

# A new anhydrous amphibole from the Hoskins mine, Grenfell, New South Wales, Australia: Description and crystal structure of ungarettiite, $\text{NaNa}_2(\text{Mn}^{2+}\text{Mn}^{3+})\text{Si}_8\text{O}_{22}\text{O}_2$

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## ABSTRACT

Ungarettiite is a new amphibole species from the Hoskins mine, near Grenfell, New South Wales, Australia. It occurs with Mn-bearing oxides, silicates, and carbonates in a stratiform schist associated with metajasper, metabasalt, and metasiltstone. Ungarettiite is brittle,  $H = 6$ ,  $D_{\text{meas}} = 3.52 \text{ g/cm}^3$ ,  $D_{\text{calc}} = 3.45 \text{ g/cm}^3$ . In plane-polarized light, it is strongly pleochroic,  $X = \text{orange red}$ ,  $Y \sim Z = \text{very dark red}$ ;  $X \wedge a = -2^\circ$  (in  $\beta$  acute),  $Y = b$ ,  $Z \wedge c = 17^\circ$  (in  $\beta$  obtuse), with absorption  $X < Y \leq Z$ . Ungarettiite is biaxial positive,  $\alpha = 1.717(2)$ ,  $\beta = 1.780(4)$ ,  $\gamma = 1.800(2)$ ;  $2V = 51(2)^\circ$ , dispersion  $r < v$ . Ungarettiite is monoclinic, space group  $C2/m$ ,  $a = 9.89(2)$ ,  $b = 18.04(3)$ ,  $c = 5.29(1) \text{ \AA}$ ,  $\beta = 104.6(2)^\circ$ ,  $V = 912(1) \text{ \AA}^3$ ,  $Z = 2$ . The strongest ten X-ray diffraction lines in the powder pattern are [ $d(I, hkl)$ ]: 2.176(10,171), 3.146(9,310), 2.544(9,202), 1.447(9,3.11.1), 3.400(8,131), 1.656(8,461), 8.522(7,110), 2.299(7,171), 2.575(6,241), and 2.047(6,202). Analysis by a combination of electron microprobe and crystal-structure refinement gives  $\text{SiO}_2$  50.66,  $\text{Al}_2\text{O}_3$  0.04,  $\text{TiO}_2$  0.03,  $\text{Fe}_2\text{O}_3$  0.50,  $\text{FeO}$  0.00,  $\text{Mn}_2\text{O}_3$  24.35,  $\text{MnO}$  12.42,  $\text{MgO}$  1.46,  $\text{ZnO}$  0.10,  $\text{CaO}$  0.18,  $\text{Na}_2\text{O}$  9.13,  $\text{K}_2\text{O}$  0.76, F not detected, sum 99.63 wt%. The formula unit calculated on the basis of 24 O atoms is  $(\text{K}_{0.15}\text{Na}_{0.82})(\text{Na}_{1.97}\text{Ca}_{0.03})(\text{Mn}_{1.66}^{2+}\text{Mg}_{0.34}\text{Mn}_{2.96}^{3+}\text{Fe}_{0.06}^{3+}\text{Zn}_{0.01})\text{Si}_{7.99}\text{Al}_{0.01}\text{O}_{22}\text{O}_2$  and is close to the ideal end-member composition of  $\text{NaNa}_2(\text{Mn}^{2+}\text{Mn}^{3+})\text{Si}_8\text{O}_{22}\text{O}_2$ .

The crystal structure of ungarettiite was refined to an  $R$  index of  $\sim 1.5\%$  using  $\text{MoK}\alpha$  X-ray intensity data. Site-scattering refinement shows that the M1, M2, and M3 sites are occupied dominantly by Mn. The  $\langle \text{M-O} \rangle$  distances are M1: 2.03; M2: 2.17; M3: 2.01  $\text{Å}$ , compatible with the site occupancies M1  $\sim$  M3  $\sim$   $\text{Mn}^{3+}$ , M2  $\sim$   $\text{Mn}^{2+}$ . All bonds to the O3 anion are very short, and a bond valence analysis indicates that the O3 site is occupied by a divalent anion:  $\text{O}^{2-}$ , as suggested by the overall electroneutrality requirement of the structural formula.

## INTRODUCTION

The discovery of leakeite (Hawthorne et al., 1992),  $\text{NaNa}_2(\text{Mg}_2\text{Fe}_2^{3+}\text{Li})\text{Si}_8\text{O}_{22}(\text{OH})_2$ , in manganiferous meta-sediments of the Kajlidongri manganese mine, Madhya Pradesh, India, and the characterization of the crystal-chemical features of  $^{6}\text{Li}$  incorporation in amphiboles (Hawthorne et al., 1994) suggest that  $^{6}\text{Li}$ -bearing amphiboles should be much more common than their relatively recent discovery would suggest. The discovery of the importance of  $^{6}\text{Li}$  in alkali amphiboles in peralkaline granites (Hawthorne et al., 1993) supports this view. Consequently, we decided to look at amphiboles from some

other geologically similar localities to see if that is true. The manganiferous amphiboles from the Hoskins mine near Grenfell, New South Wales, Australia, proved to be  $^{6}\text{Li}$ -bearing. However, they also proved to contain a radically different type of amphibole, one with no monovalent anion. Privately, we had previously speculated on the possible occurrence of (halogen-free) anhydrous amphiboles, as their existence is quite reasonable from a crystal-chemical viewpoint, but we lacked the confidence to predict their existence in print. Nature turns out to be less conservative than we were, and we discovered a Mn-rich anhydrous amphibole coexisting with the Li-bearing alkali amphiboles at the Hoskins mine. We name this amphibole ungarettiite, in honor of Luciano Ungaretti, Professor of Mineralogy, Dipartimento di Scienza della Terra, Università de Pavia, Pavia, Italy, in recognition of his great

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insights into the crystal chemistry of rock-forming silicate minerals. The new species and the new name have been approved by the International Mineralogical Association Commission on New Minerals and Mineral Names. Holotype material is deposited in the Canadian Museum of Nature, Ottawa, sample no. 81517.

