1 Crystallisation and destabilisation of eudialyte-group minerals in
2 peralkaline granite and pegmatite: a case study from the
3 Ambohimirahavavy complex, Madagascar.

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11

Abstract:

Eudialyte-group minerals (EGM) are very common in highly evolved SiO₂-undersaturated syenites and are characteristic minerals of agpaitic rocks. Conversely, they are extremely rare in peralkaline granites, with only a handful of EGM occurrences reported worldwide. Here, we study two new examples of EGM occurrence in two types of peralkaline pegmatitic granites from the Cenozoic Ambohimirahavavy complex, and assess the magmatic conditions required to crystallise EGM in peralkaline SiO₂-oversaturated rocks. In the transitional granite (contains EGM as accessory minerals) EGM occur as late phases and are the only agpaitic and major REE-bearing minerals. In the agpaitic granite (contains EGM as rock-forming minerals) EGM are early-magmatic phases occurring together with two other agpaitic minerals, nacareniobsite-(Ce), and turkestanite. In these granites, EGM are partly to completely altered and replaced by secondary assemblages consisting of zircon and quartz in the transitional granite and an unidentified Ca-Na zirconsilicate in the agpaitic granite. Ambohimirahavavy EGM, as well as those from other peralkaline granites and pegmatites, are richer in REE and poorer in Ca than EGM in nepheline syenites. We infer that magmatic EGM are rare in SiO₂-oversaturated rocks because of low Cl concentration in these melts. At Ambohimirahavavy, contamination of the parental magma of the agpaitic granite with Ca-rich material increased the solubility of Cl in the melt promoting EGM crystallisation. In both granite types, EGM were destabilised by the late exsolution of a fluid and by interaction with an external Ca-bearing fluid.

Introduction

Eudialyte-group minerals (EGM) are complex Na-Ca-Zr-cyclosilicates with the general formula $\text{Na}_{15}(\text{Ca}, \text{REE})_6(\text{Fe}, \text{Mn})_3\text{Zr}_3\text{Si}(\text{Si}_{25}\text{O}_{72})(\text{O}, \text{OH}, \text{H}_2\text{O})_3(\text{Cl}, \text{OH})_2$ (Johnsen *et al.*, 2003) characteristic of evolved peralkaline [molar $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3 > 1$] SiO₂-undersaturated syenites, also called agpaitic syenites. This mineral is generally considered as diagnostic of agpaicity, i.e., those rocks in which High Field Strength Elements (HFSE, such as Zr, Hf, Nb,

Ta, U and Th) and Rare Earth Elements (REE) are incorporated into complex Na-K-Ca-Zr-silicates, rich in volatiles (Cl, F and H₂O) (Sørensen, 1992, 1997; Khomyakov, 1995; Le Maitre *et al.*, 2002; Marks *et al.*, 2011). By contrast, when HFSE are incorporated in more common minerals (e.g. zircon, titanite), rocks are termed miaskitic. EGM can contain important amounts of REE and are considered as a potentially valuable ore of REE and Zr (e.g., the Kringlerne deposit in the Ilímaussaq complex, the Norra Kärr complex in Sweden and the Kipawa complex in Canada; Goodenough *et al.* (2016) and Saucier *et al.* (2013)). Because EGM crystallize through a range of magmatic to hydrothermal conditions, their compositional variability can be used to monitor the conditions of the environment in which they crystallized (Mitchell and Liferovich, 2006; Schilling *et al.*, 2009; Marks *et al.*, 2015; Ratschbacher *et al.*, 2015). Very commonly, EGM are partly-to-completely replaced by secondary phases, at late magmatic-to-hydrothermal stages (Salvi *et al.*, 2000; Mitchell and Liferovich, 2006; Karup-Møller *et al.*, 2010; Sheard *et al.*, 2012; Karup-Møller and Rose-Hansen, 2013).

Although EGM were initially considered to be characteristic of highly differentiated SiO₂-undersaturated rocks, these minerals have also been reported in a few SiO₂-oversaturated peralkaline rocks. The only known examples, to our knowledge, are: quartz syenite from the Carlingford complex, Ireland (Nockolds, 1950); the Pajarito mountain, Texas (McLemore, 2015); granitic dykes from the Ascension Island in the South Atlantic (Harris *et al.*, 1982); the Straumsvola complex in Antarctica (Harris and Rickard, 1987); the Windy Fork pluton in Alaska (Gunter *et al.*, 1993); pegmatitic granitic dykes from the Ambohimirahavavy complex in Madagascar (Estrade *et al.*, 2014a); the Dara-i-Pioz massif in Tajikistan (Grew *et al.*, 1993); Rockall Island in the North Atlantic (Sabine, 1957). However, in studies of most of these occurrences, EGM are only mentioned as an accessory mineral and are not completely described in terms of texture and composition, although in their recent compilation, Schilling *et al.* (2011) characterized the EGM from the Ascension Island and Straumsvola.

In place of EGM, other magmatic complex Zr-silicates are usually described in peralkaline granites and pegmatites (Table 1). The most commonly reported Zr-minerals include dalyite (K₂ZrSi₆O₁₅), wadeite (K₂ZrSi₃O₉), elpidite (Na₂ZrSi₆O₁₅·3H₂O), catapleiite (Na₂ZrSi₃O₉·2H₂O)

and, more rarely, gittinsite ($\text{CaZrSi}_2\text{O}_7$) and armstrongite ($\text{CaZrSi}_6\text{O}_{15} \cdot 2\text{H}_2\text{O}$). It is noteworthy that, among these six minerals, none contain Cl or F while three contain H_2O (elpidite, catapleiite and armstrongite). Several Zr-minerals are usually reported in the same peralkaline rocks and their complex textural relationships have often led to multiple interpretations (e.g. Strange Lake, Birkett et al., 1992; Roelofsen and Veblen, 1999). Moreover, in many cases, post-magmatic processes have destabilised the primary assemblages, greatly complicating identification of the original magmatic mineralogy.

The main factors controlling the stability of EGM in a melt are its peralkalinity and high HFSE (mainly Zr) and volatile contents (mainly Cl, F and H_2O) (Sørensen, 1997). These conditions are usually found in highly-evolved undersaturated melts derived from the differentiation of magmas under low oxygen fugacity (Markl et al., 2010). Conversely, the problem of scarcity of EGM in peralkaline granites has not been discussed so far in the literature.

