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# Ferro-ferri-hornblende from the Traversella Mine (Ivrea, Italy): occurrence, mineral description and crystal-chemistry

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2	Ferro-ferri-hornblende from the Traversella Mine (Ivrea, Italy):
3	occurrence, mineral description and crystal-chemistry.
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# ABSTRACT

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24	Ferro-ferri-hornblende is a new member of the amphibole supergroup (IMA-CNMNC 2015-054). It
25	has been found in rock specimen from the historical collection of Leandro De Magistris, which was
26	collected at the Traversella Mine (Val Chiusella, Ivrea, Piemonte, Italy). The specimen was
27	catalogued as "speziaite", and contains a wide range of amphibole compositions from
28	tremolite/actinolite to magnesio-hastingsite. The end-member formula of ferro-ferri-hornblende is
29	<sup>A</sup> $\square$ <sup>B</sup> Ca <sub>2</sub> <sup>C</sup> (Fe <sup>2+</sup> <sub>4</sub> Fe <sup>3+</sup> ) <sup>T</sup> (Si <sub>7</sub> Al) O <sub>22</sub> <sup>W</sup> (OH) <sub>2</sub> , which requires SiO <sub>2</sub> 43.41, Al <sub>2</sub> O <sub>3</sub> 5.26, FeO 29.66,
30	Fe <sub>2</sub> O <sub>3</sub> 8.24 CaO 11.57, H <sub>2</sub> O 1.86, total 100.00 wt%. The empirical formula derived from electron
31	microprobe analysis and single-crystal structure refinement for the holotype crystal is
32	${}^{A}(Na_{0.10}K_{0.13})_{\Sigma=0.23} {}^{B}(Ca_{1.93}Na_{0.07})_{\Sigma=2.00} {}^{C}(Mg_{1.16}Fe^{2+}_{3.21}Mn_{0.06}Fe^{3+}_{0.45}Al_{0.12}Ti_{0.01})_{\Sigma=5.01}$
33	<sup>T</sup> $(Si_{7.26}Al_{0.74})_{\Sigma=8.00} O_{22}$ <sup>W</sup> $(OH_{1.89}F_{0.01}Cl_{0.10})_{\Sigma=2.00}$ . Ferro-ferri-hornblende is biaxial (-), with $\alpha =$
34	1.697(2), $\beta = 1.722(5)$ , $\gamma = 1.726(5)$ and 2V (meas.) = 35.7(1.4)°, 2V (calc.) = 43.1°. The unit-cell
35	parameters are $a = 9.9307(5)$ , $b = 18.2232(10)$ , $c = 5.3190(3)$ Å, $\beta = 104.857(1)^{\circ}$ , $V = 930.40$ (9)
36	Å <sup>3</sup> , $Z = 2$ , space group $C2/m$ . The <i>a</i> : <i>b</i> : <i>c</i> ratio is 0.545:1:0.292. The strongest eight reflections in the
37	X-ray powder pattern [d values (in Å), I, (hkl)] are: 8.493, 100, (110); 2.728, 69, (151); 3.151, 47,
38	(310); 2.555, 37, (-202); 2.615, 32, (061); 2.359, 28, (-351); 3.406, 26, (131); 2.180, 25, (261). Type
39	material is deposited in the collections of the Museo di Mineralogia, Dipartimento di Scienze della
40	Terra e dell'Ambiente, Università di Pavia, under the catalogue number 2015-01. Sample
41	M/U15285 from the historical collection of Luigi Colomba, presently at the Museo Regionale di
42	Scienze Naturali di Torino, was also checked, and the presence of ferro-ferri-hornblende was
43	confirmed.
11	

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45 KEYWORDS: ferro-ferri-hornblende, electron-microprobe analysis, crystal-structure refinement, Traversella
46 mine, Italy.

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48	Introduction
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50	This paper describes a further achievement obtained during a systematic search aimed at providing
51	the mineral description of common members of the amphibole supergroup which still miss an
52	official recognition by IMA-CNMNC. This project started after approval of the new scheme for
53	amphibole classification and nomenclature (Hawthorne et al., 2012), which is strongly connected
54	with amphibole crystal-chemistry, and will provide formal approval for amphibole species that are
55	widespread in common rocks
56	The name "hornblende" was proposed in 1789 by Abraham Gottlieb Werner, who combined
57	an old German term for dark minerals of no ore value with the term "blende", meaning "to deceive".
58	This name has long been used as a group name for dark green to black amphiboles, mostly ferro-
59	hornblende or magnesio-hornblende according to the nomenclature in force. Indeed, in the book
60	"Rock-forming minerals, volume 2b, Double chain silicates" by Deer et al. (1997), the term
61	"hornblende" is used as a group name for all aluminous amphiboles in the calcium amphibole
62	subgroup. In their report on amphibole nomenclature, Hawthorne et al. (2012) give the name
63	"magnesio-hornblende" to the amphibole composition ${}^{A}\Box {}^{B}Ca_{2}{}^{C}(Mg_{4}Al) {}^{T}(Si_{7}Al) O_{22}{}^{W}(OH)_{2}$ .
64	Despite the frequent occurrence in Nature of these compositions, according to the latest
65	version of the IMA list of minerals (September 2015), only two entries contain the root-name
66	hornblende, and are the two grandfathered end-members magnesio-hornblende and ferro-
67	hornblende. In February 2015, IMA-CNMNC approved the sole hornblende species with a
68	complete mineral description, i.e. magnesio-ferro-fluoro-hornblende 2014-091 from Portoscuso
69	(Sardinia; Oberti et al., 2016).
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### MINERAL DATA FOR FERRO-FERRI-HORNBLENDE

