## Ferro-tschermakite from the Ploumanac'h granitic complex, Brittany, France: mineral description

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Abstract: The mineral description is provided for ferro-tschermakite, ideally  ${}^{A}\Box {}^{B}Ca_{2}{}^{C}(Fe_{3}^{2+}Al_{2})^{T}(Si_{6}Al_{2})O_{22}{}^{W}(OH)_{2}$ . The type specimen has been found in the dump of the Bâtiment et Granit de Ploumanac'h northern granite quarry, La Clarté, Perros-Guirec, Ploumanac'h granitic complex, Brittany, France. The empirical formula derived from electron microprobe analysis and single-crystal structure refinement is:  ${}^{A}(Na_{0.29}K_{0.08})_{\Sigma=0.37}{}^{B}(Ca_{1.69}Fe_{0.11}^{2+}Mn_{0.02}^{2}Na_{0.18})_{\Sigma=2.00}{}^{C}(Fe_{1.84}^{2+}Mg_{1.54}Al_{1.33}Fe_{0.24}^{3+}V_{0.01}^{3+}Ti_{0.04})_{\Sigma=5.00}{}^{T}(Si_{6.15}Al_{1.85})_{\Sigma=8.00}O_{22}{}^{W}(OH_{1.94}F_{0.06})_{\Sigma=2.00}$ . Ferro-tschermakite is biaxial (–), with  $\alpha = 1.666(2)$ ,  $\beta = 1.680(2)$ ,  $\gamma = 1.690(2)$  and 2V (meas.) =  $84(1)^{\circ}$ , 2V (calc.) = 79.8. The dispersion is medium (r > v), and the orientation is:  $X^{*}a = 9.5^{\circ}$  (in  $\beta$  acute),  $Y \parallel b$ ,  $Z^{*}c = 24.3^{\circ}$  (in  $\beta$  obtuse). The unit-cell parameters are a = 9.7598(6), b = 18.0220(11), c = 5.3299(3) Å,  $\beta = 104.826(1)^{\circ}$ , V = 906.27 (9) Å<sup>3</sup>, Z = 2, space group C2/m. The strongest ten reflections in the X-ray powder pattern obtained from single-crystal data [d values (in Å), I, (h k l] are: 8.359, 100, (110); 2.708, 84, (151); 3.098, 55, (310); 2.552, 43, ( $\overline{2} 0 2$ ); 2.595, 41, (061); 2.330, 33, ( $\overline{3} 5 1$ ); 2.159, 27, (261); 2.936, 27, (221); 3.338, 27, (131); 2.012, 24, ( $\overline{4} 0 2$ ; 3 51).

**Key words:** ferro-tschermakite; amphibole; electron-microprobe analysis; optical properties; powder-diffraction pattern; crystalstructure refinement; Ploumanac'h granitic complex; France.

### 1. Introduction

After the approval of the new scheme for the classification and nomenclature of the amphibole supergroup (Hawthorne et al., 2012), we have started a systematic investigation to find and characterize all the amphiboles with distinct compositions that have not yet been officially approved by IMA-CNMNC, and for which there is no proper reference in the official IMA list of minerals. We realized that the root-name "tschermakite", with the ideal  ${}^{A}\Box {}^{B}Ca_{2}{}^{C}(Mg_{3}Al_{2})^{T}(Si_{6}Al_{2})O_{22}{}^{W}(OH)_{2},$ composition) and its Fe-rich analogues are lacking proper modern characterization. We present in this paper the complete characterization of ferro-tschermakite, which was approved by the IMA-CNMNC vote 2016-116. The holotype ferro-tschermakite is deposited in the mineralogical collections of the Museo di Mineralogia of the Università di Pavia, catalogue number 2016-02.

