

The Mineralogical Diversity of Alkaline Igneous Rocks: Critical Factors for the Transition from Miaskitic to Agpaitic Phase Assemblages

MICHAEL A. W. MARKS¹*, KAI HETTMANN¹, JULIAN SCHILLING¹,
B. RONALD FROST² AND GREGOR MARKL¹

¹INSTITUT FÜR GEOWISSENSCHAFTEN, UNIVERSITÄT TÜBINGEN, WILHELMSTR. 56, D-72074 TÜBINGEN, GERMANY

²DEPARTMENT OF GEOLOGY AND GEOPHYSICS, UNIVERSITY OF WYOMING, PO BOX 3006, LARAMIE, WY

82071-3006, USA

RECEIVED APRIL 19, 2010; ACCEPTED NOVEMBER 19, 2010
ADVANCE ACCESS PUBLICATION JANUARY 3, 2011

Geochemically, the large family of alkaline plutonic rocks (both Qtz-undersaturated and -oversaturated compositions) can be subdivided into metaluminous [$(\text{Na}_2\text{O} + \text{K}_2\text{O}) < \text{Al}_2\text{O}_3$] and peralkaline [$(\text{Na}_2\text{O} + \text{K}_2\text{O}) > \text{Al}_2\text{O}_3$] types. In this paper, we discuss two important aspects of the mineralogical evolution of such rocks. With respect to their Fe–Mg phases, a major mineralogical transition observed is the precipitation of arfvedsonite or aegirine instead of fayalite or magnetite ($\pm$ ilmenite). The relative stability of these phases is controlled by oxygen fugacity and Na activity in the crystallizing melts. If Na activity in the melt is high enough, arfvedsonite + aegirine form a common assemblage in peralkaline rocks under both reduced and oxidized conditions. Major mineralogical differences within this rock group exist with respect to their high field strength element (HFSE)-rich minerals: most syenitic rocks, known as miaskites, contain zircon, titanite or ilmenite as HFSE-rich minerals, whereas in agpaites complex Na–K–Ca–(Ti, Zr) silicates incorporate the HFSE. Similarly, only a small group of peralkaline granites are found to lack zircon, titanite or ilmenite but instead contain Na–K–Ca–(Ti, Zr) silicates. Here, we present a detailed phase petrological analysis of the chemical parameters ($\mu\text{Na}_2\text{O}$, μCaO , $\mu\text{K}_2\text{O}$) that influence the transition from miaskitic to agpaitic rocks. Based on the occurrence of Ti and Zr minerals, several transitional mineral assemblages are identified and two major evolution trends for agpaites are distinguished: a high-Ca trend, which is exemplified by the alkaline rocks of the Kola Province, Russia, and a Ca-depletion trend, which is displayed by the alkaline rocks of the Gardar Province, South Greenland. Both trends show significant Na-enrichment during magmatic evolution.

High-Ca agpaites evolve from nephelinitic parental melts that did not crystallize large amounts of plagioclase. In contrast, agpaites showing Ca-depletion originate by extensive fractionation of plagioclase from basaltic parental melts. In some peralkaline granites evolutionary trends are observed that culminate in agpaitic-like HFSE-mineral associations in the most evolved rocks.

KEY WORDS: alkaline igneous rocks; oxygen fugacity; miaskitic; agpaitic; peralkaline granites; peralkaline syenites

INTRODUCTION

Alkaline igneous rocks contain either (1) modal feldspathoids or alkali amphiboles or pyroxenes or (2) normative feldspathoids or acmite (Le Maitre, 2002). Based on the molar ratios of $\text{Na}_2\text{O} + \text{K}_2\text{O}$ relative to Al_2O_3 , they can be subdivided into metaluminous [$(\text{Na}_2\text{O} + \text{K}_2\text{O}) < \text{Al}_2\text{O}_3$] and peralkaline [$(\text{Na}_2\text{O} + \text{K}_2\text{O}) > \text{Al}_2\text{O}_3$] types. Conclusively, this means that an alkaline rock should belong to the metaluminous or to the peralkaline group, although rare peraluminous [$\text{Al}_2\text{O}_3 > (\text{CaO} + \text{Na}_2\text{O} + \text{K}_2\text{O})$] nepheline syenites do occur (Frost & Frost, 2008). This classification is used for both syenitic (Qtz-undersaturated) and granitic (Qtz-saturated) rocks (see also Frost & Frost, 2008, 2010). The term peralkaline has been used synonymously with the term agpaitic, but this is not correct (Le Maitre, 2002).

*Corresponding author. E-mail: michael.marks@uni-tuebingen.de

Table 1: Important Ti and Zr phases in plutonic rocks and their abbreviations

<i>Ti-phases</i>		
Ilmenite	FeTiO ₃	Ilm
Perovskite	CaTiO ₃	Per
Titanite	CaTiSiO ₅	Tit
Aenigmatite	Na ₂ Fe ₅ TiSi ₆ O ₂₀	Aen
Astrophyllite	K ₃ Fe ₇ Ti ₂ Si ₈ O ₂₆ (OH) ₅	Ast
<i>Zr-phases</i>		
Baddeleyite	ZrO ₂	Bad
Zircon	ZrSiO ₄	Zrn
Eudialyte	Na ₁₅ Ca ₆ Fe ₃ Zr ₃ Si ₂₆ O ₇₂ (OH) ₄ Cl	Eud
Dalyite	K ₂ ZrSi ₆ O ₁₅	Dal
Wadeite	K ₂ ZrSi ₃ O ₉	Wad
Elpidite	Na ₂ ZrSi ₆ O ₁₅ ·3H ₂ O	Elp
Catapleite	Na ₂ ZrSi ₃ O ₉ ·2H ₂ O	Cat

Alkaline rocks are rich in large ion lithophile elements (LILE) such as Na, K and Li and in high field strength elements (HFSE) such as Ti, Zr, Hf, Nb, Ta, rare earth elements (REE), U and Th, potentially forming economically important deposits of these elements (e.g. Kogarko, 1980; Sørensen, 1992). As for most other plutonic rocks, the major carriers of HFSE in alkaline igneous rocks are accessory zircon and titanite $\pm$ Fe–Ti oxides (ilmenite or Ti-bearing magnetite). For metaluminous nepheline syenites with this assemblage, the term miaskitic is used (Le Maitre, 2002). Many peralkaline nepheline syenites, as well as metaluminous and peralkaline granites, also contain the same assemblage. In contrast, a special group of peralkaline nepheline syenites contains one or several complex Na–K–Ca–(Fe)–silicates, which are rich in Ti or Zr, the most prominent of these being eudialyte, aenigmatite and astrophyllite (Table 1). In these rocks, zircon, titanite and Fe–Ti oxides are either scarce or absent. This rock family is called agpaitic (Ussing, 1912; Sørensen, 1997; Le Maitre, 2002). Rarely, peralkaline granites exist that are poor in, or lack, zircon and titanite but contain Ti- and Zr-silicates such as eudialyte, elpidite, dalyite, aenigmatite or astrophyllite (Table 1; e.g. Harris & Rickard, 1987; Salvi & Williams-Jones, 1995). Although this may seem confusing, these rocks are not classified as agpaitic rocks according to the current nomenclature, as this term was originally restricted to peralkaline nepheline syenites (Le Maitre, 2002).

Agpaitic nepheline syenites are interpreted to form by extensive differentiation of parental mafic magmas at low oxygen fugacity, which is a major prerequisite for their

formation (e.g. Markl *et al.*, 2010, and references therein). The low oxygen fugacity is responsible for the often observed presence of a CH₄-rich fluid phase in such rocks (e.g. Konnerup-Madsen, 2001; Nivin *et al.*, 2005; Beeskow *et al.*, 2006; Krumrei *et al.*, 2007; Schönenberger & Markl, 2008) instead of the H₂O–CO₂ fluid mixtures typical of other less reduced rock types (e.g. Olsen & Griffin, 1984a, 1984b; Andersen, 1990; Hansteen & Burke, 1990; Fall *et al.*, 2007). This in turn results in a strong enrichment of Na, Cl, F and other volatile species in the fractionating melt, as no H₂O-rich fluid phase exsolves during the early magmatic stages, which would deplete these water-soluble elements from the melt during fluid exsolution (e.g. Signorelli & Carroll, 2000; Chevychelov *et al.*, 2008). In turn, such Na-, Cl- and F-rich melts have high solubilities for the HFSE such as Ti and Zr (e.g. Watson, 1979; Keppler, 1993; Linnen & Keppler, 2002) and will eventually crystallize agpaitic minerals such as eudialyte, lävenite and aenigmatite, which are invariably Na-rich and partly Cl- or F-bearing. If the melts were not so enriched in Na, Cl, and F, titanite and zircon would precipitate instead, as occurs in miaskitic rocks.

The field occurrence of agpaitic rocks is variable. In some localities (e.g. Ilimaussaq and Motzfeld, Greenland; Khibina and Lovozero, Russia; Mont Saint Hilaire, Canada; Pilansberg, South Africa; Nora Kärr, Sweden), a plutonic complex may consist of several intrusive bodies, which are either miaskitic or agpaitic (e.g. Ussing, 1912; Ferguson, 1964; Kogarko *et al.*, 1982; Horvarth & Gault, 1990; Mitchell & Liferovich, 2006; Schönenberger & Markl, 2008). In other areas (e.g. Tamazeght, Morocco) initially miaskitic rocks locally transform into agpaites during the late-magmatic or even hydrothermal stage within otherwise miaskitic rocks (e.g. Salvi *et al.*, 2000; Marks & Markl, 2003; Schilling *et al.*, 2009). At some localities (e.g. Langesundfjord region, Norway; Gardiner Complex, East Greenland), agpaitic assemblages are restricted to pegmatites within otherwise miaskitic rocks (Brøgger, 1890; Nielsen, 1994; Andersen *et al.*, 2010). Additionally, during the final alteration stages, mineral assemblages may be transformed to miaskitic ones and vice versa (e.g. Pilansberg; Mitchell & Liferovich, 2006; Andersen *et al.*, 2010). Lastly, rare examples of metamorphosed agpaites (e.g. Red Wine and Kipawa, Canada and Norra Kärr, Sweden) have been reported (e.g. Blaxland, 1977; Allan, 1992).

Although there is a mineralogical transition between miaskitic and agpaitic syenites (see Sørensen, 1997, and references therein), the reasons why such different groups of syenitic rocks exist, and how the transition from miaskites to agpaites happens in detail are poorly understood. In the present study, we discuss in general how this transition is related to changes in the chemical potentials of Na₂O, K₂O and CaO in the melt. We show that the

transition from miaskitic to agpaite rocks follows two distinct evolutionary trends, which allows us to distinguish two major types of agpaite rocks. Some peralkaline granites show evolutionary trends and agpaite-like mineral assemblages similar to those observed in syenitic systems, although the granitic systems appear to be more potassic than sodic.

THE STABILITY OF Fe- AND Na-Fe-MINERALS IN ALKALINE MELTS: THE COUPLED ROLE OF OXYGEN FUGACITY AND Na ACTIVITY

One of the most obvious mineralogical features of the transition from metaluminous to peralkaline igneous rocks is the precipitation of arfvedsonite or aegirine instead of fayalite or magnetite (see e.g. Markl *et al.*, 2010, and references therein). The stability of these phases can be described in terms of the chemical system Na-Fe-Si-O-H. Andersen & Sørensen (2005) presented a chemographic analysis of this system with the addition of Al to the system to investigate the stability of the rare mineral naujakasite $[\text{Na}_6(\text{Fe}, \text{Mn})\text{Al}_4\text{Si}_8\text{O}_{26}]$ relative to arfvedsonite or aegirine in unusual so-called hyper-agpaite melts (Khomyakov, 1995; Sørensen, 1997; Khomyakov *et al.*, 2001; Sørensen & Larsen, 2001).

As shown in reactions (1)–(8) (Table 2) and illustrated in Fig. 1, the chemical parameters governing the stability of Fe-bearing phases in the Na-Fe-Si-O-H system at fixed P and T are $\mu_{\text{Na}_2\text{O}}$, μ_{SiO_2} , $\mu_{\text{H}_2\text{O}}$ and μ_{O_2} . At fixed μ_{SiO_2} and $\mu_{\text{H}_2\text{O}}$, fayalite is restricted to low f_{O_2} and low $\mu_{\text{Na}_2\text{O}}$ and mixed Fe^{2+} – Fe^{3+} -phases (magnetite and arfvedsonite) occur at intermediate f_{O_2} values, depending on $\mu_{\text{Na}_2\text{O}}$. The Fe^{3+} -phases (hematite and aegirine) are stable at relatively high f_{O_2} values. The two Na-bearing phases, arfvedsonite and aegirine, occur at relatively high $\mu_{\text{Na}_2\text{O}}$. Two possible topologies of the phase diagram are illustrated in Fig. 1a and b. The major difference between the two is the position of reaction (1) relative to reaction (7). At higher silica activities, aegirine is stabilized to lower f_{O_2} values with respect to arfvedsonite, whereas the reaction between magnetite and hematite is independent of silica activity. A similar relationship applies to reaction (2), which indicates that at very low silica activities the assemblage Aeg + Fa would become stable. To our knowledge, this assemblage has not been described from natural rocks.

