(O,OH)_7$
Beryllite	$Be_3SiO_4(OH)_2 \cdot H_2O$
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	$Na_4(Ca,Ce)_2(Fe,Mn,Y)ZrSi_8O_{22}(OH,Cl)_2$
Lamprophyllite	$Na_2(Sr,Ba)_2Ti_3(SiO_4)_4(OH,F)_2$
Låvenite	$(Na,Ca)_2(Mn^{2+},Fe^{2+})(Zr,Ti)Si_2O_7(O,OH,F)_2$
Lomonosovite	$Na_2Ti_2Si_2O_9 \cdot Na_3PO_4$
Loparite-(Ce)	$(Ce,Na,Ca)(Ti,Nb)O_3$
Lovozerite	$Na_2Ca(Zr,Ti)Si_6(O,OH)_{18}$
Lorenzenite	$Na_2Ti_2Si_2O_9$
Mosandrite	an alteration product of rinkite
Murmanite	$Na_2(Ti,Nb)_2Si_2O_9 \cdot nH_2O$
Natrosilite	$Na_2Si_2O_5$
Naujakasite	$Na_6(Fe,Mn)Al_4Si_8O_{26}H_2O$
Ramsayite	syn. of lorenzenite
Rinkite	$(Ca,Ce)_4Na(Na,Ca)_2Ti(Si_2O_7)_2F_2(O,F)_2$
Sodalite	$(NaAlSiO_4)_2 \cdot 2NaCl$
Steenstrupine-(Ce)	$Na_{14}Ce_6Mn_2Fe_2(Zr,Th)(Si_6O_{18})_2(PO_4)_7 \cdot 3H_2O$
Ussingite	$NaAlSi_3O_8 \cdot NaOH$
Villiaumite	NaF
Vitusite-(Ce)	$Na_3Ce(PO_4)_2$
Vuonnemite	$Na_5Nb_3Ti(Si_2O_7)_3O_2F_2 \cdot 2Na_3PO_4$
Zirsinalite	$Na_6CaZrSi_6O_{18}$

(3) K_{alk} = 25–35 %: *Medium agpaitic* rocks with apatite, titanite, arfvedsonite, nosean, etc.

(4) K_{alk} = 15–25 %: *Low agpaitic* rocks with eudialyte, låvenite, titanite, zircon, apatite, katophorite, etc.

(5) $K_{alk} \ll 15$ % : *Miaskitic* rocks with allanite, zircon, ilmenite, hastingsite, etc.

The distinction between agpaitic and hyperagpaitic (or ultra-agpaitic) nepheline syenites is a result of the discovery in the Khibina and Lovozero complexes of numerous minerals, in part water-soluble, having unusually high contents of sodium, as reported in Khomyakov's 1995 memoir on the *Mineralogy of the Hyperagpaitic Alkaline Rocks*.

The establishment of a group of hyperagpaitic rocks is the major difference between the classification systems of Semenov and Khomyakov. The present author prefers a slightly simplified system consisting of groups of hyperagpaitic, agpaitic *sensu stricto*, transitional and miaskitic rocks. Such a system applied to the rock types of the Ilímaussaq complex (e.g. Larsen and Sørensen, 1987) classifies the pulaskite and foyaite as transitional syenites and nepheline syenites; the sodalite foyaite, naujaite, kakortokite, aegirine lujavrites and some of the eudialyte-rich arfvedsonite lujavrites as agpaitic; while the naujakasite and steenstrupine lujavrites, and a number of late veins have a hyperagpaitic mineralogy, as will be discussed below.

Occurrence

Agpaitic nepheline syenites occur in intraplate locations. They form intrusive complexes or parts of complexes, and late-stage pegmatites and veins in non-agpaitic complexes. Agpaitic phonolites are rare.

Examples of massifs are the already-mentioned Ilímaussaq, Lovozero, Khibina and Mont Saint-Hilaire complexes, and Tamazeght (Bouabdli *et al.*, 1988), the Pilanesberg complex, South Africa (Ferguson, 1973; Lurie, 1985) and Saima, China (Saima Deposit Research Group, 1978). Agpaitic rocks form a minor part of massifs such as the above-mentioned Mont Saint-Hilaire, the Motzfeldt centre, South Greenland (Jones and Larsen, 1985), and the McGerrigle complex, Gaspé, Quebec (Wallace *et al.*, 1990). In a number of complexes, agpaitic mineralogy is restricted to late pegmatites and veins; examples are the Langesundsfjord region of the Oslo province, Southern Norway (Brøgger, 1890), Fitou, Southern France (Vitrac-Michard *et al.*, 1977) and the Gardiner complex, East Greenland (Nielsen, 1994). The most developed agpaitic rocks in the Ilímaussaq, Khibina and Lovozero complexes show late-stage mineralization of water-soluble and unstable minerals such as villiaumite and natrolsilite, interstitially and as veins and veinlets (Khomyakov, 1995).

Examples of agpaitic phonolites are found in Cantal, Central France (Varet, 1969; Brousse and Rancon, 1984) and Hoggar, Algerian Sahara (Girod, 1971). Subvolcanic occurrences of agpaitic rocks have been demonstrated by means of xenoliths in volcanic rocks at Tenerife, Canary Islands (Wolff, 1987) and at Oldoinya Lengai, Tanzania (Dawson and Frisch, 1971).

