



A global review on agpaitic rocks

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ABSTRACT

Peralkaline igneous rocks are defined by a molar $(\text{Na} + \text{K})/\text{Al}$ ratio > 1 and are subdivided into miaskitic and agpaitic varieties depending on their mineralogy. In the more common miaskitic types, rare earth elements (REEs) and high field strength elements (HFSEs) are largely stored in zircon and titanite, while agpaitic varieties contain a wealth of mostly halogen-bearing Na-Ca-HFSE minerals instead. Among those, minerals of the eudialyte, rinkite, and wöhlerite groups are the most common ones. The present review on the geological and mineralogical information available on agpaitic rocks provides a summary of the fluid inclusion record of miaskitic and agpaitic rocks as fluids play a key role in the evolution of peralkaline rocks.

Magmas that crystallize peralkaline rocks are generally believed to originate from low-degree partial melting of geochemically enriched mantle lithologies, combined with prolonged differentiation processes at shallow crustal levels. Agpaitic and hyperagpaitic rocks (the latter containing appreciable amounts of water-soluble minerals) represent the most evolved stages of peralkaline systems. They form either parts of plutonic to subvolcanic composite magmatic complexes, which consist of several agpaitic and/or miaskitic intrusive units, or they occur as sills, laccoliths, domes, dykes, or even as lavas. However, as agpaitic rocks are notably rare compared to miaskitic rocks (about 100 vs. several thousand occurrences worldwide), their formation requires special conditions that are not generally met during the evolution of peralkaline rocks. Despite their rarity, agpaitic and hyperagpaitic rocks form important deposits of critical metals such as REE, Zr, Nb, and U and are interesting targets for otherwise rare elements such as F, Be, Sn, Zn, and Ga.

The relative timing when magmas reach their agpaitic stage is highly variable. Magmatic–agpaitic assemblages can form only if early-magmatic crystallization conditions were reduced enough (low f_{O_2}) to enable subsequent Fe enrichment, an increase in peralkalinity, retention of halogens, and extreme enrichment of HFSEs in the evolving magmas, as only these contribute to the direct crystallization of agpaitic minerals. Late-magmatic interstitial agpaitic assemblages indicate that the required enrichment levels of the above-mentioned constituents were reached only during the final differentiation stages of magmas. Hydrothermal agpaitic assemblages precipitate from highly saline brines released from peralkaline magmas and are capable of transporting HFSEs. All three varieties of agpaitic assemblages occur in plutonic, subvolcanic, and volcanic rocks. Although many modern and detailed studies have dealt with plutonic–subvolcanic agpaitic rocks, most volcanic occurrences are insufficiently studied, mainly because of difficult outcrop or logistic situations. However, especially the volcanic examples raise questions on the details of why and how degassing of halogens at such shallow emplacement levels is sufficiently prevented to precipitate halogen-bearing agpaitic assemblages. Thus, a thorough geochemical and petrological investigation of such localities is desired.

The presently valid definitions of agpaitic and miaskitic rocks are not appropriate, and therefore, alternative definitions are suggested. Similarly, the frequently used classification scheme for nepheline syenites must be abandoned as it is inconsistent and excludes very similar mineral assemblages observed in other partly even quartz-bearing rock types. Variable processes may produce sequences of mineral assemblages that belong to different groups of this classification. Therefore, we suggest that rather than dividing agpaitic rocks into specific subgroups, careful textural studies that distinguish early-magmatic, late-magmatic, and hydrothermal phase assemblages are warranted. This is the only way to understand the effect of various physicochemical parameters (such as P , T , f_{O_2} , a_{SiO_2} , $a_{\text{H}_2\text{O}}$, peralkalinity, and the activity of other compounds including halogens) during different evolutionary stages of these mineralogically and texturally diverse rocks.

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1. Introduction

Peralkaline igneous rocks are defined by a molar $(\text{Na} + \text{K})/\text{Al}$ ratio > 1 and include intrusive and extrusive silica-oversaturated (granitic/rhyolitic), silica-saturated (syenitic/trachytic), and silica-undersaturated (nepheline syenitic to foidolitic/phonolitic to foiditic) rocks (e.g., Le Maitre, 2003; Frost and Frost, 2008, 2010). Most peralkaline rocks are rich in large ion lithophile elements (LILE, such as Li, Na, K, Rb, and Cs), halogens (F, Cl, Br, and I), rare earth elements (REEs), high field strength elements (HFSEs, such as Zr, Hf, Nb, Ta, and U), and otherwise relatively rare elements such as Be, Sn, Zn, and Ga (e.g., Kogarko, 1980; Sørensen, 1992; Bailey et al., 2001).

In some cases, the extreme enrichment of alkalis, halogens, HFSEs, and REEs during the differentiation of peralkaline magmas may result in the precipitation of a wealth of otherwise rare minerals including F-minerals (villiaumite), Cl-minerals (sodalite), and various typical halogen-bearing Na-Ca-HFSE minerals (Table 1), the most common of them being eudialyte-group minerals (EGMs; e.g., Sørensen, 1997; Johnsen et al., 2003; Rastsvetaeva, 2007; Pfaff et al., 2010) and members of the rinkite and wöhlerite groups (e.g., Merlino and Perchiazzi, 1988; Chakhmouradian et al., 2008; Sokolova and Cámara, 2017). The presence of these diverse and structurally complex HFSEs defines the so-called agpaitic rocks as opposed to miaskitic rocks, in which HFSEs are largely hosted by zircon and titanite (Khomyakov, 1995; Sørensen, 1997; Le Maitre, 2003; Andersen et al., 2010; Marks et al., 2011), as is typical of most other igneous rocks.

The extreme geochemical composition of agpaitic rocks results in a unique wealth of different minerals. Many occurrences of agpaitic rocks are type localities for several minerals, with the extreme examples of Khibina (Russia, $N = 120$), Lovozero (Russia, $N = 106$), Mont Saint-Hilaire (Canada, $N = 65$), Dara-i-Pioz (Tajikistan, $N = 35$), and Ilímaussaq (Greenland, $N = 33$), summing up to > 350 types of minerals (mindat.org). As many agpaitic minerals contain halogens and as other halogen-bearing minerals such as sodalite and fluorite are typically associated, the retention and release of fluids carrying alkalis, halogens (F and Cl), and other fluid-mobile components during the evolution of peralkaline magmas are of critical importance for their formation (e.g., Markl et al., 2001; Andersen et al., 2010).

The magmas eventually forming agpaitic rocks are mantle derived. A combination of low melting degrees of a geochemically pre-enriched magma source and subsequent differentiation at low oxygen fugacity (f_{O_2}) and water activity ($a_{\text{H}_2\text{O}}$) is probably responsible for the unusual geochemical composition of agpaitic rocks (e.g., Kogarko, 1974; Harris, 1983; Larsen and Sørensen, 1987; Caroff et al., 1993; Kramm and Kogarko, 1994; Sørensen, 1997; Frisch and Abdel-Rahman, 1999; Markl et al., 2010). Although agpaitic rocks are relatively rare and often considered mineralogically exotic, they are of large economic interest as they represent some of the most promising sources for future HFSE and REE supply (e.g., Smith et al., 2016; Goodenough et al., 2016).

Reviews on agpaitic rocks have been presented by Sørensen (1960, 1974, 1997) and Khomyakov (1995). Since then, many detailed textural, mineralogical, petrological, and geochemical works on agpaitic and very similar rock types have been published, which revealed the complex evolution of such rocks. Therefore, we consider it timely to present an overview on the present knowledge on these diverse rocks to provide directions for future research.

The most common and classical cases of agpaitic rocks are those

containing EGM-bearing assemblages. We review the information available for the 105 EGM-bearing localities known to date (Fig. 1; Table 2) and compare them with those of other igneous rocks containing similar HFSE-rich mineral assemblages. We provide an overview on the fluid inclusion data presently available for miaskitic and agpaitic rocks and propose models for the formation of orthomagmatic, late-magmatic, and hydrothermal agpaitic mineral assemblages.

Khomyakov (1995) suggested a classification system for nepheline syenites on the basis of the presence of mostly accessory silicate minerals of the general formula $\text{A}_x\text{M}_y\text{Si}_p\text{O}_q$ ($\text{A} = \text{Na}, \text{K}$, and other strong bases; $\text{M} = \text{Nb}, \text{Ti}, \text{Zr}, \text{Be}$, and other Al-substituting elements). The compositional parameters x , y , and p were used for calculating the so-called alkalinity modulus ($K_{\text{alk}} = (x * 100) / (x + y + p)$) to distinguish five subgroups, namely miaskitic ($K_{\text{alk}} \ll 15\%$), low agpaitic ($K_{\text{alk}} = 15\text{--}25\%$), medium agpaitic ($K_{\text{alk}} = 25\text{--}35\%$), highly agpaitic ($K_{\text{alk}} = 35\text{--}40\%$), and hyperagpaitic ($K_{\text{alk}} > 40\%$) rocks, each of them defined by typical mineral assemblages (Table 3). Although helpful at a first glance, we consider this scheme to be insufficient and not appropriate because (i) early-magmatic, late-magmatic, and hydrothermal agpaitic assemblages were not distinguished, (ii) the often complex textural relations between the various mineral assemblages were not considered, (iii) quartz-bearing syenites and peralkaline granites were excluded from this scheme, and (iv) very similar mineral assemblages in some nepheline syenites and in potassic-ultrapotassic rocks were not considered. This situation is unsatisfactory and causes considerable confusion in the literature regarding whether a given rock should be called agpaitic or not and how to name alkaline rocks properly. Therefore, we propose redefinitions for the terms agpaitic and miaskitic and suggest a descriptive characterization of agpaitic rocks according to textural and mineralogical criteria.

2. Geology of agpaitic rocks

We compiled 105 EGM-bearing localities of agpaitic rocks described in the literature (Table 2) along with their age, field expression, EGM textures, rock associations, and several key references for each locality. The level of detail concerning the geological, mineralogical, and petrological information among the listed localities varies considerably. The classical localities (e.g., Ilímaussaq, Khibina, Lovozero, Mont Saint-Hilaire, and Tamazeght) have been intensely studied since the 19th century. Much of our modern views concerning the origin and evolution of agpaitic rocks originate from the study of these relatively few occurrences. Detailed work on some less studied localities became available in the last decades (e.g., Langesundfjord, Pilanesberg, Madagascar, Norra Kärr, Red Wine, and Kipawa). Many other occurrences, however, are only shortly mentioned in the accessible literature and clearly deserve further investigation (e.g., some of the occurrences in Brazil, Tajikistan, Kazakhstan, Alaska, and Libya). Some localities were only recently discovered (e.g., Sushina), partly in otherwise well-known alkaline provinces (e.g., Kaiserstuhl and Kovdor). Therefore, the presented list of EGM occurrences (Table 2) is probably not yet complete, and more localities may be added in the future.

2.1. Geodynamic setting and age distribution

The geodynamic settings in which agpaitic rocks occur resemble those for peralkaline rocks in general (e.g., Sørensen, 1974; Fitton and Upton, 1987 and references therein), including (i) continental rifts (e.g.,

Gardar rift, East African rift, Oslo rift), (ii) intraplate settings of oceanic (e.g., Ascension, Azores, Cape Verde) and continental (e.g., Monteregian Hills, Damaraland province, and Serra do Mar province) affinity, and (iii) subduction-related settings (e.g., Trans-Pecos). However, for many occurrences, no detailed geodynamic investigations are available, and no consensus on the ultimate reasons for alkaline magmatism in the respective provinces exists.

For most of the listed localities, geochronological data of variable quality and precision are available (Fig. 2; Table 2). Agpaitic rocks have occurred since the Paleoproterozoic era; the Nechalacho deposit

(Canada) represents the oldest occurrence so far (2176 ± 3 Ma; Möller and Williams-Jones, 2016a). Relatively few Proterozoic agpaitic rocks are known (such as the Gardar occurrences, Pilanesberg, Marioupol, and Stettin), including all metamorphosed/deformed occurrences (Norra Kärr, Red Wine, Kipawa, and Sushina). No examples are known in the age period from about 1100–500 Ma except for the Ilomba complex (Malawi); in fact, most agpaitic rocks are younger than 400 Ma. This overall age distribution is similar to that of alkaline rocks in general (e.g., Kogarko, 2001; Balashov and Glaznev, 2006) and can be roughly correlated with the nonexistence of supercontinents (Fig. 2).

Table 1

HFSE-rich minerals in miaskitic, agpaitic, and hyperagpaitic rocks with some remarks on their typical occurrences.

HFSE minerals typical of miaskitic rocks		
Zircon	ZrSiO ₄	Common in most igneous rocks, also as postmagmatic alteration product of other HFSE phases (see below) in agpaitic rocks
Baddeleyite	ZrO ₂	Instead of zircon in rocks with low silica activity (e.g., mafic rocks, carbonatites, and some syenites)
Titanite	CaTiSiO ₅	Common in most igneous rocks
Perovskite	CaTiO ₃	Instead of titanite in rocks with low silica activity (e.g., ultramafic to mafic rocks, carbonatites, also in some peralkaline nephelinites)
HFSE minerals typical of agpaitic rocks		
Aenigmatite	Na ₂ Fe ₅ TiSi ₆ O ₂₀	Important Ti host in many agpaitic rocks
Armstrongite	CaZr(Si ₆ O ₁₅) * 2 H ₂ O	Rare, probably only postmagmatic
Astrophyllite	K ₃ Fe ₇ Ti ₂ Si ₈ O ₂₆ (OH) ₅	Important Ti host in many agpaitic rocks
Catapleiite	Na ₂ ZrSi ₃ O ₉ * 2 H ₂ O	Mostly known from quartz-bearing peralkaline rocks, also as post-magmatic alteration product of EGM
Dalyite	K ₂ ZrSi ₆ O ₁₅	Mostly known from quartz-bearing peralkaline rocks and from potassic-ultrapotassic rocks, including lamproites and kimberlites
Elpidite	Na ₂ ZrSi ₆ O ₁₅ * 3 H ₂ O	Mostly known from quartz-bearing peralkaline rocks
Eudialyte _(sensu stricto) ¹	Na ₁₅ Ca ₆ Fe ₃ Zr ₃ Si(Si ₂₅ O ₇₃)(O,OH,H ₂ O) ₃ (Cl,OH) ₂	Major Zr host in most agpaitic rocks
Gittinsite	CaZrSi ₂ O ₇	Rare, mostly hydrothermal/metamorphic, also as alteration product of EGMs, elpidite, or zircon
Hilairite	Na ₂ ZrSi ₃ O ₉ * 3 H ₂ O	Rare, probably only very late- or even postmagmatic
Lamprophyllite	(SrNa)Ti ₂ Na ₃ Ti(Si ₂ O ₇) ₂ O ₂ (OH) ₂	Important Ti host in some agpaitic rocks
Lorenzenite	Na ₂ Ti ₂ Si ₂ O ₉	Rare
Lovozerite	Na ₃ CaZr(Si ₆ O ₁₅)(OH) ₃	Rare
Parakeldyshite	Na ₂ ZrSi ₂ O ₇	Rare, in pegmatites and hydrothermal veins, in cases as alteration product of EGM
Rinkite _(sensu stricto) ²	(Ca ₃ REE)Na(NaCa)Ti(Si ₂ O ₇) ₂ (OF)F ₂	Important Ti host in many agpaitic rocks
Vlasovite	Na ₂ ZrSi ₄ O ₁₁	Very rare, mainly (but not exclusively) known from quartz-bearing peralkaline rocks
Wadeite	K ₂ ZrSi ₃ O ₉	Mostly known from SiO ₂ -undersaturated rocks with potassic affinities, also in lamproites and kimberlites
Wöhlerite _(sensu stricto) ³	Na ₂ Ca ₄ Zr(Nb,Ti)(Si ₂ O ₇) ₂ (O,F) ₄	Important Zr host in many agpaitic rocks
HFSE minerals and other HFSE-free phases indicative of hyperagpaitic conditions		
Chkalovite	Na ₂ BeSi ₂ O ₆	Mostly in late-stage veins and pegmatites
Epididymite	Na ₂ Be ₂ Si ₆ O ₁₅ * H ₂ O	Mostly in late-stage veins
Lomonosovite	Na ₅ Ti ₂ O ₂ (Si ₂ O ₇)(PO ₄)	Mostly in late-stage veins
Zirsinalite	Na ₆ CaZr(Si ₆ O ₁₈)	
Natrophosphate	Na ₇ (PO ₄) ₂ F * 19 H ₂ O	
Natrosilite	Na ₂ Si ₂ O ₅	
Naujakasite	Na ₆ (Fe,Mn)Al ₄ Si ₈ O ₂₆	Instead of nepheline
Sørensenite	Na ₄ Be ₂ Sn(Si ₃ O ₉) ₂ * 2 H ₂ O	Mostly in late-stage veins and pegmatites
Steenstrupine-(Ce)	Na ₁₄ Ce ₆ Mn ₂ (Fe ₂ ³⁺ Zr(PO ₄) ₇ Si ₁₂ O ₃₆ * 3 H ₂ O	Instead of EGM in agpaitic rocks (except for voronkovite); major Zr host in most hyperagpaitic rocks
Thermonatrite	Na ₂ CO ₃ * H ₂ O	
Trona	Na ₃ (HCO ₃)(CO ₃) * 2 H ₂ O	
Tugtupite	Na ₄ BeAlSi ₄ O ₁₂ Cl	Mostly in late-stage veins and pegmatites

(continued on next page)

Table 1 (continued)

HFSE minerals typical of miaskitic rocks		
Ussingite	$\text{Na}_2\text{AlSi}_3\text{O}_8\text{OH}$	Mostly replacing alkali feldspar
Villiaumite	NaF	also in agpaite rocks, marking the transition toward hyperagpaite conditions
Vitusite-(Ce)	$\text{Na}_3\text{Ce}(\text{PO}_4)_2$	
Voronkovite	$\text{Na}_{15}(\text{Na,Ca,Ce})_3(\text{Mn,Ca})_3\text{Fe}_3\text{Zr}_3\text{Si}_{26}\text{O}_{72}(\text{OH,O})_4\text{Cl} \cdot \text{H}_2\text{O}$	Na-rich member of the eudialyte group; described from P-poor hyperagpaite rocks, where steenstrupine-(Ce) is absent
Vuonnemite	$\text{Na}_6\text{Nb}_2\text{Nb}_2\text{Na}_3\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{PO}_4)_2\text{O}_2(\text{OF})$	Major Ti host in most hyperagpaite rocks

1 = Eudialyte group.

$\text{Na}_{15}\text{M}_1\text{M}_2\text{M}_3\text{M}_4\text{Z}_3[\text{Si}_{24}\text{O}_{73}]\text{O}'_4\text{X}_2$; N = Na, Ca, K, Sr, REE, Ba, Mn, H_3O^+ ; M1 = Ca, Mn, REE, Na, Sr, Fe; M2 = Fe, Mn, Na, Zr, Ta, Ti, K, Ba, H_3O^+ ; M3, 4 = Si, Nb, Ti, W, Na; Z = Zr, Ti, Nb; O' = O, OH⁻, H₂O; X = H₂O, Cl⁻, F⁻, OH⁻, CO₃²⁻, SO₄²⁻, SiO₄⁴⁻ (Johnsen et al., 2003; Rastsvetaeva, 2007), with > 20 endmembers at present, including

Eudialyte $\text{Na}_{15}\text{Ca}_6\text{Fe}_3\text{Zr}_3\text{Si}(\text{Si}_{25}\text{O}_{73})(\text{O,OH,H}_2\text{O})_3(\text{Cl,OH})_2$.