This study focuses on the occurrence of EGM in peralkaline granitic pegmatites in the Ambohimirahavavy alkaline complex, northwest Madagascar. On the basis of textural and compositional data for EGM, other agpaitic minerals, clinopyroxene and amphibole, we assess the magmatic conditions required for the stability of EGM in peralkaline SiO_2 -oversaturated rocks and compare them to their undersaturated counterpart.

Geological setting and petrography

The Ambohimirahavavy alkaline complex (24.2 ± 0.6 Ma for nepheline syenite and 23.5 ± 6.8 for peralkaline granite; in situ U-Pb dating of zircon, Estrade et al., 2014b) is part of the Cenozoic alkaline province located in the north-western part of Madagascar, in the Ampasindava peninsula. The complex consists of silica-under- and -oversaturated syenites and granites as well as volcanic units of alkaline affinity, including basalt, phonolite, trachyte, and rhyolitic obsidian (Fig. 1). A network of granitic and pegmatitic dykes intruded the Isalo sedimentary units along the external flank of the south syenitic ring-dyke. The dykes are characterized by an alkaline mineralogy (i.e. contain sodic clinopyroxene and sodic amphibole)

and by the presence of minerals rich in HFSE and REE. Their local intrusion in limestone resulted in the formation of a REE-rich skarn (Estrade *et al.*, 2015).

This complex is currently under exploration by Tantalus Rare Earth AG, which focuses on the ion-adsorption REE mineralization in clays associated with laterites. The company has also evaluated the economic potential of the bedrock, as most of the HFSE and REE occur as primary mineralization in peralkaline granite and pegmatite dykes. In a previous study, we distinguished three types of dykes according to their textures and major mineralogy (Estrade *et al.*, 2014a):

(1) A coarse-grained granitic type (GR-I), characterized by an allotriomorphic granular texture, composed of quartz, perthitic alkali feldspar, Na-amphibole and Na-clinopyroxene. The main HFSE-bearing minerals form a miaskitic assemblage consisting of zircon, pyrochlore-group minerals, monazite-(Ce) and chevkinite-(Ce).

(2) A pegmatitic granitic type (GR-II), consisting of quartz, perthitic alkali feldspar, Na-clinopyroxene, Na-amphibole, and containing a agpaitic to miaskitic accessory assemblage consisting of EGM, mostly altered to a secondary miaskitic assemblage, dominated by zircon and quartz (Fig. 2a-b-c). This rock is termed transitional because of this feature and because EGM only occur as accessory minerals.

(3) A pegmatitic agpaitic granitic type (GR-III) which consists of K-feldspar, albite, Na-clinopyroxene, Na-amphibole and quartz, plus EGM as rock-forming minerals (Fig. 2d-e). Other agpaitic minerals include nacareniobsite-(Ce) $(\text{Na}_3\text{Ca}_3(\text{Ce},\text{La})(\text{Nb},\text{Ti})(\text{Si}_2\text{O}_7)_2\text{OF}_3)$ and turkestanite $(\text{Th}(\text{Ca},\text{Na})_2 \text{K}_{1-x}\square_x (\text{Si}_8\text{O}_{20}) \cdot n\text{H}_2\text{O})$.

In the following sections, we describe in detail the EGM and the complex mineralogy of both the pegmatitic transitional (GR-II) and the pegmatitic agpaitic (GR-III) dykes. These dykes form a more-or-less continuous belt around the ring-dyke of syenite. They vary in thickness from a few centimetres to a few meters. Although no relationships have been observed between GR-II and GR-III dykes, their similar mode of emplacement suggests a contemporaneous origin. GR-II dykes are far more common in the complex than GR-III, which have been only found in

boreholes. However, Lacroix (1915, 1923) and Ganzeev and Grechishchev (2003) have described similar rocks to GR-III dykes containing more than 40% of EGM, suggesting that they outcrop somewhere in the flank of the complex.

Analytical Methods

The mineralogy and textural relationships were investigated using optical microscopy and back-scattered electron (BSE) imaging using a JEOL JSM 6360LV scanning electron microscope (SEM) equipped with a silicon drift detector analysis system. The instrument was also used to obtain energy dispersive X-ray phase maps.

Major and minor element concentrations in minerals were determined using a Cameca-SX-50 electron probe microanalyser (EPMA) with SAMx automation, at the Géosciences Environment Toulouse (GET) laboratory at the University of Toulouse. Operating conditions were an accelerating voltage of 15kV and a beam current of 20nA. Standardization was obtained using, periclase (Mg), wollastonite (Ca and Si), corundum (Al), pyrophanite (Mn and Ti), hematite (Fe), barite (Ba), albite (Na), sanidine (K), zircon (Hf and Zr), graftonite (P), UO₂ (U), ThO₂ (Th), Pb₂ P₂O₇ (Pb), sphalerite (Zn), orthophosphate for REE and yttrium, Nb metal (Nb), Ta metal (Ta), topaz (F) and tugtupite (Cl).

In-situ trace element concentrations were determined by laser ablation inductively coupled plasma mass-spectrometry (LA-ICP-MS) at the University of Montpellier. The instrument used for analysis was a Geolas Q excimer CompEx 102 laser ablation system coupled to a ThermoFinnigan Element XR ICP-MS. We used a beam diameter of 60 µm for all analyses, which allowed a high detection threshold even for very low-level trace elements. For each analysis, the signal was recorded for 180 s, consisting of 60 s of background measurement followed by 120 s of ablation. To calibrate the instrument, we used NIST SRM 610 glass as external standard and NIST SRM 612 as a secondary standard. SiO₂ was used as internal standard for the correction of different ablation rates between sample and standard. Silica concentration had been previously determined by EPMA in the ablation area. Data processing

was carried out with the SILLIS software (Guillong *et al.*, 2008). Typical concentration uncertainties are ± 5 % for concentrations >10 $\mu\text{g/g}$ and ± 10 % for concentration <10 $\mu\text{g/g}$.

