

Clino-suenoite, a newly approved magnesium-iron-manganese amphibole from Valmalenco, Sondrio, Italy

ROBERTA OBERTI^{1,*}, MASSIMO BOIOCCHI², FRANK C. HAWTHORNE³, MARCO E. CIRIOTTI⁴, OLAV REVHEIM⁵ AND ROBERTO BRACCO⁶

¹ CNR-Istituto di Geoscienze e Georisorse, Sede secondaria di Pavia, via Ferrata 1, I-27100 Pavia, Italy

² Centro Grandi Strumenti, Università di Pavia, via Bassi 21, I-27100 Pavia, Italy

³ Department of Geological Sciences, University of Manitoba, Winnipeg, Manitoba, R3T 2N2, Canada

⁴ Associazione Micromineralogica Italiana, via San Pietro 55, I-10073 Devesi-Cirié, Italy

⁵ Veddetoppen 48a, N-4640 Søgne, Norway

⁶ Associazione Micromineralogica Italiana, via Montenotte 18/6, I-17100 Savona, Italy

[Received 16 March 2017; Accepted 15 May 2017; Associate Editor: Andrew Christy]

ABSTRACT

Clino-suenoite, ideally $\square\text{Mn}_2^{2+}\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$ is a new amphibole of the magnesium-iron-manganese subgroup of the amphibole supergroup. The type specimen was found at the Lower Scerscen Glacier, Valmalenco, Sondrio, Italy, where it occurs in Mn-rich quartzite erratics containing braunite, rhodonite, spessartine, carbonates and various accessory minerals. The empirical formula derived from electron microprobe analysis and single-crystal structure refinement is: $^{\text{A}}\text{Na}_{0.04}^{\text{B}}(\text{Mn}_{1.58}^{2+}\text{Ca}_{0.26}\text{Na}_{0.16})_{\Sigma 2.00}^{\text{C}}(\text{Mg}_{4.21}\text{Mn}_{0.61}^{2+}\text{Fe}_{0.04}^{2+}\text{Zn}_{0.01}\text{Ni}_{0.01}\text{Fe}_{0.08}^{3+}\text{Al}_{0.04})_{\Sigma 5.00}^{\text{T}}\text{Si}_{8.00}\text{O}_{22}^{\text{W}}[(\text{OH}_{1.94}\text{F}_{0.06})]_{\Sigma 2.00}$. Clino-suenoite is biaxial (+), with $\alpha = 1.632(2)$, $\beta = 1.644(2)$, $\gamma = 1.664(2)$ and $2V_{\text{meas.}} = 78(2)^\circ$ and $2V_{\text{calc.}} = 76.3^\circ$. The unit-cell parameters in the $C2/m$ space group are $a = 9.6128(11)$, $b = 18.073(2)$, $c = 5.3073(6)$ Å, $\beta = 102.825(2)^\circ$ and $V = 899.1(2)$ Å³ with $Z = 2$. The strongest ten reflections in the powder X-ray diffraction pattern [d (in Å), I , (hkl)] are: 2.728, 100, (151); 2.513, 77, (202); 3.079, 62, (310); 8.321, 60, (110); 3.421, 54, (131); 2.603, 42, (061); 2.175, 42, (261); 3.253, 41, (240); 2.969, 40, (221); 9.036, 40, (020).

KEYWORDS: clino-suenoite, amphibole, electron-microprobe analysis, optical properties, powder-diffraction pattern, crystal-structure refinement, Lower Scerscen Glacier, Italy.

Introduction

WE present in this paper the complete characterization of a new amphibole of the magnesio-iron-manganese subgroup, clino-suenoite, ideally $^{\text{A}}\square^{\text{B}}\text{Mn}_2^{2+}\text{C}^{\text{Mg}_5}\text{Si}_8\text{O}_{22}^{\text{W}}(\text{OH})_2$. The nomenclature of this subgroup has been significantly modified by the amphibole nomenclature scheme in force (Hawthorne *et al.*, 2012). That report recognizes that dominance of Mn^{2+} among B cations cannot be dealt with by a prefix – the use of which is hereafter confined to C cations – but requires a new rootname. Indeed, the presence of

$^{\text{B}}\text{Ca}^{2+}$ (ionic radius (hereafter abbreviated i.r.) 1.12 Å in the preferred 8-coordination; Shannon, 1976) or of $^{\text{B}}(\text{Fe}, \text{Mg}, \text{Mn})^{2+}$ (i.r. 0.78, 0.72 and 0.83 Å, respectively, in 6-coordination) induces strong modifications in the crystal structure. $^{\text{B}}(\text{Fe}, \text{Mg}, \text{Mn})^{2+}$ occur ~ 0.4 Å closer than Ca^{2+} (along the b direction) to the strip of octahedra. Because of the different anion arrangements around the $M(4)$ site, magnesium-iron-manganese amphiboles may have either $P2_1/m$ or $C2/m$ monoclinic symmetry or $Pn\bar{m}n$ or $Pnma$ orthorhombic symmetry, depending on their chemical composition and the pressure (P) and temperature (T) conditions of formation (see a short review of the different stereochemistries involved in Hawthorne and Oberti (2007) and in the discussion below). In contrast, calcium amphiboles have $C2/m$ symmetry (with the one exception

*E-mail: oberti@crystal.unipv.it

<https://doi.org/10.1180/minmag.2017.081.034>

of joersmithite, ${}^A\text{Pb}^{2+}{}^B\text{Ca}_2{}^C(\text{Mg}_3\text{Fe}^{3+})^T(\text{Si}_6\text{Be}_2)\text{O}_{22}{}^W(\text{OH})_2$, which has $P2/a$ symmetry).