### OCCURRENCE

Ungarettiite occurs in manganese silicate and oxide rocks from the abandoned Hoskins mine, a Mn deposit 3 km west of Grenfell, New South Wales, Australia (Australian Map Grid Reference 8530-039487). A steeply dipping stratiform suite of schistose metamorphosed Mn-rich rocks up to 8 m thick occurs with metajasper, metabasalt, and metasilstone. The Mn-rich rocks are submarine exhalative precipitates that were subsequently deformed and metamorphosed at upper middle to upper greenschist-facies conditions (Ashley, 1986, 1989). Amphiboles occur in rock-forming amounts in scattered samples obtained from the old mine dumps. In the former workings, the Mn-rich rocks were oxidized to manganese oxide assemblages to a depth of 45 m (Hall, 1960). The unweathered amphibole-bearing rocks are therefore likely to have come from below this depth.

Two major mineral associations are evident in the Mn-rich rocks (Ashley, 1986, 1989): (1) a reduced assemblage containing rhodonite, tephroite, hausmannite, garnet (spessartine-grossular-andradite-calderite), calcium manganese barium carbonates, quartz, Mn-bearing magnetite, Mn-rich chlorite, caryopillite, barite and pyrite, and (2) an oxidized assemblage containing Mn-rich alkali amphiboles, clinopyroxenes ranging from namansilite (Kalinin et al., 1992) to aegirine, manganian pectolite-serandite (hereafter termed serandite), braunite, norrishite (Eggleton and Ashley, 1989; Tyrna and Guggenheim, 1991), calcium and barium carbonates, quartz, albite, potassium-feldspar, Mn-bearing sugilite and barite.

Oxidized assemblage samples are moderately to strongly foliated and are commonly well laminated, with the development of mineralogically distinct layers from <0.5 mm to over 30 mm in thickness. Laminae are generally planar, but some samples display tight isoclinal folds, the shearing out of fold hinges, and the development of elongate porphyroblastic aggregates of serandite, braunite, carbonate or sugilite. The mineralogically distinct layers are interpreted to be largely a result of primary sedimentary exhalative compositional variations (cf. Huebner et al., 1992) but in places could have been enhanced by deformation partitioning. Individual laminae are rich in one or more of the minerals amphibole, clinopyroxene, braunite, serandite, norrishite, carbonate, sugilite, quartz, and alkali feldspar. Grain size ranges from <0.05 to 0.5 mm, with amphibole, serandite, norrishite, and sugilite locally attaining 1.5 mm.

Amphiboles occur in two associations, both of which display foliated, granoblastic and porphyroblastic textures: (1) a generally quartz-free assemblage containing amphibole, clinopyroxene, braunite, norrishite, and manganian pectolite-serandite, with minor alkali feldspars,

carbonate, and barite, and (2) a quartz-rich assemblage, with subordinate but variable amounts of amphibole and clinopyroxene, and minor serandite, sugilite, norrishite, and carbonate. Amphiboles are disseminated in both assemblages (e.g., 1–5 modal %) but also occur as a major component (20–90 modal %) of laminae from 0.1 to 4 mm thick in the former. In hand specimen, they occur as lustrous dark red to brownish red acicular prismatic grains. In amphibole-rich laminae, felted aggregates of elongate grains commonly display preferred orientation, in part defining the foliation. Although amphibole is locally enclosed within porphyroblastic serandite, carbonate, braunite, or sugilite and is intergrown with clinopyroxene, norrishite, and braunite, it seems to coexist with all the primary metamorphic phases. Specifically, there is no textural evidence that could be interpreted as indicating replacement of clinopyroxene by amphibole.

Ungarettiite is a major component of samples 820607 and 820240. These samples are representative of assemblages 1 and 2 above; therefore, occurrence of this amphibole is not influenced by the coexisting mineral assemblage. In sample 820607, amphibole constitutes about 10 modal % in prismatic grains up to 1 mm long. It is locally enclosed in porphyroblastic serandite and carbonate, but it most commonly occurs in foliated aggregates with norrishite, accompanied by minor clinopyroxene and braunite. In sample 820240, amphibole occurs as isolated prismatic grains and aggregates in granular quartz. It forms about 5 modal % in grains up to 1 mm long, oriented in the plane of the foliation. Amphibole in aggregates is intergrown with clinopyroxene and norrishite.

Leakeite, Mn-bearing leakite, manganian katophorite, and manganian arfvedsonite occur in both assemblages (e.g., in assemblage 2 in 820994 and 820993 and in assemblage 1 in 820236, 820237, 820239, 820241 and 820608). As indicated above, they apparently coexist with all primary minerals and show a wide range of color, consistent with variations in composition (i.e., palest types are most Mg-rich and Mn-poor).

### PHYSICAL AND OPTICAL PROPERTIES

Ungarettiite is cherry red to very dark red with a vitreous luster. It has a pale pinkish white streak and shows no fluorescence under long-wave or short-wave ultraviolet light. When separated from a coarse crush of the rock, grains are prismatic on [001] and are bounded by {110} cleavage faces with the prism direction terminated by irregular fractures. Ungarettiite has a Mohs hardness of ~6 and is brittle. It has the characteristic perfect {110} cleavage of monoclinic amphiboles, intersecting at ~56°. The density, measured by flotation, is 3.52(3) g/cm<sup>3</sup>, compared with the calculated density of 3.45 g/cm<sup>3</sup>.