Alluaivite $\text{Na}_{19}(\text{Ca,Mn})_6(\text{Ti,Nb})_3\text{Si}_{26}\text{O}_{74}\text{Cl}_2\text{H}_2\text{O}$.

Aqualite $(\text{H}_3\text{O})_8(\text{Na,K,Sr})_5\text{Ca}_6\text{Zr}_3\text{Si}_{26}\text{O}_{66}(\text{OH})_9\text{Cl}$.

Kentbrooksite $(\text{Na,REE})_{15}(\text{Ca,REE})_6\text{Mn}_3\text{Zr}_3\text{Nb}(\text{Si}_{25}\text{O}_{73})(\text{O,OH,H}_2\text{O})_3(\text{F,Cl})_2$.

Oneillite $\text{Na}_{15}\text{Ca}_3\text{Mn}_3\text{Fe}_3\text{Zr}_3\text{Nb}(\text{Si}_{25}\text{O}_{73})(\text{O,OH,H}_2\text{O})_3(\text{OH,Cl})_2$.

Raslakite $\text{Na}_{15}\text{Ca}_3\text{Fe}_3(\text{Na,Zr})_3\text{Zr}_3(\text{Si,Nb})\text{Si}_{25}\text{O}_{73}(\text{OH,H}_2\text{O})_3(\text{Cl,OH})$.

Taseqite $\text{Na}_{12}\text{Sr}_3\text{Ca}_6\text{Fe}_3\text{Zr}_3\text{NbSi}_{25}\text{O}_{73}(\text{O,OH,H}_2\text{O})_3\text{Cl}_2$.

2 = Rinkite group.

$\text{A}_6^{\text{P,M}}\text{M}_1^{\text{H}}\text{M}_2^{\text{O}}(\text{Si}_2\text{O}_7)_2(\text{X}_\text{M}^{\text{O}})_2(\text{X}_\text{A}^{\text{O}})_2$; A^P = Na, Ca, REE, Ca, Zn, Ba, Sr, K; M^H = Ti, Nb, Zr, Y, Mn, Ca, REE; M^O = Ti, Zr, Nb, Fe³⁺, Fe²⁺, Mg, Mn, Zn, Ca, Na, X_M^O, X_A^O = O, OH⁻, F⁻, H₂O (Sokolova and Cámara, 2017), with > 10 endmembers at present, including

Rinkite-(Ce) $(\text{Ca}_3\text{REE})\text{Na}(\text{NaCa})\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{OF})\text{F}_2$.

Götzenite $\text{Ca}_4\text{NaCa}_2\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{OF})\text{F}_2$.

Grenmarite $\text{Na}_2\text{Zr}_2\text{Na}_2\text{MnZr}(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$.

Hainite-(Y) $(\text{Ca}_3\text{Y,REE})\text{Na}(\text{NaCa})\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{OF})\text{F}_2$.

Kochite $\text{Ca}_2\text{MnZrNa}_3\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{OF})\text{F}_2$.

Mosandrite-(Ce) $(\text{Ca}_3\text{REE})[(\text{H}_2\text{O})_2\text{Ca}_{0.5}\square_{0.5}]\text{Ti}(\text{Si}_2\text{O}_7)_2(\text{OH})_2(\text{H}_2\text{O})_2$.

Nacareniobite-(Ce) $(\text{Ca}_3\text{REE})\text{Na}_3\text{Nb}(\text{Si}_2\text{O}_7)_2(\text{OF})\text{F}_2$.

Rosenbuschite $\text{Ca}_6\text{Zr}_2\text{Na}_6\text{ZrTi}(\text{Si}_2\text{O}_7)_4(\text{OF})_2\text{F}_4$.

3 = Wöhlerite group (also known as cuspidine group).

$\text{A}_6\text{M}_1\text{M}_2(\text{Si}_2\text{O}_7)_2(\text{F,O,OH})_4$; A = Na, Ca, REE, Fe, Mn; M1, M2 = Zr, Nb, Ti, Fe, Mn (e.g., Merlino and Perchiazzi, 1988; Chakhmouradian et al., 2008), with 10 endmembers at present, including

Wöhlerite $\text{Na}_2\text{Ca}_4\text{Zr}(\text{Nb,Ti})_2(\text{Si}_2\text{O}_7)_2(\text{O,F})_4$.

Normandite $\text{Na}_2\text{Ca}_2(\text{Mn,Fe})_2(\text{Ti,Nb,Zr})_2(\text{Si}_2\text{O}_7)_2\text{O}_2\text{F}_2$.

Hiortdahlite $(\text{Na,Ca})_2\text{Ca}_4\text{Zr}(\text{Mn,Ti,Fe})_2(\text{Si}_2\text{O}_7)_2(\text{F,O})_4$.

Låvenite $(\text{Na,Ca})_4(\text{Mn,Fe})_2(\text{Zr,Ti,Nb})_2(\text{Si}_2\text{O}_7)_2(\text{O,F})_4$.

Cuspidine $\text{Ca}_8(\text{Si}_2\text{O}_7)_2\text{F}_4$.

2.2. General occurrence

Agpaite rocks mostly occur as minor constituents in alkaline magmatic provinces (e.g., Gardar province, Kola Province, Montegian Hills, Damaraland suite, and Serra de Mar province) and are known from several oceanic islands (e.g., Ascension, Azores, and Cape Verde). Compared to miaskitic peralkaline rocks, however, they are rare and restricted to single or only very few localities within a magmatic province. This implies the special requirements for their formation that are not generally mandatory for the evolution of peralkaline rocks. The controlling factors for their formation must be related to special conditions during their final evolution and emplacement and not necessarily to large-scale, deep-seated processes defining an alkaline magmatic province (e.g., source composition and melting regime).

2.3. Rock textures and emplacement level

Very often, agpaite rocks form parts of composite magmatic complexes, which consist of several otherwise miaskitic intrusive units. The agpaite units are mostly younger than the miaskitic ones. Only at a few localities, agpaite rocks dominate a magmatic complex (Ilímaussaq, Khibina, and Lovozero), but even at these locations, genetically related miaskitic rocks are present. The general association of agpaite rocks with miaskitic ones and their temporal relationships underline the necessity of extensive magma differentiation (see below) before reaching the agpaite stage. As part of plutonic to (sub)volcanic composite magmatic complexes (group 1; Table 2), agpaite rocks are often medium-to-coarse grained, although fine grained and partly porphyritic equivalents are commonly associated (Fig. 3a–c; e.g., Ilímaussaq and Lovozero). The latter rocks may even dominate the field expression of

some localities (e.g., Pocos de Caldas) and frequently intrude the coarse-grained varieties at the same outcrop level (Fig. 3d). At some localities, coarse-grained agpaite rocks intrude temporally and genetically associated lavas and other pyroclastic rocks, which are, however, typically not of agpaite composition (e.g., Ilímaussaq and Pilanesberg; Fig. 3e). Magmatic layering is another feature often encountered in agpaite rocks (e.g., Parsons, 1987; Upton et al., 1996; Féménias et al., 2005).

Agpaite rocks may also form single very shallow-level subsurface magmatic bodies, such as sills, laccoliths, domes, and dykes (group 2; Table 2 & Fig. 3a; e.g., Saint-Amable in Canada and Toongi in Australia). Such rocks are mostly fine grained and very often vesicular with millimeter- to meter-sized cavities, which in these cases remain filled with (magmatic?) fluid (e.g., Aris in Namibia). Some EGM-bearing and partly aphanitic rocks are interpreted as effusive lavas on the basis of their close association with other volcanic/pyroclastic rocks and sedimentary units (e.g., Kontozero in Russia and Tarosero in Tanzania).

Very few examples of deformed and metamorphosed equivalents of agpaite rocks are known (group 3; Table 2), namely Red Wine and Kipawa (Canada), Norra Kärr (Sweden), and the recently discovered Sushina Hill in India (Chakrabarty et al., 2011). As the magmatic characteristics of these occurrences are variably obscured (e.g., Atanasova et al., 2017), they are not considered here further.

In general, because of the field appearance and textures of agpaite rocks, they are invariably emplaced at shallow crustal levels (< about 5 km) and occur in some cases even as effusive rocks (Fig. 4). Only a few pressure estimates for agpaite rocks are available, either based on the reconstruction of the volcano-sedimentary overburden combined with isochores from fluid inclusion studies (e.g., Jones, 1980; Konnerup-Madsen and Rose-Hansen, 1984) or based on feldspar

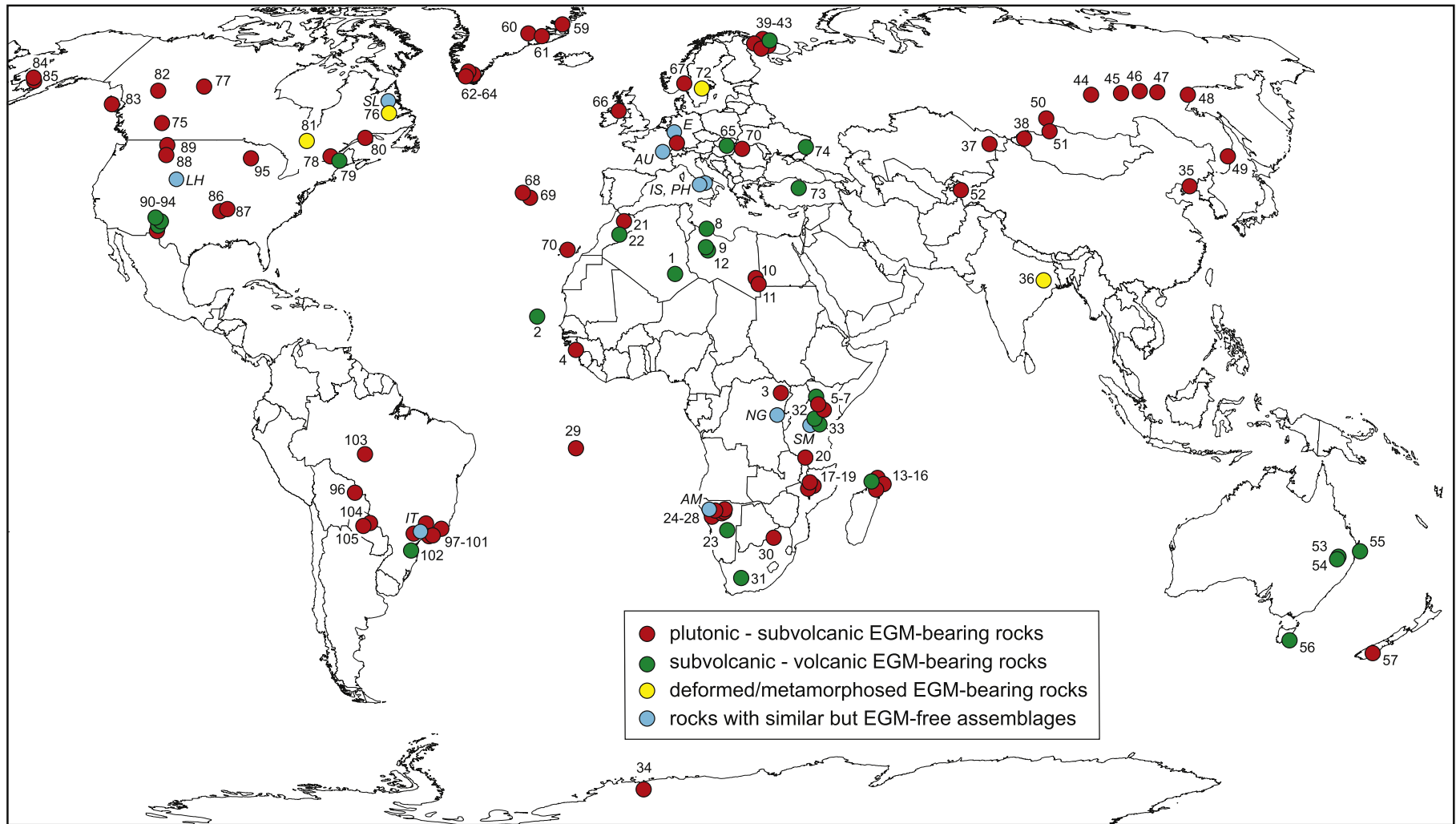


Fig. 1. Global distribution of EGM-bearing rocks (see details in Table 2) and important localities for other potentially agpaite rocks (blue dots) lacking EGMs. AM = Amis complex (Namibia), AU = Auvergne (France), E = Eifel (Germany), IS = Ischia (Italy), IT = Itatiaia (Brazil), LH = Leucite Hills (USA), NG = Nyiragongo (Democratic Republic of Congo), PH = Phlegrean fields (Italy), SL = Strange Lake complex (Canada), SM = Sadiman volcano (Tanzania).

Table 2

Compilation of EGM-bearing agpaaitic localities along with their age, field expression, rock associations, and several key references. According to their field occurrence, they are divided into 1 = plutonic to (sub)volcanic rocks with or without volcanic surface expression; 2 = subvolcanic to volcanic rocks including lavas, domes, stocks, vents, sills, laccoliths, and dykes; and 3 = Deformed/metamorphosed rocks. Field relations toward associated miaskitic rocks are categorized into A = dominantly agpaaitic rocks, B = (minor) agpaaitic unit of an otherwise miaskitic complex, C = locally developed interstitial agpaaitic assemblages in an otherwise miaskitic unit, D = agpaaitic assemblages restricted to (quartz-bearing) pegmatites/dyke rocks intruding miaskitic rocks, E = agpaaitic xenoliths in miaskitic volcanic rocks, F = skarn related. The textural appearances of EGMs are distinguished as presumably orthomagmatic (OM), late-magmatic/pegmatitic (LM), and hydrothermal (HY). The associated rock types with agpaaitic rocks are: I = Basaltic lithologies (including gabbroic and dioritic rocks), II = Basanitic lithologies, III = Nephelinitic rocks (including ijolites, urtites and meteigites), IV = Melilitite-bearing rocks, V = Carbonatitic rocks, Qtz = Quartz-bearing rocks (qtz-syenites and granites), UM = Ultramafic cumulates mostly consisting of olivine ± clinopyroxene ± garnet ± apatite ± titanite/perovskite ± nepheline ± melilite.

	Country	Area	Locality	Age	Group	Type	EGM textures	Associated rocks	Key references
234	Africa								
	1	Algeria	Hogar swell	Atakor, Azrou	23–2	2	–	?	I, II, Qtz Girod (1971); Azzouni-Sekkal et al. (2007); Ben El Khaznadj et al. (2016)
	2	Cape Verde		Boa Vista Island	15–4	2	B	LM	I, II, III, IV Dyhr and Holm (2010); Silva et al. (1989)
	3	Congo (Dem. Rep.)	Kivu	Bingo		1	B	LM	III, V Woolley et al. (1995); Williams et al. (1997)
	4	Guinea		Los Archipelago	104 ± 2	1	B	LM?	II Moreau et al. (1996)
	5	Kenya	Rift Valley Province	Kilombe	2	2	E	LM	I, (V), Qtz Ridolfi et al. (2006)
	6	Kenya	Rift Valley Province	Shombole	2	2	E	?	III, V Peterson (1989)
	7	Kenya	Homa Bay district	Ruri	11–4	1	B	LM, HY	III, V Woolley (2001)
	8	Libya	Gharyan district	Kaf El Khalef	41–38	2	–	LM	I, II Lustrino et al. (2012)
	9	Libya	Ash Shati District	Jabal Al Hasawinah	25–16	2	–	HY	I, II Oun (1991)
	10	Libya	Al Kufrah District	Jabal Archenu	40–50	1	B	?	I Woolley (2001); Flinn et al. (1991)
	11	Libya	Al Kufrah District	Uweinat	40–50	1	B	?	Woolley (2001); Flinn et al. (1991)
	12	Libya		Jabal Fezzan		2	–	OM?	I, II, III, IV, V + UM Bordet et al. (1955)
	13	Madagascar	Ampasindava Peninsula	Ambohimirahavavy (Ampasibitika)	ca. 24	1	D (qtz)	OM, LM	I, Qtz Estrade et al. (2014a, 2014b)
	14	Madagascar	Ampasindava Peninsula	Bezavona	ca. 24	1	B	LM	I Cucciniello et al. (2016); Lacroix (1922)
	15	Madagascar	Ampasindava Peninsula	Nosy Komba	ca. 21	1	D	LM	I Lacroix (1922); Cucciniello et al. (2016)
	16	Madagascar	Ampasindava Peninsula	Mont Sambirano	ca. 6	2	–	LM	I Cucciniello et al. (2016)
	17	Malawi	Chilwa Province	Jungini	137–129	1	C	LM, HY	(V) Woolley and Platt (1988)
	18	Malawi	Chilwa Province	Chenga (Mauze)		1	D	LM	(I), (III), V Garson and Walshaw (1969)
	19	Malawi	Chilwa Province	Matapon Hill (Nkallonje)		1	C	LM	III, V Garson (1963)
	20	Malawi	North Nyasa Province	Ilomba	685–655	1	C	LM	UM Wooley et al. (1992); Eby et al. (1998); Woolley et al. (1996)
	21	Morocco	High Atlas Mountains	Tamazeght	44 ± 2	1	C	LM, HY	I, V + UM Kchit (1990); Khadem-Allah (1993); Salvi et al. (2000); Marks et al. (2008a); Marks et al. (2008b); Schilling et al. (2009)
	22	Morocco	Ouarzazate Province	Saghro	10–3	2	–	HY	II, III, V + UM Berger et al. (2009)
	23	Namibia	Auas Mountains	Aris	33 ± 1	2	–	HY	II + UM Von Knorring and Franke (1987); Koller et al. (2014); Cámara et al. (2006); Piilonen et al. (2010)
	24	Namibia	Damaraland	Messum	132–127	1	D	LM	I, III, (V), Qtz + UM Harris et al. (1999)
	25	Namibia	Damaraland	Kalkfeld	173–154	1	C, D	LM	I, V, Qtz Woolley (2001); Miller (2008)
	26	Namibia	Damaraland	Etaneno	134 ± 3	1	C?	LM	Qtz Woolley (2001); Müller (1996)
	27	Namibia	Damaraland	Okorusu	127 ± 7	1	D	LM	III, V + UM Woolley (2001); Miller (2008)
	28	Namibia	Damaraland	Okenyenya	133–128	1	D	LM	I Woolley (2001); Miller (2008)
	29	Saint Helena		Ascension Island	< 1	1	D (qtz), E	LM, HY?	I, Qtz + UM Harris et al. (1982); Nielson and Sibbett (1996)
	30	South Africa	Western Bushveld Complex	Pilansberg	1395 ± 10	1	B, C	OM, LM, HY	III, Qtz Lurie (2009); Mitchell and Lifervovich (2006); Andersen et al. (2016); Elburg and Cawthorn (2016)
	31	South Africa	Sutherland	Saltpeterkop	ca. 66	2	E	?	IV, V Verwoerd et al. (1995); Verwoerd (1990)
	32	Tanzania	Rift Valley Province	Oldoinyo Lengai	< 1	2	E	LM	III, IV, V Dawson and Frisch (1971); Klaudius and Keller (2006)
	33	Tanzania	Ngorongoro Conservation Area	Tarosero	2	2	–	LM	I, III, Qtz Paslick et al. (1995); Dawson (1997); Dawson and Cooper (1997)
	Antarctica								
	34		Dronning Maud Land	Straumsvola	ca. 180	1	D (qtz)	OM?, LM, HY	I, II, III, Qtz + UM Harris and Rickard (1987); Harris and Grantham (1993); Riley et al. (2009)