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### 75 Sample description

The holotype specimen described in this work comes from the skarns at the Traversella Mine, val Chiusella, Ivrea, Piemonte, Italy. The mine has been exploited for iron ore since the XI century, but the first notes are from the Roman historian Titus Livius. During the second World War, the Traversella deposit was mined by the FIAT company. It was closed in 1971, and now can be visited only by tourists on guided tours. Mineral collecting is strictly prohibited.

81 The sample was collected in the 1960s by Leandro De Magistris, former honorary curator of 82 the Genova Mineralogical Museum, and was later acquired by Renato and Adriana Pagano (Figure 83 1a). It consists of aggregates of ferro-ferri-hornblende crystals embedded in a matrix of fibrous to 84 acicular tremolite with minor quartz and calcite (as determined by XRPD analysis). A significant inter-crystalline variation in the hastingsite component is observed, with some crystals falling in the 85 86 compositional field of hastingsite and even of magnesio-hastingsite. The sample was catalogued as 87 "speziate", a mineral first described in 1914 by Luigi Colomba (1866-1944), Mineralogy professor at the Universities of Sassari, Genova and then Torino, and named "speziate" to honour Giorgio 88 Spezia (1842-1911), also Mineralogy professor at the University of Torino, who in 1905 was the 89 first to develop a method for the hydrothermal synthesis of quartz. 90

Colomba described "speziaite" as aggregates of fibrous or acicular crystals, dark green or blackish in colour, occurring either in geodes or in druses at the Traversella mine. In the latter case, which seems to be the case of the specimen of this work, "speziaite" is embedded in a fibrous whitish to greenish amphibole. The name "speziaite", however, has never been approved by IMA; indeed, it was discredited (under its incorrect spelling "speziaite") and redefined as hornblende by Leake (1978). After the official approval of the new species, we were able to examine the original sample from the Traversella mine used by Colomba to define "speziaite", which is presently denosited in the mineralogical collection of the Musee Pagianele di Saianza Naturali di Torino.

deposited in the mineralogical collection of the Museo Regionale di Scienze Naturali di Torino,

### FERRO-FERRI-HORNBLENDE FROM TRAVERSELLA MINE

99 Sezione di Mineralogia, Petrografia e Geologia (Torino) under the catalogue number M/15285

100 (Figure 1b), and found a very similar amphibole composition. Hence, former "speziaite" is

101 definitely replaced by ferro-ferri-hornblende.

The holotype (refined and analysed) crystal described in this work has the code 1260 in the amphibole database of the CNR-IGG Pavia. Type material is deposited in the collections of the Museo di Mineralogia, Dipartimento di Scienze della Terra e dell'Ambiente, Università di Pavia, under the catalogue number 2015-01. The sample in the mineralogical collection of the Museo Regionale di Scienze Naturali di Torino (refined crystal and two pieces of the same sample) should henceforth be considered a cotype.

In this paper, we report also on the chemical and structural data obtained for another crystal from the specimen belonging to the Pagano's collection, which is still ferro-ferri-hornblende but has a composition enriched in  ${}^{A}R^{+}$  and  ${}^{T,C}R^{3+}$  cations relative to that of the holotype crystal, i.e. it occurs in the part of the ferro-ferri-hornblende compositional space closer to hastingsite. This crystal has the code 1258 in the amphibole database of the CNR-IGG Pavia. This comparison is useful to describe crystal-chemical variation in the rock-specimen and to monitor their effects on polyhedron geometries.

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# 116 **Physical and optical properties**

Ferro-ferri-hornblende occurs as acicular or lamellar crystals, is dark greenish, has vitreous lustre, is 117 transparent, and fluorescence is not present. The tenacity is brittle and single crystals show perfect 118 cleavage parallel to {110}. The calculated density is 3.35 g/cm<sup>3</sup>. Colomba (1914) measured the 119 120 density of amphiboles in sample M/U15285 using methylene iodide at 12°C, and obtained 3.362 121  $g/cm^3$ . A spindle stage was used to orient a crystal for measurement of refractive indices and 2V by 122 extinction curves (Bartelmehs et al., 1992). The optical orientation was determined by transferring 123 the crystal from the spindle stage to a single-crystal diffractometer and measuring the relative axial 124 relations by X-ray diffraction. In transmitted light, ferro-ferri-hornblende is pleochroic, X = medium

