

# Fluoroleakeite, $\text{NaNa}_2(\text{Mg}_2\text{Fe}_2^{3+}\text{Li})\text{Si}_8\text{O}_{22}\text{F}_2$ , a new mineral of the amphibole group from the Verkhnee Espe deposit, Akjailyautas Mountains, Eastern Kazakhstan District, Kazakhstan: description and crystal structure

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## ABSTRACT

Fluoroleakeite,  $\text{NaNa}_2(\text{Mg}_2\text{Fe}_2^{3+}\text{Li})\text{Si}_8\text{O}_{22}\text{F}_2$ , is a new mineral of the amphibole group from the Verkhnee Espe deposit, Akjailyautas mountains, eastern Kazakhstan district, Kazakhstan. The granites and their host rocks have been intensely reworked by post-magmatic and host-rock fluids, resulting in intense recrystallization, enrichment in F, Li and rare elements, and replacement of primary biotite and sodic-calcic amphiboles by Li-bearing riebeckite, aegirine, astrophyllite and other sodic minerals including fluoroleakeite. Crystals are prismatic parallel to [001] with {100} and {110} faces and cleavage surfaces, and the prism direction is terminated by irregular fractures. Grains are up to 3 mm long, and occur as isolated crystals, as small aggregates, and as inclusions in cámaraites. Crystals are black with a very pale grey to colourless streak. Fluoroleakeite 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  $3.245 \text{ g cm}^{-3}$ . In plane-polarized light, it is pleochroic,  $X =$  pale grey-green,  $Y =$  medium grey,  $Z =$  grey-brown;  $X^\wedge a = 14.1^\circ$  (in  $\beta$  obtuse),  $Y \parallel b$ ,  $Z^\wedge c = 75.9^\circ$  (in  $\beta$  acute). Fluoroleakeite is biaxial negative,  $\alpha = 1.663(2)$ ,  $\beta = 1.673(2)$ ,  $\gamma = 1.680(2)$ ;  $2V_{\text{obs}} = 80.9(6)^\circ$ ,  $2V_{\text{calc}} = 79.4^\circ$ .

Fluoro-leakeite is monoclinic, space group  $C2/m$ ,  $a = 9.8927(3)$ ,  $b = 17.9257(6)$ ,  $c = 5.2969(2) \text{ \AA}$ ,  $\beta = 103.990(1)^\circ$ ,  $V = 905.7(1) \text{ \AA}^3$ ,  $Z = 2$ . The strongest ten X-ray diffraction lines in the powder pattern are [ $d$  in  $\text{Å}(hkl)$ ]: 2.718(100)(151), 8.434(40)(110), 4.464(30)(021), 3.405(30)(131), 3.137(20)(310), 2.541(20)(202), 2.166(20)(261), 2.325(15)(351), 2.275(15)(312) and 2.806(10)(330). Analysis by a combination of electron microprobe and crystal-structure refinement gives  $\text{SiO}_2$  53.34,  $\text{Al}_2\text{O}_3$  0.62,  $\text{TiO}_2$  1.27,  $\text{V}_2\text{O}_5$  0.05,  $\text{Fe}_2\text{O}_3$  15.10,  $\text{FeO}$  6.00,  $\text{MnO}$  2.04,  $\text{ZnO}$  0.18,  $\text{MgO}$  6.40,  $\text{CaO}$  0.13,  $\text{Na}_2\text{O}$  9.08,  $\text{K}_2\text{O}$  1.98,  $\text{Li}_2\text{O}$  1.10,  $\text{F}$  3.33,  $\text{H}_2\text{O}_{\text{calc}}$  0.16, sum 99.39 wt.%. The formula unit, calculated on the basis of 23 O, is  $^{4}(\text{Na}_{0.64}\text{K}_{0.38})(\text{Na}_{1.98}\text{Ca}_{0.02})(\text{Li}_{0.66}\text{Mg}_{1.42}\text{Fe}_{0.75}^{2+}\text{Mn}_{0.26}^{2+}\text{Zn}_{0.02}\text{Fe}_{1.69}^{3+}\text{V}_{0.01}^{3+}\text{Ti}_{0.14}^{4+}\text{Al}_{0.03})$  ( $\text{Si}_{7.93}\text{Al}_{0.07}$ ) $\text{O}_{22}(\text{F}_{1.57}\text{OH}_{0.16}\text{O}_{0.27})$ . Crystal-structure refinement shows Li to be completely ordered at the  $M(3)$  site. Fluoroleakeite, ideally  $\text{NaNa}_2(\text{Mg}_2\text{Fe}_2^{3+}\text{Li})\text{Si}_8\text{O}_{22}\text{F}_2$ , is related to end-member leakeite,  $\text{NaNa}_2(\text{Mg}_2\text{Fe}_2^{3+}\text{Li})\text{Si}_8\text{O}_{22}(\text{OH})_2$  by the substitution  $\text{F} \rightarrow (\text{OH})$ .

