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Olmiite, $CaMn[SiO_3(OH)](OH)$, the Mn-dominant analogue of poldervaartite, a new mineral species from Kalahari manganese fields (Republic of South Africa)

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ABSTRACT

Olmiite, ideally $CaMn[SiO_3(OH)](OH)$, is a newly identified mineral from the N'Chwaning II mine of the Kalahari manganese fields (Republic of South Africa), which occurs as a product of hydrothermal alteration associated with poldervaartite, celestine, sturmanite, bultfonteinite and hematite. The mineral occurs as wheat-sheaf aggregates consisting of pale to intense reddish pink minute crystals. Olmiite is transparent with vitreous lustre, and exhibits deep-red fluorescence under short-wave UV-light. The mineral is brittle, with irregular fracture. Streak is white and Mohs hardness is 5–5½. No cleavage was observed. The measured density (pycnometer method) is 3.05(3) g/cm^3. The calculated density is 3.102 g/cm^3 or 3.109 g/cm^3 using the unit-cell volume from single-crystal or powder data, respectively. Olmiite is biaxial positive, with refractive indices α = 1.663(1), β = 1.672(1), γ = 1.694(1) (589 nm), $2V_{meas}$ = 71.8(1)°, $2V_{calc}$ = 66(8)°. The optical orientation is $X = a$, $Y = c$, $Z = b$ and dispersion: $r > v$, distinct. Pleochroism is not observed. Chemical analysis by electron microprobe yielded the chemical formula $(Ca_{2-x}Mn_xFe_y)[SiO_3(OH)](OH)$, with $0.84 \leqslant x \leqslant 0.86$, and $y \leqslant 0.01$. Olmiite is orthorhombic, space group *Pbca*, with a = 9.249(3), b = 9.076(9), c = 10.342(9) Å, V = 868(1) Å^3 and Z = 8. The strongest five powder-diffraction lines [d in Å, (I/I_o), *hkl*] are: 4.14, (45), 021; 3.19, (100), 122; 2.807, (35), 311; 2.545 (35), 312; 2.361, (40), 223. Single-crystal structure refinement (R1 = 2.74% for 1012 observed reflections) showed that the atomic arrangement of olmiite is similar to that of poldervaartite, with all Mn ordered on the *M*2 site. Significant variations in bond distances and angles are related to the pronounced difference in the Mn content. Olmiite, therefore, is the Mn-dominant analogue of poldervaartite. The name poldervaartite should be reserved for samples having Ca dominant at the *M*2 site.

Keywords: olmiite, poldervaartite, new mineral, N'Chwaning II mine, Kalahari manganese fields, crystal structure, chemical composition, South Africa.

Introduction

Poldervaartite is an acid nesosilicate of Ca and Mn first found at the Wessel mine of the Kalahari manganese fields, Republic of South Africa (Dai *et al.*, 1993). At the N'Chwaning II mine of the same area 'poldervaartite' was first reported by Cairncross *et al.* (2002) who described the mineral as spectacular, cm-sized aggregates, with colour changing from milky white to pale pink or deep pink. No chemical investigations, however, were carried out on the sample from N'Chwaning II mine, merely reported as 'poldervaartite' by

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these authors. A poldervaartite-like mineral from the same occurrence was submitted to our attention by one of the authors (RP) who had noticed that this mineral looked macroscopically different from the poldervaartite from the type locality. Preliminary chemical data showed an exceptionally high content of Mn with respect to the value reported for the poldervaartite from the type-locality (Wessel mine, Kalahari manganese fields) by Dai *et al.* (1993). According to these authors, poldervaartite from the type locality exhibits a chemical composition yielding the chemical formula $(Ca_{2-x}Mn_x)[SiO_3(OH)](OH)$, with x in the range 0.28–0.52. There are two distinct structural sites (*M*1 and *M*2) hosting divalent cations in the structure of poldervaartite (Dai *et al.*, 1993), with Mn residing at *M*2 alone. Although Dai *et al.* assigned to poldervaartite the ideal formula $Ca(Ca_{0.5}Mn_{0.5})[SiO_3(OH)](OH)$, in the official list of minerals approved by the IMA Commission on New Minerals and Mineral Names (CNMMN), poldervaartite is properly reported with the ideal formula $Ca(Ca,Mn)[SiO_3(OH)](OH)$, thus suggesting a dominance of Ca with respect to Mn, that is what actually happens in the holotype. In this view, the name poldervaartite does not fit for material with a Mn-dominant *M*2 site, as the majority of material studied by Dai *et al.* (1993) has Mn <0.5 at this site.