Mineral textures and alteration

Eudialyte-group minerals

In GR-II, EGM are accessory minerals ($<1\%$) occurring as interstitial late-formed magmatic phases surrounded by Na-clinopyroxene, Na-amphibole, perthitic alkali feldspars and quartz (Fig. 3a-b). In most samples, EGM underwent partial-to-complete alteration and have been replaced by a complex assemblage of secondary minerals, among which zircon and quartz have been identified as the main replacing phases (Estrade *et al.*, 2014a). Although most of the EGM grains are altered, rare, entirely unaffected grains may occur adjacent to altered ones. The latter crystals lack oscillatory growth or sector zoning usually observed in EGM from other alkaline complexes, although high-contrast BSE images show common small bright phases and dark grey patches, scattered along fractures.

In GR-III, EGM are rock-forming minerals (>10 vol.%) occurring as euhedral, early magmatic crystals together with Na-clinopyroxene, Na-amphibole, nacareniobsite-(Ce), turkestanite, grains of albite and K-feldspar and quartz (Fig. 3c-d). Except from quartz, all these minerals occur as individual grains and as inclusions in cores of the EGM, as well as along concentric layers that follow growth zones. Quartz mainly occurs as late anhedral crystals and as layers flanked by euhedral eudialyte. Unlike in GR-II, most of the EGM are pristine; locally-altered EGM grains occur in narrow bands, together with calcite, altered nacareniobsite-(Ce) and turkestanite. All other silicates were not altered.

Other agpaitic minerals

In addition to EGM, the agpaitic minerals nacareniobsite-(Ce) and turkestanite occur in significant modal amounts (1-2 vol.%) in GR-III, whereas EGM are the only agpaitic minerals in GR-II. Nacareniobsite-(Ce), is also a mineral typical of agpaitic SiO_2 -undersaturated rocks, but has been only rarely described in SiO_2 -saturated rocks (Vilalva *et al.*, 2013). In GR-III, it

occurs as early magmatic elongated euhedral crystals, which enclose small chadacrysts of albite, K-feldspar, Na-clinopyroxene and Na-amphibole (Fig. 4a-b). In altered portions of GR-III, nacareniobsite-(Ce) is replaced by a complex assemblage of secondary Ca-rich minerals including calcite and titanite. Turkestanite is an extremely rare mineral that has been reported in only four other alkaline complexes (Pautov *et al.*, 1997; Kabalov *et al.*, 1998; Vilalva and Vlach, 2010). In GR-III, it is an early magmatic phase occurring as diamond-shaped euhedral crystals that enclose small chadacrysts of albite, K-feldspar, Na-clinopyroxene and Na-amphibole (Fig. 4c). In BSE images, these crystals commonly show zoning and alteration textures consisting of a heterogeneous core containing a network of very thin U-rich veinlets, surrounded by a BSE-brighter homogeneous rim (Fig. 4d).

Na-Clinopyroxene and Na-amphibole

Sodic clinopyroxene is the main mafic constituent in GR-II and -III. In GR-II, it forms two main, texturally distinct generations: Na-Clinopyroxene-I (cpx-I) is relatively uncommon and forms large euhedral phenocrysts (up to 1 mm across), locally showing distinct cores and rims; Na-clinopyroxene-II (cpx-II) is more abundant and occurs as homogeneous small grains or thin acicular crystals. In GR-III, Na-clinopyroxene occurs as small euhedral crystals and as chadacryst in EGM, nacareniobsite-(Ce) and turkestanite.

Sodic amphibole is the second main mafic constituent after Na-clinopyroxene. In GR-II, its habit varies considerably and, depending on its location in the dyke, can form large euhedral pegmatitic crystals of up to 20 cm or small anhedral grains. In GR-III, Na-amphibole occurs only as small euhedral crystals.

Mineral composition

Eudialyte-group minerals

Representative compositions of EGM are shown in Table 2. Structural formulae of EGM are based on $\Sigma (\text{Si} + \text{Al} + \text{Zr} + \text{Ti} + \text{Hf} + \text{Nb}) = 29$ a.p.f.u. and were calculated using the Excel spreadsheet of Pfaff *et al.* (2010). EGM from GR-II and GR-III have different compositions,

mainly in Mn, Ca and REE and minor variations in Si, Fe, Na, and Nb. Zirconium and chlorine contents of EGM are similar in both rock types. Binary plots of Fe versus Mn and (La+Ce+Nd+Y) versus Ca expressed as atoms per formula unit are shown in Figure 5, where they are compared with EGM from other peralkaline granites (Straumsvola and Ascension Island) and foid syenites (Ílímaussaq, Mont Saint-Hilaire, Tamazeght, Pilansberg, Kipawa, Khibiny, Lovozero, Saima, Pocos de Caldas, Langesundfjord and Norra Kärr) using the data of Schilling et al. (2011). The Mn content of early-magmatic EGM from GR-III is lower than that of late-magmatic EGM from GR-II and is consistent with data from the other complexes, showing that, in a single intrusive complex, Mn/Fe ratio increases in later-formed EGM (Schilling *et al.*, 2011). Calcium correlates negatively with the sum of the major rare-earth elements La, Ce, Nd and Y; this trend is consistent with their preferential incorporation in the same structural site (M1; Johnsen and Grice, 1999). In addition, most of the EGM from quartz-bearing rocks (GR-II, Straumsvola, and Ascension Island) have lower Ca and higher La+Ce+Nd+Y contents than EGM from foid-bearing rocks. Most EGM from foid-bearing rocks with high La+Ce+Nd+Y content (Mont Saint-Hilaire and Pilansberg) have a post-magmatic origin.

Trace element analyses for EGM, apatitic minerals, clinopyroxene and amphibole are presented in an electronic supplement. Rare-earth elements and trace element distribution patterns of EGM, nacareniobsite-(Ce), turkestanite, clinopyroxene and amphibole are shown in Figure 6. Rare-earth elements and trace elements patterns of EGM are compared with patterns of EGM from other EGM-bearing granites (Straumsvola and Ascension Island) and foid-syenites using the data of Schilling et al. (2011). We only present the patterns from the most REE-rich EGM (from Ílímaussaq and Mont Saint-Hilaire) as EGM from other complexes plot far below the REE distribution patterns of GR-II and GR-III. We also compare the concentrations of the light REE (LREE; La to Sm) and the heavy REE (HREE; Gd to Lu) in EGM from different complexes in Figure 7 using the data of Schilling et al. (2011). Among all EGM, those from quartz bearing-rocks have the highest REE concentrations and are generally enriched by up to four orders of magnitude relative to chondrite (McDonough and Sun, 1995)

(Fig. 6a). Concentrations of the LREE in EGM from quartz bearing-rocks (>40 000ppm) are similar to the most LREE-rich EGM from foid-syenites in Ilímaussaq and Mont Saint-Hilaire, whereas concentrations of the HREE are significantly higher in EGM from GR-II and Ascension Island (Fig. 7). All patterns show a strong negative Eu anomaly which is also a characteristic of the whole-rock REE distribution patterns of the dykes; this is consistent with the model for the origin of the melt in the Ambohimirahavavy complex (Estrade *et al.*, 2014b), i.e., differentiation of an alkali basaltic parental melt by fractionation of plagioclase. Trace-element distribution patterns have similar overall shapes except for U and Pb, which show a negative and positive anomaly, respectively, in GR-II while they show an opposite pattern in GR-III. Such opposed trends are absent in the whole-rock patterns, which show similar concentrations for these two elements.