**KEYWORDS:** fluoroleakeite, new amphibole, leakeite, electron-microprobe analysis, optical properties, crystal-structure refinement, Verkhnee Espe deposit, Kazakhstan.

## Introduction

ALTHOUGH Li has long been known as a major constituent in amphiboles, it is only in the last 17 years that it has been recognized as a major constituent of the C-group cations in monoclinic

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amphiboles in which Na is the dominant B-group cation (Hawthorne *et al.*, 1993). Several new amphibole species have since been characterized (Table 1), and the crystal chemistry of <sup>C</sup>Li in monoclinic amphiboles was examined in detail by Hawthorne *et al.* (1993, 1994).

During work on the new Ti-silicate mineral, cámaraité, from the Verkhnee Espe deposit in Eastern Kazakhstan (Sokolova *et al.*, 2009a; Cámara *et al.*, 2009), another new amphibole was discovered coexisting with cámaraité, the 'fluoro' equivalent of leakeite, ideally  $\text{NaNa}_2(\text{Mg}_2\text{Al}_2\text{Li})\text{Si}_8\text{O}_{22}\text{F}_2$ ; a formal description of the amphibole is given here. The new species and the new name (Leake *et al.*, 1997, 2003) have been approved by the International Mineralogical Association Commission on New Minerals and Mineral Classification (2009-085). Holotype material is deposited in the Fersman Mineralogical Museum, Moscow, Russia, registration number 3828/1.

## Occurrence

Fluoroleakeite occurs in the Verkhnee Espe deposit (48°03'–48°10'N 81°26'–81°29'E), which is spatially related to two small oval outcrops of alkaline granite at the northern exo-contact of the large Akjailyautas granite massif in the northern part of the Tarbagatai mountain range, Eastern Kazakhstan (Sokolova *et al.*, 2009a). The Verkhnee Espe rare-element (Zr, Nb, REEs, Th, *etc.*) deposit formed during the later stages of the intrusion of the Akjailyautas massif.

Lithium and F in fluoroleakeite came from fluids of the alkali granites, and Mg, Mn, Ca, Ti

and Zn probably were derived mainly from the host rocks *via* contamination. The accumulation of post-magmatic fluids and their contamination by host-rock fluids resulted in intense reworking of the granites and the host rocks. The granites were intensely recrystallized with significant enrichment in F, Li and rare earth elements. Primary biotite and sodic-calcic amphiboles were replaced by Li-bearing riebeckite, aegirine and astrophyllite. Crystals of riebeckite, aegirine and lacy albite are oriented NW–SE irrespective of the orientation of the contact, suggesting that recrystallization was accompanied by strong NW–SE stress. Sokolova *et al.* (2009a) reported the discovery of cámaraité, ideally  $\text{Ba}_3\text{Na}(\text{Fe}^{2+}, \text{Mn})_8\text{Ti}_4(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{OH}, \text{F})_7$ , as platy intergrowths with bafertisite, ideally  $\text{Ba}_2\text{Ti}_2\text{Fe}_2^{3+}(\text{Si}_2\text{O}_7)_2\text{O}_2(\text{OH})_4$  (Guan *et al.*, 1963), and jinshajiangite, ideally  $\text{Ba}_2\text{Na}_2\text{Ti}_4\text{Fe}_8^{2+}(\text{Si}_2\text{O}_7)_4\text{O}_4(\text{OH})_4\text{F}_2$  (Sokolova, 2006; Sokolova *et al.*, 2009b). The holotype handspecimen of cámaraité also contained prismatic crystals of black amphibole. The widespread occurrence of Li-rich riebeckite at this locality encouraged us to examine this amphibole, and chemical analysis showed it to be a new species, the F analogue of leakeite.