We present in this paper the structural and chemical characterization of a specimen from the N'Chwaning II mine of the Kalahari manganese fields having Mn-dominant *M*2 site and therefore deserving a specific mineral name. This new mineral species, ideal formula $CaMn[SiO_3(OH)](OH)$, was named olmiite after Filippo Olmi (1959-2005), in recognition of his mineralogical studies at the CNR-Istituto di Geoscienze e Georisorse in Florence.

Holotype material has been deposited at Museo di Storia Naturale, Università di Firenze, Italy, under catalogue number 2987/I. The crystal used for the structural study is preserved at the Dipartimento di Scienze della Terra, Università di Firenze. The new mineral and mineral name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (which succeeded the CNMMN above, in 2006), (2006-026).

Occurrence and mineral data

At the N'Chwaning II mine of the Kalahari manganese fields (Republic of South Africa) olmiite occurs as cm-sized wheat-sheaf, sub-spherical aggregates consisting of minute crystals associated with celestine, bultfonteinite, poldervaartite, sturmanite and hematite. The observed mineral assemblage, as well as a variety of rather rare Mn minerals in the Kalahari manganese fields, was formed by hydrothermal alteration (250–400ºC) of the primary sedimentary and low-grade metamorphic ores. This assemblage crystallized along fault planes and lenticular bodies within the Mn ore beds or filling veins and vugs (Cairncross *et al.*, 1997). The sub-spherical aggregates of olmiite show poorly crystallized cores characterized by small cavities (up to 15 μm in size) and well crystallized rims which appear to be formed by later solutions partially reabsorbing the original crystals (Fig. 1). Portions showing different texture, however, did not exhibit significant variation of the Ca:Mn ratio (EDS microchemical analyses).

Olmiite is transparent, pale to intense reddish pink in colour and appears colourless in thin section. Under short-wave UV-light, it exhibits deep-red fluorescence. It is biaxial positive, with refractive indices $\alpha = 1.663(1)$, $\beta = 1.672(1)$, $\gamma = 1.694(1)$ (589 nm), $2V_{meas} = 71.8(1)^\circ$, $2V_{calc} = 66(8)^\circ$. The optical orientation is $X = a$, $Y = c$, $Z = b$ and dispersion: $r > v$, distinct. Pleochroism is not observed. Streak is white and lustre is vitreous. Mohs hardness is in the range 5–5½. The mineral is brittle with irregular fracture. No cleavage was observed. The measured density (pycnometer method) is 3.05(3) g/cm^3. The calculated density is 3.102 g/cm^3 or 3.109 g/cm^3 using the unit-cell volume obtained from single-crystal or powder data, respectively. The Gladstone-Dale relationship (Mandarino, 1981) provides a compatibility index of −0.005 or −0.002, superior (with unit-cell volume from single-crystal or powder diffraction data, respectively).

Chemical composition

Three crystal fragments of olmiite (labelled OL1, OL2, OL-TL) were embedded in resin and polished for electron-microprobe analysis (EMPA) carried out with a JEOL JXA 8600 equipped with four wavelength-dispersive spectrometers. Elements were determined at 15 kV accelerating voltage and 10 nA beam current, with a beam size of 2 μm and the following counting times: 10 s for Na, 15 s for other major elements. Ti, Al, Cr, Mg, Na and K were measured