125 gold/brown (weakest), Y = dark brown/black (strongest), Z = dark grey (medium);  $X^{\wedge} a = 26.2^{\circ}$  ( $\beta$ 

obtuse), Y // b,  $Z^{\wedge} c = 11.5^{\circ}$  ( $\beta$  acute). It is biaxial negative with indices of refraction  $\alpha = 1.697(2)$ ,

127  $\beta = 1.722(5), \gamma = 1.726(5)$  measured with gel-filtered Na light ( $\lambda = 590$  nm). 2V (meas.) = 35.7(4)°,

128 2V (calc.) = 43.1°.

### 129 Crystallography

Holotype ferro-ferri-hornblende from Traversella (1260) is monoclinic, space group C2/m, 130 and has a = 9.9307(5), b = 18.2232(10), c = 5.3190(3) Å,  $\beta = 104$ ,  $857(1)^{\circ}$ , V = 930.40(9) Å<sup>3</sup> (Z = 131 132 2). The *a:b:c* ratio calculated from the unit cell parameters is 0.545:1:0.292. Diffraction data were 133 collected for crystals 1260 and 1258 in the  $\theta$  range 2-35° with a Bruker-AXS CCD diffractometer, working with graphite monochromatized MoK $\alpha$  X-radiation ( $\lambda = 0.7107$  Å). Omega rotation frames 134 (scan width  $0.3^{\circ}$ , scan time 20 s, sample-to-detector distance 50 mm) were processed with the 135 SAINT software (Bruker, 2003) and intensities were corrected for Lorentz and polarization effects; 136 absorption effects were empirically evaluated by the SADABS software (Sheldrick, 1996) and an 137 absorption correction was applied to the data. Only the reflections with  $I_0 > 3\sigma_I$  were considered as 138 139 observed during unweighted full-matrix least-squares refinement on F. Scattering curves for fully 140 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)]. The first residuals in the 141 Difference Fourier map (with peaks corresponding to 3  $e/Å^2$  for sample 1258 and 1.5  $e/Å^2$  for 142 crystal 1260) are placed close to O(3), and are related to the presence of 0.10 Cl apfu (cf. Oberti et 143 144 al. 1993 for more details). Ferro-ferri-hornblende from sample M/U15285 is monoclinic, space group C2/m, and has a 145

146 = 9.9386(6), b = 18.2207(12), c = 5.3177(3) Å,  $\beta = 104$ . 874(1)°, V = 930.7(1) Å<sup>3</sup> (Z = 2).

147 Diffraction data was collected in the  $\theta$  range 4-36.6° at CrisDi (Torino) using an Oxford Gemini R

148 Ultra diffractometer equipped with a CCD area detector, with graphite-monochromatized MoKa

radiation ( $\lambda = 0.7107$  Å). Omega rotation frames (scan width 1°, scan time 22 s, sample-to-detector

150	distance 53 mm) were processed with the CrysAlis Pro, Agilent technologies (version 1.171.36.24)
151	and intensities were corrected for Lorentz and polarization effects. Data were corrected for
152	empirical absorption using spherical harmonics (Abspack, Agilent ®). All reflections with $I_0 > 2\sigma_I$
153	were considered as observed during weighted full-matrix least-squares refinement on $F^2$ . Scattering
154	curves were chosen according to the calculated chemical formulae.
155	For all the samples examined, crystallographic details are given in Table 1. Atom
156	coordinates and displacement parameters, refined site-scattering values (Hawthorne et al., 1995),
157	and selected bond lengths and angles are given in Tables 2 and 3.
158	X-ray powder-diffraction data (CuK $\alpha$ , $\lambda$ = 1.54178 Å) were obtained for the holotype crystal
159	1260 using the XPREP utility of SAINT (Bruker, 2003), which generates a 2D powder
160	
	diffractogram (Debye-Scherrer technique) starting from the $F_{obs}$ collected on the single-crystal and
161	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
161 162	

### 164 **EMP analyses**

165 Chemical analyses on crystals 1260 and 1258 used for structure refinement were done with a

166 Cameca SX-100 electron microprobe (WDS mode, 15 kV, 20 nA, counting time 20 s, 5 µm beam

diameter). The standards used are: Si and Ca: diopside (TAP); Ti: titanite (LPET); Al: andalusite

168 (TAP); Fe: fayalite (LLiF); Mn: spessartine (LLiF); Mg: forsterite (LTAP); Zn: gahnite (LLiF); Na:

albite (TAP); K: orthoclase (LPET); F: fluoro-riebeckite (TAP); Cl: tugtupite (LPET). H<sub>2</sub>O was

estimated based on 2 = (OH, F, Cl) apfu and taking into account the constraints from the structure

refinement. The oxide wt% and the calculated unit-formula are reported in Table 5. End-member

- 172 ferro-ferri-hornblende has the formula  ${}^{A}\Box {}^{B}Ca_{2}{}^{C}(Fe^{2+}{}_{4}Fe^{3+}) {}^{T}(Si_{7}Al) O_{22}{}^{W}(OH)_{2}$ , which requires
- 173 SiO<sub>2</sub> 43.41, Al<sub>2</sub>O<sub>3</sub> 5.26, FeO 29.66, Fe<sub>2</sub>O<sub>3</sub> 8.24 CaO 11.57, H<sub>2</sub>O 1.86, total 100.00 wt%.

