Ferri-fluoro-leakeite: a second occurrence at Bratthagen (Norway), with new data on Zn partitioning and the oxo component in Na amphiboles

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ABSTRACT

A second occurrence of ferri-fluoro-leakeite has been identified in the Bratthagen nepheline syenite pegmatite (Vestfold County, Norway). With respect to the holotype found at the Verkhnee Espe deposit (Akjailyautas Mountains, Kazakhstan; Cámara *et al.*, 2010), it is closer to the ideal composition because of its larger Li and Mg contents and the absence of an oxo-component; however, it has a significant Zn content (0.29 a.p.f.u.). The ideal formula of ferri-fluoro-leakeite is ^ANa^BNa₂^C(Mg₂Fe₂³⁺Li)^TSi₈O₂₂^WF₂ and the empirical formula derived from electron-microprobe analysis and single-crystal structure refinement for the sample used here is ^A(Na_{0.68}K_{0.32})_{Σ=1.00} ^BNa_{2.00}^C(Mg_{1.69}Mn_{0.25}²⁺Fe_{0.24}²⁺Zn_{0.29}Al_{0.23}Fe_{1.59}³⁺Ti_{0.02}Li_{0.78})_{Σ=5.00}^TSi₈O₂₂^W(F_{1.59}(OH)_{0.41})_{Σ=2.00}. Unitcell data are *a* = 9.788(2), *b* = 17.826(3), *c* = 5.282(1) Å, β = 104.195(5)°, *V* = 893.5 (3) Å³, *Z* = 2. Crystal-chemical analysis shows that Li is ordered at the *M*(3) site and Zn is ordered mainly at the *M*(2) site, confirming previous findings for Li-bearing amphiboles. The new data also make quantification of the oxo component in Na amphiboles possible.

Keywords: ferri-fluoro-leakeite, electron microprobe analysis, crystal-structure refinement, lithium, oxo component, Bratthagen, Norway.

Introduction

MONOCLINIC amphiboles containing Li as a C cation have been characterized only relatively recently (Hawthorne *et al.*, 1992). Rather ironically, the widespread use of electron microprobe analysis (EMPA) instead of wet-chemical analysis obscured the occurrence of ^CLi in amphiboles, which was first revealed by low site-scattering values at the M(3) site in Na amphiboles by Hawthorne *et al.* (1992). However, many occurrences of amphiboles containing variable amounts of ^CLi have been

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discovered since then and have been characterized by single-crystal structure refinement (SREF) and ion-probe (SIMS) analysis (Oberti et al., 2007a). The occurrence of ^CLi in amphiboles is now known to be restricted to ^BNa and ^BLi compositions (i.e. to the rootnames eckermannite, arfvedsonite and leakeite for ^BNa and holmquistite and pedrizite for ^BLi), whereas there is no apparent limit to homovalent substitution at the various groups of sites (which may give rise to use of the prefixes potassic, ferro-, ferri-, fluoro and even oxo- (related to the rootnames ungarettiite and dellaventuraite: Hawthorne et al., 2012). Systematic work on ^{B,C}Li-bearing samples resulted in a sound crystal-chemical model which allows detection and quantification

of Li based solely on SREF (Oberti *et al.*, 2003, 2007*b*). ^CLi is always ordered at the M(3) site and electroneutrality is maintained by additional R^{3+} cations (dominantly Fe³⁺) at the M(2) site. Moreover, ^CLi is never larger than ^AR⁺, showing that the A cations play an important role in local charge balance.

A^CLi-bearing amphibole was found recently in the mineral collection of Roy Kristiansen. The sample is from the nepheline syenite pegmatite at Bratthagen, Vestfold County, Norway, an historical locality protected by law since 1984, where no further collecting is allowed. The EMPA and crystal structure refinement showed that it is ferrifluoro-leakeite (Hawthorne et al., 2012), a mineral species described by Cámara et al. (2010) from the Verkhnee Espe deposit (Kazakhstan) under the name (in force at that time) of "fluoroleakeite". The Verkhnee Espe deposit is an intrusion of alkali granite in the northern exocontact of the Akjailyantas granite massif; it is the type locality of six species: bastnaesite-(Y), gagarinite-(Y), cámaraite, natrotitanite, tarbagataite and ferri-fluoro-leakeite (Stepanov and Sverov, 1961: Mineev et al., 1970: Sokolova et al., 2009; Cámara et al., 2010; Stepanov et al., 2012*a*,*b*). Both the difference in petro-genetic conditions and in chemical composition with respect to holotype ferri-fluoro-leakeite provide significant new information on the genesis and crystal-chemistry of ^CLi amphiboles and the longrange order of some exotic cations (i.e. Zn) in amphiboles.