Hawthorne *et al.* (2012) proposed that a new rootname should be assigned to the composition ${}^A\Box{}^B\text{Mn}_2^{2+}{}^C\text{Mg}_5\text{Si}_8\text{O}_{22}{}^W(\text{OH})_2$. A subsequent Commission on New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (IMA) decision to use the rootname *suenoite* for that composition was taken considering the data available in the literature for its orthorhombic $Pnmm$ ferro-dominant counterpart, with ideal chemical formula: ${}^A\Box{}^B\text{Mn}_2^{2+}{}^C\text{Fe}_5^{2+}{}^T\text{Si}_8\text{O}_{22}{}^W(\text{OH})_2$; this is now called *proto-ferro-suenoite* (vote 13-A, Williams *et al.*, 2013; proponents: Oberti, Hawthorne and Kurosawa). This composition was first reported by Matsuura (1984), and later by Sueno *et al.* (1998), and its complete mineral description (under the name *protomangano-ferro-anthophyllite*, PMFA) was reported by Sueno *et al.* (2002). The mineral occurs in pegmatites in Fukushima Prefecture and in a Mn mine in the Tochigi Prefecture, Japan, and has the empirical formula ${}^B(\text{Mn}_{1.40}\text{Fe}_{0.60}){}^C(\text{Fe}_{4.10}\text{Mg}_{0.90})^T\text{Si}_8\text{O}_{22}{}^W(\text{OH})_2$. In 2002, Mn was assumed to order as a B cation during the structure refinement. The crystal-chemical formula of PMFA was later confirmed by Zanazzi *et al.* (2010) on a sample provided by M. Kurosawa, for which the authors proposed the formula ${}^B(\text{Mn}_{1.39}\text{Fe}_{0.59}){}^C(\text{Fe}_{3.98}\text{Mg}_{1.02})^T\text{Si}_8\text{O}_{22}{}^W(\text{OH})_2$.

The crystal structure of a monoclinic amphibole with a composition fairly compatible with the name *clino-suenoite* had been described by Hawthorne and Grundy (1977) under the name ‘*zincian tirodite*’, but a complete mineral characterization was not provided and the sample is no longer available. Therefore, a new search was made with the help of mineral collectors. The mineral *clino-suenoite* and its name were approved by the IMA-CNMNC (IMA2016-111) The holotype material is deposited in the mineralogical collections of the Museo di Mineralogia of the Università di Pavia, under the catalogue number 2016-01.

Occurrence and optical properties

The specimen studied in this work was found in the early 2000s at the Vedretta Inferiore di Scerscen (Lower Scerscen Glacier in Stalder *et al.*, 1998), Lanzada (46°16'9"N, 9°54'8"E), Valmalenco, Sondrio, Italy (Fig. 1). At this locality, *clino-suenoite* occurs in Mn-rich quartzite erratics in which the main mineralization consists of



FIG. 1. View of the Vedretta inferiore (lower glacier) of Scerscen. The numbers indicate: 1 = rutile-rich dolomitic marble; 2 = manganese mineralization (picture taken by A. Montrasio in Bedognè *et al.*, 1993, and modified by M. E. Ciriotti)

rhodonite, braunite, pyroxmangite, rhodochrosite, Mn-bearing calcite, kutnohorite, pyrophanite, tiragalloite, magnesio-riebeckite, manganberzeliite, aegirine-augite, tephroite, albite, Mn-rich muscovite, hausmannite, bixbyite, friedelite, hematite, clinocllore, romanèchite, rancièite, Mn-bearing tremolite, jacobsite, anatase and johannsenite. *Clino-suenoite* is yellow or yellow-brown to brown, and may be found both as fibrous aggregates and as flattened elongated crystals, often in tufts up to 2 cm long (Figs 2 and 3), usually included in rhodonite or, more rarely, in small carbonate veins associated with tiragalloite and pyrophanite (Bedognè *et al.*, 1993; 2006). Anatase occurs as yellow tabular crystals in fissures inside quartz schist, at the contact with the



FIG. 2. Orange-brown *clino-suenoite* crystal aggregate in rhodonite matrix from Vedretta inferiore di Scerscen. Field of view = 3.5 mm. (photo: R. Bracco)



FIG. 3. Fascicular yellow-orange crystals of clino-suenoite from Vedretta inferiore di Scerscen. Field of view = 6 mm. (photo: R. Bracco)



FIG. 4. The holotype rock specimen studied in this work.

manganese mineralization. Pyrophanite and tiragalloite may also occur, the first as yellow-brown plates and cherry-red to blood-red hexagonal tabular crystals, often grouped in rosettes up to

1 cm in diameter, the second as orange to orange-red, transparent, wedge-like crystals up to several mm long (Bedognè *et al.*, 1993; 2006).

The geological setting of the Scerscen manganese orebody, like most Alpine manganese occurrences, belongs to the typical seafloor sequences of the Tethys Ocean and is dated mid to late Jurassic. The mineralization formed in shallow radiolaritic sediments of the Margna nappe sedimentary sequence, which were converted into quartzites by Alpine metamorphism.

In the type specimen, clino-suenoite occurs as pale yellow, honey-yellow, yellow-brown to light brown acicular to lamellar crystals embedded in a rhodonite matrix (Fig. 4). Its colour depends strongly on grain size, it does not fluoresce, and has a vitreous lustre. The calculated density of the clino-suenoite sample of this work is 3.175 g/cm³.