Alteration paragenesis of EGM

Most of the EGM in GR-II samples are entirely replaced by a secondary paragenesis, ultimately consisting of zircon and quartz. Locally, however, EGM are partly altered and replaced by an assemblage of Zr-Ca-bearing phases and REE-Ca-F-bearing phases with no zircon (Estrade *et al.*, 2014a). In this work, we have identified EGM that show partial replacement by zircon, and we consider this texture as representative of the alteration pattern of EGM in GR-II. An X-ray element map of partially-replaced EGM is shown in Figure 8 and the compositions of the phases present are reported in Table 2. In this Figure, EGM is ultimately replaced by zircon and quartz through an intermediate step consisting of an unidentified Ca-zirconosilicate with higher Ca and Zr and lower Fe and Mn contents than the original EGM. All of Na, Cl, Nb, and most of the REE have been lost. REE-rich and Zr-rich phases co-crystallized with the Ca-zirconosilicate but were not analysed with EPMA due to their very small size. Secondary zircon is characterized by a low ZrO₂ content (57.8 wt. %), a low sum of oxides (91.5 wt. %) and the presence of Fe and Ca. In GR-III, replacement of EGM involved an intermediate phase slightly enriched in Si (Fig. 9a-b). The replacing phase is an unidentified Ca-Na zirconosilicate lacking Cl, REE, Mn, and Fe.

257 *Other agpaitic minerals*

258 Representative compositions of nacareniobsite-(Ce) and turkestanite are given in Table 3. The
259 composition of different grains of nacareniobsite-(Ce) is homogeneous and comparable to that
260 of nacareniobsite-(Ce) published for other complexes (Sokolova and Hawthorne, 2008; Vilalva
261 *et al.*, 2013; Borst *et al.*, 2016). Fluorine content is higher than in the ideal formulae as the
262 calculated cations at around 3.7 a.p.f.u. exceed the ideal value of 3 cations. REE distribution
263 patterns show a steep negative slope from LREE to HREE, similarly to published patterns
264 (Vilalva *et al.*, 2013) (Fig. 6b). Trace element distribution patterns reproduce the strong
265 negative anomalies for Sr, Ti, and Li that characterize EGM. Alteration products consist mainly
266 of calcite, titanite, and quartz (Fig. 9c-d).

267 Turkestanite is characterized by a low sum of oxides (88-95 wt. %) and compositional
268 differences between crystals, and between core and rim of altered crystals (Fig. 9e-f). The low
269 total oxide sum is consistent with most of the compositions reported in the literature, and is
270 probably related to structural H₂O not analysed with EPMA (Pautov *et al.*, 1997; Vilalva and
271 Vlach, 2010). However, the very low sum of oxides of altered cores could result from porosity
272 created by alteration processes and subsequent loss of volume. Altered cores are
273 characterized by lower Si, Th, Na and K and higher Mn content compared to their rims and the
274 unaltered crystals. Similarly to nacareniobsite-(Ce), REE distribution patterns show a steep
275 negative slope from LREE to HREE, not unlike the patterns given by Vilalva and Vlach (2010)
276 (Fig. 6c).

277 *Na-Clinopyroxene and Na-amphibole*

278 Further insights into the crystallisation processes can be obtained by studying the detailed
279 chemical changes of other rock-forming, non-agpaitic minerals, which are also liable to
280 incorporate HFSE and REE. Representative compositions of Na-clinopyroxene and Na-
281 amphibole in GR-II and GR-III are reported in Table 4 and 5. Structural formulae of
282 clinopyroxene are based on four cations and six oxygens and those of amphibole have been
283 calculated using the spreadsheet of Locock (2014). All Na-clinopyroxenes analysed in both

dyke types are aegirine. In GR-II, the core of cpx-I is richer in Ca and Zr (1.0 wt. % for both CaO and ZrO₂) than the rim (0.6 wt. % CaO and 0.2 wt. % ZrO₂) whereas the Ti content increases slightly in the rim from 1.1 to 1.6 wt. %. The composition of cpx-II is similar to that of the cpx-I rim. REE distribution patterns have the same appearance in both dyke types although the REE concentrations are slightly higher in aegirine from GR-II than in GR-III (Fig. 6d). Trace elements distribution patterns are similar, except for Rb, Ba, Th, and U, which are all below detection limits in GR-II, and above them in GR-III.

BSE images and X-ray element mapping of a cpx-I phenocryst in GR-II illustrate the discontinuous zoning pattern between a homogeneous core and a zoned rim, as well as their compositional differences (Fig. 10). The qualitative X-ray Si map (Fig. 10b) shows the distribution of alkali feldspar (orange), clinopyroxene (green), quartz (red) and Zr-minerals (blue). The cpx-I shows a homogeneous light grey core enriched in Zr and Ca and depleted in Ti with respect to the external dark rim. This rim is characterized by porous, light and dark grey overgrowths containing inclusions of zircon, alkali feldspar and light grey patches (Fig. 10c-d-e-f). These features are restricted to the external rim and do not affect the light core. The light grey patches, porosity and zircon inclusions are mostly restricted to the light grey bands. The composition of zircon and light grey patches has been qualitatively analysed by EDS. Zircon contains significant concentrations of Ce, Ca, Fe, and Al, whereas the light grey patches mainly contain Si, Zr and Na.