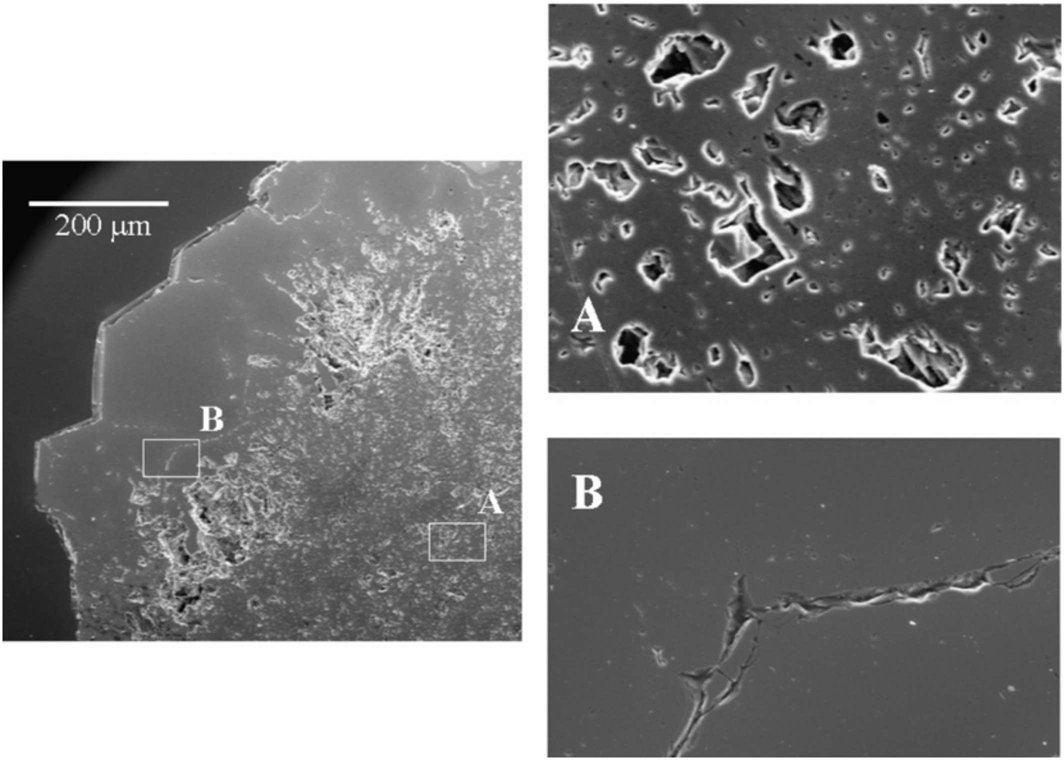

FIG. 1. Back-scattered electron SEM images of olmiite. Poorly crystallized cores characterized by small cavities (A) and well crystallized rim (B) which appears to be formed by later solutions partially reabsorbing the original crystals.

but resulting values were below the detection limit. Matrix corrections were applied using the coefficients of Bence and Albee (1968) as modified by Albee and Ray (1970). For each crystal, four spot analyses were carried out; the average of these values are reported in Table 1 along with the ranges of variation in parentheses. H_2O contents were inferred on the basis of stoichiometry (*i.e.* two hydroxyl groups per formula unit). Assuming all Mn and Fe as Mn^{2+} and Fe^{2+} respectively, the three average analyses yielded the chemical formula $(Ca_{2-x-y}Mn_xFe_y)[SiO_3(OH)](OH)$ with $0.84 \leqslant x \leqslant 0.86$, and $y \leqslant 0.01$. Individual spot analyses indicated modest variations of the Mn content ($0.82 \leqslant x \leqslant 0.92$). The empirical formula (based on 5 oxygen atoms) of the crystal used for the structure determination is $Ca(Mn_{0.85}Ca_{0.14}Fe_{0.01})[SiO_3(OH)](OH)$. The ideal formula for the end-member $CaMn[SiO_3(OH)](OH)$ requires CaO = 27.34, MnO = 34.58, SiO_2 = 29.29, H_2O = 8.79, Total 100.00 wt.%.

X-ray crystallography

Due to its greater degree of compositional homogeneity, the sample OL-TL was selected for the structural study and removed from the resin. A small fragment of it (125 μm × 150 μm × 190 μm) was mounted on a Enraf-Nonius CAD4 single-crystal diffractometer. Cell dimensions were refined from the angular settings of 25 high-θ reflections yielding an orthorhombic unit cell with a = 9.249(3), b = 9.076(9), c = 10.342(9) Å, V = 868(1) $Å^3$. Systematic absences were consistent with the space group *Pbca*. A redundant set of 2804 intensity data was collected ($\overline{13} \leqslant h \leqslant 13$, $0 \leqslant k \leqslant 12$, $0 \leqslant l \leqslant 14$) up to θ = 30º (Mo-$K\alpha$). The intensities were corrected for Lorentz-polarization effects and for absorption following the semi-empirical method of North *et al.* (1968); the values of the equivalent pairs were averaged (R_{int} = 3.66%). Structure refinement was done using the program SHELXL-97 (Sheldrick, 1997) with the non-hydrogen atomic coordinates of poldervaartite (Dai *et al.*, 1993) as starting model. Neutral

TABLE 1. Chemical composition of olmiite from N'Chwaning II mine (average of four spot analyses per crystal).