## Physical and optical properties

Fluoroleakeite is black with a vitreous lustre. It has a very pale-grey to colourless streak and shows no fluorescence under long-wave or short-wave ultraviolet light. Grains are prismatic parallel to [001] with {100} and {110} faces and cleavage faces, and the prism direction is terminated by irregular fractures. Grains are up to

TABLE 1. Leakeite-related amphiboles.

Name	End-member formula	Ref.
Leakeite	$\text{NaNa}_2(\text{Mg}_2\text{Fe}_2^{3+}\text{Li})\text{Si}_8\text{O}_{22}(\text{OH})_2$	(1)
Fluoroleakeite	$\text{NaNa}_2(\text{Mg}_2\text{Fe}_2^{3+}\text{Li})\text{Si}_8\text{O}_{22}\text{F}_2$	(2)
Fluoro-aluminoleakeite	$\text{NaNa}_2(\text{Mg}_2\text{Al}_2\text{Li})\text{Si}_8\text{O}_{22}\text{F}_2$	(3)
Fluoro-ferroleakeite	$\text{NaNa}_2(\text{Fe}^2\text{Fe}_2^{3+}\text{Li})\text{Si}_8\text{O}_{22}\text{F}_2$	(4)
Kornite	$\text{NaNa}_2(\text{Mg}_2\text{Mn}_2^{3+}\text{Li})\text{Si}_8\text{O}_{22}(\text{OH})_2$	(5)
Potassicleakeite	$\text{KNa}_2(\text{Mg}_2\text{Fe}_2^{3+}\text{Li})\text{Si}_8\text{O}_{22}(\text{OH})_2$	(6)
Dellaventuraite	$\text{NaNa}_2(\text{MgMn}_2^{3+}\text{LiTi}^{4+})\text{Si}_8\text{O}_{22}\text{O}_2$	(7)

References: (1) Hawthorne *et al.* (1992); (2) this work; (3) Oberti *et al.* (2009); (4) Hawthorne *et al.* (1996b); (5) Armbruster *et al.* (1993); (6) Matsubara *et al.* (2002); (7) Tait *et al.* (2005).

3 mm long, and occur as isolated crystals, as small aggregates, and as inclusions in cámaraité (Sokolova *et al.*, 2009a; Cámara *et al.*, 2009). Fluoroleakeite 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 ~56°. The calculated density is 3.245 gcm<sup>-3</sup>.

A spindle stage was used to orient a crystal for measurement of refractive indices and  $2V$  by extinction curves (Bartelmeys *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, fluoroleakeite is pleochroic with  $X$  = pale grey-green,  $Y$  = medium grey,  $Z$  = grey-brown,  $X \wedge a = 14.1^\circ$  (in  $\beta$  obtuse),  $Y \parallel b$ ,  $Z \wedge c = 75.9^\circ$  (in  $\beta$  acute). It is biaxial negative with indices of refraction  $\alpha = 1.663(2)$ ,  $\beta = 1.673(2)$ ,  $\gamma = 1.680(2)$  measured with gel-filtered Na light ( $\lambda = 589.9$  nm);  $2V_{\text{obs.}} = 80.9(6)$ ,  $2V_{\text{calc.}} = 79.4^\circ$ .

TABLE 2. Chemical composition (wt.%) and unit formula (a.p.f.u.) for fluoroleakeite.

SiO <sub>2</sub>	53.34	Si	7.93
TiO <sub>2</sub>	1.27	Al	0.07
Al <sub>2</sub> O <sub>3</sub>	0.62	Sum T	8.00
V <sub>2</sub> O <sub>3</sub>	0.06		
Fe <sub>2</sub> O <sub>3</sub>	15.10	Al	0.03
FeO	6.00	Ti <sup>4+</sup>	0.14
MnO	2.04	V <sup>3+</sup>	0.01
ZnO	0.18	Fe <sup>3+</sup>	1.69
MgO	6.40	Fe <sup>2+</sup>	0.75
CaO	0.13	Mn <sup>2+</sup>	0.26
Na <sub>2</sub> O	9.08	Zn	0.02
K <sub>2</sub> O	1.98	Mg	1.42
Li <sub>2</sub> O	1.10	Li	0.66
H <sub>2</sub> O	0.16	Sum C	4.98
F	3.33		
-O=F	-1.40	Ca	0.02
Total	99.39	Na	1.98
		Sum B	2.00
		Na	0.64
		K	0.38
		Sum A	1.02
		(OH)	0.16
		F	1.57
		O	0.27
		Sum W	2.00

