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► **To cite this version:**

Guillaume Estrade, Stefano Salvi, Didier Béziat. Crystallization and destabilization of eudialyte-group minerals in peralkaline granite and pegmatite: a case study from the Ambohimirahavavy complex, Madagascar. *Mineralogical Magazine*, 2018, 82 (2), pp.375-399. 10.1180/minmag.2017.081.053 . hal-02363133

HAL Id: hal-02363133

<https://hal.science/hal-02363133>

Submitted on 6 Nov 2020

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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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8 Version January 15, 2017

9 **Keywords:** eudialyte-group minerals, peralkaline granites, agpaitic rocks, zirconosilicate,

10 HFSE and REE, pegmatites.

11

12 **Abstract:**

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

32

33 **Introduction**

34 Eudialyte-group minerals (EGM) are complex Na-Ca-Zr-cyclosilicates with the general formula
35 $\text{Na}_{15}(\text{Ca}, \text{REE})_6(\text{Fe}, \text{Mn})_3\text{Zr}_3\text{Si}(\text{Si}_{25}\text{O}_{72})(\text{O}, \text{OH}, \text{H}_2\text{O})_3(\text{Cl}, \text{OH})_2$ (Johnsen *et al.*, 2003)
36 characteristic of evolved peralkaline [molar $(\text{Na}_2\text{O} + \text{K}_2\text{O})/\text{Al}_2\text{O}_3 > 1$] SiO₂-undersaturated
37 syenites, also called agpaitic syenites. This mineral is generally considered as diagnostic of
38 agpaicity, i.e., those rocks in which High Field Strength Elements (HFSE, such as Zr, Hf, Nb,

39 Ta, U and Th) and Rare Earth Elements (REE) are incorporated into complex Na-K-Ca-Zr-
40 silicates, rich in volatiles (Cl, F and H₂O) (Sørensen, 1992, 1997; Khomyakov, 1995; Le Maitre
41 *et al.*, 2002; Marks *et al.*, 2011). By contrast, when HFSE are incorporated in more common
42 minerals (e.g. zircon, titanite), rocks are termed miaskitic. EGM can contain important amounts
43 of REE and are considered as a potentially valuable ore of REE and Zr (e.g., the Kringlerne
44 deposit in the Ilímaussaq complex, the Norra Kärr complex in Sweden and the Kipawa complex
45 in Canada; Goodenough *et al.* (2016) and Saucier *et al.* (2013)). Because EGM crystallize
46 through a range of magmatic to hydrothermal conditions, their compositional variability can
47 been used to monitor the conditions of the environment in which they crystallized (Mitchell and
48 Liferovich, 2006; Schilling *et al.*, 2009; Marks *et al.*, 2015; Ratschbacher *et al.*, 2015). Very
49 commonly, EGM are partly-to-completely replaced by secondary phases, at late magmatic-to-
50 hydrothermal stages (Salvi *et al.*, 2000; Mitchell and Liferovich, 2006; Karup-Møller *et al.*,
51 2010; Sheard *et al.*, 2012; Karup-Møller and Rose-Hansen, 2013).

52 Although EGM were initially considered to be characteristic of highly differentiated SiO₂-
53 undersaturated rocks, these minerals have also been reported in a few SiO₂-oversaturated
54 peralkaline rocks. The only known examples, to our knowledge, are: quartz syenite from the
55 Carlingford complex, Ireland (Nockolds, 1950); the Pajarito mountain, Texas (McLemore,
56 2015); granitic dykes from the Ascension Island in the South Atlantic (Harris *et al.*, 1982); the
57 Straumsvola complex in Antarctica (Harris and Rickard, 1987); the Windy Fork pluton in Alaska
58 (Gunter *et al.*, 1993); pegmatitic granitic dykes from the Ambohimirahavavy complex in
59 Madagascar (Estrade *et al.*, 2014a); the Dara-i-Pioz massif in Tajikistan (Grew *et al.*, 1993);
60 Rockall Island in the North Atlantic (Sabine, 1957). However, in studies of most of these
61 occurrences, EGM are only mentioned as an accessory mineral and are not completely
62 described in terms of texture and composition, although in their recent compilation, Schilling
63 *et al.* (2011) characterized the EGM from the Ascension Island and Straumsvola.

