

## Dellaventurite, $\text{NaNa}_2(\text{MgMn}^{3+}\text{Ti}^{4+}\text{Li})\text{Si}_8\text{O}_{22}\text{O}_2$ , a new anhydrous amphibole from the Kajlidongri Manganese Mine, Jhabua District, Madhya Pradesh, India

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### ABSTRACT

Dellaventurite is a new amphibole species from the Kajlidongri manganese mine, Jhabua District, Madhya Pradesh, India. It occurs with leakeite, kornite, albite, braunite, and bixbyite associated with cross-cutting epigenetic veins that have reacted with regionally metamorphosed rocks containing Mn-rich minerals (braunite, bixbyite, jacobsonite, spessartine) to produce Mn-rich amphiboles, Mn-rich pyroxenes, Mn-rich mica, piemontite, and manganophyllite. Dellaventurite occurs as anhedral grains, the color of which varies from pink to red, depending on Mn content. It is brittle,  $H = 5$ ,  $D_{\text{calc}} = 3.184 \text{ g/cm}^3$ , has a pale pink streak, vitreous luster, and does not fluoresce in ultraviolet light; it has perfect cleavage on  $\{110\}$  and conchoidal fracture. In transmitted plane-polarized light, dellaventurite is strongly pleochroic,  $X = \text{pale mauve-brown}$ ,  $Y \sim Z = \text{dark red-brown}$ ;  $Y \wedge a = 20^\circ$  (in  $\beta$  obtuse),  $Z = b$ , with absorption  $X < Y \sim Z$ . It is biaxial positive,  $\eta_\alpha = 1.688 \pm 0.003$ ,  $\eta_\beta = 1.692 \pm 0.005$ ,  $\eta_\gamma = 1.721 \pm 0.003$ ,  $2V_{\text{(obs)}} = 49 \pm 3^\circ$ ,  $2V_{\text{(calc)}} = 41^\circ$ . Dellaventurite is monoclinic, space group  $C2/m$ ,  $a = 9.808(1)$ ,  $b = 17.840(2)$ ,  $c = 5.2848(5) \text{ \AA}$ ,  $\gamma = 104.653(1)^\circ$ ,  $V = 894.6(2) \text{ \AA}^3$ ,  $Z = 2$ . The strongest ten X-ray diffraction lines in the powder pattern are  $[d(I, hkl)]$ : 2.697(10,151), 2.542(9,-202), 3.127(8,310), 3.378(7,131), 2.154(7,261), 1.434(7,-661), 4.450(6,021), 8.459(5,110), 2.727(5,-331), 2.328(5,-351). Analysis by a combination of electron microprobe, SIMS and crystal-structure refinement gives  $\text{SiO}_2 = 54.22$ ,  $\text{Al}_2\text{O}_3 = 0.81$ ,  $\text{TiO}_2 = 5.45$ ,  $\text{Fe}_2\text{O}_3 = 6.44$ ,  $\text{Mn}_2\text{O}_3 = 7.57$ ,  $\text{ZnO} = 0.12$ ,  $\text{NiO} = 0.16$ ,  $\text{MgO} = 8.26$ ,  $\text{Li}_2\text{O} = 1.53$ ,  $\text{CaO} = 1.85$ ,  $\text{Na}_2\text{O} = 8.12$ ,  $\text{K}_2\text{O} = 2.12$ ,  $\text{H}_2\text{O} = 0.80$ , Cr, V, F, Cl not detected, sum 97.41 wt%. The formula unit, calculated on the basis of 24(O,OH,F) is  $(\text{K}_{0.46}\text{Na}_{0.61})(\text{Na}_{1.71}\text{Ca}_{0.29})(\text{Mg}_{1.81}\text{Zn}_{0.01}\text{Ni}_{0.02}\text{Li}_{0.90}\text{Fe}_{0.71}^{3+}\text{Mn}_{0.85}^{3+}\text{Ti}_{0.60}^{4+}\text{Al}_{0.10})(\text{Si}_{7.96}\text{Al}_{0.04})\text{O}_{22}[(\text{OH})_{0.80}\text{O}_{1.20}]$ ; the ideal end-member composition  $\text{NaNa}_2(\text{MgMn}^{3+}\text{LiTi}^{4+})\text{Si}_8\text{O}_{22}\text{O}_2$ .

The crystal structure of dellaventurite was refined to an  $R$  index of 3.8% using  $\text{MoK}\alpha$  X-ray intensity data. The M1 site is occupied by  $\text{Ti}^{4+}$ ,  $\text{Mn}^{3+}$ , and Mg in approximately equal amounts, the M2 site is occupied primarily by Mg and  $\text{Fe}^{3+}$ , and M3 is occupied by Li with minor Mg and  $\text{Mn}^{2+}$ . Local bond-valence considerations suggest that  $\text{O}^{2-}$  at O3 is linked to  $\text{Ti}^{4+}\text{Mg}$  or  $\text{Mn}^{3+}\text{Mn}^{3+}$  at the adjacent M1 sites, and that OH at O3 is linked to MgMg at the adjacent M1 sites.

