

TI-RICH FLUORO-RICHTERITE FROM KARIÅSEN (NORWAY): THE OXO-COMPONENT AND THE USE OF Ti^{4+} AS A PROXY

ROBERTA OBERTI[§]

CNR-Istituto di Geoscienze e Georisorse, UOS Pavia, I-27100, Pavia, Italy

MASSIMO BOIOCCHI

Centro Grandi Strumenti, Università degli Studi di Pavia, I-27100 Pavia, Italy

FRANK C. HAWTHORNE

Department of Geological Sciences, University of Manitoba, 125 Dysart Road, Winnipeg, MB, R3T 2N2, Canada

FERNANDO CÁMARA

Dipartimento di Scienze della Terra, Università degli Studi di Torino, I-10125 Torino, Italy

MARCO E. CIRIOTTI

Associazione Micromineralogica Italiana, via San Pietro 55, I-10073 Devesi-Ciriè, Italy

SVEIN A. BERGE

Hegnaveien 57, N-3235 Sandefjord, Norway

ABSTRACT

The crystal-chemical characterization of an amphibole with an unusual composition, $^{\text{A}}(\text{Na}_{0.76}\text{K}_{0.24})^{\text{B}}(\text{Ca}_{1.42}\text{Na}_{0.56}\text{Mn}^{2+}_{0.02})^{\text{C}}(\text{Mg}_{2.64}\text{Fe}^{2+}_{1.95}\text{Mn}^{2+}_{0.07}\text{Mg}_{2.64}\text{Zn}_{0.01}\text{Fe}^{3+}_{0.01}\text{Ti}^{4+}_{0.32})^{\text{I}}(\text{Si}_{7.18}\text{Al}_{0.82})\text{O}_{22}^{\text{W}}[(\text{OH})_{0.58}\text{O}_{0.27}\text{F}_{1.15}]$, found in pegmatitic veins at Kariåsen, Larvik Plutonic Complex, Norway, provides an excellent example of the detection and estimation of the oxo component in amphibole. The use of Ti as a proxy for the oxo component is discussed and a procedure to derive accurate Ti partitioning from the results of structure refinement is described. Because the presence and amount of oxo component in amphiboles are important in order to determine values of f_{O_2} and $f_{\text{H}_2\text{O}}$, especially in igneous and magmatic systems, this procedure should be applied any time the compositional data or the petrological context indicate the presence of significant Ti, or suggest that the oxo component may be a relevant issue.

Keywords: amphibole, fluoro-richterite, oxo component, titanium, Kariåsen, Norway, structure refinement.

INTRODUCTION

This paper reports on an unusual amphibole composition found in S-type alkaline pegmatitic veins in larvikite at Kariåsen (Norway), which were exposed after blasting in 1979; this composition was formerly described as “magnesio-katophorite” (Hansen 1981, Berge & Andersen 2002, Piilonen *et al.* 2013). In particular, Piilonen *et al.* (2013) reported a comprehensive petrological and geochemical study of mafic phases in

the Larvik Plutonic complex; with regard to the amphiboles, they examined the possibility that the Ti content was related to the presence of the oxo component ($^{\text{W}}\text{O}^{2-}$) according to the coupled substitution $\text{Ti}^{4+} + 2\text{O}^{2-} \leftrightarrow (\text{Mg}, \text{Fe}, \text{Mn})^{2+} + 2\text{OH}^-$; they concluded that this substitution plays a negligible role in these amphiboles and calculated all formulae on the basis of 13 cations and 2 (OH,F,Cl) atoms per formula unit (*apfu*).

However, the oxo component has recently been shown to be far more common than previously

[§] Corresponding author e-mail address: oberti@crystal.unipv.it

thought in all the amphibole subgroups (Oberti *et al.* 2007, Hawthorne *et al.* 2012, Perinelli *et al.* 2012, Zaitsev *et al.* 2013). Here, we report a single-crystal structure refinement and crystal-chemical analysis of the sodium-calcium amphibole occurring at Kariåsen, paying particular attention to the oxo component. The results indicate a different classification of this amphibole and, even more important, provide further clues on the crystal-chemical role of Ti in non-calcium amphiboles. The detection and calculation of the oxo component in sodium-calcium amphiboles are described, and the use of Ti as a proxy for deprotonation is discussed. All these issues should be taken in consideration in future petrological studies involving amphiboles.

This paper is dedicated to Ed Grew for our numerous formal and informal interactions in the pursuit of mineralogy.

OCCURRENCE AND PARAGENESIS

Two large pegmatite veins intruded in larvikite were exposed during blasting for an extension of the athletics fields for the Sandar Sports Club at Kariåsen, Vesterøya, Sandefjord, in 1979 (Fig. 1). An abundance of interesting pegmatite material was exposed for a short period of time. As the only reports available are written in Norwegian and not easy to get hold of (Hansen 1981, Berge & Andersen 2002), we give here a detailed description of the exposed rocks.

