

FERRO-FERRI-NYBØITE, $\text{NaNa}_2(\text{Fe}^{2+}_3\text{Fe}^{3+}_2)(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$, A NEW CLINOAMPHIBOLE FROM MONT SAINT-HILAIRE, QUÉBEC, CANADA: DESCRIPTION AND CRYSTAL STRUCTURE

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ABSTRACT

Ferro-ferri-nybøite, $\text{NaNa}_2(\text{Fe}^{2+}_3\text{Fe}^{3+}_2)(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$, is a new mineral of the amphibole group from Poudrette quarry, Mont Saint-Hilaire, La Vallée-du-Richelieu RCM, Montérégie (formerly Rouville County), Québec, Canada. It occurs in an igneous microbreccia associated with a eudialyte-group mineral, an astrophyllite-group mineral, albite, and nepheline. Crystals are prismatic parallel to [001] with {100} and {110} forms and cleavage surfaces, and the prism direction is terminated by irregular fractures. Grains are up to 3 cm long, and occur as blocky aggregates. Crystals are black with a greyish-green to black streak. Ferro-ferri-nybøite is brittle, has a Mohs hardness of 6 and a splintery fracture; it is non-fluorescent with perfect {110} cleavage, no observable parting, and has a calculated density of 3.424 g/cm³. Crystals show extreme optical absorption due to intervalence charge transfer, which inhibited measurement of optical properties.

Ferro-ferri-nybøite is monoclinic, space group *C2/m*, *a* 9.9190(5), *b* 18.0885(8), *c* 5.3440(3) Å, β 103.813(1)°, *V* 931.09 (13) Å³, *Z* = 2. The strongest ten X-ray diffraction lines in the powder pattern are [*d* in Å(*hkl*): 8.520(100)(110), 3.162 (55)(310), 2.834(24)(330), 1.671(19)(461), 2.732(10)(151), 2.552(10)(202), 2.344(9)(351), 3.298(7)(240), 2.606(6)(061), 1.446(6)(661,4,10,0)]. Analysis by a combination of electron microprobe and Mössbauer spectroscopy gives SiO₂ 45.80, Al₂O₃ 3.11, TiO₂ 0.50, Fe₂O₃ 11.18, FeO 23.45, MnO 2.28, ZnO 0.12, MgO 0.23, CaO 0.99, Na₂O 8.01, K₂O 1.30, F 0.81, H₂O_{calc} 1.47, O ≡ F−0.34 sum 98.91 wt%. The formula unit, calculated on the basis of 24 (O + OH + F) with (OH + F) = 2 *apfu* is $(\text{Na}_{0.66}\text{K}_{0.27})_{\Sigma 0.92}(\text{Na}_{1.83}\text{Ca}_{0.17})_{\Sigma 2.00}(\text{Mg}_{0.06}\text{Fe}^{2+}_{3.15}\text{Mn}_{0.31}\text{Zn}_{0.01}\text{Fe}^{3+}_{1.38}\text{Ti}_{0.06}\text{Al}_{0.03})_{\Sigma 5.00}(\text{Si}_{7.35}\text{Al}_{0.65})_{\Sigma 8.00}\text{O}_{22}(\text{OH}_{1.58}\text{F}_{0.42})_{\Sigma 2.00}$. Ferro-ferri-nybøite, ideally $\text{NaNa}_2(\text{Fe}^{2+}_3\text{Fe}^{3+}_2)(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$, is related to endmember nybøite, $\text{NaNa}_2(\text{Mg}_3\text{Al}_2)(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$ by the substitutions $\text{Fe}^{2+} \rightarrow \text{Mg}$ and $\text{Fe}^{3+} \rightarrow \text{Al}$.

Keywords: Ferro-ferri-nybøite, new amphibole, nybøite, electron-microprobe analysis, Mössbauer spectroscopy, crystal-structure refinement, Mont Saint-Hilaire, Canada.

