

Fluoro-aluminoleakeite, $\text{NaNa}_2(\text{Mg}_2\text{Al}_2\text{Li})\text{Si}_8\text{O}_{22}\text{F}_2$, a new mineral of the amphibole group from Norra Kärr, Sweden: description and crystal structure

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ABSTRACT

Fluoro-aluminoleakeite, ideally ${}^A\text{Na}^B\text{Na}_2^C(\text{Mg}_2\text{Al}_2\text{Li})^T\text{Si}_8\text{O}_{22}\text{F}_2$, is a new mineral of the amphibole group from Norra Kärr, Sweden (IMA-CNMMNC 2009-012). It occurs in a proterozoic alkaline intrusion that mainly comprises a fine-grained schistose agpaitic nepheline-syenite (grennaite). Fluoro-aluminoleakeite occurs as isolated prismatic crystals 0.10–2 mm long in a syenitic matrix. Crystals are light greenish-blue with a greenish-blue streak. It is brittle, has a Mohs hardness of 6 and a splintery fracture; it is non-fluorescent with perfect {110} cleavage, no observable parting, and has a calculated density of 3.14 g cm^{-3} . In plane-polarized light, it is pleochroic, X = pale green, Y = dark green, Z = pale green; X \wedge a = 62.9° (in β obtuse), Y \parallel b. Fluoro-aluminoleakeite is biaxial negative, $\alpha = 1.632(1)$, $\beta = 1.638(1)$, $\gamma = 1.643(1)$; $2V_{\text{obs.}} = 98.0(4)^\circ$, $2V_{\text{calc.}} = 95.5^\circ$.

Fluoro-aluminoleakeite is monoclinic, space group $C2/m$, $a = 9.7043(5) \text{ \AA}$, $b = 17.7341(8) \text{ \AA}$, $c = 5.2833(3) \text{ \AA}$, $\beta = 104.067(4)^\circ$, $V = 882.0(2) \text{ \AA}^3$, $Z = 2$. The eight strongest X-ray diffraction lines in the powder-diffraction pattern are [d in Å , (I), (hkl)]: 2.687, (100), ($\bar{3}31$, 151); 4.435, (80), (021, 040); 3.377, (80), (131); 2.527, (60), ($\bar{2}02$); 8.342, (50), (110); 3.096, (40), (310); 2.259, (40), ($\bar{1}71$, $\bar{3}12$) and 2.557, (30), (002, 061). Analysis, by a combination of electron microprobe and crystal-structure refinement, gives SiO_2 58.61, Al_2O_3 7.06, TiO_2 0.32, FeO 3.27, Fe_2O_3 6.05, MgO 8.61, MnO 0.73, ZnO 0.43, CaO 0.05, Na_2O 9.90, K_2O 2.43, Li_2O 1.62, F 3.37, $\text{H}_2\text{O}_{\text{calc.}}$ 0.50, sum 101.08 wt.%. The formula unit, calculated on the basis of 24 (O,OH,F,Cl) p.f.u. with (OH) + F = 2 a.p.f.u., is ${}^A(\text{Na}_{0.65}\text{K}_{0.43})_{\Sigma=1.09}{}^B(\text{Na}_{1.99}\text{Ca}_{0.01})_{\Sigma=2.00}{}^C(\text{Mg}_{1.77}\text{Fe}_{0.38}^{2+}\text{Mn}_{0.09}\text{Zn}_{0.04}\text{Fe}_{0.63}^{3+}\text{Al}_{1.16}\text{Ti}_{0.03}\text{Li}_{0.90})_{\Sigma=5.00}{}^T\text{Si}_{8.00}\text{O}_{22}{}^W(\text{F}_{1.47}\text{OH}_{0.53})_{\Sigma=2.00}$. Crystal-structure analysis shows ${}^C\text{Li}$ to be completely ordered at the $M(3)$ site, and provided reliable site populations. Fluoro-aluminoleakeite is related to the end-member leakeite, ${}^A\text{Na}^B\text{Na}_2^C(\text{Mg}_2\text{Fe}_2^3\text{Li})^T\text{Si}_8\text{O}_{22}{}^W(\text{OH})_2$, by the substitutions ${}^C\text{Fe}^{3+} \rightarrow {}^C\text{Al}$ and ${}^W\text{F} \rightarrow {}^W(\text{OH})$.