## Chemical composition

Fluoroleakeite was analyzed primarily by electron microprobe using a Cameca SX-100 operating in wavelength-dispersive mode with excitation voltage of 15 kV, specimen current 10 nA, beam diameter 5  $\mu$ m, peak-count time 20 s and background-count time 10 s. The following standards and crystals were used for  $K\text{-}\alpha$  X-ray lines: Si, Ca: diopside, TAP; Ti: titanite, LiF; Fe: fayalite, LiF; Mn: tephroite, LiF; V: VP<sub>2</sub>O<sub>7</sub>, LiF; Mg: periclase, TAP; Na: jadeite, TAP; Al: corundum, TAP; F: fluororibeckite, TAP; Zn: gahnite, LiF; K, orthoclase, PET. Data reduction was done using the  $\varphi(\rho Z)$  procedure of Pouchou and Pichoir (1985). Li was derived by SREF (see section on crystal-structure refinement). The average of 10 analyses on a single grain is given in Table 2. The Fe<sup>3+</sup>:(Fe<sup>2+</sup>+Fe<sup>3+</sup>) ratio was derived from the structure-refinement results. The end-member formula of reference is NaNa<sub>2</sub>(Fe<sub>2</sub><sup>2+</sup>Al<sub>2</sub>Li) Si<sub>8</sub>O<sub>22</sub>F<sub>2</sub>, which requires SiO<sub>2</sub> 55.52, Fe<sub>2</sub>O<sub>3</sub> 18.44, MgO 9.31, Na<sub>2</sub>O 10.74, Li<sub>2</sub>O 3.45, F 4.39, total 100.00 wt.%.

## X-ray powder diffraction

The powder-diffraction pattern was recorded from a small fragment on a Gandolfi camera with Ni-filtered 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 3. Peak intensities reported in Table 3 are those estimated by eye from the darkening on the film. 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

X-ray diffraction data were collected with a Bruker AXS diffractometer equipped with a SMART APEX CCD detector (Mo- $K\alpha$  radiation). The intensities of 11625 reflections with  $-17 < h < 17$ ,  $-31 < k < 30$ ,  $-9 < l < 9$ , of which 2535 are unique, were collected to  $77^\circ 2\theta$  using  $0.2^\circ$  frames and an integration time of 10 s. The detector-to-crystal working distance was 4 cm. Lp and empirical absorption corrections (SADABS, Sheldrick, 1998) were applied. The refined unit-cell parameters were obtained from 5246 reflections with  $I < 10\sigma(I)$  collected in the  $2\theta$  range  $4\text{--}77^\circ$ . Weighted full-matrix least-squares refine-

TABLE 3. X-ray powder diffraction pattern for fluoroleakeite.

$I_{\text{obs.}}$	$d_{\text{meas.}} (\text{Å})$	$d_{\text{calc.}} (\text{Å})$	$h k l$
40	8.434	8.420	1 1 0
30	4.464	4.476	0 2 1
<5	4.063	4.057	$\bar{1}$ 4 0
<5	3.672	3.669	$\bar{2}$ 2 1
30	3.405	3.405	1 3 1
<5	3.269	3.266	2 4 0
20	3.137	3.130	3 1 0
5	2.964	2.968	2 2 1
10	2.806	2.807	3 3 0
100	2.718	2.711	1 5 1
10	2.587	2.587	0 6 1
20	2.541	2.542	$\bar{2}$ 0 2
15	2.325	2.326	$\bar{3}$ 5 1
15	2.275	2.275	$\bar{3}$ 1 2
20	2.166	2.167	2 6 1
<5	2.074	2.071	2 0 2
<5	2.022	2.026	3 5 1

ment on  $F^2$  was done using SHELX 97 (Sheldrick, 2008) and 2423 reflections with  $I > 4\sigma(I)$  were considered as observed. 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)]. Refinement on  $F_o > 4\sigma(I)$  converged to  $R_{\text{obs}} = 2.4\%$  and  $R_{\text{all}} = 2.6\%$ . Crystal data are summarized in Table 4.