A spindle stage was used to orient a crystal for measurement of refractive indices and 2V 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, clino-suenoite is pleochroic (X = pale yellow to yellow, Y = yellow to pale orange and Z = orange brown). It is biaxial (+), $\alpha = 1.632(2)$, $\beta = 1.644(2)$, $\gamma = 1.664(2)$, $2V_{\text{meas.}} = 78(2)$ and $2V_{\text{calc.}} = 76.3^\circ$. The dispersion is weak ($v > r$), and the orientation is: $X \wedge a = 15^\circ$ (in β obtuse), $Y \parallel b$ and $Z \wedge c = 2^\circ$ (in β acute).

The compatibility index ($1 - (K_p/K_c)$; Mandarino, 1981) is 0.014 (superior).

Single-crystal and powder diffraction analysis

Diffraction data for a lamellar single crystal $350 \mu\text{m} \times 100 \mu\text{m} \times 40 \mu\text{m}$ in size (no. 1316 in

TABLE 1. Miscellaneous information for holotype clino-suenoite (crystal 1316).

a (Å)	9.6128(11)	Crystal size (mm)	$0.35 \times 0.10 \times 0.04$
b (Å)	18.073(2)	Crystal colour	Pink orange
c (Å)	5.3073(6)	Total no. of reflections	6704
β (°)	102.825(2)	No. unique reflections	1355
V (Å ³)	899.1(2)	No. observed reflections ($I > 3 \sigma_I$)	971
Space group	$C2/m$	θ range (°)	2–30
Z	2	R_{merge} (%)	4.4
D_{calc} (g cm ⁻³)	3.175	R_{obs} (%)	4.3
μ MoK α (cm ⁻¹)	21.42	R_{all} (%)	6.4

the amphibole database at CNR-IGG Pavia) were collected in the θ range 2–30° with a Bruker-AXS CCD diffractometer using graphite-monochromatized MoK α X-radiation ($\lambda = 0.7107$ Å). Omega rotation frames (scan width 0.3°, scan time 20 s and 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 with the *SADABS* software (Krause *et al.*, 2015) and an absorption correction was applied to the data. A total of 6704 collected reflections was reduced to 1355 unique reflections (mean redundancy = 5 and $R_{\text{int}} = 4.4\%$). Following the procedures and terminology described in Hawthorne *et al.* (1995) and Oberti *et al.* (1992), 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)]. Full-matrix unweighted least-squares refinement on the 971 reflections with $I > 3 \sigma I$ was done with a program locally written to handle complex solid-solutions (Cannillo *et al.*, 1983) and gave $R_{\text{obs}} = 4.3\%$ and $R_{\text{all}} = 6.4\%$. Crystallographic details are summarized in Table 1, and refined atom coordinates and displacement parameters, as well as selected bond lengths and angles are given in Tables 2 and 3, respectively. Observed structure factors have been deposited with the crystallographic information file as Supplementary materials (see below). The $a:b:c$ ratio calculated from the unit-cell parameters is 0.532:1:0.294

Powder X-ray diffraction data (CuK α , $\lambda = 1.54178$ 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}^2 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 4.

Chemical analysis

Chemical analysis (10 points) on the crystal used for structure refinement was undertaken using a with a Cameca SX-100 electron microprobe (wavelength dispersive spectroscopy mode, 15 kV, 20 nA, count time 20 s and 5 μm beam diameter). Chromium and V are below their detection limits. The standards and dispersive crystals used are as follows: Si and Ca: diopside (TAP); Ti: titanite

TABLE 2. Atom coordinates, refined site-scattering values (ss, electrons pfu) and atom-displacement parameters (B_{eq} , Å²; β_{11} , β_{22} , β_{33} , Å² × 10⁴) for clino-suenoite crystal 1316.

Site	ss	x/a	y/b	z/c	B_{eq}	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)		0.1144(4)	0.0862(2)	0.2117(6)	1.03(7)	34	9	69	-2	11	-5
O(2)		0.1217(4)	0.1720(2)	0.7188(6)	1.22(8)	42	10	83	0	18	1
O(3)		0.1127(5)	0	0.7108(9)	1.15(11)	34	11	81	-	11	1
O(4)		0.3729(4)	0.2472(2)	0.7794(6)	1.41(8)	57	9	99	-7	16	2
O(5)		0.3497(4)	0.1308(2)	0.0700(6)	1.44(8)	43	13	105	0	17	12
O(6)		0.3483(4)	0.1208(2)	0.5630(6)	1.54(8)	46	15	98	2	12	-12
O(7)		0.3423(6)	0	0.2823(10)	1.53(12)	57	8	142	-	15	-
T(1)		0.2859(2)	0.08430(7)	0.2798(2)	0.99(3)	40	7	63	-1	14	0
T(2)		0.2942(2)	0.17001(7)	0.7865(2)	1.05(3)	38	8	69	-1	13	0
M(1)	27.8(3)	0	0.08710(10)	1/2	0.90(5)	39	7	44	-	18	-
M(2)	28.7(3)	0	0.17756(11)	0	0.93(4)	34	8	55	-	15	-
M(3)	13.33(9)	0	0	0	0.96(7)	39	7	62	-	18	-
M(4)	44.8(5)	0	0.26445(8)	1/2	1.42(3)	51	13	89	-	32	-
H		0.201(8)	0	0.749(14)	1.0						

CLINO-SUENOITE

TABLE 3. Selected interatomic distances (Å), angles (°), tetrahedral and octahedral angle variances (TAV, OAV, °₂) and quadratic elongations (TQE, OQE) according to Robinson *et al.* (1971) in clino-suenoite crystal 1316.

