On the reported presence of potassium in clinopyroxene from potassium-rich lavas: a transmission electron microscope study

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Abstract

Titanian aegirine in a pegmatoid differentiate from leucitite *sensu stricto* (i.e. without modal plagio-clase) was found to contain significant K (up to 0.07 K atoms per formula unit; 0.11 wt.% K_2O) by electron probe microanalysis. A transmission electron microscope study showed that this pyroxene contained a lamellar amorphous phase and other more irregular, amorphous domains where K and Al are concentrated. The microstructures suggest that the aegirine–amorphous phase system did not achieve textural equilibrium. Also, the chemistry of this phase is variable, particularly in Ca and Mg, suggesting lack of chemical equilibrium within the liquid from which the phase derived. The average composition of the latter approaches that of the coexisting K-richterite and is interpreted as trapped residual liquid, i.e. glass, from pyroxene crystallization which failed to develop a crystalline amphibole. In view of the extensive stability of richterite coexisting with pyroxene to high pressure, the reported occurrence of 'K-bearing pyroxene' may not be considered as a homogeneous K-bearing phase and a predictable potassium carrier in the petrogenesis of K-rich rocks like leucitites and lamproites.

KEYWORDS: potassium, clinopyroxene, aegirine, transmission electron microscopy.

Introduction

THE presence of significant K, up to *c.* 0.8 wt.% has recently been reported in chrome-diopside associated with lamproites from Western Australia (Jaques, 1987). On the other hand, virtually no K (K<0.002%) was found in diopside from representative lamproites from: Western Australia; Gaussberg, Antarctica; Leucite Hills, Wyoming; and southeastern Spain (Dal Negro *et al.*, in prep.). Diopsides from ultramafic inclusions in kimberlite contain trace amounts of K (0.002–0.007 wt.%) and only exceptionally up to 0.11 wt.% (Griffin and Murthy, 1969). However, K concentrations up to *c.* 0.8 wt.% have been reported in eclogitic omphacite (Harlow and Dowty, 1982). K contents of synthetic clinopyroxene crystallized from K-rich systems under high pressure (15–100 kbar) are generally below 0.08 wt.% K and

exceptionally reach 0.22 wt.% K (Erlank and Kushiro, 1970; Shimizu, 1971). Most would agree with the statement by Papike (1960), 'The only major element that cannot be accommodated in the pyroxene structure is K...', and it seems, therefore, important to investigate the nature of pyroxenes with significant K in their chemistry and to understand the nature and conditions under which K may occur in this mineral. This is relevant to the genesis of alkaline basalts and K-rich variants like leucitites and lamproites.

In this paper we report on the nature of a titanian aegirine which yielded up to 0.07 K atoms per formula unit (a.f.u.) ($K_2O = 0.11$ wt.%) by means of electron microprobe analysis. This pyroxene occurs sparsely (less than 2% by volume) in a trachytic pegmatoid associated with leucitites (*sensu stricto*, i.e. no modal plagioclase) from

Begargo Hill, New South Wales (Cundari, 1973). The specimen investigated, 70-1039, represents a textural variant of the rock and is strongly porphyritic, with variable proportions of diopside phenocrysts up to 1 cm in length in an aphyric matrix of sanidine + nepheline. The rock is largely composed of sanidine($Or_{55-73}Ab_{40-25}Cs_{5-2}$), nepheline($Ne_{85-90}Ks_{15-10}$), and diopside($Ca_{0.9-1.0}Mg_{0.8}Fe^{2+}_{0.2}[Si_{1.85-1.90}Al_{0.07-0.10}Ti_{0.04-0.05}]O_6$), together forming c. 90% of the mode. Accessory amounts of phlogopite ($[K_{1.6}Na_{0.3}Ba_{0.1}]_{\Sigma2}[Mg_{3.1}Fe^{2+}_{1.5}Ti_{0.7}]_{\Sigma5.3}[Si_{5.6}Al_{2.0}Ti_{0.4}]_{\Sigma8}O_{20}(OH)_3F_1)$, richterite ($[K_{0.4}Na_{0.6}]_{\Sigma1}[Na_{1.6}Ca_{0.4}]_{\Sigma2}[Mg_{2.5}Fe^{2+}_{1.8}Ti_{0.5}]_{\Sigma4.8}[Si_{7.7}Al_{0.3}]_{\Sigma8}O_{22}(OH,F_{0.8})$), magnetite ($Usp_{42}Mt_{58}$), apatite, and aegirine ($[Na_{0.63}Fe_{0.62}Ca_{0.41}Mg_{0.34}]_{\Sigma2}[Si_{1.90}Ti_{0.10}]_{\Sigma2}O_6$) are also present (Cundari, 1973, and this paper). Under the petrological microscope, late-crystallized richterite and aegirine can be seen to be intergrown, with sharp to transitional boundaries (e.g. Birch, 1978; Fig. 7). The analysed bulk rock specimens (Table 1),

