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Oxo-mangani-leakeite from the Hoskins mine, New South Wales, Australia: occurrence and mineral description

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ABSTRACT

Oxo-mangano-leakeite, a newly approved end-member of the amphibole supergroup (IMA-CNMNC 2015-035), has been found in a rock containing manganese silicate and oxide at the Hoskins Mine, a Mn deposit 3 km west of Grenfell, New South Wales. The end-member formula of oxo-mangani-leakeite is $^{A}Na^{B}Na_2$ $^{C}(Mn^{3+}_4Li\ )^{T}Si_8\ O_{22}{}^{W}O_2$, which would require SiO_2 53.15, Mn_2O_3 34.91, Li_2O 1.66, Na_2O 10.28, total 100.00 wt.%. The empirical formula derived for the sample of this work from electron and ion microprobe analysis using constraints resulting from single-crystal structure refinement is $^{A}(Na_{0.65}K_{0.36})_{\Sigma=1.01}{}^{B}(Na_{1.94}Ca_{0.06})_{\Sigma=2.00}{}^{C}(Mg_{1.60}Zn_{0.01}Mn^{3+}_{2.32}Fe^{3+}_{0.44}Al_{0.03}Ti^{4+}_{0.03}\ Li_{0.58})_{\Sigma=5.01}{}^{T}(Si_{7.98}Al_{0.02})_{\Sigma=8.00}O_{22}{}^{W}(O_{1.34}OH_{0.66})_{\Sigma=2.00}$. Oxo-mangano-leakeite is biaxial (–), with α = 1.681, β = 1.712, γ = 1.738, all ± 0.002, and 2V (meas.) = 81.0(4)°, 2V (calc.) = 83.5°. The unit-cell dimensions are $a = 9.875(5)$, $b = 17.873(9)$, $c = 5.295(2)$ Å, β = 104.74(3)°, $V = 903.8\ (7)$ Å^3; the space group is $C2/m$, with $Z = 2$. The strongest ten reflections in the powder X-ray pattern [d values (in Å), I, (hkl)] are: 8.423, 100, (110); 3.377, 46, (131); 4.461, 40, (040); 4.451, 40, (021); 3.134, 37, (310); 2.694, 37, (151); 2.282, 27, ($\bar{3}12$); 2.734, 25, ($\bar{3}31$); 2.575, 24, (061); 2.331, 24, [($\bar{3}51$) ($\bar{4}21$)]. The holotype material is deposited in the Canadian Museum of Nature, Ottawa, under the catalogue number CMNMC 86895.

Keywords: oxo-mangani-leakeite, ungarettiite, amphibole, oxo component, new mineral, electron-microprobe analysis, crystal-structure refinement, Hoskins mine, Australia.

Introduction

The mineralogical and petrological community is paying increased attention to the oxo-component ($^{W}O^{2-}$) in amphiboles. Its importance in amphibole crystal-chemistry is emphasized by the use of the oxo-component as the first discriminating parameter in the new scheme for amphibole classification (Hawthorne *et al.*, 2012), where the amphibole supergroup is divided into two groups: $^{W}O^{2-}$-dominant and $^{W}(OH, F, Cl)^{-}$-dominant amphiboles. In the first group, root-names are assigned solely to Ti-dominant compositions, whereas for all other compositions, the prefix oxo- is added to the $^{W}(OH, F, Cl)^{-}$-dominant root-name of relevance. This decision was based on the observation that among the two possible mechanisms available to incorporate the oxo component in amphiboles:

$$^{M(1)}Ti^{4+}_1\ {}^{O(3)}O^{2-}_2\ {}^{M(1)}(Mg,\ Fe)^{2+}_{-1}\ {}^{O(3)}OH)^{-}_{-2}\ \left(cation{:}O^{2-}ratio\,1{:}2\right) \tag{1}$$

$$^{M(1,3)}(Mg,\ Fe)^{3+}_1\ {}^{O(3)}O^{2-}_1\ {}^{M(1,3)}(Mg,\ Fe)^{2+}_{-1}\ {}^{O(3)}OH_{-1}\ \left(cation{:}O^{2-}ratio\,1{:}1\right) \tag{2}$$

the first must occur at crystallization and the second may also occur during post-crystallization events, i.e. during HT processes under oxidizing conditions (cf. Oberti *et al.,* 2007 for a review). Moreover, accurate characterization of the amount and the

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mechanism of O^{2-} incorporation in amphiboles provides useful constraints both for the recalculation of their unit formula and for the correct determination of their petrogenetic conditions.