Amphiboles in both dyke types are Na-rich, classified using the spreadsheet of Locock (2014) as an arfvedsonite in GR-II and as a ferri-fluoro-leakeite in GR-III. Lithium and fluorine contents are twice as in amphibole from GR-III than in GR-II. The most significant difference is the very high Mg content (7.6 wt. %) in amphibole from GR-III, which is very low (< 0.1 wt. %) in amphibole from GR-II. Their REE distribution patterns have a similar appearance in the LREE portion, with a higher content of LREE in GR-III than in GR-II, and an opposed HREE portion with a steep slope in GR-III and a slightly curved shape in GR-II (Fig. 6e). Their trace element distribution patterns have minor variations except for U, which is three orders of magnitude

more concentrated in GR-III than in GR-II, and the geochemical twins Zr-Hf, which are one order of magnitude more concentrated in GR-II than in GR-III (Fig. 6e).

Discussion

Unusual occurrence of EGM in SiO₂-oversaturated rocks

Cl solubility in the melt as the main limiting factor for EGM crystallisation

The EGM described above are new examples occurring in SiO₂-oversaturated rocks, and add to the list of other complex Na-K-Ca-Zr-silicates occurring in peralkaline granites (Table 1). It is now accepted that the term agpaitic, originally used to designate SiO₂-undersaturated rocks that contain complex Na-K-Ca-Zr-silicates (Sørensen, 1997; Le Maitre *et al.*, 2002), can be extended to SiO₂-oversaturated rocks (Marks *et al.*, 2011). Marks *et al.* (2011) also point out that most Zr-minerals occurring in peralkaline granite (e.g. elpidite and dalyite) have higher molar amount of SiO₂ relative to alkalis and ZrO₂ than Zr-minerals in nepheline syenite (e.g. catapleiite and wadeite), due to the higher SiO₂ activity in this type of melt. In addition, Zr-minerals in peralkaline granite are either volatile free (e.g. dalyite and vlasovite) or H₂O-rich (e.g. elpidite). The EGM, unlike other agpaitic minerals found in peralkaline granites and pegmatites, are rich in Cl. Therefore, in addition to strongly peralkaline conditions and high Zr melt contents, the Cl content of the melt appears to be a critical parameter for crystallisation of EGM in peralkaline granites (Sørensen, 1997; Giehl *et al.*, 2014).

Chlorine is considered to be an incompatible element, thus enriched in most evolved melts, although small amounts can also be incorporated in amphibole, mica and apatite (Aiuppa *et al.*, 2009). It has been shown that the fundamental controls on the solubility of Cl in silicate melts include the composition and structure of the melt, pressure and temperature (Signorelli and Carroll, 2002; Oppenheimer *et al.*, 2014). Chlorine solubility in silicic melts increases with decreasing pressure and increasing temperature (Webster, 1992a). Chlorine is also known to have a high liquid/melt partition coefficient, leading to depletion of melts in Cl when a fluid

phase is exsolved (Webster, 1992b). The high capacity of peralkaline melts, and more particularly of agpaitic melts, to retain volatiles and rare elements has been discussed by several authors (e.g. Kogarko, 1974; Metrich and Rutherford, 1992). Several experimental studies have shown that the solubility of Cl in peralkaline SiO₂-oversaturated (pantelleritic) and undersaturated (phonolitic) melts is similar, in agreement with the concentration of Cl measured in natural samples (Metrich and Rutherford, 1992; Signorelli and Carroll, 2000, 2002). However, in granites and nepheline syenites, their intrusive equivalents, the retention of Cl is controlled by the composition of the crystallizing phases and by the eventuality of fluid exsolution. In SiO₂-undersaturated rocks such as nepheline syenite, Cl can be incorporated into the Cl-rich rock-forming mineral sodalite, but in peralkaline granite, there are no major Cl-rich minerals. Furthermore, exsolution of a NaCl-rich fluid phase is common in peralkaline granites and is usually evoked to explain the scarcity of Cl in these rocks (Webster, 1997). Thus, the window for EGM crystallization in SiO₂-oversaturated rocks is rather restricted, requiring a highly evolved peralkaline melt composition and no, or very late, exsolution of a fluid phase. We thus suggest that the scarcity of EGM in peralkaline granites is related to the unavailability of Cl in the melt due to exsolution of a fluid phase at a late stage of crystallization. In the Ambohimirahavy complex, we have shown in a previous paper that an orthomagmatic fluid exsolved from the melt at a late stage of crystallization of the peralkaline dykes (Estrade *et al.*, 2015). The interstitial texture of EGM indicates that favorable conditions for its crystallization, i.e. a sufficient amount of Cl and Zr in the melt, were only achieved at the very late magmatic stage. However, these conditions rapidly evolved towards exsolution of an orthomagmatic fluid that partly altered the EGM.

The very unusual association of early magmatic EGM and quartz in the GR-III peralkaline pegmatite.

The agpaitic GR-III granite represents the most differentiated lithology in the complex. This is shown by its agpaitic mineralogy and the coexistence of separate grains of albite and K-feldspar, indicating that the temperature of crystallization had decreased to below the

feldspar solvus, and contrasts with crystallization of perthitic alkali feldspar in GR-II. These characteristics are attributed to the extremely evolved composition of the melt from which GR-III crystallised, and its extreme enrichment in HFSE, Na, and volatiles (Estrade *et al.*, 2014a). To our knowledge, the association of early magmatic EGM and quartz in GR-III is the only known example of EGM as an early liquidus phase in granite. However, unlike other main minerals, quartz is not present as inclusions in EGM, suggesting that quartz probably crystallized late, as also indicated by its interstitial texture. This raises the question of whether quartz could have crystallized at a post-magmatic stage, i.e., from a hydrothermal fluid. However, the lack of reaction textures between these two minerals, or with any other agpaitic mineral, suggest a magmatic origin for quartz. Indeed, circulation of a hydrothermal fluid among these minerals would have severely affected the very unstable agpaitic minerals. The unusual composition of the GR-III melt compared to GR-II is further shown by the high Mg content of amphibole (Table 5, 8.0 wt. % MgO) and by the high Ca content of all the agpaitic minerals (Tables 2 and 3, 7.7 wt. % in EGM, 19.5 wt. % in nacareniobsite-(Ce) and 9.0 wt. % in turkestanite). High Mg contents, similar to those measured in GR-III, have been reported in ferri-fluoro-leakeite in nepheline syenite pegmatite from the Larvik Plutonic complex in Norway (Oberti *et al.*, 2014) and in the Verkhnee Espe deposit in Kazakhstan (Cámara *et al.*, 2010). However, in the former occurrence, the Mg enrichment is not discussed, whereas in the latter, it is unclear whether the amphibole is magmatic or crystallized at a hydrothermal stage. The high Mg and Ca contents of these minerals contrasts with the composition of agpaitic melts, which are typically highly depleted in Mg – a highly compatible and early fractionating element – and moderately depleted in Ca (Sørensen, 1997). To this effect, Marks *et al.* (2011) have shown that the Ca content of evolved agpaitic melts varies depending on the nature of the parental melt and whether or not plagioclase had fractionated from the melt. The strongly negative Eu anomaly of the whole-rock REE patterns for both GR-II and GR-III dyke types (Fig. 6a) evidences the strong fractionation of plagioclase from their parental melt; thus, the melt from which both dykes crystallized has been depleted in Ca, following an evolution similar