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

67 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
68 that, among these six minerals, none contain Cl or F while three contain H_2O (elpidite,
69 catapleiite and armstrongite). Several Zr-minerals are usually reported in the same peralkaline
70 rocks and their complex textural relationships have often led to multiple interpretations (e.g.
71 Strange Lake, Birkett et al., 1992; Roelofsen and Veblen, 1999). Moreover, in many cases,
72 post-magmatic processes have destabilised the primary assemblages, greatly complicating
73 identification of the original magmatic mineralogy.

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

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

84

85 **Geological setting and petrography**

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

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

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

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

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

111 (3) A pegmatitic agpaitic granitic type (GR-III) which consists of K-feldspar, albite, Na-
112 clinopyroxene, Na-amphibole and quartz, plus EGM as rock-forming minerals (Fig. 2d-e).
113 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
114 turkestanite $(\text{Th}(\text{Ca},\text{Na})_2 \text{K}_{1-x}\square_x (\text{Si}_8\text{O}_{20}) \cdot n\text{H}_2\text{O})$.

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

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

124

125 **Analytical Methods**

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

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

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

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

150

151 **Mineral textures and alteration**

152 *Eudialyte-group minerals*

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

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

170 *Other agpaitic minerals*

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

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

185 *Na-Clinopyroxene and Na-amphibole*

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

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

196

197 **Mineral composition**

198 *Eudialyte-group minerals*

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

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

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

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

241 *Alteration paragenesis of EGM*

242 Most of the EGM in GR-II samples are entirely replaced by a secondary paragenesis, ultimately
243 consisting of zircon and quartz. Locally, however, EGM are partly altered and replaced by an
244 assemblage of Zr-Ca-bearing phases and REE-Ca-F-bearing phases with no zircon (Estrade
245 *et al.*, 2014a). In this work, we have identified EGM that show partial replacement by zircon,
246 and we consider this texture as representative of the alteration pattern of EGM in GR-II. An X-
247 ray element map of partially-replaced EGM is shown in Figure 8 and the compositions of the
248 phases present are reported in Table 2. In this Figure, EGM is ultimately replaced by zircon
249 and quartz through an intermediate step consisting of an unidentified Ca-zirconosilicate with
250 higher Ca and Zr and lower Fe and Mn contents than the original EGM. All of Na, Cl, Nb, and
251 most of the REE have been lost. REE-rich and Zr-rich phases co-crystallized with the Ca-
252 zirconosilicate but were not analysed with EPMA due to their very small size. Secondary zircon
253 is characterized by a low ZrO₂ content (57.8 wt. %), a low sum of oxides (91.5 wt. %) and the
254 presence of Fe and Ca. In GR-III, replacement of EGM involved an intermediate phase slightly
255 enriched in Si (Fig. 9a-b). The replacing phase is an unidentified Ca-Na zirconosilicate lacking
256 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

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

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

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

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

313

314 **Discussion**

315 *Unusual occurrence of EGM in SiO₂-oversaturated rocks*

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

317 The EGM described above are new examples occurring in SiO₂-oversaturated rocks,
318 and add to the list of other complex Na-K-Ca-Zr-silicates occurring in peralkaline granites
319 (Table 1). It is now accepted that the term agpaitic, originally used to designate SiO₂-
320 undersaturated rocks that contain complex Na-K-Ca-Zr-silicates (Sørensen, 1997; Le Maitre
321 *et al.*, 2002), can be extended to SiO₂-oversaturated rocks (Marks *et al.*, 2011). Marks *et al.*
322 (2011) also point out that most Zr-minerals occurring in peralkaline granite (e.g. elpidite and
323 dalyite) have higher molar amount of SiO₂ relative to alkalis and ZrO₂ than Zr-minerals in
324 nepheline syenite (e.g. catapleiite and wadeite), due to the higher SiO₂ activity in this type of
325 melt. In addition, Zr-minerals in peralkaline granite are either volatile free (e.g. dalyite and
326 vlasovite) or H₂O-rich (e.g. elpidite). The EGM, unlike other agpaitic minerals found in
327 peralkaline granites and pegmatites, are rich in Cl. Therefore, in addition to strongly peralkaline
328 conditions and high Zr melt contents, the Cl content of the melt appears to be a critical
329 parameter for crystallisation of EGM in peralkaline granites (Sørensen, 1997; Giehl *et al.*,
330 2014).