The first oxo-end-member identified (in 1884; Dana, 1892) was kaersutite, ideally $^{A}Na^{B}Ca_2{}^{C}(Mg_3Ti^{4+}Al)^{T}(Si_6Al_2)O_{22}{}^{W}O_2$; compositions referring to root-names kaersutite (ferri-kaersutite, Gentili *et al.*, 2014) and hastingsite (oxo-magnesio-hastingsite, Zaitsev *et al.*, 2013) are typical of igneous rocks and of crystallization of calcium amphiboles under HT and low f_{H_2O} or highly oxidizing conditions. However, amphibole compositions with O^{2-} dominant among W anions have more recently also been found in sodium amphiboles. They usually occur as the $Fe^{2,3+}$- or $Mn^{2,3+}$-dominant species, and may refer either to Ti-dominant root-names, namely mangani- and ferro-ferri-obertiite, (ideally $^{A}Na^{B}Na_2{}^{C}(Mg_3Mn^{3+}Ti^{4+})^{T}Si_8O_{22}{}^{W}O_2$ and $^{A}Na^{B}Na_2{}^{C}(Fe^{2+}_3Fe^{3+}Ti^{4+})^{T}Si_8O^{W}_{22}O_2$,respectively; Hawthorne *et al.,* 2000; 2010; redefined after Hawthorne *et al.*, 2012), mangani-dellaventuraite, (ideally $^{A}Na^{B}Na_2{}^{C}(MgMn^{3+}_2Ti^{4+}Li)^{T}Si_8O_{22}{}^{W}O_2$; Tait *et al.,* 2005) or to the unique composition mangano-mangani-ungarettiite, ideally $^{A}Na^{B}Na_2{}^{C}(Mn^{2+}_2Mn^{3+}_3)^{T}Si_8O_{22}{}^{W}O_2$ (Hawthorne *et al.*, 1995*a*). All the names have been revised according to Hawthorne *et al.* (2012). Mangano-mangani-ungarettiite has two unique characteristics: (1) it has so far only been confirmed at the Hoskins and Woods mines, New South Wales, Australia (Ashley, 1986, 1989; Hawthorne *et al.*, 1995*a*; Kawachi *et al.,* 2002) however an occurrence in the Eifel region has been reported recently and the sample is presently under examination to confirm the finding; (2) all the crystals studied are close to end-member composition. The second characteristic is consistent with the observation made by Hawthorne *et al.* (1993) of a strongly relaxed *M*(2) site, to be related to the inverse pattern of order observed in mangano-mangani-ungarettiite with respect to all the other amphibole compositions known so far. Indeed, in this composition, all the R^{3+} cations (either involved in the eckermannitic charge arrangement or the oxo component occur at the *M*(1) and *M*(3) sites instead of at the *M*(2) site, as is commonly the case in $^{W}(OH, F, Cl)^{-}$-dominant compositions. This particular composition and ordering pattern gives rise to significant Jahn-Teller distortion typical of octahedrally coordinated Mn^{3+} and relaxation and distortion of the *M* (2) octahedron (the measured octahedral quadratic elongation is 1.030, whereas the angular variance is 94.75°). Hawthorne *et al.* (1995*a*) noted that the pattern of order in mangano-mangani-ungarettiite is only feasible close to its ideal stoichiometry of C cations, i.e. $Mn^{3+}_3Mn^{2+}_2$.

Many of the samples from the Hoskins mine studied by Ashley (1986, 1989) contain amphiboles with significant amounts of Li, another constituent of amphiboles which is proving to be more common than expected. In this paper, we report on the recognition and characterization of a new member of the oxo-amphiboles group, i.e. oxo-mangani-leakeite. In a second paper (Oberti *et al.*, 2017), we will report on the crystal-chemistry of Li in oxo amphiboles and on the apparent solvus between mangano-mangani-ungarettiite and oxo-mangani-leakeite (plus oxo-bearing leakeites).