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Table 2 (continued)

	Country	Area	Locality	Age	Group	Type	EGM textures	Associated rocks	Key references
Asia									
35	China	Liadong Peninsula	Saima	230–240	1	B	OM, LM, HY?	V + Qtz	Wu et al. (2010, 2015, 2016); Zhu et al. (2016)
36	India	Purulia District	Sushina Hill	1500–1300	3	–	–	Qtz	Chakrabarty et al. (2011, 2012, 2016); Goswami and Basu (2013)
37	Kazakhstan	Akjailayautas Mountains	Verkhnee Espe	250	1	D (qtz)	LM	Qtz	Stepanov et al. (2012); Sokolova et al. (2009); Cámara et al. (2010); Heinhorst et al. (2000)
38	Mongolia	Altai Range	Khaldzan-Buregtei	395–391	1	D (qtz)	LM	I, Qtz	Kovalenko et al. (2004); Baginski et al. (2016)
39	Russia	Kola Peninsula	Turiy	373 ± 6	1	D	LM	I + UM	Downes et al. (2005); Bell et al. (1996); Ivanikov et al. (1998); Dunworth and Bell (2001)
40	Russia	Kola Peninsula	Lovozero	370 ± 7	1	A	OM, LM, HY	III, IV, V + UM	Kramm and Kogarko (1994); Pekov (2000); Arzamastsev et al. (2008)
41	Russia	Kola Peninsula	Khibina (Chibiny)	ca. 370	1	A	OM, LM, HY	II, III, IV + UM	Kramm and Kogarko (1994); Arzamastsev et al. (2008)
42	Russia	Kola Peninsula	Kovdor	379 ± 2	1	D	LM, HM?	III, IV, V + UM	Verhulst et al. (2000); Krasnova et al. (2004); Pekov et al. (2001); Chukanov et al. (2005)
43	Russia	Kola Peninsula	Kontozero	370–380	2	–	OM, LM?	Qtz	Balaganskaya et al. (2002); Arzamastsev and Petrovsky (2012); Petrovsky et al. (2012)
44	Russia	Baikal Alkaline Province	Burpal(a)	287	1	D	LM, HY	I, Qtz + UM	Vladykin and Sotnikova (2016); Vladykin et al. (2014); Kotov et al. (2013); Sotnikova and Vladykin (2015)
45	Russia	Aldan Province	Little Murun	130–140	1	D	OM, LM	V + UM	Kogarko et al. (1995); Mitchell and Vladykin (1996); Reguir (2001)
46	Russia	Aldan Province	Inagli	130–140	1	D	LM, HY?	III, IV, V + UM	Kogarko et al. (1995); Naumov et al. (2008)
47	Russia	Aldan Province	Strelka		1	B	HY?		Kogarko et al. (1995)
48	Russia	Aldan Province	Konder	110–120	1	D	LM	UM	Kogarko et al. (1995); Zaitsev and Kogarko (2002)
49	Russia	Primorye	Koksharovka	160–172	1	D	OM	III, V + UM	Kogarko et al. (1995); Oktyabr'skii et al. (2010)
50	Russia	East Tuva	Dugdu	278–290	1	D	LM, HY?	Qtz	Kogarko et al. (1995); Kartashov (pers. comm.)
51	Russia	East Tuva	Korgeredaba	304 ± 12	1	B?, D	LM, HY	Qtz	Kogarko et al. (1995)
52	Tajikistan	Tien Shan Mountains	Dara-i-Pioz	150–190	1	D	LM	Qtz	Kogarko et al. (1995); Belakowski (1991); Reguir et al. (1999)
Australia									
53	Australia	New South Wales	Warrumbungle	17–13	2	–	LM	I, Qtz	Duggan (1988, 1990); Duggan and Knutson (1991)
54	Australia	New South Wales	Toongi	184 ± 19	2	–	LM	I	Spandler and Morris (2016)
55	Australia	Queensland	Mount Goonneringerrringgi		2	D	OM		Carr et al. (1976)
56	Australia	Tasmania	Port Cygnet	ca. 100	2	D	LM		Ford (1983)
57	New Zealand	East Otago province	Port Chalmers	13–3	1	E	LM?	I, II, III, Qtz + UM	Allen (1974); Coombs and Wilkinson (1969); Price et al. (2003)
Europe									
58	Germany	Rhinegraben	Kaiserstuhl	17–13	1	E	LM?	II, III, IV, V	Kolitsch (pers. comm.)
59	Greenland	East Greenland	Werner Bjerger	ca. 30	1	C	LM?	I, Qtz	Gleadow and Brooks (1979); Brooks et al. (1982); Christiansen et al. (2003)
60	Greenland	East Greenland	Kangerdlugssuaq	ca. 50	1	D	LM	I, Qtz	Wager (1965); Gleadow and Brooks (1979); Riishuus et al. (2008); Johnsen et al. (1998)
61	Greenland	East Greenland	Gardiner	ca. 55	1	D	OM, LM?	III, IV, V + UM	Frisch and Keusen (1977); Petersen and Secher (1993); Gleadow and Brooks (1979); Nielsen (1980, 1981); Nielsen et al. (1997)
62	Greenland	Gardar Province (South Greenland)	Ilímaussaq	1160 ± 5	1	A	OM, LM, HY?	I, Qtz	Ferguson (1964); Larsen and Sørensen (1987); Marks and Markl (2015)
63	Greenland	Gardar Province (South Greenland)	Motzfeldt	1273 ± 6	1	B	LM	I	Jones and Larsen (1985); Schönenberger and Markl (2008); McCreath et al. (2012, 2013)
64	Greenland	Gardar Province (South Greenland)	North Qôroq	1268 ± 60	1	B	OM, LM	I, (V)	Coulson (1997, 2003)
65	Hungary	Mecsek Mountains	Kövestető/Somlyó-Szamarhegy	135–110	2	–	LM	I, II	Dobisi (1987); Harangi (1994); Huemer (1997); Szakáll et al. (2014)

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Table 2 (continued)

	Country	Area	Locality	Age	Group	Type	EGM textures	Associated rocks	Key references
66	Ireland	Carlingford Complex	Barnavave	61 ± 1	1	D (qtz)	OM	I, Qtz	Nockolds (1950); Baxter (2008)
67	Norway	Larvik Plutonic Complex	Langesundsfjorden	299–292	1	B	OM?, LM	I, II, III, IV;Qtz	Larsen (2010); Andersen et al. (2010); Larsen et al. (2005); Corfu and Dahlgren (2008)
68	Portugal	Azores	San Miguel Island	< 1	1	E	LM	I	Ridolfi et al. (2003); Chiappino et al. (2017)
69	Portugal	Azores	Terceira Island	< 1	1	E	LM	I, Qtz	Jeffery et al. (2016); Gertisser et al. (2010)
70	Romania	Apuseni Mountains	Magureaua Vatei	70–90	1	F	LM?HY?	Qtz	Săbău and Negulescu (2014); Wiesinger et al. (2004)
71	Spain	Canary Islands	Tenerife	< 4	1	E	LM	I, II	Ferguson (1978); Wolff (1987); Ablay et al. (1998)
72	Sweden	Småland	Norra Kärr	1489 ± 8	3	–	–		Sjöqvist et al. (2013); Atanasova et al. (2017)
73	Turkey	Anatolya	Kizilcaören	24 ± 1	2	–	LM	V	Nikiforov et al. (2014)
74	Ukraine	Azov Sea Region	Mariupol (Oktyabrski)	ca. 1800	2	B	OM, LM?	Qtz	Krivdick and Tkachuk (1988); Dumańska-Słowik et al. (2012); Dumańska-Słowik (2016); Dumanska-Słowik et al. (2016); Sharygin et al. (2009)
North America									
75	Canada	British Columbia	Ice River	360 ± 4	1	B	OM, LM	III, V + UM	Currie (1975); Locock (1994)
76	Canada	Labrador	Red Wine + Mann-1, Mann-2, Seal Lake/Letitia Lake	ca. 1330	3	–	–	Qtz	Curtis and Gittins (1979); Curtis and Currie (1981); Smith (1969); Kerr (2011)
77	Canada	Northwest Territories	Thor Lake/Nechalacho	2176 ± 3	1	B	OM, LM	Qtz	Sheard et al. (2012); Möller and Williams-Jones (2016a, 2016b)
78	Canada	Monteregion Hills Province (Quebec)	Mont Saint-Hilaire	ca. 125	1	B	OM, LM, HY	I	Schilling et al. (2011a, 2011b, 2011c); Gilbert and Foland (1986)
79	Canada	Monteregion Hills Province (Quebec)	Saint-Amable	ca. 125	2	–	LM, HY		Horváth et al. (1998)
80	Canada	Québec	Mont McGerrigle	390–377	1	D	LM	I, Qtz	Wallace et al. (1990)
81	Canada	Québec	Kipawa	1389 ± 8	3	–	–	Qtz	Allan (1992); Currie and Van Breemen (1996); Edgar and Blackburn (1972);
82	Canada	Yukon	Ting Creek	53 ± 2	1	B	OM, LM	Qtz	Harrison (1982)
83	USA	Prince of Wales Island (Alaska)	Dora Bay	180–184	1	D	LM		Gunter et al. (1993); Barker and Mardock (1990); Taylor et al. (2014)
84	USA	McGrath District (Alaska)	Middle Fork	ca. 57	1	D (qtz)	LM	I, Qtz	Gunter et al. (1993); Barker (2016)
85	USA	McGrath District (Alaska)	Windy Fork	30 ± 2	1	D (qtz)	LM	I, Qtz	Solie (1983); Gunter et al. (1993)
86	USA	Arkansas	Magnet Cove	ca. 101	1	D	LM	III, V + UM	Erickson and Blade (1963); Flohr and Ross (1989, 1990)
87	USA	Little Rock (Arkansas)	Granite Mountain Syenite	95–86	1	D	LM	Qtz	Barwood (1989)
88	USA	Crazy Mountains (Montana)	Gordon Butte	ca. 48	1	D	LM		Chakhmouradian and Mitchell (2002); Emmart (1985)
89	USA	Bearpaw Mountains (Montana)	Rocky Boy Stock	40–50	1	D	LM, HY?	V + UM	Pecora (1942); Chakhmouradian and Mitchell (1999)
90	USA	Cornudas Mountains (New Mexico)	Wind Mountain	33–36	1	D	OM, LM		Boggs (1986); Boggs and Ghose (1985); Nutt et al. (1997); Clabaugh (1950); McLemore and Guilingier (1993); McLemore et al. (1996)
91	USA	New Mexico	Point of Rocks Mesa		2	–	?	I	DeMark (1984); Smith (2016)
92	USA	New Mexico	Pajarito Mountain	ca. 1180	1	A (qtz)	LM?	Qtz	Sherer (1990); McLemore (1990, 2010, 2015)
93	USA	Cornudas Mountains (Texas)	Chattfield Mountain	33–36	2	–	LM		Barker (2014); McLemore and Guilingier (1993)
94	USA	Sierra Tinaja Pinta (Texas)	Miller Mountain	33–36	2	–	LM	I, Qtz	Barwood (1989)
95	USA	Wausau Complex (Wisconsin)	Stettin	1565 ± 4	1	C, D	LM		Myers et al. (1984); Falster et al. (1999, 2014)
South America									
96	Bolivia		Velsaco Province	143–136	1	D (qtz)	LM?, HY?	(V), Qtz	Fletcher and Litherland (1981)
97	Brazil	Serro do Mar province	Poços de Caldas	75–85	1	B	OM, LM, HY?	III, (V)	Thompson et al. (1998); Ulbrich (1993); Gualda (1998); Schorscher and Shea (1992)
98	Brazil	Serro do Mar province	Passa Quatro	67 ± 3	1	C	LM		Thompson et al. (1998); Brotzu et al. (1992); Enrich et al. (2005)

(continued on next page)

Table 2 (continued)

	Country	Area	Locality	Age	Group	Type	EGM textures	Associated rocks	Key references
99	Brazil	Serro do Mar province	Monte de Trigo	ca.87	1	D	LM?	I + UM	Enrich et al. (2009, 2016)
100	Brazil	Serro do Mar province	Búzios Island	83	1	D	LM	Qtz	Alves and Gomes (2001); Enrich et al. (2012)
101	Brazil	Serro do Mar province	Itaipirapua	104–101	1	D	LM	V + UM	Gomes (1970); Gomes et al. (1970)
102	Brazil	Lages alkaline district	Morro do Tributo, Fazenda Nueva do Tributo	80–75	2	–	LM	II, III, IV, V + UM	Traversa et al. (1994)
103	Brazil	Apuí	Sucunduri	ca. 1200	1	B	LM?	I, II, III	Iwanuch (1981); Ulbrich and Gomes (1981)
104	Paraguay	Alto Paraguay province	Cerro Siete Cabezas	ca. 241	1	A?	LM?	Qtz	Velazquez et al. (1996); Comin-Chiaromonti et al. (2005)
105	Paraguay	Alto Paraguay province	Cerro Boggiani	ca. 241	1	B	LM?		Velazquez et al. (1996); Comin-Chiaromonti et al. (2015, 2016)

geothermobarometry (Petrovsky et al., 2012). Consistent with the field geology (see above), they mostly indicate shallow-level emplacement depths of about 1 kbar or less, although crystallization of some melts that formed agpaitic rocks may have started at deeper levels (e.g., Krumrei et al., 2007), and pressures of about 4 kbar were determined for the agpaitic rocks of the Nechalacho deposit in Canada (Möller and Williams-Jones, 2016a, 2016b). It is probably the unusual composition of the magmas (alkali and volatile rich) and the resulting physical properties (low density and viscosity) that allow for rapid ascent and differentiation processes by crystal settling and may influence their shallow emplacement level. However, they still must be able to retain their volatiles (see above).

2.4. Relations between miaskitic and agpaitic rocks in composite complexes

The field relations between miaskitic and agpaitic rocks in composite magmatic complexes are variable. At a few localities, agpaitic rocks constitute the dominant rock units of composite magmatic complexes (type A), where EGMs are the common rock-forming minerals in the magmatic units and in associated pegmatites and hydrothermal veins (Table 2; Fig. 5a; e.g., Ilímaussaq, Khibina, and Lovozero). Composite magmatic complexes with minor agpaitic rock units (type B) are more typical (Table 2; Fig. 5b; e.g., Pocos de Caldas, Mont Saint-Hilaire, and Langesundsfjord). Another variety (type C), which is represented, in general, by millimeter-sized interstitial EGM-bearing assemblages, occurs irregularly dispersed in spatially restricted areas of otherwise miaskitic rocks (Table 2; Fig. 5c; e.g., Tamazeght, Pilanesberg (white foyaite), and Junguni). Typically, agpaitic pegmatites and veins intruding the miaskitic host rock and the surrounding basement rocks also occur at such localities. The most common cases, however, are EGM-bearing pegmatites and dyke rocks, which crosscut otherwise miaskitic rocks with no agpaitic plutonic rocks exposed (type D; Table 2 & Fig. 5c; e.g., Magnet Cove, Burpala, and Kovdor). These occurrences show large differences in terms of areal extent and frequency of agpaitic pegmatites/dykes, while in some cases, they are documented only by a single dyke rock.

We suggest that the field expressions of agpaitic rocks and their variable field relations to miaskitic rocks in a given magmatic complex result from the present outcrop level. Plutonic agpaitic rocks are often seen to intrude overlying lava sequences or contain xenoliths of miaskitic volcanic rocks (Figs. 3e & 5a). These shallow-level composite bodies represent ancient magma chambers and magma plumbing systems that once fed larger volcanoes at the surface, which are now eroded. Thus, subvolcanic to volcanic agpaitic rocks may have been more common, but their present rock record is diminished because of erosion.

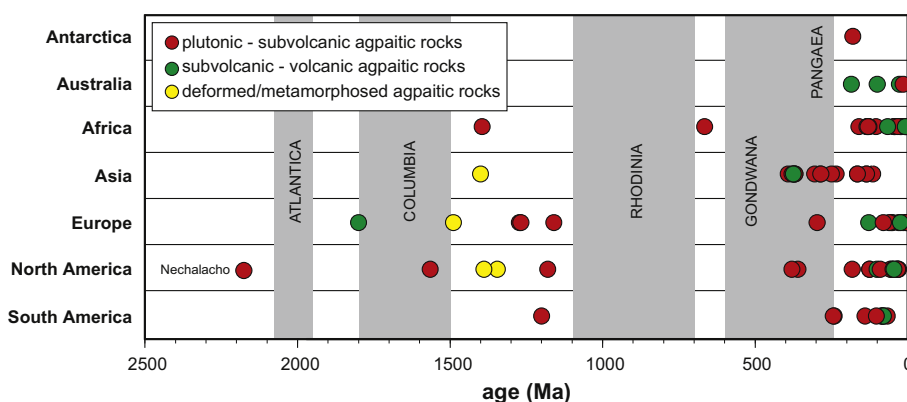
In turn, agpaitic pegmatites and veins crosscutting miaskitic plutonic rocks at many localities may imply that unexposed agpaitic plutonic bodies underlie these areas and are hidden at unknown depths (Fig. 5c). A very good example is the classic locality of the Langesundsfjord (Norway). Here, agpaitic and miaskitic pegmatites are relatively common and occur over a large area of several tens of square kilometers. These pegmatites intrude the very large (ca. 1800 km²) composite Larvik Plutonic complex, which was until recently considered to exclusively consist of miaskitic plutonic rocks. Only very detailed and recent fieldwork (Dahlgren, 2010; S. Dahlgren pers. comm. 2017) revealed the existence of a younger, type B agpaitic plutonic body, which developed interstitial agpaitic assemblages (although this body probably relates to the “ditroite schist” of Brøgger, 1890).

Similarly, coarse-grained, EGM-bearing nepheline syenites or granites found as loose blocks and xenoliths/autoliths in lavas from various volcanic islands (type E; Fig. 4 & Table 2; e.g., Azores, Canary Islands, and Ascension Island) and from volcanoes of the East African rift (Kilombe, Oldoinyo Lengai, and Shombole) imply that unexposed agpaitic plutonic bodies underlie the volcanic structures of miaskitic composition, and such conclusions may equally be derived from rare agpaitic effusive rocks interlayered with otherwise miaskitic volcanic rock sequences (Fig. 4).

Table 3

Comparison of the nomenclature scheme for nepheline syenites suggested by Khomyakov (1995) and the new classification system proposed here.