TABLE 4. Miscellaneous information for fluoroleakeite.

$a$ (Å)	9.8927(3)
$b$	17.9257(6)
$c$	5.2969(2)
$\beta$ (°)	103.990(1)
$V$ (Å <sup>3</sup> )	905.7(1)
Space group	$C2/m$
$Z$	2
$D_{\text{calc.}}$ (g cm <sup>-3</sup> )	3.245
Crystal size (µm)	$25 \times 200 \times 300$
Radiation/monochromator	Mo- $K\alpha$ /Graphite
No. of unique reflections	2535
No. $I_o > 4\sigma(I)$	2423
$R_{\text{merge}}$ %	1.93
$R_{\text{obs}}$ %	2.4
$R_{\text{all}}$ %	2.6

Table 5 lists atom coordinates and anisotropic-displacement parameters, Table 6 shows selected interatomic distances and angles. 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](http://www.minersoc.org/pages/e_journals/dep_mat_mm.html).

Site populations and Li content were derived from the results of EMP analysis and structure refinement. Based on our knowledge of the crystal-chemistry of Li in amphiboles, it is now possible to derive accurately the amount and distribution of Li without direct analytical measurement. The refined  $\langle T-O \rangle$  distances indicate that they are occupied solely by Si, and the unit formula (Table 2) has only 0.07 Al assigned to the T-group cations, in accord with site populations observed in amphiboles (Hawthorne and Oberti, 2007). Using the regression equation given by Hawthorne and Oberti (2007), and the <sup>[4]</sup>Al content indicated by the unit formula of fluoroleakeite, we obtain a calculated value for  $\langle T-O \rangle$  of 1.6257 Å, close to the observed value of 1.6265 Å. The observed scattering at the  $M(2)$  site (Table 7) indicates that this site is occupied predominantly by Fe, and the  $\langle M(2)-O \rangle$  distance of 2.040 Å indicates that most of the Fe is in the trivalent state at this site. Ti<sup>4+</sup> was assigned to the  $M(1)$  site, being incorporated into the structure in local association with O<sup>2-</sup> at the O(3) site (Oberti *et al.*, 1992; Hawthorne *et al.*, 1998), and Mg and Fe<sup>2+</sup> were assigned to  $M(1)$  to fill the site and reflect the refined site-scattering value. Minor <sup>[6]</sup>Al was assigned to  $M(2)$  in accord with the site-occupancies generally found in monoclinic amphiboles (Hawthorne, 1983; Oberti *et al.*, 1998; Oberti *et al.*, 2007a), and Fe and Mg were assigned to  $M(2)$  to fill the site and reflect the refined site-scattering value. This process used up all Mg in the unit formula, and Li and Fe were assigned to the  $M(3)$  site to reflect the refined site-scattering value. The populations of the  $M(4)$ - and A-sites were assigned from the unit formula and are in accord with the refined site-scattering values (Table 7). The resulting site-populations were then adjusted to fit the unit formula and the refined site-scattering values equally well, and the final values are given in Table 7. The A-group cations Na and K both occupy the  $A(m)$  site. It has long been established that K always occupies the  $A(m)$  site in monoclinic amphiboles (Hawthorne and Grundy, 1972; Hawthorne, 1983), and

TABLE 5. Atom coordinates and displacement factors for fluoroleakeite.