to the Ca-depleted trend of the Ilímaussaq complex (Marks *et al.*, 2011). And, as far as we know, Mg enrichment has never been documented in alkaline complexes.

A possible explanation for the high Mg and Ca contents in the GR-III melt is contamination of the dykes by the host sediments (marls, mudstone, and limestone) during emplacement. It is also possible that some of the Ca could have been introduced during fluid-rock interaction at a post-magmatic stage such as described at Strange Lake during Ca-metasomatism (Salvi and Williams-Jones, 1996; Gysi *et al.*, 2016; Vasyukova *et al.*, 2016). However, textural evidence clearly rules out a hydrothermal overprint of the primary Ca-bearing apatitic minerals and Mg-bearing amphibole at Ambohimirahavavy.

The addition of Ca to the GR-III melt by contamination would have had a strong effect on the solubility of Cl. Indeed, Chevychelov (1999) has shown that the solubility of Cl in a melt correlates positively with its CaO content and with the CaO/SiO₂ molar ratio. Using whole-rock compositional data from our previous studies on pegmatitic dykes, the CaO/SiO₂ ratios are one order of magnitude higher in GR-III (0.053, sample EU01; Estrade *et al.*, 2014a) compared with GR-II (≤ 0.007 , samples AM30, AM50 and AM113A; Estrade *et al.*, 2014b). Therefore, we propose that the contamination of the highly evolved GR-III melt by Ca-rich material allowed for crystallisation of early-magmatic eudialyte by increasing the concentration level of Cl in the melt because fluid saturation was suppressed. In GR-II, the low Mg content of amphibole and other minerals and the relatively low Ca content in cpx-I and EGM (Tables 2, 4, and 5) may indicate a lower contamination level than for GR-III.

REE and trace elements in EGM

High REE content of EGM

Figure 6a displays trace-element patterns of EGM for SiO₂-oversaturated (Ambohimirahavavy, Ascension Island, and Straumsvola) and undersaturated (Ilímaussaq and Mont Saint Hilaire) complexes. In SiO₂-oversaturated rocks, EGM generally have higher REE contents than in SiO₂-undersaturated counterparts. In addition, most of the EGM from SiO₂-undersaturated rocks that have similarly high REE contents are reported to be post-magmatic

EGM (hatched pattern in Fig. 7), so probably crystallized from a REE-rich fluid (Figs. 5b and 7). The REE enrichment in EGM in GR-II can be explained by the fact that EGM are the only REE-bearing minerals in GR-II, and thus they scavenged most of the REE in the melt. By contrast, in GR-III, nacareniobsite-(Ce) is also a major REE-bearing mineral and competed with EGM for the uptake of REE. Harris et al. (1982; 1987) considered the Ca-poor composition of peralkaline granites from Ascension Island and Straumsvola to explain the REE enrichment in EGM. They suggested that, because REE are incorporated in the same structural site as Ca in EGM, high amounts of REE entered the Ca site to compensate for its paucity in the melt from which the mineral crystallized. The negative correlation between La+Ce+Nd+Y and Ca clearly indicates that these elements compete for the same structural site (Fig. 5b). However, although whole-rock Ca contents in GR-II, Ascension Island and Straumsvola are similarly low (0.2 to 0.5 wt. %), EGM from Straumsvola are depleted in HREE compared to those in the other two localities. Thus, another mechanism must be evoked to explain the difference in HREE content.

HREE enrichment in EGM: the role of melt composition

The HREE content of the melt can be qualitatively estimated by examining the REE distribution patterns of the major minerals present in the rocks (Fig. 6). In GR-II, the major minerals aegirine, amphibole, and EGM all show HREE enrichments, suggesting that the GR-II melt was enriched in HREE. In GR-III, however, all minerals have lower HREE concentrations, surely reflecting an overall lower concentration of HREE in the GR-III melt. This difference is also evident from the whole-rock REE distribution patterns; in GR-II the HREE show a flat profile (Gd/Lu=0.97), whereas it decreases slightly in GR-III (Gd/Lu=1.73). We have pointed out above that the GR-III dykes are the most evolved lithology in the complex, and that they represent a melt produced by extensive fractionation. We suggest that at a late stage of evolution the HREE became compatible due to the abundant crystallization of phases that could incorporate them, such as aegirine and arfvedsonite, and were thus fractionated. The resulting melt, albeit very evolved, was thus relatively depleted in HREE.

U and Pb in EGM

Among all trace elements analysed in EGM from both dykes, U and Pb show the most markedly opposite behaviour (Fig. 6a). Uranium concentration in EGM, as for aegirine and amphibole, is higher in GR-III than in GR-II. As proposed for HREE above, the opposing behaviour of U in EGM might be attributed to its difference in concentration in the GR-II and GR-III melts. A much higher U concentration in the melt from which GR-III crystallized would be consistent with the presence of turkestanite in this granite, as U is a major constituent of this rare mineral, with up to 2 wt. % UO_2 . The higher U concentration in the GR-III melt thus reflects its highly incompatible behaviour, leading to an enrichment in the most evolved melts that were formed by intense fractional crystallisation. The opposite observation can be made for Pb, which shows a positive and negative anomaly compared to its neighbouring elements in EGM from GR-II and GR-III, respectively (Fig. 6a). This opposed behaviour contrasts with the bulk Pb content, which is similar in both dykes. In GR-II, EGM and K-feldspar are the only minerals that can accommodate significant amounts of Pb, as aegirine and amphibole have very low Pb contents (few ppm to below ppm, electronic supplement). In GR-III, in addition to EGM and K-feldspar, Pb is easily incorporated into turkestanite (~400 ppm, electronic supplement). As feldspars are present in similar modal amounts in GR-II and GR-III, we think that they had a similar effect on bulk Pb content of the two melts. Therefore, we attribute the relative low Pb content in EGM from GR-III to its concomitant uptakes by turkestanite.