Mineral data for oxo-mangani-leakeite

Occurrence

Similar to mangano-mangani-ungaretttite, oxo-mangani-leakeite occurs in manganese silicate and oxide rocks of the abandoned Hoskins mine, a Mn deposit 3 km west of Grenfell, New South Wales, Australia (Australian Map Grid Reference 8530-039487). The following description is reported in Hawthorne *et al.* (1995*a*), and is also applicable to the samples of this work. “A steeply dipping stratiform suite of schistose metamorphosed Mn-rich rocks up to 8 m thick occurs with metajasper, metabasalt and metasiltstone. 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. 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, caryopilite, barite and pyrite and (2) an oxidized assemblage containing Mn-rich alkali amphiboles (previously indicated as leakeite, Mn-bearing leakeite, manganoan katophorite and manganoan arfvedsonite (Hawthorne *et al.,* 1995*a*), clinopyroxenes ranging from namansilite (Kalinin *et al.*, 1992) to aegirine, manganoan pectolite–

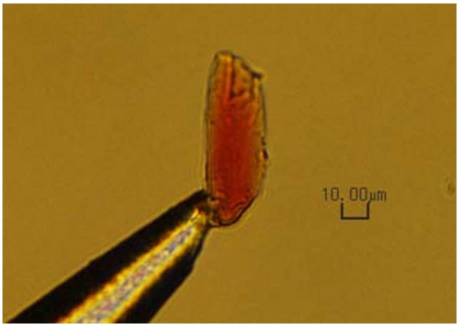

FIG. 1. Picture of an oxo-mangani-leakeite crystal from sample 820239 oriented looking down the optic normal.

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 assemblages are commonly foliated and laminated, and may be either quartz-free (amphibole, clinopyroxene, braunite, norrishite and manganoan pectolite–serandite, with minor alkali feldspars, carbonate and barite, or quartz-rich, with subordinate but variable amounts of amphibole and clinopyroxene, and minor serandite, sugilite, norrishite and carbonate. Both these assemblages, although in different specimens, may include either oxo-mangani-leakeite (quartz-free: 820236 and 820239) or mangano-mangani-ungarettiite (quartz-free: 820607; quartz rich: 820240 and 820994); Hawthorne *et al.*, 1995*a*).

Oxo-mangani-leakeite was first found in specimen 820239, and the crystal studied by X-ray diffraction (XRD) and EMP+SIMS analyses has the code 1087 in the amphibole database of the CNR-IGG Pavia. The holotype material has been deposited in the Canadian Museum of Nature, Ottawa, under the catalogue number CMNMC 86895.

Appearance, physical and optical properties

Oxo-mangani-leakeite has a prismatic habit, and is red-orange in colour; its lustre is vitreous, transparent, and it does not fluoresce in ultraviolet light. The tenacity is brittle and single crystals show perfect cleavage parallel to {110}. The density (calculated from the unit formula and cell dimensions) is 3.25 g/cm^3. A spindle stage was used to orientate a crystal for measurement of refractive indices and 2V by extinction curves (Bartelmehs *et al.*, 1992). The optical orientation was determined by transferring the crystal from the spindle stage to a single-crystal diffractometer and measuring the relative axial relations by XRD. In transmitted light, oxo-mangani-leakeite is pleochroic X = red brown, Y = Z orange red; X > Y = Z, X^c = 51.5° (β acute), Z // b, Y^a = 66.3° (β obtuse).

TABLE 1. Powder XRD data for oxo-mangani-leakeite 820239 n.1 (1087).