Table 1. Chemical analyses of the Begargo Hill pegmatoid associated with leucitite (Cundari,1973;Table 3).

wt%	70-1038	70-1039
SiO_2	42.04	45.48
TiO_2	7.98	5.45
Al_2O_3	9.81	12.10
Fe_2O_3	4.66	5.49
FeO	6.54	4.64
MnO	0.17	0.16
MgO	6.28	4.54
CaO	10.84	7.88
Na_2O	2.93	3.30
K_2O	3.70	4.54
P_2O_5	2.08	1.44
H_2O+	1.44	4.14
Σ	98.47	98.16
(ppm)		
Cr	82	80
Ni	35	23
Co	n.d	n.d
Zr	951	1091
Rb	38	44
Sr	3228	3393
Ba	2000	4547
D.I.	39.6	49.6
CIPW Q	-8.1	-5.81
(Na+K)/Al	0.90	0.85
$Mg/(Mg+Fe^{2+})$	0.63	0.64

represent the compositional variation of the pegmatoid, notable for its high alkali content, relative to Al, and silica undersaturation. A similar assemblage was figured from the Cosgrove leucitite, Victoria, which is genetically related to the New South Wales leucitite suite (Birch, 1978, Fig. 1). These pegmatoids are not uncommon in the above suite and have been interpreted as differentiates of the leucitite magma (Cundari, 1973; Birch, 1978).

TEM observations

Aegirine fragments, drilled out of conventional petrographic thin-sections, were ion-milled to electron transparency and were investigated by standard transmission electron microscopy (TEM) techniques (e.g. Griffin et al., 1985) and chemical analysis (Mellini and Menichini, 1985). It was found that K-bearing pyroxene in this assemblage is uncommon and that a K-free aegirine occurs closely intermixed with a K-bearing, amorphous phase. No evidence of crystallinity was found for this phase by electron diffraction. Therefore, in the light of the available evidence, this phase was considered to be a glass. The typical textural relationships between crystal and glass are shown in Fig. 1, where a crystalline matrix is intersected by two glassy lamellae, oriented edge on, and varying in thickness between 10^2–10^3Å (Fig. 1a). Both continuous and truncated lamellae were observed. More substantial glassy domains within aegirine were also observed with wedge-shaped glassy lamellae propagating from these domains toward the inner pyroxene (Fig. 1b). These textural relationships are reminiscent of the results obtained by Vaughan and Kohlstedt (1982) in their study of hot-pressed, olivine-basalt aggregates, especially from their shorter-time experiments. According to these results, the microstructures of the olivine-quenched melt aggregates evolved from an irregular glass distribution with narrow glassy layers at grain boundaries toward confinement of the glass to texturally equilibrated triple-junctions. This suggests that, in the present case, the natural aegirine–glass system did not achieve textural equilibrium.

It is noteworthy that the investigated aegirine displays almost identical orientations on the two sides of the grain boundaries, as indicated by electron diffraction and contrast features such as thickness fringes and curved boundaries (see also Fig. 1) This 'structural continuity' across grain boundaries excludes the possibility that the pyroxene was produced by random growth of microcrystalline aegirine under rapid cooling conditions, as occasionally observed in high-temperature augites from volcanic parageneses. On the contrary, it indicates conditions compatible with fast crystal growth, potentially capable of enclosing surrounding melt during growth.