### INTRODUCTION

During mineralogical examination of amphibole assemblages from the Kajlidongri manganese mine, Jhabua District, Madhya Pradesh, India (Tait et al. unpublished), we encountered a sodic amphibole strongly enriched in Ti and Mn. Crystal-structure refinement indicated that the Ti was ordered at the M1 site, Li is the dominant cation at the M3 site, and that both Mn and Fe are in the trivalent state, suggesting that this amphibole should be enriched in  $\text{O}^{2-}$  at the O3 site. This suspicion was confirmed by analysis of H and Li by SIMS, indicating that this amphibole is a new species, joining the increasing number of amphiboles characterized by dominant  $\text{O}^{2-}$  at the O3 site. We name this amphibole dellaventurite for Giancarlo Della Ventura, Università degli Studi di Roma Tre, for his extensive work on the crystal

chemistry of synthetic amphiboles. The species and name have been approved by the International Mineralogical Association Commission on New Minerals and Mineral Names (IMA 2003-061). Holotype material is deposited at the Canadian Museum of Nature, Ottawa, Canada.

### OCCURRENCE

The Aravalli Supergroup of metasedimentary rocks of Precambrian age (sedimentation 2300 m.y., Crawford 1969) covers parts of Western India in the states of Rajasthan and Madhya Pradesh with extensions into the state of Gujarat. Post-tectonic granite and carbonate rocks of the area are younger than the phyllite and quartzite (Lahiri 1971). Manganese-oxide and manganese-silicate minerals occur as syngenetic bands concordant with the quartzose rocks. The manganese ores of Kajlidongri (Nayak 1966, 1969a; Ostwals and Nayak 1993) occur in syngenetic bands of manganese oxides and silicates enclosed in

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quartzose rocks, interbedded with phyllites, quartz schist, and gondites (metamorphosed, non-calcareous magniferous argillites and arenites) of the Aravalli Supergroup. Subsequent to their formation, post-tectonic epigenetic activity introduced veins cutting across the above-mentioned rocks, with later supergene alteration. The presence of feldspars in quartz veins indicates their pegmatitic origin (Nayak 1966).

Dellaventuraite was found in a rock consisting of 20% amphibole, 20% aegirine-augite, 50% quartz, 10% albite ( $Ab_{100}$ ), and trace apatite. The amphiboles are anhedral to subhedral with an average grain size of 0.4 mm and a maximum size of 1.5 mm. Dellaventuraite occurs together with leakeite and kornite, commonly overgrowing aegirine-augite (Fig. 1), and is the least abundant of these three amphiboles. The pyroxene has an average grain size of 0.5 mm and a maximum size of 0.9 mm. Quartz forms the matrix of the rock, being anhedral with an average grain size of 1.2 mm and a mosaic texture. The feldspar is subhedral to anhedral with an average grain size of 0.3 mm and a maximum grain size of 1.5 mm, and shows poorly developed albite twinning in some grains. The trace apatite is very fine-grained, acicular, and occurs within the quartz and feldspar.

### Physical and optical properties

Dellaventuraite is pink to red with a pale-pink streak and transparent with a vitreous luster; it shows no fluorescence under long-wave or short-wave ultraviolet light. Crystals are anhedral, but the amphibole in the rock ranges widely in composition, from dellaventuraite to leakeite to kornite, and dellaventuraite can only be distinguished by electron-microprobe analysis. Dellaventuraite has perfect {110} cleavage intersecting at  $\sim 56^\circ$ , is brittle, has conchoidal fracture, and has a Mohs' hardness of 5. The calculated density is 3.184 g/cm<sup>3</sup>.

A spindle stage was used to orient a crystal for refractive-index measurement and determination of  $2V$  by extinction curves. The optic 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, plane-polarized light, dellaventuraite is strongly pleochroic,  $X = \text{pale mauve-brown}$ ,  $Y \sim Z = \text{dark red-brown}$ ;  $Y \wedge a = 20^\circ$  (in  $\beta$  obtuse),  $Z = b$ , with absorption  $X < Y \sim Z$ . It is biaxial positive,  $\eta_\alpha = 1.688 \pm 0.003$ ,  $\eta_\beta = 1.692 \pm 0.005$ ,  $\eta_\gamma = 1.721 \pm 0.003$ , measured with gel-filtered Na light ( $\lambda = 589.9 \text{ nm}$ );  $2V_{(\text{obs})} = 49 \pm 3^\circ$ ,  $2V_{(\text{calc})} = 41^\circ$ .