Agpaitic rocks may survive deformation and metamorphism as has been demonstrated for the Red Wine alkaline complex, Central Labrador (Curtis and Currie, 1981). The eudialyte-bearing rocks of the Kipawa syenite complex are proposed to have been formed by metasomatic reactions involving a deformed association of alkaline igneous complex, marble, and other rocks (Currie and van Breemen, 1996).

Geochemistry

The agpaitic rocks are characterized by high to extreme contents of Na, Zr, Cl, F and a number of rare elements such as Li, Be, Rb, Ga, *REE*, Nb, Ta, Hf, Zn, Sn, U and Th, and are depleted in elements such as Mg, (Ca), Cr, Sc, Co and Ni. The peralkaline character is shown by high normative contents of *ac* and *ns*.

The chemical compositions of the agpaitic rocks indicate that their melts must be extremely rich in sodium and in volatile and rare elements. This has been confirmed by the results of the examination of the interstitial glass in a block of nepheline syenite found in phonolitic pumice deposits of Tenerife, Canary Islands (Wolff, 1987; Wolff and Toney, 1993). The glass provides a sample of quenched interstitial melt in the nepheline syenite, which is estimated to have crystallized in the roof zone of a phonolitic magma chamber at a depth of about 4 km beneath the caldera. The electron microprobe analyses of the interstitial glass showed 13.4–17.0 wt.% Na_2O, 0.58–0.78 wt.% CaO, 1.4–1.8 wt.% ZrO_2, 1–1.4 wt.% F and an agpaitic index of 1.81–2.26. Normative *ne* varies from *c*. 10 to 15 wt.%, *ac* from *c*. 14 to 16, and *ns* from *c*. 7 to 12.5. These features support the view that the glass is a sample of quenched agpaitic magma.

The agpaitic rocks are characterized by a gas phase rich in methane and other hydrocarbons (Konnerup-Madsen and Rose-Hansen, 1982).

Rb-Sr data are available for a number of the occurrences of agpaitic rocks (Table 2).

In the Ilímaussaq complex, the initial $^{87}Sr/^{86}Sr$ ratio of the non-agpaitic augite syenite indicates a mantle-derived magma, whereas the higher ratio for the agpaitic kakortokite may indicate some crustal contamination (Bailey *et al.*, unpublished data).

The low initial $^{87}Sr/^{86}Sr$ ratios for the Khibina and Lovozero complexes indicate mantle-derived magmas (Kramm *et al.*, 1993).

The early rocks of Mont Saint-Hilaire have low initial $^{87}Sr/^{86}Sr$ ratios, whereas the late rocks have higher ratios, which is taken as evidence for the involvement of crustal contamination in the evolution of this complex (Currie *et al.*, 1986).

The agpaitic rocks of Los Archipelago (Moreau *et al.*, 1996) have a low initial $^{87}Sr/^{86}Sr$ ratio compatible with a mantle origin.

The agpaitic rocks of Poços de Caldas, Brazil (Shea, 1992) and of McGerrigle, Quebec (Wallace *et al.*, 1990) have rather high initial $^{87}Sr/^{86}Sr$ ratios.

The initial $^{87}Sr/^{86}Sr$ ratios for the agpaitic complexes thus fall into two groups: the Khibina and Lovozero complexes, the early rocks of Mont Saint-Hilaire and Ilímaussaq and the Los Archipelago give low initial $^{87}Sr/^{86}Sr$ ratios indicating mantle derivation of their magmas, whereas the initial ratios of the agpaitic rocks of Ilímaussaq and of the other complexes are higher, which is taken as evidence for some form of crustal contamination.

The above-mentioned agpaitic complexes show some distinct differences in their Rb and Sr contents (Table 2).

The rocks of the very large Khibina and Lovozero complexes and the Poços de Caldas complex have high contents of Sr and rather high Rb contents.

The agpaitic rocks of the much smaller Ilímaussaq, Mont Saint-Hilaire, Los Archipelago and McGerrigle complexes have high to very high contents of Rb, and low to very low contents of Sr. The low Sr contents of the agpaitic rocks of these complexes may have made their $^{87}Sr/^{86}Sr$ ratios more vulnerable to crustal contamination than those of the Kola complexes, which have high contents of Sr. This interpretation is corroborated by the low initial $^{87}Sr/^{86}Sr$ ratio and the high Rb and Sr contents of the small nepheline syenite massif at Fitou, Corbières orientales, France (Vitrac-Michard *et al.*, 1977). The high Sr content may have made this complex less vulnerable to crustal contamination than the complexes characterized by high Rb/Sr ratios and low contents of Sr. The agpaitic rocks of Poços de Caldas clearly represent a special case having high initial $^{87}Sr/^{86}Sr$ ratios and rather high contents of Sr.

As discussed in a later section, the agpaitic rocks of Ilímaussaq and some of the other complexes have been exposed to intensive late- to post-magmatic alteration leading to a redistribution of Rb and Sr, which should also be taken into consideration when interpreting the Sr-isotopic data. It may be concluded, that the Rb/Sr data should be considered with some caution.

