F-rich richterite from the Hydro quarry, Fen complex, Southern Norway: crystallographic data and crystal-chemistry

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Introduction

Sodium and sodium-calcium amphiboles are described from the contact metasomatic zones in the northwestern part of the alkaline Fen carbonatite complex, Telemark, Norway (Andersen 1989). In the fenites, amphiboles are a characteristic mineral formed as a result of fenitization (an alteration process) of country rock caused by several progressive metasomatic events related to alkali-rich fluids originating from alkaline and carbonatitic intrusions. Amphiboles are also found in the alkaline biotite-amphibole-søvite, a calcite carbonatite, found in this area of the Fen complex, and at the contact zones between the fenite wall rock and søvite, as a result of late-stage metasomatic processes (Brøgger 1921; Sæther 1957; Kresten & Morogan 1986; Kresten 1988; Andersen 1989). In these rocks, amphibole colour varies from colorless to pale greenish to blue. A systematic study of these sodium to sodium-calcium amphiboles would be relevant to understand the petrogenesis of the carbonatites in the Fen complex. However, only a few chemical analyses of amphiboles from the contact zones between the fenite and the biotite-amphibole-søvite have been published so far. In his petrographic study, Andersen (1989) provides two chemical analyses of amphiboles found at the Cappelen quarry, and concludes that amphiboles in the contact metasomatic zones range from richterite to magnesio-arfvedsonite (*sensu lato*) in composition. He does not provide any description of the amphiboles analysed.

We present in this paper the crystal-chemical (EMP analysis and single-crystal structure refinement, SREF) description of a sample of blue amphibole collected in 2012 in the Hydro quarry (neighbour to the Cappelen quarry) by one of the authors (KEL). According to the current IMA amphibole nomenclature (Hawthorne *et al*. 2012), it is classified as F-rich richterite.

Geological setting

The Fen carbonatite complex is situated near lake Norsjø in the Nome municipality in Telemark county, southeast Norway. It consists of a circular 5 km^2 core with various carbonatites and alkaline igneous rocks (mainly of the melteigite-ijolite-urtite series), intruded 583 +/- 10 Ma ago into Mesoproterozoic granitic Telemark Gneiss (ca. 1105 Ma). The intrusion was followed by intense faulting and brecciation, producing several phases through metasomatic alteration and fenitization of the country rock (Brøgger 1921; Sæther 1957; Andersen 1989; Verschure & Maijer 2005). The original minerals of the gneiss, quartz, biotite and amphibole (hornblende), were altered or replaced by aegirine-augite and sodium amphiboles. Microcline and oligoclase were also replaced by mesoperthite and chessboard albite (Verschure & Maijer 2005). A fenite aurole surrounds the western and southern parts of the complex, as well as metasomatic alteration of the fenite at the contact with the carbonatite (Kresten & Morogan 1986; Andersen 1989). Andersen (1989) observed four phases of contact metasomatism associated with different carbonatites. In the largest of these in extent, labelled the C_2-phase, fenite wall-rock alteration was caused by intrusion of biotite-amphibole-søvite and dolomite carbonatite. As a result, minerals of the fenite at the contact with dykes or smaller veins of carbonatite have been altered to phlogopite, amphibole, calcite and apatite.

Location and sample description

The Hydro quarry (in Norwegian: Hydrobruddet) is located in the nortwestern part of the complex, close to the shore of lake Norsjø (59°16'53"N, 9°16'59"). A large irregular dyke of biotite-amphibole-søvite, the so-called Hydro vein, was mined for niobium in 1953-1965, mainly in the Cappelen quarry and Tufte adit nearby. The Hydro quarry is now abandoned and partly overgrown, but veins and swarms of smaller veins of white søvite intruded along fissures in darker fenite can be observed in the quarry. Extensive phlogopitization around fractured pieces of fenite along the contacts of the søvite has been described by Kresten (1988).

A visit to the quarry in 2012 revealed that large boulders had recently fallen from the old quarry wall (Fig. 1) and exposed fresh surfaces of søvite and the contact with fenite. In one of the larger boulders, along the contact surfaces of fenite, which consist mostly of søvite, clusters of blue amphiboles are embedded in phlogopite.