A coarse, somewhat altered pegmatite vein in the southeastern part of the worked area contains microcline (as large crystals of perthitic alkali feldspar up to 30 cm long), amphibole (“magnesio-katophorite”

as large, coarse crystals up to 20 cm long), large masses of aenigmatite (as black, shiny crystals with a typical reddish streak), ferrokentbrooksite (as large brown to reddish-brown masses, sometimes altered to a yellowish skeleton-like or powdery material), albite (as small crystals in cavities), zircon (as brown-to-whitish crystals in cavities), aegirine (as small, dark-green needle-shaped crystals in cavities), and quartz (as grayish-brown crystals up to 14 mm long in cavities with albite and epididymite). A less-altered coarse pegmatite vein in the northeastern part of the worked area also contains microcline, “magnesio-katophorite”, aenigmatite, aegirine, and albite with the same characteristics as the other vein. Moreover, it contains riebeckite (as pale-blue fibrous masses of acicular crystals), annite (rare), zircon (as prismatic, brown crystals up to 2–3 cm in length, often close to “magnesio-katophorite” and aenigmatite, or as brown-to-yellow and whitish bipyramidal crystals up to 1 mm in cavities with albite and aegirine), chlorite (as globular crystal aggregates on aegirine and albite in cavities), pyrite (as small crystals in cavities, occurring as cubes, octahedra, pentagonal dodecahedra, and globular crystal aggregates), fluorapatite (as long colorless, white or yellow prismatic crystals in cavities, often covered by pyrite crystals on the prism faces, or white crystals up to 2–3 cm long in the matrix), titanite (as small, brown, striated crystals in cavities with aegirine and albite), and calcite (as well-developed crystals in cavities). Other minerals found in the cavities are parisite-(Ce) (as brownish, prismatic crystals up to 5 mm long in cavities or golden-yellow crystals covered by pyrite on the prism faces, the basal faces being uncovered), pyrochlore (as brown octahedra up to 1 cm), bastnäsite-(Ce) [partly as epitactic



FIG. 1. View of the mineral-rich pegmatite at Kariåsen athletics fields. The black mineralization mainly consists of amphiboles and aenigmatite.

intergrowths with parisite-(Ce) in cavities, partly as a brownish zone surrounding fluorapatite crystals up to 2 cm in matrix], magnetite (rare), hematite (as rosettes of thin tabular crystals), galena (as rare cube-octahedral crystals), molybdenite (as thin tabular crystals with a hexagonal outline up to 1 cm in size), thorite (as brownish-black metamict masses up to 3 cm), ilmenite (black, elongated, rounded crystals up to 14 mm long in an alkali-feldspar matrix), epididymite (as colorless, tabular, elongated crystals up to 5 × 2 mm), britholite-(Ce) (in reddish-brown zones surrounding fluorapatite), allanite-(Ce) (as aggregates of dark reddish-brown crystals up to 1 mm), grossular (as green crystals up to 1 mm), andradite (as green dodecahedra up to 1 mm), arsenopyrite (as crystal aggregates up to 0.5 mm), bertrandite (as colorless, square tabular crystals up to 0.7 mm), elpidite (as small pale-brown crystal aggregates, always somewhat altered), helvine (as aggregates of numerous sub-parallel crystals up to 2 mm in a cavity with elpidite, aegirine, and quartz), monazite-(Ce) (as small brown crystals), “polymignite” (zirconolite-3O; as black, prismatic crystal up to 2 mm long in an alkali-feldspar matrix), and sphalerite (as reddish-brown crystals up to 0.6 mm).

As stated by Dahlgren (2010), Kariåsen occurs in the Ring Section #4 (in order of age of intrusion) of the Larvik plutonic complex. In their comprehensive study of mafic phases in the Larvik plutonic complex, Piilonen *et al.* (2013) ascribed sodium-calcium amphiboles to a late-stage of the pegmatite evolution, and sodium amphiboles (rare, but present at Kariåsen) are considered a secondary hydrothermal phase. They also suggested that at Kariåsen, late-stage amphiboles formed during localized late post-magmatic alteration by fluids in the miaskitic pegmatites.

SINGLE-CRYSTAL STRUCTURE REFINEMENT (SREF)

A fragment of a large crystal, $0.43 \times 0.16 \times 0.10$ mm in size, formerly referred to as “magnesiokatophorite”, was mounted on a Philips PW-1100

four-circle diffractometer and examined with graphite-monochromatized MoK α X-radiation; crystal quality was assessed *via* profile analysis of Bragg diffraction peaks. Unit-cell dimensions were calculated from least-squares refinement of the d values obtained from 52 rows of the reciprocal lattice by measuring the gravity centroid of each reflection and its corresponding antireflection in the θ range -30° to 30° .

Intensity data were collected in the range $2^\circ < \theta < 30^\circ$. Only the monoclinic pairs hkl and $h\bar{k}l$ were collected with the Philips PW1100 point detector. Intensities (I) were corrected for absorption, Lorentz, and polarization effects, and then averaged and reduced to structure factors (F).

Reflections with $I > 3 \sigma_I$ were considered as observed during unweighted full-matrix least-squares refinement on F . In order to improve the refined model, scattering curves for fully ionized chemical species were used at those sites where chemical substitutions occur; neutral *versus* ionised scattering curves were used at the T and anion sites [except O(3)] (*cf.* Hawthorne *et al.* 1995 for a detail description of the procedure). Selected crystal data and refinement information are given in Table 1, selected interatomic distances are given in Table 2, and refined values of the atom coordinates and displacement factors as well as site-scattering values in *epfu* (electrons per formula unit; Hawthorne *et al.* 1995) are given in Table 3. This sample has the code 1130 in the CNR-IGG-Pv amphibole database.

