

Crystal structure and crystal chemistry of fluoro-potassic-magnesio-arfvedsonite from Monte Metocha, Xixano region, Mozambique, and discussion of the holotype from Quebec, Canada

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ABSTRACT

Fluoro-potassic-magnesio-arfvedsonite, ideally ${}^A K {}^B Na_2 {}^C (Mg_4 Fe^{3+}) {}^T Si_8 O_{22} {}^W F_2$, has been found in a dyke ~25 km southwest of Monte Metocha, Xixano region, northeastern Mozambique. Fluoro-potassic-magnesio-arfvedsonite and low sanidine form a fine-grained mafic, ultrapotassic, peralkaline igneous rock without visible phenocrysts. The amphibole is brittle, has a Mohs hardness of 6 and a splintery fracture; it is non-fluorescent with perfect {110} cleavage and no observable parting, and has a calculated density of 3.174 g cm^{-3} . In plane-polarized light, it is pleochroic, X = pale grey-green, Y = blue-green, Z = pale grey; $X \wedge c = 23.6^\circ$ (in β obtuse), $Y \parallel b$, $Z \wedge c = 66.4^\circ$ (in β acute). Fluoro-potassic-magnesio-arfvedsonite is biaxial negative, $\alpha = 1.652(2)$, $\beta = 1.658(2)$, $\gamma = 1.660(2)$; $2V_{\text{obs}} = 22.5(7)^\circ$, $2V_{\text{calc}} = 30.2^\circ$. The unit-cell dimensions are $a = 9.9591(4)$, $b = 17.9529(7)$, $c = 5.2867(2) \text{ \AA}$, $\beta = 104.340(1)^\circ$, $V = 919.73(10) \text{ \AA}^3$, $Z = 2$. The nine strongest X-ray diffraction lines in the experimental powder pattern are: [d in $\text{Å}(I)(hkl)$]: 2.716(100)(151), 3.410(70)(131), 8.475(50)(110), 3.178(50)(310), 3.309(30)(240), 2.762(20)($\bar{3}31$), 2.549(20)(260), 2.351(10)($\bar{3}51$), 2.269(10)(331). Electron microprobe analysis gave: SiO_2 54.25, Al_2O_3 0.03, TiO_2 1.08, FeO 6.69, Fe_2O_3 8.07, MgO 13.99, MnO 0.32, ZnO 0.05, CaO 1.16, Na_2O 6.33, K_2O 5.20, F 2.20, H_2O_{calc} 0.74, sum 99.18 wt.%. The formula unit, calculated on the basis of 24 (O,OH,F) with (OH+F) = 2–(2 Ti), is ${}^A K_{0.98} {}^B (Na_{1.81} Ca_{0.18})_{\Sigma 1.99} {}^C (Mg_{3.07} Fe_{0.83}^{2+} Mn_{0.04} Al_{0.01} Fe_{0.90}^{3+} Ti_{0.12} Zn_{0.01})_{\Sigma=4.98} {}^T Si_8 O_{22} {}^W [F_{1.03} (OH)_{0.73} O_{0.24}]_{\Sigma 2.00}$ and confirms the usual pattern of cation order in the amphibole structure. The presence of a significant oxo component (locally balanced by Ti at the $M(1)$ site) is related to the crystallization conditions. The presence of Fe^{3+} at the T sites, originally suggested for the holotype specimen, is discounted for this amphibole composition.

KEYWORDS: fluoro-potassic-magnesio-arfvedsonite, electron-microprobe analysis, optical properties, crystal-structure refinement, Mount Metocha, Xixano region, Mozambique.

Introduction

THE fluoro-potassic-magnesio- analogue of arfvedsonite, $NaNa_2(Fe_4^{2+}Fe^{3+})Si_8O_{22}(OH)_2$, was identi-

fied for the first time by Hogarth and Lapointe (1984, sample 300) from fenitized Mesoproterozoic metasediment near Cantley, Québec, Canada. A few years later, Hogarth *et al.* (1987) found several amphibole samples with nearly the same composition in Proterozoic metasedimentary rocks of the Gatineau-Perkins area, Quebec. In particular, sample 1093B from the

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Gatineau area contained prismatic F- and K-rich magnesio-arfvedsonite crystals, and those authors submitted a new-mineral proposal for “potassium fluor-magnesio-arfvedsonite” to the Commission for New Minerals and Mineral Names of the International Mineralogical Association (IMA-CNMMN) (85-023) which was accepted. Hogarth (2006) noted that a formal description of the new mineral had never been published, he stated that “petrological, optical, physical-property, compositional, Mössbauer, X-ray and unit-cell data for the type specimen were given in Hogarth *et al.* (1987, sample 1093B)”, and updated the mineral name according to Leake *et al.* (2003) and Burke and Leake (2004).