Fig. 1. *The quarry wall at the Hydro quarry. The specimen described in this work was found in one of the larger boulders to the right in the photo.*

A few centimeters away from the amphiboles in the søvite, euhedral crystals of plogopite, apatite (probably fluorapatite) and an altered pyrochlore group mineral (referred to as "koppite" in earlier literature) were observed embedded in the white calcite. A few samples of the amphiboles were collected. One was given to Roy Kristiansen, who later forwarded it to Roberta Oberti for analysis. This specimen (Fig. 2) is about 4 x 10 cm in size, and shows a felt-like mass consisting of aggregates of radiating, acicular, pale-blue amphibole crystals embedded in brownish plogopite.

Fig. 2. *The specimen studied in this work. F-rich richterite occurs as bluish acicular crystals. Photo: Roy Kristiansen.*

X-ray diffraction and crystal-structure refinement

A few crystals were analysed, and they turned out to be quite homogeneous in composition. We report in this paper the best data set, obtained on a crystal which was given the code 1318 in the amphibole database at the CNR-IGG in Pavia, Italy. Data collection was done on a Bruker-AXS Smart-Apex CCD-based diffractometer with graphite-monochromatized Mo$K\alpha$ X-radiation (λ = 0.7107 Å). We report Omega-rotation frames (scan width 0.3°, scan time 20 s, sample-to detector distance 50 mm) were processed with the SAINT software (©Bruker, 2003) and intensities were corrected for Lorentz and polarization effects; absorption effects were empirically evaluated by the SADABS software (Krause *et al.* 2015) and an absorption correction was applied to the data. Accurate unit-cell dimensions were calculated by least-squares refinement of the positions of 2129 reflections with $I_o > 10\ \sigma(I)$ in the θ range 2-30°. Reflections with $I_o > 3\ \sigma(I)$ within the same θ 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 (Cannillo *et al.* 1983). 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). The unit-cell dimensions and details of the crystallographic study are reported in Table 1. Table 2 reports refined site-scattering values (in electrons per formula unit, epfu; Hawthorne *et al.* 1995), atom coordinates and equivalent-isotropic-displacement parameters, and Table 3 reports selected interatomic distances and parameters related to the conformation of the double-chain of tetrahedra.

A sketch of the amphibole structure is provided in Fig. 3 in order to make the following discussion easier to follow.

Table 1. *Unit-cell parameters and crystallographic details for crystal 1318.*

a (Å)	9.8705(6)	Scan width (°)	0.3
b (Å)	17.9702(11)	Scan speed (°s^{-1})	20
c (Å)	5.2764(3)	Sample to detector distance (mm)	50
β (°)	104.1580(10)	R_{sym} %	2.30
V(Å^3)	907.47(9)	R_{obs} %	2.97
θ range (°)	2-30	R_{all} %	3.55
Space group (Z = 2)	*C*2/*m*	# all reflections	1372
Size (μm)	220 × 70 × 30	# obs reflections	1159

Table 2. *Atom coordinates, refined site-scattering values* (ss, epfu), and equivalent atom-displacement parameters (B_{eq}, Å^2) for crystal 1318.*

Site	ss	*x/a*	*y/b*	*z/c*	B_{eq}
O(1)		0.1123(2)	0.08570(8)	0.2168(3)	0.70(3)
O(2)		0.1188(2)	0.16914(8)	0.7271(3)	0.77(3)
O(3)	16.76(6)	0.1068(2)	0	0.7126(6)	0.91(5)
O(4)		0.3623(2)	0.24875(9)	0.7939(3)	1.01(3)
O(5)		0.3474(2)	0.13014(9)	0.0890(3)	0.95(3)
O(6)		0.3428(2)	0.11705(9)	0.5883(3)	0.98(3)
O(7)		0.3393(2)	0	0.2896(5)	1.00(5)
T(1)		0.27937(6)	0.08494(3)	0.29444(11)	0.63(2)
T(2)		0.28655(6)	0.17149(3)	0.80082(11)	0.67(2)
M(1)	24.36(6)	0	0.08888(6)	½	0.69(2)
M(2)	28.43(14)	0	0.17995(5)	0	0.90(2)
M(3)	12.31(4)	0	0	0	0.78(3)
M(4)	29.7(2)	0	0.27591(5)	½	1.24(2)
A	2.24(4)	0	½	0	2.1(2)
A(*m*)	6.62(11)	0.0377(7)	½	0.0891(13)	3.3(2)
A(2)	2.05(9)	0	0.4687(9)	0	1.2(2)
H	1.1(2)	0.184(9)	0	0.75(2)	1.0