Destabilisation of EGM and post-magmatic assemblage

Alteration of GR-II

The destabilisation of EGM and concomitant sudden change in cpx-I composition in GR-II (Figs. 8 and 10), together with the local destabilisation of the three agpaitic minerals (EGM, nacareniobsite-(Ce) and turkestanite) in GR-III (Fig. 9), indicate that both granites experienced late- to post-magmatic alteration. The occurrence of alteration is a very common feature in peralkaline granites (Salvi and Williams-Jones, 2006; Kynicky *et al.*, 2011; Kempe *et al.*, 2015; Gysi *et al.*, 2016; Vasyukova *et al.*, 2016) and in most cases the primary agpaitic

minerals in these rocks undergo complete replacement, to the point that the precursor is not always easy to recognize. Examples include the Strange Lake complex in Canada, where most of the subsolvus granitic facies contain pseudomorphs of gittinsite after a euhedral precursor phase (Birkett *et al.*, 1992; Mariano and Mariano, 2014). Rare occurrences of partial replacement from drill core samples allowed identification of the primary mineral as elpidite, which was transformed to gittinsite via an intermediate step involving armstrongite (Salvi and Williams-Jones, 1995). Other instances of complete pseudomorphism include the Khan Bogd complex (Kynicky *et al.*, 2011) and Khaldzan Buregtey complex (Kempe *et al.*, 2015). Detailed mineralogical studies in some of these localities have shown that destabilisation of these agpaite minerals is a subsolidus process, related either to interaction with external fluids or to the exsolution of a fluid from the melt at a very late-stage of crystallization. In some cases, fluid inclusion study documented the input of external fluids which may cause formation of relatively rare minerals, as it was the case at Strange Lake where Ca to form gittinsite was derived from a meteoric fluid (Salvi and Williams-Jones, 1990, 1996).

The above discussion indicates that interaction with a fluid, either of orthomagmatic or external origin, at late- to post-magmatic stages is a recurrent phenomenon in agpaite peralkaline granite. This seems also to be the case in the Ambohimirahavavy complex, as shown in GR-II where secondary assemblages are mainly characterized by the occurrence of pseudomorphs of zircon and quartz after EGM plus an unidentified Ca-zirconosilicate (Fig. 8). Interaction with a fluid is also evidenced by the rims of cpx-I, which show a porous texture associated with zircon inclusions (Fig. 10). A similar texture has been previously described by the authors in zircon in a peralkaline granitic dyke of this complex (Estrade *et al.*, 2014a). The association of Zr-rich patches, zircon inclusions and pores in the rim of the cpx-I can be interpreted in terms of coupled dissolution-reprecipitation which occurred at the fluid-cpx-I interface (Putnis, 2009). The presence of Al, Fe, and Ca in zircon inclusions, elements that are not compatible in its structure, is further evidence of their hydrothermal origin (Geisler *et al.*, 2007). The fact that the alteration is restricted to the light grey bands in the zoned rims of these crystals is intriguing (Fig. 10d, f). We suggest that this may be due to their higher content in

Zr, thus making them more prone to alteration. The outermost dark rims are poor in Zr and likely precipitated during fluid-rock interaction concomitantly with the small cpx-II grains and late hydrothermal zircon (rich in Ca, Fe, and Al) in the groundmass.

We propose that, during the interaction with a fluid, Cl and H₂O were liberated to the fluid phase, causing the destabilisation of previously formed EGM and precipitation of zircon and quartz. The elements initially present in EGM were redistributed in the rocks according to their respective mobility in the fluid phase. The precipitation of zircon within the edges of precursor EGM indicates that Zr could not be transported over a long distance. Moreover, Ti could no longer be incorporated in EGM and was therefore incorporated in the crystallising rims of cpx-I and in the secondary cpx-II crystals (Fig. 10, Table 4). The similar Na₂O content of cpx-I cores and rims indicate that Na activity did not change significantly between magmatic and late- to post-magmatic conditions. The amount of Ca incorporated in secondary phases (mainly in secondary Zr-minerals) could partly derive from the Ca released in the fluid during the replacement of EGM and cpx-I. However, it is likely that some Ca was added to the system by an external fluid.

Alteration in GR-III is local and Ca-rich

Unlike GR-II, where most of the EGM have been completely replaced, alteration of EGM in GR-III is only a local phenomenon, and most of the EGM are pristine. In the altered parts, the three main agpaitic minerals (EGM, nacareniobsite-(Ce) and turkestanite) are destabilised and replaced, but aegirine and amphibole are mostly preserved. The most significant effect of alteration is the systematic removing of alkalis from the three agpaitic minerals and the precipitation of Ca-rich phases such as calcite and titanite in secondary assemblages (Fig. 9 and Tables 2 and 3). These observations suggest that, similarly to GR-II, a Ca-rich fluid interacted with GR-III at a late- to post-magmatic stage. The origin of the fluid could be both magmatic and external (Estrade *et al.*, 2015).

Conclusions

We document two new occurrences of EGM in two types of peralkaline granitic dykes from the Ambohimirahavavy complex in northwest Madagascar. We propose that Cl availability is the main limiting factor for the crystallisation of EGM in SiO₂-oversaturated rocks. The transitional GR-II granite was produced from a melt that only achieved a sufficient Cl content to crystallize EGM at very late stages, resulting in formation of interstitial EGM. The melt rapidly evolved towards fluid exsolution, losing its Cl and thus hampering EGM crystallization. The resulting orthomagmatic fluid altered the EGM, although only to a limited extent. The agpaitic GR-III granite contains early-formed, abundant EGM. Contamination of the highly evolved GR-III melt by Ca-rich material increased Cl solubility, inducing early EGM crystallization. EGM in these granites have higher REE contents than most occurrences in undersaturated complexes. This is explained by the low Ca content of peralkaline melts, which favours REE intake in EGM as substitution for Ca. The enrichment of the heavy REE in GR-II with respect to EGM in GR-III is a feature inherited from the respective melt compositions, related to fractionation of the more compatible HREE in late-forming minerals at late stages of GR-III melt differentiation. In GR-II, exsolution of a NaCl-rich fluid caused destabilisation of EGM and precipitation of zircon and quartz. In GR-III, the exsolving fluid was rich in Ca and produced a calcic alteration assemblage.