In most feldspathic plutonic rocks at least two of the above-mentioned phases coexist. Therefore, we constructed stability fields for potential two-phase assemblages in $\mu_{\text{Na}_2\text{O}}$ – μ_{O_2} space using Schreinemaker analysis [reactions (9)–(22), Table 2; Fig. 1c]. The following 10 two-phase assemblages are potentially

Table 2: Reactions in the system Fa–Mag–Arf–Aeg–Hem (normalized to Fe)

(1)	$15 \text{ Aeg} + 3 \text{ H}_2\text{O} = 3 \text{ Arf} + 6 \text{ SiO}_2 + 3 \text{ Na}_2\text{O} + 3 \text{ O}_2$
(2)	$7.5 \text{ Fa} + 2.5 \text{ O}_2 = 5 \text{ Mag} + 7.5 \text{ SiO}_2$
(3)	$7.5 \text{ Fa} + 4.5 \text{ Na}_2\text{O} + 16.5 \text{ SiO}_2 + 3 \text{ H}_2\text{O} + 0.75 \text{ O}_2 = 3 \text{ Arf}$
(4)	$2 \text{ Arf} + 3 \text{ O}_2 = 7.5 \text{ Hem} + 3 \text{ H}_2\text{O} + 24 \text{ SiO}_2 + 4.5 \text{ Na}_2\text{O}$
(5)	$5 \text{ Mag} + 4.5 \text{ Na}_2\text{O} + 24 \text{ SiO}_2 + 3 \text{ H}_2\text{O} = 3 \text{ Arf} + 7/4 \text{ O}_2$
(6)	$5 \text{ Mag} + 7.5 \text{ Na}_2\text{O} + 30 \text{ SiO}_2 + 1.25 \text{ O}_2 = 15 \text{ Aeg}$
(7)	$5 \text{ Mag} + 1.25 \text{ O}_2 = 7.5 \text{ Hem}$
(8)	$15 \text{ Aeg} = 7.5 \text{ Hem} + 7.5 \text{ Na}_2\text{O} + 30 \text{ SiO}_2$
(9)	$2.5 \text{ Mag} + 2.25 \text{ Na}_2\text{O} + 12 \text{ SiO}_2 + 1.5 \text{ H}_2\text{O} = 1.5 \text{ Arf} + 0.875 \text{ O}_2$
(10)	$3.75 \text{ Fa} + 2.25 \text{ Na}_2\text{O} + 8.25 \text{ SiO}_2 + 1.5 \text{ H}_2\text{O} + 0.375 \text{ O}_2 = 1.5 \text{ Arf}$
(11)	$3.75 \text{ Fa} + 1.875 \text{ O}_2 = 3.75 \text{ Hem} + 3.75 \text{ SiO}_2$
(12)	$3.75 \text{ Fa} + 1.25 \text{ O}_2 = 2.5 \text{ Mag} + 3.75 \text{ SiO}_2$
(13)	$2.5 \text{ Mag} + 3.75 \text{ Na}_2\text{O} + 15 \text{ SiO}_2 + 0.625 \text{ O}_2 = 7.5 \text{ Aeg}$
(14)	$3.75 \text{ Fa} + 3.75 \text{ Na}_2\text{O} + 11.25 \text{ SiO}_2 + 1.875 \text{ O}_2 = 7.5 \text{ Aeg}$
(15)	$3.75 \text{ Hem} + 2.25 \text{ Na}_2\text{O} + 12 \text{ SiO}_2 + 1.5 \text{ H}_2\text{O} = 1.5 \text{ Arf} + 1.5 \text{ O}_2$
(16)	$2.5 \text{ Mag} + 2.25 \text{ Na}_2\text{O} + 12 \text{ SiO}_2 + 1.5 \text{ H}_2\text{O} = 1.5 \text{ Arf} + 0.875 \text{ O}_2$
(17)	$2.5 \text{ Mag} + 0.625 \text{ O}_2 = 3.75 \text{ Hem}$
(18)	$1.5 \text{ Arf} + 1.5 \text{ O}_2 = 3.75 \text{ Hem} + 2.25 \text{ SiO}_2 + 2.25 \text{ Na}_2\text{O} + 1.5 \text{ H}_2\text{O}$
(19)	$1.5 \text{ Arf} + 3 \text{ SiO}_2 + 1.5 \text{ Na}_2\text{O} + 1.5 \text{ O}_2 = 7.5 \text{ Aeg} + 1.5 \text{ H}_2\text{O}$
(20)	$2.5 \text{ Mag} + 3.75 \text{ Na}_2\text{O} + 15 \text{ SiO}_2 + 0.625 \text{ O}_2 = 7.5 \text{ Aeg}$
(21)	$2.5 \text{ Mag} + 7.5 \text{ Aeg} + 1.5 \text{ H}_2\text{O} = 1.5 \text{ Arf} + 3.75 \text{ Hem} + 1.5 \text{ Na}_2\text{O} + 3 \text{ SiO}_2 + 0.875 \text{ O}_2$
(22)	$2.5 \text{ Mag} + 2.25 \text{ Na}_2\text{O} + 12 \text{ SiO}_2 + 1.5 \text{ H}_2\text{O} = 1.5 \text{ Arf} + 0.875 \text{ O}_2$

Reactions (1)–(8) are used to construct the diagrams illustrated in Fig. 1a and b; reactions (9)–(22) are used for Fig. 1c.

important: Arf + Mag, Arf + Aeg, Mag + Aeg, Mag + Hem, Aeg + Hem, Arf + Hem, Fa + Mag, Fa + Arf, Fa + Aeg and Fa + Hem. The last two are considered to be unstable as they each comprise a pure Fe^{2+} -phase and a pure Fe^{3+} -phase and consequently, they should react to a mixed Fe^{2+} – Fe^{3+} two-phase assemblage (Fa + Arf, Fa + Mag, Mag + Hem or Arf + Hem), depending on $\mu_{\text{Na}_2\text{O}}$, μ_{O_2} and μ_{SiO_2} . Higher μ_{SiO_2} results in a decrease in the relative size of the Fa + Mag and the Mag + Hem fields, whereas Aeg-bearing assemblages become more stable (dashed line in Fig. 1c). This is in qualitative accordance with the observation that Fa-bearing syenites are more common in alkaline intrusive complexes compared with Fa-bearing granites (see, e.g. Frost *et al.*, 1988). Furthermore, at sufficiently high $\mu_{\text{Na}_2\text{O}}$ levels, the assemblage Arf + Aeg is common in both reduced and oxidized systems. At high μ_{SiO_2} , this assemblage is stabilized to lower values of $\mu_{\text{Na}_2\text{O}}$. The assemblage Arf + Aeg is common in alkaline rocks in general and is neither restricted to miaskites or agpaites nor to SiO_2 -undersaturated or SiO_2 -oversaturated alkaline rocks.

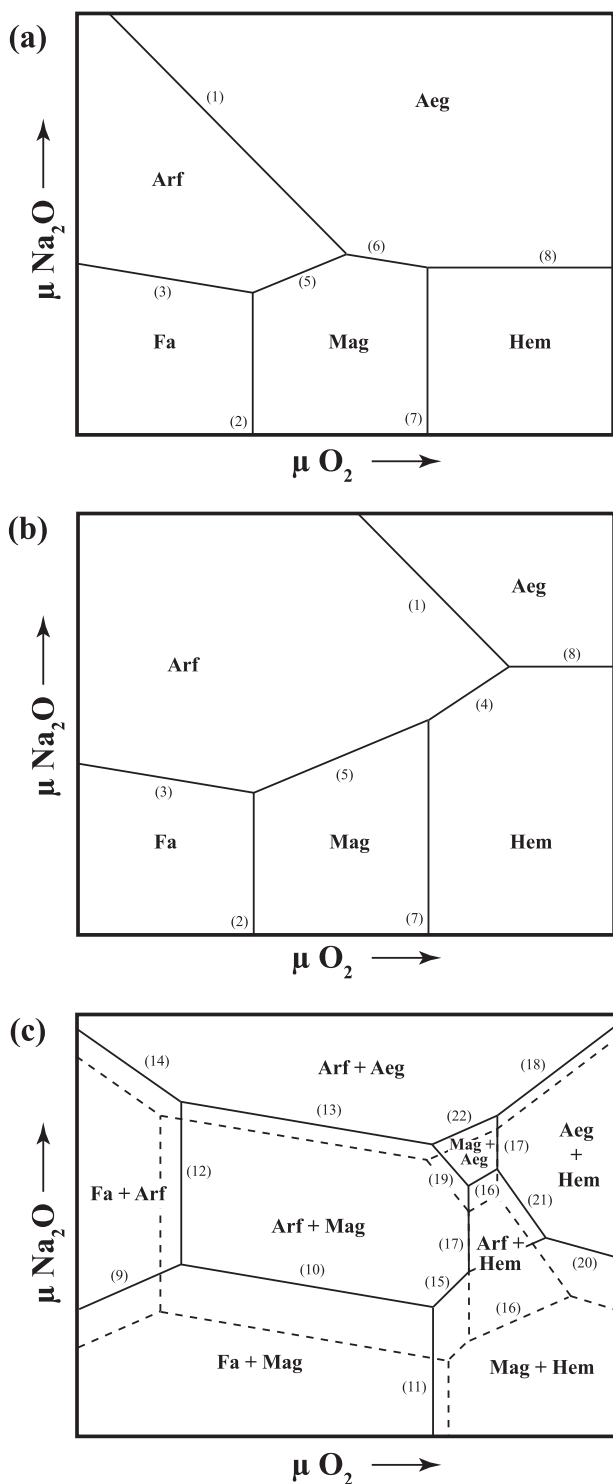


Fig. 1. Qualitative $\mu\text{Na}_2\text{O}$ vs μO_2 diagrams for the system Fa–Mag–Hem–Arf–Aeg. (a) and (b) show two possible topologies for the stability relations between the different phases [reactions (1)–(8) of Table 2]. (c) illustrates the relative stabilities of the different two-phase assemblages [reactions (9)–(22) of Table 2]. The dashed line indicates the qualitative effect of increasing a_{SiO_2} (see text for details).

Ti- AND Zr-MINERAL ASSEMBLAGES IN ALKALINE PLUTONIC ROCKS

The differences in the typical Ti and Zr mineral assemblages found in miaskitic and agpaitic nepheline syenites are obvious: in the miaskitic group, the most abundant Ti-bearing phases are ilmenite ($\pm$ Ti-bearing magnetite) and titanite. Rarely, usually in ultramafic to mafic rocks with very low silica activity, perovskite may be favored over titanite and in some rocks Ti-andradite is stable as well (e.g. Vuorinen *et al.*, 2005; Marks *et al.*, 2008a). The Zr host in these rocks is generally zircon and, in rocks of low silica activity, baddeleyite. In contrast, agpaitic rocks contain a large variety of Na–K–Ca–HFSE-phases (see e.g. Sørensen, 1997). Similarly, most granitic rocks contain zircon, ilmenite ($\pm$ Ti-bearing magnetite) and titanite. In some alkaline granites, however, a number of Na–K–Ca–HFSE-phases have been described (e.g. Kovalenko *et al.*, 1995; Salvi & Williams-Jones, 1995; Schmitt *et al.*, 2000).

Some of the Na–K–Ca–HFSE-phases are Ti- and Zr-dominated, some are Nb (+Ta)-rich, and some are dominated by REE. Not all of them are silicate minerals, but oxides, carbonates and phosphates also play an important role. As Nb and REE concentrations are significantly lower in most silicate melts than Ti and Zr concentrations, Nb- or REE-dominated minerals generally crystallize later than Ti- and Zr-rich ones, if they crystallize at all. Ti and Zr silicates (such as eudialyte) typically contain significant amounts of Nb and REE, which prevents the melts reaching concentrations that are sufficiently high to stabilize Nb or REE endmember phases at magmatic stages. Hence, a large number of other HFSE-rich minerals precipitate under late-stage magmatic to hydrothermal conditions or during metasomatic alteration of primary magmatic phases (e.g. Sørensen, 1997; Salvi *et al.*, 2000; Mitchell & Liferovich, 2006; Schilling *et al.*, 2009; Andersen *et al.*, 2010). Because this study concerns only the evolution of HFSE-mineral assemblages under magmatic conditions, such secondary minerals are not the topic of the discussion here.

Below we briefly review the typical occurrences of the most important Na–Ca–K–HFSE-phases in alkaline rocks, as described in the literature. Given the unusual variety of HFSE-rich minerals in such rocks, we decided to focus on the most common species found (Tables 1 and 3). Detailed descriptions of the textural relationships between the various Na–Ca–K–HFSE-phases are unavailable for some occurrences. It is not always clear if several Na–Ca–K–HFSE-phases in a single rock form a stable mineral assemblage or if they are simply associated within a single rock type via a series of reaction textures. We thus give only general information on the observed HFSE-rich mineral associations, which nevertheless serve as the best

Table 3: Important localities and references for some of the more common HFSE-rich silicate minerals in alkaline rocks as mentioned in the text

	Syenitic rocks	Granitic rocks
Eudialyte	Ilimaussaq (Greenland) ¹ Motzfeld (Greenland) ¹⁸ Saima (China) ² Khibiny and Lovozero (Russia) ³ Tamazeght (Morocco) ⁴ Mont Saint Hilaire (Canada) ⁵ Langesundfjord (Norway) ⁶ Gordon Butte (USA) ⁷ Red Wine and Kipawa (Canada) ⁸ Pocos de Caldas (Brazil) ¹⁴	Straumsvola (Antarctica) ⁹ Ascension Island ¹⁰
Catapleite	Langesundfjord (Norway) ⁶ Mont Saint Hilaire (Canada) ⁵ Ilimaussaq (Greenland) ¹ Khibiny and Lovozero (Russia) ³ Gordon Butte (USA) ⁷ Pocos de Caldas (Brazil) ¹⁴	Strange Lake (Canada) ¹¹
Elpidite	Mont Saint Hilaire (Canada) ⁵ Khibiny and Lovozero (Russia) ³ Pocos de Caldas (Brazil) ¹⁴ Gjerdingen (Norway) ¹³	Strange Lake (Canada) ¹¹ Khaldzan Buragtag (Mongolia) ¹² Ilimaussaq (Greenland) ¹
Wadeite	Mont Saint Hilaire (Canada) ⁵ Khibiny (Russia) ³ Gordon Butte (USA) ⁷ Pocos de Caldas (Brazil) ¹⁴	
Dalyite	Langesundfjord (Norway) ⁶ Gjerdingen (Norway) ¹³ Azores (Portugal) ¹⁵ Straumsvola (Antarctica) ⁹ Amis (Namibia) ¹⁶	Strange Lake (Canada) ¹¹
Aenigmatite	Ilimaussaq ¹ , Puklen ¹⁷ and Motzfeld ¹⁸ (Greenland) Khibiny and Lovozero (Russia) ³ Pocos de Caldas (Brazil) ¹⁴	Amis (Namibia) ¹⁶ Ascension Island ¹⁰
Astrophyllite	Langesundfjord (Norway) ⁶ Khibiny and Lovozero (Russia) ³ Ilimaussaq (Greenland) ¹ Pocos de Caldas (Brazil) ¹⁴ Mont Saint Hilaire (Canada) ⁵	Puklen (Greenland) ¹⁷ Strange Lake (Canada) ¹¹ Amis (Namibia) ¹⁶ Khaldzan Buragtag (Mongolia) ¹² Gjerdingen (Norway) ¹³

1, Ussing (1912); Ferguson (1964); Larsen (1977); Marks & Markl (2003); Müller-Lorch *et al.* (2007). 2, Chen & Saima Deposit Research Group (1978); Wu *et al.* (2010). 3, Kogarko *et al.* (1982); Pekov (1998); Arzamastsev *et al.* (2001, 2005). 4, Kchit (1990); Khadem-Allah (1993); Khadem-Allah *et al.* (1998); Salvi *et al.* (2000); Marks *et al.* (2008a, 2008b); Schilling *et al.* (2009). 5, Horvath & Gault (1990); Wight & Chao (1995). 6, Brøgger (1890); Bollinberg *et al.* (1983); Andersen *et al.* (2010). 7, Chakhmouradian & Mitchell (2002). 8, Edgar & Blackburn (1972); Blaxland (1977); Allan (1992). 9, Harris & Rickard (1987). 10, Roedder & Coombs (1967); Harris *et al.* (1982). 11, Birkett *et al.* (1992); Salvi & Williams-Jones (1995, 1996). 12, Kovalenko *et al.* (1995). 13, Raade & Mladeck (1983). 14, Atencio *et al.* (1999); Lustrino *et al.* (2003). 15, Ridolfi *et al.* (2003). 16, Schmitt *et al.* (2000). 17, Pulvertaft (1961); Parsons (1972); Marks *et al.* (2003). 18, Jones & Peckett (1980) Jones (1984); Schönerberger & Markl (2008).

source of information available. Table 3 summarizes important localities for these minerals and provides supporting references.