	OL1	OL2	OL-TL*
SiO_2	29.21 (28.92–29.45)	29.25 (29.06–29.34)	29.47 (29.29–29.52)
FeO	0.31 (0.16–0.42)	0.02 (0.00–0.05)	0.18 (0.10–0.21)
MnO	29.37 (29.01–29.76)	29.93 (29.15–31.88)	29.28 (29.11–29.53)
CaO	31.14 (31.03–31.24)	31.67 (30.08–32.34)	31.33 (30.96–31.42)
Total	90.03 (89.66–90.41)	90.87 (90.33–91.04)	90.26 (90.09–90.61)
$H_2O^{\#}$	8.87	8.87	8.89
Si	1.00	0.99	1.00
Fe^{2+}	0.01	–	0.01
Mn^{2+}	0.85	0.86	0.84
Ca	1.14	1.15	1.14
Σcat.	3.00	3.01	2.99

\# H_2O calculated from stoichiometry
* crystal used for the structural study and chosen as holotype (OL-TL)
Cations calculated on the basis of five oxygen atoms.

scattering curves from the *International Tables for X-ray Crystallography*, volume IV (Ibers and Hamilton, 1974) were used: Ca *vs*. Mn (*M*1 and *M*2 sites), Si (*T* site) and O (anion sites). All the refined occupancies were constrained to unity sum. Site scattering values obtained for the site-occupancy refinement [20.0(2), 24.2(2) and 14.0(0) for *M*1, *M*2 and *T* sites, respectively] are in excellent agreement with the measured chemical composition. Both H1 and H2 atoms were located on the difference-Fourier map. Convergence was achieved quickly to R1 = 2.74% for 1012 observed reflections [$F_o > 4\sigma(F_o)$] and 4.22% for all 1260 unique reflections. Inspection of the difference Fourier map revealed that maximum positive and negative peaks were 0.50 and −0.70 $e^-/Å^3$, respectively. Fractional atomic coordinates and anisotropic-displacement parameters are given in Table 2. The list of the F_o/F_c data is available upon request. Table 3 reports the X-ray powder pattern of olmiite compared with that calculated using the structural parameters. Unit-cell parameters refined from powder data are: *a* = 9.244(6) Å, *b* = 9.051(4) Å, *c* = 10.353(6) Å, *V* = 866(1) Å^3.

Results and description of the structure

The structure of olmiite consists of isolated $SiO_3(OH)$ tetrahedra continuously connected along the [100] direction to two $M2O_7$ polyhedra by sharing edges. The *M*2-Si chains are linked together by corner sharing to form waved sheets parallel to (010) (Fig. 2). Alternating sheets are linked together by *M*1 octahedra and hydrogen bonds, resulting in a strongly bonded polyhedral network. On the whole, the atomic arrangement of

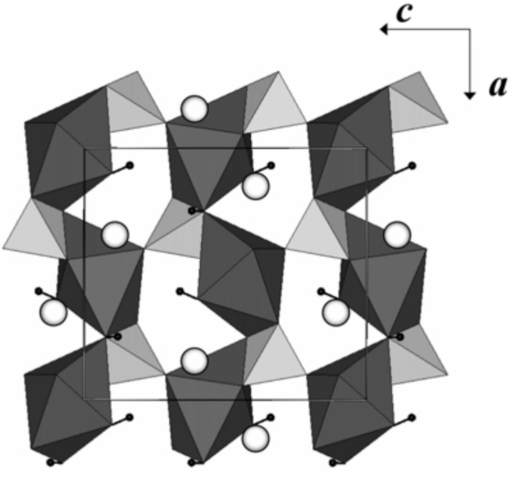

FIG. 2. Olmiite structure: layer of $M2O_7$ polyhedra (dark grey) and Si tetrahedra (pale grey) approximately located at *y* = ¼ and *M*1 cations (white circles) approximately located at *y* = ½. Black dots represent hydrogen atoms (solid lines represent O–H bonds). To simplify the picture only half of the unit content along the *b* axis has been drawn.

TABLE 2. Fractional atomic coordinates and anisotropic displacement parameters for olmiite (OL-TL)

	x	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{eq}
*M*1	0.15329(5)	0.49245(6)	0.39231(5)	0.0100(2)	0.0099(2)	0.0077(2)	−0.0003(2)	0.0005(2)	0.0002(2)	0.0092(1)
*M*2	0.50894(5)	0.33741(4)	0.43030(4)	0.0118(2)	0.0104(2)	0.0086(2)	−0.0023(2)	−0.0006(2)	−0.0001(2)	0.0103(1)
T	0.32771(8)	0.21852(7)	0.65915(7)	0.0096(3)	0.0076(3)	0.0065(3)	−0.0001(2)	−0.0001(2)	−0.0002(2)	0.0079(2)
O1	0.2509(2)	0.3568(2)	0.5767(2)	0.025(1)	0.0076(8)	0.0123(8)	0.0027(8)	−0.0067(8)	−0.0003(7)	0.0151(4)
O2	0.9441(2)	0.3544(2)	0.4391(2)	0.0101(8)	0.0128(9)	0.0094(8)	−0.0014(7)	−0.0018(7)	−0.0017(7)	0.0107(4)
O3	0.1009(2)	0.7144(2)	0.2881(2)	0.0164(9)	0.0117(9)	0.0086(8)	0.0022(7)	0.0037(7)	0.0020(7)	0.0122(4)
O4	0.4005(2)	0.5509(2)	0.4012(2)	0.0141(9)	0.0152(9)	0.0127(9)	−0.0016(8)	0.0006(8)	0.0012(8)	0.0140(4)
O5	0.1956(2)	0.3953(2)	0.1874(2)	0.0122(8)	0.0129(8)	0.0099(8)	0.0023(7)	0.0009(7)	−0.0007(7)	0.0117(4)
H1	0.249(5)	0.441(5)	0.619(4)	0.04(1)						
H2	0.430(5)	0.595(4)	0.339(4)	0.04(1)						