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753

Figure captions

Figure 1:

Geological map of the Ambohimirahavavy complex, modified after Donnot (1963).

Figure 2:

Outcrop photograph (a), scanned polished rock slab (b-d) and scanned thin sections (c-e) of the pegmatitic transitional granitic dyke (GR-II) (a, b, c) and pegmatitic agpaitic granitic dyke (GR-III) (d, e). Both rock types show pronounced layering and variable grain sizes typical of pegmatite. Abbreviations: afs: alkali feldspar, amp: amphibole, cpx: clinopyroxene, qtz: quartz.

Figure 3:

BSE images of EGM textures from GR-II (a-b) and GR-III (c-d): (a-b) Late-magmatic interstitial EGM partially altered along fractures. (c-d) Oscillatory-zoned early-magmatic euhedral EGM with mineral inclusions. Abbreviations: afs: alkali feldspar; amp: amphibole; cpx: clinopyroxene; qtz: quartz; pcl: pyrochlore.

Figure 4:

BSE images of agpaitic minerals in GR-III: (a-b) euhedral laths of nacareniobsite-(Ce) containing mineral inclusions. (c-d) zoned euhedral turkestanite containing mineral inclusions. The core of the turkestanite shows bright U-rich veinlets and inclusions. Abbreviations: amp: amphibole; cal: calcite; K-fsp: K-feldspar; qtz: quartz.

Figure 5:

(a) A plot of Fe vs Mn in atom per formula units of EGM from the Ambohimirahavavy complex (filled symbols) compared with EGM from other alkaline complexes taken from Schilling et al. (2011). (b) A plot of La+Ce+Nd+Y vs Ca in atom per formula units of EGM from the Ambohimirahavavy complex (filled symbols) compared with EGM from other alkaline complexes taken from Schilling et al. (2011).

Figure 6:

Chondrite normalised REE (left) and trace-elements (right) distribution patterns from (a) EGM, (b) nacareniobsite-(Ce), (c) turkestanite, (d) clinopyroxene, and (e) amphibole. EGM patterns from GR-II and GR-III are compared with whole-rock patterns from GR-II and GR-III (dashed lines) using data from Estrade et al. (2014b; GR-II dyke type sample AM113A) and Estrade et al. (2014a; GR-III dyke type sample EU01). EGM patterns are also compared with EGM data from other alkaline complexes taken from Schilling et al. (2011) (cf. legend). Nacareniobsite-(Ce) and turkestanite patterns are compared with data from the Morro Redondo complex (Brazil) taken from Vilalva and Vlach (2010) and Vilalva et al. (2013).

Figure 7:

Range of light (La to Sm) and heavy (Gd to Lu) REE concentrations in EGM from the Ambohimirahavavy complex and other alkaline complexes. Data are from Schilling et al. (2011). The grey colour indicates overlapping of the white and black patterns in the legends.

Figure 8:

BSE image and X-ray maps depicting the distribution of chlorine (Cl), calcium (Ca), zirconium (Zr), neodymium (Nd) and cerium (Ce), showing partial replacement of EGM (BSE image lower right hand side) by zircon and quartz (BSE image left hand side) in GR-II. Replacement takes place through formation of an intermediate Ca-zirconosilicate with Zr-rich and REE-rich phases. Abbreviations: aeg: aegirine; afs: alkali feldspars; qtz: quartz; zrn: zircon.

Figure 9:

BSE images (a, b, c, and e) and false-coloured X-ray maps (d, f) of altered agpaitic minerals in GR-III: (a-b) altered EGM replaced by Ca-Na zirconosilicate, an intermediate phase, and calcite. (c-d) altered nacareniobsite-(Ce) replaced mainly by calcite and titanite. (e-f) zoned altered turkestanite with calcite. Abbreviations: ab: albite; aeg: aegirine; amp: amphibole; cal: calcite; K-fsp; K-feldspar; qtz: quartz; ttn: titanite.

Figure 10:

Part 1: BSE images (a, c, d, e and f) and X-ray maps of a clinopyroxene-I phenocryst and surrounding phases in GR-II: (a-b) zoned clinopyroxene phenocryst (cpx-I) surrounded by

806 small clinopyroxene (cpx-II), zircon, alkali feldspar, and quartz. (c-d) BSE images of the left
807 and right (e-f) tips of the clinopyroxene phenocryst with different grey contrast. Band
808 overgrowths contain pores, zircon and alkali feldspar inclusions, and Zr-rich light grey patches.
809 Abbreviations: afs: alkali feldspars; cpx: clinopyroxene, qtz: quartz; zrn: zircon.

810 Part 2: BSE image and X-ray maps showing the distribution of zirconium (Zr), calcium (Ca),
811 and titanium (Ti) in a clinopyroxene phenocryst and surrounding phases in GR-II.

812

813 **Table captions**

814 Table 1: List of the main Zr-silicates in agpaitic peralkaline granite and pegmatite.

815 Table 2: Average compositions of EGM and their replacing phases in pegmatitic transitional
816 (GR-II) and pegmatitic agpaitic (GR-III) dykes.

817 Table 3: Average compositions of nacareniobsite-(Ce) and turkestanite in pegmatitic agpaitic
818 (GR-III) dykes.

819 Table 4: Average compositions of aegirine in pegmatitic transitional (GR-II) and pegmatitic
820 agpaitic (GR-III) dykes.

821 Table 5: Average compositions of amphibole in pegmatitic transitional (GR-II) and pegmatitic
822 agpaitic (GR-III) dykes. Lithium determined by LA-ICP-MS.

823 Electronic supplement: five tables with trace element abundances of EGM, clinopyroxene,
824 amphibole, nacareniobsite-(Ce) and turkestanite obtained by LA-ICP-MS.