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

338 phase is exsolved (Webster, 1992b). The high capacity of peralkaline melts, and more
339 particularly of agpaitic melts, to retain volatiles and rare elements has been discussed by
340 several authors (e.g. Kogarko, 1974; Metrich and Rutherford, 1992). Several experimental
341 studies have shown that the solubility of Cl in peralkaline SiO₂-oversaturated (pantelleritic)
342 and undersaturated (phonolitic) melts is similar, in agreement with the concentration of Cl
343 measured in natural samples (Metrich and Rutherford, 1992; Signorelli and Carroll, 2000,
344 2002). However, in granites and nepheline syenites, their intrusive equivalents, the retention
345 of Cl is controlled by the composition of the crystallizing phases and by the eventuality of fluid
346 exsolution. In SiO₂-undersaturated rocks such as nepheline syenite, Cl can be incorporated
347 into the Cl-rich rock-forming mineral sodalite, but in peralkaline granite, there are no major Cl-
348 rich minerals. Furthermore, exsolution of a NaCl-rich fluid phase is common in peralkaline
349 granites and is usually evoked to explain the scarcity of Cl in these rocks (Webster, 1997).
350 Thus, the window for EGM crystallization in SiO₂-oversaturated rocks is rather restricted,
351 requiring a highly evolved peralkaline melt composition and no, or very late, exsolution of a
352 fluid phase. We thus suggest that the scarcity of EGM in peralkaline granites is related to the
353 unavailability of Cl in the melt due to exsolution of a fluid phase at a late stage of crystallization.
354 In the Ambohimirahavy complex, we have shown in a previous paper that an orthomagmatic
355 fluid exsolved from the melt at a late stage of crystallization of the peralkaline dykes (Estrade
356 *et al.*, 2015). The interstitial texture of EGM indicates that favorable conditions for its
357 crystallization, i.e. a sufficient amount of Cl and Zr in the melt, were only achieved at the very
358 late magmatic stage. However, these conditions rapidly evolved towards exsolution of an
359 orthomagmatic fluid that partly altered the EGM.

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

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

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

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

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

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

412 *REE and trace elements in EGM*

413 *High REE content of EGM*

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

419 EGM (hatched pattern in Fig. 7), so probably crystallized from a REE-rich fluid (Figs. 5b and
420 7). The REE enrichment in EGM in GR-II can be explained by the fact that EGM are the only
421 REE-bearing minerals in GR-II, and thus they scavenged most of the REE in the melt. By
422 contrast, in GR-III, nacareniobsite-(Ce) is also a major REE-bearing mineral and competed
423 with EGM for the uptake of REE. Harris et al. (1982; 1987) considered the Ca-poor composition
424 of peralkaline granites from Ascension Island and Straumsvola to explain the REE enrichment
425 in EGM. They suggested that, because REE are incorporated in the same structural site as Ca
426 in EGM, high amounts of REE entered the Ca site to compensate for its paucity in the melt
427 from which the mineral crystallized. The negative correlation between La+Ce+Nd+Y and Ca
428 clearly indicates that these elements compete for the same structural site (Fig. 5b). However,
429 although whole-rock Ca contents in GR-II, Ascension Island and Straumsvola are similarly low
430 (0.2 to 0.5 wt. %), EGM from Straumsvola are depleted in HREE compared to those in the
431 other two localities. Thus, another mechanism must be evoked to explain the difference in
432 HREE content.