Fluoro-potassic-magnesio-arfvedsonite (the second occurrence) was found by Robinson *et*

al. (2008, sample AS04-36) in a dyke cutting Neoproterozoic metamorphosed sedimentary and igneous rocks from northeastern Mozambique. This gave the present authors the opportunity to characterize the crystal structure and site occupancies of fluoro-potassic-magnesio-arfvedsonite, a topic of particular interest as recalculation of the chemical analysis of Hogarth *et al.* (1987) on the basis of 24(O,OH,F) results in a significant amount of Fe³⁺ at the T sites (Table 1), an unusual feature that has never been confirmed by crystal-structure refinement in amphiboles. A complete description of fluoro-potassic-magnesio-arfvedsonite from Mozambique is reported here and compared to the available data for the holotype material from Quebec, Canada.

TABLE 1. Chemical composition and unit formula for fluoro-potassic-magnesio-arfvedsonite.

	— This work —		Holotype material ¹	End member		This work	Holotype material ¹	End member
	Range (wt.%)	(wt.%)	(wt.%)	(wt.%)		(a.p.f.u.)	(a.p.f.u.)	(a.p.f.u.)
SiO ₂	53.94–54.63	54.25	54.80	56.37	Si	8.00	7.85	8.00
TiO ₂	0.77–1.47	1.08	0.15	—	Al	—	0.03	—
Al ₂ O ₃	0.00–0.05	0.03	0.17	—	Fe ³⁺	—	0.11	—
Cr ₂ O ₃		n.a.	0.07	—	Cr	—	0.01	—
Fe ₂ O ₃ *		8.07	9.84	9.36	Sum T	8.00	8.00	8.00
FeO*	13.23<FeO _{tot} <14.52	6.69	2.61	—	Ti ⁴⁺	0.12	0.02	—
MnO	0.23–0.39	0.32	0.11	—	Al	0.01	0.00	—
ZnO	0.05	0.05	n.a.	—	Fe ³⁺	0.90	0.95	1.00
MgO	13.51–14.63	13.99	17.44	18.90	Fe ²⁺	0.83	0.31	—
BaO+SrO		n.a.	0.05	—	Mg	3.07	3.72	4.00
CaO	1.02–1.31	1.16	2.37	—	Mn	0.04	0.00	—
Na ₂ O	6.19–6.42	6.33	6.37	7.27	Zn	0.01	—	—
K ₂ O	5.11–5.34	5.20	3.44	5.52	Sum C	4.98	5.00	5.00
H ₂ O**		0.74	0.99	—	Ca	0.18	0.36	—
F	1.95–2.36	2.20	2.33	4.46	Na	1.81	1.62	2.00
–O=F		–0.93	–0.98	–1.88	Mn	0.00	0.02	—
Total		99.18	99.76	100.00	Sum B	1.99	2.00	2.00
					K	0.98	0.63	1.00
Calculated site-scattering values					Na	0.00	0.15	—
A cations		18.62	13.62	19.00	Sum A	0.98	0.78	1.00
B cations		23.51	25.52	22.00	F	1.03	1.06	2.00
C cations		85.89	77.84	74.00	OH	0.73	0.94	—
T cations		112.00	113.39	112.00	O ^{2–}	0.24	0.00	—
W anions		17.03	17.06	18.00	Sum W	2.00	2.00	2.00

¹ Sample 1093B (Hogarth *et al.* 1987)

* for this work, the FeO:Fe₂O₃ ratio was calculated from SREF results; for holotype material: FeO was determined by titration

** for this work: calculated based on 24 (O, OH, F) with (OH + F) = 2–(2 × Ti) a.p.f.u.; for holotype material: calculated based on 13 (T + C) and 2 (F, Cl, OH).