### 2. Occurrence

Ferro-tschermakite was found in a specimen found in the dump of the Bâtiment et Granit de Ploumanac'h northern granite quarry, in the Ploumanac'h granitic complex, at La

Clarté, Perros-Guirec, Brittany, France (~48°48'50" N, ~3°28′50″ W; Fig. S1 in Supplementary Material attached to this article and freely available online on the GSW website of the journal: http://eurjmin.geoscienceworld. org/). The Ploumanac'h granite complex (or Ploumanac'h plutonic complex in Decître et al., 2002), is located on the northern coast of Brittany, at the northern tip of the Trégor, between Trébeurden and Perros-Guirec. On the geological map of France at a scale of 1/1 000 000, the complex occurs at the northern end of the "red granites", which extend from the end of Finistère (Aber-Ildut, Morlaix) in the southwest to the Cotentin peninsula (Flamanville and Barfleur) in the northeast. The Ploumanac'h complex is approximately  $12 \times 8$  km in extent, and is concentrically zoned with an outer aureole (Fig. S2; Barrière, 1977). A reconstruction of geological setting, of magma composition and of the complex crystallization conditions is provided in Decître et al. (2002). The Ploumanac'h complex intrudes: (i) the Trébeurden gneisses; (ii) the granite pluton of Perros-Guirec; (iii) the orbicular granite of Milliau Island (Decître et al., 2002). The Perros-Guirec granite (Fig. S3) is a grey-pink granite batholith located east of the Ploumanac'h complex. It is a coarse-grained, porphyroid granite, where the pronounced pink colour is due to the presence of large feldspar crystals. It is emplaced in the Icartian basement, dated to the lower Brioverian (615 Ma, the beginning of the Cadomian cycle), and intruded by veins of the pink Ploumanac'h granite (Decître *et al.*, 2002).

### 3. Appearance and physical properties

The holotype specimen is shown in Fig. 1. It consists of a  $\sim$ 3 cm long aggregate of dark green bladed-to-acicular crystals of ferro-tschermakite associated with white plagioclase and occurs in miarolitic texture in a granite pegmatite. Ferro-tschermakite is dark green, is non-fluorescent, and has a dark green streak and a vitreous lustre.

A spindle stage was used to orientate a crystal to measure refractive indices and 2*V* by extinction curves (Bartelmehs *et al.*, 1992). The optical orientation was determined by transferring the crystal from the spindle stage to a single-crystal diffractometer and measuring the relative axial relations by X-ray diffraction. In transmitted plane-polarized light, ferro-tschermakite is pleochroic (*X*= pale yellow-green, *Y*= olive green, *Z*= blue green). It is biaxial (-),  $\alpha = 1.666(2)$ ,  $\beta = 1.680(2)$ ,  $\gamma = 1.690(2)$ , 2*V* (meas)=84(1), 2*V* (calc)=79.8°. The dispersion is medium (*r* > *v*), and the orientation is:  $X^{\wedge} \mathbf{a} = 9.5^{\circ}$  (in  $\beta$  acute), *Y*|| **b**,  $Z^{\wedge} \mathbf{c} = 24.3^{\circ}$  (in  $\beta$  obtuse).

The compatibility index  $(1 - (K_p/K_c); Mandarino, 1981)$  is 0.005 (superior) based on the proposed chemical formula.

# 4. Single-crystal diffraction and powder analysis

Diffraction data for a platy prismatic single crystal  $140 \times 130 \times 50$  µm in size were collected in the  $\theta$  range 2– 30° with a Bruker-AXS CCD diffractometer using graphite monochromatized ΜοΚα X-radiation  $(\lambda = 0.7107 \text{ Å})$ . Omega rotation frames (scan width  $0.3^{\circ}$ , 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. A total of 6912 collected reflections was reduced to 1377 unique reflections (mean redundancy = 5,  $R_{int}$  = 1.8%). Of these, 1249 reflections with  $I > 3\sigma I$  were considered as observed during unweighted full-matrix least-squares refinement on F done with a program locally written to handle complex solid-solutions (Cannillo et al., 1983). Scattering curves for fully ionised 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)]. Full-matrix unweighted least-squares refinement on I > 3 $\sigma I$  gave  $R_{obs} = 2.5\%$  (1249 reflections) and  $R_{all} = 2.7\%$ (1377 reflections). Refined atom coordinates and displacement parameters, and selected bond lengths and angles are given in Tables 1 and 2, respectively. Observed structure



Fig. 1. The holotype specimen of ferro-tschermakite, from the Ploumanac'h granitic complex (scale in cm).

factors have been deposited together with the CIF, as part of the supplementary material linked to this article. The refined and analysed crystal of this work has the code 1307 in the amphibole database of the CNR-IGG in Pavia, Italy.

The *a:b:c* ratio calculated from the unit cell parameters is 0.542:1:0.296.