INTRODUCTION

Amphibole compositions approximating $\text{NaNa}_2(\text{Al}_2\text{Mg}_3)(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$ were reported by Ungaretti *et al.* (1981) from the Nybø eclogite pod, Norway. The root-name “nybøite” was mentioned as being under consideration by the IMA (Ungaretti *et al.* 1981), and had been approved in 1980, but a full description was not published at that time (see detailed discussion

by Oberti *et al.* 2003). Despite subsequent reports on the occurrence, chemical composition, and crystal structure of this amphibole (*e.g.*, Hirajima *et al.* 1992, Pawley 1992, Hawthorne *et al.* 1996), a comprehensive description of “nybøite” was not reported until the formal description of “fluoro-nybøite” by Oberti *et al.* (2003). If this were not irregular enough, the previous IMA amphibole classification gave the root-name “nybøite” (Leake *et al.* 1997), whereas the current IMA

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amphibole classification gives the root-name nybøite (Hawthorne *et al.* 2012) to the composition $\text{NaNa}_2(\text{Al}_2\text{Mg}_3)(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$. As part of a preliminary examination of the crystal chemistry of amphiboles from Mont Saint-Hilaire, Quebec (Taylor 1999), a sample from an igneous breccia was found to contain an amphibole-group mineral whose chemical composition resembles that of nybøite, but which shows dominance of Fe^{2+} and Fe^{3+} at the C position of the amphibole formula. Here, we report on the characterization and occurrence of the new clinoamphibole species, ferro-ferri-nybøite.

The new species and the new name (Hawthorne *et al.* 2012) have been approved by the International Mineralogical Association Commission on New Minerals and Mineral Classification (2013-072). Holotype material is deposited in the mineral collection of the Department of Natural History, Royal Ontario Museum, 100 Queens Park, Toronto, Ontario, M5S 2C6, Canada, catalogue number M55980.

OCCURRENCE

The sample of ferro-ferri-nybøite was discovered in the Poudrette quarry, Mont Saint-Hilaire, La Vallée-du-Richelieu RCM, Montérégie (formerly Rouville County), Québec, Canada, in an igneous breccia collected by Dr. P. Tarassoff (Beaconsfield, Quebec) on 29 July, 1995. It occurs as anhedral to subhedral, stubby

crystals up to 3×3 cm, but most averaging 0.5×0.5 cm. The mineral is jet-black in color, and occurs in association with an astrophyllite-group mineral, a reddish to brownish eudialyte-group mineral, albite, and nepheline. A secondary amphibole is also present, but it is distinct in that it occurs as euhedral, prismatic greenish-brown crystals that average 100×300 μm in size. Paragenetically, ferro-ferri-nybøite is the earliest mineral formed and it commonly shows evidence of having been subsequently overgrown by nepheline.

PHYSICAL AND OPTICAL PROPERTIES

Ferro-ferri-nybøite is black with a vitreous luster. It has a greyish-green to black streak and shows no fluorescence under long-wave or short-wave ultraviolet light. Grains are prismatic parallel to $[001]$ with $\{100\}$ and $\{110\}$ forms and cleavage faces, and the prism direction is terminated by irregular fractures. They are up to 3 cm long and occur as blocky aggregates. Ferro-ferri-nybøite has a Mohs hardness of ~ 6 and is brittle with a splintery fracture; it has the characteristic perfect $\{110\}$ cleavage of amphiboles, intersecting at $\sim 56^\circ$. The calculated density (using the empirical formula and the single-crystal cell-dimensions) is 3.424 g/cm^3 .

We were unable to measure the optical properties of this amphibole despite extensive effort. The crystals show extreme optical absorption due to intervalence