KEYWORDS: Fluoro-aluminoleakeite, new amphibole, lithium, electron microprobe analysis, optical properties, crystal-structure refinement, Norra Kärr, Sweden.

Introduction

THE new amphibole species fluoro-aluminoleakeite was found during systematic work on localities where the presence of Li-rich amphiboles, possibly as new species, was considered

feasible. Lithium is a major constituent in amphibole (Oberti *et al.*, 2007). Amphiboles have the general formula $A_{0-1} B_2 C_5 T_8 O_{22} (\text{OH})_2$, where A are [8]- to [12]-coordinated cations, B are [6]- to [8]-coordinated medium (Li, Mg, Fe^{2+}) or large (Na, Ca) cations, C are [6]-coordinated cations, and T are [4]-coordinated cations. The occurrence of ${}^B\text{Li}$ has long been known in holmquistite [root composition $\text{Li}_2(\text{Mg}_3\text{Al}_2)\text{Si}_8\text{O}_{22}(\text{OH})_2$] and in clinholmquistite (Ginsburg, 1965); however, the latter was

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recently discredited by Oberti *et al.* (2005). C-group Li, strongly ordered at the $M(3)$ site, was first identified as a major constituent in leakeite [${}^A\text{Na}{}^B\text{Na}_2{}^C(\text{Mg}_2\text{Al}_2\text{Li})^T\text{Si}_8\text{O}_{22}{}^W(\text{OH})_2$, Hawthorne *et al.*, 1992] and kornite [${}^A\text{K}{}^B\text{Na}_2{}^C(\text{Mg}_2\text{Mn}_2{}^3+\text{Li})^T\text{Si}_8\text{O}_{22}{}^W(\text{OH})_2$, Armbruster *et al.*, 1993] and has since been found in the oxo-amphibole dellaventuraite [${}^A\text{Na}{}^B\text{Na}_2{}^C(\text{MgMn}_2{}^3+\text{LiTi}^{4+})^T\text{Si}_8\text{O}_{22}{}^W\text{O}_2$, Tait *et al.*, 2005]. More recently, identification of pedrizites [with the root composition ${}^A\text{Na}{}^B\text{Li}_2{}^C(\text{Mg}_2\text{Al}_2\text{Li})^T\text{Si}_8\text{O}_{22}{}^W(\text{OH})_2$; a recent review of the known compositions is given by Oberti *et al.* 2009] showed that Li can be both a B-group and a C-group cation, and that complete $\text{Na}_1\text{Li}_{-1}$ exchange is possible within the B group (Oberti *et al.*, 2003a). This latter point was investigated on different synthetic systems by Iezzi *et al.* (2003) and Della Ventura *et al.* (2005).

A significant amount of Li (1.15 wt.% Li_2O , corresponding to 0.65 atoms per formula unit, a.p.f.u.) was reported by Sundius (1945) in amphiboles from Norra Kärr (Sweden). Norra Kärr is the type locality of eckermannite [ideally ${}^A\text{Na}{}^B\text{Na}_2{}^C(\text{Mg}_4\text{Al})^T\text{Si}_8\text{O}_{22}{}^W(\text{OH})_2$], which has the charge arrangement most suitable for ${}^C\text{Li}$ incorporation in amphiboles according to the coupled exchange ${}^{M(2,3)}(\text{Mg}, \text{Fe}^{2+})_{-2}{}^{M(3)}\text{Li}_1{}^{M(2)}(\text{Al}, \text{Fe}^{3+})_1$ (Hawthorne *et al.*, 1994). Investigation of two rock samples from this locality, kindly provided by the well known mineral collectors Renato and Adriana Pagano (Cinisello Balsamo Italy), led to the discovery of the new species fluoro-aluminoleakeite (IMA-CNMNC 2009-012). This paper reports its characterization and mineral description.

Occurrence

The rock sample examined in this work (code 9717 in the Pagano's collection) was found at Norra Kärr, Gränna, Jönköping, Småland, Sweden (latitude $58^\circ 06'\text{N}$, longitude $14^\circ 40'\text{E}$). Citing Holtstam (1998), the Norra Kärr locality is a small oval (1200 m long and 400 m wide at the surface) Proterozoic alkaline intrusion, composed mainly of fine-grained schistose aegaitic nepheline-syenite (grennaite). The petrological and genetic aspects of Norra Kärr have been described extensively by Adamson (1944), von Eckermann (1968), Blaxland (1977) and Kramm and Koark (1988). In the sample studied here, isolated prismatic crystals 0.10–2 mm long occur in a syenitic matrix, together with albite and aegirine.