A spindle stage was used to orient a crystal for refractive index measurements and determination of 2*V* by extinction curves. The optical orientation was determined by transferring the crystal from the spindle stage to a precession camera and determining the relative axial relations by X-ray diffraction. In transmitted light, ungarettiite is strongly pleochroic with *X* = orange red, *Y* ~ *Z* =

very dark red,  $X \wedge a = -2^\circ$  (in  $\beta$  acute),  $Y = b$ ,  $Z \wedge c = 17^\circ$  (in  $\beta$  obtuse); absorption is  $X < Y \leq Z$ . It is biaxial positive with indices of refraction  $\alpha = 1.717(2)$ ,  $\beta = 1.780(4)$ ,  $\gamma = 1.800(2)$  measured with gel-filtered Na light ( $\lambda = 589.9$  nm);  $2V_x = 51(2)$ ,  $2V_{\text{calc}} = 57^\circ$ , and the dispersion is  $r < v$ , but it is not easily visible because of the deep color.

### CHEMICAL COMPOSITION

Ungarettiite was analyzed by electron microprobe using a Cameca SX-50 operating in the wavelength-dispersive mode with an excitation voltage of 15kV, a specimen current of 20 nA, a peak-count time of 20 s and a background-count time of 10 s. The following standards and crystals were used for  $K\alpha$  X-ray lines: Si, Ca: tremolite, PET; Ti: hornblende, LiF; Fe: arfvedsonite, LiF; Mn: tephroite, LiF; Mg: tremolite, TAP; Na, Al: albite, TAP; K: orthoclase, PET; F: fluor-riebeckite, TAP; Zn: willemite, LiF. Data reduction was done using the  $\phi$  ( $\rho, Z$ ) procedure of Pouchou and Pichoir (1984, 1985). The averages of 10 analyses on single grains are given in Table 1. Refinement of the crystal structure of ungarettiite (see later sections) shows Mn to be in the divalent and trivalent states and allows the  $\text{Mn}^{3+}$ - $\text{Mn}^{2+}$  ratio to be derived.

Ion microprobe analysis of crystal A 5 was done on a Cameca IMS 4f with an  $\text{O}^-$  primary beam 20  $\mu\text{m}$  in diameter giving a beam current of  $\sim 10$  nA. The energy-filtering technique was used to eliminate any possible molecular interference and to reduce matrix effects. Secondary positive ion currents were measured at masses 7 (Li) and 30 (Si, used as the reference element) and corrected for isotopic abundances. The results were put on a quantitative basis using empirical calibration curves based on standard silicate samples. The resulting values are small (0.02 wt%  $\text{Li}_2\text{O}$ ) but significant in terms of the limit of detection of 10 ppm Li. Further details can be found in Ottolini et al. (1993).

### X-RAY CRYSTALLOGRAPHY

X-ray precession photographs with Zr-filtered  $\text{MoK}\alpha$  X-radiation are compatible with Laue symmetry  $2/m$ , and the condition for reflections to be present,  $h + k = 2n$ , showed that the lattice is  $C$  centered. Long-exposure photographs (80 h) showed no sign of any violating reflections. The possible space groups are  $C2/m$ ,  $C2$ , and  $Cm$ ; crystal-structure refinement confirmed the space group  $C2/m$ .

The powder diffraction pattern for a bulk sample was recorded from a small fragment on a Gandolfi camera with Fe-filtered  $\text{CuK}\alpha$  X-radiation. Cell dimensions were refined from the corrected  $d$  values using the program Celref (Appleman and Evans, 1973); the indexed powder pattern and refined cell dimensions are given in Table 2. The powder diffraction pattern is not of the best quality, partly because of the difficulty in obtaining pure material, as ungarettiite tends to be intergrown with namansilite, norrishite, and other manganoan amphibole. However,

TABLE 1. Chemical compositions\* and unit formulae\*\* of ungarettiite crystals

	U1	U2
$\text{SiO}_2$	50.66	51.28
$\text{Fe}_2\text{O}_3$	0.50	0.49
$\text{Mn}_2\text{O}_3$	24.35	24.59
MnO	12.42	12.26
MgO	1.46	1.53
CaO	0.18	0.19
$\text{Na}_2\text{O}$	9.13	9.11
$\text{K}_2\text{O}$	0.76	0.75
$\text{Li}_2\text{O}$	0.02	0.02
Total	99.48	100.22
Si	8.002	8.023
$\text{Fe}^{3+}$	0.059	0.058
$\text{Mn}^{3+}$	2.927	2.928
$\text{Mn}^{2+}$	1.662	1.625
Mg	0.344	0.357
Li	0.013	0.013
Total C	5.005	4.981
Ca	0.030	0.032
Na	1.970	1.968
Total B	2.000	2.000
Na	0.826	0.795
K	0.153	0.150
Total A	0.979	0.945

\* Al, Ti, Ni, Cr, F, and Cl not detected.

\*\* Calculated on the basis of 24 O atoms.

the refined cell dimensions agree with values measured by single-crystal diffractometry (Table 3). Peak intensities reported in Table 2 are those calculated from the refined ungarettiite structure; these values agree with the values estimated by eye from the darkening on the film.

### X-ray data collection

Crystals U1 and U2 from rock samples 820240 and 820607, respectively, were selected for crystallographic analysis and intensity data collection on the basis of their optical clarity and freedom from inclusions. The crystals were mounted on a Philips PW 1100 automated four-circle diffractometer and examined with graphite-monochromated  $\text{MoK}\alpha$  X-radiation. Unit-cell dimensions were calculated from least-squares refinement of the positions of 48 rows of reflections in the range  $-35 < \theta < 35^\circ$ ; values for the crystals used in the collection of the intensity data are given in Table 3.

Intensity data were collected again for the equivalent pairs  $hkl$  and  $h\bar{k}l$  in the Laue group  $2/m$  in the range  $2 < \theta < 30^\circ$ , using the step-scan profile technique of Lehman and Larsen (1974). Full details of the data collection procedure are given in Ungaretti (1980) and Ungaretti et al. (1981). The intensity data were corrected for absorption by the method of North et al. (1968), corrected for Lorentz and polarization effects, averaged and reduced to structure factors.