EMP ANALYSIS

The crystal used for the crystallographic study was embedded in epoxy and analyzed by electron microprobe using a Cameca SX-100 operating in wavelength-dispersive mode with an excitation voltage of 15 kV, a specimen current of 10 nA, a beam diameter of 5 μ m, a peak-count time of 20 s, and a background-count time of 10 s. The following standards and crystals were used for K α X-ray lines: Si: diopside, TAP; Ca: diopside, LPET; Ti: titanite, LLiF; Fe: fayalite, LLiF; Mn: spessartine, LLiF; Cr: chromite, LLiF; Mg: forsterite, LTAP; Al: andalusite, TAP;

TABLE 1. CRYSTAL DATA AND REFINEMENT INFORMATION

a (Å)	9.9220(3)	Crystal size (mm)	$0.43 \times 0.16 \times 0.10$
b (Å)	18.1008(5)	Crystal color	blackish
c (Å)	5.2994(3)	Total no. of reflections	2740
β (°)	104.858(3)	No. unique reflections	1400
V (Å ³)	919.93(6)	No. observed reflections ($I > 3\sigma_I$)	1075
Space group	$C 2/m$	θ range (°)	1–30
Z	2	R_{merge} (%)	2.7
D_{calc} (g cm ⁻³)	3.25	R_{obs} (%)	2.2
μ MoK α (cm ⁻¹)	29.0	R_{all} (%)	3.6

TABLE 2. SELECTED BOND DISTANCES (Å) AND BOND ANGLES (°)

$\overline{T}(1)-O(1)$	1.632(2)	$\overline{T}(2)-O(2)$	1.619(2)	$\overline{M}(1)-O(1) \times 2$	2.062(2)	$\overline{M}(2)-O(1) \times 2$	2.171(2)
$\overline{T}(1)-O(5)$	1.654(2)	$\overline{T}(2)-O(4)$	1.591(2)	$\overline{M}(1)-O(2) \times 2$	2.089(2)	$\overline{M}(2)-O(2) \times 2$	2.107(2)
$\overline{T}(1)-O(6)$	1.652(2)	$\overline{T}(2)-O(5)$	1.656(2)	$\overline{M}(1)-O(3) \times 2$	2.073(2)	$\overline{M}(2)-O(4) \times 2$	2.011(2)
$\overline{T}(1)-O(7)$	1.650(1)	$\overline{T}(2)-O(6)$	1.675(2)	$<\overline{M}(1)-O>$	2.074	$<\overline{M}(2)-O>$	2.096
$<\overline{T}(1)-O>$	1.647	$<\overline{T}(2)-O>$	1.635				
$\overline{M}(3)-O(1) \times 4$	2.077(2)	$\overline{M}(4)-O(2) \times 2$	2.423(2)	$A-O(5) \times 4$	2.968(2)	$A(m)-O(5) \times 2$	3.115(2)
$\overline{M}(3)-O(3) \times 2$	2.062(2)	$\overline{M}(4)-O(4) \times 2$	2.348(2)	$A-O(6) \times 4$	3.127(2)	$A(m)-O(5) \times 2$	2.939(2)
$<\overline{M}(3)-O>$	2.072	$\overline{M}(4)-O(5) \times 2$	2.785(2)	$A-O(7) \times 2$	2.466(3)	$A(m)-O(6) \times 2$	2.719(2)
		$\overline{M}(4)-O(6) \times 2$	2.578(2)	$<A-O>$	2.931	$A(m)-O(7)$	2.486(3)
$\overline{M}(1)-\overline{M}(2)$	3.120(1)	$<\overline{M}(4)-O>$	2.534			$A(m)-O(7)$	3.143(3)
						$A(m)-O(7)$	2.590(3)
$O(5)-O(6)-O(5)$	167.2(1)	$\overline{T}(1)-O(5)-\overline{T}(2)$	136.0(1)	$\overline{T}(1)-O(7)-\overline{T}(1)$	136.2(1)	$<A(m)-O>$	2.863
$O(6)-O(7)-O(6)$	105.5(1)	$\overline{T}(1)-O(6)-\overline{T}(2)$	136.6(1)				

K: orthoclase, LPET; Na: albite, TAP; F: fluorriebeckite, LTAP; Zn: gahnite, LLiF. Data reduction was done using the $\phi(\rho Z)$ procedure of Pouchou & Pichoir (1985). Vanadium, Cr, Ni, and Cl were below the detection limit. The average of 11 analyses is given in Table 4, together with two options for formula recalculation, the second of which (column "oxo") is coherent with stoichiometric constraints and SREF results (see below for a detailed discussion).