The refined and analysed crystal of this work has the code 1122 in the amphibole database of the CNR-IGG Pavia. Holotype fluoro-aluminoleakeite is deposited at the Department of Natural History, Royal Ontario Museum, Toronto, Ontario M5S 2C6, Canada, specimen number M53897.

Physical and optical properties

Fluoro-aluminoleakeite is light greenish-blue, and has a vitreous lustre. It has a greenish-blue streak and shows no fluorescence under long-wave or short-wave UV light. Fluoro-aluminoleakeite has a Mohs hardness of ~6 and is brittle with a splintery fracture; it has the characteristic perfect $\{110\}$ cleavage of monoclinic amphiboles, intersecting at $\sim 56^\circ$. The calculated density is 3.14 g cm^{-3} .

A spindle stage was used to orientate a crystal for measurement of refractive indices and 2V by extinction curves (Bartelmehs *et al.*, 1992). The optical orientation was determined by transferring the crystal from the spindle stage to a single-crystal diffractometer and measuring the relative axial relations by X-ray diffraction. In transmitted light, fluoro-aluminoleakeite is pleochroic with $X = \text{pale green}$, $Y = \text{dark green}$, $Z = \text{pale green}$, $X \wedge a = 62.9^\circ$ (in β obtuse) and $Y \parallel b$. It is biaxial negative with indices of refraction $\alpha = 1.632(1)$, $\beta = 1.638(1)$, $\gamma = 1.643(1)$ measured with gel-filtered Na light ($\lambda = 589.9 \text{ nm}$); $2V_{\text{obs.}} = 98.0(43)$, $2V_{\text{calc.}} = 96.9^\circ$.

Chemical composition

Fluoro-aluminoleakeite was analysed primarily by electron microprobe using a Cameca SX100 operating in wavelength-dispersive mode with an accelerating voltage of 15 kV, a probe current of 10 nA, a final beam diameter of 5 μm , peak-count times of 20 s and background-count times of 10 s. The following standards (X-ray lines and analysing crystals) were used: synthetic fluorophlogopite (F- $K\alpha$ on LTAP); jadeite (Na- $K\alpha$ on TAP); periclase (Mg- $K\alpha$ on LTAP); corundum (Al- $K\alpha$ on TAP); wollastonite (Si- $K\alpha$ on TAP, Ca- $K\alpha$ on LPET); orthoclase (K- $K\alpha$ on LPET); rutile (Ti- $K\alpha$ on LPET); Mn metal (Mn- $K\alpha$ on LLIF); magnetite (Fe- $K\alpha$ on LLIF); Zn metal (Zn- $K\alpha$ on LLIF).

Data reduction was carried out using the $\phi(\rho Z)$ procedure of Pouchou and Pichoir (1985). Lithium was derived by SREF (Structure REfinement, see section on crystal-structure refinement), and the $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio was derived

so as to attain charge balance with the calculated amount of Li_2O . The average of 10 analyses on a single grain is given in Table 1. The refined mean bond lengths at the M sites show that both Fe and Mn are in the divalent state. The end-member formula is $\text{NaNa}_2(\text{Mg}_2\text{Al}_2\text{Li})\text{Si}_8\text{O}_{22}\text{F}_2$, which corresponds to SiO_2 60.60, Al_2O_3 12.86, MgO 10.16, Na_2O 11.72, Li_2O 1.88, F 4.79, Total 100.00 wt.%. The compatibility index $(1-K_p/K_c)$ is 0.0015 (superior).

X-ray crystallography

The powder-diffraction pattern was recorded from a small fragment on a Gandolfi camera with Fe-filtered $\text{Cu-K}\alpha$ X-radiation. Cell dimensions were refined from the corrected d values; the indexed powder pattern and refined cell dimensions are given in Table 2. Peak intensities reported in Table 3 as I_{obs} are those estimated by eye from the darkening on the film; those reported as I_{calc} have been calculated based on single-crystal data.