Khomyakov (1995)		Suggested here	
Group	Diagnostic minerals	Modifier	Diagnostic minerals, excluding postmagmatic and secondary minerals
Miaskitic	Allanite, zircon, ilmenite, hastingsite	Miaskitic	Zircon/baddeleyite, perovskite/titanite
Low agpaitic	Eudialyte, l��venite, titanite, zircon, apatite, katophorite	Transitional agpaitic	Minerals being typical for miaskitic and agpaitic rocks ^a
Medium agpaitic	Apatite, titanite, nosean, arfvedsonite, etc.	Miaskitic	Zircon/baddeleyite, perovskite/titanite
Highly agpaitic	Eudialyte, lamprophyllite, aenigmatite, astrophyllite, Li-arfvedsonite, nepheline, analcime, sodalite, villiaumite, etc.	Agpaitic	Minerals of the eudialyte, rinkite, and w��hlerite groups and aenigmatite, astrophyllite, dalyite, elpidite, hilairite, lamprophyllite, lorenzite, lovozerite, parakeldyshite, vlasovite, wadeite ^b
Hyperagpaitic	Zirsinalite, vuonnemite, vitusite, steenstrupine, chkalovite, Li-arfvedsonite, ussingite, natrosilite, villiaumite, etc.	Hyperagpaitic	Steenstrupine-(Ce)/voronkovite, naujakasite, lovozerite/zirsinalite, lomonosovite, natrophosphate, vitusite, natrosilite, ussingite, and others ^c

^a See details in Marks et al. (2011).^b See Table 1.^c See Table 1 and details in S  rensen, 1997; S  rensen and Larsen, 2001; Andersen and S  rensen, 2005; S  rensen et al., 2011; Andersen and Friis, 2015.**Fig. 2.** Available age data for EGM-bearing agpaitic rocks (Table 2). Yellow dots represent the magmatic ages of the metamorphosed agpaites from Norra K  rr (Sweden), Sushina Hill (India), and Redwine and Kipawa (Canada). The gray fields represent the approximate times of major supercontinent assemblies (Atlantica, Columbia, Rhodinia, Gondwana/Pangaea) after Rogers and Santosh (2003).

2.5. Temporal evolution of agpaitic assemblages

In general, EGMs show variable textural appearances: They occur as a cumulus or intercumulus phase in plutonic rocks and as a phenocryst or groundmass phase in volcanic rocks. In pegmatites, they form euhedral or interstitial phases, and in hydrothermal veins or late-stage geodes, they form euhedral, subhedral, or anhedral aggregates and may even occur as thin coatings in late-stage vugs and clefts. Some localities show all of these textural appearances in a given magmatic unit, whereas at other places, only one of them occurs at the present outcrop level (Table 2). Globular and spheroidal textures, which suggest immiscibility among silicate liquids, have been reported from several EGM-rich agpaitic rocks (Fig. 3h; Markl, 2001a; S  rensen et al., 2003; Spandler and Morris, 2016) and from other peralkaline rocks (e.g., Petrella et al., 2014; Vasyukova and Williams-Jones, 2014). Such phenomena cause extreme fractionation of major, minor, and trace elements (including halogens) between immiscible Na-Al-H₂O-rich and Fe-P-REE-S-F-Cl-rich melts (e.g., Markl, 2001a; Lester et al., 2013). In very rare cases, evolution toward extreme alkali enrichment permits the crystallization of the so-called hyperagpaitic assemblages. In these very unusual rocks, ussingite and naujakasite crystallize instead of or in addition to alkali feldspar and feldspathoids; steenstrupine-(Ce) forms at the expense of EGMs (see Table 1 for mineral formulas); and numerous water-soluble minerals such as villiaumite, trona, thermommatite, natrosilite, and natrophosphate are stable (e.g., Khomyakov, 1995; S  rensen, 1997; S  rensen and Larsen, 2001; Andersen and S  rensen, 2005; S  rensen et al., 2011; Andersen and Friis, 2015 and references therein). During the final evolutionary stages of agpaitic

systems, the coexistence of an aluminosilicate melt and an ionic melt of almost pure NaF (villiaumite) composition was suggested (Kogarko and Krigmann, 1970; Kogarko and Romanchev, 1983), and a gradual transition from melt to hydrothermal fluid in such systems was proposed (Kogarko, 1977; Khomyakov, 1995).

Overall, the variable textural appearance of agpaitic mineral assemblages clearly shows that the conditions necessary for stabilizing agpaitic minerals may be reached during different evolutionary stages of a given magmatic system. Accordingly, magmatic, late-magmatic, and hydrothermal agpaitic mineral assemblages must be distinguished (Table 2). However, the importance of the relative timing of their formation in a given magmatic complex and the role of magmatic and hydrothermal fluids in HFSE transport in such systems are not well understood.

3. Sources and parental magmas of peralkaline rocks

The composition of the source rocks from which melts are produced and the resulting parental magma compositions are the starting points for any further physicochemical evolution of the magmas that may eventually crystallize agpaitic rocks. In the following subsections, we review the present knowledge on magma sources and parental magma compositions of peralkaline rocks.

3.1. Magma sources

Numerous isotope studies demonstrated that magmas evolving toward peralkaline SiO₂-undersaturated rocks are ultimately mantle derived (e.g.,

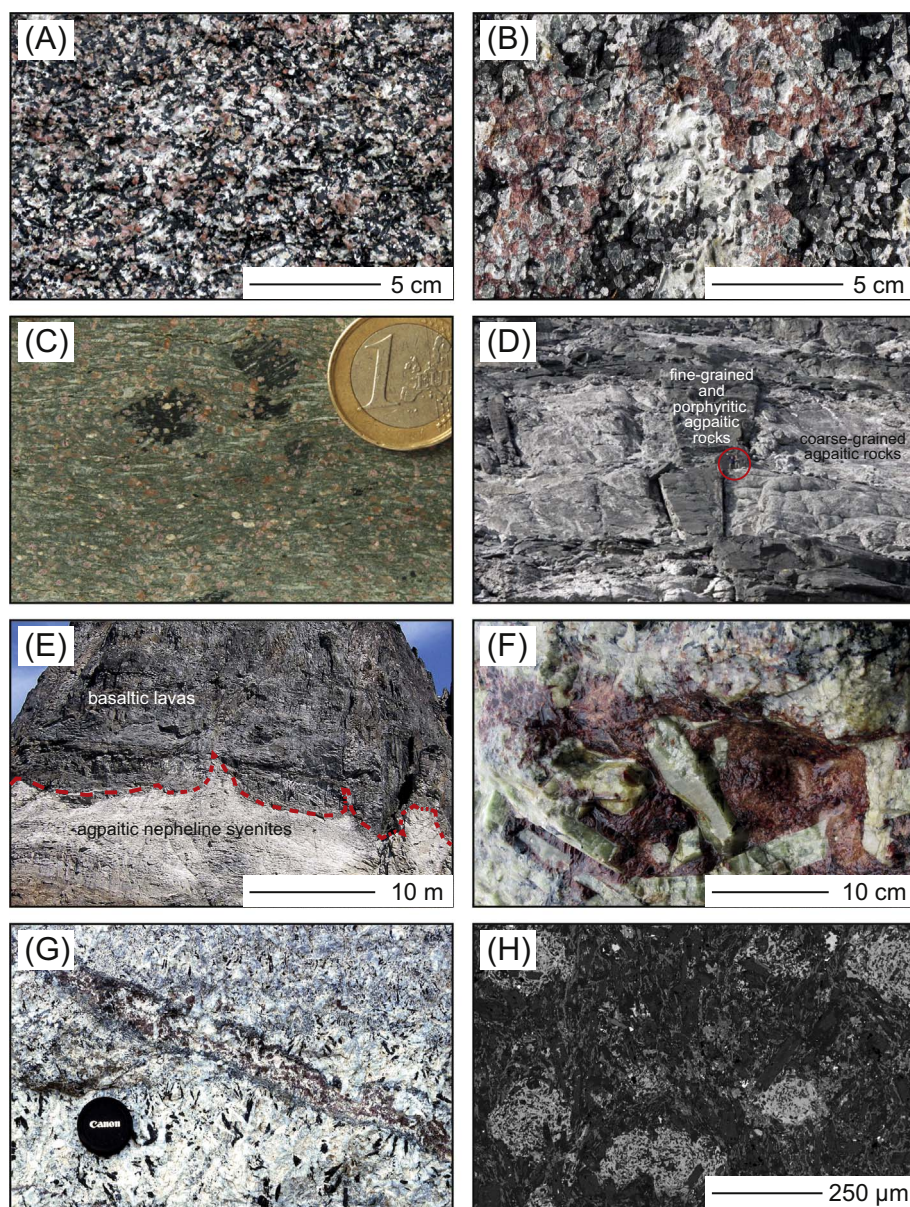


Fig. 3. Field characteristics of agpaite rocks and textural variations of EGMs. (A) Coarse-grained agpaite nepheline syenite (kakortokite) from the Ilímaussaq complex (Greenland) with cumulus EGMs (red) associated with sodic amphibole (black) and alkali feldspar + nepheline (white). (B) Coarse-grained agpaite nepheline syenite (naujaite) from the Ilímaussaq complex (Greenland) consisting of euhedral sodalite (greenish gray) and interstitial EGMs (red), sodic amphibole (black), and alkali feldspar + nepheline (white). (C) Fine-grained and porphyritic agpaite nepheline syenite (lujavrite) from the Ilímaussaq complex (Greenland) with euhedral phenocrysts of alkali feldspar (pale gray laths), EGMs (purple), nepheline (orange), and sodalite (white) set in a foliated matrix of sodic pyroxene (green) with occasional poikilitic sodic amphibole (black). (D) Fine-grained agpaite rocks (dark gray) intruding coarse-grained agpaite rocks (pale gray) in the Ilímaussaq complex (Greenland). Note the two persons for scale (red circle). (E) Coarse-grained agpaite rocks (pale) intruding overlying basaltic lavas (dark) in the roof zone of the Ilímaussaq complex (Greenland). (F) Agpaite pegmatite from the Lovozero complex (Russia) with euhedral alkali feldspar (greenish-gray) and interstitial EGMs (red). (G) Euhedral EGMs (reddish-brown) together with alkali feldspar (white) and fine-grained sodic pyroxene (dark greenish) in an agpaite vein crosscutting miaskitic nepheline syenites from the Tamazeght complex (Morocco). (H) Globular inclusion-rich bleb EGMs (pale gray) set in a fine-grained matrix consisting of albite, K-spar, and aegirine from the Toongi deposit (Australia).

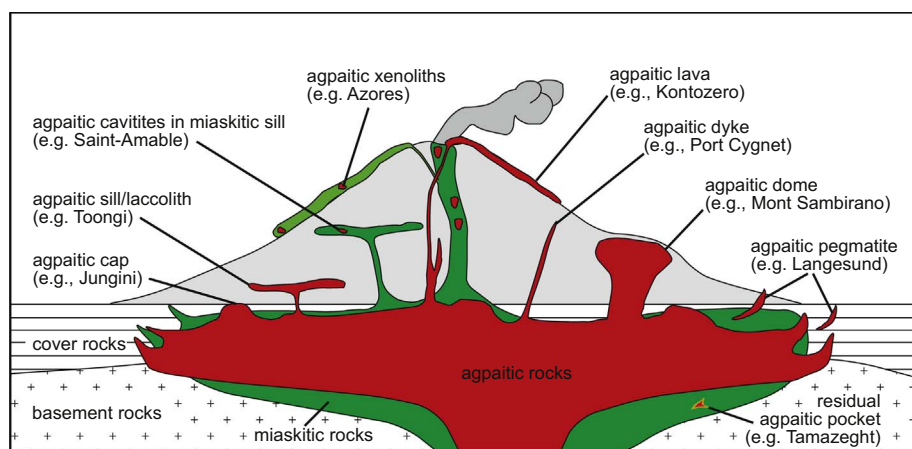


Fig. 4. Schematic illustrations of various field characteristics of miaskitic and agpaite peralkaline rocks.

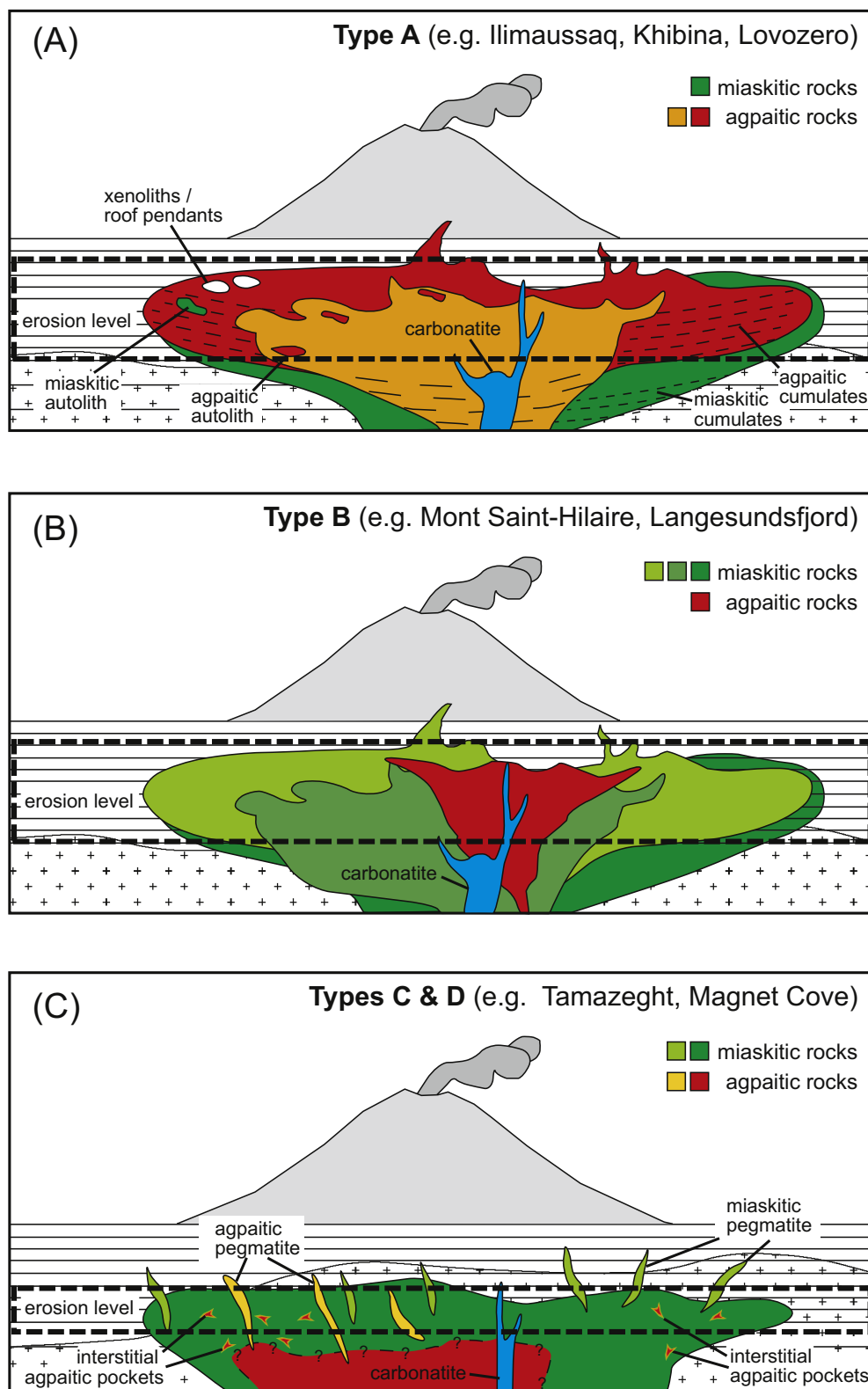


Fig. 5. Sketch of a composite miaskitic–agpaitic alkaline complex with associated carbonatite. The stippled box marks the present erosion level. (A) Dominated by agpaitic units and (B) by minor agpaitic units only. (C) Field relations between miaskitic plutonic rocks, agpaitic pockets therein, and associated pegmatites, implying potentially unexposed agpaitic plutonic rocks.

Eby, 1985; Kramm and Kogarko, 1994; Dunworth and Bell, 2001), although variable sources (e.g., asthenosphere, (subcontinental) lithosphere, and plume-derived) have been proposed (e.g., Kogarko et al., 2009; Upton et al., 2003; Trumbull et al., 2000). However, most researchers agree that a combination of low melting degrees in the mantle source and a prolonged subsequent differentiation history is not sufficient to explain the unusual enrichment of halogens, HFSEs, REEs, and other rare and incompatible

elements in peralkaline rocks. Therefore, the metasomatic pre-enrichment of these elements in the mantle sources, from which peralkaline melts are generated, is generally assumed as a prerequisite for peralkaline rock formation (Upton and Emeeus, 1987; Arzamastsev et al., 2001; Goodenough et al., 2002; Upton et al., 2003).

The proposed reasons for such pre-enrichment processes are diverse and include the recycling of oceanic and continental crust,

delamination and downwelling of the subcontinental lithosphere, and mantle metasomatism induced by diverse melts and fluids (e.g., McKenzie and O'Nions, 1983; White and Hofmann, 1982; Zindler et al., 1979; Foley, 1992; O'Reilly and Griffin, 2013; and references therein). Subsequent melting events in such modified mantle regions would initially produce alkaline melts that are enriched in incompatible elements if the degree of melting is low enough. The higher the degree of melting, the less alkaline the resultant melts will be. From mineralogical and geochemical evidence, the proposed source rocks for peralkaline melts include phlogopite-, amphibole-, apatite-, and partly carbonate-bearing garnet or spinel lherzolites (e.g., Upton and Emeleus, 1987; Upton, 1990; Paslick et al., 1995; Arzamastsev et al., 2001; Marks et al., 2008a; Köhler et al., 2009; Melluso et al., 2016). Further evidence for variably metasomatized mantle lithologies that give rise to peralkaline magmatism include the presence of associated mafic potassic or ultrapotassic rocks (mostly lamprophyres) and carbonatites (e.g., Goodenough et al., 2002; Coulson et al., 2003).

Alternatively, some peralkaline magmas were considered to represent the primary products of partial melting of metasomatically altered mantle rocks or lower crustal lithologies (e.g., Bailey, 1987). This model was put forward for agpaite phonolites from Kontozero (Russia) and was mainly based on the presence of various types of xenocrysts or inclusions in other minerals (e.g., omphacite and Mg-bearing ilmenite) and REE data.

3.1.1. Role of crustal contamination

Studies on a number of composite complexes containing both foid- and quartz-bearing rocks suggest that the amount of assimilation of (generally quartz-bearing) country rocks plays a critical role in the formation of SiO₂-oversaturated versus SiO₂-undersaturated peralkaline rocks (Davies and Macdonald, 1987; Wallace et al., 1990; Foland et al., 1993; Harris, 1995; Mingram et al., 2000; Schmitt et al., 2000; Späth et al., 2001; Marks et al., 2003). Similarly, isotope data for quartz-bearing agpaite rocks from Madagascar confirm the role of crustal contamination during their genesis (Estrade et al., 2014a).