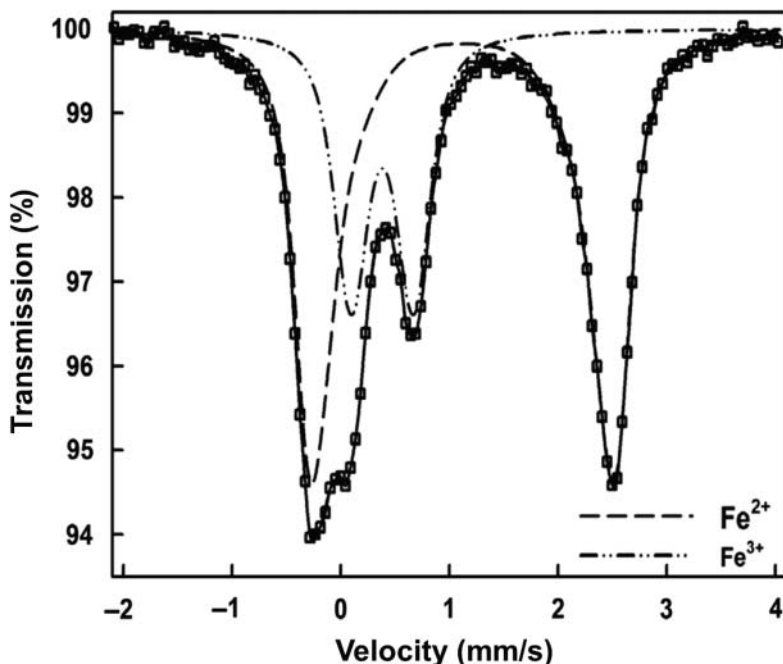


FIG. 1. The ^{57}Fe Mössbauer spectrum of ferro-ferri-nybøite.

charge transfer. When attempting to measure extinction curves on a spindle stage, the strongly anisotropic absorption due to IVCT was superimposed on the extinction curves, giving curves with two sets of maxima and minima (instead of the one set normally observed). In addition, the resultant maxima and minima were displaced (by an undetermined amount) from their ideal positions. Consequently, we could not properly orient the crystals optically so as to measure their optical properties. We tried crystals as small as 5 microns in size, but could not eliminate this effect. In tiny grains and on the thin edges of larger grains, the amphibole is strongly pleochroic in shades of dark greenish blue to black.

MÖSSBAUER SPECTROSCOPY

Fragments of ferro-ferri-nybøite were ground with an agate mortar and pestle, placed on a Pb ring (2 mm inner diameter), and secured in place with tape. The Mössbauer spectrum was acquired in transmission geometry at room temperature using a $^{57}\text{Co}(\text{Rh})$ point source, and the spectrometer was calibrated with the room-temperature spectrum of $\alpha\text{-Fe}$. The spectrum was analyzed in terms of a Voigt-function-based quadrupole-splitting distribution (Rancourt & Ping 1991) using the RECOIL® software package. Figure 1 shows the Mössbauer spectrum of ferro-ferri-nybøite fit to a model having two generalized sites. The Fe^{2+} site (dashed line) has three Gaussian components and

TABLE 1. CHEMICAL COMPOSITION (wt.%) AND UNIT FORMULA (*apfu*) FOR FERRO-FERRI-NYBØITE

SiO_2	45.80	Si	7.35
TiO_2	0.50	Al	0.65
Al_2O_3	3.61	Sum T	8.00
Fe_2O_3	11.74		
FeO	23.45	Al	0.03
MnO	2.28	Ti^{4+}	0.06
ZnO	0.12	Fe^{3+}	1.38
MgO	0.23	Fe^{2+}	3.15
CaO	0.99	Mn	0.31
Na_2O	8.01	Zn	0.01
K_2O	1.30	Mg	0.06
H_2O	1.47	Sum C	5.00
F	0.81		
–O=F	–0.34	Ca	0.17
Total	99.48	Na	1.83
		Sum B	2.00
		Na	0.66
		K	0.27
		Sum A	0.93
		(OH)	1.58
		F	0.42
		Sum W	2.00