### Structure refinement

Fully ionized scattering factors were used for nontetrahedral cation, and both neutral and ionized scattering factors were used for tetrahedral cations and O atoms (Ungaretti et al., 1983).  $R$  indices are of the standard form and are given as percentages.

TABLE 2. Indexed powder pattern for ungarrettiite

<i>hkl</i>	<i>d</i> <sub>calc</sub> (Å)	<i>d</i> <sub>obs</sub> (Å)	<i>I</i> *
020	8.969	8.998	16
110	8.400	8.426	45
111	4.881	4.882	9
040	4.484	4.481	54
111	4.031	4.033	11
131	3.868	3.867	6
221	3.658	3.660	10
131	3.402	3.404	57
240	3.262	3.262	12
310	3.120	3.122	29
241	2.988	2.985	38
151	2.929	2.929	6
330	2.800	2.800	12
151	2.710	2.710	100
061	2.587	2.585	38
202	2.536	2.536	92
170	2.474	2.472	9
350	2.375	2.376	5
351	2.322	2.322	19
171	2.287	2.287	12
312	2.268	2.268	21
331	2.268	2.268	21
242	2.208	2.207	5
261	2.165	2.165	26
202	2.069	2.068	10
351	2.024	2.024	8
402	2.003	2.003	7
242	1.878	1.878	4
512	1.735	1.734	6
133	1.695	1.695	12
0,10,1	1.695	1.695	12
550	1.680	1.680	9
282	1.680	1.680	9
461	1.654	1.654	12
481	1.634	1.634	7
480	1.631	1.632	8
1,11,0	1.607	1.607	8
153	1.586	1.586	25
403	1.586	1.586	25
402	1.570	1.570	3
263	1.515	1.515	21
0,12,0	1.495	1.495	9
443	1.495	1.495	9
2,10,2	1.464	1.465	4
642	1.442	1.442	4
572	1.442	1.442	4
661	1.430	1.430	9
533	1.420	1.419	4
711	1.394	1.394	4
590	1.376	1.376	6
313	1.376	1.376	6
710	1.354	1.354	5
553	1.354	1.354	5
263	1.345	1.345	6
333	1.344	1.345	6
1,11,2	1.340	1.340	6
204	1.328	1.327	4
681	1.317	1.317	8
114	1.317	1.317	8
552	1.288	1.288	12
2,12,2	1.288	1.288	12
404	1.268	1.268	5

Note: cell:  $a = 9.89(2)$ ,  $b = 18.04(3)$ ,  $c = 5.29(2)$  Å,  $\beta = 104.6(2)^\circ$ .

\* Intensities were calculated from the refined crystal structure.

All refinements were done in the space group  $C2/m$  and converged to  $R$  indices of <2% for full-matrix refinement of all atomic positions, those site-occupancies considered as variable, and anisotropic displacement factors. Final atomic coordinates and equivalent isotropic displacement parameters are given in Table 4, selected interatomic dis-

TABLE 3. Unit-cell dimensions and structure refinement information for ungarrettiite

	U1	U2
<i>a</i> (Å)	9.889(4)	9.893(3)
<i>b</i> (Å)	18.033(7)	18.041(7)
<i>c</i> (Å)	5.296(2)	5.295(3)
$\beta$ ( $^\circ$ )	105.08(2)	105.10(3)
<i>V</i> (Å <sup>3</sup> )	911.9	912.6
$F_{\text{tot}}$	1384	1385
$F_{\text{obs}}$	938	932
$R_{\text{sym}}$ (%)	2.2	1.5
$R_{\text{obs}}$ (%)	1.8	1.4
$R_{\text{int}}$ (%)	4.2	2.8

tances and angles are given in Tables 5 and 6, refined site-scattering powers are listed in Table 7, and observed and calculated structure factors are given in Table 8.<sup>1</sup>

### SITE POPULATIONS

Site populations were derived from site-scattering refinement results, electron and ion microprobe analyses, and mean bond lengths. The  $\langle \text{T1-O} \rangle$  and  $\langle \text{T2-O} \rangle$  bond lengths (Table 5) indicate negligible <sup>141</sup>Al, and the electron microprobe results (Table 1) are in accord with that.

Examination of the unit formulae in Table 1 shows that the C-group cations are dominated by Mn:  $\langle \text{Mn} \rangle = 4.57$  apfu (atoms per formula unit), and this is in accord with the observed scattering at the M1, M2, and M3 sites. However, the difference in mean bond lengths at these sites indicates that Mn is present in two valence states, with  $\text{Mn}^{3+}$  ( $r = 0.645$  Å; Shannon, 1976) dominating at M1 and M3, and  $\text{Mn}^{2+}$  ( $r = 0.83$  Å) dominating at M2. Ungaretti et al. (1981) and Hawthorne (1978, 1983) have determined relations between mean bond lengths and the aggregate size of the constituent cations at the M1, M2, and M3 sites in  $C2/m$  amphiboles, using ideal mean bond lengths for specific cations or aggregate ionic radii. Their relations were determined for amphiboles with monovalent anions ( $\text{OH}^-$  and  $\text{F}^-$ ) at O3. This is not the case for ungarrettiite. In addition, the observed mean bond lengths lie far outside the range of values for other  $C2/m$  calcic, sodic-calcic, and alkali amphiboles. Thus it is not clear if these relations are as reliable as they are for OH- and F-containing amphiboles. However, we must use these relations to approach the site-population problem in ungarrettiite, while bearing in mind that the results must be concordant with the electron microprobe results on the same crystals. We have assumed that the small amount of Fe present is in the trivalent state because of the oxidized environment, and we include  $\text{Fe}^{3+}$  and  $\text{Mn}^{3+}$  as they have the same ionic radius (Shannon, 1976).