TABLE 2. Rb-Sr data and initial $^{87}Sr/^{86}Sr$ ratios for some agpaitic complexes

Complex	ppm Rb	ppm Sr	$^{87}Sr/^{86}Sr$
Khibina-Lovozero	av. 230	av. 610	0.703–0.704
	80–270	100–1800	
		(- > 1%)	
Poços de Caldas	148.8–194.6	1385–3263	0.7051
Fitou	216	653	0.7036
Ilímaussaq			
augite syenite^1	93.6–132.7	337.8–889.2	
agpaitic rocks^1	194.9–644.0	56.9–139.7	0.7096
		(-521.5)	
augite syenite^2	160	284	0.7039
kakortokite	250–1200	8–90	0.711
(agpaitic rocks)^2		(–160)	
Mont Saint Hilaire	87.31–261.4	20.5–138.3	
early rocks			0.7030–0.7040
late rocks			0.7037–0.7051
Los Archipelago	296–445	2.66–17.80	0.7040
McGerrigle	166–188	7–149	>0.71

References:
Khibina and Lovozero complexes, Kola Peninsula,Russia: Kramm *et al.*, 1993.
Poços de Caldas complex, Brazil: Shea, 1992.
Fitou, Corbières Orientales, France: Vitrac-Michard *et al.*, 1977.
Ilímaussaq, South Greenland:^{1} Blaxland *et al.*, 1976; ^{2} Bailey *et al.*, unpublished data.
Mont Saint-Hilaire, Quebec, Canada: Currie *et al.*, 1986.
Los Archipelago, Guinea: Moreau *et al.*, 1996.
McGerrigle, Gaspé, Quebec, Canada: Wallace *et al.*, 1990.

The Sm-Nd data throw some light on the problem of the origin of the agpaitic magmas. Kramm *et al.* (1993) report whole-rock $^{143}Nd/^{144}Nd$ ratios varying from 0.512517 to 0.512733 and an ε_{Nd} value for the Khibina and Lovozero complexes of *c.* +5. This is in accordance with the low $^{87}Sr/^{86}Sr$ initial ratios for these complexes, and a further confirmation of formation from mantle-derived magmas. The ε_{Nd} of the nepheline syenites of the Poços de Caldas complex is $-3.4 \pm 0{,}0$ and ε_{Sr} $+9.8 \pm 0.3$. This is interpreted to represent a Mid-Ocean Ridge basalt-type source magma contaminated by continental igneous and metamorphic rocks, which is in accordance with the Rb-Sr data (Shea, 1992).

Very little information about the Sm/Nd system is available for the Ilímaussaq complex. Paslick *et al.* (1993) reported a whole-rock $^{143}Nd/^{144}Nd$ ratio of 0.512017 for the augite syenite. Ross Stevenson (pers.information) has obtained $^{143}Nd/^{144}Nd$ values of 0.511645 to 0.512060 for Ilímaussaq rocks, and an ε_{Nd} value of *c.* 0.0 to −3.56, which may indicate contamination processes or derivation from a primitive or metasomatically altered mantle. Further data are obviously needed.

The McGerrigle complex (Wallace *et al.*, 1990) has, as mentioned above, a very high initial $^{87}Sr/^{86}Sr$ ratio, but the ε_{Nd} is reported to be +4.2 to +5.2, that is juvenile or mantle-like values.

The $\delta^{18}O$ values for Ilímaussaq (Sheppard, 1986), Lovozero (Khomyakov, 1995), McGerrigle (Wallace *et al.*, 1990) and Poços de Caldas (Shea, 1992) are all juvenile, in the range of $\delta^{18}O$ = +6 to +10 ‰ (SMOW). Sheppard points out, however, that the $\delta^{18}O$ values for the Ilímaussaq agpaitic rocks are higher than in the other Gardar complexes examined and may indicate, together with information obtained from the hydrogen isotopes, an involvement of deep crustal contamination of the agpaitic melts. Also in the case of Poços de Caldas the influence of surficial processes and crustal assimilation may have played a role (Shea, 1992).

The $\delta^{13}C$ values for Ilímaussaq (methane) (Konnerup-Madsen *et al.*, 1988), and Khibina and Lovozero (carbonates) (Khomyakov, 1995) are +0.7

to −5.7 ‰ (PDB), that is also juvenile values. The somewhat controversial isotopic data will be discussed further below.

Origin and evolution

The geochemical data indicate that agpaitic melts may be formed by extreme fractionation of alkali basaltic (Larsen and Sørensen, 1987), nephelinitic (Kramm and Kogarko, 1994) or melanephelinitic (Nielsen, 1994) magmas.

In the case of the Ilímaussaq complex, low-pressure feldspar fractionation may have been involved as seen from xenoliths of anorthosite cumulates in some of the rocks of the complex, and from the distinct negative Eu anomalies in the agpaitic rocks (Bailey *et al.*, 1978). The low contents of Mg, Cr, Co, Ni and Sc indicate that there has also been a fractionation of mafic minerals. This evolution is envisaged to have taken place in a large alkali basaltic magma chamber, a view that is supported by information about a marked gravity high coinciding with the Tugtutôq-Ilímaussaq zone (Blundell, 1978) which is interpreted as an accumulation of mafic minerals in a deep magma chamber. The top part of this heavy mass is estimated to lie at depths of 2–5 km and the bottom at a minimum depth of 20 km (Forsberg and Rasmussen, 1978).