TABLE 2. X-RAY POWDER DIFFRACTION DATA FOR FERRO-FERRI-NYBØITE

$l_{\text{est.}}^*$	$d_{\text{meas}} \text{ \AA}$	$d_{\text{calc}} \text{ \AA}$	<i>h</i>	<i>k</i>	<i>l</i>
100	8.520	8.502	1	10	0
4	4.822	4.816	2	0	0
5	4.524	4.522	0	4	0
3	3.430	3.431	1	3	1
7	3.298	3.297	2	4	0
55	3.162	3.161	3	1	0
4	2.992	2.994	2	2	1
24	2.834	2.834	3	3	0
3	2.742	2.742	$\bar{3}$	3	1
10	2.732	2.733	1	5	1
6	2.606	2.607	0	6	1
3	2.599	2.597	2	4	1
10	2.552	2.553	2	0	2
5	2.402	2.401	3	5	0
9	2.344	2.345	$\bar{3}$	5	1
2	2.304	2.306	$\bar{1}$	7	1
1	2.286	2.287	$\bar{3}$	1	2
2	2.197	2.197	1	7	1
4	2.186	2.185	2	6	1
2	2.085	2.086	2	0	2
3	2.045	2.045	3	5	1
1	2.022	2.022	4	0	2
2	1.961	1.961	4	2	1
3	1.885	1.885	$\bar{4}$	6	1
2	1.835	1.836	4	4	1
3	1.809	1.809	0	10	0
2	1.753	1.753	5	1	2
2	1.693	1.693	2	10	0
	1.693	1.693	$\bar{2}$	8	2
1	1.684	1.683	$\bar{3}$	9	1
19	1.671	1.672	4	6	1
1	1.648	1.648	4	8	0
3	1.621	1.621	1	11	0
3	1.605	1.605	6	0	0
		1.596	$\bar{1}$	5	3
5	1.539	1.540	6	0	2
2	1.524	1.525	$\bar{2}$	6	3
		1.524	5	5	1
2	1.520				
2	1.507	1.507	0	12	0
4	1.463	1.464	3	11	0
6	1.446	1.447	6	6	1
	1.446	1.446	4	10	0

*The ten most intense lines are bolded.

the Fe^{3+} site (dash-dot line) has one Gaussian component. We do not know the relative recoil-free fractions of Fe^{2+} and Fe^{3+} in ferro-ferri-nybøite, but measurements on riebeckite (Eeckhout & De Grave 2003) suggest differences on the order of 10%. Using these in conjunction with the area ratio derived from the

Mössbauer spectrum of ferro-ferri-nybøite gives an $\text{Fe}^{3+}/\text{Fe}^{\text{tot}}$ value of 0.30(2).

CHEMICAL COMPOSITION

Ferro-ferri-nybøite was analyzed using a Cameca SX-100 operating in the wavelength-dispersive mode with an excitation voltage of 15 kV, specimen current 10 nA, beam diameter 5 μm , peak-count time 20 s, and background-count time 10 s. The following standards and crystals were used for $K\alpha$ X-ray lines: Si, Ca: diopside, TAP, LPET; Ti: titanite, LPET; Fe: fayalite, LLiF; Mn: spessartine, LLiF; Mg: forsterite, TAP; Na: albite, LTAP; Al: andalusite, TAP; F: fluoro-riebeckite, LTAP; Zn: gahnite, LLiF; K, orthoclase, PET. Data reduction was done using the $\varphi(\rho Z)$ procedure of Pouchou & Pichoir (1985). The average of 10 analyses on a single grain is given in Table 1. The $\text{Fe}^{3+}/(\text{Fe}^{2+} + \text{Fe}^{3+})$ ratio was derived by Mössbauer spectroscopy. The chemical formula was calculated on the basis of 24 (O + OH + F) with OH + F = 2 *apfu* (atoms per formula unit) and is as follows: $\text{A}(\text{Na}_{0.66}\text{K}_{0.27})_{\Sigma 0.93}(\text{Na}_{1.83}\text{Ca}_{0.17})_{\Sigma 2.00}(\text{Mg}_{0.06}\text{Fe}^{2+}_{3.15}\text{Mn}_{0.31}\text{Zn}_{0.01}\text{Fe}^{3+}_{1.38}\text{Ti}_{0.06}\text{Al}_{0.03})_{\Sigma 5.00}(\text{Si}_{7.35}\text{Al}_{0.65})_{\Sigma 8.00}\text{O}_{22}(\text{OH}_{1.58}\text{F}_{0.42})_{\Sigma 2.00}$.