Eudialyte [$\text{Na}_{15}\text{Ca}_6\text{Fe}_3\text{Zr}_3\text{Si}_{26}\text{O}_{72}(\text{OH})_4\text{Cl}$] is by far the most common Zr-mineral in agpaitic rocks. It occurs as a magmatic phase (e.g. in Ilimaussaq, Saima, Khibina and Lovozero), and in late-magmatic patches, pegmatites and veins (e.g. Tamazeght, Langesundfjord, Gordon Butte); it has also been described from metamorphosed agpaites (Red Wine and Kipawa). In some occurrences, eudialyte is reported to be associated with zircon, catapleite, dalyite, titanite, aenigmatite or astrophyllite. Eudialyte also occurs as a magmatic phase in some granitic rocks from Straumsvola (Antarctica) associated with dalyite and from Ascension Island associated with aenigmatite, vlasovite, dalyite and zircon.

Catapleite ($\text{Na}_2\text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$) mainly occurs in agpaitic rocks and associated pegmatites (e.g. Langesundfjord, Mont Saint Hilaire, Ilimaussaq, Khibina and Lovozero) and may be associated with zircon, eudialyte and astrophyllite. It also occurs as a late-magmatic phase in peralkaline granites from the Strange Lake Complex.

Elpidite ($\text{Na}_2\text{ZrSi}_6\text{O}_{15} \cdot 3\text{H}_2\text{O}$) is mainly known from peralkaline granites (e.g. Strange Lake Complex, Khaldzan Buragtag Massif, Ilimaussaq, Gjerdingen) where it occurs as a magmatic phase associated with zircon, vlasovite, dalyite, aenigmatite and astrophyllite. Rarely, it occurs in the late-magmatic to hydrothermal stages of agpaitic syenites (e.g. Mont Saint Hilaire, Khibina and Lovozero).

The K–Zr silicates wadeite ($\text{K}_2\text{ZrSi}_3\text{O}_9$) and dalyite ($\text{K}_2\text{ZrSi}_6\text{O}_{15}$) are known from several lamproite and kimberlite occurrences (e.g. Salvioli-Marini & Venturelli, 1996). Dalyite has also been observed as an accessory mineral in peralkaline granites and quartz-syenites (e.g. Strange Lake, the Azores, Gjerdingen, Straumsvola, Amis Complex). It is associated with eudialyte, zircon, titanite, aenigmatite or astrophyllite. It has also been described from late-magmatic pegmatites of the Oslo region. Wadeite is only known from agpaitic pegmatites and hydrothermal veins and late-stage vugs (e.g. Mt Saint Hilaire, Khibina, Gordon Butte; Pocos de Caldas) together with astrophyllite or eudialyte.

Aenigmatite ($\text{Na}_2\text{TiFe}_5\text{Si}_6\text{O}_{20}$) is frequently observed in both alkaline syenites and granites as a magmatic or late-magmatic phase (e.g. Ilimaussaq, Puklen and Motzfeld in Greenland; Khibina and Lovozero in Russia; the Amis complex). Commonly, it replaces Fe–Ti oxides and is reported to coexist with zircon, eudialyte, dalyite, titanite and astrophyllite.

Astrophyllite [$\text{K}_3\text{Fe}_7\text{Ti}_2\text{Si}_8\text{O}_{26}(\text{OH})_5$] occurs as a late-magmatic phase in syenites, granites and associated pegmatites. Important locations are the Langesund region, the Kola complexes, the Ilimaussaq and Puklen complexes,

Strange Lake, Mont Saint Hilaire, Amis, Red Wine, Pilansberg and Khaldzan Buragtag. Astrophyllite may be associated with zircon, eudialyte, catapleite, elpidite, dalyite and aenigmatite.

In addition to the above-mentioned minerals, there are additional Na–Ca–HFSE phases in agpaitic rocks that contain significant amounts of fluorine, including minerals of the wöhlerite [e.g. $\text{Na}_2\text{Ca}_4\text{ZrNb}(\text{Si}_2\text{O}_7)\text{O}_3\text{F}$], rosenbuschite $[(\text{Ca},\text{Na})_3(\text{Zr},\text{Ti})\text{Si}_2\text{O}_7\text{FO}]$ and rinkite groups $[\text{Ti}(\text{Na},\text{Ca})_3(\text{Ca},\text{Ce})_4(\text{Si}_2\text{O}_7)(\text{O},\text{F})_4]$. These are not considered further here, as most of their described occurrences are either late-magmatic or hydrothermal (e.g. Andersen *et al.*, 2010) or they form as a result of secondary Ca-metasomatism (e.g. Khadem-Allah *et al.*, 1998; Salvi *et al.*, 2000). Vlasovite ($\text{Na}_2\text{ZrSi}_4\text{O}_{11}$) occurs in very similar environments to elpidite, but is extremely rare (e.g. Currie & Zaleski, 1985). It is therefore not discussed further. Gittinsite ($\text{CaZrSi}_2\text{O}_7$) has been described from the metamorphosed agpaites of the Kipawa Complex, Canada (Ansell *et al.*, 1980) and from silicocarbonatites of the Afrikanda Complex, Russia, replacing primary zircon (Chakhmouradian & Zaitsev, 2002). In addition, it also occurs in the peralkaline granites of the Strange Lake Complex (Canada) and the Khaldzan Buragtag massif (Mongolia), where it forms a secondary alteration product after elpidite caused by the influx of external Ca-rich fluids (Birkett *et al.* 1992; Kovalenko *et al.*, 1995; Salvi & Williams-Jones, 1995; Roelofsen & Veblen, 1999). Thus, gittinsite seems not to form by primary magmatic processes. The same is true for armstrongite ($\text{CaZrSi}_6\text{O}_{15}\cdot 3\text{H}_2\text{O}$), which occurs associated with or replacing gittinsite (Salvi & Williams-Jones, 1995). Consequently, these two minerals are not considered further in our discussion. Minerals of the lovozerite group are also extremely rare and some of them (e.g. zirsinallite, $\text{Na}_6\text{CaZrSi}_6\text{O}_{18}$) form only under hyper-agpaitic conditions (e.g. Sørensen, 1997). From a magmatic perspective, this is well beyond the transition from miaskitic to agpaitic rocks. Detailed accounts of the occurrence of these minerals and the factors influencing their relative stability have been given by, for example, Khomyakov (1995), Sørensen (1997), Sørensen & Larsen (2001) and Andersen *et al.* (2010).

THE ROLE OF Na, K AND Ca ACTIVITIES IN SILICATE MELTS IN THE FORMATION OF SPECIFIC HFSE-MINERAL ASSEMBLAGES

Below we investigate the influence of the chemical potentials of Na, K and Ca oxides in the melt on the formation of specific HFSE-rich mineral assemblages. For our purpose, we consider ilmenite, titanite, aenigmatite and astrophyllite as the relevant Ti-phases and zircon, eudialyte,

elpidite, catapleite, dalyite and wadeite as the relevant Zr-phases (see Table 1 for the simplified endmember formulae used). These minerals are the most common primary Ti- and Zr-phases in alkaline igneous rocks. In most alkaline igneous rocks, complex Zr-silicates are more abundant than complex Ti-silicates and in some samples Ti-silicates may be absent. This is probably an effect of the early fractionation history of the parental melts, as significant fractionation of Fe–Ti oxides strongly depletes the melts in Ti (e.g. Larsen, 1976; Marks & Markl, 2001; Marks *et al.*, 2004; Ryabchikov & Kogarko, 2006). To evaluate the relative stabilities of both Zr- and Ti-silicates, the calculations below are performed assuming sufficient Zr and Ti to form the relevant phases.

Most of the Zr-phases contain small amounts of Ti and vice versa, but for simplicity we treat them here as pure phases (Table 1). The same simplifications are applied to Na and K: for example, eudialyte generally contains small amounts of K, but Na dominates by far (Pfaff *et al.*, 2008, 2010). The opposite is true for astrophyllite, which typically contains large amounts of K and only minor amounts of Na (Piilonen *et al.*, 2003; Macdonald *et al.*, 2007). Solid solution will expand the stability field of the phases that accept the dissolving component, but should have minimal effect on the topologies and slopes of the reactions in activity–activity diagrams.

Based on the commonly observed assemblages of Zr-silicates (see above), syenitic and granitic systems show significant differences, as follows.

- (1) In terms of pure Na–Zr silicates, catapleite seems to be restricted to syenitic systems, whereas elpidite mainly occurs in peralkaline granites. There are no reports of primary magmatic catapleite in peralkaline granites in the literature, although catapleite has been reported as a late- to post-magmatic phase in peralkaline granites from the Strange Lake Complex, Canada (Birkett *et al.*, 1992).
- (2) In terms of pure K–Zr silicates, dalyite occurs as an accessory mineral in peralkaline granites and quartz-syenites, whereas wadeite has been described only from nepheline syenites and associated pegmatites.

Consequently, we discuss syenitic and granitic systems separately.

SYENITIC SYSTEMS: THE TRANSITION FROM MIASKITIC TO AGPAITIC ASSEMBLAGES

To evaluate the relative stabilities of the HFSE-phases in syenitic systems and to investigate the chemical controls on the transition of miaskites to agpaites, we constructed a set of μ – μ diagrams using Schreinemaker's analysis,

where Na_2O , K_2O and CaO are treated as mobile components (Fig. 2):

- (1) μCaO vs $\mu\text{Na}_2\text{O}$ (considering ilmenite, titanite, aenigmatite, catapleite, eudialyte and zircon);
- (2) μCaO vs $\mu\text{K}_2\text{O}$ (considering ilmenite, titanite, astrophyllite, zircon and wadeite);
- (3) $\mu\text{Na}_2\text{O}$ vs $\mu\text{K}_2\text{O}$ (considering ilmenite, aenigmatite, astrophyllite, zircon and wadeite).

Some of the phases involved contain Fe, some do not. Consequently, a donor for Fe is needed to balance the relevant reactions (Table 4). Depending on f_{O_2} and $\mu\text{Na}_2\text{O}$, the iron-bearing phases considered are fayalite, magnetite, hematite, arfvedsonite or aegirine (Fig. 1). Reaction (23) in Table 4 may serve as an example as it can be balanced in four different ways in which the iron donor is (1) FeO in the melt, (2) fayalite, (3) magnetite and hematite and (4) arfvedsonite and aegirine. The only difference between the first reaction and the second is silica, because fayalite can be written $2\text{FeO} + \text{SiO}_2$. The only difference between the first reaction and the third is Fe^{3+} , because the difference between magnetite and hematite is FeO (i.e. $\text{FeO} + \text{Fe}_2\text{O}_3 = \text{Fe}_3\text{O}_4$). Obviously, there is no effect on the slope of the reactions in the respective μ - μ diagrams and consequently no influence on their topology. Thus, the relative stability of the respective Ti and Zr phase pairs in miaskitic vs agpaite rocks does not directly depend on f_{O_2} ; instead, $\mu\text{Na}_2\text{O}$, μCaO and $\mu\text{K}_2\text{O}$ are the governing parameters. Hence, all further reactions are balanced using fayalite as the Fe donor, even though fayalite itself may not be in the assemblage involved. The fourth reaction involves arfvedsonite and aegirine, which changes the slope of the reactions (Table 4). The resulting topology (Fig. 3a), however, is considered to be not useful here, as reaction (23), the formation of aenigmatite at the expense of ilmenite, would be independent of Na_2O and would thus not appear in the diagram and reactions (25) and (29), reactions (27) and (31) and reactions (28) and (32) would have the same slope. Consequently, ilmenite and aenigmatite would be equivalent and one could not distinguish between the assemblages $\text{ilm} + \text{zrn}$ and $\text{aen} + \text{zrn}$, $\text{ilm} + \text{eud}$ and $\text{aen} + \text{eud}$ or $\text{ilm} + \text{cat}$ and $\text{aen} + \text{cat}$ in the diagrams. The dependence on Na_2O is eliminated because the $\text{aeg} + \text{arf}$ assemblage itself implies a high $\mu\text{Na}_2\text{O}$ environment where ilmenite is not stable. Otherwise, the use of fayalite and Fe-oxides for Fe-balancing is strictly valid only for the medium to low $\mu\text{Na}_2\text{O}$ region of the diagrams. This might imply that the stability fields for the $\text{ilm} + \text{eud}$ and the $\text{ilm} + \text{cat}$ assemblages do not exist at all. To our knowledge these assemblages have not been reported from natural samples, which implies that the assemblages do not occur in nature or have very narrow stability fields that are rarely attained. The Ca-K subsystem is not affected by using arfvedsonite and aegirine to balance

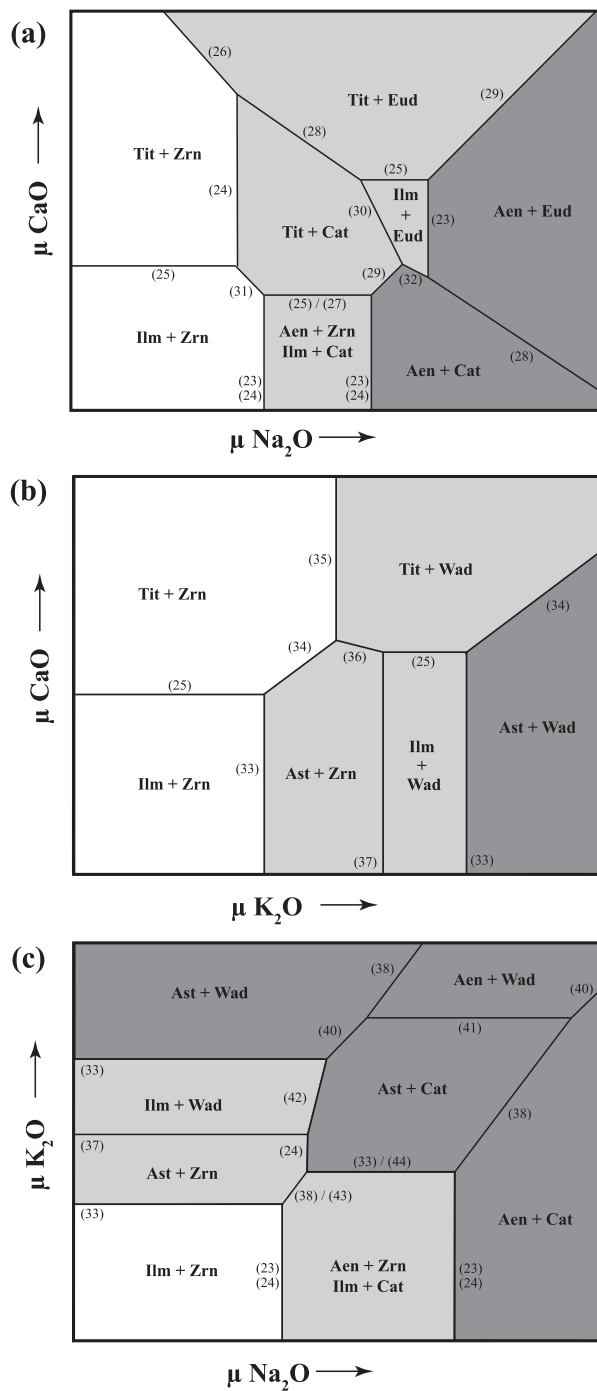


Fig. 2. Qualitative μ - μ diagrams illustrating the transformation from miaskitic (white) to agpaite (dark gray) rocks and transitional assemblages (light gray).

the equations (as arfvedsonite and aegirine are here treated as Ca- and K-free). For the Na-K subsystem, similar flaws as for the Na-Ca subsystem would arise, as ilmenite and aenigmatite could not be distinguished (Fig. 3b).