Occurrence and sample description

The specimen studied in this work was collected in 1978 by Roy Kristiansen in the Bratthagen nepheline syenite pegmatite of the Larvik Plutonic complex (LPC), Norway (Larsen, 2010, 2013). The pegmatite is situated in a road cut on the main road RV 8, ~200 m SE of the Bratthagen farm (59°09'26" N 10°00'39" E) in Lågendalen, Hedrum, Vestfold County, Norway. The locality has been protected by law since November 1984 and mineral collecting is now prohibited. The large roadcut was blasted through a trachytoid nepheline syenite dyke in which there are several cross-cutting nepheline syenite pegmatites up to 30 cm thick. The syenite was first analysed and described by Brøgger (1897).

The lardalite/foyaite rocks in Lågendal contain the last segments of the LPC. The foyaites are younger than the lardalites and belong to the igneous rock complex of the Oslo region and the extreme mineral association in the Bratthagen syenite pegmatite shows mineralogical and geochemical features quite different from most of the syenite pegmatites in the LPC. Textural features suggest that these pegmatites are related to the host foyaite, which is younger than the lardalites. The mineral association is diagnostic of agpaitic pegmatites (Dahlgren, 2010).

According to Piilonen et al. (2012), the major minerals in the Bratthagen nepheline syenite are aegirine, hastingsite, magnesio-hastingsite, taramite, ferropargasite, albite, analcime, catapleiite, microcline, natrolite, kupletskite and polylithionite. Almost 60 different species have been characterized, many of which are typical of latestage mineralization in highly evolved agpaitic intrusions. The mineralogy comprises mostly silicates of Zr, Be, Ti and Na, including rare minerals like barylite (Sæbø, 1965, 1966), kupletskite (Piilonen et al., 2003), lorenzenite (Larsen et al., 1992), parakeldyshite (Raade and Mladeck, 1977) and more recently micheelsenite (Berge, 2011) and surkhobite (Kristiansen, 2013). The occurrence of chrysoberyl (rather uncommon in a syenite pegmatite) has also been reported (Sæbø, 1965). Notably, ferri-fluoro-leakeite is the second mineral containing Li (after polylithionite) from this pegmatite: Raade and Larsen (1980) reported up to 1.35 wt.% Li2O in arfvedsonite from Vøra, Sandefjord.

The Norwegian locality, a nepheline syenite pegmatite, is very different from the type locality in Kazakhstan, an alkaline granite; however, there are similarities in both the geochemistry and the mineralogy. Indeed, astrophyllite-kupletskite, aegirine, ilmenite, pyrochlore, polylithionite, zircon, monazite and now ferri-fluoro-leakeite have been found at both localities. Notably, in the Bratthagen locality the diversity of Be minerals is more extensive, with at least eight species reported, whereas the Verkhnee Espe deposit is characterized mainly by Y-bearing minerals and rare Ba minerals such as cappelenite-(Y), cámaraite, bafertisite and barylite; the latter is also found as a rarity in Bratthagen along with a recent finding of another Ba mineral, surkhobite (Kristiansen, 2013).

The rock specimen containing ferri-fluoroleakeite from Bratthagen is $\sim 6 \text{ cm} \times 5 \text{ cm} \times 4 \text{ cm}$ in size and also contains, as major constituents, anorthoclase and broken crystals of aegirine and, as minor constituents, catapleïte, pyrochlore, pyrophanite and zircon. In the crystalchemical database for amphiboles at CNR-IGG-Pv, ferri-fluoro-leakeite from Bratthagen has the code jym-1226.