Kramm and Kogarko (1994) point out that the rocks of the Khibina and Lovozero complexes show very weak negative Eu anomalies, which give evidence that the agpaitic magmas in the Kola region did not form from basaltic liquids by fractional crystallization of plagioclase or anorthoclase at crustal levels. They consider formation from nephelinitic or nepheline benmoreitic magmas at mantle pressures more likely, possibly as a result of dynamic flow crystallization. The low $^{87}Sr/^{86}Sr$ ratios determined on the rocks of these complexes is in accordance with this view (Kramm *et al.* 1993). The high concentration of rare elements in the agpaitic rocks of the Khibina and Lovozero complexes is explained by an enrichment of the mantle prior to magma formation. The suggested deep origin of the agpaitic magmas explains the pure line of magmatic evolution with a minimum of crustal contamination. The large volumes of melts involved in the formation of these complexes, much larger than in the case of the other agpaitic complexes considered in this paper, have also counteracted any contamination of the melts.

The Sm-Nd data from the Poços de Caldas complex indicate a Mid Ocean Ridge basalt source magma contaminated by continental rocks (Shea, 1992). The lack of a negative Eu anomaly also indicates that feldspar fractionation has not been important in the formation of these rocks (Schorscher and Shea, 1992).

With regard to the other complexes discussed here, the origin of the melts is less clear. As mentioned above, the Nd-Sm information about the McGerrigle complex points to mantle-derived melts, whereas the high intial $^{87}Sr/^{86}Sr$ ratio indicates the involvement of crustal contamination of the melts. This disagreement, which also applies to the Ilímaussaq and Mont Saint-Hilaire complexes, should be seen in the light of the very low Sr contents in the agpaitic rocks of these complexes. The addition of small amounts of radiogenic Sr from the country rocks to the melts would have a great effect on the measured initial Sr-isotope ratios. In the Ilímaussaq complex, intense late- and post-magmatic alteration of the rocks may have contributed to the elevated initial Sr-isotope ratios.

The isotopic data thus indicate that agpaitic melts may be formed by fractionation of magmas deep in the mantle as has been suggested for the two large Kola massifs, or by fractionation of feldspar and mafic minerals in crustal magma chambers as has been proposed for the Ilímaussaq complex.

The above-mentioned quenched sample of a possible agpaitic melt found at Tenerife (Wolff, 1987; Wolff and Toney, 1993) occurs interstitially in a xenolith of nepheline syenite nepheline syenite, which is composed of alkali feldspar, sodalite, nepheline, pyroxene (with Na/(Na + Ca) < 0.2), magnetite, biotite and titanite. These minerals reacted with the trapped interstitial liquid resulting in the conversion of the pyroxene to Na-rich compositions, continued growth of felsic minerals, partial to complete consumption of biotite, magnetite, titanite and apatite, and growth of stellate aegirine, arvedsonite, låvenite, loparite, Mn-rich ilmenite, and trace amounts of ramsayite and eudialyte/eucolite, that is an agpaitic mineralogy. The glass contains no Zr-mineral in spite of the high Zr content, in accordance with the well-known high capacity of peralkaline melts to retain rare and volatile elements in solution (Kogarko, 1974). The sequence of formation of minerals in the nepheline syenite in contact with the interstitial melt recalls the evolution in the Ilímaussaq complex in which early fayalite, hedenbergite, apatite and titanomagnetite reacted out and were substituted by arfvedsonite, aegirine, aenigmatite and eudialyte (Larsen and Sørensen, 1987).

The rarity of examples of quenched agpaitic melts such as that described from Tenerife, and the corresponding rarity of agpaitic phonolites in comparison with plutonic agpaitic complexes, are best explained by the assumption that special conditions of crystallization govern their formation. The high capacity of agpaitic melts to retain volatiles and rare elements (Kogarko, 1974) is one necessary condition; another is that consolidation takes place in a closed system as proposed for the Ilímaussaq complex (Larsen and Sørensen, 1987).

The temperature during the interstitial stage of crystallization of the above-mentioned nepheline syenite from Tenerife (Wolff, 1987) is, from the presence of hypersolvus alkali feldspar and geothermometry on the associated phonolite, constrained to 750 to 680°C. This is in good agreement with the temperatures estimated for the agpaitic magma of the Ilímaussaq complex. The initial temperature is estimated to 900°C at a pressure of about 1 kbar and contents of H_2O + F around 4 wt.% (Larsen and Sørensen, 1987). The initial magma was volatile undersaturated; saturation was achieved around 700°C. According to Curtis and Currie (1981) the coexistence of alkali pyroxene and arfvedsonite requires temperatures in the range 625–675°C with water pressure greater than half total pressure and oxygen fugacities well below the QFM buffer, that is at a lower oxygen fugacity than suggested by Larsen (1976). Solidus temperatures are around 450°C according to melting experiments by Edgar and Parker (1974) and others. This is in conformity with the coexistence of separate grains of low albite and low microcline in the most developed rocks, such as the lujavrites of the Ilímaussaq complex, indicating that the temperature of crystallization has decreased to below the feldspar solvus (Larsen and Sørensen, 1987).