I_{rel}	d(calc)	$h\ k\ l$	I_{rel}	d(calc)	$h\ k\ l$	I_{rel}	d(calc)	$h\ k\ l$	I_{rel}	d(calc)	$h\ k\ l$
17	8.935	0 2 0	11	2.926	$\bar{1}$ 5 1	7	2.209	$\bar{2}$ 4 2	9	1.787	0 10 0
100	**8.423**	**1 1 0**	20	2.808	3 3 0	12	2.166	1 7 1			1 9 1
23	5.055	1 3 0	**25**	**2.734**	**$\bar{3}$ 3 1**	23	2.154	2 6 1	8	1.752	$\bar{5}$ 1 2
14	4.890	$\bar{1}$ 1 1	**37**	**2.694**	**1 5 1**	5	2.128	$\bar{1}$ 5 2	8	1.720	1 7 2
40	**4.461**	**0 4 0**	6	2.618	$\bar{1}$ 1 2	10	2.049	2 0 2			$\bar{5}$ 5 1
40	**4.451**	**0 2 1**	**24**	**2.575**	**0 6 1**	13	2.016	$\bar{4}$ 0 2	13	1.687	$\bar{5}$ 3 2
5	4.212	2 2 0	23	2.542	$\bar{2}$ 0 2			3 5 1			$\bar{1}$ 3 3
22	3.996	1 1 1	9	2.466	1 7 0	5	1.965	$\bar{3}$ 7 1	12	1.678	$\bar{2}$ 8 2
11	3.867	$\bar{1}$ 3 1	7	2.418	$\bar{1}$ 3 2	11	1.944	1 9 0			0 2 3
17	3.683	$\bar{2}$ 2 1	9	2.378	3 5 0	13	1.934	$\bar{3}$ 5 2	12	1.649	4 6 1
46	**3.377**	**1 3 1**	**24**	**2.331**	**$\bar{3}$ 5 1**			4 2 1	9	1.632	4 8 0
23	3.263	2 4 0			$\bar{4}$ 2 1	6	1.899	5 1 0	8	1.602	1 11 0
37	**3.134**	**3 1 0**	7	2.310	1 1 2	8	1.874	$\bar{4}$ 6 1	6	1.592	6 0 0
13	3.033	$\bar{3}$ 1 1	**27**	**2.282**	**$\bar{3}$ 1 2**	11	1.863	2 4 2	11	1.579	$\bar{1}$ 5 3
6	2.998	$\bar{2}$ 4 1			$\bar{1}$ 7 1			$\bar{5}$ 3 1	5	1.568	$\bar{4}$ 2 3
17	2.944	2 2 1	7	2.258	3 3 1	7	1.850	$\bar{1}$ 9 1			6 2 0

Note: The strongest ten lines are in bold.

TABLE 2. Unit-cell parameters (Å, °, Å^3) and crystallographic details for oxo-mangani-leakeite 820239 n.1 (1087).

a	9.8753(45)	θ range	2–30
b	17.8730(86)	R_{sym} %	3.10
c	5.2952(22)	R_{obs} %	2.01
β	104.737(25)	R_{all} %	6.47
V	903.86(71)	# all	1372
Space group	*C*2/*m*	# obs	769

It is biaxial (–) with indices of refraction $\alpha = 1.681$, $\beta = 1.712$, $\gamma = 1.738$, all ± 0.002, measured with gel-filtered Na light ($\lambda = 590$ nm); 2V (meas.) = 81.0(4)°, 2V (calc.) = 83.5°. The crystal used to measure the optical properties is reported in Fig. 1.

Crystallography

Holotype oxo-mangani-leakeite is monoclinic, space group *C*2/*m*, and has $a = 9.875(5)$, $b = 17.873(9)$, $c = 5.295(2)$ Å, $\beta = 104.74(3)°$, $V = 903.8(7)$ Å^3 ($Z = 2$). Unit-cell parameters were calculated by a least-squares procedure from the positions of reflections belonging to 60 selected rows of reciprocal space and occurring in the θ range –30 to +30°. Measurements were performed using a 4-circle diffractometer equipped with a point detector and Mo*K*α-radiation ($\lambda = 0.7107$ Å). Powder XRD data (Cu*K*α, $\lambda = 1.54178$ Å) were obtained using the *XPREP* utility of *SAINT* (Bruker, 2003), which generates a 2D powder diffractogram (Debye-Scherrer technique) starting from the F_{obs} collected on the single-crystal and taking into account solely the information concerning the unit-cell dimensions and the Laue symmetry. No Lorentz and polarization correction was applied. Data are given in Table 1.

X-ray diffraction analysis was carried out with a Philips PW1100 4-circle diffractometer ($\lambda =$ Mo*K*α) on a crystal 200 μm×50 μm×50 μm in size. Two monoclinic equivalents were collected in the 2θ range 4–60°; corrections for absorption and Lp were applied and the collected data were merged to obtain a set of unique reflections. Unit-cell parameters were calculated from least-squares refinement of the d* values obtained for 60 rows of the reciprocal lattice by measuring the centre of gravity of each reflection and of its antireflection in the 2θ range –70 to 70°.