UNIT FORMULA AND CRYSTAL CHEMISTRY

Based on the measured values of wt.% oxides, an electroneutral and stoichiometric unit-formula cannot be obtained using the standard procedure based on 22 O and 2 (OH,F,Cl) *apfu*. The only solution to avoid negative values of the oxidation ratio $[\text{Fe}^{3+}/(\text{Fe}^{3+}+\text{Fe}^{2+})]$ is

accepting a total sum of cations = 15.91, a low but significant amount of Ti^{4+} , and a deficit in C cations (column "non oxo" in Table 4). To improve the balance, we may either lower the positive charges or raise the negative ones. There are only two possibilities left to obey these constraints: (1) assume the presence of Li , or (2) assume the presence of an oxo component, *i.e.*, partial deprotonation at the O(3) site. Recalculation based on the first assumption results in an even more significant Ti partitioning between the C and T cations. However, the refined values of the mean bond-length and angular variance at $\overline{T}(2)$, which should both significantly increase with the incorporation of Ti^{4+} (Oberti *et al.* 1992), show that Ti is present only as a C cation. Recalculation based on the second assumption shows that the minimum amount of the oxo component required (*i.e.*, that obtained without considering the

TABLE 3. REFINED ATOM COORDINATES AND DISPLACEMENT PARAMETERS, (B_{EQ} , Å²; $\beta_{ij} \times 10^4$), AND REFINED SITE-SCATTERING VALUES (SS, *EPFU*)

Site	ss	x/a	y/b	z/c	B_{EQ}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)		0.11030(18)	0.08590(9)	0.21909(34)	0.71(4)	19(2)	5(1)	69(6)	-1(1)	8(3)	-1(1)
O(2)		0.11993(18)	0.17048(9)	0.72565(33)	0.74(4)	18(2)	6(1)	69(6)	-1(1)	6(2)	-1(1)
O(3)	17.40(5)	0.10646(24)	0	0.71302(46)	1.02(6)	29(2)	6(1)	112(9)	-	13(4)	-
O(4)		0.36314(19)	0.24836(10)	0.79098(37)	0.92(4)	31(2)	5(1)	98(6)	-4(1)	22(3)	-5(1)
O(5)		0.34772(19)	0.13371(10)	0.09774(38)	1.15(4)	21(2)	12(1)	103(7)	1(1)	11(3)	14(2)
O(6)		0.34499(19)	0.11738(10)	0.59598(36)	0.97(4)	21(2)	9(1)	99(6)	1(1)	16(3)	-10(2)
O(7)		0.34104(27)	0	0.28937(54)	1.13(6)	29(3)	5(1)	154(10)	-	12(4)	-
$\overline{T}(1)$		0.28041(7)	0.08459(3)	0.29867(13)	0.51(1)	14(1)	3(1)	53(2)	-1(1)	5(1)	-1(1)
$\overline{T}(2)$		0.28874(6)	0.17117(3)	0.80514(12)	0.49(1)	13(1)	4(1)	49(2)	-1(1)	6(1)	0(1)
$\overline{M}(1)$	34.56(16)	0	0.08766(5)	$1/2$	0.85(2)	23(1)	8(1)	69(3)	-	14(1)	-
$\overline{M}(2)$	41.07(14)	0	0.17868(3)	0	0.58(2)	16(1)	4(1)	67(3)	-	12(1)	-
$\overline{M}(3)$	16.24(4)	0	0	0	0.61(3)	20(1)	3(1)	60(5)	-	4(2)	-
$\overline{M}(4)$	34.57(18)	0	0.27751(4)	$1/2$	0.92(2)	31(1)	5(1)	116(4)	-	36(1)	-
<i>A</i>	4.37(4)	0	$1/2$	0	3.7(2)	75(8)	49(3)	274(29)	-	114(13)	-
<i>A(m)</i>	7.84(11)	0.0457(6)	$1/2$	0.0998(11)	2.9(2)	80(7)	26(2)	264(25)	-	85(10)	-

TABLE 4. AVERAGED EMP ANALYSIS AND UNIT FORMULA*

Oxide	wt.%			apfu	
	non oxo	oxo		non oxo	oxo
SiO ₂	47.76	47.76	Si	7.136	7.176
TiO ₂	2.83	2.83	Al	0.826	0.824
Al ₂ O ₃	4.69	4.69	Ti ⁴⁺	0.038	-
Fe ₂ O ₃	0.05	0.04	Sum T	8.000	8.000
FeO	15.50	15.50	Ti ⁴⁺	0.280	0.320
FeO _{TOT}	15.54	15.54	Al	0.000	0.007
MgO	11.79	11.79	Fe ³⁺	0.006	0.005
MnO	0.71	0.71	Fe ²⁺	1.936	1.948
ZnO	0.09	0.09	Mg	2.624	2.639
CaO	8.83	8.83	Mn ²⁺	0.090	0.071
Na ₂ O	4.53	4.53	Zn	0.010	0.010
K ₂ O	1.25	1.25	Sum C	4.946	5.000
H ₂ O*	0.85	0.58	Ca	1.414	1.422
F	2.42	2.42	Mn ²⁺	-	0.019
-O=F	1.02	1.02	Na	0.586	0.559
Total	100.28	100.00	Sum B	2.000	2.000
Site scattering (epfu)			Na	0.726	0.761
EMP			K	0.238	0.240
non oxo			Sum A	0.964	1.001
EMP			F	1.144	1.150
oxo			OH	0.847	0.581
C cations	90.69	91.65	O ²⁻	0.009	0.269
B cations	34.73	35.06	Sum W	2.000	2.000
A cations	12.51	12.93			

* calculated based on 24 (O, OH, F) with (OH, F) = 2 apfu (non oxo) or (O, OH, F) = 2 apfu (oxo).

occurrence of ^CFe³⁺) is = 0.27 apfu, which corresponds to 0.58 H₂O wt.% in the chemical composition (Table 4). Notably, the resulting agreement between the refined and calculated group site-scattering values is excellent. This agreement would not change, however, if a greater amount of the oxo component were accepted and balanced by a correspondingly greater amount of ^CFe³⁺. Therefore, the next issue is to find further constraints to fix the amount of the oxo component.