Atom	x	y	z	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$	$U_{eq}$
O(1)	0.11078(7)	0.09014(3)	0.21362(13)	0.0076(2)	0.0127(3)	0.0095(3)	0.00002(19)	0.00207(19)	-0.00075(18)	0.00991(11)
O(2)	0.11920(7)	0.16992(4)	0.73373(12)	0.0082(2)	0.0110(2)	0.0089(2)	-0.00015(18)	0.00150(18)	-0.00027(18)	0.00944(11)
O(3)	0.10913(9)	0	0.70342(18)	0.0154(4)	0.0129(4)	0.0162(4)	0	0.0022(3)	0	0.0151(2)
O(4)	0.36339(7)	0.24943(4)	0.80227(13)	0.0156(3)	0.0085(2)	0.0120(3)	-0.00113(19)	0.0051(2)	-0.0039(2)	0.01171(11)
O(5)	0.34893(6)	0.12816(4)	0.08488(11)	0.0092(2)	0.0131(3)	0.0087(3)	0.00384(19)	0.00230(19)	0.00006(19)	0.01029(11)
O(6)	0.34229(6)	0.11962(4)	0.58347(12)	0.0104(2)	0.0130(3)	0.0082(2)	-0.00354(19)	0.00213(19)	0.00027(19)	0.01056(11)
O(7)	0.33426(10)	0	0.30020(19)	0.0148(4)	0.0064(3)	0.0167(4)	0	0.0027(3)	0	0.01284(16)
T(1)	0.27887(2)	0.08582(1)	0.29429(4)	0.00766(10)	0.00623(9)	0.00587(10)	-0.00013(6)	0.00148(7)	-0.00038(6)	0.00661(6)
T(2)	0.28871(2)	0.17057(1)	0.80265(4)	0.00769(10)	0.00703(9)	0.00603(10)	-0.00028(6)	0.00198(7)	-0.00109(6)	0.00686(6)
M(1)	0	0.08850(2)	1/2	0.01029(13)	0.01067(13)	0.00812(13)	0	0.00320(9)	0	0.00953(9)
M(2)	0	0.18135(1)	0	0.00769(8)	0.00761(8)	0.00746(8)	0	0.00214(5)	0	0.00753(5)
M(3)	0	0	0	0.0130(3)	0.0084(3)	0.0093(3)	0	0.0015(2)	0	0.01039(18)
M(4)	0	0.27730(3)	1/2	0.0219(4)	0.0143(3)	0.0220(4)	0	0.0129(2)	0	0.0181(3)
A	0.0307(2)	1/2	0.0681(3)	0.0696(16)	0.0310(6)	0.0720(16)	0	0.0603(13)	0	0.0502(7)

TABLE 6. Selected interatomic distances (Å) and angles (°) in fluoroleakeite.

$T(1)-O(1)$	1.605(1)	$M(2)-O(1) \times 2$	2.132(1)
$T(1)-O(5)$	1.628(1)	$M(2)-O(2) \times 2$	2.050(1)
$T(1)-O(6)$	1.625(1)	$M(2)-O(4) \times 2$	1.939(1)
$T(1)-O(7)$	1.630(1)	$\langle M(2)-O \rangle$	2.040
$\langle T(1)-O \rangle$	1.622		
$T(2)-O(2)$	1.618(1)	$M(3)-O(1) \times 4$	2.117(1)
$T(2)-O(4)$	1.593(1)	$M(3)-O(3) \times 2$	2.106(1)
$T(2)-O(5)$	1.654(1)	$\langle M(3)-O \rangle$	2.113
$T(2)-O(6)$	1.660(1)		
$\langle T(2)-O \rangle$	1.631		
$M(1)-O(1) \times 2$	2.070(1)	$M(4)-O(2) \times 2$	2.431(1)
$M(1)-O(2) \times 2$	2.082(1)	$M(4)-O(4) \times 2$	2.374(1)
$M(1)-O(3) \times 2$	2.066(1)	$M(4)-O(5) \times 2$	2.887(3)
$\langle M(1)-O \rangle$	2.073	$M(4)-O(6) \times 2$	2.519(1)
		$\langle M(4)-O \rangle$	2.553
$T(1)-O(5)-T(2)$	135.4(1)	$A(m)-O(5) \times 2$	2.793(1)
$T(1)-O(6)-T(2)$	138.6(1)	$A(m)-O(5) \times 2$	2.928(2)
$T(1)-O(7)-T(1)$	141.5(1)	$A(m)-O(6) \times 2$	2.907(2)
$O(5)-O(6)-O(5)$	172.8(1)	$A(m)-O(7)$	2.527(2)
$O(6)-O(7)-O(6)$	110.7(1)	$A(m)-O(7)$	2.612(2)
		$A(m)-O(7)$	3.288(4)
		$\langle A(m)-O \rangle$	2.853

Hawthorne *et al.* (1996a) showed that the occupancy of the  $A(m)$  and  $A(2)$  sites by Na is affected by the patterns of short-range order around the  $A$  site. In particular, where O(3) is occupied by F,  $^A\text{Na}$  is ordered at the  $A(m)$  site.