A long interval of crystallization is characteristic for the agpaitic rocks and may be combined with intervals of liquid immiscibility (Kogarko, 1977; Kogarko and Romanchev, 1983). There is a transition from low-temperature peralkaline volatile-rich melts to hydrothermal solutions containing 'excess' sodium as pointed out already by Tuttle and Bowen (1958), cf. Krauskopf (1961), and indicated by experimental data (Kogarko, 1977; Khomyakov, 1995). The content of normative *ns* of up to 12.5 wt.% in the above-mentioned interstitial glass from Tenerife (Wolff and Toney, 1993) should be compared with the *ns* contents of most Ilímaussaq rocks of up to about 5 wt.% suggesting a loss of sodium etc. during crystallization of the rocks. The late separation of sodium-rich fluid phases, by immiscibility processes or transition from low-temperature melt into hydrothermal fluids, is the cause of late- and post-magmatic alteration of the rocks. In the hyperagpaitic stage, this results in the formation of ussingite and analcime at the expense of the primary sodalite, nepheline, microcline and albite. The low-temperature alteration is represented by analcime and natrolite at the expense of nepheline, feldspars and sodalite, acmite at the expense of arfvedsonite, and catapleiite and various ill-defined pigmentary material formed at the expense of eudialyte. In some Ilímaussaq lujavrites, analcime is the only felsic mineral. It forms a matrix in which all other minerals are embedded. In these rocks magmatic consolidation has very probably passed gradually into hydrothermal partial recrystallization that has resulted not only in a neo-mineralization but also in a redistribution of elements such as Rb and Sr which may explain some of the above-mentioned problems with the Rb-Sr system. The contents of Li, U and Th in the Ilímaussaq rocks (Bailey and Gwozdz, 1994; Bailey *et al.*,1983) indicate that a redistribution of these elements has taken place.

The sodium-rich fluid phase is furthermore involved in the formation of hyperagpaitic rocks and mineralizations.

Hyperagpaitic rocks

The hyperagpaitic rocks form sodium-rich mineral associations, which are characterized by minerals such as natrosilite, ussingite, villiaumite, analcime, Li-arfvedsonite, zirsinalite, vuonnemite, lomonosovite, vitusite, chkalovite and steenstrupine (Khomyakov, 1995).

The hyperagpaitic associations of the Khibina complex are confined to pegmatites and late veins in the deep central part of the complex, while the Lovozero complex in addition to hyperagpaitic pegmatites and veins also has hyperagpaitic rocks: foyaites containing lomonosovite, murmanite and villiaumite, and lovozerite-murmanite lujavrites.

Khomyakov (1995) distinguishes three stages of mineral formation: 1 increasing alkalinity, 2 maximum alkalinity, and 3 decreasing alkalinity, where stage 1 mineral associations usually are similar to the mineralogy of the host rocks or form the marginal zones of complex pegmatites. This principle is well illustrated by the associations of eudialyte and zircon in the rocks of the Tamazeght complex. In some rocks, eudialyte is later than zircon; in others eudialyte crystals are rimmed by zircon; hyperagpaitic minerals have, however, not been found (Khadem Allah, 1993).

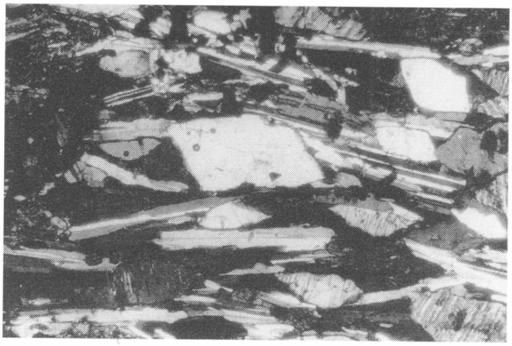
In Khibina and Lovozero it is shown (Khomyakov, 1995), that eudialyte, which may be considered the distinctive mineral of agpaitic rocks, becomes unstable in the hyperagpaitic stage, where its place is taken by zirsinalite. Zirsinalite again has a narrow interval of stability and reacts with water to form lovozerite. The minerals lomonosovite and vuonnemite are also characteristic for the hyperagpaitic rocks of Khibina and Lovozero, but are under decreasing alkalinity replaced by respectively murmanite and epistolite.

The Ilímaussaq complex provides additional information about the relationship between agpaitic and hyperagpaitic rocks. In this complex, hyperagpaitic mineral associations are found in pegmatites and late veins (cf. Sørensen, 1962; Semenov, 1969; and Engell *et al.*, 1971), in rocks such as arfvedsonite lujavrites carrying steenstrupine and naujakasite to be discussed below, and in metasomatized volcanic rocks of the roof of the complex (Sørensen *et al.*, 1974; Karup-Møller, 1983). Zirsinalite has not been found. Eudialyte is of widespread occurrence and lovozerite has been found in some lujavrites and in ussingite-bearing late veins (Sørensen, 1962). Lomonosovite and vuonnemite have been found (Karup-Møller, 1983; Rønsbo *et al.*, 1983), but their secondary minerals, murmanite and epistolite, are much more widespread. The hyperagpaitic associations in the Ilímaussaq complex are especially characterized by minerals such as ussingite, sodalite, analcime, naujakasite, villiaumite, chkalovite and steenstrupine. The very unstable mineral natrosilite has not been observed, but its presence is inferred from numerous cavities in ussingite in late veins, and from chemical analysis of the water flowing from the Kvanefjeld gallery in the northern part of the complex. The pH of this water was 11, the dissolved material consisted 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).

In the hyperagpaitic lujavrites of the Ilímaussaq complex naujakasite and steenstrupine are important rock-forming minerals, whereas steenstrupine is a rare pegmatite mineral in the Lovozero and Mont Saint-Hilaire complexes.