<sup>1</sup> A copy of Table 8 may be ordered as Document AM-95-572 from the Business Office, Mineralogical Society of America, 1130 Seventeenth Street NW, Suite 330, Washington, DC 20036, U.S.A. Please remit \$5.00 in advance for the microfiche.

**TABLE 4.** Atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ ) for ungarrettiite

		U1	U2
O1	x	0.1201	0.1200
	y	0.0832	0.0832
	z	0.2075	0.2085
	$B_{\text{eq}}$	0.69	0.63
O2	x	0.1170	0.1171
	y	0.1594	0.1592
	z	0.7087	0.7079
	$B_{\text{eq}}$	0.64	0.63
O3	x	0.0913	0.0914
	y	0	0
	z	0.7186	0.7186
	$B_{\text{eq}}$	0.64	0.72
O4	x	0.3488	0.3490
	y	0.2484	0.2485
	z	0.7904	0.7906
	$B_{\text{eq}}$	0.96	0.94
O5	x	0.3504	0.3504
	y	0.1263	0.1262
	z	0.0716	0.0712
	$B_{\text{eq}}$	0.86	0.85
O6	x	0.3486	0.3488
	y	0.1185	0.1186
	z	0.5752	0.5755
	$B_{\text{eq}}$	0.84	0.83
O7	x	0.3502	0.3502
	y	0	0
	z	0.2934	0.2941
	$B_{\text{eq}}$	0.93	0.93
T1	x	0.2885	0.2885
	y	0.0840	0.0841
	z	0.2863	0.2862
	$B_{\text{eq}}$	0.51	0.47
T2	x	0.2870	0.2870
	y	0.1680	0.1680
	z	0.7861	0.7863
	$B_{\text{eq}}$	0.50	0.50
M1	x	0	0
	y	0.0814	0.0815
	z	1/2	1/2
	$B_{\text{eq}}$	0.47	0.47
M2	x	0	0
	y	0.1834	0.1834
	z	0	0
	$B_{\text{eq}}$	0.61	0.58
M3	x	0	0
	y	0	0
	z	0	0
	$B_{\text{eq}}$	0.42	0.40
M4	x	0	0
	y	0.2730	0.2729
	z	1/2	1/2
	$B_{\text{eq}}$	1.58	1.47
Am*	x	0.0362	0.0364
	y	1/2	1/2
	z	0.0782	0.0794
	$B_{\text{eq}}$	2.77	2.98
A2*	x	0	0
	y	0.4873	0.4896
	z	0	0
	$B_{\text{eq}}$	2.68	3.04

\* Sites are only partly occupied. All standard deviations are  $\leq 1$  in the final digit.

### M1 site

The refined site-scattering values (Table 7) are compatible with complete occupancy of this site by Mn. When one assumes all  $\text{Mn}^{3+}$  and  $\text{O}^{2-}$  at O3, the curve of Hawthorne (1983) predicts a  $\langle \text{M1-O} \rangle$  distance on 2.032  $\text{\AA}$ . This is equal to the  $\langle \text{M1-O} \rangle$  distance in U1, indicating com-

**TABLE 5.** Selected interatomic distances ( $\text{\AA}$ ) and angles ( $^\circ$ ) in ungarrettiite\*

	U1	U2	U1	U2	
T1-O1	1.607	1.610	T2-O2	1.631	1.630
-O5	1.615	1.616	-O4	1.571	1.574
-O6	1.615	1.617	-O5	1.659	1.657
-O7	1.631	1.631	-O6	1.664	1.665
$\langle \text{T1-O} \rangle$	1.617	1.619	$\langle \text{T2-O} \rangle$	1.631	1.632
QE	1.002	1.003	QE	1.005	1.005
AV	9.78	9.97	AV	20.15	21.07
M1-O1	2.184	2.179	M3-O1 $\times 4$	2.047	2.049
-O2	1.968	1.964	-O3 $\times 2$	1.933	1.934
-O3	1.941	1.942	$\langle \text{M3-O} \rangle$	2.009	2.010
$\langle \text{M1-O} \rangle$	2.031	2.039	QE	1.009	1.010
QE	1.021	1.020	AV	26.60	27.34
AV	48.82	47.96	M4-O2	2.468	2.470
M2-O1	2.282	2.284	-O4	2.438	2.438
-O2	2.199	2.204	-O5	2.982	2.985
-O4	2.068	2.027	-O6	2.557	2.558
$\langle \text{M2-O} \rangle$	2.170	2.172	$\langle \text{M4-O} \rangle$	2.611	2.613
QE	1.029	1.030			
AV	94.15	94.75			
Am-O5	2.921	2.921	A2-O5	2.611	2.643
-O5	2.745	2.746	-O6	3.032	3.057
-O6	2.855	2.851	-O7	2.420	2.421
-O7	2.413	2.404			
-O7	3.224	3.214			
-O7	2.507	2.515			
			T1-O5-T2	137.1	137.1
O5-O6-O5	110.3	110.4	T1-O6-T2	137.2	137.1
O5-O7-O5	125.4	125.2	T1-O7-T1	136.7	136.8
M1-M1	2.935	2.940	M1-M2	3.225	3.224
M1-M3	3.028	3.028	M2-M3	3.307	3.309

\* Standard deviations are  $\leq 1$  in the last digit for both distances and angles.

plete occupancy by  $\text{Mn}^{3+}$  (Table 9). In U2,  $\langle \text{M1-O} \rangle$  is 2.039  $\text{\AA}$ , indicating a small amount of a larger cation. The site scattering indicates that this larger cation must be  $\text{Mn}^{2+}$  or  $\text{Fe}^{2+}$ ; as Fe is probably completely in the trivalent state, the difference must be due to  $\text{Mn}^{2+}$  (Table 9).