X-RAY POWDER DIFFRACTION

The powder-diffraction pattern was recorded using a D5000 Bruker powder diffractometer (Ni-filtered $\text{CuK}\alpha$ radiation, $\lambda = 1.54178 \text{ \AA}$). No internal standard was used. The indexed powder pattern is listed in Table 2. Unit-cell parameters refined from the powder data (Table 2) are as follows: *a* 9.918(1), *b* 18.087(2), *c* 5.342(1) Å , β 103.81(1)°, *V* 930.6(1) Å^3 . The pattern was indexed on the space group *C2/m* as indicated by single-crystal structure refinement.

CRYSTAL-STRUCTURE REFINEMENT

A crystal was attached to a tapered glass fibre and mounted on a Bruker P4 diffractometer equipped with a 4K CCD detector (Mo $K\alpha$ radiation). A total of 8188 intensities was collected to 65° 2 θ using 10 s per 0.2°

frame, with a crystal-to-detector distance of 5 cm. Empirical absorption corrections (SADABS; Sheldrick 2008) were applied and equivalent reflections were corrected for Lorentz, polarization, and background effects, averaged and reduced to structure factors. The unit-cell dimensions were obtained by least-squares refinement of the positions of 6593 reflections with $I > 10\sigma I$ and are given in Table 3, together with other information pertaining to data collection and structure refinement. All calculations were done with the SHELXTL PC (Plus) system of programs; *R* indices are of the form given in Table 3 and are expressed as percentages. The structure was refined to convergence by full-matrix least-squares methods with anisotropic-displacement parameters for all atoms except those in the *A* cavity. At a later stage of refinement, difference-Fourier maps showed a weak density maximum approximately 1 Å from the O(7) anion. This maximum was entered into the structure model as an H atom and its parameters were refined with the soft constraint that the O(7)–H distance be approximately 0.98 Å . The structure converged to a final R_1 index of 3.14%. Refined atom coordinates and anisotropic-displacement parameters are listed in Table 4; selected interatomic distances and angles are given in Table 5. A table of structure-factors and a cif file may be obtained from The Depository of Unpublished Data on the MAC website [document ferro-ferri-nybøite CM52_10.3749/canmin.1400057].

DERIVATION OF SITE POPULATIONS

Site populations were derived from the results of EMP analysis and structure refinement. The refined $\langle T\text{--O} \rangle$ distances (Table 5) indicate the presence of appreciable Al at the *T* sites, in accord with the chemical formula (Table 1). Using the regression equation given by Hawthorne & Oberti (2007), and the ^{14}Al content indicated by the unit formula of ferro-ferri-nybøite, we obtain a calculated value for $\langle T\text{--O} \rangle$ of 1.638 Å , in accordance with the observed value of 1.639 Å .

Minor Ti was assigned to *M*(2) in accord with the site occupancy generally found in monoclinic

TABLE 3. MISCELLANEOUS INFORMATION FOR FERRO-FERRI-NYBØITE

<i>a</i> (Å)	9.9190(5)	crystal size (μm)	200 × 200 × 330
<i>b</i>	18.0885(8)	radiation/monochromator	Mo $K\alpha$ /Graphite
<i>c</i>	5.3440(3)	No. unique reflections	1402
β (°)	103.813(1)	No. $I_o > 4\sigma I$	1382
<i>V</i> (Å^3)	931.09(13)	$R_{\text{merge}}\%$	1.88
Sp. Gr.	<i>C2/m</i>	$R_{\text{obs}}\%$	3.14
<i>Z</i>	2	$R_{\text{all}}\%$	7.21
D_{calc} (g cm^{-3})	3.424		