3.2. Parental magmas

The importance of extensive differentiation processes of mantle-derived magmas by crystal fractionation for the origin of agpaite rocks is supported by coarse-grained mafic to ultramafic rocks typically associated with evolved (miaskitic and agpaite) peralkaline rocks at the present outcrop level or by geophysical evidence for the presence of dense cumulates in deeper levels of the crust (e.g., Neumann et al., 2004). Such cumulate rocks mostly consist of olivine ± clinopyroxene ± garnet ± apatite ± titanite/perovskite ± nepheline ± melilite. Although these rocks are certainly far from real magma compositions, they provide qualitative information on fractionating mineral assemblages.

3.2.1. Record from primitive volcanic and subvolcanic rocks

Two groups of primitive volcanic and dyke rocks are commonly associated with agpaite rocks. These are either plagioclase-bearing with (alkali) basaltic to basanitic compositions (e.g., Gardar province, Aris, and Canary Islands) or feldspar-free with mostly nephelinitic (and relatively rarely melilititic) compositions (Kola Peninsula, Gardiner, Magnet Cove, and Oldoinyo Lengai). From these observations and petrological and geochemical considerations, it is assumed that alkali basaltic, basanitic, and nephelinitic compositions are likely to represent the most important types of parental melts for peralkaline rocks.

Numerous experimental and field-based works provide important constraints on the generation of nephelinites, melilitites, basanites, and alkali olivine basalts. Some of these data suggest that alkali basaltic, basanitic, and nephelinitic magmas may evolve toward peralkaline phonolitic compositions by crystal fractionation (e.g., Bultitude and Green, 1967; Green, 1970; Brey and Green, 1975; Brey, 1978; Yagi and Onuma, 1978; Segalstad, 1979; Wilkinson and Stolz, 1983; Melluso et al., 2016). For example, a recent work on the agpaite rocks from the

Toongi deposit (Australia) used state-of-the-art geochemical modeling to show that polybaric differentiation processes may drive alkali basaltic magmas toward the evolution of peralkaline compositions (Spandler and Morris, 2016), and similar concepts have been applied elsewhere (e.g., Neumann, 1990; Platz et al., 2004).

Quite frequently, alkali basaltic, basanitic, and nephelinitic rocks are described from the same composite alkaline magmatic complex (e.g., Tamazeght, Boa Vista Island, Jabal Fezzan, and Messum), which may imply that diverse parental magma compositions are involved in the evolution of peralkaline complexes (e.g., Marks et al., 2008a). However, experimental evidence suggests that nephelinites, basanites, and alkali basalts may be related to each other through differentiation processes (e.g., Yagi and Onuma, 1978; Green, 1970). This would make it difficult to ultimately identify the parental melts of peralkaline rocks in a given magmatic complex depending on the presence or absence of one of these candidates in the field alone. However, detailed geochemical work on the volcanic Ankaratra Complex (Madagascar) implies that although nephelinites, basanites, and alkali basaltic rocks may all evolve toward peralkaline phonolites, these three primitive rock types represent primitive melts from mineralogically distinct mantle domains and are not related to each other by fractional crystallization (Melluso et al., 2016; Cucciniello et al., 2017).

Melilite-bearing rocks are occasionally associated with miaskitic and agpaite nepheline syenites (e.g., Kola Peninsula; Gardiner complex, Oldoinyo Lengai), but their specific role as potential parental magmas remains unclear. Although it was suggested that some nephelinite varieties may originate from the differentiation of initially melilititic compositions (Yagi and Onuma, 1978), the derivation of peralkaline phonolites by the differentiation of melilite-bearing rocks was excluded on the basis of phase petrological and geochemical work (e.g., Wilkinson and Stolz, 1983; Melluso et al., 2016; Cucciniello et al., 2017). Clearly, more detailed work is needed to evaluate the importance of melilititic rocks and their potential role as primary magma compositions for peralkaline trachytic to phonolitic compositions by differentiation processes.

3.2.2. Compositional record from agpaite rocks and EGMs

The mineralogical composition of agpaite rocks and the composition of EGMs themselves reflect their parental melt composition and the subsequent differentiation history (e.g., Schilling et al., 2011a; Marks et al., 2011; Enrich et al., 2016). Considering the potential effect of plagioclase fractionation (see above), Sr-rich and Sr-poor agpaite rocks can be distinguished, allowing for a first distinction of potential parental magma compositions, even in the absence of primitive rock types in a given magmatic complex. Fractionation of large amounts of plagioclase from basaltic magmas will deplete the residual magmas in Sr and Eu. Hence, EGMs from rocks that were derived from alkali basaltic magmas normally have low Sr levels and show pronounced negative Eu anomalies (e.g., Schilling et al., 2011a; Rojas et al., 2016). In contrast, nephelinitic magmas do not typically fractionate plagioclase, and consequently, EGMs in agpaite rocks of nephelinitic derivation typically have high Sr levels and do not show pronounced negative Eu anomalies (Marks et al., 2008b; Wu et al., 2010; Schilling et al., 2011a). For similar reasons, the presence of lamprophyllite-group minerals (which are typically Sr rich; Zaitsev and Kogarko, 2002) in agpaite rocks may imply nephelinitic as opposed to basaltic parental magma compositions. The potential role of melilite fractionation in this context has been only poorly studied to date (e.g., Platz et al., 2004), and as melilite may be Sr rich and can develop positive Eu anomalies (e.g., Mason and Martin, 1974), distinguishing melilite from plagioclase fractionation may be difficult. However, depending on a_{H2O} and f_{O2} in parental basaltic magmas, the typical fractionation assemblage olivine + plagioclase may change to amphibole + clinopyroxene, which allows for Sr (and Ba) enrichment during differentiation, and only minimal Eu anomalies will develop. Consequently, deciphering the parental melt composition of agpaite rocks, where mafic lithologies in the respective complex are absent, may be difficult, as recently shown for the Pilanesberg case (Elburg and Cawthorn, 2016).

4. Petrological evolution of peralkaline rocks

Extensive fractionation of plagioclase from broadly alkali basaltic compositions (alkalinity index < 1) is a potential mechanism for driving magmas toward peralkaline compositions (alkalinity index > 1), resembling the “plagioclase effect” of Bowen (1945). The additional fractionation of other Al-bearing but (Na + K)-poor phases (e.g., spinel or Al-bearing clinopyroxene) will enhance this process, and once it exceeds an alkalinity index of 1, the extensive fractionation of alkali feldspar will drive the evolving magmas to even higher peralkalinity (e.g., Giehl et al., 2013).

4.1. Combined effects of oxygen fugacity and peralkalinity

Oxygen fugacity is a crucial factor for the geochemical and mineralogical evolution of magmas in general. At oxidized conditions (high f_{O_2}), extensive magnetite precipitation will lead to FeO* depletion and SiO₂ enrichment in more evolved magmas. In contrast, at reduced conditions (low f_{O_2}), magnetite crystallization is suppressed, and/or co-crystallization of olivine will result in the enrichment of FeO and depletion of SiO₂ in the more evolved magma compositions. These two opposing trends have been frequently observed in nature and in experimental studies and are well known as the so-called Bowen and Fenner trends of metaluminous calc-alkaline and tholeiitic rock associations, respectively.

Similar trends are known from alkaline rock series, culminating either in rather melanocratic Fe-rich and strongly SiO₂-undersaturated peralkaline rocks (e.g., Ilímaussaq) or in relatively leucocratic Fe-poor compositions (e.g., Tamazeght). The less evolved members of such rock associations contain either olivine–augite–Fe–Ti oxide assemblages or augite–Fe–Ti oxide–garnet (± titanite) assemblages. Those with typically fayalite-rich olivine and mostly ulvöspinel-rich magnetite (or ilmenite) indicate much reduced (low f_{O_2}) and dry ($a_{H_2O} \ll 1$) magma compositions that crystallized around or below the FMQ buffer (Fig. 6a; e.g., Marks and Markl, 2001; Schilling et al., 2011b, 2011c). In contrast, assemblages involving garnet (typically andradite–schorlomite solid solutions) and Ti-poor magnetite indicate equilibration conditions well above the FMQ buffer (Fig. 6b; e.g., Marks et al., 2008a; Zaitsev et al., 2012). The various equilibria among these phases show variable dependencies from f_{O_2} and a_{SiO_2} and are the basis for any geochemical and mineralogical evolution of the subsequently evolving magmas.

Further differentiation processes of peralkaline rock associations are commonly expressed by the presence of sodic amphibole

(nyboite–arfvedsonite), sodic pyroxene (aegirine), or aenigmatite (or combinations of these) in the more evolved peralkaline rocks instead of fayalite, augite, or magnetite/ilmenite in the less differentiated ones. The relative stability of these phases depends on peralkalinity, silica activity (a_{SiO_2}), f_{O_2} , and a_{H_2O} (e.g., Ernst, 1962; Nicholls and Carmichael, 1969; Marsh, 1975; Andersen and Sørensen, 2005; Markl et al., 2010; Marks et al., 2011). Changes in these parameters during the evolution of peralkaline rocks are well documented by abundant disequilibrium textures where the precursors fayalite, hedenbergite, and typically ulvöspinel-rich magnetite are resorbed and replaced by arfvedsonite, aenigmatite, and aegirine (Larsen, 1977; Melluso et al., 2014; Lustrino et al., 2012; Marks and Markl, 2003, 2015). The common presence of such textures suggests that this transition is a continuous process, which may occur at different stages during the evolution of magmatic systems.

4.2. Halogen-bearing minerals in peralkaline rocks

Experimental evidence provides important information on the solubility of halogens in peralkaline melts, their influence on the stability of apatitic minerals, and their importance for inducing an unusually large crystallization interval commonly observed in peralkaline and, especially in, apatitic rocks (e.g., Piotrowski and Edgar, 1970; Sood and Edgar, 1970; Kogarko, 1974; Burnham, 1979; Bureau and Métrich, 2003; Giehl et al., 2013, 2014). Peralkaline magmas have high solubilities for halogens (e.g., Kogarko, 1974; Burnham, 1979; Bureau and Métrich, 2003; Giehl et al., 2013, 2014). The solubility of F reaches 8 wt% in rhyolitic melts (e.g., Webster, 1990; Webster and Halloway, 1990; Scaillet and Macdonald, 2004) and may reach similar levels in phonolitic melt compositions, although experimental constraints on the F solubility in peralkaline compositions are scarce (Giehl et al., 2014). The solubility of Cl in silicate melts increases with an increase in peralkalinity and FeO* content and decrease in SiO₂ content and may reach approximately 0.8–0.9 wt% (e.g., Métrich and Rutherford, 1992; Signorelli and Carroll, 2000, 2002; Giehl et al., 2014). Therefore, peralkaline magmas that evolved under reduced conditions may have a higher capacity for dissolving halogens compared to those that evolved under relatively oxidized conditions (see above).

4.2.1. Chlorine-rich minerals

Lowenstern (1994) suggested that peralkaline magmatic systems may only appear to be Cl rich compared to metaluminous ones because in peralkaline systems, Cl partitions into the melt phase rather than into

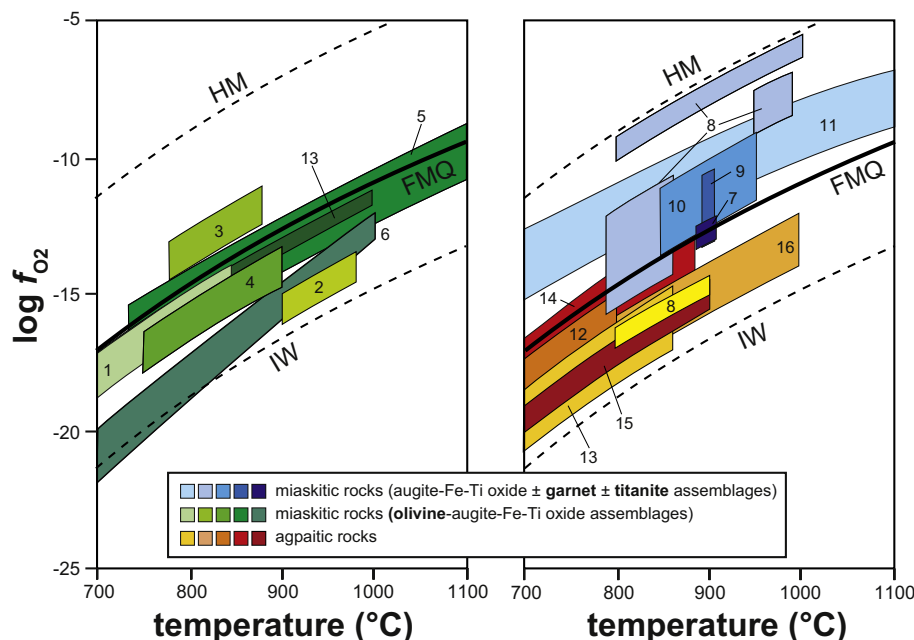


Fig. 6. Redox conditions during magmatic crystallization of alkaline rock sequences, grouped into rocks with (A) olivine–augite–Fe–Ti oxide assemblages (green) and (B) assemblages involving garnet and/or titanite (blue) and apatitic rocks (red, orange and yellow). Localities: 1 = Tugtutoq (Greenland; Upton and Thomas, 1980; Upton et al., 1985), 2 = Igdlertfigssalik (Greenland; Powell, 1978), 3 = Katzenbuckel (Germany; Mann et al., 2006), 4 = Puklen (Greenland; Marks et al., 2003), 5 = Mont Saint-Hilaire (Canada; Schilling et al., 2011b, 2011c), 6 = Ilímaussaq (Greenland; Marks and Markl, 2015), 7 = Khibina (Russia; Ryabchikov and Kogarko, 2006), 8 = Tamazeght (Morocco; Marks et al., 2008a), 9 = Sadiman (Tanzania; Zaitsev et al., 2012), 10 = Oldoinyo Lengai (Tanzania; Zaitsev et al., 2012), 11 = Itatiaia (Brazil; Brotzu et al., 1997; Enrich et al., 2005; Melluso et al., 2017), 12 = Motzfeldt (Greenland; Schönerberger and Markl, 2008), 13 = Ambohimarahavavy (Madagascar; Estrade et al., 2014a), 14 = Nechalacho (Canada; Möller and Williams-Jones, 2016a), 15 = Pilanesberg (South Africa; Andersen et al., 2016), 16 = Nyiragongo (Democratic Republic of Congo; Andersen et al., 2012b). HM, FMQ, and IW are hematite–magnetite, fayalite–magnetite–quartz, and iron–wüstite oxygen buffers, respectively, at 1 kbar.

coexisting fluids, and hence, degassing of Cl is much stronger for metaluminous compositions than that for peralkaline ones (e.g., Bacon et al., 1992; Webster et al., 1993). The most important sinks for Cl in many peralkaline rocks are typically early-magmatic sodalite-group minerals (SGMs), which can be divided into Cl rich (sodalite sensu stricto) and S rich (haüyne and nosean). Importantly, there is a profound difference between SGMs in miaskitic and agpaite varieties: In miaskitic rocks, SGMs are often sulfate rich, while they are typically S poor and Cl dominated in agpaite rocks (e.g., Parat et al., 2011; Krumrei et al., 2007). The variation in the S speciation of SGMs was shown to correlate with redox conditions. Sulfur-bearing sodalites from agpaite rocks (Ilímaussaq, Mont Saint-Hilaire) were shown to be sulfide dominated as opposed to SGMs from miaskitic rocks (Eifel), which are sulfate rich (Hettmann et al., 2012; Zahoransky et al., 2016), indicating reduced magmas for agpaite rocks. Experimental work showed that sodalite joins the stable assemblage alkali feldspar + nepheline at high temperatures ($> 800\text{ }^{\circ}\text{C}$) if a_{Cl} in the melt is high enough, while at lower temperatures, alkali feldspar may coexist with sodalite without nepheline. Both nepheline and sodalite are stable only at low $a_{\text{H}_2\text{O}}$ (e.g., Stormer and Carmichael, 1970; Giehl et al., 2013, 2014). Sodalite crystallization buffers the Cl content in residual melts to lower Cl concentrations with a decrease in temperature (e.g., from about 0.4 wt% Cl at $800\text{ }^{\circ}\text{C}$ to about 0.2 wt% Cl at $650\text{ }^{\circ}\text{C}$). Therefore, sodalite fractionation can have a major impact on the evolution of F/Cl ratios in evolving peralkaline systems (e.g., Giehl et al., 2014).

In agpaite rocks, Cl-bearing EGMs combine with sodalite at a certain point in the differentiation history. In addition to sufficient Cl, EGM crystallization additionally requires Zr content of around 0.7 wt% in the melt (e.g., Kogarko et al., 1982; Giehl et al., 2014). In this regard, the early crystallization of Zr-rich aegirine, which has been observed in some peralkaline but EGM-free rocks (e.g., Mann et al., 2006; Andersen et al., 2012a), could have an additional influence on the stability of EGMs. Most EGMs contain variable amounts of H_2O , generally as OH on the Cl site (e.g., Schilling et al., 2011a). This may reflect a potential temperature dependence on the incorporation of Cl into EGMs or on the Cl/ H_2O activity ratio in the coexisting melts/fluids (e.g., Ratschbacher et al., 2015; Giehl et al., 2014).

4.2.2. Fluorine-rich minerals

The most common F-bearing early magmatic minerals in peralkaline rocks are apatite, titanite, mica, and amphibole. Apatite is typically F rich and very Cl poor (e.g., Rae et al., 1996; Liferovich and Mitchell, 2006; Zirner et al., 2015; Ladenburger et al., 2016; Wang et al., 2016) but is relatively scarce in peralkaline rocks (especially in agpaite varieties), probably because of apatite fractionation during earlier differentiation stages, as suggested by their relatively low P_2O_5 contents (e.g., Bailey et al., 2001; Marks et al., 2003). In hyperagpaite rocks, however, various phosphates (e.g., natrophosphate, vitusite-(Ce)) and silico-phosphate minerals (e.g., steenstrupine-(Ce)) may be common again (Table 1; e.g., Andersen and Friis, 2015). Similar to apatite, titanite, biotite, and amphibole in peralkaline rocks are typically Cl poor (normally well below 0.1 wt%) but often contain F at the wt% level. In contrast to sodalite (see above), however, the halogen composition of apatite, titanite, mica, and amphibole in peralkaline magmas may be misleading. Their typically F-rich but Cl-poor character does not necessarily indicate F-rich and Cl-poor magmas or melts with high F/Cl ratios as the incorporation of halogens in these minerals is largely influenced by crystal chemical effects, and mineral-melt partitioning coefficients for F are > 1 , whereas those for Cl are $\ll 1$ (e.g., Zhu and Sverjensky, 1991; Zhang et al., 2012; and references therein).

Fluorite was reported as an early magmatic phenocryst in peralkaline rhyolites (e.g., Marshall et al., 1998). In SiO_2 -undersaturated systems, however, fluorite normally occurs as a late-magmatic interstitial phase (e.g., Marks and Markl, 2003; Melluso et al., 2011; Wang et al., 2016) or during hydrothermal conditions (e.g., Salvi et al., 2000). Until recently, experimental studies on the solubility of fluorite were

restricted to SiO_2 -oversaturated systems (e.g., Webster et al., 1987; Price et al., 1999; Scaillet and MacDonald, 2001, 2003); however, Giehl et al. (2014) showed that fluorite may form in phonolitic compositions at $\leq 825\text{ }^{\circ}\text{C}$, depending on CaO and F contents in the melt.