### M2 site

For both U1 and U2, the refined site-scattering values indicate a combination of Mg and Fe + Mn that can be calculated directly from the refined values (Table 7). The predicted  $\langle \text{M2-O} \rangle$  distances of 2.164  $\text{\AA}$  are somewhat less than the observed values of 2.170 and 2.172  $\text{\AA}$ , but they confirm that Mn at M2 must be in the divalent state.

### M3 site

The refined site-scattering values (Table 7) indicate a small amount of Mg at M3, and the observed  $\langle \text{M3-O} \rangle$  distances indicate that Mn at this site is in the trivalent state. However, it should be noted that the predicted values for  $\langle \text{M3-O} \rangle$  calculated using the curves of Hawthorne (1983) are both 2.045  $\text{\AA}$ , considerably larger than the observed distances of 2.010  $\text{\AA}$ . Presumably this difference reflects the very different structural relaxation in ungarrettiite resulting from the unusual ordering scheme and the divalent anion at the O3 site.

**TABLE 6.** Selected interatomic distances (Å) and internal angles (°) for the M octahedra in ungarrettiite\*

	U1	U2		U1	U2
O1 <sup>u</sup> -O2 <sup>d</sup> × 2	2.851	2.850	O1 <sup>u</sup> -M1-O2 <sup>d</sup> × 2	86.56	86.77
O1 <sup>u</sup> -O2 <sup>u</sup> × 2	2.997	2.986	O1 <sup>u</sup> -M1-O2 <sup>u</sup> × 2	92.23	92.09
O1 <sup>u</sup> -O3 <sup>d</sup> × 2	2.684	2.682	O1 <sup>u</sup> -M1-O3 <sup>d</sup> × 2	80.94	80.99
O1 <sup>u</sup> -O3 <sup>u</sup> × 2	3.172	3.166	O1 <sup>u</sup> -M1-O3 <sup>u</sup> × 2	100.36	100.24
O2-O2	2.753	2.750	O2-M1-O2	88.76	88.86
O2-O3 × 2	2.887	2.886	O2-M1-O3 × 2	95.23	95.23
O3-O3	2.540	2.540	O3-M1-O3	81.73	81.65
(O-O) M1	2.873	2.869	(O-M1-O)	90.09	90.10
O1-O1	2.785	2.790	O1-M2-O1	75.23	75.28
O1 <sup>u</sup> -O2 <sup>d</sup> × 2	2.851	2.850	O1 <sup>u</sup> -M2-O2 <sup>d</sup> × 2	79.01	78.82
O1 <sup>u</sup> -O2 <sup>u</sup> × 2	2.971	2.978	O1 <sup>u</sup> -M2-O2 <sup>u</sup> × 2	83.04	83.13
O1-O4 × 2	3.052	3.053	O1-M2-O4 × 2	89.97	89.96
O2 <sup>u</sup> -O4 <sup>d</sup> × 2	2.739	2.743	O2 <sup>u</sup> -M2-O4 <sup>d</sup> × 2	93.21	93.25
O2 <sup>u</sup> -O4 <sup>u</sup> × 2	3.074	3.078	O2 <sup>u</sup> -M2-O4 <sup>u</sup> × 2	100.53	100.53
O4-O4	3.187	3.190	O4-M2-O4	105.38	105.35
(O-O)M2	2.946	2.949	(O-M2-O)	89.34	89.33
O1 <sup>u</sup> -O1 <sup>d</sup> × 2	2.785	2.790	O1 <sup>u</sup> -M3-O1 <sup>d</sup> × 2	85.75	85.83
O1 <sup>u</sup> -O1 <sup>u</sup> × 2	3.000	3.001	O1 <sup>u</sup> -M3-O1 <sup>u</sup> × 2	94.25	94.17
O1 <sup>u</sup> -O3 <sup>d</sup> × 4	2.684	2.684	O1 <sup>u</sup> -M3-O3 <sup>d</sup> × 4	84.75	84.73
O1 <sup>u</sup> -O3 <sup>u</sup> × 4	2.941	2.946	O1 <sup>u</sup> -M3-O3 <sup>u</sup> × 4	95.25	95.37
(O-O)M3	2.839	2.842	(O-M3-O)	90.00	90.03

\* Standard deviations are  $\leq 1$  in the last digit; u = up and d = down with respect to the (100) projection.

### O3 site

As discussed in the next section, the O3 site is occupied by  $\text{O}^{2-}$ . However, certain aspects of the assigned site populations (Table 9) suggest that small amounts of  $\text{OH}^-$  may be present at O3. If the positive and negative charges are summed for both structures using the site populations of Table 9, there are small charge deficiencies of  $0.05^-$  and  $0.19^-$  for U1 and U2, respectively. These may be compensated by small amounts of  $\text{OH}^-$  replacing  $\text{O}^{2-}$  at O3. In this regard, it is notable that U2 contains  $0.10 \text{ Mn}^{2+}$  apfu at M1; if this  $\text{Mn}^{2+}$  is associated with  $\text{OH}^-$  at adjacent O3 sites, it would imply an  $\text{OH}^-$  content of  $0.20$  apfu at O3, almost exactly compensating the charge deficiency of  $0.19$  for crystal U2.

### BOND-VALENCE CONSIDERATIONS

The bond valence arrangement for ungarrettiite (Table 10) was calculated with the parameters of Brown (1981). The sum of the bond valence incident at the O3 position is  $1.81 \text{ vu}$ , reasonably close to the ideal sum of  $2.0 \text{ vu}$  for the occurrence of  $\text{O}^{2-}$  at O3 and larger than the value of

**TABLE 7.** Refined site-scattering values (epfu) from SREF and comparison with EMP results\* for ungarrettiite

	N**	U1		U2	
		SREF	EMP	SREF	EMP
M1	2	50.02	—	50.14	—
M2	2	47.14	—	47.20	—
M3	1	24.20	—	24.10	—
Total		121.36	120.74	121.44	120.10
M4	2	22.22	22.27	22.44	22.29
A	1	12.16	12.00	12.36	11.60

\* Standard deviations are in the range 2–12 in the last digit.