<i>T</i> (1)–O(1)	1.608(4)	<i>T</i> (2)–O(2)	1.617(4)	<i>M</i> (4)–O(2) ×2	2.216(2)
<i>T</i> (1)–O(5)	1.620(4)	<i>T</i> (2)–O(4)	1.590(4)	<i>M</i> (4)–O(4) ×2	2.131(2)
<i>T</i> (1)–O(6)	1.629(4)	<i>T</i> (2)–O(5)	1.641(4)	<i>M</i> (4)–O(5) ×2	3.068(2)
<i>T</i> (1)–O(7)	1.616(2)	<i>T</i> (2)–O(6)	1.656(4)	<i>M</i> (4)–O(6) ×2	2.599(2)
< <i>T</i> (1)–O>	1.618	< <i>T</i> (2)–O>	1.626	< <i>M</i> (4)–O> ^[6]	2.315
TAV	1.67	TAV	17.91	< <i>M</i> (4)–O> ^[8]	2.503
TQE	1.0004	TQE	1.0046		
<i>M</i> (1)–O(1) ×2	2.073(3)	<i>M</i> (2)–O(1) ×2	2.156(4)	<i>M</i> (3)–O(1) ×4	2.086(3)
<i>M</i> (1)–O(2) ×2	2.114(4)	<i>M</i> (2)–O(2) ×2	2.093(3)	<i>M</i> (3)–O(3) ×2	2.066(5)
<i>M</i> (1)–O(3) ×2	2.089(4)	<i>M</i> (2)–O(4) ×2	2.020(4)	< <i>M</i> (3)–O>	2.079
< <i>M</i> (1)–O>	2.092	< <i>M</i> (2)–O>	2.090	OAV	39.80
OAV	32.14	OAV	24.45	OQE	1.0122
OQE	1.0098	OQE	1.0079		
O(3)–H	0.82(8)	O(6)–O(7)–O(6)	111.8(2)	<i>T</i> (1)–O(6)– <i>T</i> (2)	140.3(2)
O(5)–O(6)–O(5)	172.2(2)	<i>T</i> (1)–O(5)– <i>T</i> (2)	139.3(2)	<i>T</i> (1)–O(7)– <i>T</i> (1)	141.0(4)

(LPET); Al: andalusite (TAP); Fe: fayalite (LLiF); Mn: spessartine (LLiF); Mg: forsterite (LTAP); Zn: gahnite (LLiF); Ni: pentlandite (LLiF); Na: albite (TAP); K: orthoclase (LPET); F: fluoro-riebeckite (TAP); and Cl: tugtupite (LPET). The amount of H₂O used in the calculation is that required for F+OH+Cl = 2 anions pfu and 15.04 cations pfu (as required to obtain a non-negative value for Fe²⁺). The oxide wt.% and the calculated unit-formula are reported in Table 5. The proposed empirical formula for crystal 1316 is: ^ANa_{0.04}^B(Mn_{1.58}²⁺Ca_{0.26}Na_{0.16})_{Σ2.00}^C(Mg_{4.21}Mn_{0.61}²⁺Zn_{0.01}Ni_{0.01}Fe_{0.08}³⁺Al_{0.04})_{Σ5.00}^TSi_{8.00}O₂₂^W[(OH)_{1.94}F_{0.06}]_{Σ2.00}

(where the dominant cations/anions are in bold). Note that the Fe³⁺ content is that required for electroneutrality. The end-member formula of clino-suenoite is ^A□^BMn₂²⁺^CMg₅^TSi₈O₂₂^W(OH)₂, which requires SiO₂ 57.08, MgO 23.93, MnO 16.85 H₂O 2.14, total 100.00 wt.%.

The crystal-chemistry of clino-suenoite

The site populations were obtained by distributing the ions of the unit formula under the constraints of the refined site-scattering values (Hawthorne *et al.*, 1995) and mean bond lengths (for the C cations

TABLE 4. Powder X-ray diffraction data for clino-suenoite crystal 1316.

<i>I</i> _{rel}	<i>d</i>	<i>h k l</i>	<i>I</i> _{rel}	<i>d</i>	<i>h k l</i>	<i>I</i> _{rel}	<i>d</i>	<i>h k l</i>	<i>I</i> _{rel}	<i>d</i>	<i>h k l</i>
39.5	9.036	0 2 0	5.3	3.143	2 0 1	17.7	2.264	$\bar{4}$ 2 1	16.8	1.701	$\bar{5}$ 1 2
60.2	8.321	1 1 0	61.9	3.079	3 1 0	20.4	2.236	$\bar{3}$ 1 2	17.3	1.697	$\bar{1}$ 3 3
10.2	5.175	0 0 1	40.4	2.969	2 2 1	17.2	2.194	$\bar{2}$ 4 2	7.3	1.681	$\bar{2}$ 8 2
5.3	5.068	1 3 0	10.6	2.937	$\bar{1}$ 5 1			1 7 1	28.6	1.652	4 6 1
26.6	4.843	$\bar{1}$ 1 1	14.8	2.773	3 3 0	41.5	2.175	2 6 1	6.5	1.626	4 8 0
13.7	4.518	0 4 0	100.0	2.728	1 5 1	5.0	2.111	$\bar{3}$ 3 2	13.4	1.618	1 11 0
14.6	4.160	2 2 0	15.8	2.674	$\bar{3}$ 3 1	22.0	2.078	2 0 2	26.0	1.588	$\bar{1}$ 5 3
5.0	4.051	1 1 1	42.1	2.603	0 6 1	13.2	2.025	3 5 1	7.0	1.572	4 0 2
5.2	3.934	$\bar{2}$ 0 1	76.9	2.513	2 0 2	14.5	1.967	$\bar{4}$ 0 2	6.7	1.567	2 10 1
27.3	3.860	$\bar{1}$ 3 1	5.0	2.364	3 5 0	13.2	1.865	$\bar{1}$ 9 1	7.1	1.563	6 0 0
53.5	3.421	1 3 1	33.8	2.300	$\bar{3}$ 5 1	9.4	1.804	$\bar{4}$ 4 2	17.3	1.697	$\bar{1}$ 3 3
41.3	3.253	2 4 0			$\bar{1}$ 7 1						

Note: the strongest ten reflections are in bold. Only peaks with *I*_{rel} ≥ 5 are reported.