433 *HREE enrichment in EGM: the role of melt composition*

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

446 *U and Pb in EGM*

447 Among all trace elements analysed in EGM from both dykes, U and Pb show the most
448 markedly opposite behaviour (Fig. 6a). Uranium concentration in EGM, as for aegirine and
449 amphibole, is higher in GR-III than in GR-II. As proposed for HREE above, the opposing
450 behaviour of U in EGM might be attributed to its difference in concentration in the GR-II and
451 GR-III melts. A much higher U concentration in the melt from which GR-III crystallized would
452 be consistent with the presence of turkestanite in this granite, as U is a major constituent of
453 this rare mineral, with up to 2 wt. % UO₂. The higher U concentration in the GR-III melt thus
454 reflects its highly incompatible behaviour, leading to an enrichment in the most evolved melts
455 that were formed by intense fractional crystallisation. The opposite observation can be made
456 for Pb, which shows a positive and negative anomaly compared to its neighbouring elements
457 in EGM from GR-II and GR-III, respectively (Fig. 6a). This opposed behaviour contrasts with
458 the bulk Pb content, which is similar in both dykes. In GR-II, EGM and K-feldspar are the only
459 minerals that can accommodate significant amounts of Pb, as aegirine and amphibole have
460 very low Pb contents (few ppm to below ppm, electronic supplement). In GR-III, in addition to
461 EGM and K-feldspar, Pb is easily incorporated into turkestanite (~400 ppm, electronic
462 supplement). As feldspars are present in similar modal amounts in GR-II and GR-III, we think
463 that they had a similar effect on bulk Pb content of the two melts. Therefore, we attribute the
464 relative low Pb content in EGM from GR-III to its concomitant uptakes by turkestanite.

465 *Destabilisation of EGM and post-magmatic assemblage*

466 *Alteration of GR-II*

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

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

487 The above discussion indicates that interaction with a fluid, either of orthomagmatic or external
488 origin, at late- to post-magmatic stages is a recurrent phenomenon in agpaite peralkaline
489 granite. This seems also to be the case in the Ambohimirahavy complex, as shown in GR-
490 II where secondary assemblages are mainly characterized by the occurrence of
491 pseudomorphs of zircon and quartz after EGM plus an unidentified Ca-zirconosilicate (Fig. 8).
492 Interaction with a fluid is also evidenced by the rims of cpx-I, which show a porous texture
493 associated with zircon inclusions (Fig. 10). A similar texture has been previously described by
494 the authors in zircon in a peralkaline granitic dyke of this complex (Estrade *et al.*, 2014a). The
495 association of Zr-rich patches, zircon inclusions and pores in the rim of the cpx-I can be
496 interpreted in terms of coupled dissolution-precipitation which occurred at the fluid-cpx-I
497 interface (Putnis, 2009). The presence of Al, Fe, and Ca in zircon inclusions, elements that are
498 not compatible in its structure, is further evidence of their hydrothermal origin (Geisler *et al.*,
499 2007). The fact that the alteration is restricted to the light grey bands in the zoned rims of these
500 crystals is intriguing (Fig. 10d, f). We suggest that this may be due to their higher content in

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

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

516 *Alteration in GR-III is local and Ca-rich*

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

526

527 **Conclusions**

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

545

546 **Acknowledgements**

547 Financial support for this research was provided by a CESSUR grant from the French Institut
548 National des Sciences de l'Univers to Stefano Salvi, and by the company Tantalus Rare Earth
549 A.G., who also kindly provided access to the Ambohimirahavavy complex and logistical
550 support during fieldwork. We would like to thank Wolfgang Hampel for his invaluable help in
551 the field, Olivier Bruguier for laboratory assistance with the LA-ICP-MS and Sophie Gouy,
552 Philippe De Parseval and Thierry Aigouy for assistance with EPMA and SEM analyses. We
553 are grateful to Roger H. Mitchell and Iain Samson for their constructive and thorough reviews,
554 which helped improve the quality of this manuscript.

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- 753

754 **Figure captions**

755 Figure 1:

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

757 Figure 2:

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

762 Figure 3:

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

767 Figure 4:

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

772 Figure 5:

773 (a) A plot of Fe vs Mn in atom per formula units of EGM from the Ambohimirahavavy complex
774 (filled symbols) compared with EGM from other alkaline complexes taken from Schilling et al.
775 (2011). (b) A plot of La+Ce+Nd+Y vs Ca in atom per formula units of EGM from the
776 Ambohimirahavavy complex (filled symbols) compared with EGM from other alkaline
777 complexes taken from Schilling et al. (2011).

778 Figure 6:

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

787 Figure 7:

788 Range of light (La to Sm) and heavy (Gd to Lu) REE concentrations in EGM from the
789 Ambohimirahavavy complex and other alkaline complexes. Data are from Schilling et al.
790 (2011). The grey colour indicates overlapping of the white and black patterns in the legends.

791 Figure 8:

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

797 Figure 9:

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

803 Figure 10:

804 Part 1: BSE images (a, c, d, e and f) and X-ray maps of a clinopyroxene-I phenocryst and
805 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.