*Hawthorne *et al.* (1995)

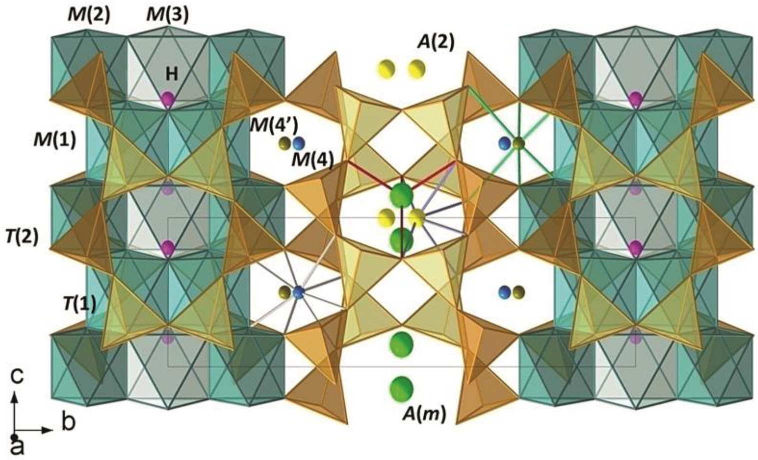

***Fig. 3.** The amphibole structure projected onto (100).*

***Table 3.** Selected interatomic distances (Å), polyhedral volumes (V, Å^3), angles (°), bond angle variances (°^{2}) and quadratic elongations (AV and QE; Robinson et al., 1971) refined for crystal 1318.*

T(1)–O(1)	1.599(2)	*T*(2)–O(2)	1.606(2)	*M*(4)–O(2) ×2	2.409(2)
T(1)–O(5)	1.625(2)	*T*(2)–O(4)	1.582(2)	*M*(4)–O(4) ×2	2.340(2)
T(1)–O(6)	1.629(2)	*T*(2)–O(5)	1.667(2)	*M*(4)–O(5) ×2	2.868(2)
T(1)–O(7)	1.6394(10)	*T*(2)–O(6)	1.682(2)	*M*(4)–O(6) ×2	2.584(2)
<*T*(1)–O>	1.623	< T(2)–O>	1.634	<*M*(4)–O>	2.550
V	2.186	*V*	2.220	*V*	27.373
TAV	11.34	TAV	27.55		
TQE	1.0026	TQE	1.0064		
M(1)–O(1) ×2	2.0676(14)	*M*(2)–O(1) ×2	2.188(2)	*M*(3)–O(1) ×4	2.071(2)
M(1)–O(2) ×2	2.050(2)	*M*(2)–O(2) ×2	2.077(2)	*M*(3)–O(3) ×2	2.048(3)
M(1)–O(3) ×2	2.084(2)	*M*(2)–O(4) ×2	1.987(2)	<*M*(3)–O>	2.063
<*M*(1)–O>	2.067	<*M*(2)–O>	2.084	*V*	11.495
V	11.588	*V*	11.865	OAV	40.46
OAV	36.12	OAV	38.84	OQE	1.0124
OQE	1.0109	OQE	1.0127	O(3)-H	0.74(9)
A–O(5) ×4	2.882(2)	*A*(*m*)–O(5) ×2	2.999(4)	*A*(2)–O(5) ×2	2.448(12)
A–O(6) ×4	3.147(2)	*A*(*m*)–O(5) ×2	2.857(4)	*A*(2)–O(6) ×2	2.803(9)
A–O(7) ×2	2.457(2)	*A*(*m*)–O(6) ×2	2.781(5)	*A*(2)–O(7) ×2	2.521(4)
<*A*–O>	2.903	*A*(*m*)–O(7)	2.443(7)	<*A*(2)–O>	2.590
V	45.506	*A*(*m*)–O(7)	3.205(7)		
		A(*m*)–O(7)	2.580(6)	*M*(1)-*M*(2)	3.1047(7)
T(1)–O(5)–*T*(2)	135.69(10)	<*A*(*m*)–O>	2.833		
T(1)–O(6)–*T*(2)	136.72(10)			O(6)–O(7)–O(6)	106.61(11)
T(1)–O(7)–*T*(1)	137.20(10)			O(5)–O(6)–O(5)	169.63(10)