In calcium amphiboles and in richterites from mantle environments, there is a strong correlation between the amount of the oxo component (measured by SIMS analysis on H) and the *M*(1)–*M*(2) distance (Fig. 2, modified after Oberti *et al.* 2007). Whereas the slopes of the two experimental trends are almost equal (0.54 and 0.51, respectively), the value measured for *M*(1)–*M*(2) at (OH, F, Cl) = 2 apfu definitively depends on composition, especially on the ^BNa content, but possibly also on the F and Fe contents. The *M*(1)–*M*(2) distance measured in mantle richterites with no oxo component and low F content is 3.120 Å, the same as that measured for the fluoro-amphibole of this work, which suggests that the *M*(1)–*M*(2) distance of reference (*i.e.*, that

corresponding to oxo component = 0 apfu) for fluoro-calcium-sodium amphiboles should be shorter. Hence, the issue here is to find a sample with composition similar to that of the sample of this work but free of oxo component. A good candidate is available in the CNR-IGG-Pv database: the fluoro-katophorite (borderline to fluoro-richterite) BL10 (sample code 721) described by Hawthorne *et al.* (2006), which has the composition: ^A(Na_{0.51}K_{0.30}) ^B(Na_{0.77}Ca_{1.23}) ^C(Mg_{3.43}Fe²⁺_{0.91}Mn_{0.05}Zn_{0.01}Fe³⁺_{0.48}Al_{0.03}Ti_{0.06}Li_{0.02}) ^T(Si_{7.37}Al_{0.63})O₂₂ ^W(F_{1.21}OH_{0.79}). Because the sample studied here contains more Fe and less F [which may imply an increase in the *M*(1)–*M*(2) distance], we can use sample BL10 to calculate the maximum amount of the oxo-component. The length of the *M*(1)–*M*(2) distance in BL10 is 3.103 Å, hence the maximum amount of the oxo component in the sample from Kariåsen is (3.120–3.103)/0.051 = 0.33 ^WO²⁻ apfu, in good agreement with the minimum estimate based on the recalculation of the unit formula.

The amount of the oxo-component in amphiboles can be further constrained based on the calculation of the site populations of the *M*(1–3) sites. The best site populations obtained for the (oxo) unit formula reported in Table 4 are shown in Table 5. They

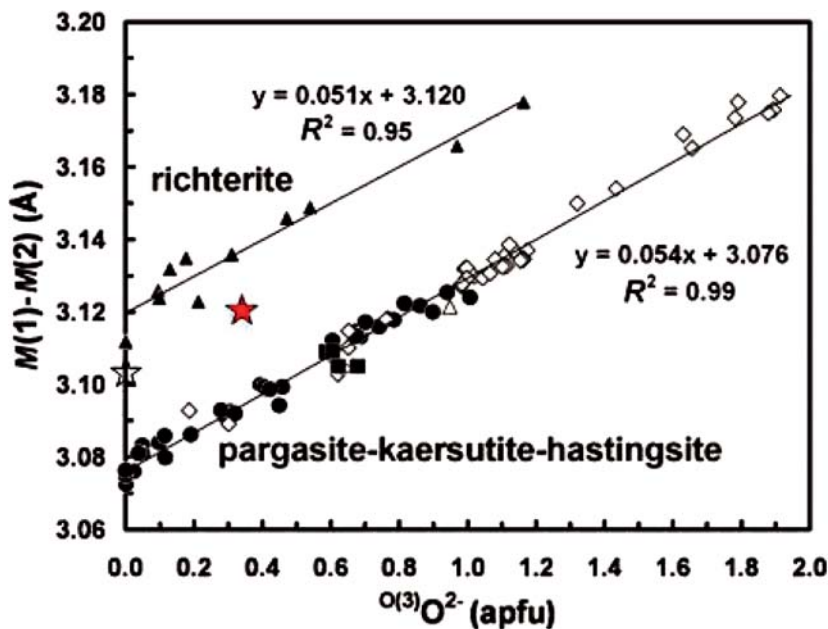


FIG. 2. The relation between the $M(1)$ – $M(2)$ distances and the oxo component in amphiboles. The red star is the sample studied here and the white star is fluoro-katophorite (borderline with richterite) BL10 from Hawthorne *et al.* (2006). Modified after Oberti *et al.* (2007).

confirm that the oxo component is unlikely to be greater than 0.27 *apfu*; in that case, larger amounts of Fe^{3+} would imply shorter $\langle M(1,3)\text{--O} \rangle$ distances. A further feature to be taken into account is the value of Δ ($\sum_{i=1,6} [((M\text{--O})_i - \langle M\text{--O} \rangle) / \langle M\text{--O} \rangle]^2 / 6 \times 10^4$; Brown & Shannon 1973), a measure of the deformation of the $M(1)$ octahedron, which increases significantly (beyond 1–2) when Fe^{3+} occurs at the $M(1)$ site to help balance the oxo component. The Δ value is very low (0.292) in the sample studied here (it is 0.258 in sample BL10 in Hawthorne *et al.* 2006),

confirming that no significant amount of Fe^{3+} occurs at the $M(1)$ site.