Table 4: Reactions in the Ca–Na, Ca–K and Na–K sub-systems used to construct the μ – μ diagrams shown in Fig. 2

(a) Reactions in the Ca–Na-subsystem

(23) IW:	$\text{Ilm} + \text{Na}_2\text{O} + 6 \text{ SiO}_2 + 4 \text{ FeO} = \text{Aen}$	[∞]
(23) FMQ:	$\text{Ilm} + \text{Na}_2\text{O} + 4 \text{ SiO}_2 + 2 \text{ Fa} = \text{Aen}$	[∞]
(23) HM:	$\text{Ilm} + \text{Na}_2\text{O} + 6 \text{ SiO}_2 + 4 \text{ Mag} = \text{Aen} + 4 \text{ Hem}$	[∞]
(23) Arf–Aeg:	$\text{Ilm} + \text{Arf} = \text{Aen} + \text{Aeg} + \text{H}_2\text{O}$	[–]
(24)	$\text{Zrn} + \text{Na}_2\text{O} + 2 \text{ SiO}_2 + 2 \text{ H}_2\text{O} = \text{Cat}$	[∞]
(25) IW:	$\text{Ilm} + \text{SiO}_2 + \text{CaO} = \text{Tit} + \text{FeO}$	[0]
(25) FMQ:	$\text{Ilm} + 1.5 \text{ SiO}_2 + \text{CaO} = \text{Tit} + 0.5 \text{ Fa}$	[0]
(25) HM:	$\text{Ilm} + \text{SiO}_2 + \text{CaO} + \text{Hem} = \text{Tit} + \text{Mag}$	[0]
(25) Arf–Aeg:	$\text{Ilm} + 0.25 \text{ Aeg} + 0.25 \text{ Na}_2\text{O} + \text{CaO} + 2.5 \text{ SiO}_2 + 0.25 \text{ H}_2\text{O} = \text{Tit} + 0.25 \text{ Arf}$	[–0.25]
(26) IW:	$3 \text{ Zrn} + 6 \text{ CaO} + \text{NaCl} + 2 \text{ H}_2\text{O} + 23 \text{ SiO}_2 + 7 \text{ Na}_2\text{O} + 3 \text{ FeO} = \text{Eud}$	[–1.17]
(26) FMQ:	$3 \text{ Zrn} + 6 \text{ CaO} + \text{NaCl} + 2 \text{ H}_2\text{O} + 21.5 \text{ SiO}_2 + 7 \text{ Na}_2\text{O} + 1.5 \text{ Fa} = \text{Eud}$	[–1.17]
(26) HM:	$3 \text{ Zrn} + 6 \text{ CaO} + \text{NaCl} + 2 \text{ H}_2\text{O} + 23 \text{ SiO}_2 + 7 \text{ Na}_2\text{O} + 3 \text{ Mag} = \text{Eud} + 3 \text{ Hem}$	[–1.17]
(26) Arf–Aeg:	$3 \text{ Zrn} + 0.75 \text{ Arf} + 1.25 \text{ H}_2\text{O} + \text{NaCl} + 18.5 \text{ SiO}_2 + 6 \text{ CaO} + 6.25 \text{ Na}_2\text{O} = \text{Eud} + 0.75 \text{ Aeg}$	[–1.04]
(27) IW:	$\text{Aen} + \text{Zrn} + \text{CaO} + 2 \text{ H}_2\text{O} = \text{Tit} + \text{Cat} + 3 \text{ SiO}_2 + 5 \text{ FeO}$	[0]
(27) FMQ:	$\text{Aen} + \text{Zrn} + \text{CaO} + 2 \text{ H}_2\text{O} = \text{Tit} + \text{Cat} + 0.5 \text{ SiO}_2 + 2.5 \text{ Fa}$	[0]
(27) HM:	$\text{Aen} + \text{Zrn} + \text{CaO} + 2 \text{ H}_2\text{O} + 5 \text{ Hem} = \text{Tit} + \text{Cat} + 3 \text{ SiO}_2 + 5 \text{ Mag}$	[0]
(27) Arf–Aeg:	$\text{Aen} + \text{Zrn} + \text{CaO} + 3.25 \text{ H}_2\text{O} + 1.25 \text{ Aeg} + 1.25 \text{ Na}_2\text{O} + 4.5 \text{ SiO}_2 = \text{Tit} + \text{Cat} + 1.25 \text{ Arf}$	[–1.25]
(28) IW:	$3 \text{ Cat} + 6 \text{ CaO} + 4 \text{ Na}_2\text{O} + \text{NaCl} + 3 \text{ FeO} + 17 \text{ SiO}_2 = \text{Eud} + 4 \text{ H}_2\text{O}$	[–0.67]
(28) FMQ:	$3 \text{ Cat} + 6 \text{ CaO} + 4 \text{ Na}_2\text{O} + \text{NaCl} + 1.5 \text{ Fa} + 15.5 \text{ SiO}_2 = \text{Eud} + 4 \text{ H}_2\text{O}$	[–0.67]
(28) HM:	$3 \text{ Cat} + 6 \text{ CaO} + 4 \text{ Na}_2\text{O} + \text{NaCl} + 3 \text{ Mag} + 17 \text{ SiO}_2 = \text{Eud} + 3 \text{ Hem} + 4 \text{ H}_2\text{O}$	[–0.67]
(28) Arf–Aeg:	$3 \text{ Cat} + 0.75 \text{ Arf} + 6 \text{ CaO} + 3.25 \text{ Na}_2\text{O} + \text{NaCl} + 12.5 \text{ SiO}_2 = \text{Eud} + 0.75 \text{ Aeg} + 4.75 \text{ H}_2\text{O}$	[–0.54]
(29) IW:	$\text{Tit} + 5 \text{ SiO}_2 + \text{Na}_2\text{O} + 5 \text{ FeO} = \text{Aen} + \text{CaO}$	[1]
(29) FMQ:	$\text{Tit} + 2.5 \text{ SiO}_2 + \text{Na}_2\text{O} + 2.5 \text{ Fa} = \text{Aen} + \text{CaO}$	[1]
(29) HM:	$\text{Tit} + 5 \text{ Mag} + 5 \text{ SiO}_2 + \text{Na}_2\text{O} = \text{Aen} + \text{CaO} + 5 \text{ Hem}$	[1]
(29) Arf–Aeg:	$\text{Tit} + 1.25 \text{ Arf} = \text{Aen} + \text{CaO} + 0.25 \text{ Na}_2\text{O} + 2.5 \text{ SiO}_2 + 1.25 \text{ H}_2\text{O} + 1.25 \text{ Aeg}$	[–0.25]
(30) IW:	$3 \text{ Tit} + 3 \text{ Cat} + 14 \text{ SiO}_2 + 3 \text{ CaO} + 4 \text{ Na}_2\text{O} + \text{NaCl} + 6 \text{ FeO} = 3 \text{ Ilm} + \text{Eud} + 4 \text{ H}_2\text{O}$	[–1.33]
(30) FMQ:	$3 \text{ Tit} + 3 \text{ Cat} + 11 \text{ SiO}_2 + 3 \text{ CaO} + 4 \text{ Na}_2\text{O} + \text{NaCl} + 3 \text{ Fa} = 3 \text{ Ilm} + \text{Eud} + 4 \text{ H}_2\text{O}$	[–1.33]
(30) HM:	$3 \text{ Tit} + 3 \text{ Cat} + 14 \text{ SiO}_2 + 3 \text{ CaO} + 4 \text{ Na}_2\text{O} + \text{NaCl} + 6 \text{ Mag} = 3 \text{ Ilm} + \text{Eud} + 6 \text{ Hem} + 4 \text{ H}_2\text{O}$	[–1.33]
(30) Arf–Aeg:	$3 \text{ Tit} + 3 \text{ Cat} + 1.5 \text{ Arf} + \text{NaCl} + 2.5 \text{ Na}_2\text{O} + 3 \text{ CaO} + 5 \text{ SiO}_2 = 3 \text{ Ilm} + \text{Eud} + 1.5 \text{ Aeg} + 5.5 \text{ H}_2\text{O}$	[–0.83]
(31) IW:	$\text{Ilm} + \text{Zrn} + 3 \text{ SiO}_2 + \text{CaO} + \text{Na}_2\text{O} + 2 \text{ H}_2\text{O} = \text{Tit} + \text{Cat} + \text{FeO}$	[–1]
(31) FMQ:	$\text{Ilm} + \text{Zrn} + 3.5 \text{ SiO}_2 + \text{CaO} + \text{Na}_2\text{O} + 2 \text{ H}_2\text{O} = \text{Tit} + \text{Cat} + 0.5 \text{ Fa}$	[–1]
(31) HM:	$\text{Ilm} + \text{Zrn} + 3 \text{ SiO}_2 + \text{CaO} + \text{Na}_2\text{O} + 2 \text{ H}_2\text{O} + \text{Hem} = \text{Tit} + \text{Cat} + \text{Mag}$	[–1]
(31) Arf–Aeg:	$\text{Ilm} + \text{Zrn} + 0.25 \text{ Aeg} + 4.5 \text{ SiO}_2 + \text{CaO} + 1.25 \text{ Na}_2\text{O} + 2.25 \text{ H}_2\text{O} = \text{Tit} + \text{Cat} + 0.25 \text{ Arf}$	[–1.25]
(32) IW:	$3 \text{ Aen} + 3 \text{ Cat} + 6 \text{ CaO} + \text{Na}_2\text{O} + \text{NaCl} = 3 \text{ Ilm} + \text{Eud} + \text{SiO}_2 + 9 \text{ FeO} + 4 \text{ H}_2\text{O}$	[–0.17]
(32) FMQ:	$3 \text{ Aen} + 3 \text{ Cat} + 6 \text{ CaO} + \text{Na}_2\text{O} + \text{NaCl} + 3.5 \text{ SiO}_2 = 3 \text{ Ilm} + \text{Eud} + 4.5 \text{ Fa} + 4 \text{ H}_2\text{O}$	[–0.17]
(32) HM:	$3 \text{ Aen} + 3 \text{ Cat} + 6 \text{ CaO} + \text{Na}_2\text{O} + \text{NaCl} + 9 \text{ Hem} = 3 \text{ Ilm} + \text{Eud} + \text{SiO}_2 + 9 \text{ Mag} + 4 \text{ H}_2\text{O}$	[–0.17]
(32) Arf–Aeg:	$3 \text{ Aen} + 3 \text{ Cat} + 2.25 \text{ Aeg} + 6 \text{ CaO} + 3.25 \text{ Na}_2\text{O} + \text{NaCl} + 12.5 \text{ SiO}_2 = 3 \text{ Ilm} + \text{Eud} + 2.25 \text{ Arf} + 1.75 \text{ H}_2\text{O}$	[–0.54]

(b) Additional reactions in the Ca–K-subsystem

(33) IW:	$2 \text{ Ilm} + 1.5 \text{ K}_2\text{O} + 5 \text{ FeO} + 8 \text{ SiO}_2 + 2.5 \text{ H}_2\text{O} = \text{Ast}$	[∞]
(33) FMQ:	$2 \text{ Ilm} + 1.5 \text{ K}_2\text{O} + 5.5 \text{ SiO}_2 + 2.5 \text{ Fa} + 2.5 \text{ H}_2\text{O} = \text{Ast}$	[∞]
(33) HM:	$2 \text{ Ilm} + 1.5 \text{ K}_2\text{O} + 5 \text{ Mag} + 8 \text{ SiO}_2 + 2.5 \text{ H}_2\text{O} = \text{Ast} + 5 \text{ Hem}$	[∞]
(34) IW:	$\text{Ast} + 2 \text{ CaO} = 2 \text{ Tit} + 1.5 \text{ K}_2\text{O} + 7 \text{ FeO} + 6 \text{ SiO}_2 + 2.5 \text{ H}_2\text{O}$	[0.75]
(34) FMQ:	$\text{Ast} + 2 \text{ CaO} = 2 \text{ Tit} + 1.5 \text{ K}_2\text{O} + 2.5 \text{ SiO}_2 + 3.5 \text{ Fa} + 2.5 \text{ H}_2\text{O}$	[0.75]
(34) HM:	$\text{Ast} + 2 \text{ CaO} + 7 \text{ Hem} = 2 \text{ Tit} + 1.5 \text{ K}_2\text{O} + 7 \text{ Mag} + 6 \text{ SiO}_2 + 2.5 \text{ H}_2\text{O}$	[0.75]
(35)	$\text{Zrn} + \text{K}_2\text{O} + 2 \text{ SiO}_2 = \text{Wad}$	[∞]
(36) IW:	$\text{Ast} + 2 \text{ Zrn} + 2 \text{ CaO} + 0.5 \text{ K}_2\text{O} = 2 \text{ Tit} + 2 \text{ Wad} + 2 \text{ SiO}_2 + 7 \text{ FeO} + 2.5 \text{ H}_2\text{O}$	[–0.25]
(36) FMQ:	$\text{Ast} + 2 \text{ Zrn} + 2 \text{ CaO} + 0.5 \text{ K}_2\text{O} + 1.5 \text{ SiO}_2 = 2 \text{ Tit} + 2 \text{ Wad} + 3.5 \text{ Fa} + 2.5 \text{ H}_2\text{O}$	[–0.25]

(continued)