The chemical composition of the investigated aegirine, as determined by TEM/EDS microanalysis is:

$$[Na_{0.63}Fe^{2+}_{0.62}Ca_{0.41}Mg_{0.34}]_{\Sigma2}[Si_{1.90}Ti_{0.10}]_{\Sigma2}O_6$$

While neither K nor Al were detected, these two elements are concentrated in the adjacent
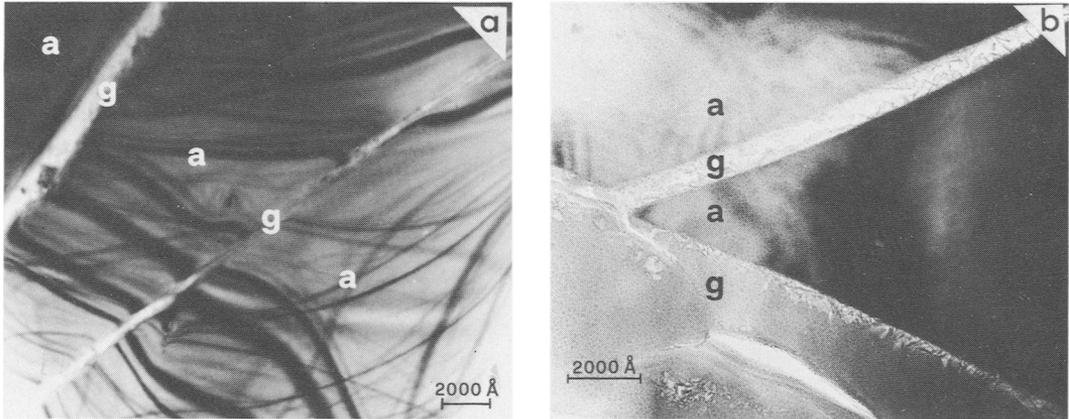
FIG. 1(a) TEM image of glassy lamellae (g) within aegirine (a). (b) Wedge-shaped glassy lamella (g) infiltrating aegirine (a) from relatively large glassy domain in the lower left corner.

Table2.TEM/EDS microanalysis of glass in titanian aegirine from 70-1039, on a fluorohydroxyl-free basis, expressed on the basis of two silicon atoms.Analyst: M. Mellini.

Cations	1	2	3	4	mean(4)
Si	2.00	2.00	2.00	2.00	2.000
Ti	0.06	0.08	0.12	0.08	0.085
Al	0.56	0.66	0.60	0.92	0.685
*Fe^{2+}	0.40	0.40	0.40	0.46	0.415
Mg	0.32	0.88	1.26	1.44	0.975
Ca	0.34	0.32	0.22	0.18	0.265
K	0.30	0.30	0.26	0.32	0.295
Σ	3.98	4.64	4.86	5.40	4.720

Table3.Partial chemical analysis of glass in titanian aegirine from 70-1039 (Table2), recalculated to 16 cations, and compared to the coexisting amphibole and other amphiboles from similar parageneses. Amphibole structural formulae,expressed in term of cations per formula unit, a.f.u.,were calculated according to Leake(1978).

Cations	1	2 (core)	3 (rim)	4	5	6	7 (gm)
Si	6.78	7.62	7.69	7.53	7.79	7.51	7.62
Ti	0.29	0.28	0.79	0.36	0.26	0.40	0.70
Al	2.32	0.33	0.26	0.36	0.16	1.40	1.19
*Fe^{2+}	1.41	1.55	1.77	1.83	1.90	0.37	1.03
Mg	3.30	3.11	2.25	2.84	2.85	2.25	0.85
Ca	0.90	0.80	0.08	0.94	0.86	1.91	0.30
Na	<0.3	1.97	2.86	1.64	1.63	0.30	0.85
K	1.00	0.45	0.21	0.40	0.42	0.79	1.77
Σ	16.00	16.11	15.91	15.90	15.87	14.93	14.31
T	8.00	8.00	8.00	8.00	8.00	8.00	8.00
(M1+M2+M3)	5.00	4.89	4.76	4.92	4.96	3.93	3.39
M4	1.97	2.00	2.00	2.00	2.00	2.00	2.00
A	1.02	1.22	1.15	0.98	0.91	1.00	0.92
mg	0.70	0.58	0.56	0.61	0.60	0.85	0.45