Occurrence and sample description

During regional geological mapping of Neoproterozoic metamorphosed sedimentary and igneous rocks in northeastern Mozambique (Bingen *et al.* 2006), sample AS04-36 was collected, characterized as a complex mafic ultrapotassic peralkaline igneous rock, and classified as a high-silica lamproite. Its complete petrological description was given by Robinson *et al.* (2008). In particular, electron microprobe analysis showed that the composition of the amphiboles spans the compositional space defined by three end-members with ideal formulae: ${}^A\text{K}{}^B\text{Na}_2{}^C(\text{Mg}_4\text{Fe}^{3+}){}^T\text{Si}_8\text{O}_{22}{}^W\text{F}_2$ (fluoro-potassic-magnesio-arfvedsonite), ${}^A\text{K}{}^B\text{Na}_2{}^C(\text{Mg}_3\text{Fe}^{3+}\text{Ti}){}^T\text{Si}_8\text{O}_{22}{}^W\text{O}_2$ (to be named “potassic-obertiite” according to the present classification scheme) and ${}^A\text{K}{}^B\text{Na}_2{}^C(\text{Mg}_2\text{Fe}_3^{3+}){}^T\text{Si}_8\text{O}_{22}{}^W\text{O}_2$ (to be named “magnesio-ferriungarettiite”). Due to their very peculiar compositions, the amphiboles were checked system-

atically by single-crystal X-ray diffraction and structure refinement.

In sample AS04-36, amphibole and low sanidine form a fine-grained rock with no phenocrysts. The smallest amphibole crystals are platy limpid prisms of fluoro-potassic-magnesio-arfvedsonite $\sim 0.02 \text{ mm} \times 0.04 \text{ mm} \times 0.10 \text{ mm}$ in size, and with good X-ray diffraction quality. Associated minerals are Fe^{3+} -bearing low sanidine, Sr-bearing fluor-apatite, rutile, Sr-bearing baryte, quartz, zircon and hematite.

Physical and optical properties

The physical and optical properties for fluoro-potassic-magnesio-arfvedsonite from Mozambique are reported in Table 2 and compared to those of sample 1093B from Quebec, which is the holotype for this mineral species (Hogarth, 2006). The amphibole from this second occurrence is enriched in Fe^{2+} (0.83 vs. 0.31 a.p.f.u., atoms per formula unit) and depleted

TABLE 2. Physical and optical properties for the fluoro-potassic-magnesio-arfvedsonite.

	This work	Holotype material ¹
Colour	Bluish-grey	Pale greyish blue
Lustre	Vitreous	—
Streak	White	—
Fluorescence	None (long UV, short UV)	—
Hardness	6	6
Tenacity	Brittle	—
Fracture	Splintery	—
Cleavage	{110}perfect	{110}perfect
Forms	{110} and {100}	Elongated parallel to <i>c</i>
$D_{\text{calc.}}$ (g cm^{-3})	3.174	—
$D_{\text{meas.}}$	—	3.14
Pleochroism	<i>X</i> = pale grey-green	<i>X</i> = blue
	<i>Y</i> = blue-green	<i>Y</i> = blue-violet
	<i>Z</i> = pale grey	<i>Z</i> = green
Orientation	$X \wedge c$ 23.6 (in β obtuse)	—
	$Y \parallel b$	$Y \parallel b$
	$Z \wedge c$ 66.4 (in β acute)	$Z \wedge c$ 54 (in β obtuse)
Optic sign	(—)	(—)
α (Na light, $\lambda = 589.9 \text{ nm}$)	1.652(2)	1.631(2)
β (Na light, $\lambda = 589.9 \text{ nm}$)	1.658(2)	1.638(2)
γ (Na light, $\lambda = 589.9 \text{ nm}$)	1.660(2)	1.642(2)
$2V_{\text{obs}} - 2V_{\text{calc}}$ (°)	22.5(7) — 30.2	71–74.2
Absorption	$X < Z < Y$	$X \approx Y > Z$
Dispersion	$r < v$ strong	$r < v$ weak
Compatibility index	0.007 (superior)	0.023 (excellent)

¹ Sample 1093B (Hogarth *et al.*, 1987)

in C_{Mg} (3.07 vs. 3.73 a.p.f.u.) relative to the holotype sample, accounting for the observed differences in refraction indices and in other optical properties.

