

Manganvesuvianite and tweddillite, two new Mn³⁺-silicate minerals from the Kalahari manganese fields, South Africa

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ABSTRACT

The new minerals manganvesuvianite and tweddillite, both formed by hydrothermal alteration of primary manganese ores, are described from the Kalahari manganese fields (Republic of South Africa). In addition, single-crystal X-ray structure refinements of both new minerals are presented.

Manganvesuvianite is a tetragonal vesuvianite mineral with the simplified formula $\text{Ca}_{19}\text{Mn}^{3+}(\text{Al},\text{Mn}^{3+},\text{Fe}^{3+})_{10}(\text{Mg},\text{Mn}^{2+})_2\text{Si}_{18}\text{O}_{69}(\text{OH})_9$, characterized by Mn³⁺ occupying the five-coordinated position (square pyramid). The crystals have simple prismatic forms: {100}, {110} terminated by {101} and exhibit deep maroon red colour. With polarized light the crystals are strongly pleochroic, yellowish parallel to E and dark red to lilac parallel to O.

Tweddillite is an epidote-group mineral (space group space group $P2_1/m$, $a = 8.932(5)$, $b = 5.698(4)$, $c = 10.310(5)$ Å, $\beta = 114.56(4)$, $V = 477.3(8)$ Å³) with the simplified formula $\text{CaSr}(\text{Mn}^{3+},\text{Fe}^{3+})_2\text{Al}[\text{Si}_3\text{O}_{12}](\text{OH})$, closely related to strontio Piemontite. The difference between strontio Piemontite and tweddillite is the concentration of octahedral Mn³⁺. Strontio Piemontite has Mn³⁺ mainly on the M3 site whereas tweddillite has Mn³⁺ with minor Fe³⁺ on M3 and M1. Tweddillite forms aggregates of very thin dark red {001} blades characterized by striking pleochroism. The crystals appear dark red parallel to *b* and orange-yellow parallel to *a*. Perpendicular to (001) the blades appear magenta to red.

KEYWORDS: manganvesuvianite, tweddillite, Kalahari, manganese fields, South Africa, epidote group, vesuvianite.

Introduction

A variety of rather rare manganese minerals formed in the Kalahari manganese fields by hydrothermal alteration (250–400°C) of the primary sedimentary and low-grade metamorphic manganese ores. Such minerals crystallized along fault planes and lenticular bodies within the manganese ore beds or filling veins and vugs (Cairncross *et al.*, 1997).

Recently, the IMA Commission on New Minerals and Mineral Names (CNMMN) approved two new mineral species from this locality which are characterized, including their crystal structures. Both new species manganvesuvianite (CNMMN-2000-40) and tweddillite (CNMMN-2001-14) belong to well established mineral groups, the vesuvianite and epidote minerals, respectively.

Manganvesuvianite

General aspects of vesuvianite crystal chemistry.

A simplified formula of tetragonal vesuvianite ($a \approx 15.5$, $c \approx 11.8$ Å, $Z = 2$), taking into account

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the various cation coordinations and its domain structure, may be written as $X_{18}X'Y'Y_2Y_4Y_3Z_{18}O_{69}(OH,F)_9$ where X and X' are seven to nine-coordinated, Y_2 and Y_3 have octahedral coordination, Y' has square pyramidal coordination, and Z represents tetrahedral coordination. X and X' are commonly occupied by Ca. Y and Y' host elements with an average valence of 2.85 (c.g. 11 Al and 2 Mg) and Z is mainly occupied by Si. X' and Y' occupy strings along the 4-fold axes. In space group $P4/nnc$, these strings have the sequence $Y'X'X'Y'$ but due to short $X'X'$ and $Y'X'$ distances, occupied sites always alternate with vacancies (\square). Thus a string along a 4-fold axis has locally either a $Y'\square X'\square$ or a $\square X'\square Y'$ arrangement. If we assume for electrostatic reasons that two adjacent vacancies do not occur, each string itself is fully ordered (short range ordering). However, adjacent strings are either long-range disordered (space group $P4/nnc$) or they follow some specific ordering patterns leading to decreased symmetry (Giuseppetti and Mazzi, 1983; Fitzgerald *et al.*, 1986; Allen and Burnham, 1992; Ohkawa *et al.*, 1994; Pavese *et al.*, 1998; Armbruster and Gnos, 2000a,b,c).