TABLE 1. Chemical composition (wt.%) and unit formula (a.p.f.u.) for fluoro-aluminoleakeite.

SiO_2	58.16	Si	8.00
TiO_2	0.32	Sum T	8.00
Al_2O_3	7.06	Ti^{4+}	0.03
Fe_2O_3^*	6.05	Al	1.16
FeO	3.27	Fe^{3+}	0.63
MnO	0.73	Fe^{2+}	0.38
ZnO	0.43	Mn	0.09
MgO	8.61	Zn	0.04
CaO	0.05	Mg	1.77
Na_2O	9.90	Li	0.90
K_2O	2.43	Sum C	5.00
Li_2O^*	1.62	Ca	0.01
H_2O^{**}	0.50	Na	1.99
F	3.37	Sum B	2.00
Sub total	102.50	K	0.43
Less $\text{O}\equiv\text{F}$	1.42	Na	0.65
Total	101.08	Sum A	1.09
		F	1.47
		OH	0.53
		Sum W	2.00

* from structure refinement;

** based on $(\text{OH}) + \text{F} = 2$ a.p.f.u.

The possible space groups are $C2/m$, $C2$ and Cm ; crystal-structure refinement confirmed the space group $C2/m$.

Crystal-structure refinement and crystal chemistry

A single crystal was selected for data collection and structure refinement based on optical and diffraction properties. Unit-cell dimensions were calculated by least-squares refinement of the d values obtained from 47 rows of the reciprocal lattice by measuring the centroid of gravity of each reflection and of the corresponding anti-reflection in the range $-60^\circ < 2\theta < 60^\circ$. Two monoclinic equivalents were collected in the 2θ range $4-60^\circ$, and corrections were applied for absorption and Lp. Reflections with $I_o > 3\sigma(I)$ were considered as observed during an unweighted full-matrix least-squares refinement on F done using a program written at CNR-IGG-PV specifically to deal with complex solid-solutions. Scattering curves for fully ionized scattering 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)]. Crystal data are summarized in Table 3. Table 4 reports the atomic coordinates and the components of the anisotropic-displacement parameters, and Table 5 reports selected interatomic distances and parameters related to the conformation of the double-chain of tetrahedra. A table listing the observed and calculated structure factors has been deposited with the Principal Editor of *Mineralogical Magazine* and is available from www.minersoc.org/pages/e_journals/dep_mat_mm.html.

Site populations and Li quantification were derived from the results of EMP analysis and structure refinement. The present knowledge of the crystal-chemistry of Li in amphiboles allows determination of the amount and distribution of Li directly by SREF. The indications of the structure refinements are as follows: (1) the mean bond lengths of the tetrahedra ($\langle T1-O \rangle = 1.620 \text{ \AA}$ and $\langle T2-O \rangle = 1.621 \text{ \AA}$) indicate that the amount of Al at the $T(1)$ site, if any, is very low; (2) the mean bond length (2.064 \AA) and site-scattering (28.85 e.p.f.u.) refined at the $M(1)$ site indicate that Mg and Zn occur at this site; (3) comparison of the refined- and calculated-bond distances at the three M octahedra (Table 6) indicates that Mn is in the divalent state and is ordered at the $M(3)$ site, and that Fe^{2+} is distributed between the $M(1)$

TABLE 2. X-ray powder-diffraction data for fluoro-aluminoleakeite.