*Fe^{2+}:total Fe as Fe^{2+}
mg:$Mg/(Mg+Fe^{2+})$

1. Glass in titanian aegirine from 70-1039.Analyst:M.Mellini
2,3.K-richterites from 70-1038(Ferguson,1978) F=1.00 and 0.82 a.f.u.,respectively.
4,5.Mg-arfvedsonites from pegmatoid in the Cosgrove leucitite (Birch,1978).
6. K-richterite from the Gaussberg-Antarctica leucitite (BMR77284755)
   F=0.054 a.f.u.;OH=1.95 a.f.u.Analyst:A.K.Ferguson.
7. K-richterite from Gaussberg-Antarctica leucitite pegmatoid(N4881141).Ba=0.051 a.f.u. . Analyst:A.Cundari.

glass (Table 2). The chemistry of the latter is variable, particularly with respect to Ca and Mg, probably due, at least in part, to possible contamination from fine-scale glass/pyroxene intergrowth and/or poor glass contrast within aegirine. However, the recorded glass composition essentially reflects lack of chemical equilibrium within the glass, and, presumably, within the liquid from which the glass derived.

The average composition of the glass, recalculated on the basis of 16 cations and 22 oxygens, is very close to that of the coexisting amphibole and other amphiboles from similar parageneses (Table 3). Notably, the F content of the investigated richterites is up to 1.00 a.f.u.

Concluding remarks

The investigated titanian aegirine is a composite system consisting of clinopyroxene + glass. The latter may represent potential amphibole of richteritic composition which failed to develop a crystalline phase. Therefore, the presence of K in clinopyroxene compositions obtained by conventional electron microprobe analysis, as reported by Jaques (1987) and Harlow and Dowty (1982), may derive from a distinct phase(s) crystallographically independent from the host clinopyroxene (Buseck and Veblen, 1978; Veblen and Buseck, 1981).

The close association of aegirinic pyroxene and amphibole in alkaline assemblages is character-

ized by distinct crystallization paths showing a pyroxene 'compositional gap' in the system Na–Mg–ΣFe(Ca) filled by amphibole compositions (Ferguson, 1978). These paths imply unique crystallization conditions for each pyroxene–amphibole paragenesis and support the role of F in stabilizing richterite in the investigated pegmatoid (Ferguson, 1978). They relate to the strong Na-enrichment, relative to K, in the BEH leucitite crystallization residuum, where the K/Na ratio is reduced by a factor of 0.6 that of the parental leucitite (BEH-D; K/Na = 1.5. Cundari, 1973; Table II). The pyroxene trend toward aegirine, with enrichment in Ca, K and Al in the residual liquid, is consistent with the composition of the aegirine intracrystalline glass. Therefore, this glass probably represents a primary, metastable phase, derived from the leucitite liquid line of thermal descent by differentiation. After an initial slow-cooling rate, which promoted diopside phenocrystal growth, more rapid cooling of the pegmatoid residuum ensued, resulting in the sporadic development of aegirine and richterite, notably as diopside pseudomorphs. Possible loss of fluorohydroxyl components and/or sluggish diffusion of these in the relatively more viscous residuum would account for 'freezing in' the aegirine–richterite paragenesis.

The crystallization temperature of the investigated aegirine is not known, but it must be close to that of the solidus of the host rock, roughly estimated at c. 700 °C (Cundari, 1973). The observed glass in aegirine is, therefore, interpreted as trapped residual liquid from aegirine crystallization, formed under conditions unfavourable to amphibole crystallization. In contrast, the pyroxene 'compositional gap' would correspond to a near-equilibrium amphibole crystallization under favourable growth conditions. It should be noted that amorphous substance may be found also in metamict and diaplectic minerals and has been reported as replacement of cordierite (Haslam, 1983). While the detailed nature of the process responsible for this substance in the present paragenesis is beyond the scope of this paper, we believe that it probably reflects an extreme case in the kinetics of the structural change of biopyriboles (Akai, 1982). Development of submicroscopic amphibole in pyroxene

has been reported from a variety of parageneses and explained in terms of different mechanisms, essentially replacement and exsolution (e.g. Veblen and Buseck, 1981). The present occurrence may be considered as a special intergrowth defect, where K is not bonded by the pyroxene lattice and is, therefore, independent of the pyroxene stoichiometry. Consequently, the geochemical role of the pyroxene as a predictable K carrier is suspect and may not be generalized. On the other hand, K-richterite coexisting with diopside would be stable at least to 30 kbar under water saturated conditions (Kushiro and Erlank, 1970) and may play an important role in the genesis of K-rich, mantle-derived melts like leucitites (*sensu stricto*) and lamproites.

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