In addition to these 'common vesuvianites' there are also excess Y -group vesuvianites (Groat *et al.*, 1994a,b) with additional sites occupied that are vacant in ordinary vesuvianites. These additional sites may also be occupied by boron leading to wiluite (Groat *et al.*, 1998) of simplified composition $Ca_{19}(Al,Mg,Fe,Ti)_{13}(B,Al,\square)_5Si_{18}O_{68}(O,OH)_{10}$.

The IMA CNMMN (Nickel and Grice, 1998) has defined the general guideline for compositional criteria that at least one structural site in the potential new mineral should be predominantly occupied by a different chemical component than that which occurs in the equivalent site in an existing mineral species. This rule expands vesuvianite to a mineral group with various mineral species distinguished by different cations occupying the square pyramidal Y' site. Ohkawa *et al.* (1992) suggest that Mn^{2+} , Fe^{2+} , Cu^{2+} , Fe^{3+} and Mg^{2+} may occupy the five-coordinated Y' site. However, interatomic distances obtained from diffraction experiments of disordered $P4/nnc$ vesuvianites are not reliable for assignments of cation radii to the Y' site because in $P4/nnc$ symmetry this site is only 50% occupied with the remaining 50% being vacancies. In other words, the valence of Mn and Fe cannot simply be derived from interatomic distances. High-resolution solid-state ^{27}Al NMR

spectroscopy (Phillips *et al.*, 1987; Olejniczak and Zabinski, 1996) indicated that in Mg-rich (Fe-poor) vesuvianites also, Al may dominate the five-coordinated site. In a combined X-ray and neutron diffraction study Pavese *et al.* (1998) have shown that in a $P4/n$ vesuvianite from Val d'Ala (Italy) the square pyramidal Y' site is occupied by Fe^{3+} . The examples above demonstrate that the vesuvianite group is much more complex than hitherto assumed, requiring definition of new mineral species.

Definition

Manganvesuvianite is a vesuvianite group mineral where the five-coordinated (Y') position (square pyramid) is occupied by Mn^{3+} . The simplified formula is $Ca_{19}Mn^{3+}(Al,Mn^{3+},Fe^{3+})_{10}(Mg,Mn^{2+})_2Si_{18}O_{69}(OH)_9$.

Identification criteria

(1) Manganvesuvianite is macroscopically deep red and strongly pleochroic E: colourless–yellowish, O: dark red or lilac. More detailed optical absorption spectra of five-coordinated Mn^{3+} in vesuvianite are discussed by Hälenius and Annersten (1994) and Platonov *et al.* (1995).

(2) If the chemical formula of a boron-poor vesuvianite is either normalized to 50 cations or $(Ca + Sr + Ba + Na + K) = 19$, there are 13 Y type cations (Al, Fe^{3+} , Mn^{3+} , Mg, Fe^{2+} , Mn^{2+} , Cu^{2+} , Ti^{4+}). For stoichiometry reasons the average charge of the Y cations must be 2.85⁺. If Ti^{4+} can be ignored (which is the case for the Mn-rich samples described here) two Y cations are divalent and eleven Y cations are trivalent. The divalent Y cations are Mg, Cu^{2+} and Mn^{2+} . If the analysis reveals, after correction for Mn^{2+} ($2 - (Mg + Cu)$ p.f.u. = Mn^{2+} p.f.u.), more than 1 Mn^{3+} p.f.u. and in addition $Mn^{3+} > Fe^{3+}$, the mineral is manganvesuvianite.

(3) Crystal structure analysis of manganvesuvianite indicates that Mn^{3+} occupies the five-coordinated square pyramidal Y' position leading to Jahn-Teller distortion where the four-fold axis of the square pyramid is elongated.

Occurrence

Manganvesuvianite (Wessels mine and N'Chwaning II mine) occurs as long prismatic (up to 1.5 cm) crystals filling veins and vugs. Larger crystals are nearly black and opaque with

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TABLE 1. Electron microprobe analyses of manganvesuvianites from the N'Chwaning II mine.