Chemical composition

The crystal of fluoro-potassic-magnesio-arfvedsonite used for the crystallographic study was analysed by electron microprobe using a Cameca SX-100 operating in wavelength-dispersive mode with excitation voltage 15 kV, specimen current 10 nA, beam diameter 5 μm , peak-count time 20 s and background-count time 10 s. The following reference materials and crystals were used for $K\alpha$ X-ray lines: Si: diopside, TAP; Ca: diopside, LPET; Ti: titanite, LPET; Fe: fayalite, LLiF; Mn: spessartine, LLiF; Cr: chromite, LLiF; Mg: forsterite, LTAP; Al, andalusite, TAP; K: orthoclase, LPET; Na: albite, TAP; F: fluorioriebeckite, LTAP; Zn: gahnite, LLiF. Data reduction was carried out using the 'PAP' $\phi(\rho Z)$ procedure of Pouchou and Pichoir (1985). The average of 10 analyses is given in Table 1, together with the chemical analysis of the holotype and the oxide composition of the ideal end-member formula: ${}^A\text{K}{}^B\text{Na}_2{}^C(\text{Mg}_4\text{Fe}^{3+}){}^T\text{Si}_8\text{O}_{22}{}^W\text{F}_2$. The crystal analysed is somewhat zoned in Ti and F; however, the average analysis corresponds closely to the refined site-scattering (ss) values (Table 7). The Fe^{2+} - Fe^{3+} ratio and the H_2O content were derived from the results of crystal-structure refinement. The oxo component (O^{2-} at the O(3) site) was estimated based on the

Ti content (0.12 a.p.f.u.), as suggested by structure refinement and by the paragenesis, where the other two corners of the amphibole compositional space are oxo-amphiboles. There is no Fe^{3+} or Cr occurring as the T cation, and the stoichiometry is closer to that of the end-member than the holotype sample. The compatibility index is 0.007 (superior).

X-ray diffraction and crystal-structure refinement

The powder-diffraction pattern was recorded from a small fragment on a 114.6 mm Debye-Scherrer powder camera with a Gandolfi attachment and Ni-filtered Cu- $K\alpha$ X-radiation. Peak intensities were estimated by eye from the darkening on the film, and were not corrected for shrinkage; no internal standard was used. Cell dimensions refined from the corrected d values are as follows: $a = 10.014(17)$, $b = 17.99(4)$, $c = 5.324(24)$ \AA , $\beta = 104.3(2)^\circ$, $V = 929.3(31)$ \AA^3 . The indexed powder pattern is given in Table 3 where the observed intensities from the sample from Mozambique are also compared to those measured on the type material (Hogarth *et al.*, 1987) and to powder-diffraction intensities simulated from the results of single-crystal Structure REfinement (SREF). The amphiboles in this rock are extremely heterogeneous, which accounts for the lack of accord between unit-cell dimensions and relative intensities obtained from Gandolfi and CCD single-crystal diffraction on different crystals.

TABLE 3. The most intense X-ray powder-diffraction data for fluoro-potassic-magnesio-arfvedsonite.

I_{obs}^1	I_{HOLO}^2	I_{SREF}^1	d_{obs} (\AA)	d_{calc} (\AA)	$h k l$
50	58	58	8.475	8.539	1 1 0
70	13	81	3.410	3.412	1 3 1
30	28	43	3.309	3.298	2 4 0
50	100	60	3.178	3.183	3 1 0
20	9	43	2.762	2.759	$\bar{3}$ 3 1
100	19	100	2.716	2.718	1 5 1
20	5	70	2.549	2.551	2 6 0
10	9	37	2.351	2.352	$\bar{3}$ 5 1
10	3	32	2.269	2.290	3 3 1

¹ I_{obs} and I_{SREF} = relative intensities estimated on a Debye-Scherrer Cu- $K\alpha$ powder camera with Gandolfi attachment and simulated from the structure refinement results for the sample of this work

² I_{HOLO} = relative intensities for the holotype sample (Hogarth *et al.* 1987) measured with a Cu- $K\alpha$ powder diffractometer