Focusing on the site partitioning of the other cations, the amount of $^{\text{T}}\text{Al}$ calculated in Table 4 is in excellent agreement with that calculated based on the $\langle T(1)\text{--O} \rangle$ distance (Oberti *et al.* 1995, Hawthorne & Oberti 2007), confirming that $^{\text{T}}\text{Al}$ is ordered at the $T(1)$ site. Also, the A cations are completely ordered at the $A(m)$ site, as expected when F is greater than 1.0 *apfu* (Hawthorne *et al.* 1996). Note that the A site (with multiplicity 1) has been inserted in the refined

TABLE 5. SITE POPULATIONS OBTAINED BY COMBINING EMP AND SREF RESULTS*

Site	Site populations	SS _{SREF}	SS _{EMP} (oxo)	mbl _{SREF}	mbl _{EMP}
$T(1)$	$\text{Si}_{3.18} \text{Al}_{0.82}$			1.647	1.645
$T(2)$	$\text{Si}_{4.00}$			1.635**	
$M(1)$	$\text{Mg}_{1.21} \text{Fe}^{2+}_{0.66} \text{Ti}^{4+}_{0.13}$	34.56	34.54	2.074	2.071
$M(2)$	$\text{Mg}_{0.72} \text{Fe}^{2+}_{1.01} \text{Mn}^{2+}_{0.07}$	41.07	41.13	2.096	2.094
	$\text{Zn}_{0.01} \text{Ti}^{4+}_{0.19}$				
$M(3)$	$\text{Mg}_{0.71} \text{Fe}^{2+}_{0.28} \text{Fe}^{3+}_{0.01}$	16.24	16.06	2.072	2.073
$M(4)$	$\text{Ca}_{1.42} \text{Na}_{0.56} \text{Mn}^{2+}_{0.02}$	34.57	35.06		
A	$\text{Na}_{0.76} \text{K}_{0.24}$	12.21	12.92		
O(3)	$\text{F}_{1.15} \text{OH}_{0.58} \text{O}^{2-}_{0.27}$				

*ss = site scattering in *apfu*; mbl = mean bond length in Å;

**as a reference, the $\langle T(2)\text{--O} \rangle$ distance observed in sample BL10 in Hawthorne *et al.* (2006) is 1.633 Å.

model solely to better reproduce the bilobate shape of the electron density at the $A(m)$ site (with multiplicity 2).

DISCUSSION AND IMPLICATIONS

Nomenclature and classification

Sodium-calcium amphiboles from Kariåsen and other localities in the Larvik plutonic complex have always been referred to as “magnesio-katophorite” (to be converted to katophorite after Hawthorne *et al.* 2012). Katophorite is a rare composition, and all analyses attributed to its compositional field have turned out to be ferro-, ferri-, or ferro-ferri- katophorite ($\pm$ fluoro-). A sample of authentic katophorite (IMA-CNMNC 2013-140) has only recently been described by Oberti *et al.* (2015) from a sample first analyzed by Harlow & Olds (1987) and found near Hpakan, Jade Mine Tract, Kachin State, Myanmar.

Katophorite has the endmember formula $^A\text{Na}^B(\text{NaCa})^C(\text{Mg}_4\text{Al})^T(\text{Si}_7\text{Al})\text{O}_{22}^W(\text{OH})_2$. The composition of the amphibole described in this work is: $^A(\text{Na}_{0.76}\text{K}_{0.24})_{\Sigma 1.00}^B(\text{Ca}_{1.42}\text{Na}_{0.56}\text{Mn}^{2+}_{0.02})_{\Sigma 2.00}^C(\text{Mg}_{2.64}\text{Fe}^{2+}_{1.95}\text{Mn}^{2+}_{0.07}\text{Zn}_{0.01}\text{Fe}^{3+}_{0.01}\text{Ti}^{4+}_{0.32})_{\Sigma 5.00}^T(\text{Si}_{7.18}\text{Al}_{0.82})_{\Sigma 8.00}^W\text{O}_{22}[(\text{OH})_{0.58}\text{O}_{0.27}\text{F}_{1.15}]_{\Sigma 2.00}$. The new report on amphibole nomenclature and classification (Hawthorne *et al.* 2012) states that only the charge arrangement at the A, B, and C cations must be taken into consideration, and that the amount of the high-charged cations related to deprotonation has to be subtracted to calculate the effective charge of the C-group cations. In the present case, we obtain $^C\text{R}^{3+} = ^C\text{Al} + ^C\text{Fe}^{3+} + 2^C\text{Ti}^{4+} - ^W\text{O} = 0.38$, a value lower than 0.50. Hence, the sample studied here has to be named (Ti-rich) fluoro-richterite. If this sample had (OH, F, Cl) = 2 *apfu*, this composition would have had the charge arrangement of rootname katophorite, but it would have needed a new rootname, because Ti^{4+} is the dominant high-charged cation.