olmiite (OL-TL) is quite similar to that of poldervaartite from the type locality (PD-TL) as determined by Dai *et al.* (1993). Nonetheless, significant variations in bond distances and angles (Table 4) can be observed, which are related to the pronounced difference of the Mn content in the *M*2 site [$(Ca_{0.67}Mn_{0.33})$ and $(Mn_{0.85}Ca_{0.14}Fe_{0.01})$ in PD-TL and OL-TL, respectively]. The atomic arrangement is also identical to that of the structure of the synthetic $Ca_2[SiO_3(OH)](OH)$ [$a = 9.487(4)$, $b = 9.179(4)$, $c = 10.666(7)$ Å, $V = 928.8(8)$ Å^3], first determined by Yano *et al.* (1993) in the non-centrosymmetric $P2_12_12_1$ space group and then revised by Marsh (1994) who concluded that it is better described in the space group *Pbca*. On the other hand, the chemically related mineral nchawaningite, $Mn_2^{2+}SiO_3(OH)_2{\cdot}H_2O$, exhibits a different structural arrangement which can be described as a pyroxene-related chain structure (Nyfeler *et al.*, 1995). Olmiite, poldervaartite and α-dicalcium silicate hydrate (CSH) alone, therefore, will be compared in the following discussion.

Crystal chemical remarks

In both the olmiite and the poldervaartite structures, Mn^{2+} completely orders on the *M*2 site. Accordingly, the most pronounced geometrical variations affect the *M*2 polyhedron. As pointed out by Dai *et al.* (1993), the (5+2) coordination of *M*2 can be described as a distorted trigonal bipyramid with two additional distant O1 atoms approximately located on the equatorial plane to form an irregular pentagonal bipyramid. In poldervaartite, where *M*2 is dominated by Ca, the mean $\langle M2{-}O\rangle^{V}$ and $\langle M2{-}O\rangle^{VII}$ distances are 2.269 and 2.433 Å, respectively, whereas $\langle M2{-}O\rangle^{V} = 2.191$ Å (−3.4%) and $\langle M2{-}O\rangle^{VII} = 2.376$ Å (−2.3%) in olmiite. The analogous values for the CaO_7 polyhedron in CSH (Marsh, 1994) are $\langle Ca{-}O\rangle^{V} = 2.317$ Å and $\langle Ca{-}O\rangle^{VII} = 2.468$ Å. The effect of Mn^{2+} replacing Ca, indeed, merely affects the five shorter distances, while the sixth (*M*2−O1) and the seventh longest ($M2{-}O1^{f}$) distances appear substantially unrelated. As shown in Fig. 3*a*, $\langle M2{-}O\rangle^{V}$ distance correlates perfectly with the Mn^{2+} content in the *M*2 site ($r = -0.999$). This feature is quite common in minerals wherein Mn^{2+} substitutes for Ca in high-coordination polyhedra. As an example, in the minerals belonging to the piemontite-androsite series of the epidote, group the length difference between the seventh and the

TABLE 3. X-ray powder-diffraction data for olmiite.