$I_{\text{obs.}}$	$I_{\text{calc.}}$	$d_{\text{obs.}}$ (Å)	$d_{\text{calc.}}$ (Å)	$h k l$	$I_{\text{obs.}}$	$I_{\text{calc.}}$	$d_{\text{obs.}}$ (Å)	$d_{\text{calc.}}$ (Å)	$h k l$
20	14	8.907	8.866	0 2 0		22		2.254	$\bar{3}$ 1 2
50	42	8.342	8.309	1 1 0	<5	7	2.197	2.193	$\bar{2}$ 4 2
80	43	4.435	4.443	0 2 1	10	33	2.148	2.144	2 6 1
	51		4.433	0 4 0	5	14	2.128	2.121	$\bar{3}$ 3 2
10	15	4.002	4.004	1 1 1	10	14	2.053	2.055	2 0 2
<5	6	3.626	3.629	$\bar{2}$ 2 1	10	11	2.000	2.004	3 5 1
80	84	3.377	3.374	1 3 1	<5*	6	1.922	1.928	1 9 0
20	25	3.225	3.226	2 4 0		7		1.920	4 2 1
40	57	3.096	3.087	3 1 0	5	8	1.870	1.871	5 1 0
5	10	2.966	2.976	$\bar{3}$ 1 1	*	8		1.864	2 4 2
	2		2.963	$\bar{2}$ 4 1	5	6	1.833	1.835	$\bar{1}$ 9 1
	2		2.955	0 6 0	10*	10	1.777	1.777	1 9 1
10	22	2.921	2.939	2 2 1		7		1.778	3 1 2
20	30	2.766	2.770	3 3 0		7		1.773	0 10 0
100	60	2.687	2.688	$\bar{3}$ 3 1	<5	4	1.720	1.720	$\bar{5}$ 1 2
	100		2.685	1 5 1		3		1.718	1 7 2
30	24	2.557	2.567	0 0 2	<5	7	1.685	1.687	$\bar{1}$ 3 3
	36		2.561	0 6 1	<5	7	1.666	1.665	$\bar{2}$ 8 2
60	59	2.527	2.523	$\bar{2}$ 0 2	15	27	1.638	1.637	4 6 1
<5	1	2.342	2.351	4 0 0		13		1.636	5 1 1
	8		2.349	3 5 0	<5	12	1.613	1.613	4 8 0
20	21	2.294	2.299	$\bar{3}$ 5 1	<5	10	1.590	1.589	1 11 0
	11		2.284	$\bar{4}$ 2 1	10	11	1.576	1.576	$\bar{4}$ 0 3
40	19	2.259	2.264	$\bar{1}$ 7 1		21		1.577	$\bar{1}$ 5 3

114.6 mm Debye-Scherrer powder camera with Gandolfi attachment using Ni-filtered Cu radiation (λ Cu- $K\alpha$ = 1.54178 Å). Intensities estimated visually (obs.) and calculated from SREF (calc.).

Not corrected for shrinkage, and no internal standard was used.

* lines omitted for unit-cell refinement.

Indexed on $a = 9.691(6)$ Å, $b = 17.731(9)$ Å, $c = 5.290(3)$ Å, $\beta = 103.92(5)^\circ$, $V = 882.2(7)$ Å³.

and $M(2)$ sites; in contrast, Fe^{3+} is ordered at the $M(2)$ site. Based on these constraints and on the results of the EMP analysis, the Li_2O content was calculated, and the corresponding value of Li in a.p.f.u. is in good agreement with the refined site-

scattering values at the $M(3)$ site. The final site populations (Table 6) are also in accord with the crystal-chemical constraint derived for ${}^{\text{C}}\text{Li}$ amphiboles, i.e. ${}^{\text{A}}(\text{Na,K}) = {}^{\text{C}}\text{Li}$ (Oberti *et al.*, 2003a). They differ only slightly from the unit

TABLE 3. Miscellaneous information for fluoro-aluminoleakeite.

a (Å)	9.7043(5)	Crystal size (μm)	300 × 115 × 65
b (Å)	17.7341(8)	Radiation/monochromator	Mo- $K\alpha$ /Graphite
c (Å)	5.2833(3)	Total no. of reflections	2590
β	104.067(4)	No. unique reflections	1339
V (Å ³)	882.0(2)	No. observed reflections	1071
Space group	$C2/m$	R_{merge} %	1.80
Z	2	R_{obs} %	1.63
$D_{\text{calc.}}$ (g cm^{-3})	3.14	R_{all} %	2.66

FLUORO-ALUMINOLEAKEITE

TABLE 4. Atomic coordinates, refined site-scattering values (ss, e.p.f.u.), atomic-displacement parameters (B_{eq} , \AA^2 ; $\beta_{11} \times 10^4$) for fluoro-aluminoleakeite.