TABLE 4. ATOM COORDINATES FOR FERRO-FERRI-NYBOITE

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂	<i>U</i> _{eq}
<i>T</i> (1)	0.27830(7)	0.08604(4)	0.29111(13)	0.0079(3)	0.0062(3)	0.0065(3)	0.0002(2)	0.0009(2)	0.0001(2)	0.00703(18)
<i>T</i> (2)	0.28889(7)	0.17093(4)	0.80075(13)	0.0081(3)	0.0084(3)	0.0079(3)	-0.0002(2)	0.0021(2)	-0.0011(2)	0.00808(18)
<i>M</i> (1)	0	0.09148(3)	½	0.0118(3)	0.0102(3)	0.0086(3)	0	0.00319(19)	0	0.01009(19)
<i>M</i> (2)	0	0.18347(3)	0	0.0082(3)	0.0069(3)	0.0088(3)	0	0.00238(18)	0	0.00791(18)
<i>M</i> (3)	0	0	0	0.0116(4)	0.0069(4)	0.0085(4)	0	0.0017(3)	0	0.0091(3)
<i>M</i> (4)	0	0.27795(9)	½	0.0203(9)	0.0130(8)	0.0210(9)	0	0.0134(6)	0	0.0167(5)
<i>O</i> (1)	0.1096(2)	0.09085(10)	0.2069(4)	0.0097(8)	0.0119(9)	0.0086(8)	-0.0006(6)	0.0016(7)	-0.0012(6)	0.0102(4)
<i>O</i> (2)	0.12071(19)	0.17298(10)	0.7349(4)	0.0093(8)	0.0113(8)	0.0113(8)	-0.0013(7)	0.0012(7)	0.0002(7)	0.0108(4)
<i>O</i> (3)	0.1099(3)	0	0.7074(5)	0.0227(13)	0.0216(13)	0.0218(13)	0	0.0046(11)	0	0.0221(6)
<i>O</i> (4)	0.3650(2)	0.24827(11)	0.7975(4)	0.0165(9)	0.0111(9)	0.0141(9)	-0.0019(7)	0.0064(7)	-0.0054(7)	0.0134(4)
<i>O</i> (5)	0.3476(2)	0.12845(12)	0.0800(4)	0.0125(9)	0.0185(10)	0.0125(8)	0.0056(7)	0.0029(7)	0.0007(7)	0.0145(4)
<i>O</i> (6)	0.3394(2)	0.11873(11)	0.5821(4)	0.0132(9)	0.0165(10)	0.0133(9)	-0.0056(7)	0.0034(7)	-0.0003(7)	0.0143(4)
<i>O</i> (7)	0.3327(3)	0	0.2940(6)	0.0134(13)	0.0098(12)	0.0221(14)	0	0.0023(11)	0	0.0155(6)
H	0.213(2)	0	0.754(10)	0.01500(0)						
<i>A</i> (2)	0	0.5127(5)	0	0.0171(15)						
<i>A</i> (<i>m</i>)	0.0368(17)	½	0.091(3)	0.0171(15)						
<i>A</i> (<i>m</i>)'	0.085(5)	½	0.160(7)	0.0171(15)						

TABLE 5. SELECTED INTERATOMIC DISTANCES (Å) FOR FERRO-FERRI-NYBØITE

T(1)–O(1)	1.628(2)	M(1)–O(1)	×2	2.109(2)	A(2)–O(5)	×4	2.676(7)
T(1)–O(5)	1.644(2)	M(1)–O(2)	×2	2.113(2)	A(2)–O(6)	×4	3.084(6)
T(1)–O(6)	1.638(2)	M(1)–O(3)	×2	2.139(2)	A(2)–O(7)	×4	2.553(3)
T(1)–O(7)	1.647(1)	<M(1)–O>		2.120			
<T(1)–O>	1.639				A(m)–O(5)	×2	2.837(4)
		M(2)–O(1)	×2	2.153(2)	A(m)–O(5)	×2	2.978(4)
T(2)–O(2)	1.621(2)	M(2)–O(2)	×2	2.070(2)	A(m)–O(6)	×2	2.856(12)
T(2)–O(4)	1.592(2)	M(2)–O(4)	×2	1.948(2)	A(m)–O(7)		2.514(8)
T(2)–O(5)	1.656(2)	<M(2)–O>		2.057	A(m)–O(7)		2.678(8)
T(2)–O(6)	1.669(2)				A(m)–O(7)		3.23(2)
<T(2)–O>	1.635	M(3)–O(1)	×4	2.129(2)			
		M(3)–O(3)	×2	2.108(3)	A(m)'–O(5)	×2	2.81(1)
		<M(3)–O>		2.122	A(m)'–O(5)	×2	3.26(3)
					A(m)'–O(6)	×2	2.56(2)
		M(4)–O(2)	×2	2.430(2)	A(m)'–O(7)		2.73(2)
		M(4)–O(4)	×2	2.359(2)	A(m)'–O(7)		2.76(3)
		M(4)–O(6)	×2	2.560(2)	A(m)'–O(7)		2.83(4)
		<M(4)–O>		2.45			