### Chemical composition

Dellaventuraite was analyzed by electron-microprobe using a Cameca SX-50 at the University of Manitoba operating in the wavelength-dispersive mode with excitation voltage 15 kV, specimen current 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: diopside (Si and Ca-PET); titanite (Ti-LiF); arfvedsonite (Fe-LiF); spessartine (Mn-LiF); olivine albite (Na-TAP); Kyanite (Al-TAP); orthoclase (K-PET); fluororibeckite (F-TAP); gahnite (Zn-LiF); and pentlandite (Ni-LiF). Data reduction was done using the  $\varphi(\rho Z)$  procedure of Pouchou and Pichoir (1984, 1985). The average of 10 analyses on a single grain is given in Table 1 [analysis(1)]. Analysis (2) (Table 1) is the mean of 10 analyses on the crystal used to collect

X-ray intensity data for crystal-structure refinement.

Ion-microprobe analysis of the crystal used for X-ray data collection was done on a Cameca IMS 4f at Pavia, Italy. Due to the very small dimensions of the amphibole crystal, an  $^{16}\text{O}^-$  primary beam  $\leq 5$  micrometers in diameter, corresponding to a beam current of  $\sim 1.2\text{--}2.0$  nA, was used. The sample was left in the ion-microprobe sample chamber to degas for two days, together with H standards that were used in the calibration procedure. The energy-filtering technique was used to eliminate any possible molecular interference and to reduce matrix effects affecting light-element ionization. Secondary positive-ion currents were measured at masses 1 (H), 7 (Li), and 30 (Si) was 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. In particular, for H quantification, we used a sample of tremolite (Hawthorne and Grundy 1976) ( $\text{SiO}_2 = 56.57 \text{ wt\%}$ ;  $\text{H}_2\text{O} = 1.46 \text{ wt\%}$ ) and high-Fe amphibole standards, and corrections were done to take into account the variation of the ion-yield relative to Si for H [=Y(H/Si)] vs. (Fe + Mn) (at. content) in the sample (Ottolini and Hawthorne 2001; Ottolini et al. 2002). Lithium quantification was done according to the procedure of Ottolini et al. (1993). The accuracy of H and Li analysis is estimated to be in the order of 10% relative.

The unit formula was calculated on the basis of  $24(\text{O,OH,F})$ . When calculating the unit formulae of amphiboles characterized by *SREF* (Site-scattering REFinement) from microprobe data, we derive the  $\text{Fe}^{3+}/\text{Fe}^{2+}$  ratio from stereochemical criteria (Hawthorne 1983). When there is significant Mn present, it is usually assumed that Mn is in the divalent state (e.g., Hawthorne et al. 1993). However, the situation in dellaventuraite is somewhat different as the O3 site is occupied predominantly by  $\text{O}^{2-}$ . Hawthorne et al. (1995) described another amphibole, ungarrettiite, in which  $\text{O}^{2-}$  is dominant at the O3 site. In ungarrettiite, the M1A site is occupied by  $\text{Mn}^{3+}$ , and the unusual pattern of bond lengths (involving a very short bond to O3) is promoted by the Jahn-Teller distortion typical

**TABLE 1.** Average chemical composition (wt%) and unit formula (apfu) of dellaventuraite

	(1)*	(2)†	(1)	(2)	
SiO <sub>2</sub>	56.65	54.22	Si	8.04	7.96
Al <sub>2</sub> O <sub>3</sub>	0.75	0.81	Al	–	0.04
TiO <sub>2</sub>	5.40	5.45	ΣT	8.04	8.00
Fe <sub>2</sub> O <sub>3</sub>	5.42	6.44			
MgO	8.23	8.26	Al	0.13	0.10
Mn <sub>2</sub> O <sub>3</sub>	9.34	7.57	Ti	0.58	0.60
ZnO	–	0.12	Fe <sup>3+</sup>	0.58	0.71
NiO	–	0.16	Mg <sup>2+</sup>	1.74	1.81
CaO	2.16	1.85	Mn <sup>3+</sup>	1.01	0.85
Na <sub>2</sub> O	7.83	8.12	Zn	–	0.01
K <sub>2</sub> O	2.44	2.12	Ni	–	0.02
H <sub>2</sub> O	0.80‡	0.80	Li	0.87	0.90
Li <sub>2</sub> O	1.53‡	1.53	ΣC	4.91	5.00
Total	100.55	97.45			
			Ca	0.33	0.29
			Na	1.67	1.71
			ΣB	2.00	2.00
			Na	0.49	0.60
			K	0.44	0.40
			ΣA	0.93	1.00
			OH	0.76	0.80
			O <sup>2-</sup>	1.24	1.20

\* F, Cr, V not detected; mean of 10 determinations.

† Ni, Cr, V, F, Cl not detected.

‡ Values taken from crystal (2).



FIGURE 1. View in plane-polarized light of dellaventuraite (OPTK) as an overgrowth on aegirine-augite (AE-AG) in a matrix of rounded quartz (QZ) with minor rounded (high relief) apatite grains. The field of view is 2.5 cm wide.

for the  $d^4$  electron configuration of  $Mn^{3+}$ . As both  $Mn^{3+}$  and  $Fe^{3+}$  have the same cation radius (Shannon 1976) and the radii of  $Fe^{2+}$  (0.78 Å) and  $Mn^{2+}$  (0.83 Å) are fairly similar, it is not possible to distinguish between  $Fe^{3+}$  and  $Mn^{3+}$  in these circumstances. However, as shown later, the mean bond-lengths indicate that Fe and Mn are both in the trivalent state.