\*\* Number of sites in the structural formula.

**TABLE 9.** Assigned site populations (apfu) in ungarrettiite

	N*	U1	U2
M1	2	$2.00\text{Mn}^{3+}$	$1.90\text{Mn}^{3+} + 0.10\text{Mn}^{2+}$
M2	2	$1.78\text{Mn}^{2+} + 0.22\text{Mg}$	$1.78\text{Mn}^{2+} + 0.22\text{Mg}$
M3	1	$0.94\text{Mn}^{3+} + 0.06\text{Mg}$	$0.93\text{Mn}^{3+} + 0.07\text{Mg}$
M4	2	$1.97\text{Na} + 0.03\text{Ca}$	$1.97\text{Na} + 0.03\text{Ca}$
A	1	$0.83\text{Na} + 0.15\text{K}$	$0.80\text{Na} + 0.15\text{K}$

\* Number of sites in the structural formula.

$1.78 \text{ vu}$  at O4 ( $=\text{O}^{2-}$ ). Thus the local bond valence sums are in accord with the overall electroneutrality principle, both requiring the occurrence of a divalent anion at the O3 position. The O3 anion is coordinated by two M1 and one M3 cations, and inspection of Table 10 shows that the bonds to O3 are the strongest in each octahedron. Indeed, comparison of the octahedral bond lengths in ungarrettiite with amphiboles from the CSCC data base shows that ungarrettiite has the shortest bonds to O3 recorded in norrishite, and for the same reason.

### STRUCTURAL RELAXATION AROUND O3

First of all, let us examine the relative distortion of the three octahedra (M1–M3) in ungarrettiite. According to both quadratic elongation (QE) and angle variance (AV) parameters (Table 5), the relative distortion of the three octahedra is  $\text{M2} > \text{M1} > \text{M3}$ . Interestingly enough, this is the same sequence of relative octahedral distortion as was observed in winchite and “juddite” by Ghose et al. (1986); in these minerals, the ordering scheme (with  $\text{Mn}^{3+}$  ordered at M2) was rationalized as being due to the relative distortion of the three octahedra. In ungarrettiite, the occurrence of  $\text{O}^{2-}$  at O3 forces the ordering of  $\text{Mn}^{3+}$  at M1 and M3 in order to satisfy the anion bond-valence requirements at the O3 position.

Now  $\text{Mn}^{3+}$  has a high-spin  $d^4$  configuration and hence has a degenerate electronic state in a perfectly octahedral ligand field. The Jahn-Teller theorem (Jahn and Teller, 1937) indicates that a holosymmetric octahedral arrangement is unstable relative to a distortion that lifts the electronic degeneracy and will spontaneously distort away from holosymmetric symmetry (the Jahn-Teller effect). Obviously, this is not directly applicable to the amphibole structure, as no site in this structure can have holosymmetric octahedral symmetry. However,  $\text{Mn}^{3+}$  in a fairly regular octahedral ligand field will only have a small stabilization energy relative to its electronically degenerate state and is still unstable with regard to a distortion that increases the splitting of the nearly degenerate state. Typically,  $\text{Mn}^{3+}$  shows four short equatorial bonds and two long apical bonds when in an octahedral environment (Burns et al., 1994). This is exactly the case for the M1 octahedron; it has four short bonds ( $1.955 \text{ \AA}$ ) and two long bonds ( $2.184 \text{ \AA}$ ), and the long bonds are in a trans configuration. That is not the case for the M3 octahedron in ungarrettiite (Table 5), with four long bonds ( $2.047 \text{ \AA}$ ) to the equatorial O1 atoms and two short bonds ( $1.933$

TABLE 10. Bond valence\* table for ungarrettiite

	M1	M2	M3	M4	A	T1	T2	$\Sigma$
O1	0.314 <sup>x2</sup> ↓	0.263 <sup>x2</sup> ↓	0.448 <sup>x4</sup> ↓			1.041		2.066
O2	0.556 <sup>x2</sup> ↓	0.324 <sup>x2</sup> ↓		0.166 <sup>x2</sup> ↓			0.977	2.023
O3	0.600 <sup>x2</sup> ↓ →		0.614 <sup>x2</sup> ↓					1.814
O4		0.457 <sup>x2</sup> ↓		0.175 <sup>x2</sup> ↓			1.147	1.779
O5				0.073 <sup>x2</sup> ↓	0.09 <sup>x4</sup> ↓	1.019	0.908	2.090
O6				0.142 <sup>x2</sup> ↓	0.05 <sup>x4</sup> ↓	1.019	0.896	2.107
O7					0.15 <sup>x2</sup> ↓	0.977		2.104
$\Sigma$	2.940	2.088	3.020	1.112	0.86	4.056	3.928	

\* Calculated from the parameters of Brown (1981).

Å) to the apical O3 atoms. The symmetry arguments associated with the Jahn-Teller effect predict that octahedral coordination around  $\text{Mn}^{3+}$  will show a tetragonal distortion, but they do not predict whether the apical bonds are long or short relative to the equatorial bonds. As  $\text{Mn}^{3+}\text{O}_6$  octahedra usually have long apical bonds (Burns et al., 1994), it seems reasonable to conjecture that this is the energetically favorable arrangement. However, the symmetry arguments still hold, and there should be a significant stabilization for a (2+4)-distorted octahedral configuration around  $\text{Mn}^{3+}$ , as is the case for  $\text{Cu}^{2+}$  (Burns and Hawthorne, 1990, 1991). That is presumably the case at the M3 site in ungarrettiite. The  $2/m$  point symmetry requires the four M3-O1 bonds to be identical, and the two apical M3-O3 bonds are required to be short by the bond valence requirements of the  $\text{O}^{2-}$  anion at the O3 site. Hence for M3, the local anion bond-valence requirements interact with the Jahn-Teller mechanism to produce an axially compressed octahedral coordination rather than the more usual axially elongated arrangement.