X-ray powder-diffraction data (CuK $\alpha$ ,  $\lambda = 1.54178$  Å) were obtained using the XPREP utility of SAINT (Bruker, 2003), which generates a 2D powder diffractogram (Debye–Scherrer technique) starting from the  $F_{obs}$ collected on the single crystal and taking into account solely the information concerning the unit-cell dimensions and the Laue symmetry. No Lorentz and polarization corrections were applied. Data are given in Table 3.

#### 5. Chemical analysis and unit-formula

Chemical analysis (10 points) of the crystal used for structure refinement was done with a Cameca SX-100 electron microprobe (WDS mode, 15 kV, 20 nA, counting time 20 s, 5  $\mu$ m beam diameter). The standards used are as follows: Si and Ca, diopside (TAP); Ti, titanite (LPET); Al, and alusite (TAP); Cr, chromite (LPET); V,  $VP_2O_7$ (LLiF); Fe, fayalite (LLiF); Mn, spessartine (LLiF); Mg, forsterite (LTAP); Zn, gahnite (LLiF); Ni, pentlandite (LLiF); Na, albite (TAP); K, orthoclase (LPET); F, fluororiebeckite (TAP); Cl, tugtupite (LPET). The amount of H<sub>2</sub>O used in the calculation is that required to give F + OH + Cl = 2 anions and 15.37 cations per formula unit, in accord with amphibole stoichiometry and the results of the structure refinement (which constrains the total number of cations and excludes the presence of the oxo-component). These assumptions fix the  $Fe^{3+}/Fe_{tot}$ ratio. The oxide wt% and the calculated unit-formula are reported in Table 4. The proposed empirical formula (based on 24 anions pfu and 15.37 cations pfu, a value compatible with the results of the structure refinement) is  ${}^{A}(Na_{0.29}K_{0.08})_{\Sigma=0.37}{}^{B}(Ca_{1.69}Fe_{0.11}^{2+}Mn_{0.02}^{2+}Na_{0.18})_{\Sigma=2.00}$ 

Site	Ss	x	у	Ζ	B <sub>eq</sub>	$\beta_{11}$	β <sub>22</sub>	β <sub>33</sub>	$\beta_{12}$	$\beta_{13}$	β <sub>23</sub>
O(1)		0.1041(2)	0.09409(8)	0.2089(3)	1.01(3)	27	8	100	-2	18	-2
O(2)		0.1193(2)	0.17647(8)	0.7443(3)	0.96(3)	24	7	103	0	9	2
O(3)	16.30(10)	0.1114(2)	0	0.7098(4)	1.10(5)	28	8	118	_	14	_
O(4)		0.3722(2)	0.25142(8)	0.7958(3)	1.15(3)	39	6	124	-3	23	3
O(5)		0.3525(2)	0.14032(8)	0.1103(3)	1.13(3)	29	9	104	-1	11	9
O(6)		0.3413(2)	0.12069(9)	0.6025(3)	1.20(3)	31	10	117	1	14	-7
O(7)		0.3312(3)	0	0.2850(5)	1.56(5)	42	10	173	_	15	_
T(1)		0.28060(6)	0.08693(3)	0.30164(11)	0.72(2)	22	5	71	-1	9	-1
T(2)		0.29292(6)	0.17407(3)	0.81664(11)	0.74(2)	22	5	75	-1	12	0
M(1)	38.67(11)	0	0.09024(3)	1/2	0.79(2)	28	5	71	_	14	_
M(2)	30.73(10)	0	0.17824(4)	0	0.78(2)	24	5	82	_	12	_
M(3)	22.42(4)	0	0	0	0.80(2)	29	5	76	_	14	_
M(4)	38.0(2)	0	0.28043(4)	$\frac{1}{2}$	1.06(2)	33	8	105	_	27	_
M(4')	1.51(7)	0	0.2578(12)	$\frac{1}{2}$	1.0						
A	1.49(6)	0	1/2	0	2.0						
A(m)	1.32(9)	0.033(3)	1/2	0.085(7)	2.0						
A(2)	1.72(9)	0	0.4675(13)	0	2.0						
Н	1.8(2)	0.183(8)	0	0.765(13)	1.0						

Table 1. Atom coordinates, refined site-scattering values (ss, epfu), atom-displacement parameters ( $B_{eq}$ , Å<sup>2</sup>;  $\beta_{ij} \times 10^4$ ) for ferro-tschermakite crystal 1307.