Petrology

In their study of mafic phases from the Larvik plutonic Complex, Piilonen *et al.* (2013) have recently reported many amphibole compositions and discussed their relation to the geological evolution of that area. In particular, in Figure 14, they showed a correlation between total Ti^{4+} and total $(\text{Mg}, \text{Mn}, \text{Fe})^{2+}$, and concluded that the oxo component is not relevant in this system because the experimental compositions do not fall on the 1:1 line. Indeed, the distance from the 1:1 line in such a diagram depends on the crystal-chemical role (*i.e.*, site partitioning) of Ti^{4+} . This study shows that Ti^{4+} is not totally involved in the coupled substitution implying deprotonation. However, having ignored the presence of the oxo component in amphiboles from the Larvik Plutonic Complex, Piilonen *et al.* (2013) reported a number of unit formulae

where the assumption that (OH,F,Cl) = 2 *apfu* produces either a considerable amount of $^T\text{Ti}^{4+}$ (up to 0.21 *apfu*) or low sums of C cations. Both these features should be considered as a signal of the oxo component. In amphiboles, $^T\text{Ti}^{4+}$ has been reported only in richterite and fluoro-richterites occurring in (HT, LP) lamproites and in their synthetic analogues (Oberti *et al.* 1992, Della Ventura *et al.* 1991), and vacancy has never been confirmed as a C-group constituent. All these incorrect features in the amphibole formulae were caused by ignoring the presence of the oxo-component.

Formula calculations and Ti^{4+} partitioning

There are two important considerations that can improve how the Ti^{4+} content is dealt with in amphibole analyses. The first is that the use of Ti^{4+} as a proxy for the oxo component is unsound for the following reasons: (1) only $^C\text{Ti}^{4+}$ should be used for this purpose (although $^T\text{Ti}^{4+}$ has so far been described solely in richterite and fluoro-richterite crystallized under the HT/LP conditions typical of lamproites; Oberti *et al.* 1992); (2) $^C\text{Ti}^{4+}$ may or may not be involved in the local charge balance of deprotonation, so that an estimate which does not distinguish between $^M(1)\text{Ti}^{4+}$ and $^M(2)\text{Ti}^{4+}$ may provide only an estimate of the maximum amount of the oxo component in upper-mantle systems; (3) in many cases, where the Ti^{4+} content in the system is low and especially where deprotonation occurred after crystallization, the oxo component is balanced by oxidation of Fe^{2+} mainly at the $M(1)$ and, to a lesser extent, at the $M(3)$ site (Oberti *et al.* 2007); hence considering only $^C\text{Ti}^{4+}$ in these geological systems (*e.g.*, in volcanic systems) will lead to underestimation of the oxo component.

For the sample studied here, where around 40% of $^C\text{Ti}^{4+}$ is involved in balancing the oxo component, this procedure is particularly successful because a careful recalculation of the unit formula already gives the correct amount of oxo component (although we could arrive at this conclusion only after a complete crystal-chemical analysis). Good estimates of deprotonation can be obtained only by crystal-structure refinement, which is now rapid and straightforward, and hence worthwhile also in petrological studies. If the equivalent atomic-displacement parameter at the $M(1)$ site is higher than those at the $M(2)$ and $M(3)$ sites, this must now be considered as proof of the presence of $^M(1)\text{Ti}^{4+}$ (Tiepolo *et al.* 1999, Oberti *et al.* 2007). Deprotonation related to Fe^{2+} oxidation can be detected by values of Δ at $M(1)$ higher than 2, and measured by the $M(1)$ – $M(2)$ distance. This method works very well for calcium amphiboles and richterites from mantle environments (for a list, see Oberti *et al.* 2007; for more recent cases, see Perinelli *et al.* 2012 and Bonadiman *et al.* 2014), and will be

developed further for other amphibole compositions. However, differences in the oxo component (*e.g.*, during experimental annealing) can now be successfully estimated by the difference in the $M(1)$ – $M(2)$ distances measured before and after annealing (Oberti *et al.* 2013 and manuscript in preparation).

The issue of the correct calculation of the oxo component in amphiboles is of great relevance to petrogenetic studies, especially in igneous and magmatic environments, where an accurate estimate of fO_2 is crucial to establish the conditions of formation and evolution of the system.

ACKNOWLEDGMENTS

A careful revision of the manuscript by Andreas Ertl and Aaron Lussier is gratefully acknowledged. This work was supported by the Natural Sciences and Engineering Research Council of Canada in the form of a Canada Research Chair in Crystallography and Mineralogy, and a Discovery grant to FCH, and by Canada Foundation for Innovation grants to FCH.