Atom	ss	x/a	y/b	z/c	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)		0.1079(1)	0.0930(1)	0.2106(2)	0.62(2)	13	6	55	-1	4	-1
O(2)		0.1177(1)	0.1711(1)	0.7415(2)	0.60(2)	14	5	57	1	1	0
O(3)	17.28(8)	0.1138(1)	0	0.6958(3)	0.92(3)	25	6	101	-	2	-
O(4)		0.3664(1)	0.2517(1)	0.8066(2)	0.74(2)	28	4	69	-3	14	-2
O(5)		0.3519(1)	0.1290(1)	0.0882(2)	0.66(2)	15	7	52	-1	3	7
O(6)		0.3419(1)	0.1206(1)	0.5856(2)	0.68(2)	19	7	48	0	3	-6
O(7)		0.3321(2)	0	0.3016(3)	0.86(3)	25	4	113	-	8	-
T(1)		0.2773(1)	0.0871(1)	0.2948(1)	0.38(1)	12	3	34	-1	2	-1
T(2)		0.2895(1)	0.1725(1)	0.8068(1)	0.42(1)	12	3	34	-1	2	0
M(1)	28.85(9)	0	0.0875(1)	1/2	0.54(1)	17	4	46	-	7	-
M(2)	37.00(9)	0	0.1792(1)	0	0.46(1)	13	4	43	-	3	-
M(3)	4.81(5)	0	0	0	0.94(1)	29	6	93	-	6	-
M(4)	22.30(6)	0	0.2768(1)	1/2	1.07(1)	35	7	123	-	35	-
A	3.75(3)	0	1/2	0	2.84(13)	122	12	386	-	195	-
A(m)	10.69(7)	0.0453(3)	1/2	0.0969(5)	2.50(5)	93	15	277	-	103	-
H	1.10(5)	0.1891(10)	0	0.7501(20)	1.00						

TABLE 5. Selected interatomic distances (Å) and angles (°) in fluoro-aluminoleakeite.

$T(1)-O(1)$	1.599(1)	$T(2)-O(2)$	1.618(1)
$T(1)-O(5)$	1.628(1)	$T(2)-O(4)$	1.591(1)
$T(1)-O(6)$	1.624(1)	$T(2)-O(5)$	1.654(1)
$T(1)-O(7)$	<u>1.630(1)</u>	$T(2)-O(6)$	<u>1.661(1)</u>
$\langle T(1)-O \rangle$	1.620	$\langle T(2)-O \rangle$	1.631
$M(1)-O(1) \times 2$	2.055(1)	$M(2)-O(1) \times 2$	2.025(1)
$M(1)-O(2) \times 2$	2.103(1)	$M(2)-O(2) \times 2$	1.987(1)
$M(1)-O(3) \times 2$	<u>2.035(1)</u>	$M(2)-O(4) \times 2$	<u>1.893(1)</u>
$\langle M(1)-O \rangle$	2.064	$\langle M(2)-O \rangle$	1.968
$M(3)-O(1) \times 4$	2.119(1)	$M(4)-O(2) \times 2$	2.395(1)
$M(3)-O(3) \times 2$	<u>2.160(1)</u>	$M(4)-O(4) \times 2$	2.362(1)
$\langle M(3)-O \rangle$	2.133	$M(4)-O(5) \times 2$	2.842(1)
$A-O(5) \times 4$	2.800(1)	$M(4)-O(6) \times 2$	<u>2.492(1)</u>
$A-O(6) \times 4$	3.177(1)	$\langle M(4)-O \rangle$	2.523
$A-O(7) \times 2$	<u>2.541(2)</u>	$A(m)-O(5) \times 2$	2.952(1)
$\langle A-O \rangle$	2.899	$A(m)-O(5) \times 2$	2.767(1)
$T(1)-O(5)-T(2)$	133.7(1)	$A(m)-O(6) \times 2$	2.774(1)
$T(1)-O(6)-T(2)$	139.0(1)	$A(m)-O(7)$	2.557(2)
$T(1)-O(7)-T(1)$	142.6(1)	$A(m)-O(7)$	3.111(2)
$O(5)-O(6)-O(5)$	172.4(1)	$A(m)-O(7)$	<u>2.659(2)</u>
$O(6)-O(7)-O(6)$	110.6(1)	$\langle A(m)-O \rangle$	2.813

formula reported in Table 1. In fact, the amount of SiO_2 (wt.%) obtained from EMPA does not allow Al to be a T cation, and implies a number of A cations >1.0 a.p.f.u. A small amount of $T^{(1)}\text{Al}$ is suggested from the refined $\langle T(1)-O \rangle$ and is in accord with the need for more trivalent cations

(i.e. a slightly higher $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratio) at the $M(2)$ site, which in turn derives from the very short value of the refined $\langle M(2)-O \rangle$ distance. Two distinct sites, $A(2)$ and $A(m)$, have been used to account for the highly anisotropic distribution of the electron density in the A cavity (Hawthorne et

TABLE 6. Site populations, site scattering and mean bond-lengths for fluoro-aluminoleakeite calculated based on EMP and SREF analysis.