### X-ray crystallography

The powder diffraction pattern was recorded from a small fragment on a Gandolfi camera with Fe-filtered  $CuK\alpha$  X-radiation. Cell dimensions were refined using the program Celref (Appleman and Evans 1973); the indexed powder pattern and refined cell dimensions are given in Table 2.

### Crystal-structure refinement

A small optically homogeneous crystal was mounted on a Siemens P4 automated four-circle diffractometer; reflections were aligned using  $MoK\alpha$  radiation. The cell dimensions were

TABLE 2. Powder x-ray diffraction data for dellaventuraite

$l_{est}$	$d_{(meas.)}$ (Å)	$d_{(calc.)}$ (Å)	$hkl$	$l_{est}$	$d_{(meas.)}$ (Å)	$d_{(calc.)}$ (Å)	$hkl$
50	8.459	8.402	1 1 0	50	2.278	2.279	$\bar{3}$ 1 2
60	4.450	4.448	0 2 1	70	2.154	2.154	2 6 1
40	3.977	3.999	1 1 1	30	2.052	2.052	2 0 2
70	3.378	3.379	1 3 1	30	2.013	2.016	4 0 2
40	3.264	3.257	2 4 0	30	2.013	2.014	3 5 1
80	3.127	3.124	3 1 0	30	1.929	1.933	$\bar{3}$ 5 2
20	3.031	3.022	$\bar{3}$ 1 1	30	1.929	1.930	4 2 1
30	2.923	2.923	$\bar{1}$ 5 1	10	1.684	1.689	$\bar{1}$ 3 3
20	2.798	2.801	3 3 0	20	1.646	1.647	4 6 1
50	2.727	2.726	$\bar{3}$ 3 1	30	1.581	1.580	$\bar{1}$ 5 3
100	2.697	2.695	1 5 1	10	1.535	1.533	$\bar{6}$ 0 2
40	2.579	2.575	0 6 1	30	1.512	1.513	$\bar{2}$ 6 3
90	2.542	2.541	$\bar{2}$ 0 2	20	1.449	1.450	$\bar{6}$ 4 2
50	2.328	2.327	$\bar{3}$ 5 1	70	1.434	1.434	$\bar{6}$ 6 1
50	2.278	2.281	$\bar{1}$ 7 1				

Notes: Refined cell dimensions:  $a$  9.838(4),  $b$  17.868(14),  $c$  5.300(3) Å,  $\beta$  104.61(4)°,  $V$  901.5(6) Å<sup>3</sup>.

TABLE 3. Miscellaneous information for dellaventuraite

$a$ (Å)	9.808(1)	crystal size (Fm)	40 × 25 × 40
$b$	17.840(2)	radiation/filter	MoK $\alpha$ /graphite
$c$	5.2848(5)	total reflections	4565
$\beta$ (°)	104.653(1)	$F > 4\sigma F$	762
$V$ (Å <sup>3</sup> )	894.6(2)	$R$ (merge)%	3.8
Space Group	$C2/m$	$R$ (obs)%	4.0
$Z$	2	$wR$ (obs)%	4.0

$$R = \frac{\sum (F_o - F_c)^2}{\sum F_o^2}$$

$$wR = \left[ \frac{\sum w(F_o - F_c)^2}{\sum w F_o^2} \right]^{1/2}, w = 1$$

determined by least-squares refinement of the setting angles, and the values are given in Table 3. A total of 4565 intensities was collected according to the procedures of Hawthorne and Groat (1985). The intensities were reduced to structure factors with the usual geometrical and absorption corrections, resulting in 1349 reflections, 762 of which are considered as observed ( $|F_o| > 4\sigma F$ ). Subsequent to the collection of the X-ray intensity data, the crystal used was mounted in epoxy, ground, polished, carbon coated, and analyzed by electron-microprobe according to the procedure described above.

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 refined rapidly to an  $R_1$  index of 3.8% for anisotropic-displacement parameters for all atoms except those occupying the A cavity. A difference-Fourier map through the A site with the A cations omitted from the refinement showed two maxima in the mirror plane. These were designated as the Am and Am' sites, and their occupancies were refined with their isotropic-displacement parameters constrained to be equal (in order to reduce variable correlation during refinement). Full-matrix, least-squares refinement of all variables converged to an  $R$ -index of 3.8%. Final atom positions and displacement parameters are listed in Table 4, selected interatomic distances and angles are given in Table 5, refined site-scattering values are given in Table 6, and structure factors are listed in Table 7<sup>1</sup>.

### SITE POPULATIONS

The site populations were derived from consideration of the site-scattering refinement results, the unit formula calculated from the electron-microprobe analysis and the observed mean bond-lengths.