Only the reflections with $I_o > 3\sigma_I$ were considered as observed during unweighted full-matrix least-squares refinement on *F* carried out with an extensively modified version of the program *ORFLS* (Busing and Levy, 1962) which is able to deal with complex solid-solutions (Cannillo *et al.*, 1983). Scattering curves for fully ionized chemical

TABLE 3. Refined site-scattering values (ss), atom coordinates and displacement parameters ($\beta_{ii} \times 10^4$) in oxo-mangani-leakeite 820239 n.1 (1087).

Atom	ss (epfu)	*x*/*a*	*y*/*b*	*z*/*c*	B_{eq} (Å^2)	β^{11}	β^{22}	β^{33}	β^{12}	β^{13}	β^{23}
O(1)		0.11263(25)	0.08887(12)	0.21149(48)	0.98(6)	22	10	83	–4	6	–3
O(2)		0.11944(22)	0.16649(13)	0.72061(45)	0.93(6)	18	10	74	1	2	6
O(3)		0.10787(35)	0	0.70332(69)	1.08(8)	28	7	114	–	8	–
O(4)		0.35918(26)	0.24965(12)	0.79938(50)	1.17(6)	51	5	122	–4	43	–1
O(5)		0.34828(24)	0.12752(11)	0.08029(47)	0.86(5)	22	8	68	1	8	7
O(6)		0.34510(24)	0.11867(11)	0.58238(45)	0.89(5)	21	9	57	2	–1	–5
O(7)		0.33694(36)	0	0.29630(69)	1.23(8)	40	4	161	–	12	–
T(1)		0.27993(9)	0.08588(4)	0.29089(18)	0.55(2)	15	4	53	–1	2	–1
T(2)		0.28841(8)	0.17033(4)	0.79675(17)	0.57(2)	17	4	49	0	3	3
M(1)	39.04(18)	0	0.08525(5)	$^1/_2$	0.70(2)	20	7	50	–	9	–
M(2)	45.94(16)	0	0.18075(4)	0	0.62(2)	16	5	62	–	5	–
M(3)	8.99(5)	0	0	0	0.50(7)	16	3	41	–	–8	–
M(4)	22.60(23)	0	0.27540(11)	$^1/_2$	1.30(6)	40	9	155	–	48	–
A	4.08(4)	0	$^1/_2$	0	2.6(2)	57	21	374	–	116	–
A(*m*)	9.73(11)	0.0437(5)	$^1/_2$	0.0991(9)	2.6(1)	80	19	261	–	70	–

epfu – electrons per formula unit.

TABLE 4. Selected interatomic distances (Å), interatomic angles in the double-chain of tetrahedra (°), tetrahedral and octahedral angle variance (TAV, OAV, $°^2$) and quadratic elongation (TQE, OQE; Robinson *et al.*, 1971) in oxo-mangani-leakeite 820239 n.1 (1087).