I/I_o	I_{calc}	d_{meas}	d_{calc}	*h*	*k*	*l*
5	8	5.46	5.4850	1	1	1
15	23	5.16	5.1765	0	0	2
5	4	4.60	4.6220	2	0	0
10	3	4.51	4.5166	1	0	2
45	**27**	**4.14**	**4.1466**	**0**	**2**	**1**
25	25	4.10	4.1163	2	1	0
15	14	4.03	4.0413	1	1	2
20	20	3.82	3.8251	2	1	1
3	2	3.77	3.7834	1	2	1
20	33	3.44	3.4477	2	0	2
5	3	3.40	3.4071	0	2	2
20	11	3.23	3.2336	2	2	0
	9		3.2219	2	1	2
100	**100**	**3.19**	**3.1968**	**1**	**2**	**2**
3	3	3.08	3.0865	2	2	1
3	2	3.05	3.0446	1	1	3
35	**42**	**2.807**	**2.8076**	**3**	**1**	**1**
30	33	2.762	2.7640	1	3	1
20	14	2.737	2.7442	0	2	3
13	13	2.650	2.6477	3	0	2
10	11	2.627	2.6307	1	2	3
20	22	2.594	2.5883	0	0	4
35	**37**	**2.545**	**2.5412**	**3**	**1**	**2**
30	23	2.521	2.5264	2	3	0
20	21	2.472	2.4732	3	2	1
5	4	2.450	2.4544	2	3	1
5	9	2.402	2.4030	1	1	4
40	**63**	**2.361**	**2.3596**	**2**	**2**	**3**
3	3	2.286	2.2853	3	2	2
10	5	2.269	2.2704	2	3	2
5	5	2.247	2.2467	0	2	4
10	7	2.187	2.1886	4	1	1
5	3	2.113	2.1105	3	3	1
	9		2.1103	4	0	2
5	5	2.074	2.0733	0	4	2
5	7	2.057	2.0582	4	2	0
10	10	2.039	2.0385	2	3	3
15	5	2.031	2.0323	2	4	0
20	14	2.024	2.0231	1	4	2
3	3	1.988	1.9942	2	4	1
3	6	1.931	1.9360	3	1	4
5	10	1.919	1.9125	4	2	2
10	11	1.894	1.8923	0	4	3
20	14	1.747	1.7512	2	4	3
	18		1.7437	2	2	5
3	5	1.729	1.7255	0	0	6
15	10	1.682	1.6885	3	1	5
	9		1.6803	1	5	2
10	13	1.612	1.6168	4	4	0
	5		1.6165	2	0	6
5	8	1.559	1.5584	5	3	1
10	11	1.543	1.5434	3	5	1
15	4	1.508	1.5085	0	6	0
3	9	1.485	1.4841	5	1	4
3	1	1.462	1.4641	4	4	3
5	4	1.450	1.4483	0	6	2

Footnote to Table 3
Powder XRD data obtained with a Philips diffractometer (Bragg-Brentano geometry) and Ni-filtered Cu-$K\alpha$ radiation
d values calculated on the basis of unit-cell parameters from powder data [a = 9.244(6), b = 9.051(4), c = 10.353(6) Å]
Intensities calculated with the atomic coordinates reported in Table 2 using XPOW software version 2.0 (Downs *et al.*, 1993).
Five strongest reflections are given in bold.

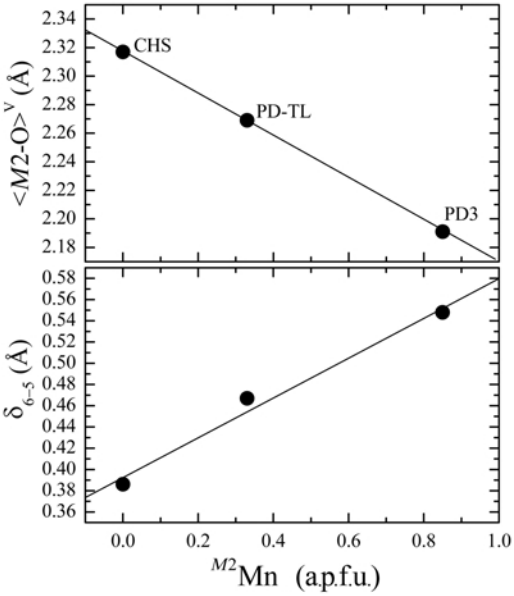

FIG. 3. The mean $<M2-O>^V$ distance (*a*) and the length difference between the sixth and the fifth longest distance, δ_{6-5}, (*b*) plotted *vs.* the Mn^{2+} content (a.p.f.u.) in the *M*2 polyhedron of α-dicalcium silicate hydrate (CSH), poldervaartite (PD-TL) and olmiite (OL-TL) respectively. Regression lines fit the equations: $y = 2.3174(6) - 0.148(1)x$ ($r = -0.999$) and $y = 0.39(1) + 0.19(2)x$ ($r = 0.992$), respectively.

sixth longest distance (δ_{7-6}) was found to be a parameter to estimate the amount of Mn^{2+} on the *A*1 site, commonly occupied by Ca in most epidote group minerals (Bonazzi *et al.*, 1996). Analogously, the length difference between the sixth and the fifth longest distance (δ_{6-5}) in olmiite and poldervaartite, together with the homologous value in CSH, is linearly related to the Mn^{2+} content (Fig. 3*b*).