Villiaumite was reported as an interstitial phase in some plutonic agpaite rocks, extremely evolved hyperagpaite rocks (see below), pegmatites, andmiarolitic cavities and vugs (e.g., Khomyakov, 1995; Horváth et al., 1998; Sørensen and Larsen, 2001; Sørensen et al., 2011; Andersen and Friis, 2015).

In some peralkaline rocks and even in some metaluminous rocks (see below), F-rich Zr–Ti silicates of the wöhlerite and rinkite groups may occur (e.g., Varet, 1969; Andersen et al., 2010, 2012b; Melluso et al., 2011, 2014, 2017). Experimental data indicated that hiortdahlite may form together with fluorite instead of clinopyroxene if F contents in the melt are high enough (Giehl et al., 2014).

5. Fluids in peralkaline rocks

During ascent, cooling, and crystallization, most silicate magmas experience saturation with various types of fluids as it is evident from the fluid inclusions found in various intrusive and extrusive rocks. In the C–O–H system, the speciation of fluids mainly depends on temperature and oxygen fugacity and is based on the following schematic reaction.



It is obvious that under high f_{O_2} conditions, CO_2 and H_2O are the dominant fluid species. In contrast, CH_4 -rich fluids are stable under strongly reduced conditions. In contrast to CH_4 - and CO_2 -rich fluids, H_2O -rich fluids typically contain variable amounts of dissolved salts, such as NaCl, KCl, and CaCl_2 (e.g., Liebscher and Heinrich, 2007 and references therein). The NaCl– H_2O system is characterized by immiscibility under a wide range of p–T conditions in the upper crust, which results in the separation of a low-density vapor and a high-density hydrosaline melt (Hack et al., 2007). Indeed, some silicate rocks show evidence for the coexistence of silicate melt, vapor, and hydrosaline melt (e.g., Frost and Touret, 1989; Lowenstern, 1994). The fixed a_{Cl} in the two fluids determines the concentration of Cl in the silicate melt at a given P and T, and the high Cl contents in some peralkaline rocks may therefore be considered as evidence for their coexistence with immiscible vapor and hydrosaline melt (Lowenstern, 1994). As the type and speciation of the magmatic fluids coexisting with the silicate melt are of prime importance for understanding the difference between the transition of miaskitic and agpaite rocks, a brief review on the fluid inclusion record of miaskitic and agpaite peralkaline rocks is provided in the following subsections. This will include two localities (Motzfeldt, South Greenland and new data from Tamazeght, Morocco) where the transition from miaskitic to agpaite assemblages could be documented particularly well.

5.1. Fluids in miaskitic rocks

In miaskitic rocks, f_{O_2} is typically buffered by magnetite–titanite assemblages, indicating redox conditions around or above the FMQ buffer (e.g., Wones, 1989). Magmatic fluids from such rock types are either CO_2 – H_2O mixtures or H_2O dominated with a wide range of salinities. This has been shown, e.g., for various metaluminous and peralkaline monzonites, syenites, nepheline syenites, quartz-syenites, and granites from the Oslo Graben system and from the Gardar province (Olsen and Griffin, 1984a, 1984b; Hansteen and Burke, 1990; Andersen, 1990; Konnerup-Madsen, 1984; Köhler et al., 2004). For example, primary fluids in miaskitic nepheline syenites from the Ditrau massif (Romania) are invariably aqueous (albeit partly carbonate rich), showing a trend of decreasing salinities from the early-magmatic (35–40 wt% NaCl equivalent) to late-magmatic (20–25 wt% NaCl equivalent) and hydrothermal stages ($< 10\text{ wt\% NaCl equivalent}$; Fall

et al., 2007). The authors suggested that the crystallizing melt reached fluid saturation of an H₂O-rich fluid at an early stage (at up to about 600 °C) and at 2.5–5 kbar. Some of the most Cl-rich volcanic rocks on Earth are the peralkaline rhyolites from Pantelleria Island (Italy), reaching about 1 wt% Cl in bulk-rock samples (e.g., Lowenstern, 1994). Fluid and melt inclusion studies on these rocks confirmed the coexistence of silicate melt (with up to about 0.9 wt% Cl), aqueous hydro-saline melts (about 60–80 wt% NaCl equivalent), and almost Cl-free H₂O–CO₂ vapor (Lowenstern, 1994; Neave et al., 2012).

A rather unusual example is represented by the peralkaline Strange Lake granitic complex (Canada). Here, the earliest fluids are saline brines (about 25 wt% NaCl equivalent) that coexisted with immiscible CH₄ + H₂ gas. The fluids were exsolved from the silicate melt at about 450–500 °C (Vasyukova et al., 2016). Oxygen fugacity at the onset of fluid exsolution was estimated to be at least 2 log units below the FMQ buffer (Salvi and Williams-Jones, 1992, 1997; Gysi and Williams-Jones, 2013). During further cooling down to about 300 °C, the CH₄-dominated, low-density fluid was oxidized to a CO₂-dominated type, and the apparent salinity of the primary aqueous fluids successively decreased down to about 4.5 wt% NaCl equivalent. Various late-stage alteration reactions consumed the carbonic component and H₂O, resulting again in an increase in salinity (up to about 19 wt% NaCl equivalent) in secondary fluids. Vasyukova et al. (2016) further suggested that the saline fluids are capable of remobilizing and transporting REEs, Ti, and Zr over variable scales, with a change from hydroxy or hydroxy-fluoride complexes at higher T and pH toward chloride or hydroxy-chloride complexes at lower T and pH (because of the increase in activity of dissolved CO₂).

5.2. Fluids in agpaitic rocks

Numerous fluid inclusion studies on the classic agpaitic complexes (Ilímaussaq, South Greenland; Lovozero and Khibina, Russia) show that CH₄ (and minor molecular H₂) is the dominant or at least important fluid species during the magmatic stage in these rocks (e.g., Konnerup-Madsen, 2001; Krumrei et al., 2007; Beeskow et al., 2006; Nivin et al., 2005). Despite many studies, there is considerable debate whether such fluids are of magmatic origin and represent primary high-temperature conditions (mantle gas theory) or are the result of various secondary processes (e.g., Konnerup-Madsen, 2001; Potter and Konnerup-Madsen, 2003; Krumrei et al., 2007; Graser et al., 2008; Beeskow et al., 2006; Nivin et al., 1995, 2001, 2005; Potter et al., 1998, 2004; Potter and Longstaffe, 2007; Ryabchikov and Kogarko, 2006). However, today, scientists largely agree on the abiogenic origin of CH₄-rich fluids found in the Ilímaussaq rocks and in similar agpaitic complexes in Russia. The estimated redox conditions for agpaitic rocks are variable but are mostly below the FMQ buffer (Fig. 6b). At such reduced to extremely reduced conditions, high-temperature fluids are invariably CH₄ dominated. However, because of the temperature dependence of equilibrium (1), CH₄-rich fluids can also develop by the cooling and respeciation of initial CO₂–H₂O fluids (e.g., Konnerup-Madsen, 2001; Ryabchikov and Kogarko, 2006).

Late-magmatic to hydrothermal fluids in the same rocks and in hydrothermal veins are either CH₄ dominated (containing traces of higher hydrocarbons such as ethane and propane) or of mixed CH₄–H₂O–NaCl compositions with variable, but generally high salinities of up to about 30 wt% NaCl equivalent (e.g., Konnerup-Madsen, 2001; Markl et al., 2001; Krumrei et al., 2007; Graser et al., 2008). This is in accordance with experimental work, which showed the existence of p- and T-dependent miscibility gaps in CH₄–H₂O–NaCl system; in addition, saline brines coexist with CH₄-dominated fluids at temperatures below about 600 °C (e.g., Lamb et al., 1996; Duan et al., 2003).

Detailed investigation on some of the late-stage agpaitic rocks and associated hydrothermally overprinted rocks from Ilímaussaq revealed a large temperature range (from about 600 to 200 °C), which marks the transition from the late-magmatic to the hydrothermal stage (e.g.,

Markl, 2001a). The aqueous fluids in such veins are extremely sodic and characterized by high pH (up to 10–12), thus enabling the formation of ussingite and hyperagpaitic mineral assemblages, which are described below (Markl and Baumgartner, 2002). Kogarko (1977) and Khomyakov (1995) proposed a gradual transition from melt to hydrothermal fluid in such systems. Furthermore, various kinds of bitumen are known from some Ilímaussaq rocks (Petersilie and Sørensen, 1970; Konnerup-Madsen et al., 1988; Laier and Nytoft, 2012). Although they occur finely dispersed (not visible through the naked eye) in most Ilímaussaq rocks, rare millimeter-sized droplets are common in some of the late-stage pegmatites and hydrothermal veins (Konnerup-Madsen, 1988; H. Friis, pers. comm. 2013).

5.3. Fluids in rocks showing the transition from miaskitic to agpaitic assemblages

Fluid inclusion data from mixed miaskitic to agpaitic localities are particularly interesting as they may provide insight on the importance of fluid composition and speciation for the stability of miaskitic vs. agpaitic assemblages. One such example is Motzfeldt (South Greenland), which is a composite nepheline syenite complex dominated by miaskitic rocks except for the latest magmatic unit where EGM-bearing assemblages developed, resembling type B in Table 2. For miaskitic rocks, redox conditions between 0.5 and 2 log units below the FMQ buffer were proposed (Schönenberger and Markl, 2008). The presumably magmatic fluids of these units are of the H₂O–NaCl type (< 10 wt% NaCl equivalent) with occasional calcite daughter crystals, implying the presence of CO₂ or HCO₃[–] in the original fluid phase. In contrast, rocks of the agpaitic unit contain mixed CH₄–H₂O–NaCl fluids with salinities of up to 18 wt% NaCl equivalent (Schönenberger and Markl, 2008).

In Tamazeght (Morocco), interstitial EGM–sodalite assemblages occur irregularly dispersed in several spatially restricted areas (generally < 100 m²) within an otherwise miaskitic nepheline syenite body (Fig. 7a & b; Schilling et al., 2009). The redox conditions of these agpaitic pods were estimated to be about 2 log units below the FMQ buffer (yellow field 8 in Fig. 6b; Marks et al., 2008a). Further EGM-bearing assemblages are found in late-stage dyke rocks, pegmatites, and hydrothermal veins crosscutting otherwise miaskitic units and limestone country rocks (Fig. 7a & b). Hydrothermally altered agpaitic pegmatites contain high salinity aqueous fluids (up to 25 wt% NaCl equivalent), with assumed trapping conditions of about 300 °C (Salvi et al., 2000). These fluids are proposed to result from the interaction of a hydrothermal brine released from agpaitic pegmatites with the surrounding limestones. This caused alteration in nepheline and EGMs and resulted in the formation of secondary HFSEs (e.g., catapleiite) and fluorite (Salvi et al., 2000), similar to the alteration zones described for the peralkaline (but EGM free) Strange Lake complex in Canada (e.g., Salvi and Williams-Jones, 2006).

Additional fluid inclusion data from several localities in the Tamazeght complex, where millimeter-sized agpaitic pockets occur in several spatially restricted areas of an otherwise miaskitic nepheline syenite body, provide new insight into this transition. Several samples from miaskitic nepheline syenites and agpaitic pods therein, as well as from miaskitic and agpaitic dyke rocks, were investigated (Fig. 7a & b). Miaskitic and agpaitic rocks contained aqueous fluid inclusions in nepheline and EGMs (the latter only in the agpaitic samples, obviously) with different salinities that partly overlapped. However, fluid inclusions from miaskitic samples had salinities mostly below 10 wt% NaCl equivalent, with only few inclusions showing higher salinities. In contrast, the salinities of fluid inclusions from agpaitic samples were mostly above 10 wt% NaCl equivalent, and salinities well above 20 wt% were frequently found (Fig. 7c). Homogenization temperatures in miaskitic and agpaitic samples varied between about 150 and > 400 °C (heating limit of the used heating-freezing stage), with texturally primary fluid inclusions homogenizing mostly at > 400 °C. No systematic difference

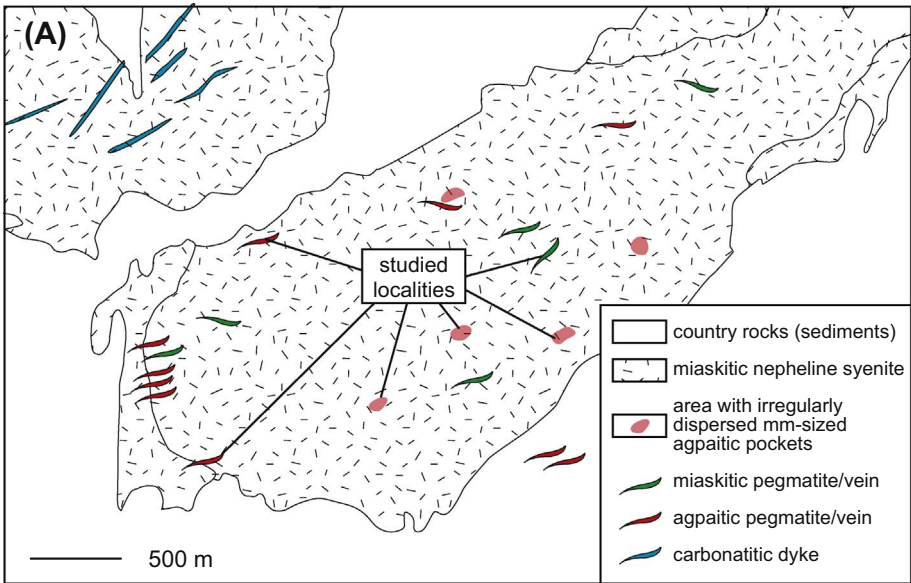
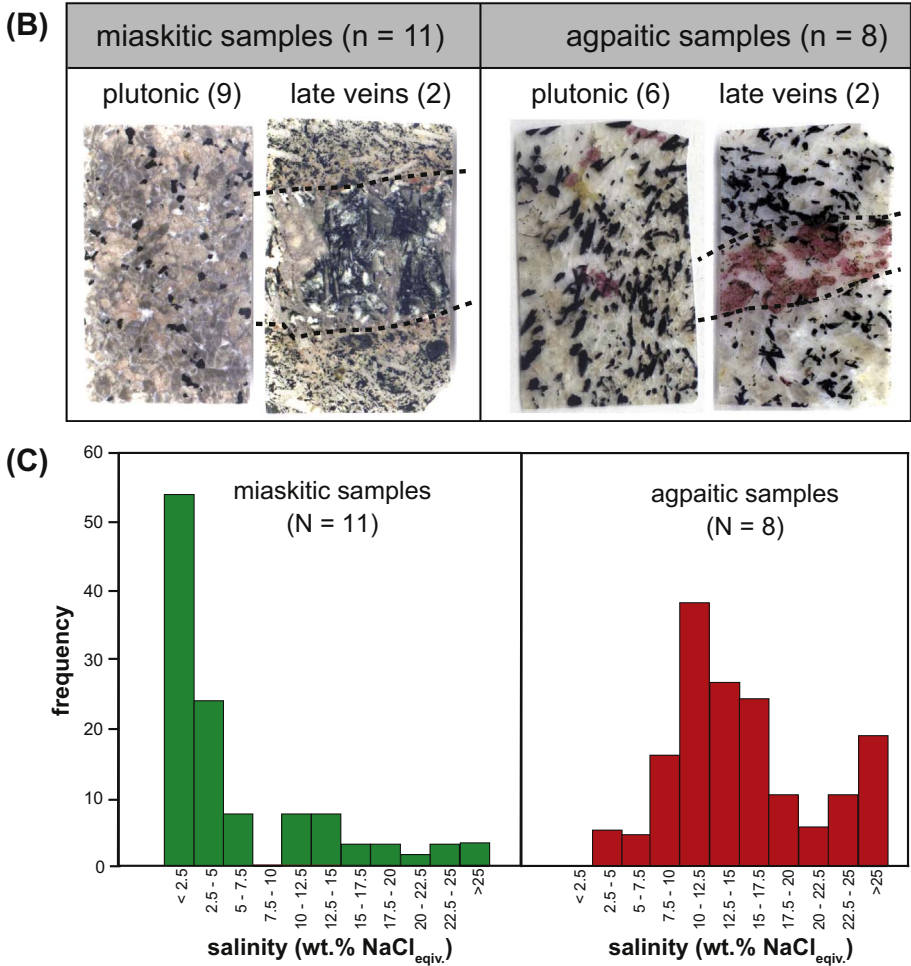


Fig. 7. (A) Field occurrence of agpaitic rocks in the Tamazeght complex (Morocco). Besides agpaitic pegmatites and veins (not to scale), millimeter-sized agpaitic assemblages are found in several spatially very restricted areas (pale red areas) in a miaskitic nepheline syenite body (see details in Schilling et al., 2009). (B) Scanned thick sections of the various types of samples investigated. (C) Salinity of fluid inclusions (expressed as wt% NaCl equivalent) from miaskitic and agpaitic samples.



on homogenization temperatures between miaskitic and agpaitic samples existed, and no universal correlation between homogenization temperature, melting temperature, or salinity was detected (for details, see the electronic appendix). Fluid inclusions from miaskitic samples did not contain any CH₄, whereas in agpaitic samples, traces of methane were found. Late-stage EGM-bearing veins contained even pure methane fluid inclusions with traces of molecular hydrogen and/or higher hydrocarbons (ethane and propane).

5.4. Potential implications

Magmatic fluids in agpaitic rocks are dominated by CH₄-rich/high-salinity and H₂O-poor compositions, whereas those in miaskitic rocks tend to be H₂O rich instead, with the notable exception of the Strange Lake complex (see above). These differences are ultimately related to the prevailing redox conditions: Most miaskitic rocks form at relatively oxidized conditions, thus causing the early exsolution of H₂O-

dominated fluids or H₂O–CO₂ mixtures that deplete the remaining melt in water-soluble species, such as Na and halogens. In contrast, agpaite rocks and some peralkaline granites evolve during reduced conditions (Fig. 6b), and the components that would normally be expelled by aqueous fluids will be retained and enriched during further evolution. Such Na- and halogen-rich compositions have high solubilities for HFSEs (e.g., Watson, 1979; Keppler, 1993; Linnen and Keppler, 2002) and are capable of precipitating EGMs during magmatic stages, as soon as the required enrichment level for Zr (about 0.7 wt% ZrO₂; see above) is reached in the magma.

Late-magmatic to hydrothermal fluids in miaskitic and agpaite peralkaline rocks may contain variable amounts of CH₄ or CO₂ but are generally aqueous. Compared to early-magmatic fluids, such late-stage fluids may show higher or lower salinities (see above). The partitioning behavior of Cl between silicate melt and coexisting fluid is pressure dependent: At pressures below about 1.5 kbar (as in the case for most agpaite rocks, see above), the salinity of exsolving fluids increases with progressive crystallization. At higher pressures (e.g., at Ditrau, see above), however, the salinity of late-stage fluids is lower than that of early-magmatic fluids (e.g., Cline and Bodnar, 1991; Kilinc and Burnham, 1972; Shinohara et al., 1989; Signorelli and Carroll, 2000). This may influence the transport capacity for HFSE in variably saline fluids (see Section 8) and could explain why agpaite rocks are generally restricted to low-pressure environments. Therefore, some peralkaline magmatic systems may end up miaskitic (although their geochemical composition would allow for the formation of late-magmatic to hydrothermal agpaite assemblages), not only because their crystallization environment was too oxidized but simply because they were emplaced at very deep crustal levels.