174 The final  $[1 - (K_P/K_C)]$  compatibility index for holotype ferro-ferri-hornblende 1260 is -175 0.029 (excellent).

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# **Crystal chemistry**

### 178 Site populations and chemical variability

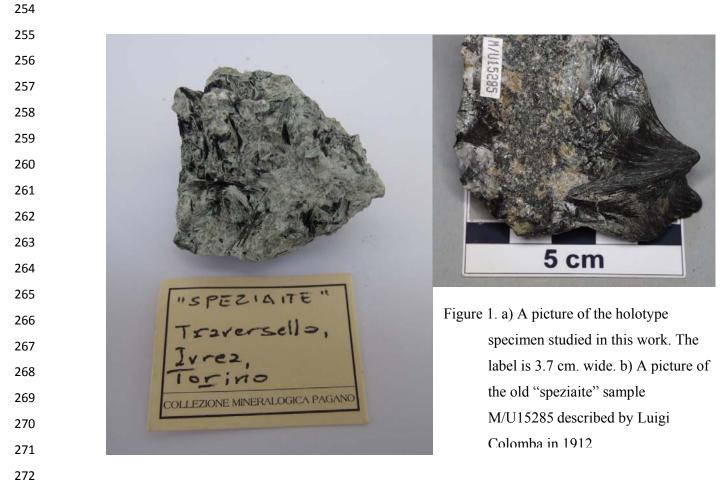
The chemical analyses available for crystals 1260 and 1258 were combined with the refined site-179 scattering values (in electrons per formula unit, epfu) to obtain site populations (Hawthorne et al., 180 181 1995). They are reported in Table 6, together with a comparison between the observed mean bond-182 lengths (mbl) and those calculated from the site populations based on the values of the distinct <cat-183 O> optimized for amphiboles during extensive crystal chemical work at IGG-CNR-Pv (Mg: 2.078 Å, Al: 1.929 Å Ti: 1.960 Å, Mn<sup>2+</sup>: 2.173 Å, Fe<sup>2+</sup> 2 .125 Å, Fe<sup>3+</sup>: 2.025 Å). The agreement between 184 the refined and calculated site-scattering values is excellent, and validates the averaged composition 185 186 of the crystal, the recalculation of the unit formula, and the partitioning of cations among the 187 different groups of sites. Inspection of the geometrical variations reported in Tables 3 and 5 confirms the calculated 188 amounts of <sup>T</sup>Al and its ordering at the T(1) site; the small increase in <sup>T</sup>Al in crystal 1258 decreases 189 slightly but significantly the stretching (along c) of the double chain of tetrahedra, measured by the 190 191 O(5)-O(6)-O(5) angle. As far as the C cations are concerned, the comparison of the observed and 192 calculated distances reported in Table 5, in particular the shorter  $\langle M(2) - O \rangle$  distance measured in 193 crystal 1258, confirm the ordering of high-charged cations at the M(2) site, which is expected in <sup>W</sup>(OH,F,Cl) amphiboles (Hawthorne and Oberti, 2007, Oberti *et al.*, 2007). 194 195 The chemical variability observed in the two crystals (which is representative of that 196 observed in a total of 8 crystals refined and analyzed) indicates variation from tremolite/actinolite to

197 magnesio-hastingsite/hastingsite, where an increasing amount of  ${}^{T}R^{3+}$  is balanced by an increase in