TABLE 5. Chemical composition (average of 10 points), unit formula (based on 24 anions and 15.04 cations; cf. text) and a comparison between observed and calculated site scattering values for clino-suenoite (1316).

Oxide	wt.% (esd)	Oxide	wt.% (esd)				apfu		apfu	
SiO ₂	54.95(26)	H ₂ O*	1.80		Si	8.00	Na		0.16	
TiO ₂	0.01(1)	F	0.14(32)		Al	0.00	Ca		0.26	
Al ₂ O ₃	0.22(2)	Cl	0.01(1)		Sum T	8.00	Mn		1.58	
Fe ₂ O ₃	0.75	O = F,Cl	-0.06				Sum B		2.00	
FeO	0.32	Total	97.93		Al	0.04				
[FeO] _{tot}	[1.00(7)]				Fe ³⁺	0.08	Na		0.04	
MnO	17.81(41)				Mg	4.21	Sum A		0.04	
MgO	19.40(16)	Group site-scattering (epfu)			Mn ²⁺	0.61				
NiO	0.12(5)		obs (SREF)	calc (EMP)	Fe ²⁺	0.04	(OH) ⁻		1.94	
ZnO	0.10(8)		C	69.84	70.12	Ni	0.01	F ⁻		0.06
CaO	1.65(3)		B	44.81	46.49	Zn	0.01	Sum W		2.00
Na ₂ O	0.70(5)	A	-	0.44	Sum C	5.00				
K ₂ O	0.01(1)	Total	114.65	117.05						

* calculated based on 15.04 cations and 24 (O, OH, F, Cl) with (OH + F + Cl) = 2 apfu.

occurring at the *M*(1), *M*(2) and *M*(3) sites). The correct distribution of Mn among the *M*(1), *M*(2) and *M*(3) sites could be determined because of the very low amount of Fe²⁺ in the formula, and was checked via the refined mean bond-lengths. The Mn site preference is *M*(4) >> *M*(1) > *M*(2) >> *M*(3). The results are reported in Table 6. The agreement between the refined and calculated site-scattering values is close.

The residual electron density at the *A* site is very low, in agreement with the presence of 0.04 Na atoms per formula unit (apfu) in the chemical analysis; therefore *A* sites were not inserted in the refined model. The *M*(4) site is [6 + 2]-coordinated, as expected where small cations are the dominant B cations: the *M*(4)–O(5) distance of 3.068 Å is even longer than the distance *M*(4)–*T*(2), i.e. 2.994 Å. The <*T*–O> distances are very short, confirming

TABLE 6. Site populations for clino-suenoite, crystal 1316. There is close agreement 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
<i>T</i> (1)	4.00 Si			1.618	
<i>T</i> (2)	4.00 Si			1.626	
<i>M</i> (1)	1.68 Mg + 0.32 Mn ²⁺	27.77	28.16	2.092	2.093
<i>M</i> (2)	1.63 Mg + 0.23 Mn ²⁺ + 0.01 Zn + 0.01 Ni + 0.08 Fe ³⁺ + 0.04 Al	28.74	28.49	2.090	2.084
<i>M</i> (3)	0.90 Mg + 0.06 Mn ²⁺ + 0.04 Fe ²⁺	13.33	13.34	2.079	2.085
Σ C cations		69.84	69.99		
B cations	1.58 Mn ²⁺ + 0.26 Ca + 0.16 Na	44.81	46.46		
A cations	0.04 Na	—	0.44		
W anions	1.94 (OH) ⁻ + 0.06 F ⁻	16.00	16.06		

*Hawthorne *et al.* (1995)

that no ^TAl is present, and the $M(1,3)$ octahedra are quite distorted, in accord with the presence of Mn^{2+} . Oberti and Ghose (1993; Fig. 3) observed that in monoclinic amphiboles, the value of the β angle is linearly related to the average ionic radius of the B cations; the β angle measured for clino-suenoite is in perfect agreement with this behaviour.

Relation with other species and a review of related compositions

As noted in the Introduction, Sueno *et al.* (1998, 2002) described an orthorhombic amphibole ($Pn\bar{m}n$ symmetry) with the empirical formula $^B(\text{Mn}_{1.40}\text{Fe}_{0.60})^C(\text{Fe}_{4.10}\text{Mg}_{0.90})^T\text{Si}_8\text{O}_{22}^W(\text{OH})$ (root composition $^A\Box^B\text{Mn}_2^+{}^C\text{Fe}_5^+{}^T\text{Si}_8\text{O}_{22}^W(\text{OH})_2$) and called it ‘protomangano-ferro-anthophyllite’ (PMFA). According to the rules currently in force, this mineral must now be referred to as proto-ferro-suenoite (Williams *et al.*, 2013). Proto-ferro-suenoite was discovered in a fayalite pegmatite associated with laihunite, magnetite and quartz and in mineralized blocks associated with pyrox-mangite, rhodonite, rhodochrosite and spessartine at: (1) Suishoyama pegmatite, Iizaka, Kawamata, Fukushima Prefecture, Tohoku Region; and (2) Nippyo and Yokoneyama mines, Awano, Kanuma City, Tochigi Prefecture, Kanto Region, both in Honshu Island, Japan. It occurs as fibrous yellow-brown crystals, a few mm long, sometimes in aggregates resembling sheaves of wheat (Sueno *et al.*, 2002).