#### The T-sites

The  $\langle T1-O \rangle$  distance of 1.618 Å indicates that there is negligible Al at the T1 site. The observed scattering at T2 indicates that there is no Ti at this site (Ti does occur at T2 in Ti-rich richterite; Oberti et al. 1992). Thus the T sites are occupied entirely by Si.

#### The M1, M2, M3 sites

The total refined scattering at the M1, M2, and M3 sites is 77.8 electrons per formula unit (epfu); the total effective scattering of the C-group cations in the formula unit of Table 1, crystal 2, is 78.3 epfu. These values are sufficiently close to allow us to derive site populations from the data in Tables 1 and 6.

Examination of the M-M distances (Table 5) shows that the M1-M1 distance is much shorter than the other M-M distances, indicating that the M1 cations are displaced toward the O3-O3 edge relative to their position in most amphiboles (Hawthorne 1983). This behavior is typical of amphiboles containing much O<sup>2-</sup> (instead of OH) at the O3 site and

<sup>1</sup>For a copy of Table 7, deposit item AM-05-007, contact the Business Office of the Mineralogical Society of America (see inside front cover of recent issue) for price information. Deposit items may also be available on the American Mineralogist web site at <http://www.minsocam.org>.

**TABLE 4.** Atom parameters for dellaventuraite

	x	y	z	U <sub>11</sub>	U <sub>22</sub>	U <sub>33</sub>	U <sub>23</sub>	U <sub>13</sub>	U <sub>12</sub>	U <sub>eq</sub>
O1	0.1108(4)	0.0890(2)	0.2176(8)	0.010(2)	0.013(2)	0.009(2)	-0.0006(14)	0.0027(16)	-0.0025(15)	0.0107(13)
O2	0.1172(4)	0.1662(2)	0.7229(8)	0.0084(19)	0.016(2)	0.0109(19)	0.0001(15)	0.0045(15)	0.0005(15)	0.0115(12)
O3	0.1087(6)	0	0.6925(12)	0.011(3)	0.013(3)	0.014(3)	0	0.002(2)	0	0.0127(18)
O4	0.3596(5)	0.2500(2)	0.8029(8)	0.016(2)	0.0105(18)	0.014(2)	-0.0022(15)	0.0080(17)	-0.0029(15)	0.0125(13)
O5	0.3476(4)	0.1279(2)	0.0849(8)	0.0093(18)	0.0155(18)	0.0104(18)	0.0024(15)	0.0042(15)	0.0012(15)	0.0115(11)
O6	0.3461(4)	0.1190(2)	0.5862(8)	0.0126(19)	0.0144(18)	0.0079(18)	-0.0009(15)	0.0032(15)	0.0027(15)	0.0115(11)
O7	0.3364(6)	0	0.3005(12)	0.010(3)	0.009(3)	0.017(3)	0	0.002(2)	0	0.0124(17)
T1	0.27918(18)	0.08596(8)	0.2951(3)	0.0092(8)	0.0092(8)	0.0060(8)	-0.0001(5)	0.0027(6)	0.0006(6)	0.0080(5)
T2	0.28818(17)	0.17064(8)	0.8011(3)	0.0086(7)	0.0067(7)	0.0064(7)	-0.0001(5)	0.0025(6)	-0.0005(5)	0.0071(5)
M1	0	0.08163(10)	1/2	0.0087(10)	0.0167(10)	0.0057(9)	0	0.0041(7)	0	0.0100(6)
M2	0	0.17930(10)	0	0.0084(10)	0.0073(9)	0.0062(9)	0	0.0032(7)	0	0.0070(6)
M3	0	0	0	0.027(9)	0.014(7)	0.024(8)	0	-0.003(6)	0	0.023(5)
M4	0	0.27565(18)	1/2	0.0202(19)	0.0137(17)	0.0197(18)	0	0.0154(13)	0	0.0160(11)
Am	0.017(3)	1/2	0.039(5)							0.018(2)
Am'	0.051(2)	1/2	0.104(4)							0.018(2)

high-valence cations (e.g., Ti<sup>4+</sup>, Mn<sup>3+</sup>) at the M1 site, as is the case in ungarettiite [ideally NaNa<sub>2</sub>(Mn<sup>2+</sup>Mn<sup>3+</sup>)Si<sub>8</sub>O<sub>22</sub>O<sub>2</sub>, Hawthorne et al. 1995] and obertiite [ideally NaNa<sub>2</sub>(Mg<sub>3</sub>Fe<sup>3+</sup>Ti<sup>4+</sup>)Si<sub>8</sub>O<sub>22</sub>O<sub>2</sub>, Hawthorne et al. 2000]. It is also in accord with the low content of OH at O3 and the high Ti content of the amphibole (Table 1). Hence, all Ti<sup>4+</sup> was assigned to the M1 site. Tiepolo et al. (1999) refined the structures of Fe-free synthetic kaersutite crystals, and showed that where Ti<sup>4+</sup> is present in significant amounts at M1, then the equivalent isotropic-displacement value at M1 [ $\langle U_{eq}^{M1} \rangle = 0.012$ ] is larger than the corresponding values at M2 and M3 [ $\langle U_{eq}^{M2} \rangle = 0.008$ ,  $\langle U_{eq}^{M3} \rangle = 0.009$ ]. This is also the case for M1 and M2 in dellaventuraite (Table 4), but the M3 site is affected by the presence of dominant Li. Thus the displacement factors at the M1 and M2 sites in dellaventuraite are in accord with the occurrence of the majority of Ti<sup>4+</sup> at M1. This conclusion is also in accord with the arguments of Oberti et al. (2000).