Naujakasite is known only from Ilímaussaq, where it is a major mineral in the variety of arfvedsonite lujavrite called naujakasite lujavrite. This rock is a late highly developed type of lujavrite characterized by high Na_2O – 12.6 to >14 wt.%, and higher than 15 wt.% in villiaumite-bearing varieties (Kunzendorf *et al.*, 1982). The highly alkaline state of this lujavrite variety is seen in the normative values, *ne* ~ 20, *ac* ~ 13, and *ns* ~ 9 in villiaumite-free rocks (Table 3). The very low contents of CaO (0.30 wt.%), and MgO (~ 0.10 wt.%) (Sørensen *et al.*, 1969; Gerasimovsky, 1969; Engell, 1973; and unpublished data) are also indications of the highly evolved nature of this rock. The agpaitic index is around 1.7. These values should be compared with the data for the common eudialyte-bearing arfvedsonite lujavrite of the Ilímaussaq complex, *ne* <10, *ac* ~ 20, *ns* < 5, agpaitic index ~ 1.5, and the same low contents of MgO and CaO as the naujakasite lujavrite. The porphyritic lovozerite–murmanite lujavrite of the Lovozero complex (Gerasimovsky *et al.*, 1966, and Bussen and Sakharov, 1972), which is a higly developed rock in that complex, has *ne* ~ 15, *ac* ~ 20, *ns* ~ 2–3 and the agpaitic index 1.4. It has higher contents of SiO_2, MgO and CaO and K_2O and lower Na_2O than the naujakasite lujavrite (Table 2). These data show that the naujakasite lujavrite of the Ilímaussaq complex has a very high alkalinity; it is indeed hyperagpaitic. This may explain why naujakasite, $Na_6(Fe,Mn)Al_4Si_8O_{26}{\cdot}H_2O$, which is composed of common rock-forming elements, is restricted to the Ilímaussaq complex. The lujavrites of the upper part of the Ilímaussaq complex are more enriched in sodium and volatiles than the rocks of other agpaitic complexes.

Nepheline is an important rock-forming mineral of the Ilímaussaq lujavrites, but is generally absent from the naujakasite lujavrites in which naujakasite occurs



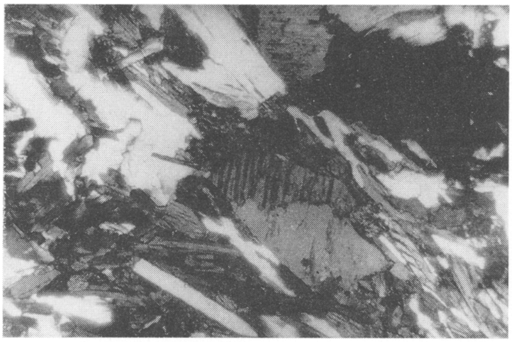
FIGS 1 and 2. Fig. 1 (*left*). Arfvedsonite lujavrite from Kvanefjeld in the northern part of the Ilímaussaq complex. Corroded grains of nepheline enveloped by laths of albite and acicular grains of arfvedsonite and with interstitial analcime. Crossed polarized light, the section measures 3 mm from left to right. Fig. 2 (*right*). Naujakasite lujavrite, drill core no.7 at 110.90 m, Kvanefjeld. Rhomb-shaped crystals of naujakasite enveloped by laths of albite and microcline and needles of arfvedsonite with interstitial analcime. Crossed polarized light. The section measures 3 mm from left to right.

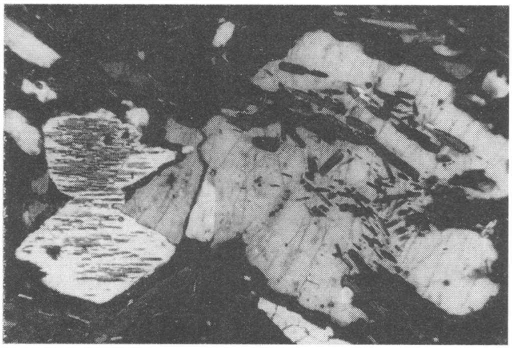
TABLE 3. Selected chemical analyses of lujavrites from the Ilímaussaq and Lovozero complexes

	Ilímaussaq complex			Lovozero complex
	Arfvedsonite lujavrite (154373-2)	Naujakasite lujavrite (154364)	Naujakasite lujavrite (77100)	Murmanite–lovozerite lujavrite (C-11)
SiO_2	53.47	50.33	50.58	53.86
TiO_2	0.41	0.22	0.22	1.49
ZrO_2	0.78	0.37	0.34	1.64
Al_2O_3	12.51	13.39	14.97	14.40
Fe_2O_3	6.28	4.17	4.42	6.83
FeO	5.45	10.53	9.03	1.08
MnO	0.52	1.06	1.04	0.60
MgO	0.10	0.15	0.08	0.85
CaO	0.49	0.31	0.31	1.39
Na_2O	9.17	12.61	14.04	9.13
K_2O	3.93	1.82	2.10	5.24
P_2O_5	0.25	0.26	0.18	0.25
S	0.06	0.11	0.11	0.11
Cl	0.02	0.00	0.00	0.20
F	0.08	0.10	0.14	–
H_2O+	3.85	2.67	1.66	1.76
H_2O-	0.16	0.65	0.42	0.34
CO_2	0.04	0.11	–	–
	97.57	98.86	99.75	99.33
Less O = F, Cl,S	0.07	0.10	0.06	0.10
Other elements	1.74	0.91	?	0.61
Total	99.24	99.67	99.69	99.84
CIPW weight norms				
ap	0.58	0.64	0.54	0.59
il	0.83	0.31	0.63	2.27
zr	1.35	0.58	0.56	2.41
tn	–	–	–	0.95
or	25.06	11.44	12.88	32.46
ab	34.15	33.72	26.57	20.69
ne	6.27	15.33	21.68	14.70
ac	19.53	12.71	13.06	20.86
ns	3.74	8.43	9.33	2.37
di	0.22	–	0.21	1.80
ol	8.23	16.79	14.10	0.79
agpaitic index	1.55	1.68	1.69	1.43
	Geological Survey of Denmark and Greenland and Institute of Geology, University of Copenhagen		Gerasimovsky, 1969	Gerasimovsky *et al.*, 1966: composite sample.