	NC14-38 ¹	NCII-1 ²	St. dev.	NCII-2 ³	St. dev.
SiO ₂	34.13	36.69	0.16	36.15	0.43
TiO ₂	0.00	0.00	0.00	0.00	0.00
Al ₂ O ₃	10.63	16.19	0.32	14.73	0.63
Fe ₂ O ₃	0.00	1.83	0.16	1.12	0.60
Mn ₂ O ₃	15.96	3.78	0.19	6.79	1.01
MgO	0.09	2.47	0.24	2.35	0.30
CaO	34.33	36.07	0.16	35.73	0.22
CuO	0.41	0.06	0.05	0.02	0.02
SrO	0.05	0.12	0.06	0.11	0.06
BaO	0.00	0.00	0.00	0.00	0.00
Na ₂ O	0.00	0.05	0.03	0.03	0.02
K ₂ O	0.01	0.00	0.01	0.00	0.00
F	0.12	0.05	0.04	0.12	0.06
Cl	0.00	0.01	0.01	0.01	0.01
H ₂ O (calc.)	2.52	2.74	0.02	2.67	0.04
-(F+Cl)	-0.06	-0.03		-0.07	
Sum	98.19	100.03		99.76	
Formulae normalized to (Ca + Sr + Ba + Na + K) = 19					
Si	17.611	17.962		17.885	
Ti	0.000	0.000		0.000	
Al	6.467	9.341		8.589	
Mn ³⁺	4.498	1.226		2.300	
Mn ²⁺	1.770	0.175		0.260	
Fe ³⁺	0.000	0.675		0.418	
Fe ²⁺	0.000	0.000		0.000	
Mg	0.072	1.803		1.733	
Ca	18.972	18.918		18.940	
Cu	0.158	0.022		0.007	
Sr	0.014	0.034		0.032	
Ba	0.000	0.000		0.000	
Na	0.000	0.047		0.029	
K	0.009	0.000		0.000	
F	0.191	0.077		0.188	
Cl	0.000	0.008		0.008	
H (calc.)		8.914		8.804	
Sum Y ⁴	12.965	13.242		13.308	

¹ Armbruster and Gnos (2000b)

² Sample for refractive index measurement (average of 15 point analyses)

³ Sample for crystal structure analysis (average of 19 point analyses)

⁴ Excess of Y cations (Al + Fe + Mg + Mn + Cu + Ti) > 13 is well documented for vesuvianites (Groat *et al.*, 1994a,b), Mn²⁺ was calculated as Mn²⁺ = 2 - (Fe²⁺ + Mg²⁺ + Cu²⁺)

dark-red internal reflections, smaller crystals are red to lilac and transparent. The crystals are characterized by prism faces: dominant {100}, minor {110}, both often with striations, terminated by {101}.

At the N'Chwaning II mine, manganvesuvianite is also rock-forming, densely intergrown with

either manganese-poor grossular or xonotlite and calcite in lenticular calcsilicate bodies within manganese ore beds. Those manganvesuvianite crystals are short to long prismatic (<0.2 mm) and strongly zoned. Additional associated minerals are calcite, serandite-pectolite, strontioepimontite-tweddillite, moztartite and hydrogrossular-

TABLE 2. Single-crystal X-ray data collection and refinement of manganvesuvianite NCII-2.

Space group	$P4/n$, No. 85 (origin at $\bar{1}$)
a, c (Å), V (Å ³)	15.575(2), 11.824(2), 2868.5(6)
Crystal size (mm ³)	0.150 × 0.150 × 0.280
X-radiation	Mo- $K\alpha$
Upper θ limit	30°
h, k, l limit	$21 \geq h \geq 0, 21 \geq k \geq 0, 16 \geq l \geq 0$
Reflections measured	4660
Unique reflections	4189
Reflections $> 4\sigma$ (F)	3870
Absorption corr.	empirical: ψ scans
$R_{\text{int}}, R_{\sigma}$ (%)	2.2, 1.4
Twinning, ratio	merohedral (110), 0.722(3): 0.278
Number of parameters	272; U_{eq} of Si sites constraint
$R1$ (on F) %	3.5
$wR2$ (on F^2) %	8.2

$$R1 = (\sum ||F_o| - |F_c||) / (\sum |F_o|)$$

$$wR2 = \sqrt{(\sum (w(F_o^2 - F_c^2)^2)) / (\sum w(F_o^2)^2)}$$

henritermierite. Manganvesuvianite from the N'Chwaning II mine has been deposited (NMBE 35474) at the Natural History Museum in Bern, Switzerland.

manganvesuvianite cannot be distinguished from other vesuvianites (e.g. with Fe^{3+} , Cu^{2+} or Al on the square pyramidal Y' site) on the basis of its X-ray powder pattern.