TABLE 4. Selected bond distances (Å) and angles (º) in the crystal structure of olmiite OL-TL and poldervaartite PD-TL.

	OL-TL	PD-TL
*M*1−O5	2.328(3)	2.330(2)
−O3	2.335(3)	2.333(2)
−O4	2.349(2)	2.336(2)
−O2^{a}	2.355(2)	2.374(2)
−O2^{b}	2.405(2)	2.447(2)
−O1	2.443(2)	2.506(2)
<*M*1−O>	2.369	2.388
*M*2−O3^{c}	2.107(2)	2.204(2)
−O5^{d}	2.177(2)	2.259(2)
−O4^{b}	2.183(2)	2.265(2)
−O4	2.202(3)	2.275(2)
−O2^{e}	2.284(2)	2.340(2)
−O1	2.832(3)	2.881(2)
−O1^{f}	2.850(3)	2.807(2)
<*M*2−O>^{V}	2.191	2.269
<*M*2−O>^{VII}	2.376	2.433
Si −O3^{g}	1.608(2)	1.603(2)
−O2^{e}	1.622(2)	1.625(2)
−O5^{h}	1.627(2)	1.619(2)
−O1	1.675(2)	1.696(2)
<Si−O>	1.633	1.636
O3^{g}−Si−O2^{e}	113.7(1)	114.8(1)
−O5^{h}	113.6(1)	114.4(1)
−O3^{g}	108.2(1)	107.2(1)
O2^{e}−Si−O5^{h}	110.6(1)	110.1(1)
−O1	105.6(1)	104.8(1)
O5^{h}−Si−O1	104.4(1)	104.5(1)
H1−O1	0.88(4)	0.84(4)
···O5^{g}	1.72(4)	1.81(4)
O1···O5^{g}	2.573(3)	2.636(3)
H2−O4	0.81(4)	0.84(4)
···O3^{d}	2.32(4)	2.38(4)
O4···O3^{d}	3.077(3)	3.086(3)

The superscripts denote the symmetry code: a = $-1+x, y, z$; b = $1-x, 1-y, 1-z$; c = $½-x, -½+y, z$; d = $½+x, y, ½-z$; e = $-½+x, ½-y, 1-z$; f = $½+x, ½-y, 1-z$; g = $½-x, 1-y, ½+z$; h = $x, ½-y, ½+z$.

The *M*1 site is coordinated by four O atoms and two OH groups to form a distorted octahedron, and it is completely occupied by Ca in both poldervaartite and olmiite. Nonetheless, the contraction of the *M*2 polyhedron due to the entry of Mn^{2+} causes geometrical changes in the adjacent *M*1 octahedron, which shares two edges (O1−O4 and O1−O2) with the *M*2 polyhedron. Thus, the mean <*M*1−O> decreases from 2.388 Å (PD-TL) to 2.369 Å (OL-TL), whereas the homologous value in CSH is 2.404 Å.

The Si tetrahedron shares two edges (O1−O5 and O1−O2) with two adjacent $M2O_7$ polyhedra. However, the O1 atom is only weakly bonded to *M*2. In other words, there is no edge sharing in the *M*2+Si layer when a five-fold coordination for *M*2 is considered. Nonetheless, the *M*2−Si distances are the shortest cation–cation contacts in the structure (3.154 and 3.159 Å in PD-TL; 3.094 and 3.131 Å in OL-TL). On the other hand, O1−O2 and O1−O5 are the shortest tetrahedral edges, thus minimizing the repulsive forces between Mn^{2+} and Si^{4+}; as a consequence, the corresponding tetrahedral angles deviate from the ideal O−Si−O value for a regular tetrahedron [O1−Si−O5 = 104.5º (PD-TL), 104.4º (OL-TL); O1−Si−O2 = 104.8º (PD-TL), 105.6º (OL-TL)]. Furthermore, due to the acid character of the Si tetrahedron, the accommodation of the long Si−OH distances (1.697 and 1.675 Å in PD-TL and in OL-TL, respectively) causes a considerable distortion in terms of bond lengths and angles. The values of tetrahedral mean quadratic elongation (λ) and angular distortion (σ^2), calculated following Robinson *et al*. (1971), are: $\lambda = 1.0049$ and $\sigma^2 = 20.71$ in PD-TL; $\lambda = 1.0037$ and $\sigma^2 = 15.70$ in OL-TL.