T(1)–O(1)	1.599(3)	*T*(2)–O(2)	1.615(2)
T(1)–O(5)	1.624(2)	*T*(2)–O(4)	1.579(2)
T(1)–O(6)	1.623(3)	*T*(2)–O(5)	1.654(3)
T(1)–O(7)	1.633(2)	*T*(2)–O(6)	1.667(2)
<*T*(1)–O>	1.620	<T(2)–O>	1.629
T(1) TQE	1.0032	*T*(2) TQE	1.0049
T(1) TAV	13.13	*T*(2) TAV	21.17
M(1)–O(1) × 2	2.107(3)	*M*(2)–O(1) × 2	2.134(3)
M(1)–O(2) × 2	2.040(2)	*M*(2)–O(2) × 2	2.129(2)
M(1)–O(3) × 2	2.008(2)	*M*(2)–O(4) × 2	1.964(3)
<*M*(1)–O>	2.052	<*M*(2)–O>	2.076
M(1) OQE	1.0091	*M*(2) OQE	1.0155
M(1) OAV	28.17	*M*(2) OAV	48.35
M(3)–O(1) × 4	2.093(2)	*M*(4)–O(2) × 2	2.417(3)
M(3)–O(3) × 2	2.110(4)	*M*(4)–O(4) × 2	2.402(3)
<*M*(3)–O>	2.099	*M*(4)–O(5) × 2	2.915(3)
M(3) OQE	1.0156	*M*(4)–O(6) × 2	2.541(3)
M(3) OAV	50.83	<*M*(4)–O>	2.569
A–O(5) × 4	2.819(2)	*A*(*m*)–O(5) × 2	2.972(6)
A–O(6) × 4	3.163(2)	*A*(*m*)–O(5) × 2	2.784(5)
A–O(7) × 2	2.518(4)	*A*(*m*)–O(6) × 2	2.758(6)
<*A*–O>	2.896	*A*(*m*)–O(7)	2.519(9)
		A(*m*)–O(7)	3.118(9)
T(1)–O(5)–*T*(2)	136.1(1)	*A*(*m*)–O(7)	2.651(10)
T(1)–O(6)–*T*(2)	136.6(1)	<*A*(*m*)–O>	2.813
T(1)–O(7)–*T*(1)	140.2(1)		
O(5)–O(6)–O(5)	173.0(1)	O(6)–O(7)–O(6)	109.6(1)

species were used at sites where chemical substitutions occur; neutral *vs*. ionized scattering curves were used at the *T* and anion sites. More details on the refinement procedure and on the advantages of using ionized scattering curves are given in Oberti *et al.* (1992) and Hawthorne *et al.* (1995*b*). The absence of residual electron density along the **b** direction at ~ 0.40 Å from the *M*(4) site (i.e. at the *M*(4') site) confirms the absence of significant amounts of the smaller B cations (e.g. Li^+, Fe^{2+}, Mg^{2+}) at this site.

Crystallographic details and agreement factors are reported in Table 2; refined coordinates, atom displacement parameters, and selected bond lengths and angles are reported in Tables 3 and 4. The observed structure factors have been deposited with the Principal Editor of *Mineralogical Magazine* as a cif and are available from www.minersoc.org/pages/e_journals/dep_mat.html.

EMP and SIMS analyses

All chemical analyses were performed on the crystal used for the structure refinement. Electron microprobe (EMP) analyses were done with a Cameca SX-50 electron microprobe (WDS mode, 15 kV, 20 nA, counting time 20 s, 5 µm beam diameter). Zn, Cr and Cl contents are below detection limits. Li was estimated based on structure-refinement (SREF) results and H_2O was estimated by assuming complete oxidation of both Fe and Mn, in analogy to what is observed in all other studied samples from the Hoskins Mine with the exception of the very peculiar amphibole ungarettiite, where Mn^{2+} is strongly ordered at the *M*(2) site. Any other assumption for the calculation of the unit formula results in violations to the correct amphibole stoichiometry, such as a low sum of T cations, and/or too high ^{C}Li contents. The oxide wt.% and the calculated unit-formula are reported in Table 5. End-member oxo-mangani-leakeite has the formula $^{A}Na^{B}Na_2$ $^{C}(Mn^{3+}_4Li\ )^{T}Si_8O_{22}{}^{W}O_2$, which would require SiO_2 53.15, Mn_2O_3 34.91, Li_2O 1.66, Na_2O 10.28, total 100.00 wt.%. Li_2O and H_2O were analysed by Secondary Ion Mass Spectrometry (SIMS) following the procedure described in Oberti *et al.* (2003).

The compatibility index ($1 - (K_P/K_C)$, Mandarino, 2007) calculated for holotype oxo-mangani-leakeite 1087 is 0.006 (superior).

The crystal-chemistry of oxo-mangani-leakeite

Site populations

The chemical analyses available for the refined crystals were combined with the refined site-scattering values to obtain site populations which adhere to the correct stoichiometry and maintain overall electroneutrality. They are reported in Table 6, together with a comparison between the observed mean bond-lengths (mbl) and those calculated from the site populations based on the <cation–O> distances optimized for [6]-coordination in amphiboles during extensive

TABLE 5. Chemical composition and unit formula (based on 24 anions) for oxo-mangani-leakeite 820239 n.1 (1087).