Table 4: Continued

(36) HM:	$\text{Ast} + 2 \text{Zrn} + 2 \text{CaO} + 0.5 \text{K}_2\text{O} + 7 \text{Hem} = 2 \text{Tit} + 2 \text{Wad} + 2 \text{SiO}_2 + 7 \text{Mag} + 2.5 \text{H}_2\text{O}$	[−0.25]
(37) IW:	$\text{Ast} + 2 \text{Zrn} + 0.5 \text{K}_2\text{O} = 2 \text{Ilm} + 2 \text{Wad} + 4 \text{SiO}_2 + 5 \text{FeO} + 2.5 \text{H}_2\text{O}$	[∞]
(37) FMQ:	$\text{Ast} + 2 \text{Zrn} + 0.5 \text{K}_2\text{O} = 2 \text{Ilm} + 2 \text{Wad} + 1.5 \text{SiO}_2 + 2.5 \text{Fa} + 2.5 \text{H}_2\text{O}$	[∞]
(37) HM:	$\text{Ast} + 2 \text{Zrn} + 0.5 \text{K}_2\text{O} + 5 \text{Hem} = 2 \text{Ilm} + 2 \text{Wad} + 5 \text{Mag} + 4 \text{SiO}_2 + 2.5 \text{H}_2\text{O}$	[∞]
<i>(c) Additional reactions in the Na-K-subsystem</i>		
(38) IW:	$\text{Ast} + 2 \text{Na}_2\text{O} + 3 \text{FeO} + 4 \text{SiO}_2 = 2 \text{Aen} + 1.5 \text{K}_2\text{O} + 2.5 \text{H}_2\text{O}$	[1.33]
(38) FMQ:	$\text{Ast} + 2 \text{Na}_2\text{O} + 1.5 \text{Fa} + 2.5 \text{SiO}_2 = 2 \text{Aen} + 1.5 \text{K}_2\text{O} + 2.5 \text{H}_2\text{O}$	[1.33]
(38) HM:	$\text{Ast} + 2 \text{Na}_2\text{O} + 3 \text{Mag} + 4 \text{SiO}_2 = 2 \text{Aen} + 1.5 \text{K}_2\text{O} + 3 \text{Hem} + 2.5 \text{H}_2\text{O}$	[1.33]
(38) Arf-Aeg:	$\text{Ast} + 0.75 \text{Arf} + 1.25 \text{Na}_2\text{O} = 2 \text{Aen} + 0.75 \text{Aeg} + 1.5 \text{K}_2\text{O} + 3.25 \text{H}_2\text{O} + 0.5 \text{SiO}_2$	[0.83]
(39) IW:	$\text{Ast} + 2 \text{Zrn} + 2 \text{Na}_2\text{O} + 3 \text{FeO} + 8 \text{SiO}_2 + 0.5 \text{K}_2\text{O} = 2 \text{Aen} + 2 \text{Wad} + 2.5 \text{H}_2\text{O}$	[−4]
(39) FMQ:	$\text{Ast} + 2 \text{Zrn} + 2 \text{Na}_2\text{O} + 1.5 \text{Fa} + 6.5 \text{SiO}_2 + 0.5 \text{K}_2\text{O} = 2 \text{Aen} + 2 \text{Wad} + 2.5 \text{H}_2\text{O}$	[−4]
(39) HM:	$\text{Ast} + 2 \text{Zrn} + 2 \text{Na}_2\text{O} + 3 \text{Mag} + 8 \text{SiO}_2 + 0.5 \text{K}_2\text{O} = 2 \text{Aen} + 2 \text{Wad} + 2.5 \text{H}_2\text{O} + 3 \text{Hem}$	[−4]
(39) Arf-Aeg:	$\text{Ast} + 2 \text{Zrn} + 0.75 \text{Arf} + 1.25 \text{Na}_2\text{O} + 0.5 \text{K}_2\text{O} + 3.5 \text{SiO}_2 = 2 \text{Aen} + 2 \text{Wad} + 0.75 \text{Aeg} + 3.25 \text{H}_2\text{O}$	[−2.5]
(40)	$\text{Wad} + \text{Na}_2\text{O} + 2 \text{H}_2\text{O} = \text{Cat} + \text{K}_2\text{O}$	[1]
(41) IW:	$\text{Ast} + 2 \text{Cat} + 0.5 \text{K}_2\text{O} + 3 \text{FeO} + 4 \text{SiO}_2 = 2 \text{Aen} + 2 \text{Wad} + 6.5 \text{H}_2\text{O}$	[0]
(41) FMQ:	$\text{Ast} + 2 \text{Cat} + 0.5 \text{K}_2\text{O} + 1.5 \text{Fa} + 2.5 \text{SiO}_2 = 2 \text{Aen} + 2 \text{Wad} + 6.5 \text{H}_2\text{O}$	[0]
(41) HM:	$\text{Ast} + 2 \text{Cat} + 0.5 \text{K}_2\text{O} + 3 \text{Mag} + 4 \text{SiO}_2 = 2 \text{Aen} + 2 \text{Wad} + 3 \text{Hem} + 6.5 \text{H}_2\text{O}$	[0]
(41) Arf-Aeg:	$\text{Ast} + 2 \text{Cat} + 0.75 \text{Arf} + 0.5 \text{K}_2\text{O} = 2 \text{Aen} + 2 \text{Wad} + 0.75 \text{Aeg} + 0.75 \text{Na}_2\text{O} + 0.5 \text{SiO}_2 + 7.25 \text{H}_2\text{O}$	[1.5]
(42) IW:	$2 \text{Ilm} + 2 \text{Wad} + 8 \text{SiO}_2 + 2 \text{Na}_2\text{O} + 5 \text{FeO} + 6.5 \text{H}_2\text{O} = \text{Ast} + 2 \text{Cat} + 0.5 \text{K}_2\text{O}$	[4]
(42) FMQ:	$2 \text{Ilm} + 2 \text{Wad} + 5.5 \text{SiO}_2 + 2 \text{Na}_2\text{O} + 2.5 \text{Fa} + 6.5 \text{H}_2\text{O} = \text{Ast} + 2 \text{Cat} + 0.5 \text{K}_2\text{O}$	[4]
(42) HM:	$2 \text{Ilm} + 2 \text{Wad} + 8 \text{SiO}_2 + 2 \text{Na}_2\text{O} + 5 \text{Mag} + 6.5 \text{H}_2\text{O} = \text{Ast} + 2 \text{Cat} + 5 \text{Hem} + 0.5 \text{K}_2\text{O}$	[4]
(42) Arf-Aeg:	$2 \text{Ilm} + 2 \text{Wad} + 1.25 \text{Arf} + 0.5 \text{SiO}_2 + 0.75 \text{Na}_2\text{O} + 5.25 \text{H}_2\text{O} = \text{Ast} + 2 \text{Cat} + 1.25 \text{Aeg} + 0.5 \text{K}_2\text{O}$	[1.5]
(43) IW:	$\text{Ast} + 2 \text{Zrn} + 2 \text{Na}_2\text{O} + 1.5 \text{H}_2\text{O} = 2 \text{Ilm} + 2 \text{Cat} + 1.5 \text{K}_2\text{O} + 5 \text{FeO} + 4 \text{SiO}_2$	[1.33]
(43) FMQ:	$\text{Ast} + 2 \text{Zrn} + 2 \text{Na}_2\text{O} + 1.5 \text{H}_2\text{O} = 2 \text{Ilm} + 2 \text{Cat} + 1.5 \text{K}_2\text{O} + 2.5 \text{Fa} + 1.5 \text{SiO}_2$	[1.33]
(43) HM:	$\text{Ast} + 2 \text{Zrn} + 2 \text{Na}_2\text{O} + 1.5 \text{H}_2\text{O} + 5 \text{Hem} = 2 \text{Ilm} + 2 \text{Cat} + 1.5 \text{K}_2\text{O} + 5 \text{Mag} + 4 \text{SiO}_2$	[1.33]
(43) Arf-Aeg:	$\text{Ast} + 2 \text{Zrn} + 1.25 \text{Aeg} + 3.25 \text{Na}_2\text{O} + 3.5 \text{SiO}_2 + 2.75 \text{H}_2\text{O} = 2 \text{Ilm} + 2 \text{Cat} + 1.25 \text{Arf} + 1.5 \text{K}_2\text{O}$	[2.17]
(44) IW:	$2 \text{Aen} + 2 \text{Zrn} + 1.5 \text{K}_2\text{O} + 6.5 \text{H}_2\text{O} = \text{Ast} + 2 \text{Cat} + 3 \text{FeO}$	[∞]
(44) FMQ:	$2 \text{Aen} + 2 \text{Zrn} + 1.5 \text{SiO}_2 + 1.5 \text{K}_2\text{O} + 6.5 \text{H}_2\text{O} = \text{Ast} + 2 \text{Cat} + 1.5 \text{Fa}$	[∞]
(44) HM:	$2 \text{Aen} + 2 \text{Zrn} + 1.5 \text{K}_2\text{O} + 6.5 \text{H}_2\text{O} + 3 \text{Hem} = \text{Ast} + 2 \text{Cat} + 3 \text{Mag}$	[∞]
(44) Arf-Aeg:	$2 \text{Aen} + 2 \text{Zrn} + 0.75 \text{Aeg} + 1.5 \text{K}_2\text{O} + 0.75 \text{Na}_2\text{O} + 4.5 \text{SiO}_2 + 7.25 \text{H}_2\text{O} = \text{Ast} + 2 \text{Cat} + 0.75 \text{Arf}$	[−0.5]
(45) Arf-Aeg:	$2 \text{Ilm} + 1.25 \text{Arf} + 1.5 \text{K}_2\text{O} + 0.5 \text{SiO}_2 + 1.25 \text{H}_2\text{O} = \text{Ast} + 1.25 \text{Aeg} + 1.25 \text{Na}_2\text{O} + 0.75 \text{SiO}_2$	[0.83]
(46) Arf-Aeg:	$\text{Aen} + \text{Zrn} + \text{Aeg} + \text{K}_2\text{O} + 2 \text{SiO}_2 + \text{H}_2\text{O} = \text{Ilm} + \text{Wad} + \text{Arf}$	[0]
(47) Arf-Aeg:	$2 \text{Ilm} + 2 \text{Wad} + 1.25 \text{Arf} + 1.25 \text{H}_2\text{O} = \text{Ast} + 2 \text{Zrn} + 1.25 \text{Aeg} + 0.5 \text{K}_2\text{O} + 1.25 \text{Na}_2\text{O} + 3.5 \text{SiO}_2$	[−2.5]

The first three of each set of reactions [calculated at iron-wüstite (IW), fayalite-magnetite-quartz (FMQ) and hematite-magnetite (HM) conditions] demonstrate that oxygen fugacity does not change the slopes of the respective reactions (in brackets). Thus, the topology of the diagrams remains unchanged. The fourth reaction is oxygen balanced using arfvedsonite and aegirine. The meaning of these reactions is discussed in the text in detail and illustrated in Fig. 3.

In each of the diagrams in Fig. 2, several possible two-phase assemblages consisting of one Ti- and one Zr-phase can be identified. An important conclusion from these diagrams is that the typical miaskitic assemblages (ilm + zrn and tit + zrn) are separated from the fully agpaitic assemblages (aen + eud and aen + cat for the Na-Ca system, ast + wad for the K-Ca system and ast + wad, ast + cat, aen + wad and aen + cat for the Na-K system) by several transitional two-phase assemblages (tit + eud, tit + cat, ilm + eud, aen + zrn, tit + wad, ast + zrn and ilm + wad). This implies that a broad range

of transitional assemblages should exist in nature between truly agpaitic and miaskitic assemblages.

Eudialyte vs catapleite: the influence of NaCl and H₂O activity

The stability of catapleite relative to eudialyte is a function of H₂O and NaCl activities [reactions (28), (30) and (32), Table 4]. High H₂O activities favor catapleite over eudialyte (Fig. 4a). In turn, the formation of magmatic eudialyte requires a certain level of NaCl activity in the melt and the stability of eudialyte in the $\mu\text{Na}_2\text{O}$ – μCaO system is

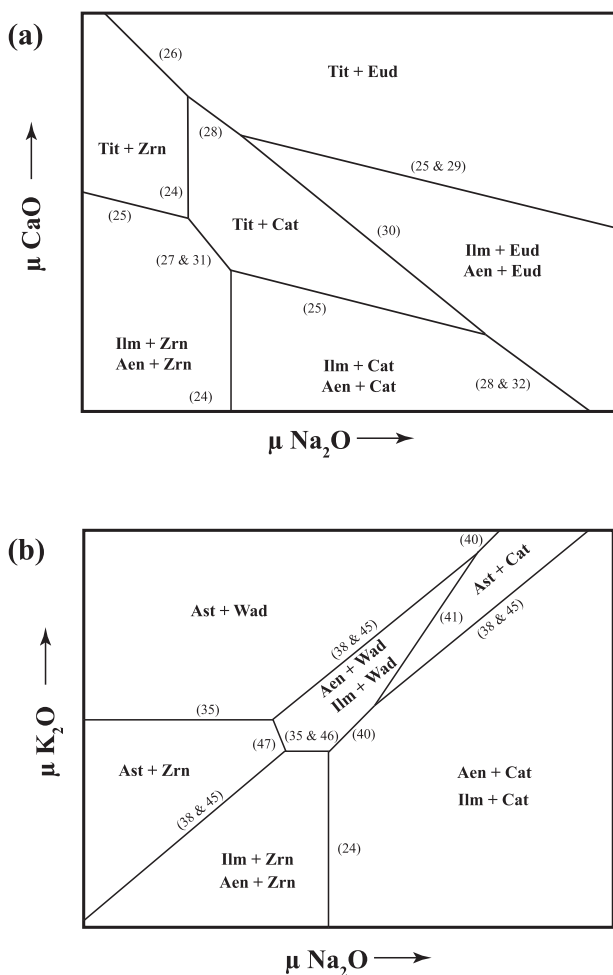


Fig. 3. Alternative topologies possible for the two systems $\mu\text{Na}_2\text{O}$ – μCaO (a) and $\mu\text{Na}_2\text{O}$ – $\mu\text{K}_2\text{O}$ (b) shown in Fig. 2 if Arf–Aeg balanced reactions (Table 4) are used. Their significance is discussed in detail in the text.

defined by NaCl-consuming reactions (26), (28), (30) and (32). Thus, increased NaCl activity in the melt enlarges the eudialyte stability field at the expense of catapelite and zircon (Fig. 4b). Another good indicator for high NaCl activity in silicate melts is the presence of sodalite (e.g. Sharp *et al.*, 1989). The magmatic association of eudialyte with sodalite, as observed in the Ilimaussaq Complex, indicates high NaCl activity in the melt. In these systems magmatic catapelite seems to be unstable. If present at all, it occurs only as a secondary phase replacing eudialyte (e.g. Ferguson, 1964). However, eudialyte also occurs in sodalite-poor or sodalite-free systems (e.g. Tamazeght or Norra Kärr). In these cases, either eudialyte is stabilized only during late-magmatic conditions, or eudialyte is associated with catapelite, indicating less chlorine-rich melt compositions. We infer that magmatic eudialyte is far more common in peralkaline syenitic systems than

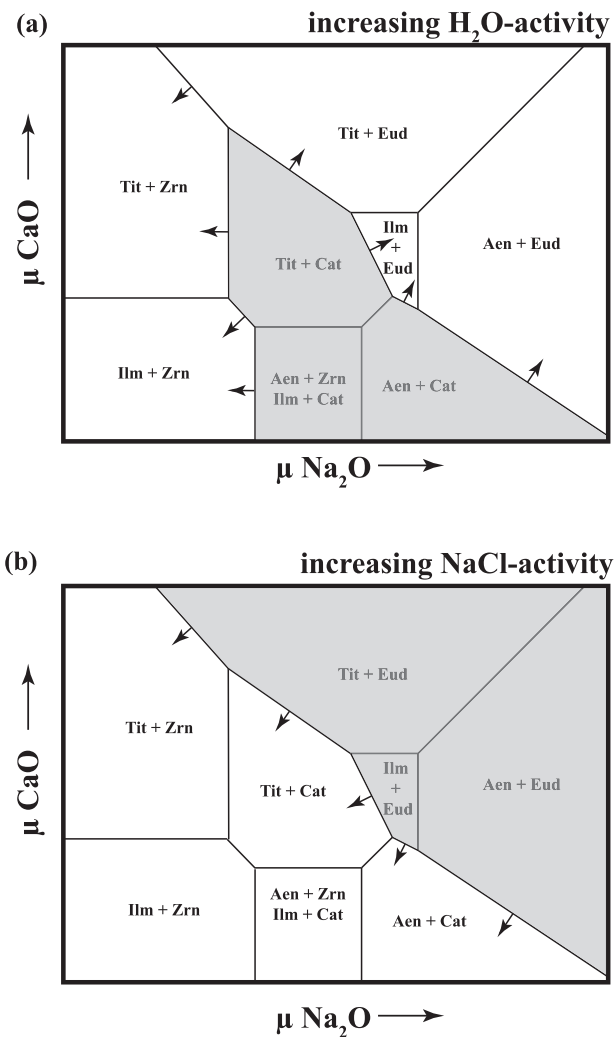


Fig. 4. Qualitative effects (arrows) of (a) increasing H_2O activity and (b) increasing NaCl activity on the stability fields of eudialyte and catapelite, respectively in the $\mu\text{Na}_2\text{O}$ – μCaO diagram.

catapelite because, as noted above, peralkaline syenite magmas are commonly reduced and have relatively high Cl activities. This could also explain why magmatic catapelite-bearing assemblages are only rarely reported from syenitic systems.