Table 2. Selected interatomic distances (Å), angles (°), bond angle variances (°<sup>2</sup>) and quadratic elongations (AV and QE; Robinson *et al.*, 1971) in ferro-tschermakite crystal 1307.

$ \frac{T(1)-O(1)}{T(1)-O(5)} \\ \frac{T(1)-O(6)}{T(1)-O(7)} \\ < T(1)-O> \\ TAV \\ TQE $	1.671(2) 1.681(2) 1.675(2) 1.6519(9) 1.670 3.60 1.0009	T(2)-O(2) T(2)-O(4) T(2)-O(5) T(2)-O(6) < T(2)-O> TAV TQE	1.639(2) 1.612(2) 1.641(2) 1.651(2) 1.636 18.23 1.0047	$\begin{array}{l} M(4)-O(2) \times 2 \\ M(4)-O(4) \times 2 \\ M(4)-O(5) \times 2 \\ M(4)-O(6) \times 2 \\ < M(4)-O \\ < M(4)-O \\ > \end{array}$	2.405(2) 2.319(2) 2.626(2) 2.511(2) 2.465
$M(1)-O(1) \times 2 M(1)-O(2) \times 2 M(1)-O(3) \times 2  OAV OQE$	2.0621(14) 2.166(2) 2.111(2) 2.113 65.50 1.0207	$M(2)-O(1) \times 2 M(2)-O(2) \times 2 M(2)-O(4) \times 2  OAV OQE$	1.998(2) 2.0066(14) 1.911(2) 1.972 19.58 1.0064	$M(3)-O(1) \times 4$ $M(3)-O(3) \times 2$ < M(3)-O> OAV OQE	2.137(2) 2.106(2) 2.127 114.31 1.0363
$A-O(5) \times 4  A-O(6) \times 4  A-O(7) \times 2    M(4')-O(2) \times 2  M(4')-O(4) \times 2$	3.041(2) 3.153(2) 2.510(3) 2.979 2.10(2) 2.253(2)	$A(2)-O(5) \times 2$ $A(2)-O(6) \times 2$ $A(2)-O(7) \times 2$ < A(2)-O>	2.57(2) 2.780(14) 2.578(6) 2.64	$\begin{array}{l} A(m) - O(5) \times 2 \\ A(m) - O(5) \times 2 \\ A(m) - O(6) \times 2 \\ A(m) - O(7) \\ A(m) - O(7) \\ A(m) - O(7) \\ < A(m) - O(7) \\ < A(m) - O> \end{array}$	3.10(2) 3.06(2) 2.82(2) 2.46(3) 3.28(3) 2.65(2) 2.93
$ \begin{array}{l} M(4') - O(5) \times 2 \\ M(4') - O(6) \times 2 \\ < M(4') - O > \end{array} $	2.869(14) 2.82(2) 2.51	T(1)-O(5)-T(2) T(1)-O(6)-T(2) T(1)-O(7)-T(1)	133.62(10) 141.21(10) 143.0(2)	O(5)-O(6)-O(5) O(6)-O(7)-O(6)	164.22(9) 104.96(11)

 $\label{eq:started_$ 

Based on the empirical formula, the calculated density of the ferro-tschermakite sample of this work is  $3.260 \text{ g/cm}^3$ .

### 6. The crystal-chemistry of ferro-tschermakite

The site populations were obtained by distributing the ions of the unit formula (Table 4) under the constraints of the refined site-scattering values (Hawthorne *et al.*, 1995) and mean bond-lengths for the C cations (Table 2). The results are reported in Table 5. The agreement between the refined and calculated site-scattering values for the B and C cations is very close. In particular, the calculated