The different crystallographic symmetries observed in amphiboles containing small B cations (i.e. in the magnesium-iron-manganese subgroup) derive from the different stacking of the I beams along the *a* direction: a ++++ stacking corresponds to the monoclinic structure (possible space groups $C2/m$ and $P2_1/m$), whereas alternating positive and negative stackings correspond to the orthorhombic structure (++ — to $Pnma$, implying a doubling of the *a* edge, and +—+— to $Pn\bar{m}n$) (Hawthorne and Oberti, 2007, fig. 14). The relative stability of the monoclinic and orthorhombic structures is determined mainly by the B cations, the Ca- and Na-rich compositions having monoclinic $C2/m$ symmetry. Evans and Ghiorso (1995) showed that orthorhombic ($Pnma$) anthophyllite is more stable than cummingtonite for $\text{Fe}/(\text{Fe}+\text{Mg}) > 0.10$ at 600–700°C, the opposite of what is observed for the Fe- and Mn-rich species. In monoclinic amphiboles, $P2_1/m$ symmetry is

preferred to $C2/m$ symmetry at high Mg/Mg+Fe values. Displacive phase transitions are observed at different *T* values, as shown by many studies reviewed in Welch *et al.* (2007).

The available data for amphiboles related to the rootname suenoite are given in Table 7. Comparison of the geometry observed in clino-suenoite and in proto-ferro-suenoite is quite interesting. The sizes of the $T(1-2)$ tetrahedra are very similar, but the $M(1-3)$ octahedra are larger in proto-ferro-suenoite, in agreement with its higher $^C\text{Fe}^{2+}$ content. As a result, the double chain of tetrahedra is almost completely extended (as measured by the O(5)–O(6)–O(5) angle) in proto-ferro-suenoite, a situation which is never observed in monoclinic amphiboles. The $M(4)$ site in amphibole acts as a hinge between the double chain of tetrahedra and the strip of octahedra. In proto-ferro-suenoite, it is not only much smaller, (which again is consistent with the low Ca^{2+} content, 0.03 apfu), but has a different coordination. The individual distances are: $M(4)$ –O(2) = 2.155 Å, $M(4)$ –O(4) = 2.032 Å and $M(4)$ –O(6) = 2.582 Å (Sueno *et al.*, 2002) so that a [4 + 2] coordination could even be considered.

Monoclinic amphiboles with composition close to $^A\Box^B\text{Mn}_2^+{}^C\text{Mg}_5^+{}^T\text{Si}_8\text{O}_{22}^W(\text{OH})_2$ have previously been reported as ‘tirodite’ after the Tirodi locality (Madhya Pradesh, India; Dunn and Roy, 1938; Segeler, 1961; Hawthorne and Grundy, 1977) and later as ‘manganocummingtonite’. The name ‘tirodite’ was discredited by Leake *et al.* (1997), and the name ‘manganocummingtonite’ was discredited by Hawthorne *et al.* (2012), who stated that the prefix mangano- has to be used only when Mn^{2+} is dominant among C cations. Analyses close to the ideal composition $^A\Box^B\text{Mn}_2^+{}^C\text{Mg}_5^+{}^T\text{Si}_8\text{O}_{22}^W(\text{OH})_2$ are listed from 55 localities in mindat.org [<https://www.mindat.org/>]. They typically occur in metamorphic manganese ores, and a closer examination of papers on the petrology and ore geology of these deposits would undoubtedly increase the number of localities.

Incidentally, the composition $\text{Ca}_{0.1}\text{Mn}_{1.9}\text{Mg}_{1.25}\text{Fe}_{3.56}^{2+}\text{Fe}_{0.38}^{3+}\text{Si}_{7.81}\text{O}_{22}(\text{OH})_2$ described from Dannemora, Sweden, and thus called ‘dannemorite’ (first reported by Kenngott (1855) and Dana (1892); see Anthony *et al.* (2018) at <http://www.handbookofmineralogy.org/pdfs/dannemorite.pdf>) should hereafter be called clino-ferro-suenoite (Table 7). Kenngott (1855) referred to the analysis of Erdmann (1851): $^B(\text{Mn}_{1.13}\text{Fe}_{0.74}\text{Ca}_{0.12})_{\Sigma 1.99}^C(\text{Fe}_{4.04}\text{Mg}_{0.69}\text{Fe}_{0.27}^{3+})_{\Sigma 5.00}^T(\text{Si}_{7.73}\text{Al}_{0.27})_{\Sigma 8}\text{O}_{22}^W(\text{OH})_2$.

TABLE 7. A comparison of the optical and crystallographic properties reported for the three amphiboles related to the rootname suenoite.