The unusual pattern of bond length variations in ungarrettiite also results in some unusual octahedral shapes in the form of edge lengths and angles (Table 6). The O3-O3 edge that links the two M1 octahedra is the shortest yet recorded, and yet the corresponding O3-M1-O3 angle is much larger than the trends documented by Hawthorne (1983, Fig. 47) would suggest: 81.7 vs.  $\sim 76^\circ$ . A similar configuration occurs in norrishite, and norrishite has an even shorter  $\text{Mn}^{3+}$ - $\text{Mn}^{3+}$  approach than ungarrettiite: 2.72 vs. 2.93 Å. The M3 octahedron is extremely regular from edge length and bond angle criteria. The shared edges, O1<sup>u</sup>-O1<sup>d</sup> and O1<sup>u</sup>-O3<sup>d</sup>, are quite large relative to the size of the octahedron. The former is shared with the M2 octahedron and hence will be forced to be long by the large size of the M2 octahedron (which is occupied by  $\text{Mn}^{2+}$ ). The O1<sup>u</sup>-O3<sup>d</sup> is shared with M1 and hence is much the shorter of the two shared edges. However, it is the unshared edges of the M3 octahedron, O1<sup>u</sup>-O1<sup>u</sup> and O1<sup>u</sup>-O3<sup>u</sup>, that are most unusual. In all amphiboles considered by Hawthorne (1983, Fig. 47), all the unshared edges of the M3 octahedron are larger than 3.2 Å. In ungarrettiite, the corresponding edges lie close to 2.97 Å, in the center of the gap between the shared and unshared edge lengths (2.84–3.20 Å; Hawthorne, 1983, Fig. 47). It is apparent that the shared edges are constrained to be long because

some of them are shared with M2, which, in ungarrettiite, is the largest octahedron observed in amphiboles. In order for the mean edge length to be in accord with the very short mean bond length, the unshared edges have to be anomalously short. Thus there is a very unusual pattern of octahedral distortions in ungarrettiite, arising from the stringent bond valence requirements of the  $\text{O}^{2-}$  at the O3 site and the requirement of linking very disparately sized octahedra together to form the octahedral strip.

#### RELATIONSHIP TO OTHER AMPHIBOLES

Ungarrettiite may be derived from glaucophane by the chemical substitution  $\text{Na} + \text{R}^{3+} + 2\text{O} \rightarrow \text{O} + \text{R}^{2+} + 2\text{H} [\text{NaR}^{3+}\text{O}_2(\text{O}^{2+}\text{H}_2)_{-1}]$  or from eckermannite by the substitution  $\text{R}_2^{3+} + \text{O}_2 \rightarrow \text{R}_2^{2+} + \text{H}_2 [\text{R}_2^{3+}\text{O}_2(\text{R}_2^{3+}\text{H}_2)_{-1}]$ , if one ignores the homovalent substitution  $\text{Mn}^{2+} \rightarrow \text{Mg}$ ; either of these schemes is satisfactory from an algebraic point of view. However, they pay no attention to the structural importance of the cation-ordering pattern in ungarrettiite. From a crystal-chemical viewpoint, it is more informative to write the substitution involving eckermannite as  ${}^{\text{M1}}\text{R}_2^{3+} + {}^{\text{M2}}\text{R}^{2+} + {}^{\text{M3}}\text{R}^{3+} + \text{H}\text{O}_2 \rightarrow {}^{\text{M1}}\text{R}_2^{3+} + {}^{\text{M2}}\text{R}^{3+} + {}^{\text{M3}}\text{R}^{2+} + \text{H}\text{H}_2 ({}^{\text{M1}}\text{R}_2^{3+} + {}^{\text{M2}}\text{R}^{2+} + {}^{\text{M3}}\text{R}_2^{3+} + \text{H}\text{O}_2 [{}^{\text{M1}}\text{R}_2^{3+} - {}^{\text{M2}}(\text{R}^{3+}){}^{\text{M3}}\text{R}^{2+} + \text{H}\text{H}_2]_{-1})$ .

Notable features of ungarrettiite are that it is very close to end-member composition and that it is extremely Mn-rich, almost to the exclusion of any other medium-sized divalent or trivalent cation. The question thus arises as to whether the ungarrettiite structure is stable just for Mn-rich compositions. As we have noted above, the octahedral distortions, particularly at the M1 site, are compatible with the geometry expected for a Jahn-Teller distorted  ${}^{6\text{S}}\text{Mn}^{3+}$  environment. Could Al or  $\text{Fe}^{3+}$  substitute for  $\text{Mn}^{3+}$  and form other amphiboles free of monovalent anions? We know that Al can occur in significant quantities at the M3 site in calcic amphiboles (Oberti et al., 1995), but that is not the case at the M1 site. In addition, Al is significantly smaller than  $\text{Mn}^{3+}$ , which might produce difficulties in linking the octahedral strip to the tetrahedral double chain. However,  $\text{Fe}^{3+}$  is the same size as  $\text{Mn}^{3+}$ , and size problems are not an issue. The possible occurrence of an Fe analogue of ungarrettiite,  $\text{NaNa}_2(\text{Fe}_3^{3+}\text{Fe}_2^{3+})\text{Si}_8\text{O}_{22}\text{O}_2$ , hinges on whether or not  $\text{Fe}^{3+}$  can assume the same type of distorted coordination as  $\text{Mn}^{3+}$  (without the benefit of a Jahn-Teller effect). We cannot predict limits of coordi-

nation distortion with any great accuracy, and therefore this question must remain unanswered. Certainly it is worthwhile looking for the Fe equivalent of ungarrettiite in highly oxidizing Fe-rich environments, perhaps in some low-grade Fe formations.

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