Chemical composition

The crystal used for the crystallographic study was analysed by electron microprobe at the Department of Geological Sciences of the University of Manitoba in Winnipeg 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*α X-ray lines: Si: diopside, TAP; Ca: diopside, LPET; Ti: titanite, LPET; Fe: fayalite, LLiF; Mn: spessartite, LLiF; Cr: chromite, LLiF; Mg: forsterite, LTAP; Al, andalusite, TAP; K: orthoclase, LPET; Na: albite, TAP; F: fluoro-riebeckite, LTAP; Zn: gahnite, LLiF; Ni: pentlandite, LLiF. Data reduction was done using the φ(ρZ) procedure of Pouchou & Pichoir (1985). Cl, Cr and V were below detection. The average of 10 analyses is given in Table 4, together with a formula (in atoms per formula unit, apfu) based on stoichiometric constraints and SREF results (see below for a detailed discussion).

Table 4. *Chemical composition and unit formula (based on 24 anions) for crystal 1318.*

Oxide	wt.%		apfu
SiO_2	58.42(27)	Si	7.967
TiO_2	0.02(1)	Al	0.016
Al_2O_3	0.10(2)	Ti^{4+}	0.002
FeO_{TOT}	1.86(9)	Sum T	7.985
FeO*	0.90	Fe^{3+}	0.110
Fe_2O_3*	1.07	Fe^{2+}	0.102
MnO	0.13(4)	Mg	4.771
ZnO	0.02(2)	Mn^{2+}	0.014
NiO	0.01(2)	Zn	0.002
MgO	23.86(19)	Ni	0.001
CaO	5.96(7)	Sum C	5.000
Na_2O	7.46(16)	Ca	0.872
K_2O	0.56(2)	Na	1.053
H_2O**	1.54	Mg	0.075
F	1.40(52)	Sum B	2.000
-O=F	-0.59	K	0.097
Total	100.86	Na	0.918
Calculated site scattering (epfu)		Sum A	1.015
C cations	63.20	F	0.600
B cations	29.92	OH	1.400
A cations	11.94	Sum W	2.000

* FeO:Fe_2O_3 ratio calculated from single-crystal structure-refinement results.
** calculated based on 24 (O,OH,F) with (OH + F) = 2 apfu.

Crystal chemistry and discussion

Based on the nomenclature rules in force (Hawthorne *et al.* 2012), the amphibole of this work is richterite, quite close to the end-member composition but for the enrichment in F. The results of the SREF procedure were interpreted in light of the present knowledge of amphibole crystal-chemistry (Oberti *et al.* 2007). In particular, the refined <*T*(1)-O> distance (1.623 Å) shows that the small amount of Al is a T cation. The refined site-scattering value at the *M*(4) site suggest that Mg and not $(Fe,Mn)^{2+}$ enter this site; those refined at the *M*(1-3) sites suggest that any C cations other than Mg order at the *M*(2) site.

The results of the structure refinement in terms of refined site-scattering values are in close agreement with those of the EMP analysis: ΣC cations = 65.10 epfu, ΣB cations = 29.70 epfu, ΣA cations = 10.91 epfu, total = 105.71 epfu (Table 2), to be compared with 63.20, 29.92, 11.94 and 106.06 epfu, respectively, calculated from the unit formula reported in Table 4.