Oxide	wt.%	Range	Oxide	wt.%	Range		apfu		apfu
SiO_2	53.53(63)	52.88–53.96	Na_2O	8.96(7)	8.72–9.07	Si	7.98	Na	1.94
TiO_2	0.28(5)	0.20–0.32	K_2O	1.90(5)	1.79–2.03	Al	0.02	Ca	0.06
Al_2O_3	0.29(7)	0.21–0.35	H_2O**	0.64					
Fe_2O_3*	3.91		F	n.d.		Sum T	8.00	Sum B	2.00
$[FeO]_{tot}$	[3.52(11)]	3.14–3.86	Cl	n.d.					
Mn_2O_3*	20.46					Li	0.58	K	0.36
$[MnO]_{tot}$	[18.43(21)]	17.74–18.98	Total	98.68		Ti^{4+}	0.03	Na	0.65
MgO	7.20(8)	7.02–7.43							
ZnO	0.13(3)	0.05–0.19	Group site-scattering (epfu)			Al	0.03	Sum A	1.01
NiO	0.06(3)	0.00–0.11		obs. (SREF)	calc. (EMP)	Fe^{3+}	0.44		
Li_2O**	0.96		C	93.97	91.73	Mn^{3+}	2.32	O^{2-}	1.34
CaO	0.36(9)	0.22–0.46	B	22.60	22.54	Zn	0.01	OH^-	0.66
			A	13.81	13.99	Mg	1.60		
								Sum W	2.00
			Total	130.38	128.26	Sum C	5.01		

*FeO:Fe_2O_3 and MnO:Mn_2O_3 ratio calculated from single-crystal structure-refinement results.
**Measured by SIMS analyses.
apfu – atoms per formula unit.

crystal chemical work at IGG-CNR-Pv (Li: 2.118, Mg: 2.078, Al: 1.929, Ti: 1.960, Mn^{2+}: 2.173, Fe^{2+}: 2.125, Mn^{2+}, Fe^{3+}: 2.025, Zn: 2.120 Å). The agreement between the refined and calculated site-scattering values is excellent. In contrast, all the three *M* octahedra – and in particular *M*(2) – have longer measured mbl than those calculated, suggesting strong distortion of the octahedra, which is also evident from anomalous values of octahedral angular variance (OAV) and quadratic elongation (OQE; Robinson *et al.*, 1971).

Discussion and comparison with other species

Table 7 compares unit-cell parameters and optical properties for oxo-mangani-leakeite and other

TABLE 6. Site populations calculated for oxo-mangani-leakeite 820239 n.1 (1087).

		Site scattering (epfu)		Mean bond lengths (Å)	
	Site population (apfu)	measured	calculated*	measured	calculated*
T(1)	3.98 Si + 0.02 Al			1.620	1.620
T(2)	4 Si				
M(1)	0.84 Mg + 1.13 Mn^{3+} + 0.03 Ti^{4+}	39.04	38.99	2.052	2.046
M(2)	0.48 Mg + 0.03 Al + 0.44 Fe^{3+} + 1.04 Mn^{3+} + 0.01 Zn	45.94	43.89	2.076	2.047
M(3)	0.27 Mg + 0.15 Mn^{3+} + 0.58 Li	8.99	8.73	2.099	2.093
C cations		93.97	91.60		
B cations	1.94 Na + 0.06 Ca	22.60	22.54		
A cations	0.64 Na + 0.36 K	13.81	13.88		
W anions	1.31 O^{2-} + 0.69 OH				

*Calculated from the chemical analysis (but with a model which does not take into account peculiar polyhedral distortion).