Physical and optical properties

The megascopic colour is deep maroon-red with vitreous lustre. Other properties: the streak is colourless; Mohs' hardness: 6–7; brittle tenacity; cleavage not observed; and subconchoidal fracture. The density was not measured because of strong chemical zoning. The calculated density for crystal NCII-1 is 3.404 g/cm³ using a cell volume of 2868.5 Å³. The mineral is uniaxial negative. At 589 nm, crystal NCII-1 has the refractive indices $\epsilon = 1.731(1)$ and $\omega = 1.719(1)$; extrapolated from small prism measurements at 546 nm: $\omega = 1.7353$, $\epsilon = 1.7236$; at 576.9 nm: $\omega = 1.7320$, $\epsilon = 1.7200$; at 643.8 nm: $\omega = 1.7274$, $\epsilon = 1.7159$. The crystal is strongly pleochroic, E: yellowish, O: dark red. Some of the manganvesuvianites analysed by Armbruster and Gnos (2000b), in addition to Mn^{3+} , also exhibit significant Cu^{2+} leading to lilac hues parallel to O. Such crystals are often colour zoned (Fig. 1) where the dark red core is more Mn^{3+} rich (typically 6–9 wt.% MnO) and the lilac rim is less Mn^{3+} -rich (typically 1.5–5 wt.% MnO). Because of the strong chemical zoning, an X-ray powder pattern was not collected. In addition,

Chemical composition

Vesuvianites were analysed with a Cameca SX-50 microprobe using beam conditions of 15 kV and 20 nA, wavelength-dispersive spectrometers, and when possible, an enlarged spot size of ~10 μm . Natural and synthetic minerals were used as standards. Results are given in Table 1. Even within one crystal the Mn^{3+} concentration is strongly variable. Mn^{3+} completely occupies the Y' site with square pyramidal coordination and may partly substitute the octahedral Y sites, commonly occupied by Al.

Crystal structure refinement

Single-crystal X-ray data collection on a maroon red crystal NCII-2 (for average chemical composition see Table 1) was performed with an ENRAF NONIUS CAD4 single crystal diffractometer with graphite monochromated Mo- $K\alpha$ X-radiation. Cell dimensions were refined from the angular settings of 20 reflections (16 0 0, 0 16 0, 0 0 16, 12 12 0, 12 12 8, and their symmetry equivalent reflections). Experimental details of the data collection and refinement are summarized

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TABLE 3. Atomic positional parameters and B_{cqq} values for manganvesuvianite NCH-2.