198	${}^{C}R^{3+}$ and ${}^{A}R^{+}$ in nearly equal proportions. Indeed, these latter compositions have been found in this
199	rock-specimen, and always occur as strongly zoned dark-green crystals. Tremolitic amphiboles
200	have been also identified (based on XRPD analysis) in the white microcrystalline matrix embedding
201	hornblende and hastingsite.
202	The results of the structure refinement of ferro-ferri-hornblende from sample M/U15285
203	(Table 5) show that it is very close in composition and in crystal-chemistry to crystal 1260. The
204	absence of the $A(2)$ and $M(4')$ subsites may be due to the different models used during the
205	refinement. Indeed, the site-scattering values refined for M/U15258 are very similar to those of
206	crystal 1260 and, together with refined mean bond distances, may indicate a composition only
207	slightly richer in <sup>C</sup> Fe and poorer in <sup>T</sup> Al and <sup>A</sup> Na, and thus even slightly closer to the end-member
208	composition [ <i>M</i> (1): 46.47 vs. 45.02, <i>M</i> (2): 45.70 vs. 43.63, <i>M</i> (3): 23.18 vs. 22.64, total C: 115.35
209	vs. 111.29 epfu; total B: 39.95 vs. 39.81 epfu; total A: 1.99 vs. 2.95 epfu].
210	
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	Holotype ferro-ferri- hornblende 1260	Ferro-ferri- hornblende 1258	Cotype ferro-ferri- hornblende M/U15285 n.4		Holotype ferro-ferri- hornblende 1260	Ferro-ferri- hornblende 1258	Cotype ferro-ferri- hornblende M/U15285 n.4
Size (µm)	210 x 100 x 60	200 x 80x 60	392 x 144 x 63	$R_{\rm merge} \ge 100$	1.6	1.6	2.8
a (Å)	9.9307(5)	9.9412(5)	9.9386(6)	$R_{\rm obs}$ x 100	2.5	2.9	3.5
b	18.2232(10)	18.2218(10)	18.2207(12)	$R_{\rm all}$ x 100	3.0	3.4	4.8
с	5.3190(3)	5.3318(3)	5.3177(3)				
β (°)	104.857(1)	104.946(1)	104.874(7)	# <sub>collected</sub>	10773	10752	4355
$V(\text{\AA}^3)$	930.40(9)	933.16(9)	930.70(10)	Mean redund.	5	5	2
a:b:c	0.545:1:0.292	0.546:1:0.293	0.545:1:292	$\#_{all}$	2110	2120	2259
θ range (°)	2-35	2-35	2-36.6				

# 274 **TABLE 1.** Crystallographic details

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277 TABLE 2. Atomic coordinates, refined site-scattering values (ss, epfu), atom-displacement parameters ( $B_{eq}$ ,  $Å^2;\beta_{ij} \ge 10^4$ ) for ferro-ferri-hornblende 1260 and 1258. 278

Site	SS	x/a	y/b	z/c	$B_{ m eq}$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
1260											
O(1)		0.11015(12)	0.08865(6)	0.21398(21)	0.93(2)	24	8	81	-3	12	-1
O(2)		0.12079(9)	0.17450(3)	0.72604(33)	0.94(2)	23	8	85	-1	10	2
O(3)		0.11225(19)	0	0.71347(33)	1.06(3)	39	7	84	-	20	-
O(4)		0.36742(13)	0.24700(7)	0.79182(23)	1.11(2)	36	7	104	-4	22	-2
O(5)		0.34602(12)	0.13469(7)	0.09832(23)	1.13(2)	27	11	91	1	13	9
O(6)		0.34243(12)	0.11921(7)	0.59039(23)	1.07(2)	28	9	97	0	14	-6
O(7)		0.33333(19)	0	0.29115(36)	1.26(4)	34	6	156	-	18	-
T(1)		0.27963(4)	0.08455(2)	0.29672(8)	0.67(1)	20	5	60	-1	9	0
T(2)	45.02(9)	0.28950(4)	0.17120(2)	0.80539(8)	0.72(1)	21 25	6	63	-1	12	0
M(1) $M(2)$	45.02(8) 43.63(8)	0 0	0.08961(2) 0.17880(2)	<sup>1</sup> / <sub>2</sub> 0	0.78(1) 0.73(1)	23 22	6 5	65 72	-	14 13	-
M(2) M(3)	43.03(8) 22.64(4)	0	0.17880(2)	0	0.73(1) 0.77(1)	22	5 5	69	-	10	-
M(3) M(4)	38.88(54)	0	0.27907(13)	<sup>1</sup> / <sub>2</sub>	1.07(2)	34	7	122	_	35	_
A	0.99(3)	0	$\frac{1}{2}$	0	0.7(2)	51	,	122		55	
A(m)	1.21(7)	0.0271(28)	$\frac{1}{2}$	0.0679(57)	1.9(3)						
A(2)	0.75(7)	0	0.4682(17)	0	1.1(4)						
Н	1.8	0.184(4)	0	0.749(8)	1.0						
<i>M</i> (4')	0.93(4)	0	0.2594(42)	<sup>1</sup> / <sub>2</sub>	1.0						
1258											
O(1)		0.10779(14)	0.09004(8)	0.21379(25)	1.00(3)	25	9	86	-3	13	-1
O(2)		0.12103(14)	0.17577(8)	0.73027(26)	1.01(3)	24	8	91	0	9	3
O(3)		0.11438(23)	0	0.71372(38)	1.29(4)	64	6	77	-	30	-
O(4)		0.36792(15)	0.24799(8)	0.79179(27)	1.15(3)	37	8	108	-4	24	-2
O(5)		0.34694(14)	0.13652(8)	0.10171(27)	1.18(3)	29	11	95	0	10	10
O(6)		0.34230(14)	0.11956(8)	0.59638(27)	1.16(3)	28	9	114	1	15	-8
O(7)		0.33310(22)	0	0.29010(43)	1.41(4)	35	8	167	_	15	-
<i>T</i> (1)		0.27912(5)	0.08522(3)	0.29925(10)	0.75(1)	22	5	69	-1	9	0
T(2)		0.29018(5)	0.17216(3)	0.80880(9)	0.74(1)	20	5	68	-1	12	0
<i>M</i> (1)	46.56(11)	0	0.09038(2)	<sup>1</sup> / <sub>2</sub>	0.84(1)	27	6	68		15	-
<i>M</i> (2)	44.14(11)	0	0.17884(2)	0	0.75(1)	22	5	74	_	12	_
<i>M</i> (3)	24.00(5)	0	0	0	0.85(1)	27	5	76	_	10	_
<i>M</i> (4)	39.26(90)	0	0.28010(20)	<sup>1</sup> / <sub>2</sub>	1.09(3)	34	7	122		34	_
A	2.87(4)	0	<sup>1</sup> / <sub>2</sub>	0	1.1(1)	51	,	122		51	
A(m)	2.19(9)	0.0300(16)	1/2	0.0722(33)	1.6(2)						
A(2)	1.83(9)	0	0.4682(13)	0	2.4(3)						
Н	1.8	0.184(5)	0.4082(13)	0.767(8)							
	0.63(8)	0.184(3)	0.2638(69)	$\frac{1}{2}$	1.0 1.0						
<i>M</i> (4')	0.03(8)	U	0.2030(09)	/2	1.0						
M/U152	85										
O(1)		0.11052(12)	0.08864(8)	0.2132(2)	0.79	19	8	61	-2	8	-2