Only small single crystals show satisfactory optical and diffraction properties; the crystal selected for data collection and structure refinement was $\sim 0.02 \text{ mm} \times 0.04 \text{ mm} \times 0.10 \text{ mm}$ in size. Data collection carried out using a Bruker-AXS Smart-Apex CCD-based diffractometer with graphite-monochromatized Mo- $K\alpha$ X-radiation. Omega-rotation frames (scan width 0.3° , scan time 30 s, sample-to detector distance 50 mm) were processed using the *SAINTE* software (Bruker, 2003) and intensities were corrected for Lorentz and polarization effects; absorption effects were evaluated empirically using the *SADABS* software (Sheldrick, 1998) and an absorption correction was applied to the data. Accurate unit-cell dimensions were calculated by least-squares refinement of the positions of 5475 reflections with $I_o > 10\sigma(I)$ in the 2θ range $2-70^\circ$. Reflections with $I_o > 3\sigma(I)$ were considered as observed during unweighted full-matrix least-squares refinement on F using a program written at CNR-IGG-PV to deal with complex solid solutions. Scattering curves for fully ionized chemical species were used at sites where chemical substitutions occur; neutral vs. ionized scattering curves were used at the T and anion sites [except O(3)]. The unit-cell dimensions for the Mozambique and Quebec samples are compared in Table 4. Table 5 reports atom coordinates and anisotropic-displacement parameters, and Table 6 reports selected interatomic distances and parameters related to the conformation of the double-chain of tetrahedra. The site populations derived from site-scattering results and crystal-chemical analysis (Oberti *et al.*, 2007)

are reported in Table 7. The observed and calculated structure factors have been deposited with the Principal Editor of *Mineralogical Magazine*, and are available from www.minersoc.org/pages/e_journals/dep_mat.html.

Crystal chemistry and discussion

Inspection of the unit-cell parameters (Table 4) shows: (1) a longer a edge in the Mozambique sample, in accordance with its larger K content; (2) nearly identical b edges, which implies that the effect of the greater Fe/Mg ratio in this sample is opposite but complementary to that of Ti; (3) nearly identical c edges.

Hogarth *et al.* (1987) published a ^{57}Fe Mössbauer spectrum of holotype fluoro-potassic-magnesio-arfvedsonite in which they show a doublet (labelled 'a') which they assigned to tetrahedrally coordinated Fe^{3+} , and that corresponded, for sample 1093B, to an occupancy of 0.11 Fe^{3+} . Preferred orientation in a sample commonly results in an asymmetric distribution of intensity between high- and low-velocity components of a Mössbauer spectrum, making it easy to fit non-existent doublets under a complex low-velocity envelope. Moreover, there are no inflection points in the envelope that correspond to the maxima of doublet a in the spectrum of Hogarth *et al.* (1987). Therefore, we contend that this doublet is an artifact of the fitting process.

Observed mean $\langle T-O \rangle$ distances, distortion of the tetrahedra and refined B_{eq} values for the Mozambique sample show that the T sites are occupied solely by Si (Hawthorne and Oberti,

TABLE 4. Unit-cell dimensions and miscellaneous information for fluoro-potassic-magnesio arfvedsonite.

	This work	Holotype material ¹	
a (Å)	9.9591(4)	9.906(1)	
b (Å)	17.9529(7)	17.953(2)	
c (Å)	5.2867(2)	5.287(1)	
β (°)	104.340(1)	104.3(1)	
V (Å ³)	915.78(7)	911.1(5)	
2θ range (°)	2–70	No. of unique reflections	2066
Space group	$C2/m$	No. of observed reflections [$I_o > 3\sigma I$]	1877
Z	2	R_{merge} %	1.40
D_{calc} (g cm ⁻³)	3.174	$R_{\text{obs}}\%$ – $R_{\text{all}}\%$	2.20 – 2.61
Largest diff. peak/hole (e Å ⁻³)	0.38/–0.31	GoF	0.989

¹ Sample 1093B (Hogarth *et al.* 1987), calculated from powder-diffraction data.

TABLE 5. Atomic coordinates, refined site-scattering values (ss, e.p.f.u.), and atomic-displacement parameters (B_{eq} , \AA^2 ; $\beta_{ii} \times 10^4$) for fluoro-potassic-magneso-arfvedsonite.