I <sub>rel</sub>	d(calc)	h	k	l	I <sub>rel</sub>	d(calc)	h	k	l	I <sub>rel</sub>	d(calc)	h	k	l	$I_{\rm rel}$	d(calc)	h	k	l
16.3	9.010	0	2	0	27.0	2.936	2	2	1	5.8	2.221	2	4	2	5.0	1.699	0	10	1
100.0	8.359	1	1	0	7.9	2.786	3	3	0	5.6	2.179	1	7	1			1	3	3
8.2	5.067	1	3	0	83.6	2.708	1	5	1	27.2	2.159	2	6	1	8.7	1.688	$\overline{2}$	8	2
15.5	4.912	1	1	1	41.4	2.595	0	6	1	13.8	2.051	2	0	2			0	2	3
14.8	4.505	0	4	0	43.3	2.552	$\overline{2}$	0	2	23.5	2.012	4	0	2	20.0	1.643	4	6	1
10.9	3.890	1	3	1	6.4	2.369	3	5	0			3	5	1	5.4	1.629	4	8	0
26.8	3.388	1	3	1	32.8	2.330	3	5	1	6.3	1.993	3	7	0	12.3	1.614	1	11	0
21.4	3.258	2	4	0	15.9	2.309	4	2	1	11.3	1.865	1	9	1	18.1	1.590	1	5	3
55.4	3.098	3	1	0	19.2	2.284	3	1	3	8.1	1.801	0	1	0	5.7	1.553	4	0	2

Table 3. Powder X-ray diffraction data for ferro-tschermakite crystal 1307.

*Note*: The strongest ten reflections are in bold. Only peaks with  $I_{rel} \ge 5$  are reported.

Table 4. Chemical composition (10 points), unit formula (based on 24 anions and 15.37 cations) and a comparison between observed and calculated group site-scattering for ferro-tschermakite crystal 1307. \* Calculated on a 2 (OH,F) apfu basis.

Oxide	wt%(esd)	Range	Oxide	wt%(esd)	Range	apfu		apfu	
SiO <sub>2</sub>	41.32(21)	40.61-42.55	H <sub>2</sub> O*	1.96		Si	6.15	Са	1.69
$TiO_2$	0.37(2)	0.35-0.39	F	0.12(15)	0.00-0.24	Al	1.85	Na	0.29
$Al_2O_3$	18.13(13)	17.72-18.41	Cl	-		Sum T	8.00	Fe <sup>2+</sup>	0.11
$Fe_2O_3$	2.09		O=F	-0.05				$Mn^{2+}$	0.02
$Cr_2O_3$	0.02(24)	0.00-0.03	Total	99.47		Ti <sup>4+</sup>	0.04	Sum B	2.00
$V_2 O_3$	0.05(4)	0.01-0.08				$Al^{3+}$	1.33		
FeO	15.66					Fe <sup>3+</sup>	0.24	Na	0.29
[FeO] <sub>tot</sub>	[17.55(27)]	17.18-17.82				$V^{3+}$	0.01	Κ	0.08
MgO	6.94(7)	6.73-7.15				Cr <sup>3+</sup>	_	Sum A	0.37
MnO	0.20(5)	0.15-0.22	Group si	ite-scattering (epfu	1)	Mg	1.54		
NiO	0.01(2)	0.00-0.03	1	obs (SREF)	calc (EMP)	$Mn^{2+}$	_	$OH^{-}$	1.94
ZnO	0.02(6)	0.00-0.04	С	91.82	90.96	Fe <sup>2+</sup>	1.84	$F^{-}$	0.06
CaO	10.58(32)	18.48-10.64	В	39.47	39.15	Ni	_	Sum W	2.00
Na <sub>2</sub> O	1.61(32)	1.30-1.74	А	4.53	4.71	Zn	_		
K <sub>2</sub> O	0.45(2)	0.42–0.46	Total	135.81	134.82	Sum C	5.00		

Table 5. Site populations for ferro-tschermakite crystal 1307. There is close agreement (see text for more detail) between the refined values of site-scattering (ss, electrons per formula unit) and mean bond-lengths (mbl, Å) and those calculated based on the proposed site populations.