The position of the H1 and H2 atoms in olmiite leads to the same hydrogen bonding scheme as found by Dai *et al.* (1993) in poldervaartite. The O1−H1···O5 bonding in olmiite (2.573 Å), however, appears to be even stronger than that observed in poldervaartite (2.636 Å), whereas minor differences are found in the length of donor–acceptor distances for the weak O4−H2···O3 bonding (3.077 and 3.086 Å in OL-TL and in PD-TL, respectively). The partition of the bond valence between donor and acceptor oxygen atoms was estimated from the graph showing the correlation between the H···O bond strength and the O···O distance (Brown and Altermatt, 1985). The bond strength on the donor oxygen was consequently determined by subtracting the obtained values from 1.0. As shown in Table 5, the model matches perfectly the charge balance requirement of all oxygen atoms.

The unit-cell parameters are linearly related to the amount of Mn^{2+} entering the *M*2 site. Using data of CSH, PD-TL and OL-TL, the following linear models are obtained: a (Å) = 9.488−0.281 $[Mn]^{M2}$ (a.p.f.u.); b (Å) = 9.179−0.121 $[Mn]^{M2}$ (a.p.f.u.), and c (Å) = 10.664−0.380

TABLE 5. Bond valences (v.u.) in olmiite.

	O1	O2	O3	O4	O5	Total
*M*1	0.28	0.35 0.31	0.37	0.36	0.38	2.05
*M*2	0.07 0.06	0.29	0.46	0.38 0.36	0.38	2.00
Si	0.91	1.05	1.09	–	1.04	4.09
H1	0.74	–	–	–	0.26	1.00
H2	–	–	0.08	0.92	–	1.00
Total	2.06	2.00	2.00	2.02	2.06	

*M*2−O bond strengths are calculated assuming *M*2 = 85% Mn^{2+} + 15% Ca; bond-valence parameters were taken from Brese and O'Keeffe (1991).

$[Mn]^{M2}$(a.p.f.u.). As shown by the angular coefficient of the above equations, the parameter which mostly decreases with the substitution of Mn^{2+} for Ca is *c*, and, to a lesser extent, *a*; the repeat unit along the stacking axis (*b*), in contrast, is only slightly related to composition. In other words, the Mn incorporation, which causes a more pronounced decrease of the shortest *M*2−O distances (i.e. $M2{-}O3^{c}$ and $M2{-}O5^{d}$), mainly strengthens the linkage within the *M*2+Si layer rather than the linkage between adjacent layers.

Concluding remarks

The structure of both poldervaartite and olmiite can be schematically described, for convenience, as a sequence along [010] of alternating layers containing *M*2+Si and *M*1 polyhedra, respectively. Nonetheless, the strong three-dimensional linkage among the polyhedral units results in a rather isotropic framework which, as pointed out by Dai *et al.* (1993), accounts for the lack of cleavage in these minerals. Indeed, the shortest *M*2−*M*2 contacts are not found within the *M*2+Si layer, but occur along [010] between pairs of edge-sharing *M*2 polyhedra belonging to different layers. The variation of the refractive indices along the join poldervaartite-olmiite could be tentatively related to this feature. Due to the different optical orientation in poldervaartite ($X = b$, $Y = a$, $Z = c$) with respect to olmiite ($X = a$, $Y = c$, $Z = b$), the refractive indices $\beta = 1.640$, $\gamma = 1.656$, $\alpha = 1.634$ in poldervaartite should be compared to $\alpha = 1.663$, $\beta = 1.672$, $\gamma = 1.694$ in olmiite, respectively. The increase in refractive indices as a function of the Mn content is rather small (1.4−1.0%) for waves vibrating within the (010) plane, whereas it is more pronounced (3.7%) for waves vibrating along [010], i.e. the direction of the *M*2−*M*2 contacts (3.379 and 3.289 Å in PD-TL and OL-TL). With the increase of the Mn content, dispersion changes from weak with $r < v$ (poldervaartite) to distinct with $r > v$ (olmiite). However, the inversion of dispersion along the poldervaartite–olmiite join does not necessarily match the 50% rule for naming the solid solutions; thus, with the lack of structural data, a chemical criterion should be used properly to name a member of the solid solution poldervaartite–olmiite. Provided that the name poldervaartite should be reserved only to samples having Ca dominant at the *M*2 site, and taking into consideration that Mn is completely ordered on *M*2, samples with Ca > 1.5 a.p.f.u. (Mn < 0.5 a.p.f.u.) should be named poldervaartite, whereas the name olmiite is for members with Mn > 0.5 a.p.f.u. (Ca < 1.5 a.p.f.u.).

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