The low OH content of dellaventuraite requires the transition metals to be predominantly in their higher valence states, and hence Fe was assigned as Fe<sup>3+</sup> and considered to occupy the M2 site, together with the small amount of VI Al. Li was assigned to the M3 site, following Hawthorne et al. (1993, 1994), and this assignment is in accord with the very low site-scattering value at M3 (Table 6). This assignment leaves Mg and Mn to be assigned over the M1, M2, and M3 sites. This assignment was done by writing the equation for the site scattering in terms of the available cations species, and solving for the amounts of Mg and Mn: e.g.,

$$M1: 0.60 \times 22(Ti) + 12x(Mg) + (1.40 - x) 25(Mn) = 37.8$$

The resulting values gave the following cation totals:  $\Sigma Mg = 1.81(1.93)$ ,  $\Sigma Mn = 0.85(0.76)$  where the values for the unit formula are given in parentheses. The site populations were adjusted to fit the site-scattering values and the unit formula (Table 1) equally well, and the values are given in Table 6.

We now have to decide on the valence state of Mn at the various sites. Hawthorne (1983) presented relations between mean bond-length and constituent-cation radius for the M1, M2, and M3 sites and the constituent-anion radius for the O3 site. As Mn<sup>2+</sup> ( $r = 0.83 \text{ \AA}$ ) and Mn<sup>3+</sup> ( $r = 0.645 \text{ \AA}$ ; Shannon 1976) are significantly different in size, the valence can be derived in a straightforward manner from the relations of Hawthorne (1983). For the M1 site, the calculated  $\langle M1-O \rangle$  distances are

**TABLE 5.** Selected interatomic distances (Å) and angles (°) for dellaventuraite

T1-O1	1.599(4)	M2-O1	×2	2.114(4)	
T1-O5	1.619(5)	M2-O2	×2	2.091(5)	
T1-O6	1.623(4)	M2-O4	×2	1.961(3)	
T1-O7	1.631(3)	<M2-O>		2.055(4)	
<T1-O>	1.618(4)				
T2-O2	1.624(4)	M3-O1	×4	2.095(4)	
T2-O4	1.579(3)	M3-O3	×2	2.157(7)	
T2-O5	1.651(4)	<M3-O>		2.116(5)	
T2-O6	1.670(5)				
<T2-O>	1.631(4)	M4-O2	×2	2.416(5)	
		M4-O4	×2	2.405(5)	
M1-O1	×2	2.060(4)	M4-O5	×2	2.889(4)
M1-O2	×2	2.074(4)	M4-O6	×2	2.524(5)
M1-O3	×2	1.935(4)	<M4-O>		2.559(5)
<M1-O>		2.023(4)			
Am-O5	×2	2.87(2)	Am'-O5	×2	2.77(2)
Am-O5	×2	2.80(2)	Am'-O5	×2	3.01(2)
Am-O6	×2	2.98(2)	Am'-O6	×2	2.71(1)
Am-O7		2.51(3)	Am'-O7		2.57(3)
Am-O7		2.57(3)	Am'-O7		2.65(3)
<Am-O>		2.80(2)	<Am'-O>		2.78(2)
M1-M1		2.913(4)	T1-O5-T2		136.4(3)
M1-M2		3.165(1)	T1-O6-T2		136.0(3)
M1-M3		3.017(1)	T1-O7-T1		140.2(4)
M1-M4		3.461(4)			
M2-M3		3.199(2)			
M2-M4		3.152(2)			

**TABLE 6.** Refined site-scattering values (epfu) and site populations (apfu) for dellaventuraite

Site	Refined site scattering	Calculated site-scattering	Assigned site-populations
M1	37.8(6)	38.2	0.60 Ti <sup>4+</sup> + 0.63 Mn <sup>3+</sup> + 0.77 Mg
M2	35.6(6)	36.5	0.71 Fe <sup>3+</sup> + 1.00 Mg + 0.19 Mn <sup>2+</sup> + 0.10 Al
M3	4.4(2)	4.3	0.90 Li + 0.03 Mn <sup>3+</sup> + 0.07 Mg
M1,2,3	77.8	-	-
M1,2,3 <sup>EMP</sup>	78.3	-	-
M4	24.6(5)		1.71 Na + 0.29 Ca
B <sup>EMP</sup>	24.6		-
Am	6.4(8)	6.6	0.60 Na
Am'	7.3(4)	7.6	0.40 K
Sum A	13.7	-	-
A <sup>EMP</sup>	14.2	-	-