The refined <*M*(2)-O> distance is somewhat longer than that calculated based on the site populations (2.084 vs. 2.075 Å), a pattern which has been already observed for richterites and especially for F-rich richterites (Oberti *et al.* 1992). The refined <*M*(1)-O> and <*M*(3)-O> are in agreement with full Mg occupancy and the analysed F content. Preferential ordering of A cations at the *A*(*m*) subsite is also in accord with the presence of a significant amount of F at the O(3) site (Hawthorne *et al.* 1996).

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References

Andersen, T. (1989): Carbonatite-related contact metasomatism in the Fen complex, Norway: effects and petrogenetic implications. *Mineralogical Magazine* **53**, 395-414.

Bruker (2003): SAINT-NT Software Reference Manual.Version 6. Bruker AXS Inc., Madison, Wisconsin, USA.

Brøgger, W.C. (1921): Die Eruptivgesteine des Kristianiagebietes. IV. Das Fengebiet in Telemark, Norwegen. *Skrifter udgit av Videnskabsselskabet i Kristiania. I. Math. Nat. Klasse* **No. 9**, 1-408.

Cannillo, E., Germani, G. & Mazzi, F. (1983): New crystallographic software for Philips PW1100 single crystal diffractometer. *CNR Centro di Studio per la Cristallografia, Internal Report* **2**, Pavia, Italy.

Hawthorne, F.C., Ungaretti, L. & Oberti, R. (1995): Site populations in minerals: terminology and presentation of results. *The Canadian Mineralogist*, **33**, 907-911.

Hawthorne, F.C., Oberti, R. & Sardone, N. (1996): Sodium at the A site in clinoamphiboles: the effects of composition on patterns of order. *The Canadian Mineralogist* **34**, 577-593.

Hawthorne, F.C., Oberti, R. (Co-Chairs), Harlow, G.E., Maresch, W.V., Martin, R.F., Schumacher, J.C. & Welch, M.D. (2012): Nomenclature of the amphibole supergroup. *American Mineralogist* **97**, 2031-2048.

Krause, L., Herbst-Irmer, R., Sheldrick, G.M. & Stalke, D. (2015): Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *Journal of Applied Crystallography* **48**, 3-10.

Kresten, P. (1988): The chemistry of fenitization: Examples from Fen, Norway. *Chemical Geology* **68,** 329-349.

Kresten, P. & Morogan, V. (1986): Fenitization at the Fen complex, southern Norway *Lithos* **19**, 27-42.

Oberti, R., Ungaretti, L., Cannillo, E. & Hawthorne, F.C. (1992): The behaviour of Ti in amphiboles: I. Four- and six-coordinated Ti in richterites. *European Journal of Mineralogy* **4**, 425-439.

Oberti, R., Hawthorne, F.C., Cannillo, E. & Cámara, F. (2007): Long-range order in amphiboles. Pp. 125–171 in: *Amphiboles: Crystal Chemistry, Occurrence and Health Issues* (F.C. Hawthorne, R. Oberti, G. Della Ventura and A. Mottana, editors). Reviews in Mineralogy and Geochemistry, **67**, Mineralogical Society of America, Washington, D.C., and the Geochemical Society, St. Louis, Missouri, USA.

Pouchou, J.L. & Pichoir, F. (1985): `PAP' φ(ρZ) procedure for improved quantitative microanalysis, p. 104-0160. *Microbeam analysis – 1985.* San Francisco Press, San Francisco.

Sæther, E. (1957): The alkaline rock province of the Fen area in southern Norway. *Det Konglige Norske Videnskabsselskaps Skrifter* **1957 (1)**, 1-150.

Verschure, R.H. & Maijer, C. (2005): A new Rb-Sr isotropic parameter for metasomatism, Δt, and its application in a study of pluri-fenitized gneisses around the Fen ring complex, south Norway. *Norges Geologiske Undersøkelse Bulletin* **445**, 45-71.