TABLE 7. Comparison of unit-cell parameters and optical properties for published compositions of the amphibole supergroup which are crystal-chemically related to oxo-mangani-leakeite.

	potassic-mangani-leakeite	oxo-mangani-leakeite	mangani-dellaventuraite	mangano-mangani-ungarettiite
a (Å)	9.94(1)	9.875(5)	9.808(1)	9.8087(7)
b (Å)	17.80(2)	17.873(9)	17.840(2)	17.8448(13)
c (Å)	5.302(4)	5.295(2)	5.2848(5)	5.2905(4)
β (°)	105.5(2)	104.74(3)	104.653(1)	103.660(1)
V (Å^3)	904.0(15) 851.5(2)	903.8(7)	864.6(2)	899.8(1)
Space group	*C*2/*m**	*C*2/*m*	*C*2/*m*	*C*2/*m*
Optic sign	Biaxial (–)	Biaxial (–)	Biaxial (+)	Biaxial (+)
α	1.654 pink	1.681 red brown	1.688 pale mauve	1.717(2) orange red
β	1.675 dark red	1.712 orange red	1.692 dark red brown	1.780(4) dark red
γ	1.696 orange red	1.738 orange red	1.721 dark red brown	1.800(2) dark red
$2V_{meas}$ (°)	88–92	81.0	49	51.0
Ref.	Armbruster *et al.* (1993)	This work	Tait *et al.* (2005)	Hawthorne *et al.* (1995*a*)

*Space groups $P2_1/m$ or $P2/a$ had been proposed by Armbruster *et al.* (1993), but a recent re-evaluation has confirmed that the correct space group is *C*2/*m* (Armbruster, in press).

crystal-chemically related $^{B}Na^{+}$- and $^{C}Mn^{3+}$-dominant amphiboles of the amphibole supergroup reported in the literature.

Deprotonation of Mn^{2+}-rich amphiboles would generally require oxidation of $(Mn, Fe)^{2+}$ at the *M*(1) and *M*(3) sites. Because ^{C}Li in amphiboles is strongly ordered at the *M*(3) site, in the case of oxo-mangani-leakeite, oxidation must occur predominantly at the *M*(1) site. Similarly, direct crystallization of oxo-mangani-leakeite must imply the incorporation of either Ti^{4+} or $(Mn,Fe)^{3+}$ predominantly at the *M*(1) site. Therefore, in oxo-mangani-leakeite, small *M*(1) and *M*(2) octahedra filled with R^{3+} cations ($r = 0.645$ Å $(Mn,Fe)^{3+}$, 0.605 Å for Ti^{4+}; Shannon, 1976) must coexist with an *M*(3) octahedron occupied by the (large and monovalent) Li^{+} ion ($r = 0.76$ Å). Although the composition of holotype oxo-mangani-leakeite contains ~0.58 ^{C}Li apfu and 0.66 ^{W}OH apfu, both of which lower the required amounts of R^{3+} cations at the *M*(1,3) sites, we observe a peculiar pattern of distortion in the strip of *M*(1–3) octahedra (Table 4), where the measured OAV values are 28.4, 48.3 and 50.9. For comparison, these values are 32.1, 38.7 and 66.1 in ferri-leakeite (Hawthorne *et al.,* 1992).

It is interesting to compare oxo-mangani-leakeite with the other oxo amphibole occurring at the Hoskins mine, i.e. mangano-mangani-ungarettiite, $^{A}Na^{B}Na_{2}{}^{C}(Mn^{2+}_{2}Mn^{3+}_{3})^{T}Si_{8}O_{22}{}^{W}O_{2}$. This amphibole has so far been found only with a near-stoichiometric composition. Indeed, mangano-mangani-ungarettiite has a completely reverse ordering of C cations, where both the R^{3+} related to the basic ‘eckermannitic’ charge arrangement and those related to the oxo component are ordered at the *M*(1) and *M*(3) sites. As a consequence, a peculiar but different pattern of distortion is observed, where the *M*(2) octahedron, occupied solely by Mn^{2+} ($r = 0.83$ Å), is strongly elongated and distorted (OAV: 94.2), whereas the *M*(1) and *M*(3) octahedra (OAV: 48.8 and 26.6) have [4 + 2] coordinations compatible with Jahn-Teller distortion for Mn^{3+} (Hawthorne *et al.,* 1995*a*). In particular, the *M*(3)–O(3) distance is very short in mangano-mangani-ungarettiite, whereas it is equal to the other *M*(3)–O distances in oxo-mangani-leakeite.

This is a further indication that the *M*(3) cations have an ancillary (minority) role in balancing H loss at the O(3) site.

The different schemes of cation order in the two oxo-end-members present at the Hoskins mine is quite unusual and very interesting to investigate. The issue of solid solution between them is addressed in detail in Oberti *et al.* (2017).

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