Site	Site population (a.p.f.u.)	Site scattering (e.p.f.u.)		Mean bond length (Å)	
		Refined	Calculated	Refined	Calculated
$T(1)$	0.04 Al + 3.96 Si	–	–	1.620	1.620
$T(2)$	4 Si	–	–	1.631	
$M(1)$	1.76 Mg + 0.20 Fe^{2+} + 0.04 Zn	28.85	27.52	2.064	2.064
$M(2)$	1.13 Al + 0.75 Fe^{3+} + 0.09 Fe^{2+} + 0.03 Ti	37.00	37.19	1.968	1.972
$M(3)$	0.09 Mn + 0.91 Li	4.81	4.95	2.133	2.104
ΣC		70.66	69.66		
$M(4)$	1.99 Na + 0.01 Ca	22.30	22.09		
$A(m)$	0.57 Na + 0.43 K	14.44	14.44		
$O(3)$	1.40 F + 0.60 (OH)	17.28	17.40		

al., 1996); in the fluoro-amphiboles $^A(\text{Na,K})$ are ordered at the off-centred A(m) position, similar to all the fluoro-amphiboles refined so far.

Discussion

The identification of fluoro-aluminoleakeite is important for two reasons. The first is that until a couple of years ago, all characterized amphiboles with significant Li at the M(3) site had $^C\text{Fe}^{3+} > ^C\text{Al}$, both in metamorphic and in magmatic environments, and thus end-member leakeite was defined as $^A\text{Na}^B\text{Na}_2^C(\text{Mg}_2\text{Fe}^{3+}\text{Li})^T\text{Si}_8\text{O}_{22}^W(\text{OH})_2$ (Hawthorne *et al.*, 1992). Two possible explanations were suggested for the observation that $^C\text{Fe}^{3+} > ^C\text{Al}$: (1) it is a geochemical constraint related to crystallization of the amphibole from fluids rich in Li, Fe, Mn; (2) it is related to some geometrical constraint requiring large trivalent cations at M(2). The identification of fluoro-sodic-pedrizite at the Tastyg spodumene deposit, Siberia (Oberti *et al.*, 2005), and now of fluoro-aluminoleakeite at Norra Kärr, indicates that a geometrical constraint is not operative, although the occurrence of Al at the M(2) site is still correlated with that of F at the O(3) site, which in turn allows contraction of the M(1) and M(3) octahedra.

Fluoro-aluminoleakeite has a crystal-chemical feature deserving of comment. The M(3) octahedron has a much shorter calculated mean bond length (based on stoichiometry) than the refined values (Table 6). Relaxation of some M(1–3) octahedra in amphiboles is well known in compositions such as glaucophane, nyböite and fluoronyböite where the M(1) and (especially) the M(3) octahedra are larger than expected from the refined site-population (Oberti *et al.*, 2003b). The maximum relaxation previously reported is 0.011 Å (2.087 vs. 2.076 Å) at the M(3) site in fluoronyböite, much smaller than that in fluoro-aluminoleakeite: 0.032 Å (2.133 vs. 2.101 Å; Table 6). Such relaxation was not present in the fluoro-ferroleakeites reported by Hawthorne *et al.* (1993), and the reason for relaxation has thus to be ascribed to the bond-valence requirements of this amphibole composition.

The second important issue arising from this work is the fact that the presence of Li was not recognized in the characterization of holotype eckermannite from Norra Kärr (Adamson, 1942), a problem first noted by Sundius (1945). The chemical and optical data reported by Fleischer (1944) (biaxial negative, $\alpha = 1.636$ (bluish-green),

$\beta = 1.644$ (bright bluish-green), $\gamma = 1.649$ (pale yellowish-green); $2V(\text{obs.}) = 74$) are compatible with those reported here for fluoro-aluminoleakeite. As a consequence, we are planning a systematic crystal-chemical work on eckermannitic amphiboles reported in the literature.

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