amphiboles (Hawthorne 1983, Oberti *et al.* 1998, Oberti *et al.* 2007), and Fe* (= Fe + Mn + Ti) was assigned to *M*(2) to fill the site and reflect the refined site-scattering value. The <*M*(2)–O> distance of 2.057 Å (Table 5) indicates a significant amount of small (trivalent) cations at *M*(2) in accordance with the presence of major amounts of Fe³⁺ in this amphibole (Fig. 1). The only way we can differentiate between ¹⁶Fe²⁺ (*r* = 0.78 Å) and ¹⁶Fe³⁺ (*r* = 0.645 Å) (radii from Shannon 1976) is by using the relation between the <*M*(2)–O> bond length and the aggregate radii of the constituent *M*(2) cations (Hawthorne & Oberti 2007): <*M*(2)–O> = 1.476 + 0.845 <*r*^{*M*(2)}>, *R* = 0.991, *σ* = 0.005 Å. Substituting the <*M*(2)–O> distance of 2.057 Å into this equation gives us the mean radius of the aggregate *M*(2) cations: 0.688 Å. The *M*(2) site is occupied by 0.06 Ti (Table 6) and the balance of the cations are Fe²⁺ (= *a apfu*) and Fe³⁺ (= 1.94 – *a apfu*). Thus

$0.06 \times 0.605 + 0.78 \times a + (1.94 - a) \times 0.645 = 2 \times 0.688 \text{ \AA}$. Solving for *a*, we get *M*(2) = 0.66 Fe²⁺ + 1.28 Fe³⁺ + 0.06 Ti *apfu*.

The observed site-scattering values at the *M*(1) and *M*(3) sites (Table 6) indicate that the small amount of Mg present occurs at the *M*(3) site, as the refined site-scattering value of 24.7 *epfu* is slightly less than that expected for complete occupancy of the site by Fe (= 26 *epfu*; or slightly less if the effect of Mn is taken into account). We have no indication of the possible ordering of Mn and hence Fe²⁺ is written as Fe²⁺ = Fe²⁺ + Mn²⁺ here. The amount of Fe³⁺ in this amphibole (1.36 Fe³⁺ *apfu*, Table 1) is slightly greater than the amount of Fe³⁺ at *M*(2): 1.28 Fe³⁺ *apfu*, and hence a small amount of Fe³⁺ must occur at *M*(1) and/or *M*(3).

The populations of the *M*(4) and *A* sites were assigned from the unit formula and are in accord with the refined site-scattering values (Table 6). The resulting

TABLE 6. SITE POPULATIONS (*apfu*) FOR FERRO-FERRI-NYBØITE

Site	Site population (<i>apfu</i>)	Site scattering (<i>epfu</i>)	
		Refined	Calculated
T(1)	0.65 Al + 3.35 Si		
T(2)	4 Si		
M(1)	1.80 Fe + 0.20 Mn	51.3(2)	51.8
M(2)	0.56 Fe ²⁺ + 1.38 Fe ³⁺ + 0.06 Ti	51.2(2)	50.9
M(3)	0.84 Fe + 0.10 Mn + 0.06 Mg	24.7(1)	25.1
M(4)	1.83 Na + 0.17 Ca	23.2(2)	23.5
A	0.66 Na + 0.27 K	12.4(6)	12.6
O(3)	1.57 (OH) + 0.43 F	15.5	16.4

site populations were then adjusted to fit the unit formula and the refined site-scattering values equally well, and the final values are given in Table 6.