Site	Site population (apfu)	SS	(epfu)	mbl (Å)		
		Refined	Calculated	Refined	Calculated	
$\overline{T(1)}$ T(2)	2.15 Si + 1.85 Al 4 00 Si			1.670	1.673	
M(1) M(2)	$1.04 \text{ Fe}^{2+} + 0.96 \text{ Mg}$ $0.34 \text{ Mg} + 0.04 \text{ Fe}^{2+} + 1.33 \text{ Al} + 0.24 \text{ Fe}^{3+} + 0.01 \text{V}^{3+} + 0.04 \text{ Ti}^{4+}$	38.67 30.73	38.56 29.76	2.113	2.102 1.971	
M(3) $\Sigma$ C cations	$0.76 \text{ Fe}^{2+} + 0.24 \text{ Mg}$	22.42 91.82	22.64 90.96	2.127	2.113	
B cations A cations W anions	1.69 Ca + 0.11 Fe <sup>2+</sup> + 0.02 Mn <sup>2+</sup> + 0.18 Na 0.29 Na + 0.08 K 1.94 OH + 0.06 F	39.47 4.53	39.15 4.71			

< M(2)-O> distance – which is a linear function of the averaged ionic radius of the constituents and is thus sensitive to the Fe<sup>3+</sup>/Fe<sup>2+</sup> ratio (Hawthorne & Oberti, 2007; Oberti *et al.*, 2007) – is in excellent agreement with the refined value, which confirms the assumption done during the formula recalculation. In contrast, the calculated < M(1)-O> and < M(3)-O> distances are

significantly shorter than the measured values, a feature which is coherent with a unusual distortion of the relevant octahedra (Table 2). However, this difference excludes the presence of trivalent cations at the M(1) and M(3) sites, and hence any deprotonation, so that the assumption of 24 (O,OH,F) atoms per formula unit (apfu) in the calculation of the formula unit is further supported.

	"Tschermakite" <sup>1</sup>	Ferro-tschermakite <sup>2</sup>	"Ferri-tschernakite" <sup>3</sup>
Colour	Green	Dark green	Pale green
Optical class		Biaxial (–)	Biaxial (–)
Pleochroism		X = pale yellow-green,	X = pale yellowish green,
		Y = olive green,	Y = Z = pale brownish green
		Z = blue-green	
Orientation	$Z \wedge c = 20^{\circ^*}$	Y    <b>b</b>	
		$Z \wedge c = 24.3^{\circ}$ (in $\beta$ acute)	
α	1.657*	1.666	1.652
β		1.680	1.664
γ		1.690	1.675
$2V_{\text{meas}}$ (°)	80°*	84°	58°
Space group	C2/m	C2/m	
a (Å)	9.8059(5)	9.7598(6)	
b (Å)	17.9721(8)	18.022(1)	
<i>c</i> (Å)	5.3012(2)	5.3299(3)	
β (°)	105.063(1)	104.826(1)	
$V(A^3)$	902.15	906.27	
< T(1) - O > (A)	1.661	1.670	
< T(2) - O > (Å)	1.637	1.636	
< M(1) - O > (A)	2.088	2.113	
< M(2) - O > (Å)	2.018	1.972	
< M(3) - O > (Å)	2.080	2.127	
< M(4) - O > (Å)	2.476	2.465	
T(1) - O(5) - T(2)	133.6	133.6	
T(1) - O(6) - T(2)	138.8	141.2	
T(1) - O(7) - T(1)	138.4	143.0	
Reference	Abdu & Hawthorne (2009)	This work	Ogura (1958)

Table 6. A comparison of the optical and crystallographic properties available for "tschermakite" (no longer such after Hawthorne et al., 2012), ferro-tschermakite (this work) and "ferri-tschermakite".

The presence of the A(m) and M(4') subsites confirm, respectively, the presence of  $A^{(m)}K$  and of a significant amount of small B cations.