Atom	ss (e.p.f.u.)	x/a	y/b	z/c	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)		0.1098 (1)	0.0877 (1)	0.2161 (2)	0.67(2)	14	6	64	-1	8	-1
O(2)		0.1181 (1)	0.1696 (1)	0.7305 (2)	0.68(2)	16	6	63	0	6	-1
O(3)	17.18(4)	0.1048 (1)	0	0.7119 (2)	0.90(2)	26	7	80	-	9	-
O(4)		0.3608 (1)	0.2491 (1)	0.8014 (2)	0.89(2)	31	5	80	-5	15	-1
O(5)		0.3441 (1)	0.1284 (1)	0.0886 (2)	0.76(2)	19	8	62	0	12	8
O(6)		0.3393 (1)	0.1189 (1)	0.5877 (2)	0.79(2)	22	7	54	0	8	-7
O(7)		0.3307 (1)	0	0.3056 (2)	0.84(2)	24	4	114	-	16	-
T(1)		0.2758 (1)	0.0858 (1)	0.2976 (1)	0.47(1)	14	4	41	0	6	-1
T(2)		0.2853 (1)	0.1714 (1)	0.8040 (1)	0.47(1)	14	4	41	-1	7	-1
M(1)	29.86(11)	0	0.0894 (1)	1/2	0.76(1)	22	7	63	-	13	-
M(2)	41.13(8)	0	0.1825 (1)	0	0.57(1)	16	4	55	-	8	-
M(3)	13.82(3)	0	0	0	0.58(1)	20	4	46	-	6	-
M(4)	24.19(11)	0	0.2775 (1)	1/2	1.35(1)	43	8	164	-	48	-
A	2.82(3)	0	1/2	0	1.09(7)	36	13	34	-	24	-
A(m)	14.88(5)	0.0313 (1)	1/2	0.0701 (2)	1.59(3)	56	10	195	-	79	-
H	0.80(1)	0.188(7)	0	0.740 (13)	0.80(8)	-	-	-	-	-	-

FLUORO-POTASSIC-MAGNESIO-ARFVEDSONITE

TABLE 6. Selected interatomic distances (Å) and angles (°) in fluoro-potassic-magnesio-arfvedsonite.

$T(1)-O(1)$	1.603(1)	$T(2)-O(2)$	1.614(1)
$T(1)-O(5)$	1.626(1)	$T(2)-O(4)$	1.586(1)
$T(1)-O(6)$	1.621(2)	$T(2)-O(5)$	1.663(1)
$T(1)-O(7)$	<u>1.631(1)</u>	$T(2)-O(6)$	<u>1.670(1)</u>
$\langle T(1)-O \rangle$	1.620	$\langle T(2)-O \rangle$	1.633
$M(1)-O(1) \times 2$	2.064(1)	$M(2)-O(1) \times 2$	2.186(1)
$M(1)-O(2) \times 2$	2.057(1)	$M(2)-O(2) \times 2$	2.073(1)
$M(1)-O(3) \times 2$	<u>2.083(1)</u>	$M(2)-O(4) \times 2$	<u>1.952(1)</u>
$\langle M(1)-O \rangle$	2.068	$\langle M(2)-O \rangle$	2.070
$M(3)-O(1) \times 4$	2.088(1)	$M(4)-O(2) \times 2$	2.431(1)
$M(3)-O(3) \times 2$	<u>2.048(2)</u>	$M(4)-O(4) \times 2$	2.405(1)
$\langle M(3)-O \rangle$	2.075	$M(4)-O(5) \times 2$	2.884(1)
$A-O(5) \times 4$	2.882(1)	$M(4)-O(6) \times 2$	<u>2.569(1)</u>
$A-O(6) \times 4$	3.185(1)	$\langle^{[6]}M(4)-O \rangle$	2.468
$A-O(7) \times 2$	<u>2.608(1)</u>	$\langle^{[8]}M(4)-O \rangle$	2.573
$\langle A-O \rangle$	2.948	$A(m)-O(5) \times 2$	2.982(1)
$O(3)-H$	0.809(1)	$A(m)-O(5) \times 2$	2.842(1)
$T(1)-O(5)-T(2)$	136.1(1)	$A(m)-O(6) \times 2$	2.887(1)
$T(1)-O(6)-T(2)$	137.6(1)	$A(m)-O(7)$	2.603(1)
$T(1)-O(7)-T(1)$	141.5(1)	$A(m)-O(7)$	3.246(1)
$O(5)-O(6)-O(5)$	172.3(1)	$A(m)-O(7)$	<u>2.681(1)</u>
$O(6)-O(7)-O(6)$	110.8(1)	$\langle A(m)-O \rangle$	2.883

2007; Oberti *et al.*, 2007). The equality of the c dimension in the two samples is not compatible with the presence of ${}^T\text{Fe}^{3+}$ in the holotype sample, and thus the conclusion of Oberti *et al.* (2007) that

${}^{[4]}\text{Fe}^{3+}$ is incompatible with the amphibole structure still holds.

The same argument holds for potassic-arfvedsonite (Pekov *et al.* 2004; sample 7 in Table 8), where

TABLE 7. Site populations, site scattering and mean bond lengths for fluoro-potassic-magnesio-arfvedsonite.