Atom	Population	x/a	y/b	z/c	$B_{\text{cqq}} (\text{\AA}^2)$
Z1A	Si	-1/4	1/4	0	0.734(7)*
Z1B	Si	-1/4	1/4	1/2	0.734(7)*
Z2A	Si	-0.04035(8)	0.31890(8)	0.1292(1)	0.734(7)*
Z2B	Si	-0.04115(8)	0.18017(8)	0.3719(1)	0.734(7)*
Z3A	Si	0.08686(7)	0.34911(7)	-0.1352(1)	0.734(7)*
Z3B	Si	0.08199(7)	0.15100(7)	0.6357(1)	0.734(7)*
Y2A	0.90(1)Al + 0.10Mn	0	0	0	0.69(3)
Y2B	0.95(1)Al + 0.05Mn	-1/2	0	1/2	0.69(4)
Y3A	0.81(1)Al + 0.19Mn	-0.11226(7)	0.11962(7)	0.12497(9)	0.73(2)
Y3B	0.84(1)Al + 0.16Mn	-0.38839(7)	0.12156(7)	0.37384(9)	0.74(2)
X1	Ca	-1/4	1/4	0.2504(1)	0.81(1)
X2A	Ca	0.18951(6)	-0.04395(6)	0.62112(7)	0.84(1)
X2B	Ca	-0.04570(6)	0.18816(5)	-0.12041(7)	0.81(1)
X3A	Ca	0.09891(6)	0.17897(6)	0.11669(8)	1.35(1)
X3B	Ca	-0.39895(6)	-0.18214(6)	-0.39052(8)	1.27(1)
O1A		-0.2212(2)	0.1725(2)	0.0858(2)	0.86(4)
O1B		-0.2808(2)	0.1724(2)	0.4148(2)	0.84(4)
O2A		-0.1174(2)	0.3385(2)	0.2212(3)	0.98(4)
O2B		-0.1177(2)	0.1588(2)	0.2803(3)	0.90(4)
O3A		-0.0470(2)	0.2219(2)	0.0751(3)	0.94(4)
O3B		-0.0478(2)	0.2767(2)	0.4253(3)	0.80(4)
O4A		-0.0614(2)	0.3934(2)	0.0321(3)	1.01(5)
O4B		-0.0620(2)	0.1059(2)	0.4711(2)	0.88(4)
O5A		-0.0104(2)	0.3272(2)	-0.1771(3)	1.16(5)
O5B		-0.0150(2)	0.1701(2)	0.6797(3)	1.08(5)
O6A		0.1256(2)	0.2728(2)	-0.0572(3)	1.37(5)
O6B		0.1181(2)	0.2285(2)	0.5598(3)	1.34(5)
O7A		0.0561(2)	0.3262(2)	0.1805(3)	1.24(5)
O7B		0.0554(2)	0.1722(2)	0.3232(3)	1.06(5)
O8A		0.0928(2)	0.4386(2)	-0.0660(3)	0.84(4)
O8B		0.0909(2)	0.0610(2)	0.5678(3)	0.95(5)
O9		0.1479(2)	0.3562(2)	-0.2496(3)	1.09(5)
O10A		1/4	1/4	0.1344(5)	1.34(7)
O10B		-1/4	-1/4	-0.3648(5)	1.27(8)
O11A	OH	-0.0048(2)	0.0600(2)	0.1367(3)	0.95(5)
O11B	OH	-0.4960(2)	0.0626(2)	0.3645(3)	1.02(5)
X4B	0.324(8) Ca	1/4	1/4	-0.1469(5)	1.1(1)
Y1B	0.324(8) Mn	1/4	1/4	0.5428(3)	0.92(9)
X4A	0.676(8) Ca	1/4	1/4	0.6475(2)	0.95(3)
Y1A	0.676(8) Mn	1/4	1/4	-0.0454(2)	0.81(3)

Refined formula $Ca_{19}Mn_{2.72}Al_{10.28}Si_{18}O_{69}(OH)_9$; notice that due to similarity in X-ray scattering behaviour the pairs Fe,Mn and Al,Mg can not be distinguished.

To reduce the number of parameters, the Si displacement parameters were refined isotropically and constrained to identical values.

Note that in this paper we used the site nomenclature scheme of Groat (1992b) which is different from the scheme used by us in previous papers on vesuvianite (Armbruster and Gnos, 2000a,b,c).

in Table 2. Data reduction, including background and Lorentz polarization correction was carried out with the SDP program system (Enraf Nonius, 1983). The crystal did not show systematic

extinctions of X-ray reflections. This is characteristic of low- T vesuvianites assembled of $P4/n$ and $P4nc$ polymorphs (e.g. Allen and Burnham, 1992; Armbruster and Gnos, 2000a,b,c). However,

TABLE 4. Selected interatomic distances of manganvesuvianite.