Ferri-fluoro-leakeite occurs as elongated striated crystals of mustard yellow to brownish yellow colour growing parallel to a broken aegirine crystal. Holotype ferri-fluoro-leakeite occurs as large black crystals (Cámara *et al.*, 2010). The sample studied in the present work has a large Zn content, a feature which is in accord with the occurrence of sphalerite, willemite and genthelvite (close to endmember composition) at Bratthagen (Larsen, 1988).

X-ray diffraction and crystal-structure refinement

The crystal selected for data collection and structure refinement was ~0.04 mm× $0.04 \text{ mm} \times 0.14 \text{ mm}$ in size. Data collection was performed using a Bruker-AXS Smart-Apex CCDbased diffractometer with graphite-monochromatized MoKa radiation. Omega-rotation frames (scan width 0.3°, scan time 20 s, sample-todetector distance 50 mm) were processed with the SAINT software (Bruker, 2003) and intensities were corrected for Lorentz and polarization effects; absorption effects were evaluated empirically by 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 2285 reflections with $I > 10\sigma(I)$ in the 2 θ range $4-70^{\circ}$. Reflections with $I > 3\sigma(I)$ within the same 2θ range 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)] according to the procedures described in Hawthorne *et al.* (1995). Unit-cell dimensions and details of the crystallographic study are reported in Table 1, atom coordinates and anisotropic displacement parameters are in Table 2 and selected interatomic distances and parameters related to the conformation of the double chain of tetrahedra are in Table 3. Observed and calculated structure factors have been deposited with the Principal Editor of *Mineralogical Magazine* and are available from w w w m in ersoc.org/pages/e_journals/ dep_mat.html.

A sketch of the amphibole structure is shown in Fig. 1 in order to make the following discussion easier to follow.

Chemical composition

The crystal 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 standards and crystals were used for $K\alpha$ X-ray lines: Si: diopside, TAP: Ca: diopside, LPET: Ti: titanite, LPET: Fe: favalite, LLiF; Mn: spessartite, LLiF; Cr: chromite, LLiF; Mg: forsterite, LTAP; Al: andalusite, TAP; K: orthoclase, LPET; Na: albite, TAP; F: fluororiebeckite, LTAP; Zn: gahnite, LLiF. Data reduction was undertaken using the $\varphi(\rho Z)$ procedure of Pouchou and Pichoir (1985). Calcium, Cr and V were below detection limits. The average of 11 analyses is given in Table 4, together with a formula based on stoichiometric constraints and SREF results (see below for a detailed discussion).

$a(\text{\AA})$	9.7879(18)	Crystal size (mm)	$0.04 \times 0.04 \times 0.14$
c (Å)	5.2822(10)	Total no. of reflections	10,970
β(Å)	104.195(5)	No. unique reflections	2025
$V(Å^3)$	893.5(3)	No. observed reflections $(I > 3\sigma(I))$	1576
Space group	C2/m	θ range (°)	2-35
Ζ	2	R_{merge} (%)	2.90
$D_{\rm calc} \ ({\rm g \ cm^{-3}})$	3.24	$R_{\rm obs}$ (%)	2.92
μ MoKa (cm ⁻¹)	27.9	$R_{\rm all}$ (%)	4.16

TABLE 1. Miscellaneous information for ferri-fluoro-leakeite.

Site	SS	x/a	y/b	z/c	$B_{ m eq}$	β^{11}	β^{22}	β^{33}	β^{12}	β^{13}	β^{23}
O(1)		0.10999(14)	0.09052(8)	0.21480(27)	0.77(3)	18	7	72		6	1
O(2)		0.11870(14)	0.16982(8)	0.73519(26)	0.76(3)	20	8	09		6	Ξ
O(3)	17.8(8)	0.11156(19)	0	0.69993(36)	1.20(4)	35	6	111	ı	9	'
0(4)		0.36408(16)	0.25057(8)	0.80404(28)	0.95(3)	32	9	89	-5	14	0
O(5)		0.35024(15)	0.12889(8)	0.08870(28)	0.88(3)	24	6	64	0	13	8
O(6)		0.34317(15)	0.11995(8)	0.58672(28)	0.88(3)	24	6	67	0	12	L
0(1)		0.33512(22)	0	0.30177(43)	1.05(4)	31	5	132	ı	11	'
T(1)		0.27835(5)	0.08608(3)	0.29590(10)	0.62(1)	20	5	55	0	10	Ξ
T(2)		0.28890(5)	0.17125(3)	0.80506(10)	0.61(1)	18	5	50		6	Ξ
M(1)	31.20(12)	0	0.08684(4)	1/2	0.84(2)	26	7	70	ı	15	'
M(2)	49.82(12)	0	0.17950(2)	0	0.66(1)	20	5	59	ı	10	'
M(3)	5.35(5)	0	0	0	0.93(8)	29	9	89	ı	6	'
M(4)	22.55(18)	0	0.27692(7)	1/2	1.42(4)	47	10	149	ı	47	'
A V	4.14(4)	0	1/2	0	2.25(12)	67	21	224	ı	98	'
A(m)	9.43(9)	0.03800(38)	1/2	0.08142(66)	2.00(9)	77	14	210	ı	66	'