### FERRO-FERRI-HORNBLENDE FROM TRAVERSELLA MINE

O(2)		0.12117(12)	0.17439(8)	0.7252(2)	0.81	17	7	75	-1	4	3
O(3)		0.11150(19)	0	0.7127(3)	0.82	22	6	75	-	10	-
O(4)		0.36739(12)	0.24674(8)	0.7924(2)	0.94	30	6	94	-3	18	-3
O(5)		0.34546(11)	0.13430(9)	0.0968(2)	0.96	22	10	73	1	9	9
O(6)		0.34215(11)	0.11920(8)	0.5887(2)	0.88	22	8	76	0	8	-7
O(7)		0.33269(17)	0	0.2917(4)	1.02	29	5	130	-	14	-
<i>T</i> (1)		0.27980(5)	0.08433(3)	0.29558(9)	0.43	13	3	37	-1	5	0
T(2)		0.28981(4)	0.17083(3)	0.80469(9)	0.56	16	4	49	-1	9	0
<i>M</i> (1)	46.46(7)	0	0.08953(2)	<sup>1</sup> / <sub>2</sub>	0.60	20	4	46	-	10	-
<i>M</i> (2)	45.70(7)	0	0.17904(2)	0	0.61	19	4	57	-	9	-
<i>M</i> (3)	23.18(8)	0	0	0	0.60	20	4	50	-	6	-
<i>M</i> (4)	39.95(8)	0	0.27871(3)	<sup>1</sup> / <sub>2</sub>	0.98	30	6	109	-	32	-
Α	1.39(18)	0.032(7)	<sup>1</sup> / <sub>2</sub>	0.076(16)	2.01						
A(m)	0.6(3)	0	<sup>1</sup> / <sub>2</sub>	0	0.16						
Н	2	0.179(4)	0	0.748(6)	0.35						