Comparison with observed assemblages in nature

Most of the two-phase assemblages shown for the Na–Ca system (Fig. 5) have been reported in the literature. Exceptions are the transitional assemblages tit + cat, ilm + eud and ilm + cat. The potential reasons for this are discussed above. Some classical occurrences of agpaite rocks define distinct evolution trends in the $\mu\text{Na}_2\text{O}$ – μCaO diagram. Assemblages in Tamazeght evolved from tit + zrn to tit + eud and the Kola rocks evolved from

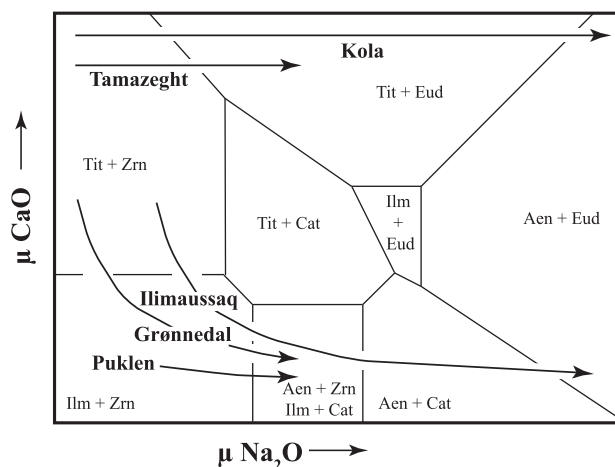


Fig. 5. Observed evolution trends for different natural suites of agpaite rocks, showing two distinct evolutionary paths: a Ca-depleted trend (e.g. Ilmaussaq) and a high-Ca trend (e.g. Tamazeght, Kola).

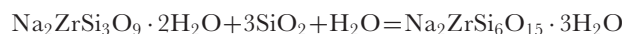
tit + zrn via tit + eud to aen + eud, reaching higher $\mu\text{Na}_2\text{O}$ than Tamazeght. This evolution can be described as a high-Ca trend. In contrast, the rocks of the Gardar province display the assemblages tit + zrn and ilm + zrn followed by aen + zrn and finally aen + eud. In some complexes, such as Grønnedal–Ika (Halama *et al.*, 2005), only parts of this path are observed, and the rocks record only transitional assemblages. In the Ilmaussaq complex and associated dyke rocks (Larsen & Steenfelt, 1974; Marks & Markl, 2003), however, the complete transition from miaskites to agpaite is observed—indicating the highest grade of Na-enrichment after significant Ca-depletion. It is evident from Fig. 5 that the evolution of $\mu\text{Na}_2\text{O}$ relative to μCaO has an important influence on the type of agpaite rock that forms.

In the Ca–K and the Na–K systems (Fig. 2b and c), several transitional (tit + wad, ast + zrn, ilm + wad, ilm + cat and aen + zrn) and truly agpaite assemblages (ast + wad, aen + wad, ast + cat and aen + cat) are of potential importance. Based on our literature research, the only transitional assemblage that was reported to occur at magmatic conditions is aen + zrn. From the four truly agpaite assemblages, only ast + wad has been reported from late-stage vugs and fractures in syenitic rocks from Pocos de Caldas, Brazil (Atencio *et al.*, 1999), implying that a K-rich agpaite assemblage is generally not achieved in syenitic systems during magmatic evolution stages. This is not surprising, as potassic alkaline rocks are much less common than sodic alkaline rocks and are generally more oxidized (Markl *et al.*, 2010). The typical occurrence of astrophyllite in late-stage veins and pegmatites within the nepheline syenites of Ilmaussaq (e.g. Macdonald *et al.*, 2007; Müller-Lorch *et al.*, 2007) could be related to the

late-stage stability of zeolites instead of alkali feldspar and related changes in $\mu\text{K}_2\text{O}$, as discussed by Müller-Lorch *et al.* (2007). In any case, the general observation is that K-rich HFSE-phases (astrophyllite or wadeite) formed during magmatic conditions are relatively rare in syenitic systems compared with granitic systems. This will be discussed in more detail below.

PERALKALINE GRANITES: THE STABILITY OF ELPIDITE AND DALYITE

In general, peralkaline granitic systems have been less well studied than syenitic suites and, consequently, much less information about the evolution of such rocks with respect to their HFSE-rich silicates is available. As mentioned above, the two major mineralogical differences between syenitic and granitic alkaline systems with respect to their Zr-phases are the presence of elpidite or dalyite in peralkaline granites instead of catapleite or wadeite in syenites. Qualitatively, this can be explained by the higher modal amount of SiO_2 relative to $(\text{Na}_2\text{O} + \text{ZrO}_2)$ and $(\text{K}_2\text{O} + \text{ZrO}_2)$ in the elpidite and dalyite formulae (Table 1):



Catapleite = Elpidite



Wadeite = Dalyite.

Thus (at constant P , T , $a\text{H}_2\text{O}$), elpidite and dalyite formation requires higher SiO_2 activities in the melt than catapleite or wadeite formation. Consequently, we plot elpidite instead of catapleite and dalyite instead of wadeite in the phase diagrams for granitic systems in Fig. 6. Additionally, the stability of elpidite relative to catapleite is also influenced by changes in water activity, which has, however, no effect in these diagrams as both mineral pairs have the same $\text{Na}_2\text{O}/\text{ZrO}_2$ and $\text{K}_2\text{O}/\text{ZrO}_2$ ratios in their structural formula (Table 1).

Agpaite-like mineral assemblages in granitic systems

The original definition of agpaite rocks as bearing complex HFSE-silicates such as eudialyte is restricted to peralkaline syenitic rocks (Sørensen, 1997; Le Maitre, 2002). However, mineral assemblages involving Zr- and Ti-minerals in Qtz-bearing systems that closely resemble those of the agpaite systems allow for comparison with syenitic systems.

- (1) Eudialyte has been reported in peralkaline granitic rocks from Antarctica (Harris & Rickard, 1987) and the assemblage aen + eud is known from peralkaline

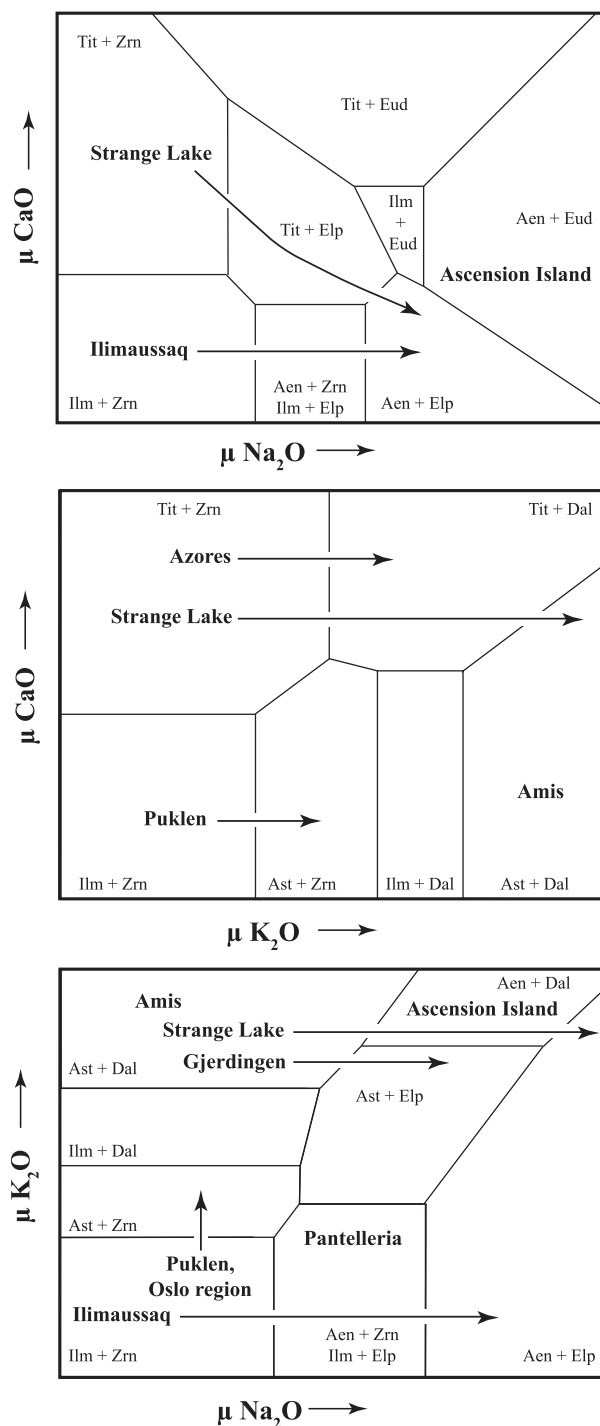


Fig. 6. Qualitative μ - μ diagrams for alkaline granitic systems. (For details, see text.)

granitic rocks from Ascension Island (Harris *et al.*, 1982).

- (2) Na- and K-dominated equivalents of this assemblage (ast + dal, aen + dal and ast + elp) were reported

from the Strange Lake Complex, Canada (e.g. Birkett *et al.*, 1992; Salvi & Williams-Jones, 1995, 1996), from the Amis Complex, Namibia (Schmitt *et al.*, 2000), from Gjerdingen, Norway (Raade & Mladeck, 1983) and from a number of other occurrences.

In some of the above occurrences, an evolutionary path similar to that in syenitic systems can be reconstructed. For example, the well-studied peralkaline granites from the Strange Lake Complex (Canada) show an evolution from early magmatic tit + zrn via transitional assemblages (tit + elp and tit + dal) to a number of agpaite-like assemblages (ast + dal, aen + dal and aen + elp) during the later stages of crystallization (Fig. 6). Peralkaline granites from the Ilmaussaq Complex, Greenland (Ferguson, 1964, and our own observations) show an evolution from ilm + zrn via transitional aen + zrn to aen + elp, again resembling an agpaite-like mineral assemblage. Peralkaline granites from the Puklen Complex, Greenland evolve from ilm + zrn to ast + zrn, reaching transitional stages (Marks *et al.*, 2003). Granites from Gjerdingen, Norway (Raade & Mladeck, 1983) show the two agpaite-like assemblages ast + dal and ast + elp. Consequently, we see no reason against using the term agpaite granite for granitic rocks showing one of the above-mentioned agpaite-like assemblages.

The distinct role of potassium in granitic systems

K-rich agpaite-like assemblages are more commonly observed in granitic than in syenitic systems. The occurrence of magmatic K-rich HFSE-phases (astrophyllite or dalyite) in peralkaline granites suggests that granites have higher μK_2O than nepheline syenites. This may be related to crustal contamination, which would result in increases in both μK_2O and μSiO_2 (up to quartz-saturation). As discussed in detail by Frost & Frost (2010), the origin of peralkaline granites can be explained by two end-member processes: extreme differentiation of basaltic melts that had normative anorthite [the 'plagioclase effect' of Bowen (1945)] or contamination of nepheline syenites with crustal melts. The most strongly peralkaline granites most probably form by the latter process (e.g. Marks *et al.*, 2003).

A POSSIBLE LINK BETWEEN PARENTAL MAGMA COMPOSITIONS AND THE EVOLUTION TREND IN AGPAITES

As discussed above, two types of agpaite evolutionary trends can be distinguished in syenites: (1) the Ca-depleted Ilmaussaq type and (2) the Tamazeght-Kola trend showing no such Ca-depletion. Obviously, however, both

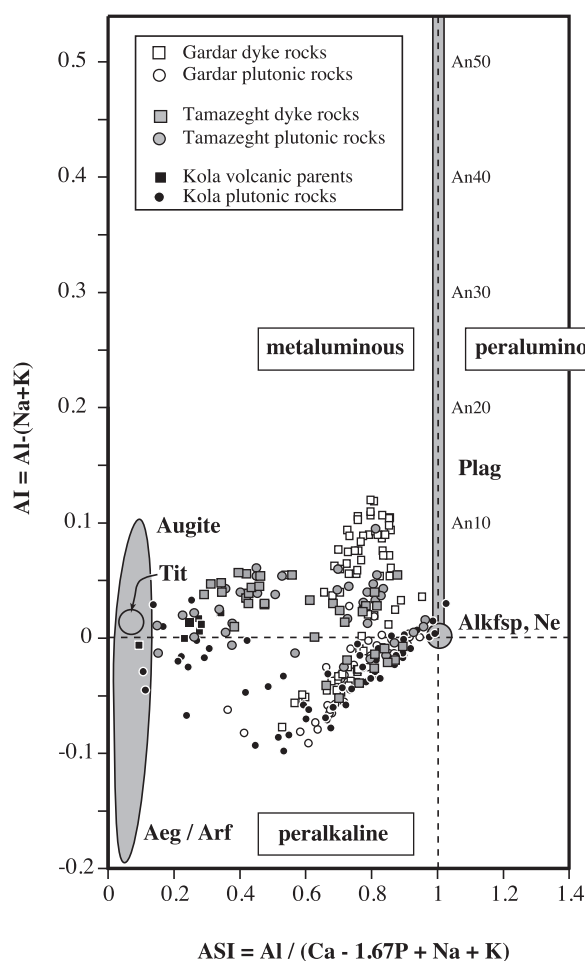


Fig. 7. Whole-rock data for representative rocks of the Gardar Province, the Kola Province and the Tamazeght complex plotted in an AI vs ASI diagram using the definitions given by Frost & Frost (2008). Gray fields indicate the composition of important fractionating mineral phases.

trends involve an increase in Na. The deeper reason for these different evolutionary paths can be evaluated by comparing whole-rock data for the respective alkaline provinces and taking into account the proposed parental melt compositions for the different rock series. In Fig. 7, whole-rock data for representative rocks of the Gardar Province, the Kola Province and the Tamazeght complex are plotted in an alkalinity index (AI) vs aluminium saturation index (ASI) diagram using the definitions given by Frost & Frost (2008).