REFERENCES

- BERGE, S.A. & ANDERSEN, F. (2002) Mineralforekomster i Sandefjordområdet. *Norsk Bergverksmuseum Skrift* **20**, 50–59 (in Norwegian).
- BONADIMAN, C., NAZZARENI, S., COLTORTI, M., COMODI, P., GIULI, G., & FACCINI, B. (2014) Crystal-chemistry of amphiboles: implications for oxygen fugacity and water activity in lithospheric mantle beneath Victoria Land, Antarctica. *Contributions to Mineralogy and Petrology* **167**, 984–1014.
- BROWN, I.D. & SHANNON, R.D. (1973) Empirical bond strength–bond lengths curves for oxides. *Acta Crystallographica* **A29**, 266–282.
- DAHLGREN, S. (2010) The Larvik Plutonic Complex: The larvikite and nepheline syenite plutons and their pegmatites. In *The Langesundsfjord – History, Geology, Pegmatites, Minerals* (A.O. Larsen, ed.). Bode Verlag GmbH, Salzhemmendorf, Germany.
- DELLA VENTURA, G., ROBERT, J.-L., & BENY, J.-M. (1991) Tetrahedrally coordinated Ti^{4+} in synthetic Ti-rich potassic richterites: evidence from XRD, FTIR and Raman study. *American Mineralogist* **76**, 1134–1140.
- HANSEN, R. (1981) Mineralnotater. *NAGS-nytt* **8**, 18 (in Norwegian).
- HARLOW, G.E. & OLDS, E.P. (1987) Observations on terrestrial ureyite and ureyitic pyroxene. *American Mineralogist* **72**, 126–136.
- HAWTHORNE, F.C. & OBERTI, R. (2007) Amphiboles: Crystal chemistry. In *Amphiboles: Crystal Chemistry, Occurrence and Health Issues* (F.C. Hawthorne, R. Oberti, G. Della Ventura, & A. Mottana, eds.). *Reviews in Mineralogy and Geochemistry* **67**, 1–54.
- HAWTHORNE, F.C., UNGARETTI, L., & OBERTI, R. (1995) Site populations in minerals: terminology and presentation of results of crystal-structure refinement. *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. *Canadian Mineralogist* **34**, 577–593.
- HAWTHORNE, F.C., OBERTI, R., & MARTIN, R.F. (2006) Short-range order in amphiboles from the Bear Lake diggings, Ontario. *Canadian Mineralogist* **44**, 1171–1179.
- HAWTHORNE, F.C., OBERTI, R., 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.
- 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., UNGARETTI, L., CANNILLO, E., HAWTHORNE, F.C., & MEMMI, I. (1995) Temperature-dependent Al order-disorder in the tetrahedral double-chain of $C2/m$ amphiboles. *European Journal of Mineralogy* **7**, 1049–1063.
- OBERTI, R., HAWTHORNE, F.C., CANNILLO, E., & CÁMARA, F. (2007) Long-range order in amphiboles. In *Amphiboles: Crystal Chemistry, Occurrence and Health Issues* (F.C. Hawthorne, R. Oberti, G. Della Ventura, & A. Mottana, eds.). *Reviews in Mineralogy and Geochemistry* **67**, 125–172.
- OBERTI, R., BOIOCCHI, M., WELCH, M.D., & ZEMA, M. (2013) Towards a model for HT behaviour of (orthorhombic and monoclinic) amphiboles. GAC-MAC Meeting Abstracts, Winnipeg, Manitoba, Canada, May 22nd–24th, 153 p.
- OBERTI, R., BOIOCCHI, M., HAWTHORNE, F.C., BALL, N.A., & HARLOW, G.E. (2014) Katophorite from the Jade Mine Tract, Myanmar: mineral description of a rare (grandfathered) end-member of the amphibole supergroup. *Mineralogical Magazine* **79**, 355–363.
- PERINELLI, C., ANDREOZZI, G.B., CONTE, A.M., OBERTI, R., & ARMIENTI, P. (2012) Redox state of subcontinental lithospheric mantle and metasomatism relationships: insights from spinel-peridotites from northern Victoria Land (Antarctica). *Contributions to Mineralogy and Petrology* **164**, 1053–1067.
- PILONEN, P.C., McDONALD, A.M., POIRER, G., ROWE, R., & LARSEN, A.O. (2013) Mafic minerals of the alkaline pegmatites in the Larvik Plutonic Complex, Oslo rift, Southern Norway. *Canadian Mineralogist* **51**, 735–770.
- POUCHOU, J.L. & PICOIR, F. (1985) ‘PAP’ ϕ (ρZ) procedure for improved quantitative microanalysis. In *Microbeam*

- Analysis. (J.T. Armstrong, ed.). San Francisco Press, San Francisco, California, United States (104–106).
- TIEPOLO, M., ZANETTI, A., & OBERI, R. (1999) Detection, crystal-chemical mechanisms and petrological implications of $^{6}\text{Ti}^{4+}$ partitioning in pargasite and kaersutite. *European Journal of Mineralogy* **11**, 345–354.
- ZAITSEV, A.N., AVDONTSEVA, E.YU., BRITVIN, S.N., DEMÉNY, A., HOMONNAY, Z., JEFFRIES, T.E., KELLER, J., KRIVOVICHEV, V.G., MARKL, G., PLATONOVA, N.V., SIIDRA, O.I., SPRATT, J., & VENNEMANN, T. (2013) Oxo-magnesian hastingsite, $\text{NaCa}_2(\text{Mg}_2\text{Fe}^{3+}_3)(\text{Al}_2\text{Si}_6)\text{O}_{22}\text{O}_2$, a new anhydrous amphibole from the Deeti volcanic cone, Gregory rift, northern Tanzania. *Mineralogical Magazine* **77**, 2773–2792.
- ZAITSEV, A.N., AVDONTSEVA, E.YU., BRITVIN, S.N., DEMÉNY, A., HOMONNAY, Z., JEFFRIES, T.E., KELLER, J., KRIVOVICHEV, V.G., MARKL, G., PLATONOVA, N.V., SIIDRA, O.I., SPRATT, J., & VENNEMANN, T. (2013) Oxo-magnesian hastingsite, $\text{NaCa}_2(\text{Mg}_2\text{Fe}^{3+}_3)(\text{Al}_2\text{Si}_6)\text{O}_{22}\text{O}_2$, a new anhydrous amphibole from the Deeti volcanic cone, Gregory rift, northern Tanzania. *Mineralogical Magazine* **77**, 2773–2792.

Received July 31, 2014, Revised manuscript accepted December 5, 2014.