On the basis of field evidence and fluid inclusion data, fluid exsolution, fluid migration, and fluid–rock interaction have to be considered as dynamic processes rather than singular events. As fluid exsolution may occur relatively late in agpaite systems (see above), this may be a locally heterogeneous process because convection and diffusion in the residual crystal–melt mush at this stage are not sufficient any more to homogenize the system. Strong chemical heterogeneity in residual silicate melt–brine–fluid systems on a local scale was demonstrated for granitic systems by, for example, Kamenetsky et al. (2004), who suggested it to occur because of the failure of individual phases to re-equilibrate. Thus, the patchy occurrence of only locally developed interstitial EGM–sodalite assemblages in otherwise miaskitic rocks, as observed in Tamazeght and many other localities (e.g., Junguni, Stettin; type C in Table 2), can be explained by variably saline fluids that exsolved during slightly different stages with only the high salinity fluids being able to transport considerable amounts of HFSEs.

6. Formation of agpaite and agpaite-like mineral assemblages

The minerals originally defining agpaite rocks are a diverse group of halogen-bearing and Zr–Ti-rich minerals, which commonly contain variable amounts of Na, K, Ca, and Fe. These phases are typically either Cl rich (EGMs) or F rich (wöhlerite and rinkite groups) and are commonly associated with a range of other sodic and/or volatile-bearing minerals, such as alkali feldspar, nepheline, sodalite, sodic amphibole/pyroxene, and aenigmatite (e.g., Khomyakov, 1995; Sørensen, 1997). However, the spatiotemporal formation of such assemblages is highly variable (see Sections 2.3–2.5), and several mineralogical variants of agpaite assemblages are known, which are discussed in the following subsections.

6.1. Mineralogical varieties of agpaite rocks

The classical case of agpaite rocks is represented by nepheline syenites containing Na- and Cl-rich EGM–sodalite assemblages, with the type locality of the Ilímaussaq complex (South Greenland), where the locality “Agpat” is situated (Ussing, 1912). Similar assemblages, partly

lacking EGMs but comprising halogen-free, Na-rich Zr–Ti silicates, being either H₂O rich (e.g., hilarite) or anhydrous (e.g., parakelydshite, lorenzenite), have been reported from several occurrences, such as Pílanesberg (Andersen et al., 2016) and Langesundfjord (Larsen, 2010). Compared to miaskitic rocks (where zircon is stable) and F-rich Zr–Ti silicate assemblages (see below), EGM formation requires a higher peralkalinity and a higher a_{HCl} in the melt (e.g., Andersen et al., 2010; Marks et al., 2011) combined with the required enrichment of Zr (e.g., Giehl et al., 2014). In addition to Zr, EGMs may contain appreciable amounts of other HFSEs (Hf, Nb, Ta, and REEs). Combined with generally low Pb, U, and Th contents, EGMs are attractive ore minerals for HFSEs, which were recently explored, for example, at Toongi (Australia), Ilímaussaq (Greenland), and Norra Kärr (Sweden).

Fluorine-rich Zr–Ti silicates may form if a_{HF} in a magma increases above a certain level. As a result, the stable assemblage zircon + fluorite shifts to assemblages with wöhlerite- and rinkite-group minerals + fluorite (Andersen et al., 2010; Giehl et al., 2014). Such assemblages are observed, for example, not only from lava domes in the Auvergne (France; Varet, 1969; Brousse and Rançon, 1984), the Eifel (Germany; Hentschel, 1980), the Kaiserstuhl (Germany; Czygan, 1973), the Phlegrean Fields (Italy; Melluso et al., 2011), Ischia (Italy, Melluso et al., 2014), and the plutonic Itatiaia complex in Brazil (e.g., Melluso et al., 2017) but also in some carbonatites (e.g., Oka and Kaiserstuhl; Mariano and Riedder, 1989; Keller et al., 1995).

Mixed assemblages consisting of F-rich Zr–Ti silicates and EGMs are quite commonly observed and are known from Libya, Madagascar, Greenland, China, and Morocco (Larsen and Steenfelt, 1974; Lustrino et al., 2012; Berger et al., 2009; Wu et al., 2016; Cucciniello et al., 2016). The perhaps best-investigated rocks of this type are the pegmatites of the Langesundfjord region in Norway. From the textural and chemographic analysis of these pegmatites, Andersen et al. (2010) suggested that alkali enrichment of magmas crystallizing F-rich Zr–Ti silicates along with fluorite is terminated by the formation of mixed assemblages, eventually crystallizing additional EGMs. Further evolution to mineral assemblages with villiaumite and other minerals typical of hyperagpaite rocks (see above) is considered as highly unlikely, and hence, only melts crystallizing Cl-rich EGM–sodalite assemblages can reach the extreme case of alkali enrichment and are the only ones with the potential to form hyperagpaite assemblages (Andersen et al., 2010; see above). This is indeed mirrored in whole-rock data for subvolcanic to volcanic rocks from various localities (Fig. 8), which show that rocks containing primary F-rich Zr–Ti silicates (with or without associated EGMs) do not reach alkalinities as high as rocks containing pure EGM–sodalite assemblages. Importantly, pure F-rich Zr–Ti silicate assemblages and mixed assemblages with additional EGMs are not restricted to peralkaline rocks, they also occur in metaluminous compositions (Fig. 8). It is, however, not clear whether the magma composition at the time when the F-rich Zr–Ti silicates crystallized was still metaluminous or already peralkaline (at least in some parts of a crystallizing crystal mush) as these minerals mostly occur interstitially. Pure EGM–sodalite assemblages lacking F-rich Zr–Ti silicates are, however, largely restricted to rocks with an alkalinity index of > 1.2 that show maximum Fe enrichment and very high Zr contents (Fig. 8). Exceptions from this are three phonolitic rocks from Libya and Hungary (alkalinity index of 0.87, 0.94, and 1.04, respectively), where although EGMs are of hydrothermal origin (Oun, 1991; S. Szakáll, pers. comm. 2017). We consider the pronounced Fe enrichment, as shown in Fig. 8, as further evidence that reduced conditions during early stages are an important prerequisite for the magmatic formation of EGMs (see above).

We further suggest that the type of Zr–Ti silicate–sodalite assemblages developed in a given rock (pure EGMs, pure F-rich Zr–Ti silicates, or mixed) monitors the geochemical evolution of peralkaline magmas with respect to their halogen contents: Most mixed assemblages contain early magmatic sodalite, texturally later F-rich Zr–Ti silicates, and even later EGMs, in cases replacing precursor F-

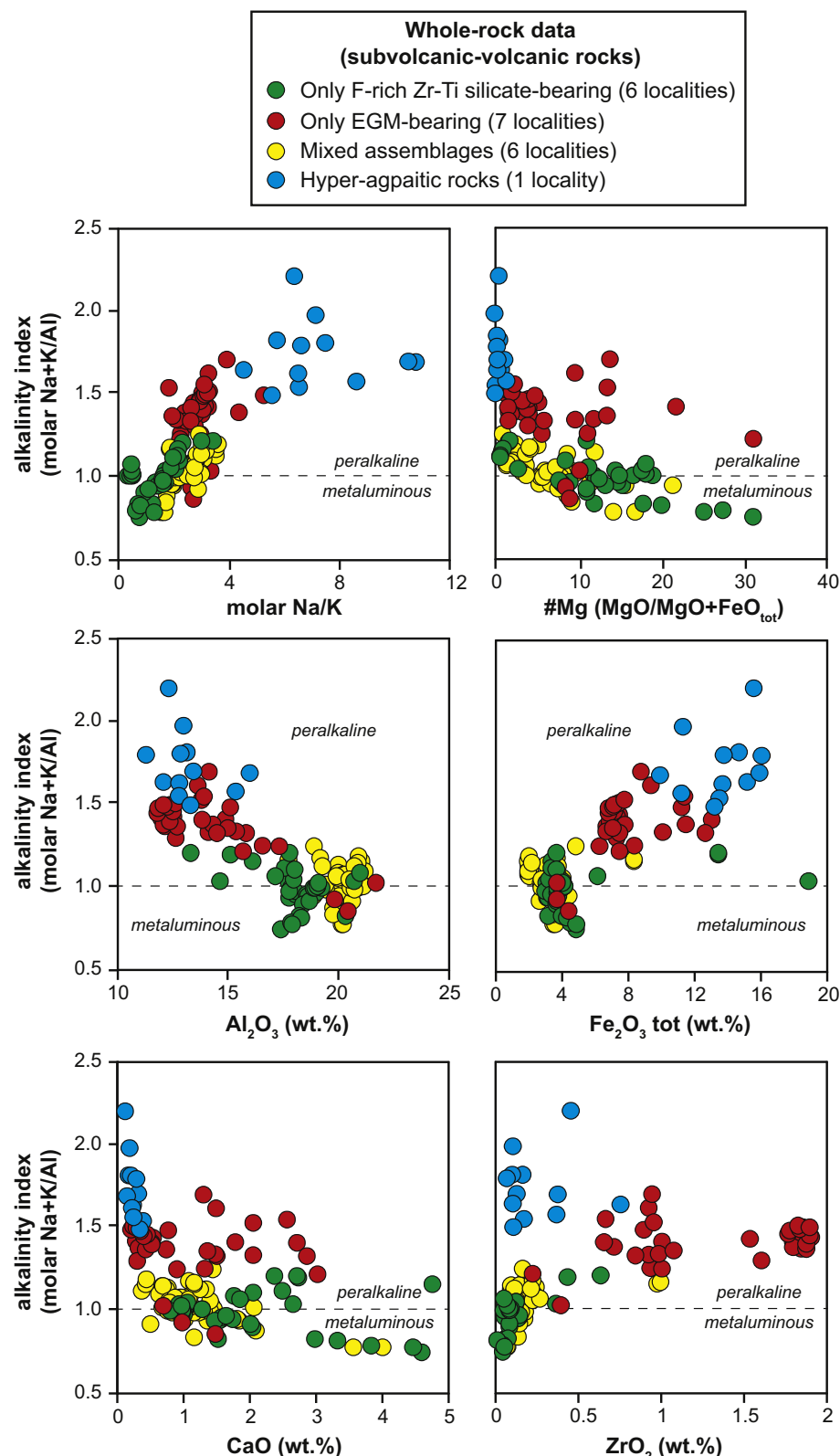


Fig. 8. Whole-rock data for subvolcanic-volcanic rocks containing pure F-rich Zr-Ti silicate assemblages (6 localities), mixed assemblages (6 localities), pure EGM assemblages (7 localities), and hyperagpaitic assemblages (1 locality). Note that only whole-rock data are plotted in this figure to minimize potential cumulate effects as would be expected in plutonic rocks. Data sources are Varet, 1969; Larsen and Steenfelt, 1974; Dobisi, 1987; Oun, 1991; Traversa et al., 1994; Horváth et al., 1998; Arzamastsev et al., 2001; Bailey et al., 2001; Khomyakov et al., 2001; Berger et al., 2009; Sørensen et al., 2011; Melluso et al., 2011, 2014; Petrovsky et al., 2012; Lustrino et al., 2012; Wu et al., 2016; Cucciniello et al., 2016; Spandler and Morris, 2016.

rich Zr-Ti silicates (e.g., Fig. 3a in Lustrino et al., 2012), which is in line with the suggestions of Andersen et al. (2010). Early magmatic sodalite fractionation from Cl-rich magmas continuously increases the F/Cl ratio in the evolving melt (see above). Subsequently, this may stabilize either EGM or fluorite + F-rich Zr-Ti silicate

assemblages, depending on the initial peralkalinity and Ca, Zr, and F contents in the melt. The latter case will further deplete the residual magma in Ca, Zr, and F, and only if peralkalinity remains high enough and Cl and Zr contents still reach the required levels for stabilizing EGM, mixed assemblages will form. Texturally, such

mixed assemblages form during late-magmatic stages and probably resemble small-scale differentiation processes involving locally closed systems on the centimeter to decimeter scale.

6.2. Hydrothermal alteration and (auto)metasomatism

Late-stage (auto)metasomatism and hydrothermal alteration, which are typically quite intense and diverse in peralkaline rocks, produce a wealth of secondary mineral assemblages. Early magmatic olivine-augite-ulvöspinel assemblage may be replaced by katophorite-arfvedsonite $\pm$ aenigmatite $\pm$ aegirine-augite assemblages (see above), and in particular, amphibole may be further transformed to aegirine + biotite or albite $\pm$ epidote $\pm$ ilvaite $\pm$ garnet assemblages (e.g., Schönerberger et al., 2006; Graser and Markl, 2008). Primary nepheline and alkali feldspar can be converted to secondary sodalite $\pm$ albite $\pm$ analcite assemblages (e.g., Finch, 1991; Markl et al., 2001), cancrinite ((Na,Ca, $\square$)₈(Al₆Si₆)O₂₄(CO₃,SO₄)₂ * 2 H₂O) may replace primary sodalite or nepheline (e.g., Schilling et al., 2009; Dumanska-Slowik et al., 2016), and late-stage assemblages involving albite and a range of zeolites (e.g., natrolite and analcite) are commonly observed (e.g., Schilling et al., 2011b; Weisenberger et al., 2014). These assemblages place important constraints on the composition of the acting fluids and on T, f_{O_2} , a_{SiO_2} , and a_{H_2O} during these late-stage processes.

Subsolidus hydrothermal-deuteric alteration of EGMs and other primary Zr–Ti silicates may produce secondary EGMs of distinct composition and a range of other secondary Zr silicates, which are Na rich (e.g., catapleiite) or Ca rich (e.g., gittinsite), and even zircon (which is indeed typical for miaskitic rocks) may form (e.g., Salvi and Williams-Jones, 1995; Mitchell and Liferovich, 2006; Graser and Markl, 2008; Schilling et al., 2009; Andersen et al., 2010; Borst et al., 2016). The exact type of secondary assemblages depends on the composition and the pH of hydrothermal fluids, which may be locally distinct, including Na-, Cl-, and F-rich or Ca- and Sr-rich compositions (e.g., Salvi et al., 2000; Markl and Baumgartner, 2002; Graser et al., 2008; Borst et al., 2016). The solubility of EGMs in various agents is currently investigated for ore-processing purposes, and recent studies have shown that EGMs are relatively easily dissolved in weak acids (e.g., Zakharov et al., 2011). In addition, assemblages involving various Be silicates are common in some late-stage agpaite rocks (Engell et al., 1971; Markl, 2001b).

6.3. Agpaite-like assemblages in peralkaline granites, nephelinites, melilitolites, and potassic-ultrapotassic rocks

About 10 localities are known where EGM-bearing SiO₂-oversaturated rocks occur, and except for one of them (Pajarito Mountain, New Mexico, USA), they represent pegmatites or dyke rocks that are mostly intruding otherwise miaskitic granite and syenite bodies (Table 2). Although the original definition of agpaite rocks was restricted to peralkaline syenitic rocks (e.g., Sørensen, 1997), the case has been changed so that such occurrences are included in the agpaite rock group (Marks et al., 2011). A recent study on such granites from Madagascar (Estrade et al., 2014a) implied considerable crustal contamination during their genesis and very reduced conditions (low f_{O_2}) for their formation, which is very similar to typical SiO₂-undersaturated agpaite rocks (orange field 12 in Fig. 6b).

High a_{H_2O} in a peralkaline magma may stabilize catapleiite- or elpidite-bearing assemblages in favor of zircon or EGM (e.g., Andersen et al., 2010; Marks et al., 2011). Such assemblages are typically observed in peralkaline granites but are only rarely studied in sufficient detail (e.g., Ferguson, 1964; Raade and Mladeck, 1983). The Strange Lake granite (Canada) represents a well-studied example where catapleiite was interpreted as a magmatic phase along with elpidite, post-dating the early magmatic crystallization of zircon, vlasovite, and the rare K–Zr silicate dalyite (Birkett et al., 1992). Secondary phases in

these assemblages include Ca-rich but F-free Zr silicates such as armstrongite and gittinsite (Salvi and Williams-Jones, 1995).

Dalyite occurs in several other quartz-bearing rocks, e.g., in the Amis Complex in Namibia (Schmitt et al., 2000), and Ascension (Portugal) and Straumsvola (Antarctica) represent two localities where dalyite is associated with EGMs. In SiO₂-undersaturated rocks with potassic affinity, wadeite may be present instead (e.g., Saima, Khibina, Gordon Butte; Marks et al., 2011) and has been described as a groundmass phase in some of the K-rich lavas from the Leucite Hills (USA; Barton and van Bergen, 1981). In the globally unique case of the Murun complex (Russia), ultrapotassic rocks comprise EGM–wadeite–dalyite–kalsilite assemblages among many other exceptional rock types (Mitchell and Vladyskin, 1996). Kalsilite-bearing plutonic rocks are very scarce (see the recent review of Bea et al., 2014), and only two examples that contain additional EGMs are known, namely the Murun complex (see above) and the rischorrites of the Khibina complex (e.g., Ageeva et al., 2012).

Rare peralkaline nephelinites from the Nyiragongo and Oldoinyo Lengai volcanoes of the East African rift (partly with potassic affinities) and melilitolites from Italy and elsewhere may contain agpaite-like mineral assemblages, including halogen-rich Na–Ca–HFSE minerals (götzenite) and a number of HFSE-free Na–Ca minerals that are either halogen bearing (zirconian cuspidine, delhayelite, and umbrianite) or halogen free (combeite), along with very rare Ba and Ba–Ti silicates (e.g., Andersen et al., 2012a, 2014; Stoppa et al., 1997; Sharygin et al., 2013; Stoppa and Schiazza, 2014 and references therein). Some of these rocks contain volcanic glass with an extreme alkalinity index of up to 18 (Dawson, 1998; Dawson and Hill, 1998; Mitchell, 2009; Andersen et al., 2014).

Apparently, a mineralogical continuum is present between “classic” sodic agpaite rocks (nepheline or quartz + EGM), sodic–potassic peralkaline rocks (assemblages consisting of nepheline or quartz $\pm$ kalsilite $\pm$ EGM $\pm$ K–HFSE silicates), and potassic–ultrapotassic rocks (kalsilite $\pm$ EGM $\pm$ K–HFSE silicates), with the number of known examples drastically decreasing in this order. However, this does not necessarily imply that these different varieties are interconnected with each other by a single or a common process. Potassium-rich agpaite-like assemblages seem to be more common in peralkaline SiO₂-oversaturated systems than in SiO₂-undersaturated systems, which suggests that peralkaline granites may reach higher a_{K_2O} than nepheline syenites because of crustal contamination. However, not all EGM-bearing granites contain additional K-rich Zr silicates, and for example, the SiO₂-undersaturated wadeite-bearing assemblages in the Saima rocks lack any signs of significant crustal input (Wu et al., 2016). Therefore, high a_{K_2O} and/or high K/Na ratios in peralkaline magmas are not related to crustal contamination alone.