### 7. Relation to other species

Ferro-tschermakite is a newly characterized member of the calcium amphibole group with the end-member formula <sup>A</sup> $\square$ <sup>B</sup>Ca<sub>2</sub><sup>C</sup>(Fe<sub>3</sub><sup>2+</sup>Al<sub>2</sub>)<sup>T</sup>(Si<sub>6</sub>Al<sub>2</sub>)O<sub>22</sub><sup>W</sup>(OH)<sub>2</sub> (Hawthorne *et al.*, 2012). It forms a series with tschermakite, <sup>A</sup> $\square$ <sup>B</sup>Ca<sub>2</sub><sup>C</sup>(Mg<sub>3</sub>Al<sub>2</sub>)<sup>T</sup>(Si<sub>6</sub>Al<sub>2</sub>)O<sub>22</sub><sup>W</sup>(OH)<sub>2</sub>, the only composition related to the rootname "tschermakite" so far recognized as a valid mineral species by IMA-CNMNC (Winchell, 1945; Abdu & Hawthorne, 2009). However, the composition reported by Abdu & Hawthorne (2009) should no longer be called tschermakite according to the classification rules in force, because the amount of trivalent C cations (which was not an issue in the previous classification schemes of Leake, 1978, and Leake et al., 1997) is much lower than 1.50 apfu, and that amphibole now falls in the compositional field of magnesiohornblende (although with a significant pargasite component). A comparison of the results of the structure refinement for "tschermakite" and ferro-tschermakite reported in Table 6 is coherent with the reported unit formulae. In particular, crystal 1307 has: (i) a lower amount of A cations (as inferred from the refined sitescattering values at the A sites); (ii) a higher amount of  ${}^{1}Al$ , ordered at the T(1) site (as inferred from the longer < T(1)-O> distance); (iii) a higher amount of trivalent C cations ordered at the M(2) site (as inferred from the shorter <M(2)–O> distance); (iv) a higher  $Fe^{2+}$  content (from the higher refined site-scattering values at the M(1) and M(3)sites and the longer  $\langle M(1) - O \rangle$  and  $\langle M(3) - O \rangle$ distances). As a consequence of (ii) and (iii), the double chain of tetrahedra in ferro-tschermakite is more stretched along both the b and c directions (as inferred from the T-O-T angles).

Given the absence of proper mineral description in the literature, tschermakite  $\Box$ Ca<sub>2</sub>(Mg<sub>3</sub>Al<sub>2</sub>)(Si<sub>6</sub>Al<sub>2</sub>)O<sub>22</sub>(OH)<sub>2</sub>, ferri-tschermakite  $\Box Ca_2(Mg_3Fe_2^{3+})(Si_6Al_2)O_{22}(OH)_2$  and  $\Box Ca_2(Fe_3^{2+}Fe_2^{3+})(Si_6Al_2)$ ferro-ferri-tschermakite,  $O_{22}(OH)_2$ , have to be considered as named amphiboles (Burke & Leake, 2004) and potential new minerals.

Of the 25 analysis reported by Deer et al. (1997) with reference to the tschermakite-ferro-tschermakite series (Table 12, pp. 248–249), only nine fit the stoichiometric requirement for C cations fixed by Hawthorne et al. (2012). Of those, five can be referred to as ferro-tschermakite: #15 from a garnet-staurolite amphibolite at Ovala (Gabon; Demange, 1976), #17 from a metacarbonate rock at Waits River (Vermont; Léger & Ferry, 1991), #19 from a hornblende schist at Lake Kutemajärvi (Finland; Seitsaari, 1951), #22 from an amphibolite at Permiö (Finland; Seitsaari, 1952), and #24a from an almandine-biotitechlorite gneiss at Joyceville (Massachusetts; Doolan et al., 1978), which is closest to the end-member composition. Hawthorne & Grundy (1973) report a ferro-tschermakite from the Frood Mine, Sudbury, Canada, that is close to the composition reported here. Only analysis #14 in Deer et al. (1997), which refer to a sample from a gneissose quartzdiorite at Furudono, Gosaisyo-Takanuki district (Japan; Ogura, 1958), where  $Fe^{3+}=0.669$  and Al=0.612 apfu, conforms to the ferri-dominant species.

Acknowledgements: FCH was supported by a Discovery Grant from the Natural Sciences and Engineering Research Council of Canada and Innovation Grants from the Canada Foundation for Innovation. Careful reviews by two anonymous referees are gratefully acknowledged.