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2	8	2
2	8	3

1260 1258 M/U15285 1260 1258 M/U15285 T(1) - O(1)1.629(1) 1.648(1)1.628(1)T(2) - O(2)1.621(1)1.626(1) 1.621(1)1.655(1) T(1) - O(5)1.675(1)1.651(1)T(2) - O(4)1.594(1)1.597(1)1.593(1)1.650(1) T(1)-O(6)1.652(1)1.668(1)1.650(1)T(2) - O(5)1.654(1)1.651(1)1.648(1)1.670(1)1.665(1)T(1) - O(7)1.633(1)1.626(1)T(2) - O(6)1.668(1) < T(1) - O >1.639 < T(2) - O >1.635 1.635 1.642 1.660 1.633 2.134(1) 2.089(1) 2.079(1) 2.096(1)2.106(1) 2.137(1)  $M(1) - O(1) \times 2$  $M(2) - O(1) \times 2$  $M(1) - O(2) \times 2$ 2.130(1)2.148(1)2.130(1) $M(2) - O(2) \times 2$ 2.113(1)2.100(1)2.120(1)2.010(1) 1.996(1)  $M(1) - O(3) \times 2$ 2.133(1)2.153(1)2.127(1) $M(2) - O(4) \times 2$ 2.010(1) <*M*(1)–O> 2.086 2.117 2.127 2.118 <*M*(2)–O> 2.067 2.089  $M(3) - O(1) \times 4$ 2.113(1)2.124(1)2.112(1) $M(4) - O(2) \times 2$ 2.403(2)2.410(3)2.399(1)2.106(2) 2.105(1)  $M(4) - O(4) \times 2$ 2.327(1) $M(3) - O(3) \times 2$ 2.126(2)2.337(2) 2.328(1)< M(3) - O >2.111 2.124 2.110  $M(4) - O(5) \times 2$ 2.774(2)2.732(2)2.789(1)2.550(2) $M(4) - O(6) \times 2$ 2.546(3)2.554(1)2.514  $A-O(5) \times 4$ 3.008(1)3.037(2)3.003(2)<*M*(4)–O> 2.506 2.518 A-O(6) ×4 3.188(1) 3.177(1)3.194(2) $A-O(7) \times 2$ 2.18(9)2.540(2)2.543(2)2.549(2) $M(4') - O(2) \times 2 2.13(6)$ <A-O> 2.987 2.994 2.989  $M(4') - O(4) \times 2 \quad 2.28(1)$ 2.29(1)  $M(4') - O(5) \times 2 = 2.99(5)$ 2.91(8)A(m)-O(5) ×2 3.07(2) 3.11(1) 3.09(4) $M(4') - O(6) \times 2 = 2.82(6)$ 2.77(9)  $A(m) - O(5) \times 2 2.99(1)$ 3.02(1)2.98(2)< M(4') - O >2.56 2.54  $A(m) - O(6) \times 2 2.91(2)$ 2.89(1) 2.89(6) A(m)–O(7) 2.51(2)2.52(2)2.53(4) $A(2)-O(5) \times 2 = 2.56(2)$ 2.58(2)A(m) - O(7)3.34(3) 3.32(2) 3.29(4)  $A(2)-O(6) \times 2$ 2.83(2)2.81(1)A(m)–O(7) 2.63(2)2.63(1)2.64(5)2.61(1) $A(2)-O(7) \times 2$ 2.61(1)<A(m)-O>2.94 2.95 2.93 <A(2)–O> 2.66 2.67 T(1) - O(5) - T(2) 136.7(1) 136.0(1)137.2(1)O(5)-O(6)-O(5) 167.8(1) 166.6(1)168.1(1)139.5(1) O(6)-O(7)-O(6) 108.3(1) 107.0(1) 108.7(1)T(1)-O(6)-T(2) 139.1(1) 139.0(1)

T(1) - O(7) - T(1) = 141.3(1)

140.9(1)

141.9(1)

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**TABLE 3.** Selected interatomic distances (Å), and interatomic angles in the double-chain of tetrahedra (°) in ferro-ferri-hornblende 1260, 1258 and M/U15285.

$I_{\rm rel}$	d(calc)	h k	l	$I_{\rm rel}$	d(calc)	h k	l	$I_{\rm rel}$	d(calc)	h k l	$I_{\rm rel}$	d(calc)	hk	l
9	9.110	0 2	0	8	2.831	3 3	0	6	2.199	1 7 1	7	1.699	-2 8	
100	8.493	1 1	0	17	2.757	-3 3	1	25	2.180	2 6 1			-1 3	
11	4.920	-1 1	1	69	2.728	1 5	1	14	2.057	2 0 2	16	1.663	4 6	]
11	4.556	0 4	0	32	2.615	06	1	23	2.033	-4 0 2	5	1.652	4 8	(
7	3.910	-1 3	1	37	2.555	-2 0	2			3 5 1	11	1.633	1 11	
26	3.406	1 3	1	5	2.402	3 5	0	5	1.895	-4 6 1	5	1.599	6 0	(
14	3.304	2 4	0	28	2.359	-3 5	1	4	1.882	-1 9 1	15	1.590	-1 5	
47	3.151	3 1	0	7	2.319	-1 7	1	4	1.763	-5 1 2	4	1.565	4 0	2
13	2.961	2 2	1	16	2.296	-3 1	2				7	1.548	-6 0	