2.090 (Mn<sup>2+</sup>) and 2.042 (Mn<sup>3+</sup>), and the observed value is 2.023 Å (Table 5). The difference of 0.019 Å between the calculated (Mn<sup>3+</sup>) and observed  $\langle M1-O \rangle$  values is larger than expected, and raises the possibility of Mn<sup>4+</sup> at M1. The corresponding calculated  $\langle M1-O \rangle$  value is 2.012 (Mn<sup>4+</sup>) Å, with a difference

of 0.011 Å. Note that ungarrettiite, with  $M1 = Mn^{3+}$ , has an observed  $\langle M1-O \rangle$  distance of 2.031 Å, exactly equal to the corresponding calculated  $\langle M1-O \rangle$  distance. Moreover, ungarrettiite shows a strongly Jahn-Teller-distorted M1 octahedron, whereas dellaventuraite shows no such distortion of the M1 octahedron, perhaps favoring  $Mn^{4+}$ . However, incorporating  $Mn^{4+}$  at M1 produces a major charge imbalance in the structure, and hence we assign  $Mn^{3+}$  to M1. There are only small amounts of Mn at M2 and M3, and radii criteria do not give a clear indication of valence state at these sites. The final assigned site-populations are given in Table 6.

### The A sites

The Am and the Am' sites both show significant electron density. From the detailed work of Hawthorne et al. (1996a) on A-site stereochemistry in monoclinic amphiboles, we may assign Na to the Am site and K to the Am' site; this assignment (Table 6) is in accord with the amounts of Na and K within the A cavity (Table 1).

### The end-member formula of dellaventuraite

We may approach the issue of the end-member formula by filling those sites in the structure at which a single species has over 50% occupancy; thus  $T1 = T2 = Si$ ,  $M3 = Li$ ,  $M4 = Na$ ,  $A = Na$ ,  $O3 = O$ , producing  $NaNa_2M1_2M2_2LiSi_8O_{22}O_2$ . For electroneutrality, the total charge required at the M1 and M2 sites is +12, and inspection of Table 6 indicates that the principal components of the M1 and M2 sites are  $Ti^{4+}$ ,  $Mn^{3+}$ , and Mg. There are three possible integer combinations of these three cations that will result in an aggregate charge of +12 at four sites; (1)  $Ti_4^{4+} + Mg_2$ ; (2)  $Mn_4^{3+}$ ; (3)  $Ti^{4+} + Mg + Mn_3^{3+}$ . Inspection of Tables 1 and 6 show that  $Ti^{4+}$ ,  $Mn^{3+}$ , and Mg are all significant species at M1 and M2, indicating that arrangement (3) is the appropriate choice. This result indicates in the following ideal end-member formula for dellaventuraite:  $NaNa_2(MgMn_3^{3+}Ti^{4+}Li)Si_8O_{22}O_2$ . As noted below, the presence of  $O^{2-}$  at O3 is compatible with occupancy of M1 by  $Ti^{4+}$  and  $Mn^{3+}$  for the end-member composition. This occupancy leaves 1.0  $Mn^{3+}$  pfu to be incorporated at the M2 site (as M1 is already full and M3 is occupied by Li). The M2 site may not be able to incorporate  $Mn^{3+}$  because  $Mn^{3+}$  usually needs a very distorted environment when in octahedral coordination. In turn, this suggests that 1.0  $Mn^{3+}$  apfu may be a limit on the amount of  $Mn^{3+}$  stereochemically possible in dellaventuraite. Note, however, that replacement of 1 apfu of  $Mn^{3+}$  by  $Fe^{3+}$  avoids this problem.

### Related species

Dellaventuraite is the third ideally anhydrous amphibole described recently, the others being ungarrettiite,  $NaNa_2(Mn_2^{3+}Mn_3^{3+})Si_8O_{22}O_2$  (Hawthorne et al. 1995), and obertiite,  $NaNa_2(Mg_3Fe^{3+}Ti^{4+})Si_8O_{22}O_2$  (Hawthorne et al. 2000). Dellaventuraite is the eighth amphibole containing essential Li as a C-group cation. The others are as follows: leakeite,  $NaNa_2(Mg_2Fe_3^{3+}Li)Si_5O_{22}(OH)_2$  (Hawthorne et al. 1992); ferroleakeite,  $NaNa_2(Fe_2^{3+}Fe_3^{3+}Li)Si_8O_{22}(OH)_2$  (Hawthorne et al. 1996b); potassic leakeite,  $KNa_2(Mg_2Fe_3^{3+}Li)Si_8O_{22}(OH)_2$  (Matsubara et al. 2002); kornite,  $KNa_2(Mg_2Mn_3^{3+}Li)Si_8O_{22}(OH)_2$  (Armbruster et al. 1993); ferriwhitakerite,  $Na(NaLi)(Mg_2Fe_3^{3+}Li)Si_8O_{22}(OH)_2$  (Oberti et al. 2004);

sodic-ferripedrizite,  $NaLi_2(Mg_2Fe_3^{3+}Li)Si_8O_2(OH)_2$  (Oberti et al. 2000); sodic-ferri-ferropedrizite,  $NaLi_2(Fe_2^{3+}Fe_3^{3+}Li)Si_8O_{22}(OH)_2$  (Oberti et al. 2003).