### References

- Abdu, Y.A. & Hawthorne, F.C. (2009): Crystal structure and Mössbauer spectroscopy of tschermakite from the ruby locality at Fiskenaesset, Greenland. *Can. Mineral.*, 47, 917–926.
- Barrière, M. (1977): Carte géologique au 1/25 000 du complexe granitique centré de Ploumanac'h – Massif armoricain. BRGM, Ed., Paris, France.
- Bartelmehs, K.L., Bloss, F.D., Downs, R.T., Birch, J.B. (1992): EXCALIBR II. Z. Kristallogr., 199, 185–196.
- Bruker (2003): SAINT Software Reference Manual. Version 6. Bruker AXS Inc., Madison, Wisconsin, USA.
- Burke, E.A.J. & Leake, B.E. (2004): "Named amphiboles": a new category of amphiboles recognized by the International Mineralogical Association (IMA), and the proper order of prefixes to be used in amphibole names. *Can. Mineral.*, **14**, 1881–1884.
- 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.
- Decître, S., Gasquet, D., Marignac, C. (2002): Genesis of orbicular granitic rocks from the Ploumanac'h Plutonic Complex (Brittany, France): petrographical, mineralogical and geochimical constraints. *Eur. J. Mineral.*, 14, 715–731.
- Deer, W.A., Howie, R.A., Zussman, J. (1997): Rock-forming Minerals: Double-Chain Silicates, Volume 2B. Geological Society of London, 764 p.
- Demange, M. (1976): Une paragenèse à staurolite et tschermakite d'Ovala (Gabon). Bull. Soc. fr. Minéral. Cristallogr., 99, 379–402.
- Doolan, B.l., Zen, E-an, Bence, A. (1978): High-aluminous hornblende: compositions and occurrences from southwestern Massachusetts. Am. Mineral., 63, 1088–1099.

- Hawthorne, F.C. & Grundy, H.D. (1973): The crystal chemistry of the amphiboles. I. Refinement of the crystal structure of ferrotschermakite. *Mineral. Mag.*, **39**, 36–48.
- Hawthorne, F.C. & Oberti, R. (2007): Amphiboles: Crystalchemistry. InAmphiboles: Crystal Chemistry, Occurrence and Health Issues (F.C. Hawthorne, R. Oberti, G. Della Ventura & A. Mottana, eds.). *Rev. Mineral. Geochem.*, **67**, 1–54.
- Hawthorne, F.C., Ungaretti, L., Oberti, R. (1995): Site populations in minerals: terminology and presentation of results of crystalstructure refinement. *Can. Mineral.*, **33**, 907–911.
- 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. *Am. Mineral.*, 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. *J. Appl. Crystallogr.*, 48, 3–10.
- Leake, B.E. (1978): Nomenclature of amphiboles. *Can. Mineral.*, **16**, 511–520.
- Leake, B.E., Woolley, A.R., Arps, C.E.S., Birch, W.D., Gilbert, M. C., Grice, J.D., Hawthorne, F.C., Kato, A., Kisch, H.J., Krivovichev, V.G., Linthout, K., Laird, J., Mandarino, J.A., Maresch, W.V., Nickel, E.H., Rock, N.M.S., Schumacher, J.C., Smith, D.C., Stephenson, N.C.N., Ungaretti, L., Whittaker, E.J. W., Guo, Y. (1997): Nomenclature of amphiboles: report of the subcommittee on amphiboles of the International Mineralogical Association, Commission on New Minerals and Mineral Names. *Eur. J. Mineral.*, 9, 623–651.
- Léger, A. & Ferry, J.M. (1991): Highly aluminous hornblende from low-pressure metacarbonates and a preliminary thermodynamic model for the Al content in calcic amphiboles. *Am. Mineral.*, 76, 1002–1007.
- Mandarino, J.A. (1981): The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Can. Mineral.*, 19, 441–450.
- Oberti, R., Hawthorne, F.C., Cannillo, E., Cámara, F. (2007): Longrange order in amphiboles. In: Amphiboles: Crystal Chemistry, Occurrence and Health Issues (eds. F.C. Hawthorne, R. Oberti, G. Della Ventura & A. Mottana). *Rev. Mineral. Geochem.*, 67, 125–172.
- Ogura, Y. (1958): On the granitization of some basic rocks of the Gosaisyo-Takanuki district, southern Abukuma plateau, Japan. *Jpn. J. Geol. Geogr.*, **29**, 171–185.
- Robinson, K., Gibbs, G.V., Ribbe, P.H. (1971): Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science*, **172**, 567–570.
- Seitsaari, J. (1951): The schist belt north-east of Tampere in Finland. Bull. Comm. Géol. Finlande, 153.
- ---- (1952): On association of cummingtonite and hornblende. Ann. Acad. Sci. Fennica, series A, III, (Geol. Geogr.), 30.
- Winchell, A.N. (1945): Variations in composition and properties of the calciferous amphiboles. *Am. Mineral.*, 30, 27–50.

Received 9 May 2017 Modified version received 18 August 2017 Accepted 30 August 2017