The small contents of Cl, F and S have not been included in the norm calculation.

in the same textural setting as nepheline, i.e. enveloped by laths of feldspar and acicular grains of arfvedsonite (Figs. 1 and 2). Danø and Sørensen (1959) and Engell (1973) therefore proposed that nepheline in some way has been substituted by naujakasite in these rocks. It may be argued that nepheline is unstable and naujakasite stable in the hyperagpaitic environment. This relationship can be demonstrated in samples from a drill core from Kvanefjeld in the northern part of the complex, in





FIGS. 3 and 4. Fig. 3 (*left*). Naujakasite lujavrite, drill core no. 11 at 166.91 m. Corroded grain of nepheline overgrown by naujakasite. Note hole after villiaumite. Crossed polarized light. The section measures 3 mm from left to right. Fig. 4 (*right*). Naujakasite lujavrite, drill core no. 11 at 166.91 m. Corroded grain of nepheline overgrown by naujakasite with narrow intervening zone of analcime. Crossed polarized light. The section measures 3 mm from left to right.

which corroded grains of nepheline are overgrown by grains of naujakasite (Figs. 3 and 4). The relationship between nepheline and naujakasite may be illustrated by the following reaction:

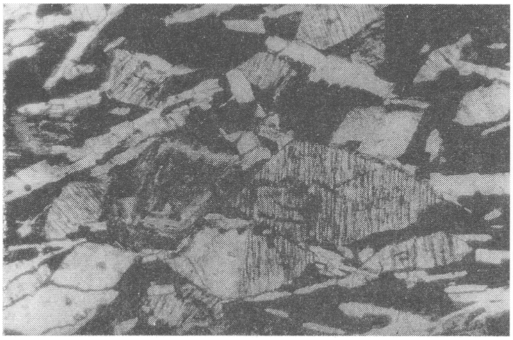
$$\underset{\text{nepheline}}{4(NaAlSiO_4)} + Na_2O + FeO + 4SiO_2 + H_2O = \underset{\text{naujakasite}}{Na_6FeAl_4Si_8O_{26}.H_2O}$$

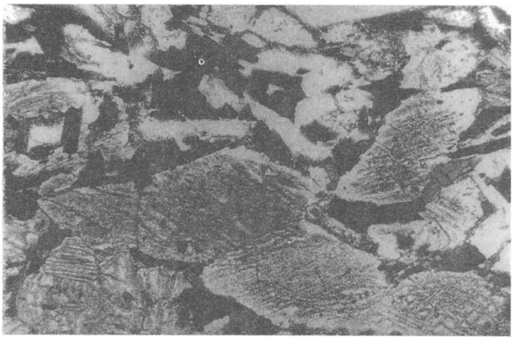
Another indication of the high alkalinity of the naujakasite lujavrite is the fact that ussingite here and there replaces the feldspars.

Naujakasite may make up more than 50 vol. % of the rocks (Fig. 5). It appears to have a very narrow stability interval. Unaltered grains are only found in rocks in which the feldspars are unaltered. The alteration of the feldspars into analcime and natrolite is accompanied by the alteration of naujakasite into analcime and pigmentary material (Fig. 6).

Eudialyte is not stable in the naujakasite lujavrite. Its place is taken by lovozerite or steenstrupine. The content of steenstrupine is so high that the naujakasite lujavrite may contain more than 300 ppm U and is a part of the Kvanefjeld uranium deposit. The Zr/U ratio of the rock is less than 10, the lowest determined in any rock at Ilímaussaq (Andersen *et al.*, 1981).

The change in alkalinity necessary for the substitution of eudialyte by steenstrupine can be estimated from a comparison of the chemical formulae of the two minerals:





FIGS. 5 and 6. Fig. 5 (*left*). Naujakasite lujavrite, drill core no. 7 at 110.90 m. Densely packed crystals of naujakasite and crystal of steenstrupine (centre left). Plane polarized light. The section measures 3 mm from left to right. Fig. 6 (*right*). Naujakasite lujavrite, drill core 25 at 33.95 m. Densely packed crystals of naujakasite partially altered into analcime and pigmentary material. Plane polarized light. The section measures 3 mm from left to right.

$$3(Na_4(Ca,Ce)_2(Fe,Mn,Y)ZrSi_8O_{22}(OH,Cl)_2 + Na_2O + 7(PO_4) + 3H^+ + (Ce,Th,U)$$

eudialyte

$$= Na_{14}Ce_6(Mn,Fe)_2(Zr,Th)(Si_6O_{18})_2(PO_4)_7{\cdot}3H_2O + 2ZrO_2 + FeO + 12SiO_2 + 3Cl + (Ca)$$

steenstrupine

In the pegmatites of the Ilímaussaq complex steenstrupine forms independent crystals and rims around eudialyte crystals (Sørensen, 1962). The latter situation is found in ussingite-bearing pegmatites and veins. This is an indication of a high alkalinity; the formula of ussingite, $NaAlSi_3O_8{\cdot}NaOH$, can also be presented as albite plus NaOH.