For the Gardar suite, the most primitive basaltic volcanic and dyke rocks (i.e. those with the highest X_{Mg} values and Ni, Cr and Sc contents) are metaluminous with AI values up to about 0.12, whereas evolved dyke rocks have peralkaline compositions (AI < 0). The primitive basaltic rocks and their pyroxenes do not show any Eu anomaly whereas the most evolved rock types have pronounced negative Eu anomalies (e.g. Halama *et al.*, 2002, 2003,

2004; Marks *et al.*, 2004; Köhler *et al.*, 2009). Thus, extensive plagioclase fractionation occurred and these rocks are good examples of the 'plagioclase effect' of Bowen (1945). This is consistent with the generally accepted assumption that the parental Gardar magmas were basalts with high Al_2O_3/CaO ratios that accumulated at the crust–mantle boundary, giving rise to extensive plagioclase $\pm$ cpx $\pm$ ol fractionation (e.g. Upton *et al.*, 2003, and references therein). The frequent occurrence of anorthositic xenoliths throughout the province supports this model (e.g. Bridgewater, 1967; Bridgewater & Harry, 1968; Halama *et al.*, 2002). From these plagioclase- and therefore Ca-depleted melts (the mean core composition of the plagioclase xenocrysts is around An₅₀; Halama *et al.*, 2002), the alkaline to peralkaline Gardar plutonic rocks evolved by fractionation or accumulation of nepheline, alkali feldspar and aegirine–arfvedsonite, eventually giving rise to Ca-depleted high-Na agpaites (Fig. 5).

In contrast, rocks from the Palaeozoic Kola suite generally lack plagioclase, Eu anomalies are generally absent or very minor, and there is no other indication for significant amounts of plagioclase fractionation prior to the formation of the peralkaline plutonic rocks (Kogarko, 1987; Kramm & Kogarko, 1994; Arzamastsev *et al.*, 2001, 2005). The assumed parental melts for the peralkaline Kola rocks (Fig. 7) are much less aluminous compared with the basaltic Gardar parent magmas and may even be peralkaline in composition (olivine nephelinites–melteigites, Kramm & Kogarko, 1994; Arzamastsev *et al.*, 2001). Thus, unlike in the Gardar province, the Kola magmas underwent no significant depletion of Ca early in their history, which allows high-Ca agpaites (tit + eud assemblage) to form (Fig. 5). The formation of the Kola plutonic rocks themselves can be explained by fractional crystallization combined with different amounts of accumulation of alkali feldspar, nepheline and clinopyroxene.

The evolution of the Tamazeght suite is slightly more complex because two trends are present, indicating that the Tamazeght rocks did not evolve from a single parental melt composition (Marks *et al.*, 2008a, 2008b). Given the absence of significant Eu anomalies in the Tamazeght rocks and minerals (e.g. Marks *et al.*, 2008b), plagioclase fractionation probably occurred only to a very minor extent compared with the Gardar province, although some rock types contain plagioclase, which formed probably during final low-pressure emplacement. The formation of the peralkaline rock types in Tamazeght might be explained by fractionation and accumulation of alkali feldspar, nepheline and clinopyroxene, and for some of the rock types titanite also plays a significant role (Marks *et al.*, 2008b). Similar to Kola, the absence of significant plagioclase fractionation prevented the strong depletion in Ca and thus led to the formation of similar Ca-rich agpaites (Fig. 5). A multi-source evolution of the

Tamazeght complex is also recorded by its petrology and isotope geochemistry (Marks *et al.*, 2008a, 2008b, 2009).

CONCLUSIONS

Alkaline syenitic rocks form from highly fractionated parental magmas, which originated from partial melting of mantle rocks (e.g. Sørensen, 1997; Markl *et al.*, 2010). The formation of peralkaline granites is attributed to extreme differentiation of basaltic melts or assimilation of crustal melts by nepheline syenite magmas. Mineralogically, evolved alkaline igneous rocks are characterized by large amounts of alkali feldspar (plagioclase is absent in many cases owing to their evolved character) and, for the SiO₂-undersaturated examples, the presence of nepheline, sodalite and other Na–Al-rich silicates. Biotite and Fe–Ti oxides are typically unstable (at least in the most evolved and generally peralkaline varieties) and are replaced by Na–Fe-silicates, mostly arfvedsonite (sodic amphibole) and aegirine (sodic–ferric pyroxene).

Within the syenitic group, both miaskitic and agpaitic varieties can be distinguished; however, Sørensen (1997) noted the occurrence of transitional rocks, which contain minerals typical of both miaskitic and agpaitic varieties at the same time. Our work here shows how this mineralogical transition depends on variations in the chemical potentials of Na₂O, K₂O and CaO in the melt and identifies two evolutionary paths: (1) a Ca-depleted trend, which is represented by the alkaline to peralkaline rocks of the Gardar Province; (2) a high-Ca trend, which is typical of the rocks of the Kola Peninsula and of the Tamazeght Complex. Ca-depleted agpaites evolve from basaltic parental melts by extensive fractionation of plagioclase prior to the formation of the peralkaline plutonic rocks. In contrast, high-Ca agpaites can form only if no such plagioclase fractionation (and thus, Ca-depletion) occurred during the early fractionation history of the precursor melts that are probably nephelinitic in composition.

Thus far, the distinction between agpaitic and miaskitic varieties of syenitic rocks has been based on the presence of minerals that incorporate the HFSE. As complex HFSE-bearing silicates such as eudialyte are not restricted to SiO₂-undersaturated rocks, we see no reason against an extension of this classification to the generally rare peralkaline granites containing eudialyte ± aen, ast + dal, aen + dal or ast + elp; for example, from Ascension Island, Antarctica and the Strange Lake Complex in Canada (Harris *et al.*, 1982; Harris & Rickard, 1987; Salvi & Williams-Jones, 1995, 1996).

ACKNOWLEDGEMENTS

The reviews of T. Andersen, H. Sørensen, S. Salvi and R. Mitchell on an earlier version of this paper are highly appreciated.

FUNDING

Funding for this work by the Deutsche Forschungsgemeinschaft (grant Ma 2135/11-1 and 11-2) is gratefully acknowledged. We are also grateful to the Alexander-von-Humboldt Foundation, Bonn, Germany, for providing the opportunity for B.R.F. to come to Tübingen.

REFERENCES

- Allan, J. F. (1992). Geology and mineralization of the Kipawa yttrium–zirconium prospect, Quebec. *Exploration and Mining Geology* **1**, 283–295.
- Andersen, T. (1990). Melt–mineral–fluid interaction in peralkaline silicic intrusion in the Oslo rift, Southeast Norway. IV: Fluid inclusions in the Sande nordmarkite. *Norske Geologiske Undersøkelser Bulletin* **417**, 41–54.
- Andersen, T. & Sørensen, H. (2005). Stability of naujakasite in hyperagpaitic melts, and the petrology of naujakasite lujavrite in the Ilimaussaq alkaline complex, South Greenland. *Mineralogical Magazine* **69**, 125–136.
- Andersen, T., Erambert, M., Larsen, A. O. & Selbekk, R. S. (2010). Petrology of nepheline syenite pegmatites in the Oslo rift, Norway: Zirconium silicate mineral assemblages as indicators of alkalinity and volatile fugacity in mildly agpaitic magma. *Journal of Petrology* **51**, 2303–2325.
- Ansell, H. G., Roberts, A. C., Platt, A. G. & Sturman, B. D. (1980). Gittinsite, a new calcium zirconium silicate from the Kipawa agpaitic syenite complex, Quebec. *Canadian Mineralogist* **18**, 201–203.
- Arzamastsev, A. A., Bea, F., Glaznev, V. N., Arzamastseva, L. V. & Montero, P. (2001). Kola alkaline province in the Paleozoic: evaluation of primary mantle magma composition and magma generation conditions. *Russian Journal of Earth Sciences* **3**, 1–32.
- Arzamastsev, A. A., Bea, F., Arzamastsev, L. V. & Montero, P. (2005). Trace elements in minerals of the Khibina Massif as indicators of mineral formation evolution: Results of LA-ICP-MS study. *Geochemistry International* **43**, 71–85.
- Atencio, D., Coutinho, J. M. V., Ulbrich, M. N. C. & Vlach, S. R. F. (1999). Hainite from Pocos de Caldas, Minas Gerais, Brazil. *Canadian Mineralogist* **37**, 91–98.
- Beeskow, B., Treloar, P. J., Rankin, A. H., Vennemann, T. W. & Spangenberg, J. (2006). A reassessment of models for hydrocarbon generation in the Khibina nepheline syenite complex, Kola Peninsula, Russia. *Lithos* **91**, 1–18.
- Birkett, T. C., Miller, R. R., Roberts, A. C. & Mariano, A. N. (1992). Zirconium-bearing minerals of the Strange Lake intrusive complex, Quebec–Labrador. *Canadian Mineralogist* **30**, 191–205.
- Blaxland, A. B. (1977). Agpaitic magmatism at Norra Kärr? Rb–Sr isotopic evidence. *Lithos* **10**, 1–8.
- Bollingberg, H. J., Ure, A. M., Sørensen, I. & Leonardsen, E. S. (1983). Geochemistry of some eudialyte–euclite specimens and a coexisting catapleite from Langesund, Norway. *Tschermaks Mineralogische und Petrographische Mitteilungen* **32**, 153–169.
- Bowen, N. L. (1945). Phase equilibria bearing on the origin and differentiation of alkaline rocks. *American Journal of Science* **243-A**, 75–89.
- Bridgwater, D. (1967). Feldspathic inclusions in the Gardar igneous rocks of South Greenland and their relevance to the formation of major Anorthosites in the Canadian Shield. *Canadian Journal of Earth Sciences* **4**, 995–1014.

- Bridgwater, D. & Harry, W. T. (1968). Anorthosite xenoliths and plagioclase megacrysts in Precambrian intrusions of South Greenland. *Meddelelser om Grønland* **185**, 243.
- Brogger, W. C. (1890). Die Mineralien der Syenitpegmatitgänge der süd-norwegischen Augit- und Nephelinsyenite. *Zeitschrift für Kristallographie* **16**, 1–663.
- Chakhmouradian, A. R. & Mitchell, R. H. (2002). The mineralogy of Ba- and Zr-rich alkaline pegmatites from Gordon Butte, Crazy Mountains (Montana, USA): comparisons between potassic and sodic agpaite pegmatites. *Contributions to Mineralogy and Petrology* **143**, 93–114.
- Chakhmouradian, A. R. & Zaitsev, A. N. (2002). Calcite–amphibole–clinopyroxene rock from the Afrikanda complex, Kola Peninsula, Russia: mineralogy and a possible link to carbonatites. III. Silicate minerals. *Canadian Mineralogist* **40**, 1347–1374.
- Chen, Z. B. (1978). Saima Deposit Research Group Uranium deposit in the Saima alkaline massif, northeast China. *Sciences in China* **21**, 365–389.
- Chevychelov, V. U., Botcharnikov, R. E. & Holtz, F. (2008). Partitioning of Cl and F between fluid and hydrous phonolitic melt of Mt. Vesuvius at 850–1000°C and 200 MPa. *Chemical Geology* **256**, 172–184.
- Currie, K. L. & Zaleski, E. (1985). The relative stability of elpidite and vlasovite: a *P–T* indicator for peralkaline rocks. *Canadian Mineralogist* **23**, 577–582.
- Edgar, A. D. & Blackburn, C. E. (1972). Eudialyte from the Kipawa Lake area, Temiscamingue County, Quebec. *Canadian Mineralogist* **11**, 554–559.
- Fall, A., Bodnar, R. J., Szabó, C. & Pál-Molnár, E. (2007). Fluid evolution in the nepheline syenites of the Ditrau alkaline massif, Transylvania, Romania. *Lithos* **95**, 331–345.
- Ferguson, J. (1964). *Geology of the Ilímaussaq alkaline intrusion, South Greenland*. Bulletin Grønlands Geologiske Undersøgelse **39**, 82 pp.
- Frost, B. R. & Frost, C. D. (2008). A geochemical classification for feldspathic igneous rocks. *Journal of Petrology* **49**, 1955–1969.
- Frost, C. D. & Frost, R. R. (2010). On ferroan (A-type) granitoids: Their compositional variability and modes of origin. *Journal of Petrology* (in press).
- Frost, B. R., Lindsley, D. H. & Andersen, D. J. (1988). Fe–Ti oxide–silicate equilibria: Assemblages with fayalitic olivine. *American Mineralogist* **73**, 727–740.
- Halama, R., Waight, T. & Markl, G. (2002). Geochemical and isotopic zoning patterns of plagioclase megacrysts in gabbroic dykes from the Gardar Province, South Greenland: implications for crystallisation processes in anorthositic magmas. *Contributions to Mineralogy and Petrology* **144**, 109–127.
- Halama, R., Wenzel, T., Upton, B. G. J., Siebel, W. & Markl, G. (2003). A geochemical and Sr–Nd–O isotopic study of the Proterozoic Eriksfjord Basalts, Gardar Province, South Greenland: Reconstruction of an OIB-signature in crustally contaminated rift-related basalts. *Mineralogical Magazine* **67**, 831–853.
- Halama, R., Marks, M., Brüggemann, G. E., Siebel, W., Wenzel, T. & Markl, G. (2004). Crustal contamination of mafic magmas: evidence from a petrological, geochemical and Sr–Nd–Os–O isotopic study of the Proterozoic Isortoq dike swarm, South Greenland. *Lithos* **74**, 199–232.
- Halama, R., Vennemann, T., Siebel, W. & Markl, G. (2005). The Grønndal–Ika carbonatite–syenite complex, south Greenland: Carbonatite formation by liquid immiscibility. *Journal of Petrology* **46**, 191–217.
- Hansteen, T. H. & Burke, E. A. J. (1990). Melt–mineral–fluid interaction in peralkaline silicic intrusions in the Oslo Rift, Southeast Norway; II. High-temperature fluid inclusions in the Eikeren–Skrim complex. *Norges Geologiske Undersøkelse Bulletin* **417**, 15–32.
- Harris, C. (1983). The petrology of lavas and associated plutonic inclusions of Ascension island. *Journal of Petrology* **24**, 424–470.
- Harris, C. & Rickard, R. S. (1987). Rare-earth-rich eudialyte and dalyite from a peralkaline granite dyke at Strumsvola, Dronning Maud Land, Antarctica. *Canadian Mineralogist* **25**, 755–762.
- Harris, C., Cressey, G., Bell, J. D., Atkins, F. B. & Besewetherick, S. (1982). An occurrence of rare-earth-rich eudialyte from Ascension Island, South Atlantic. *Mineralogical Magazine* **46**, 421–425.
- Horvath, L. & Gault, R. A. (1990). The mineralogy of Mont Saint Hilaire, Quebec. *Mineralogical Record* **21**, 284–392.
- Jones, A. P. (1984). Mafic silicates from the nepheline syenites of the Motzfeldt centre, south Greenland. *Mineralogical Magazine* **48**, 1–12.
- Jones, A. P. & Peckett, A. (1980). Zirconium-bearing aegirines from Motzfeldt, South Greenland. *Contributions to Mineralogy and Petrology* **75**, 251–255.
- Kchit, A. (1990). Le plutonisme alcalin du Tamazeght (Haut Atlas de Midelt, Maroc). PhD thesis, Université Paul Sabatier, Toulouse, 178 p.
- Keppeler, H. (1993). Influence of fluorine on the enrichment of high field strength trace elements in granitic rocks. *Contributions to Mineralogy and Petrology* **111**, 113–121.
- Khadem-Allah, B. (1993). Syénites et pegmatites nephéliniques du complexe alcalin du Tamazeght (Haut Atlas de Midelt, Maroc). Thèse, Université Paul Sabatier, Toulouse, 240 p.
- Khadem-Allah, B., Fontan, F., Kadar, M., Monchoux, P. & Sørensen, H. (1998). Reactions between agpaite nepheline syenitic melts and sedimentary carbonate rocks, exemplified by the Tamazeght complex, Morocco. *Geochemistry International* **36**, 569–581.
- Khomyakov, A. (1995). *Mineralogy of Hyperagpaite Alkaline Rocks*. Oxford: Clarendon Press, 222 p.
- Khomyakov, A., Sørensen, H., Petersen, O. V. & Vailey, J. C. (2001). Naujakasite from the Ilímaussaq alkaline complex, South Greenland, and the Lovozero alkaline complex, Kola Peninsula, Russia: a comparison. *Geology of Greenland Survey Bulletin* **190**, 95–108.
- Kogarko, L. N. (1980). Ore-forming potential of alkaline magmas. *Lithos* **26**, 167–175.
- Kogarko, L. N. (1987). Alkaline rocks of the eastern part of the Baltic Shield (Kola Peninsula). In: Fitton, J. G. & Upton, B. G. J. (eds) *Alkaline Igneous Rocks*. Geological Society, London: Special Publications **30**, 531–544.
- Kogarko, L. N., Lazutkina, L. N. & Romanchev, B. P. (1982). The origin of eudialyte mineralization. *Translations from Geokhimiya* **10**, 1415–1432.
- Köhler, J., Schönerberger, J., Upton, B. & Markl, G. (2009). Halogen and trace-element geochemistry in the Gardar Province, South Greenland: Subduction-related metasomatism and fluid exsolution from alkalic melts. *Lithos* **113**, 731–747.
- Konnerup-Madsen, J. (2001). A review of the composition and evolution of hydrocarbon gases during solidification of the Ilímaussaq alkaline complex, South Greenland. *Geology of Greenland Survey Bulletin* **190**, 159–166.
- Kovalenko, V. I., Tsaryeva, G. M., Goreglyad, A. V., Yarmolyuk, V. V. & Troitsky, V. A. (1995). The peralkaline granite-related Khaldzan–Buregtey rare metal (Zr, Nb, REE) deposit, Western Mongolia. *Economic Geology* **90**, 530–547.
- Kramm, U. & Kogarko, L. N. (1994). Nd and Sr isotope signatures of the Khibina and Lovozero agpaite centres, Kola Province, Russia. *Lithos* **32**, 225–242.
- Krumrei, T. V., Pernicka, E., Kaliwoda, M. & Markl, G. (2007). Volatiles in a peralkaline system: Abiogenic hydrocarbons and