	Clino-suenoite ¹	Clino-ferro-suenoite ²	Proto-ferro-suenoite ³
Colour	Pale yellow to brown yellow	Yellowish brown to greenish grey	Brownish yellow
Optical class	Biaxial (+)	Biaxial (–)	Biaxial (–)
Pleochroism	X = pale yellow, Y = yellow to pale orange, Z = orange-brown	X = red violet, Y = pale violet, Z = blue	Weak, X, Y, Z = pale yellow
Orientation	$X \wedge a = 15^\circ$ (β obtuse) $Y \parallel b$ $Z \wedge c = 2^\circ$ (β acute)	$Y \parallel b$ $Z \wedge c = 15^\circ$	$X \parallel a$ $Y \parallel b$ $Z \parallel c$
α	1.632	1.666	1.695
β	1.644	1.682	1.714
γ	1.664	1.698	1.731
$2V_{\text{meas}} (^\circ)$	78	88	76
Space group	$C2/m$	n.d.	$Pnmm$
a (Å)	9.6128(11)	9.561	9.425(2)
b (Å)	18.073(2)	18.28	18.303(4)
c (Å)	5.3073(6)	5.348	5.345(1)
β (°)	102.825(2)	102.09	
V (Å ³)	899.04	914.0	922.0
$\langle T(1)-O \rangle$ (Å)	1.618		1.619
$\langle T(2)-O \rangle$ (Å)	1.626		1.627
$\langle M(1)-O \rangle$ (Å)	2.092		2.121
$\langle M(2)-O \rangle$ (Å)	2.090		2.122
$\langle M(3)-O \rangle$ (Å)	2.079		2.113
$\langle M(4)-O \rangle$ (Å)	2.315		2.256
$O(5)-O(6)-O(5)$ (°)	172.2		178.6
Reference	This work	Anthony <i>et al.</i> (2018)	PMFA in Sueno <i>et al.</i> (1998, 2002)

- (1): ${}^A\text{Na}_{0.04}{}^B(\text{Mn}^{2+}_{1.58}\text{Ca}_{0.26}\text{Na}_{0.16})_{\Sigma 2.00}{}^C(\text{Mg}_{4.21}\text{Mn}^{2+}_{0.61}\text{Fe}^{2+}_{0.04}\text{Zn}_{0.01}\text{Ni}_{0.01}\text{Fe}^{3+}_{0.08}\text{Al}_{0.04})_{\Sigma 5.00}{}^T\text{Si}_{8.00}\text{O}_{22}{}^W[(\text{OH})_{1.94}\text{F}_{0.06}]_{\Sigma 2.00}$
(2): $(\text{Fe}^{2+}_{3.10}\text{Mg}_{2.42}\text{Mn}_{0.96}\text{Ca}_{0.33}\text{Fe}^{3+}_{0.21}\text{Na}_{0.07}\text{Ti}_{0.01}\text{K}_{0.01})_{\Sigma 7.11}(\text{Si}_{7.80}\text{Al}_{0.16})_{\Sigma 7.96}\text{O}_{22}[(\text{OH})_{1.99}\text{F}_{0.03}]_{\Sigma 2.02}$
(3): ${}^B(\text{Mn}_{1.38}\text{Fe}_{0.59}\text{Ca}_{0.03}){}^C(\text{Fe}_{4.10}\text{Mg}_{0.9})\text{Si}_8\text{O}_{22}{}^W(\text{OH})_2$

Vassileva and Bonev (2001) analysed amphiboles occurring in Pb–Zn skarn ore deposits in the Madan district, Central Bulgaria, and found compositions ranging from manganoan ferro-actinolite to clino-suenoite and clino-ferro-suenoite. Among the latter, the ${}^T\text{Al}$ and ${}^A(\text{Na},\text{K})$ contents are always zero or very low, whereas the ${}^B\text{Ca}$ content ranges from 0.14 to 0.28 apfu. These amphiboles were described as “developed by partial replacement of ferroan johansennite”, occur as fibres of fibrous aggregates with rounded voids formed by the dissolution of calcite, and are associated with rhodonite, quartz and Mn-rich ilvaite.

Clino-suenoite can form a continuous series with cummingtonite ${}^A\Box{}^B\text{Mg}_2{}^C\text{Mg}_5{}^T\text{Si}_8\text{O}_{22}{}^W(\text{OH})_2$ and

grunerite ${}^A\Box{}^B\text{Fe}^{2+}{}^C\text{Fe}^{2+}{}^T\text{Si}_8\text{O}_{22}{}^W(\text{OH})_2$, which are commonly associated with metamorphic manganese ores. Many of the analyses reported in the literature (cf. mindat.org) show $\text{MnO} \approx 8\%$, which is more or less equivalent to 1 apfu, thus close to the midpoint between cummingtonite and/or grunerite and clino-suenoite.

Acknowledgements

Andrew Christy, Peter Leverett and Ritsuro Miyawaki are grateful acknowledged for their helpful comments. 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.

Supplementary material

To view supplementary material for this article, please visit <https://doi.org/10.1180/minmag.2017.081.034>