## Discussion

Inspection of Table 1 indicates that leakeite-type amphiboles show no unusual compositional

features apart from the presence of Li. Table 8 reports a comparison of the characteristics of leakeite-related amphiboles. It is particularly significant that several of these amphiboles were known as constituents of their host rocks long before their status as new species was recognized. It is apparent that the difficulty in routinely analyzing for Li had inhibited the recognition of their correct chemical compositions. This suggests that leakeite-type amphiboles and other

TABLE 7. Refined site-scattering values and assigned site-populations in fluoroleakeite.

Site	Site population (a.p.f.u.)	— Site scattering (e.p.f.u.) —	
		Refined	Calculated
$T(1)$	0.07 Al + 3.93 Si	—	—
$T(2)$	4 Si	—	—
$M(1)$	1.23 Mg + 0.63 Fe <sup>2+</sup> + 0.14 Ti	35.9	34.2
$M(2)$	1.70 Fe <sup>3+</sup> + 0.04 Al + 0.20 Mg + 0.06 Fe <sup>2+</sup>	51.1	48.7
$M(3)$	0.66 Li + 0.26 Mn <sup>2+</sup> + 0.08 Fe <sup>2+</sup>	11.0	10.6
$M(4)$	1.98 Na + 0.02 Ca	22.6	22.2
$A$ site	0.63 Na + 0.37 K	13.6	13.9
O(3)	1.56 F + 0.16 (OH) + 0.28 O	17.8	17.5

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TABLE 8. Comparative table of known leakeite-related amphiboles.

	Fluoro-aluminoleakeite	Leakeite	Fluoro-ferroleakeite	Fluoro-leakeite	Kornite	Potassic leakeite
<i>a</i> (Å)	9.7043(5)	9.822(3)	9.792(1)	9.8297(3)	9.94(1)	9.922(5)
<i>b</i> (Å)	17.7341(8)	17.836(6)	17.938(1)	17.9257(6)	17.80(2)	17.987(7)
<i>c</i> (Å)	5.2833(3)	5.286(2)	5.3133(4)	5.2969(2)	5.302(4)	5.286(2)
$\beta$ (°)	104.067(4)	104.37(3)	103.87(7)	103.990(1)	105.5(2)	104.07(3)
<i>V</i> (Å <sup>3</sup> )	882.02(2)	897.1(5)	906.0(1)	905.7(1)	904(4)	915.1(7)
Space group	<i>C2/m</i>	<i>C2/m</i>	<i>C2/m</i>	<i>C2/m</i>	<i>P2<sub>1</sub>/m</i> or <i>P2<sub>1</sub>/a</i>	<i>C2/m</i>
Optic sign	Biaxial (–)	Biaxial (–)	Biaxial (+)	Biaxial (–)	Biaxial (–)	Biaxial (+)
$\alpha$	1.632	1.667	1.675	1.663(2)	1.654(4)	1.672(2)
$\beta$	1.638	1.675	1.683	1.673(2)	1.675	1.680(2)
$\gamma$	1.643	1.691	1.694	1.680(2)	1.696(4)	1.682(2)
2 <i>V</i> (°)	98	59–71	87	81	88–92	79
Colour	Light greenish blue	pale pink	Bluish black	Black	Dark red to brownish lilac	Reddish brown
Pleochroism	Dark-green to pale-green	Light-pink to mauve-red	Dark-blue to yellow-green	Pale grey-green to grey-brown	Pink to red orange	Yellowish brown to reddish brown
Ref.	(1)	(2)	(3)	(4)	(5)	(6)

References: (1) Oberti *et al.* (2009); (2) Hawthorne *et al.* (1992); (3) Hawthorne *et al.* (1996b); (4) this work; (5) Armbruster *et al.* (1993); (6) Matsubara *et al.* (2002).

Li amphiboles, particularly the <sup>B</sup>Li amphiboles (Oberti *et al.*, 2007b), may be a lot more common than is generally realized.

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