TABLE 2. Atom coordinates, refined site-scattering values (ss, e.p.f.u.) and atom displacement parameters (B_{ea} , \mathring{A}^2 ; $\beta^{ij} \times 10^4$) for ferri-fluoro-leakeite.

Crystal chemistry and discussion

The results of the SREF procedure were interpreted in light of the present knowledge of amphibole crystal chemistry (Oberti et al., 2007b). In particular, the refined < T(1) - O > distance shows that Al is present solely as a C cation and the very small Ti content does not suggest the presence of significant deprotonation. After a careful calibration based on accurate SIMS analysis for H₂O, the amount of the oxo component (O^{2-}) in amphiboles can be estimated directly from the M(1)-M(2)distance. As shown by Oberti et al. (2007b), this procedure works quite well for Ca amphiboles (pargasite/hastingsite) and oxo-amphiboles (kaersutite and oxohastingsite) and Na-Ca amphiboles (richterites); however, although the two experimental trends are nearly parallel, suggesting a constant slope for any amphibole composition, no calibration of the intercept is yet available for ^BNa amphiboles.

Holotype ferri-fluoro-leakeite from Kazakhstan described by Cámara et al. (2010) has the formula $^{A}(Na_{0.64}K_{0.38})$ authors showed that Ti (specifically 0.14 atoms per formula unit (a.p.f.u.)) occurs at the M(1) site, which implies an oxo component of 0.28 a.p.f.u. The difference in the observed M(1) - M(2) distances in the two ferri-fluoro-leakeite samples (3.128 and 3.115 Å, respectively) is compatible with a difference in the oxo component of ~0.25 a.p.f.u., which validates the suggestion made by Cámara et al. (2010) and confirms that no oxo component is present in the sample examined in the present work. Therefore, in the absence of further data on ^BNa oxoamphiboles, an estimate of the oxo component can be obtained using the M(1)-M(2)distances of the studied sample and the average slope of the trends proposed for Ca and Na-Ca oxo-amphiboles $(O^{2-}(a.p.f.u.) =$ M(1)-M(2) - 3.115/0.052). In order to test this procedure, the O^{2-} content for ferroferri-obertiite was calculated in this way and 1.21 a.p.f.u. was obtained, in comparison with the reported experimental value of 1.16 a.p.f.u. (Hawthorne et al., 2010).