- F–Cl–Br systematics in the naujaite of the Ilimaussaq intrusion, South Greenland. *Lithos* **95**, 298–314.
- Larsen, L. M. (1976). Clinopyroxenes and coexisting mafic minerals from the alkaline Ilimaussaq intrusion, south Greenland. *Journal of Petrology* **17**, 258–290.
- Larsen, L. M. (1977). Aenigmatites from the Ilimaussaq intrusion, south Greenland: Chemistry and petrological implications. *Lithos* **10**, 257–270.
- Larsen, L. M. & Steenfelt, A. (1974). Alkali loss and retention in an iron-rich peralkaline phonolite dyke from the Gardar province, south Greenland. *Lithos* **7**, 81–90.
- Le Maitre, R. W. (2002). *International Union of Geological Sciences. Subcommission on the Systematics of Igneous Rocks. Igneous Rocks: A Classification and Glossary of Terms*. Cambridge: Cambridge University Press, 236 p.
- Linnen, R. L. & Keppler, H. (2002). Melt composition control of Zr/Hf fractionation in magmatic processes. *Geochimica et Cosmochimica Acta* **66**, 3293–3301.
- Macdonald, R., Karup-Møller, S. & Rose-Hansen, J. (2007). Astrophyllite-group minerals from the Ilimaussaq complex, South Greenland. *Mineralogical Magazine* **71**, 1–16.
- Markl, G., Marks, M. A. W. & Frost, B. R. (2010). On the controls of oxygen fugacity in the generation and crystallization of peralkaline rocks. *Journal of Petrology* **51**, 1831–1847.
- Marks, M. A. W. & Markl, G. (2001). Fractionation and assimilation processes in the alkaline augite syenite unit of the Ilimaussaq Intrusion, South Greenland, as deduced from phase equilibria. *Journal of Petrology* **42**, 1947–1969.
- Marks, M. A. W. & Markl, G. (2003). Ilimaussaq “en miniature”: closed-system fractionation in an agpaitic dike rock from the Gardar Province, South Greenland. *Mineralogical Magazine* **67**, 893–919.
- Marks, M., Vennemann, T. W., Siebel, W. & Markl, G. (2003). Quantification of magmatic and hydrothermal processes in a peralkaline syenite–alkali granite complex based on textures, phase equilibria, and stable and radiogenic isotopes. *Journal of Petrology* **44**, 1247–1280.
- Marks, M. A. W., Halama, R., Wenzel, T. & Markl, G. (2004). Trace element variations in clinopyroxene and amphibole from alkaline to peralkaline syenites and granites: implications for mineral–melt trace-element partitioning. *Chemical Geology* **211**, 185–215.
- Marks, M. A. W., Schilling, J., Coulson, I. M., Wenzel, T. & Markl, G. (2008a). The alkaline–peralkaline Tamazeght complex, High Atlas Mountains, Morocco: Mineral chemistry and petrological constraints for derivation from a compositionally heterogeneous mantle source. *Journal of Petrology* **49**, 1097–1131.
- Marks, M. A. W., Coulson, I. M., Schilling, J., Jacob, D. E., Schmitt, A. K. & Markl, G. (2008b). The effect of titanite and other HFSE-rich mineral (Ti-bearing andradite, zircon, eudialyte) fractionation on the geochemical evolution of silicate melts. *Chemical Geology* **257**, 153–172.
- Marks, M. A. W., Neukirchen, F., Vennemann, T. & Markl, G. (2009). Textural, chemical, and isotopic effects of late-magmatic carbonatitic fluids in the carbonatite–syenite Tamazeght complex, High Atlas Mountains, Morocco. *Mineralogy and Petrology* **97**, 23–42.
- Mitchell, R. H. & Liferovich, R. P. (2006). Subsolidus deuteric/hydrothermal alteration of eudialyte in lujavrite from the Pilansberg alkaline complex, south Africa. *Lithos* **91**, 353–372.
- Müller-Lorch, D., Marks, M. A. W. & Markl, G. (2007). Na and K distribution in agpaitic pegmatites. *Lithos* **95**, 315–330.
- Nielsen, T. F. D. (1994). Alkaline dike swarms of the Gardiner complex and the origin of ultramafic alkaline complexes. *Geochemistry International* **31**, 37–56.
- Nivin, V. A., Treloar, P. J., Konopleva, N. G. & Ikorsky, S. V. (2005). A review of the occurrence, form and origin of C-bearing species in the Khibiny alkaline igneous complex, Kola Peninsula, Russia. *Lithos* **85**, 93–112.
- Olsen, K. I. & Griffin, W. L. (1984a). Fluid inclusion studies of the Drammen Granite, Oslo Paleorift, Norway. I. Microthermometry. *Contributions to Mineralogy and Petrology* **87**, 1–14.
- Olsen, K. I. & Griffin, W. L. (1984b). Fluid inclusion studies of the Drammen Granite, Oslo Paleorift, Norway. II. Gas and leachate analyses of microlytic quartz. *Contributions to Mineralogy and Petrology* **87**, 15–23.
- Parsons, I. (1972). Petrology of the Puklen syenite–alkali granite complex, Nunarsuit, South Greenland. *Meddelelser om Grønland*, Vol. 3, 73p.
- Pekov, I. V. (1998). *Minerals first discovered on the territory of the former Soviet Union*. Moscow: Ocean Pictures, 369 p.
- Pfaff, K., Krumrei, T. V., Marks, M., Wenzel, T., Rudolf, T. & Markl, G. (2008). Chemical and physical evolution of the ‘lower layered series’ from the nepheline syenitic Ilimaussaq intrusion, South Greenland: Implications for the origin of magmatic layering in peralkaline felsic liquids. *Lithos* **106**, 280–296.
- Pfaff, K., Wenzel, T., Schiulling, J., Marks, M. & Markl, G. (2010). A fast and easy-to-use approach to cation site assignment for eudialyte-group minerals. *Neues Jahrbuch für Mineralogie, Abhandlungen* **187**(1), 69–81.
- Piilonen, P. C., Lalonde, A. E., McDonald, A. M., Gault, R. A. & Larsen, A. O. (2003). Insights into astrophyllite-group minerals. I. Nomenclature, composition and development of a standardized general formula. *Canadian Mineralogist* **41**, 1–26.
- Pulvertaft, T. C. R. (1961). The Puklen intrusion, Nunarsuit, SW Greenland. *Meddelelser om Grønland* **123**, 35–49.
- Raade, G. & Mladek, M. H. (1983). Janhaugite, $\text{Na}_2\text{Mn}_3\text{Ti}_2\text{Si}_4\text{O}_{15}(\text{OH},\text{F},\text{O})_3$, a new mineral from Norway. *American Mineralogist* **68**, 1216–1219.
- Ridolfi, F., Renzulli, A., Santi, P. & Upton, B. G. J. (2003). Evolutionary stages of crystallization of weakly peralkaline syenites: evidence from ejecta in the plinian deposits of Agua de Pau volcano (São Miguel, Azores Islands). *Mineralogical Magazine* **67**, 749–767.
- Roedder, E. & Coombs, D. S. (1967). Immiscibility in granitic melts, indicated by fluid inclusions in ejected granitic blocks from Ascension Island. *Journal of Petrology* **8**, 417–451.
- Roelofsen, J. N. & Veblen, D. R. (1999). Relationships among zirconosilicates: examination by cathodoluminescence and transmission electron microscopy. *Mineralogy and Petrology* **67**, 71–84.
- Ryabchikov, I. D. & Kogarko, L. N. (2006). Magnetite compositions and oxygen fugacity of the Khibina magmatic system. *Lithos* **91**, 35–45.
- Salvi, S. & Williams-Jones, A. E. (1995). Zirconosilicate phase relations in the Strange Lake (Lac Brisson) pluton Quebec–Labrador, Canada. *American Mineralogist* **80**, 1031–1040.
- Salvi, S. & Williams-Jones, A. E. (1996). The role of hydrothermal processes in concentrating high-field strength elements in the Strange Lake peralkaline complex, northeastern Canada. *Geochimica et Cosmochimica Acta* **60**, 1917–1932.
- Salvi, S., Fontan, F. & Monchoux, P. (2000). Hydrothermal mobilization of high field strength elements in alkaline igneous systems: Evidence from the Tamazeght Complex, (Morocco). *Economic Geology* **95**, 559–576.
- Salvioli-Marini, E. & Venturelli, G. (1996). Temperature of crystallization and evolution of the Jumilla and Cancarix lamproites (SE

- Spain) as suggested by melt and solid inclusions in minerals. *European Journal of Mineralogy* **8**, 1027–1039.
- Schilling, J., Marks, M., Wenzel, T. & Markl, G. (2009). Reconstruction of magmatic to sub-solidus processes in an agpaitic system using eudialyte textures and composition: a case study from Tamezghet, Morocco. *Canadian Mineralogist* **47**, 351–365.
- Schmitt, A. K., Emmermann, R., Trumbull, R. B., Bühn, B. & Henjes-Kunst, F. (2000). Petrogenesis and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology of the Brandberg Complex, Namibia: Evidence for a major mantle contribution in metaluminous and peralkaline granites. *Journal of Petrology* **41**, 1207–1239.
- Schönenberger, J. & Markl, G. (2008). The magmatic and fluid evolution of the Motzfeld Intrusion in South Greenland: Insights into the formation of agpaitic and maskitic rocks. *Journal of Petrology* **49**, 1549–1577.
- Sharp, Z. D., Helfrich, G. R., Bohlen, S. R. & Essene, E. J. (1989). The stability of sodalite in the system $\text{NaAlSi}_3\text{O}_8\text{--NaCl}$. *Geochimica et Cosmochimica Acta* **53**, 1943–1954.
- Signorelli, S. & Carroll, M. R. (2000). Solubility and fluid–melt partitioning of Cl in hydrous phonolitic melts. *Geochimica et Cosmochimica Acta* **64**, 2851–2862.
- Sørensen, H. (1992). Agpaitic nepheline syenites: a potential source of rare elements. *Applied Geochemistry* **7**, 417–427.
- Sørensen, H. (1997). The agpaitic rocks—an overview. *Mineralogical Magazine* **61**, 485–498.
- Sørensen, H. & Larsen, L. M. (2001). The hyper-agpaitic stage in the evolution of the Ilimaussaq alkaline complex, South Greenland. *Geology of Greenland Survey Bulletin* **190**, 83–94.
- Upton, B. G. J., Emeleus, C. H., Heaman, L. M., Goodenough, K. M. & Finch, A. A. (2003). Magmatism of the mid-Proterozoic Gardar Province, South Greenland: chronology, petrogenesis and geological setting. *Lithos* **68**, 43–65.
- Ussing, N. V. (1912). Geology of the country around Julianehaab, Greenland. *Meddelelser om Grønland* **38**, 426.
- Vuorinen, J. H. & Hålenius, U. (2005). Nb-, Zr- and LREE-rich titanite from the Alnö alkaline complex: Crystal chemistry and its importance as a petrogenetic indicator. *Lithos* **83**, 128–142.
- Watson, E. B. (1979). Zircon saturation in felsic liquids: experimental results and applications to trace element geochemistry. *Contributions to Mineralogy and Petrology* **70**, 407–419.
- Wight, Q. & Chao, G. (1995). Mont Saint Hilaire revisited, article 2. *Rocks and Minerals* **70**, 90–103.
- Wu, F.-Y., Yang, Y. H. *et al.* (2010). *In situ* U–Pb, Sr, Nd and Hf isotopic analysis of eudialyte by LA-(MC)-ICP-MS. *Chemical Geology* **273**, 8–34.