DISCUSSION

As with other amphiboles with (OH + F) dominant at the O(3) site, octahedrally coordinated trivalent cations in ferro-ferri-nybøite are ordered at the M(2) site. Ferro-ferri-nybøite, ideally $\text{NaNa}_2(\text{Fe}^{2+}_3\text{Fe}^{3+}_2)(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$, is related to endmember nybøite, $\text{NaNa}_2(\text{Mg}_3\text{Al}_2)(\text{Si}_7\text{Al})\text{O}_{22}(\text{OH})_2$, by the substitutions $\text{Fe}^{2+} \rightarrow \text{Mg}$ and $\text{Fe}^{3+} \rightarrow \text{Al}$.

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REFERENCES

- ECKHOUT, S.G. & DE GRAVE, E. (2003) Evaluation of ferrous and ferric Mossbauer fractions. Part II. *Physics and Chemistry of Minerals* **30**, 142–146.
- HAWTHORNE, F.C. (1983) The crystal chemistry of the amphiboles. *Canadian Mineralogist* **21**, 173–480.
- HAWTHORNE, F.C. & OBERTI, R. (2007) Amphiboles: Crystal Chemistry. *Reviews in Mineralogy and Geochemistry* **67**, 1–54.
- HAWTHORNE, F.C., OBERTI, R., & SARDONE, N. (1996) Sodium at the A site in clinoamphiboles: the effects of composition on patterns of order. *Canadian Mineralogist* **34**, 577–593.
- HAWTHORNE, F.C., OBERTI, R., HARLOW, G.E., MARESCH, W., MARTIN, R.F., SCHUMACHER, J.C., & WELCH, M.D. (2012) Nomenclature of the amphibole super-group. *American Mineralogist* **97**, 2031–2048.
- HIRAJIMA, T., ZHANG, R., LI, J., & CONG, B. (1992) Petrology of the nybøite-bearing eclogite in the Donghai area, Jiangsu province, eastern China. *Mineralogical Magazine* **56**, 37–46.
- 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. *Canadian Mineralogist* **35**, 219–246.
- OBERTI, R., HAWTHORNE, F.C., CAMARA, F., & RAUDSEPP, M. (1998) Synthetic fluoro-amphiboles: site preferences of Al, Ga, Sc and inductive effects on mean bond-lengths of octahedra. *Canadian Mineralogist* **36**, 1245–1252.
- OBERTI, R., BOIOCCHI, M., & SMITH, D.C. (2003) Fluoronybøite from Jianchan (Su-Lu, China) and nybøite from Nybø (Nordfjord, Norway): a petrological and crystal-chemical comparison of these two high-pressure amphiboles. *Mineralogical Magazine* **67**, 769–784.
- OBERTI, R., HAWTHORNE, F.C., CANNILLO, E., & CAMARA, F. (2007) Long-range order in amphiboles. *Reviews in Mineralogy and Geochemistry* **67**, 125–171.
- PAWLEY, A. (1992) Experimental study of the compositions and stabilities of synthetic nybøite-glaucophane amphiboles. *European Journal of Mineralogy* **4**, 171–192.
- POUCHOU, J.L. & PICOIR, F. (1985) “PAP” $\phi(\rho Z)$ procedure for improved quantitative microanalysis. In *Microbeam Analysis* (J.T. Armstrong, ed.). San Francisco Press, San Francisco, California, United States (104–106).
- RANCOURT, D.G. & PING, J.Y. (1991) Voigt-based methods for arbitrary-shape static hyperfine parameter distributions in Mössbauer spectroscopy. *Nuclear Instruments and Methods in Physics Research* **B58**, 85–97.
- SHANNON, R.D. (1976) Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica* **A32**, 751–767.
- SHELDRIK, G.M. (2008) A short history of SHELX. *Acta Crystallographica* **A64**, 112–122.
- TAYLOR, R. (1999) *The Crystal Chemistry of Amphiboles from Mont-Saint Hilaire (sic)*, Quebec. Honors B.Sc. Thesis, Laurentian University, Sudbury, Ontario, Canada.
- UNGARETTI, L., SMITH, D.C., & ROSSI, G. (1981) Crystal-chemistry by X-ray structure refinement and electron microprobe analysis of a series of sodic-calcic to alkali amphiboles from the Nybø eclogite pod, Norway. *Bulletin de la Société Française Minéralogie et de Cristallographie* **104**, 400–412.

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