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T(1)-O(1) T(1)-O(5) T(1)-O(6) T(1)-O(7) <t(1)-o></t(1)-o>	$\begin{array}{c} 1.600(2) \\ 1.629(2) \\ 1.627(2) \\ \underline{1.630(1)} \\ 1.621 \end{array}$	T(2) - O(2) T(2) - O(4) T(2) - O(5) T(2) - O(6) < T(2) - O>	$\begin{array}{c} 1.616(2) \\ 1.595(2) \\ 1.654(2) \\ \underline{1.658(2)} \\ 1.631 \end{array}$
$M(1)-O(1) \times 2 M(1)-O(2) \times 2 M(1)-O(3) \times 2 $	2.056(1) 2.091(2) <u>2.034(1)</u> 2.061	$M(2)-O(1) \times 2 M(2)-O(2) \times 2 M(2)-O(4) \times 2 < M(2)-O>$	2.089(1) 2.033(1) <u>1.929(2)</u> 2.017
$M(3) - O(1) \times 4 M(3) - O(3) \times 2 A - O(5) \times 4$	2.110(1) <u>2.134(2)</u> 2.118 2.826(2)	$ \begin{array}{l} M(4) - O(2) & \times 2 \\ M(4) - O(4) & \times 2 \\ M(4) - O(5) & \times 2 \\ M(4) - O(6) & \times 2 \\ < M(4) - O> \end{array} $	2.415(2) 2.374(2) 2.851(2) 2.508(2) 2.537
$A-O(6) \times 4 A-O(7) \times 2 $ T(1)-O(5)-T(2) T(1)-O(6)-T(2) T(1)-O(7)-T(1)	3.170(2) 2.531(2) 2.905 134.6(1) 138.1(1) 140.6(1)	$A(m) - O(5) \times 2 A(m) - O(5) \times 2 A(m) - O(6) \times 2 A(m) - O(7) A(m) - O(7) A(m) - O(7) $	2.948(2) 2.787(2) 2.828(2) 2.536(2) 3.190(2) <u>2.622(2)</u>
O(5)-O(6)-O(5) O(6)-O(7)-O(6)	172.5(1) 110.3(1)	<a(m)-o></a(m)-o>	2.830

TABLE 3. Selected interatomic distances (Å) and angles (°) in ferri-fluoro-leakeite.

Recalculation of the unit formula based on crystal-chemical evidence and taking into account stoichiometric constraints results in 0.78 Li a.p.f.u. The complete formula based on 24 O and ^W(OH + $F + O^{2-}$) = 2 a.p.f.u. is ^A(Na_{0.68}K_{0.32})_{Σ =1.00}^BNa_{2.00} ^C(Mg_{1.69}Mn²⁺_{0.25}Fe²⁺_{0.24}Zn_{0.29}Al_{0.23}Fe³⁺_{1.50}Ti_{0.02}

 $Li_{0.78})_{\Sigma=5.00}$ ^TSi₈O₂₂^W(F_{1.59}(OH)_{0.41})_{$\Sigma=2.00$}. The calculated site-scattering value of the C cations is 86.42 electrons per formula unit (e.p.f.u.), in excellent agreement with that obtained by SREF (86.37 e.p.f.u.). Assuming that ^CLi is ordered at the *M*(3) site (Hawthorne *et al.*, 1994), the site



FIG. 1. A projection onto (100) of the structure of ferri-fluoro-leakeite from Bratthagen, showing the site nomenclature relevant to the discussion.

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Oxide	Wt.%		a.p.f.u.
SiO ₂	54.99(51)	Si	7.995
TiO ₂	0.22(9)	Al	0.005
$Al_2 \tilde{O}_3$	1.36(10)	Sum T	8.000
FeO _{TOT}	14.33(31)	Ti ⁴⁺	0.024
FeO*	1.96	Al	0.228
Fe ₂ O ₃ *	13.75	Fe ³⁺	1.504
MnO	2.10(70)	Fe ²⁺	0.238
ZnO	2.67(83)	Mg	1.687
MgO	7.79(26)	Mn^{2+}	0.254
Na ₂ O	9.51(16)	Zn	0.287
K ₂ Õ	1.70(9)	Li	0.778
Li ₂ O**	1.33	Sum C	5.000
H ₂ O***	0.43	Na	1.995
F	3.45(26)	Mn^{2+}	0.005
-O=F	-1.45	Sum B	2.000
Total	99.81	К	0.315
		Na	0.685
Calculated site scattering (e.p.f.u.)		Sum A	2.000
C sites	86.32	F	1.587
B sites	22.07	ОН	0.413
A sites	13.52	Sum W	2.00
W sites	17.59		

TABLE 4. Chemical composition and unit formula (based on 24 anions) for ferri-fluoro-leakeite.

* FeO:Fe₂O₃ ratio calculated from single-crystal structure refinement results;

** calculated taking into account stoichiometric constraints;

*** calculated based on 24 (O, OH, F) with (OH + F) = 2 a.p.f.u.

populations reported in Table 5 were calculated by minimizing the differences between the calculated and the observed values of site scatterings and mean bond lengths at the M(1-3) sites and also taking into account the shortening of the < M(1,3)-O> distances due to the presence of F

TABLE 5. Site populations, site scattering and mean bond lengths for ferri-fluoro-leakeite.