### Short-range order around the O3 site

Let us first consider the possible order around O3 in dellaventuraite of end-member composition. The composition of the C-group sites is  $(MgMn_2^{3+}Ti^{4+}Li)$ , and the ideal site-populations are as follows:  $M1 = Ti^{4+}Mn^{3+}$ ,  $M2 = MgMn^{3+}$ ,  $M3 = Li$ ,  $O3 = O^{2-}$ . The O3 is coordinated by  $M1_2M3$ , and as O3 is occupied only by  $O^{2-}$ , an ordered coordination is  $Ti^{4+}Mn^{3+}Li$ . Will this coordination satisfy the incident bond-valence requirements of  $O^{2-}$  at O3? We do not know the *local* bond lengths associated with this arrangement as the crystal of dellaventuraite examined here contains significant Mg that will perturb the bond lengths from their values for an end-member composition. Nevertheless, we know that the observed bond lengths in dellaventuraite are much shorter than in amphiboles with no  $O^{2-}$  at O3, and hence expect the actual bond lengths in end-member dellaventuraite to be significantly smaller than the values observed here. We may get an estimate of the ideal distances by comparison of the M1-O3 bond length in tremolite (2.083 Å, Papike et al. 1969) for  $M1 = Mg_2$  with that in dellaventuraite (1.935 Å) for  $M1 = Mg_{0.77}(Ti^{4+} \approx Mn^{3+})_{1.23}$ . Extrapolating to zero Mg at M1 gives a bond length of 1.842 Å for  $M1 = (Ti^{4+} \approx Mn^{3+})_2$ . Now we need to correct for local distances involving  $M1 = Ti^{4+}$  and  $M1 = Mn^{3+}$ . We may do this approximately by considering the sizes of the two cations:  ${}^VIr(Ti^{4+}) = 0.605$ ,  ${}^VIr(Mn^{3+}) = 0.645$  Å. Subtracting and adding half the difference between the radii of the two cations leads to the following distances: 1.822 and 1.862 Å, respectively, for  $Ti^{4+}$  and  $Mn^{3+}$ . Calculation of the bond valences associated with this local arrangement gives  $0.96(Ti^{4+}) + 0.75(Mn^{3+}) + 0.17(Li) = 1.88$  vu incident at  $O^{2-}$  at O3, in accord with the valence-matching principle. Thus we expect the following short-range arrangement around O3 in end-member dellaventuraite:  $O^{2-}, Ti^{4+}Mn^{3+}Li$ .

In dellaventuraite of the composition of Table 2, what do we expect in terms of short-range order around O3? Where  $O3 = O^{2-}$ , we expect the local arrangement  ${}^{M1}Ti^{4+}{}^{M1}Mn^{3+}{}^{M3}Li$ . If this is the case, then  ${}^{M1}Ti^{4+} = {}^{M1}Mn^{3+}$  and  $O^{2-} = {}^{M1}Ti^{4+} + {}^{M1}Mn^{3+}$ , inspection of Tables 1 and 6 show this to be the case;  ${}^{M1}Ti^{4+} \approx {}^{M1}Mn^{3+} = 0.61$  apfu and  $O^{2-} = 1.20 \approx {}^{M1}Ti^{4+} + {}^{M1}Mn^{3+} = 1.23$  apfu. When  $O3 = (OH)$ , then O3 is locally coordinated by  $M1M1 = MgMg$  and  $M3 = Li$ , whereby  ${}^{M1}Mg = 0.77 \approx {}^{O3}(OH) = 0.80$  apfu (Table 2).

### ${}^{M3}Li-O_3O^{2-}$ avoidance and the role of $Mn^{3+}$

In general, when O3 is occupied by  $O^{2-}$ , the locally associated M3 site cannot be occupied by Li as the local incident bond-valence is too low to satisfy  $O^{2-}$  at O3. This situation is relaxed when  $Mn^{3+}$  is present in the structure, as holosymmetric  ${}^VI Mn^{3+}$  has an energetically degenerate  $e_g$  electronic state and spontaneous distortion of the octahedron will occur. Typically, this mechanism leads to much shorter (and much longer) bonds than is normally the case for cations without this electronic degeneracy, and hence with  $Mn^{3+}$  at M1, one will have much shorter (and stronger) bonds to O3 than is the case when M1 is occupied by Al or  $Fe^{3+}$ . Hence Li is capable of being associated with  $O^{2-}$  at O3 when  $Mn^{3+}$  (as well as  $Ti^{4+}$ ) is also present at M1.

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