In the naujakasite lujavrites and in the metasomatized roof rocks, steenstrupine is a rock-forming mineral. It occurs as well-developed crystals and as larger poikilitic grains which enclose the minerals of the matrix of the rock, including small grains of lovozerite (Buchwald and Sørensen, 1961; Sørensen, 1962).

The stability relations of steenstrupine have been investigated by Sørensen *et al.* (1985). Steenstrupine was seen to form at 1000 atm. in the whole temperature range investigated, 700–400°C, but only in sodium-rich systems. In less sodium-rich runs, monazite, britholite and lessingite were formed. The presence of steenstrupine as a rock-forming mineral in lujavrites and metasomatized roof rocks, therefore, also suggests extremely alkaline, hyperagpaitic conditions of formation of these rocks. Clusters of small grains of monazite and rare crystals of britholite in some lujavrites (Danø and Sørensen, 1959; Buchwald and Sørensen, 1961) may therefore represent the products of crystallization in less alkaline systems. Lessingite has not been identified in any of the Ilímaussaq rocks. It should, however, be pointed out that Pekov *et al.* (1997) have shown that clusters of monazite-rhabdophane described under the name erikite in Ilímaussaq (Bøggild, 1903) and in Lovozero (Gerasimovsky, 1937) are vitusite pseudomorphs. Vitusite is only stable under hyperagpaitic conditions and is easily altered into erikite:

$$\text{vitusite} + H_2O = \text{monazite/rhabdophane} + NaOH + x(PO_4)\ (= \text{erikite})$$

The above-mentioned clusters of monazite may therefore also mark the former presence of vitusite and hyperagpaitic conditions and are in any case a result of crystallization under decreasing alkalinity.

Economic geology

The agpaitic rocks represent an important future source of a variety of rare elements (Sørensen, 1992). Exploitation of deposits of apatite and loparite has already taken place in the Khibina and Lovozero complexes, and uranium has been mined in Poços de Caldas and in the Saima massif, Northern China. Deposits of eudialyte have been examined in Lovozero and Ilímaussaq as sources of a number of elements, first of all Zr, Hf, *REE*, Y and Nb.

Conclusions

During the last few decades occurrences of agpaitic rocks have been studied in many parts of the world, which has resulted in a wealth of information about their mineralogy, geochemistry and petrology.

The now available information about these rocks has made it clear, that agpaitic rocks do not form a homogeneous group. Agpaitic rocks *sensu strictu* are characterized by minerals such as eudialyte and rinkite, and the absence of zircon and titanite. These last-named minerals are characteristic for the miaskitic nepheline syenites. Transitional rocks between agpaitic and miaskitic may contain eudialyte together with zircon and titanite and should therefore be distinguished as a separate group of rocks. The discovery in the Khibina and Lovozero complexes of strongly alkaline agpaitic rocks, in which eudialyte is unstable, has made it necessary to establish a group of hyperagpaitic rocks.

The isotopic data indicate that agpaitic rocks are formed from highly developed magmas derived by extreme fractionation of nephelinitic or alkali basaltic, mantle-derived melts. In some occurrences, such as the Khibina and Lovozero complexes, a deep origin and a pure line of evolution of the agpaitic magmas is proposed; in others, such as the Ilímaussaq complex, the agpaitic melts are suggested to have been formed by fractionation of alkali basaltic magmas in crustal magma chambers. The rocks of the last-named complexes show moderately elevated initial $^{87}Sr/^{86}Sr$ ratios, which may indicate some crustal contamination. These rocks have, however, very high Rb/Sr ratios and have furthermore been exposed to late- and post magmatic alteration, which may have been the cause of redistribution of elements, including Rb and Sr.

A possible quenched sample of an agpaitic melts has been found at Tenerife. It shows very high contents of Na, Zr and F and an agpaitic index of 1.81–2.26. It contains 14–16 wt. % normative *ac* and 7–12.5 % *ns*. Agpaitic rocks in general have normative *ns* lower than 5 %. This indicates that there has been a loss of sodium, etc. during the crystallization of these rocks, possibly as a result of a gradual transition from low-temperature melts into hydrothermal fluids. These fluids are the cause of late- and post-magmatic alteration of the rocks and of the formation of mineral-rich pegmatites and hydrothermal mineralizations, including the hyperagpaitic mineral associations.

The hyperagpaitic stage of evolution of agpaitic complexes is characterized by sodium-rich minerals, such as natrosilite and ussingite. Eudialyte, which is a distinctive mineral for agpaitic rocks, is unstable under hyperagpaitic conditions and is in the Khibina and Lovozero complexes replaced by zirsinalite. In the hyperagpaitic rocks of the Ilímaussaq complex, eudialyte is substituted by steenstrupine and nepheline by naujakasite. Steenstrupine is a rare pegmatite mineral in Lovozero and Mont Saint-Hilaire, but a rock-forming mineral in Ilímaussaq. Naujakasite is also a rock-forming mineral in Ilímaussaq, where it may make up more than 50 vol. % of late stage lujavrites. This mineral, which is composed of common rock-forming elements, is only known from Ilímaussaq. This indicates, that the hyperagpaitic Ilímaussaq lujavrites are the most alkaline rocks known from agpaitic complexes.

Acknowledgements

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