Site	Site population (a.p.f.u.)	Site scatter Refined	ring (e.p.f.u.) Calculated	Mean bon Refined	d length (Å) Calculated
T(1)	4.00 Si			1.621	1.620
T(2)	4.00 Si			1.631	1.631
<i>M</i> (1)	$1.51 \text{ Mg} + 0.22 \text{ Fe}^{2+} + 0.21 \text{ Mn}^{2+} + 0.06 \text{ Zn}$	31.20	30.89	2.061	2.074
<i>M</i> (2)	0.23 Zn + 0.02 Fe ²⁺ + 1.50 Fe ³⁺ + 0.23 Al + 0.02 Ti	49.82	49.98	2.017	2.026
M(3)	$0.78 \text{ Li} + 0.18 \text{ Mg} + 0.04 \text{ Mn}^{2+}$	5.35	5.55	2.118	2.093
ΣĊ	C	86.37	86.42		
В	$1.99 \text{ Na} + 0.01 \text{ Mn}^{2+}$	22.55	22.14		
А	0.68 Na + 0.32 K	13.58	13.56		
W	$1.59 \text{ F}^- + 0.41 \text{ OH}^-$	17.80	17.59		

at the O(3) site (Oberti *et al.*, 1993). The results show a very good agreement, validating the proposed site populations.

Three further issues are worth noting as far as site populations and cation ordering are concerned. The site population of the (largest) M(3) octahedron does not include cations with high Z and large ionic radius. The Mn²⁺ is almost completely ordered at the M(1) site, confirming the absence at that site of highly charged cations related to deprotonation. The Zn content of this sample is among the largest observed so far in Li-bearing amphiboles. Indeed, Zn is a rare constituent in amphiboles and is confined to specific environments such as syenites. Zinc is almost completely ordered at the M(2) site in ferri-fluoro-leakeite from Bratthagen, with only a very small amount at the M(1) site. The same ordering scheme for Zn was derived by Oberti et al. (2003) for ^{B,C}Li-bearing monoclinic amphiboles (rootname pedrizite; Oberti et al., 2000) in episyenites of the Pedriza massif (Spain), where in one case, the Zn content reached 0.48 a.p.f.u. In contrast, Hawthorne and Grundy (1977) reported an ordering pattern of the type $M(1) > M(3) \approx$ M(2) for a ^B(Mg-Fe-Mn) amphibole with 0.75 Zn a.p.f.u. (at that time called "zincian tirodite", now "clino-suenoite" after Hawthorne et al., 2012). This assumption was based on unconstrained refinement and should be re-examined in the light of present knowledge of amphibole crystal chemistry. The A cations order at the A(m) site in fluoro-^CLi-bearing amphiboles (Hawthorne *et al.*, 1996) and the displacement of the A(m) site from the centre of the A cavity (0.50 Å in the studied)sample) is related inversely to the content of the larger K cation (Oberti et al., 1993). The A cations contribute to local charge balance at the O(7) anion which bridges the T(1) tetrahedra in amphiboles; in the presence of ^CLi, Si at T(1)increases its bond valence to O(1) (shortening the T(1) - O(1) distance to 1.600 Å in the studied sample) and hence decreases its bond valence to O(7) (lengthening the T(1)-O(7) distance to 1.630 Å in the studied sample, so that the O(6)-O(7)-O(6) angle, which is related inversely to stretching of the double chain of tetrahedra, shrinks to the very low value of 110.34°).

To conclude, but for the presence of a significant amount of Zn, the ferri-fluoro-leakeite sample studied in this work is even closer to the ideal composition than the sample reported by Cámara *et al.* (2010) and its crystal-chemical

analysis confirms the procedures proposed and the trends observed for ^CLi amphiboles. Also, comparison of the two sets of data was useful to confirm the derivation of the site populations and to show the structural effect of deprotonation in ^BNa amphiboles, a feature that has not yet been explored satisfactorily.

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