In general, the origin of potassic and ultrapotassic rocks is related to low-degree partial melting of metasomatized phlogopite- and/or amphibole(K-richertite)-bearing mantle sources (e.g., Foley, 1992). Such rocks probably evolve in more oxidized conditions than sodic rocks (e.g., Markl et al., 2010 and references therein), which may play a role in their capacity to enrich HFSE to levels allowing the crystallization of K–HFSE minerals. Hence, variations in Na/K ratio, a_{SiO_2} , a_{H_2O} , a_{K_2O} , and f_{O_2} may explain this mineralogical variety. These parameters are largely governed by source composition, degree of partial melting, crustal contamination, and late-magmatic to hydrothermal metasomatism, with the relative importance of the various (partly interconnected) factors being different for each single occurrence.

7. Economic significance of agpaite rocks

Peralkaline rocks and especially their agpaite varieties are typically enriched in HFSEs (such as Zr, Hf, Nb, Ta, U); REEs; and otherwise relatively rare elements, such as Li, Be, Sn, Ga, and Zn (see above). Their potential economic importance has long been known (e.g., Sørensen, 1992), and some occurrences have a prospection history

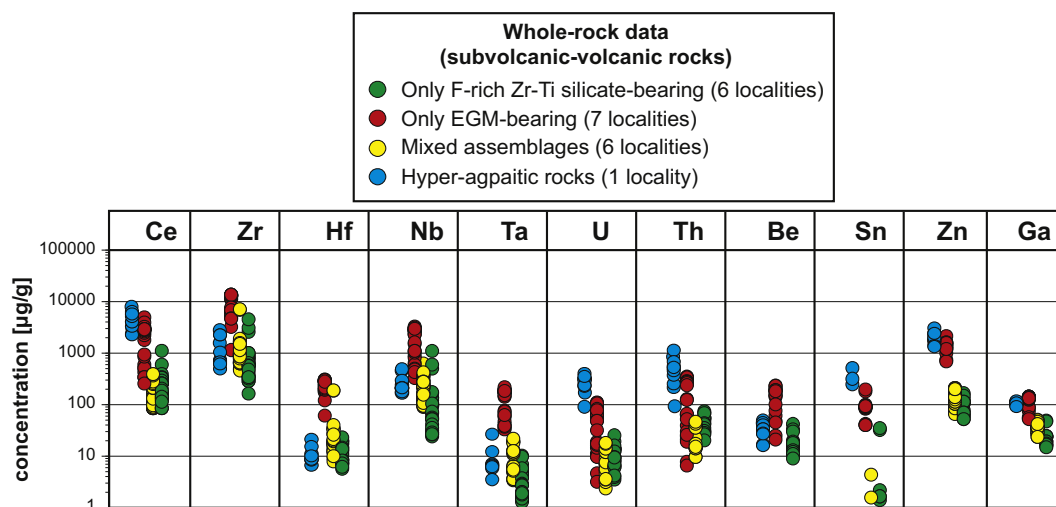


Fig. 9. Same whole-rock data as in Fig. 8 showing a range of economically interesting elements in rocks containing pure F-rich Zr–Ti silicate assemblages (6 localities), mixed assemblages (6 localities), pure EGM assemblages (7 localities), and hyperagpaitic assemblages (1 locality).

dating back to the 50s to 80s of the 20th century (e.g., Ilímaussaq, Red Wine, Letitita Lake, Strange Lake) and even earlier (Khibina and Lovozero). The demand for HFSE and REE rapidly increased over the last decades because of their broad application in high-tech products (e.g., Chakhmouradian and Wall, 2012; Weng et al., 2015). This caused a boost in exploration activities and scientific research related to peralkaline rocks. As a result, several HFSE and REE deposits were further developed (e.g., Dora Bay, Windy and Middle Fork, Pajarito Mountain, Wind Mountain), and some of them reached very advanced stages (e.g., Kvanefjeld and Kringlerne in Ilímaussaq, Strange Lake and Thor Lake/Nechalacho in Canada, Toongi in Australia, and Norra Kärr in Sweden), as is reviewed in numerous recent publications (e.g., Orris and Grauch, 2002; Verplanck et al., 2010; Weng et al., 2015; Smith et al., 2016; Goodenough et al., 2016). To date, only two agpaitic complexes in Russia are actively mined: Khibina for nepheline, apatite, and titanite and Lovozero for loparite ((Na,REE,Ca,Sr,Th)(Ti,Nb,Ta)O₃); Kalashnikov et al., 2016). Depending on the evolution of the volatile HFSE and REE market, some of the above-mentioned advanced projects may eventually go into production. As the market for these elements is comparatively small, any substantial additional REE or HFSE mine will have a substantial impact on the world-production of these elements, thereby potentially influencing the economic and political situation not only in the country of production but also worldwide.

The ore minerals in agpaitic (e.g., EGMs) and hyperagpaitic (e.g., steenstrupine-(Ce)) rocks are potentially of high economic interest as they partly show elevated heavy REEs, which are at present considerably more valuable than the light REEs (e.g., Paulick and Machacek, 2017). A further major advantage of HFSE/REE deposits in agpaitic rocks is their large potential for a number of valuable by-products. This is because of their prolonged differentiation history during generally reduced conditions (see above, Fig. 6) allowing for the enrichment of not only REE and HFSE but also Be, Sn, Zn, Ga, and others, especially in agpaitic rocks devoid of F-rich Zr silicates (Fig. 9). Some late-stage veins associated with agpaitic rocks in Ilímaussaq contain substantial amounts of various Na-Be-(Sn)-silicates, such as chkalovite, tugtupite, sørensenite, and epididymite (e.g., Engell et al., 1971; Markl, 2001b). In fact, the world-class Kvanefjeld deposit (Ilímaussaq) is a multi-commodity REE project that is also expected to produce U and Zn as U contents in steenstrupine-(Ce) (the ore mineral) are at the wt% level and sphalerite (ZnS) is a common accessory in the partly hyperagpaitic rocks to be exploited there. Further possibilities for recovering other elements such as F, Ga, Ge, Li, and Sc from these rocks are currently being tested (J. Mair, pers. comm. 2017). Similarly, the

Kringlerne project (Ilímaussaq) is anticipated to produce Zr, Hf, Nb, and Ta besides REEs as these elements are enriched in EGM.

Although the compositional complexity of EGM and steenstrupine-(Ce) may be beneficial for the economic viability of the relevant HFSE/REE projects, this poses some challenges as well: Compared to the classical REE ore minerals (e.g., bastnäsite, xenotime, and monazite), EGM and steenstrupine-(Ce) are compositionally rather complex and their economically viable processing is a problem that is yet to be solved by the mining/beneficiation industry. Further, because of the typically complex late-magmatic and hydrothermal evolution of agpaitic rocks, diverse secondary phase assemblages may develop from the primary ores (Section 6). This causes additional challenges for processing the ores, potentially complicating the mining operations with a likely impact on the operating efficiency of such deposits. Currently, extraction and beneficiation methods for REE-bearing silicate minerals are being intensively tested (e.g., Zakharov et al., 2011; Davris et al., 2017; Stark et al., 2017; Voßenkaul et al., 2017), and depending on their feasibility and potential for up-scaling to industrial processes, it remains to be awaited if, how, and when ores from agpaitic and hyperagpaitic rocks will be of importance for the global HFSE and REE market.

8. Synthesis

Peralkaline igneous rocks are geochemically and mineralogically diverse. Source composition, parental magma compositions, crustal contamination, and redox conditions during their early-magmatic stages govern their petrological evolution and exert a major control on their late-magmatic to hydrothermal compositional evolution. Compared to the more common miaskitic varieties, rare agpaitic rocks can only form if special requirements are fulfilled. The most important of them are reduced crystallization conditions (low f_{O_2}) and relatively dry magmas (low a_{H_2O}), which enables subsequent Fe enrichment, increase in peralkalinity, retention of halogens, and extreme enrichment of HFSEs in the evolving magmas, all of which are interconnected to each other (Section 4). Importantly, agpaitic rocks are themselves diverse, and there is a mineralogical continuum between F-rich Zr–Ti silicate assemblages that occur in metaluminous rocks and EGM-sodalite assemblages, being mostly restricted to extremely evolved and Fe-rich rocks with a peralkalinity index of ≥ 1.2 (Section 6). For the latter type, only reduced crystallization conditions during early magmatic stages seem to allow their formation, which is further evidenced by generally CH₄-dominated magmatic fluids in such rocks (Section 5).

Further, similar mineral assemblages occur in some peralkaline granites, nephelinites, melilitolites, and potassic-ultrapotassic rocks.

8.1. Formation of early-magmatic, late-magmatic, and hydrothermal agpaaitic assemblages

Texturally, agpaaitic mineral assemblages may form during orthomagmatic, late-magmatic, and hydrothermal stages (Section 2.5; Table 2). Thus, the conditions necessary for stabilizing agpaaitic minerals may be reached during different evolutionary stages of a given peralkaline magmatic system, and different magmatic and hydrothermal processes may result in very similar agpaaitic mineral assemblages. Orthomagmatic EGM-sodalite assemblages clearly point to extremely HFSE-, Na-, and halogen-rich magma compositions. Such unusual magma compositions must be assumed for about 25 of the listed localities in Table 2—as a primary feature of their parental magmas (ultimately related to their source composition or to extremely low degrees of melting) and/or because of extensive differentiation prior to their emplacement. Interstitial agpaaitic assemblages formed during late magmatic to pegmatitic stages are more common and suggest that the required enrichment levels of the above-mentioned constituents can be reached by most melts only during their final differentiation stages, maybe even involving locally closed systems on the centimeter scale. Hydrothermal agpaaitic assemblages as veins and fracture fillings indicate HFSE transport at low temperatures by aqueous salt brines rather than being crystallized from extremely HFSE-, Na-, and halogen-rich melts. Explanations involve late-stage alteration processes in environments with changing pH and f_{O_2} , which may influence the HFSE transport capacity of the acting fluids (e.g., Salvi et al., 2000; Salvi and Williams-Jones, 2006; Vasyukova et al., 2016). Experimental data provide evidence that the capacity for HFSE transport of fluids increases largely with salinity and fluorine concentration (e.g., Van Baalen, 1993; Migdisov et al., 2009, 2011; Williams-Jones et al., 2012; Timofeev et al., 2015).

Potential precipitation mechanisms for hydrothermal agpaaitic minerals have been discussed by Salvi and Williams-Jones (2006), where precipitation of HFSE from Ca-poor and F-bearing high-salinity fluids occurred because of interaction (mixing) with Ca-rich meteoric fluids. This caused fluorite precipitation, thereby decreasing the activity of fluorine and destabilizing HFSE-fluoride complexes, in consequence causing HFSE precipitation. Similarly, the pseudomorphic replacement of EGM in agpaaitic rocks from Ilímaussaq suggests that the mobilization of Zr, Nb, and REEs during these hydrothermal processes is limited (e.g., Borst et al., 2016). This was interpreted to be because of the relatively high pH of late-stage fluids, which caused the precipitation of fluorite and various other F-bearing phases, diminishing HFSE mobility. Similar models may be applicable to other hydrothermal EGM-assemblages associated with fluorite (e.g., Tamazeght) and offer general ideas on the parameters to be considered when trying to explain such mineral associations—a research field, which clearly deserves more detailed studies.

8.2. Retention of volatiles in agpaaitic volcanic rocks: a conundrum

Subvolcanic to volcanic agpaaitic rocks raise general questions on mechanisms that prevent degassing of halogens necessary to stabilize agpaaitic assemblages. The textural appearance of EGM and F-rich Zr–Ti silicates in such rocks (group 2 in Table 2) is as diverse as in plutonic rocks (group 1 in Table 2) and may contain EGM as (micro)phenocrysts, as interstitial groundmass phases, as globules possibly related to liquid-liquid immiscibility, as minerals in late-stage miarolitic cavities, and as very late coatings along clefts. Probably, the early magmatic stabilization of sodalite and/or fluorite is critical for retaining sufficient halogens in the magma and allow for the subsequent formation of agpaaitic assemblages in volcanic rocks (e.g., Marshall et al., 1998; Wang et al., 2014; Giehl et al., 2014; see above). However, many of these

occurrences have only been roughly described in the literature and are not studied in appropriate detail to develop models for the origin of EGM-bearing assemblages in volcanic rocks. A thorough petrological investigation of such examples considering modern views for fluid-melt partitioning of volatiles and halogens, fluid-immiscibility, and degassing processes of magmas (e.g., Lowenstern, 1994; Larsen and Gardner, 2004; Stelling et al., 2008; Balcone-Boissard et al., 2010; Neave et al., 2012) is needed.

8.3. Toward a new definition and nomenclature of agpaaitic rocks

Agpaaitic rocks were initially defined as rocks having a whole-rock composition of $(Na + K)/Al \geq 1.2$ (Ussing, 1912). This purely geochemical definition was later abandoned and instead mineralogical criteria were applied to define agpaaitic rocks (Sørensen, 1974). To date, the terms “agpaite” and “agpaaitic” are defined as being “restricted to peralkaline nepheline syenites characterised by complex Zr and Ti minerals, such as eudialyte and mosandrite, rather than simple minerals such as zircon and ilmenite” (Le Maitre, 2003). The term “miaskite” is defined as “a leucocratic variety of biotite nepheline monzosyenite with oligoclase and perthitic oligoclase,” while “miaskitic” is as “a general term for nepheline syenites in which the molecular ratio of $Na_2O + K_2O / Al_2O_3 < 1$ ” (Le Maitre, 2003). In practice, this often causes confusion, and these terms are frequently used in a much wider sense. We consider these definitions as not appropriate because (i) taken together, they do not cover all types of nepheline syenites, and according to definition, titanite- or zircon-bearing peralkaline nepheline syenites (which are not uncommon) do not belong to either of these two groups; (ii) complex Ti–Zr minerals such as eudialyte and mosandrite occur in metaluminous and peralkaline plutonic, subvolcanic, and volcanic rocks; (iii) some quartz-syenites and granites contain EGM-bearing assemblages; and (iv) very similar mineral assemblages (although lacking EGMs or mosandrite) are excluded from this definition.

We suggest that the terms “agpaite” and “miaskite” as rock names should be abandoned, while the terms “agpaaitic” and “miaskitic” should not be restricted to peralkaline and metaluminous nepheline syenites but should be used as descriptive terms to distinguish igneous rocks according to their primary magmatic HFSE mineralogy irrespective of their whole-rock composition (Tables 1 & 3): Igneous rocks (c.f. plutonic, volcanic, SiO_2 -oversaturated, SiO_2 -undersaturated, peraluminous, metaluminous, and peralkaline variants) should be characterized as **miaskitic** when containing zircon/baddeleyite and titanite/perovskite as major primary HFSE carriers and as **agpaaitic** if the major primary magmatic HFSE carriers are complex Na–Ca–HFSE minerals (minerals of the eudialyte, rinkite, and wöhlerite groups and aenigmatite, astrophyllite, catapleite, dalyite, elpidite, hilairite, lamprophyllite, lorenzenite, lovozerite, parakeldyshite, vlasovite, and wadeite; Table 1) instead. Note that by applying this definition, the presence of the volatile-bearing but HFSE-free Na–Ca silicates delhayelite, umbrianite, and combeite described from some nephelinites and melilitites (see above) would be not sufficient to characterize a rock as agpaaitic, although some of them indicate highly peralkaline conditions (see details in Andersen et al., 2012a, 2012b, 2014). Igneous rocks should be termed as **transitional agpaaitic** if they contain HFSEs that are typical of agpaaitic and miaskitic rocks (e.g., titanite and eudialyte). Accordingly, Khomyakov’s classes “low agpaaitic” and “medium agpaaitic” must be abandoned as they resemble “transitional agpaaitic” and “miaskitic” rocks, respectively (Table 3). In **hyperagpaaitic** rocks, minerals such as ussingite, naujakasite, and steensrupine-(Ce); members of the lovozerite and lomonosovite groups; and other partly water-soluble minerals (e.g., villiaumite and natrosilite) form a part of magmatic mineral assemblages (Table 3).

This leaves us with the task of characterizing agpaaitic rocks (Khomyakov’s “highly agpaaitic” group). The mineral list used by Khomyakov (1995) to define his “highly agpaaitic” group is certainly not appropriate because (i) it includes some HFSE-free minerals that are

clearly not restricted to agpaite rocks (Table 3; e.g., Li-arfvedsonite, analcime), (ii) this scheme is restricted to nepheline syenites, although very similar mineral assemblages occur in other rock types (see above); and (iii) very similar mineral assemblages in some nepheline syenites containing minerals of the rinkite group and others (Table 1) are not covered in this scheme. Therefore, the often-applied classification scheme of Khomyakov (1995) should not be used anymore. Instead, we suggest a descriptive way for fully characterizing agpaite rocks on the basis of the following aspects:

1. The evolutionary stage during which agpaite mineral assemblages are formed must be taken into account, and we suggest that only (early and late) magmatic mineral assemblages should be considered when characterizing an igneous rock as agpaite or miaskitic. In other words, miaskitic rocks that contain agpaite minerals only in hydrothermal veins or as cleft fillings should not be called agpaite.
2. The HFSE assemblage in a given rock should be categorized according to its **volatile content** as Cl-rich (e.g., EGM), F-rich (e.g., minerals of the rinkite- and wöhlerite groups), H₂O-rich (e.g., catapleiite, hilarite, elpidite), or anhydrous (e.g., dalyite, wadeite, parakeldyshite) assemblages (and combinations thereof) can be distinguished. Further, the **alkali-alkali earth proportions** of the HFSEs are suitable for distinguishing Ca-Na- (e.g., wöhlerite- and rinkite-group minerals), Na-Ca (e.g., EGM $\pm$ wöhlerite and rinkite group minerals), pure Na (e.g., catapleiite $\pm$ elpidite), Na-K (e.g., EGM + dalyite), and K (e.g., dalyite $\pm$ wadeite) assemblages. Finally, the **Ti-Zr proportions** in agpaite assemblages need to be considered. Most common are Zr-dominated assemblages (e.g., EGM) and mixed (e.g., aenigmatite-EGM) assemblages, while Ti-dominated (e.g., götzenite) assemblages in agpaite rocks are comparatively rare. Most Ti and Zr silicates (e.g., aenigmatite or EGMs) typically contain considerable amounts of Nb and REE, which prevents the melts from reaching concentrations that are sufficiently high to stabilize Nb or REE endmember phases at magmatic stages.
3. Closed system evolution and subsequent metasomatism in both metaluminous and peralkaline rocks may produce sequences of HFSE assemblages that belong to different groups of the classification suggested above (Table 3). A given magma that crystallizes early magmatic miaskitic assemblages can later precipitate (various types of) agpaite assemblages and may subsequently experience hydrothermal alteration, resulting in secondary miaskitic assemblages again (e.g., Mitchell and Liferovich, 2006). Therefore, a strict categorization of such rocks into a specific number of subgroups is simply not appropriate. Rather, careful textural studies distinguishing early-magmatic, late-magmatic, and hydrothermal mineral assemblages are the only way to understand petrologically complex processes at work during the evolution of such rocks, as exemplified by several recent studies (e.g., Salvi et al., 1995; Andersen et al., 2010; Wu et al., 2015; Borst et al., 2016).

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Appendix A. Supplementary data

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