References

- Anthony, J.W., Bideaux, R.A., Bladh, K.W. and Nichols, M.C. (editors) (2018) *Handbook of Mineralogy*. Mineralogical Society of America, Chantilly, Virginia, USA. [data for 'dannemorite' at <http://www.handbookofmineralogy.org/> accessed 15 March 2018]
- Bedognè, F., Montrasio, A. and Sciesa, E. (1993) *I Minerali della Provincia di Sondrio – Valmalenco*. Tipografia Bettini, Ed., Sondrio, 275 pp. [in Italian].
- Bedognè, F., Montrasio, A. and Sciesa, E. (2006) *I minerali della media-alta Valtellina, delle Orobie valtellinesi e della Val Poschiavo. Aggiornamenti sulle altre località della provincia di Sondrio*. Tipografia Bettini, Ed., Sondrio, 255 pp. [in Italian].
- Bartelmebs, K.L., Bloss, F.D., Downs, R.T. and Birch, J. B. (1992) EXCALIBUR II. *Zeitschrift für Kristallographie*, **199**, 185–196.
- Bruker (2003) *SAINT Software Reference Manual. Version 6*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cannillo, E., Germani, G. and Mazzi, F. (1983) *New crystallographic software for Philips PW1100 single crystal diffractometer*. Internal report 2 CNR Centro di Studio per la Cristallografia, Pavia, Italy.
- Dana, E.S. (1892) *The System of Mineralogy, Sixth Edition with Appendices I, II, and III, Completing the Work to 1915*. John Wiley & Sons, New York, pp. 386, 391, 395.
- Dunn, J.A. and Roy, O.C. (1938) Tirodite, a new Mn mineral. *Records of the Geological Survey of India – Miscellaneous Notes*, **73**, 295.
- Erdmann, A. (1851) Dannemora jernmalmsfelt. *Öfversigt af Kongliga Vetenskaps-Akademiens Förhandlingar*, **8**–19.
- Evans, B.W. and Ghiorso, M.S. (1995) Thermodynamics and petrology of cummingtonite. *American Mineralogist*, **80**, 649–663.
- Hawthorne, F.C. and Grundy, H.D. (1977) The crystal structure and site-chemistry of a zincian tirodite by least-squares refinement of X-Ray and Mossbauer data. *Canadian Mineralogist*, **15**, 309–320.
- Hawthorne, F.C. and Oberti, R. (2007) Amphiboles: Crystal-chemistry. Pp. 1–54 in: *Amphiboles: Crystal Chemistry, Occurrence and Health Issues* (F.C. Hawthorne, R. Oberti, G. Della Ventura and A. Mottana, editors). Reviews in Mineralogy & Geochemistry, **67**. Mineralogical Society of America and the Geochemical Society, Chantilly, Virginia, USA.
- Hawthorne, F.C., Ungaretti, L. and 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., Harlow, G.E., Maresch, W.V., Martin, R.F., Schumacher, J.C. and Welch, M.D. (2012) Nomenclature of the amphibole supergroup. *American Mineralogist*, **97**, 2031–2048.
- Kenngott, A. (1855) *Mineralogischen Forschungen*. T.O. Weigel, Leipzig, Germany, pp. 174 [in German].
- Krause, L., Herbst-Irmer, R., Sheldrick, G.M. and Stalkeand, D. (2015) Comparison of silver and molybdenum microfocus X-ray sources for single-crystal structure determination. *Journal of Applied Crystallography*, **48**, 3–10.
- 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. and Guo, Y. (1997) Nomenclature of amphiboles: Report of the subcommittee on amphiboles of the International Mineralogical Association, Commission on New Minerals and Mineral Names. *Canadian Mineralogist*, **35**, 219–246.
- Mandarino, J.A. (1981) The Gladstone-Dale relationship: Part IV. The compatibility concept and its application. *Canadian Mineralogist*, **19**, 441–450.
- Matsuura, S. (1984) *Crystal chemical study of space group Pnmn type Fe, Mn amphiboles*. PhD Dissertation, University of Tsukuba, Tsukuba, Japan.
- Oberti, R. and Ghose, S. (1993) Crystal-chemistry of a complex Mn-bearing alkali amphibole on the verge of exsolution. *European Journal of Mineralogy*, **5**, 1153–1160.
- 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.
- Robinson, K., Gibbs, G.V. and Ribbe, P.H. (1971) Quadratic elongation: a quantitative measure of distortion in coordination polyhedra. *Science*, **172**, 567–570.
- Segeler, C.G. (1961) First U.S. occurrence of manganoan cummingtonite, tirodite. *American Mineralogist*, **46**, 637–641.
- Shannon, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica*, **A32**, 751–767.
- Stalder, H.A., Wagner, A., Graeser, S. and Stuker, P. (1998) *Mineralienlexikon der Schweiz*. Verlag Wepf & Co. AG, Basel, Germany, 405 pp. [in German].
- Sueno, S., Matsuura, S., Gibbs, G.V. and Boisen, M.B. (1998) A crystal chemical study of

- protoanthophyllite: orthoamphiboles with the proto-amphibole structure. *Physics and Chemistry of Minerals*, **25**, 366–377.
- Sueno, S., Matsuura, S., Bunno, M. and Kurosawa, M. (2002) Occurrence and crystal chemical features of protoferro-anthophyllite and protomanganoferroanthophyllite from Cheyenne Canyon and Cheyenne Mountain, U.S.A., and Hirukawa-mura, Suisho-yama, and Yokone-yama, Japan. *Journal of Mineralogical and Petrological Sciences*, **97**, 127–136.
- Vassileva, R.D. and Bonev, I.K. (2001) Manganoan amphiboles from the skarn-ore Pb-Zn deposits in the Madan District, Central Rhodopes, Bulgaria. *Bulgarian Academy of Science, Geochemistry, Mineralogy and Petrology*, **38**, 45–53.
- Welch, M.D., Cámara, F., Della Ventura, G. and Iezzi, G. (2007) Non-ambient studies of amphiboles. Pp. 223–260 in: *Amphiboles: Crystal Chemistry, Occurrence and Health Issues* (F.C. Hawthorne, R. Oberti, G. Della Ventura and A. Mottana, editors). Reviews in Mineralogy & Geochemistry, **67**. Mineralogical Society of America and the Geochemical Society, Chantilly, Virginia, USA.
- Williams, P.A., Hatert, F., Pasero, M. and Mills, S.J. (2013) IMA Commission on New Minerals, Nomenclature and Classification (CNMNC) Newsletter 16 – New minerals and nomenclature modifications approved in 2013. *Mineralogical Magazine*, **77**, 2695–2709.
- Zanazzi, P.F., Nestola, F. and Pasqual, D. (2010) Compressibility of protoamphibole: a high-pressure single-crystal diffraction study of protomanganoferroanthophyllite. *American Mineralogist*, **95**, 1758–1764.