**TABLE 4.** Powder X-ray data for ferro-ferri-hornblende 1260.

288 Note: The strongest eight lines are in bold.

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Oxide	wt%	Range	Oxide	wt%	Range		apfu		apfu
1260									
SiO <sub>2</sub>	46.63(1.83)	44.59-49.09	H <sub>2</sub> O**	1.82		Si	7.26	Na	0.07
ГiO <sub>2</sub>	0.05(2)	0.03-0.08	F	0.02(3)	0.00-0.10	Al	0.74	Ca	1.93
$Al_2O_3$	4.67(1.19)	2.88-5.74	Cl	0.38(3)	0.12-0.64	Sum T	8.00	Sum B	2.00
Fe <sub>2</sub> O <sub>3</sub> *	3.81		O = F,Cl	-0.09	_	Ti <sup>4+</sup>	0.01	Κ	0.13
FeO*	24.65		Total	100.22		Al	0.12	Na	0.10
[FeO] <sub>tot</sub>	[28.08(94)]	26.50-29.06				Fe <sup>3+</sup>	0.45	Sum A	0.23
MnO	0.48(5)	0.40-0.58	Group site	e-scattering (e	pfu)	$Mn^{2+}$	0.06	OH-	1.89
MgO	4.99(68)	4.30-6.03		obs (SREF)	calc (EMP)	Fe <sup>2+</sup>	3.21	F <sup>-</sup>	0.01
ZnO	0.03(3)	0.00-0.08	С	111.29	112.36	Mg	1.16	Cl	0.10
CaO	11.59(9)	11.40-11.73	В	39.81	39.37	Sum C	5.01	Sum W	2.000
Na <sub>2</sub> O	0.56(15)	0.33-0.70	А	2.95	3.57				
K <sub>2</sub> O	0.63(29)	0.34-0.96	Total	154.05	155.30				
1258									
SiO <sub>2</sub>	42.87(1.55)	41.00-45.03	H <sub>2</sub> O**	1.81		Si	6.72	$Mn^{2+}$	0.04
TiO <sub>2</sub>	0.14(4)	0.11-0.21	F	0.02(2)	0.00-0.05	Al	1.28	Na	0.07
$Al_2O_3$	9.14(0.62)	8.56-10.17	Cl	0.38(3)	0.35-0.46	Sum T	8.00	Ca	1.89
Fe <sub>2</sub> O <sub>3</sub> *	3.70		O = F,Cl	-0.10		Ti <sup>4+</sup>	0.02	Sum B	2.00
FeO*	25.21		Total	100.22		Al	0.40	Κ	0.25
[FeO] <sub>tot</sub>	[28.54(32)]	27.94-28.99				Fe <sup>3+</sup>	0.44	Na	0.23
MnO	0.40(3)	0.37-0.46	Group site	e-scattering (e	pfu)	Mn <sup>2+</sup>	0.02	0.02	0.48
MgO	3.53(69)	2.55-4.38		obs (SREF)	calc (EMP)	Fe <sup>2+</sup>	3.30	OH-	1.89
ZnO	0.02(2)	0.00-0.05	С	114.70	113.22	Mg	0.82	F <sup>-</sup>	0.0
CaO	11.26(34)	10	В	39.90	39.57	Sum C	5.00	Cl	0.10
Na <sub>2</sub> O	1.07(9)	1.93-1.21	А	6.89	7.28			Sum W	2.000
K <sub>2</sub> O	1.13(8)	1.05-1.27	Total	161.49	160.07				

TABLE 5. Chemical composition (10 points) and unit formula (based on 24 anions) for ferro-ferri-hornblende
 (1260).

**293** \* FeO:Fe<sub>2</sub>O<sub>3</sub> ratio calculated from single-crystal structure-refinement results;

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

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# **Table 6.** Site populations in ferro-ferri-hornblende 1260 and 1258.

Site	Site population ( <i>apfu</i> )	site scattering (epfu)		bond distance (Å)	
		refined	calculated	refined	calculated
1260					
<i>T</i> (1)	3.26 Si + 0.74 Al			1.642	1.641
<i>T</i> (2)	4 Si				
<i>M</i> (1)	$0.48 \text{ Mg} + 1.52 \text{ Fe}^{2+}$	45.02	45.28	2.117	2.114
<i>M</i> (2)	$0.46 \text{ Mg} + 0.97 \text{ Fe}^{2+} + 0.12 \text{ Al} + 0.45 \text{ Fe}^{3+} + 0.01 \text{ Ti}^{4+}$	43.63	44.22	2.086	2.090
<i>M</i> (3)	$0.22 \text{ Mg} + 0.72 \text{ Fe}^{2+} + 0.06 \text{ Mn}$	22.64	22.86	2.111	2.118
C cations		111.29	112.36		
B cations	1.93 Ca + 0.07 Na	39.81	39.37		
A cations	0.10 Na + 0.13 K	2.95	3.57		
W anions	1.89 OH + 0.10 Cl + 0.01 F				
1258					
<i>T</i> (1)	6.72 Si + 1.28 Al			1.660	1.657
T(2)	4 Si				
<i>M</i> (1)	$0.42 \text{ Mg} + 1.58 \text{ Fe}^{2+}$	46.56	46.12	2.127	2.115
<i>M</i> (2)	$0.24 \text{ Mg} + 0.90 \text{ Fe}^{2+} + 0.40 \text{ Al} + 0.44 \text{ Fe}^{3+} + 0.02 \text{ Ti}^{4+}$	44.14	43.36	2.067	2.057
<i>M</i> (3)	$0.16 \text{ Mg} + 0.82 \text{ Fe}^{2+} + 0.02 \text{ Mn}$	24.00	23.74	2.124	2.118
C cations		114.70	113.22		
B cations	1.89 Ca + 0.04 Mn <sup>2+</sup> + 0.07 Na	39.90	39.57		
A cations	0.23 Na + 0.25 K	6.89	7.28		
W anions	1.89 OH + 0.10 Cl + 0.01 F				