Site	Site population (a.p.f.u.)	Site scattering (e.p.f.u.)		Mean bond length (Å)	
		Refined	Calculated	Refined	Calculated
$T(1)$	4 Si			1.620	1.620
$T(2)$	4 Si			1.633	1.632
$M(1)$	1.54 Mg + 0.34 Fe^{2+} + 0.12 Ti	29.86	29.96	2.068	2.066
$M(2)$	0.90 Fe^{3+} + 0.68 Mg + 0.40 Fe^{2+} + 0.01 Al + 0.01 Zn	41.13	42.39	2.070	2.069
$M(3)$	0.87 Mg + 0.09 Fe^{2+} + 0.04 Mn	13.82	13.78	2.075	2.073
Σ C cations		84.81	86.13		
$M(4)$	1.81 Na + 0.19 Ca	24.19	23.71		
$A(m)$	0.98 K	17.70	18.62		
$O(3)$	1.03 F + 0.73 OH + 0.24 O	17.18	17.03		

TABLE 8. Monoclinic $C2/m$ amphiboles related to arfvedsonite.

Name	Potassic- arfvedsonite ¹	Li-rich fluoro- arfvedsonite ²	Fluoro-magnesian- arfvedsonite ³	Fluoro-potassic- magnesian- arfvedsonite ⁴	Li-rich magnesio- arfvedsonite ⁵	Potassic magnesio- arfvedsonite ⁶	Li-rich potassic arfvedsonite ⁷
IMA status ⁹	A	N	A	A	Rd	N	A
Ideal formula	$A^k B^l Na_2$ $C(Fe_4^{2+}Fe^{3+})$ $T^1 Si_8 O_{22}^w F_2$	$A^k Na^l Na_2$ $C(Fe_4^{2+}Fe^{3+})$ $T^1 Si_8 O_{22}^w F_2$	$A^k Na^l Na_2$ $C(Mg_4 Fe^{3+})$ $T^1 Si_8 O_{22}^w F_2$	$A^k K^l Na_2 C(Mg_4 Fe^{3+})$ $T^1 Si_8 O_{22}^w F_2$	$A^k Na^l Na_2$ $C(Mg_4 Fe^{3+})$ $T^1 Si_8 O_{22}^w (OH)_2$	$A^k B^l Na_2$ $C(Mg, Fe, Ti)_5$ $T^1 Si_8 O_{22}^w (OH)_2$	$A^k B^l Na_2$ $C(Fe_4^{2+}Fe^{3+})$ $T^1 Si_8 O_{22}^w (OH)_2$
a (Å)	10.007(2)	9.832(3)	9.81(9)	9.9591(4)	9.743(3)	—	10.002(2)
b (Å)	18.077(2)	17.990(7)	18.01(3)	17.9529(7)	17.874(6)	—	18.054(3)
c (Å)	5.332(1)	5.316(3)	5.28(1)	5.2867(2)	5.288(2)	—	5.319(1)
β (°)	104.101(7)	103.79(3)	103.8(2)	104.340(1)	103.81(2)	—	103.90(3)
V (Å ³)	935.5	913.2	905.9	919.73	894.4	—	932.4
¹ (K _{0.71} Na _{0.29}) (Na _{1.84} Ca _{0.16}) (Mg _{0.11} Mn _{0.13} Fe _{3.60} Fe _{0.92} Al _{0.14} Ti _{0.10}) (Si _{3.84} Al _{0.16}) ((OH) _{1.76} F _{0.10} O _{0.14} ⁻)							
² (K _{0.25} Na _{0.75}) Na ₂ (Li _{0.48} Fe _{2.84} Mn _{0.11} Zn _{0.05} Fe _{1.45} Ti _{0.07}) (Si _{7.89} Al _{0.11}) O ₂₂ (F _{1.35} (OH) _{0.65})							
³ (Na _{0.44} K _{0.29}) (Na _{1.57} Ca _{0.43}) (Mg _{1.14} Mn _{0.03} Fe _{0.60} Fe _{3.00} Ti _{0.05} Al _{0.09}) (Si _{7.85} Al _{0.15}) O ₂₂ (F _{1.22} (OH) _{0.78})							
⁴ K _{0.98} (Na _{1.81} Ca _{0.19}) (Mg _{3.09} Fe _{0.83} Mn _{0.04} Al _{0.01} Fe _{0.90} Ti _{0.12} Zn _{0.01}) T ₁ Si ₈ O ₂₂ ^w [F _{1.03} (OH) _{0.73} O _{0.24}]							
⁵ (Na _{0.48} K _{0.12}) (Na _{1.78} Ca _{0.17} Li _{0.05}) (Mg _{3.15} Mn _{0.13} Fe _{3.00} Fe _{0.90} Ti _{0.28} Ti _{0.05} Al _{0.10} Li _{0.30}) Si ₈ O ₂₂ (F _{1.53} (OH) _{0.43})							
⁶ (Na _{0.45} K _{0.69}) (Na _{1.86} Ca _{0.14}) (Mg _{2.80} Mn _{0.05} Fe _{1.69} Ti _{0.46}) (Si _{7.92} Ti _{0.08}) O ₂₂ (OH) ₂ based on 13 C+T cations							
⁷ (K _{0.67} Na _{0.22}) (Na _{1.95} Ca _{0.05}) (Fe _{3.29} Fe _{3.26} Li _{0.29} Mn sub>0.19Ti _{0.05} Zn _{0.02} Mg _{0.01})Σ5.11 (Si _{7.76} Fe _{0.13} Al _{0.11})O ₂₂ ((OH) _{1.8} F _{0.18})							

¹ Hawthorne (1976); ² Hawthorne *et al.* (1996); ³ Bazhenov *et al.* (2000), ucp from powder diffraction; ⁴ this work; ⁵ Hawthorne *et al.* (2008); ⁶ Hall (1982); ⁷ Pekov *et al.* (2004) A = approved, N = named (published without formal approval), Rd = redefinition approved (Nickel and Nichols, 2009).

calculation of the unit formula based on 13 C+T cations and 46 charges gave 0.13 Fe³⁺ a.p.f.u. at the T sites. In that case, however, Mössbauer analysis was not in accord with this assignment, and the *c* edge and <T(1)–O> distance reported by Pekov *et al.* (2004) indicate that ^TAl is ~0.25 a.p.f.u.

Inspection of the mean bond lengths (Table 6) shows an unusual sequence in the dimensions of the *M* octahedra: *M*(1) < *M*(2) < *M*(3), indicating an unusually small aggregate cation size at the *M*(1) site. This is accompanied by a large *B*_{eq} value at the *M*(1) site (Table 5: 0.76 vs. 0.57 and 0.58 Å² at *M*(2) and *M*(3), respectively). Together with a small *M*(1)–*M*(2) distance, these stereochemical parameters indicate the presence of a significant oxo-component at the O(3) site, which is locally balanced by Ti at *M*(1) (Oberti *et al.*, 1992, 2007; Hawthorne and Della Ventura, 2007). This is the only unusual feature of this amphibole composition, and is related to the crystallization conditions.

Another interesting feature of fluoro-potassic-magnesio-arfvedsonite from Mozambique is the distribution of the *A* cations, completely ordered at the *A*(*m*) site (the *A*(2/*m*) position has been inserted in the refined model simply to better reproduce the bilobate shape of the electron density, where the maxima occur at 0.44 Å from the centre of the *A* cavity). Indeed, the dominance of (F + O²⁻) at the O(3) site cancels any steric hindrance and repulsion between the K and H cations, and allows local order between F and K at the *A*(*m*) site (Hawthorne *et al.* 2008).

Site populations were calculated from the refined site-scattering values and are reported in Table 7, together with a comparison of observed and calculated site-scattering values and bond lengths (following a well established procedure reviewed by Oberti *et al.*, 2007). No anomalies in the cation order were observed.

Unit-cell parameters and crystal-chemical formulae for arfvedsonite-related amphiboles reported in the literature are listed in Table 8. These amphiboles are related to arfvedsonite by the homovalent substitutions ^AK → ^ANa, ^CMg → ^CFe²⁺, and ^WF → ^W(OH). As expected, based on present knowledge of amphibole crystal-chemistry, potassic species have longer *a* edges, and ^TAl-rich species have longer *c* edges. The presence of Li in arfvedsonitic compositions is related to smaller β angles (cf. Hawthorne and Oberti, 2007 for a review).

The potassic-magnesio-arfvedsonite reported by Hall (1982) in the Pendennis peralkaline

minette (having strong affinities with lamproitic lavas) has considerable Ti contents (2.32–4.74 wt.% oxide) and recalculation of the unit-formulae suggests the presence of a significant oxo-component.

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