Z1A–O1A 4x	1.639(3)	X1–O1A 2x	2.333(3)
		O1B 2x	2.339(3)
Z1B–O1B 4x	1.646(3)	O2A 2x	2.507(3)
		O2B 2x	2.528(3)
Z2A–O7A	1.625(3)	mean	2.427
O3A	1.644(3)	X2A–O8B	2.329(3)
O2A	1.648(3)	O5B	2.337(3)
O4A	1.665(3)	O3B	2.375(3)
mean	1.646	O2B	2.410(3)
Z2B–O7B	1.615(3)	O5A	2.456(3)
O3B	1.635(3)	O4B	2.463(3)
O2B	1.645(3)	O1B	2.491(3)
O4B	1.679(3)	O6B	2.920(3)
mean	1.644	mean	2.473
Z3A–O8A	1.620(3)	X2B–O8A	2.329(3)
O6A	1.621(3)	O5A	2.333(3)
O5A	1.630(4)	O3A	2.371(3)
O9	1.657(4)	O4A	2.426(3)
mean	1.632	O2A	2.427(3)
Z3B–O6B	1.606(3)	O5B	2.428(3)
O8B	1.622(3)	O1A	2.462(3)
O5B	1.625(3)	O6A	3.068(3)
O9	1.664(4)	mean	2.481
mean	1.629	X3A–O7A	2.364(3)
Y2A–O11A 2x	1.869(3)	O3A	2.420(3)
O8A 2x	1.901(3)	O11A	2.469(3)
O4A 2x	1.953(3)	O7A	2.505(4)
mean	1.908	O7B	2.536(3)
Y2B–O11B 2x	1.876(3)	O6A	2.556(3)
O8B 2x	1.884(3)	O10A	2.609(1)
O4B 2x	1.941(3)	O8A	2.609(3)
mean	1.900	mean	2.509
Y3A–O11A	1.919(3)	X3B–O7B	2.340(3)
O2B	1.937(3)	O3B	2.441(3)
O1A	1.943(3)	O6B	2.452(3)
O3A	1.980(3)	O11B	2.498(3)
O5A	2.041(4)	O7B	2.508(3)
O4A	2.069(3)	O10B	2.567(1)
mean	1.982	O7A	2.583(4)
Y3B–O2A	1.911(3)	O8B	2.608(3)
O11B	1.915(3)	mean	2.500
O1B	1.915(3)	X4A–O6B 4x	2.325(4)
O3B	1.967(3)	O9 4x	2.597(3)
O5B	1.997(4)	mean	2.461
O4B	2.057(3)	X4B–O6A 4x	2.237(4)
mean	1.960	O9 4x	2.596(4)
Y1A–O6A 4x	1.975(4)	mean	2.417
O10A	2.125(7)		
Y1B–O6B 4x	2.091(4)		
O10B	2.105(8)		

reflections of the type $hk0$ with $h+k=2n+1$ were mostly weak and were ignored. The strongest reflections of this type were 1 6 0, 1 10 0, 2 7 0, and 2 15 0 with $10 < I/\sigma(I) < 15$. Reflections of the type $0kl$ with $k+l=2n+1$ and of the type hhl with $l=2n+1$ were considerably stronger indicating predominance of the $P4/n$ polytype. Subsequently, the structure refinement was carried out in space group $P4/n$ using the program SHELX-97 (Sheldrick, 1997) and applying the $P4/n$ starting coordinates given by Armbruster and Gnos (2000a). Note that in this paper we use the site nomenclature scheme of Groat *et al.* (1992b) which is different from the scheme used by us in previous papers on vesuvianite (Armbruster and Gnos, 2000a,b,c).

Crystal structure of manganvesuvianite

The structurally investigated crystal (NCII-2) represents an intergrowth of polymorphs with $P4/n$ and $P4nc$ symmetry. A distinction of the two polymorphs is possible on the basis of characteristic X-ray reflections (e.g. Armbruster and Gnos, 2000a,b,c). However, the $P4/n$ polymorph is more dominant and so a structure refinement in space group $P4/n$ was successful. The crystal exhibits merohedral $\{110\}$ twinning that converged to a refined twin ratio of 0.722(3)/0.278. In addition to twinning, there is occupational disorder leading to string A and B occupations (e.g. Armbruster and Gnos, 2000a,b,c) of 67.2(8) and 32.8%, respectively. This disorder could be an artifact caused by the presence of the subordinate $P4nc$ polymorph.

Z1A,B and Z2A,B are orthosilicate groups whereas Z3A and Z3B form a disilicate unit with an angle Z3A–O9–Z3B of $136.1(2)^\circ$. The strong bending of the angle is balanced by increased Z3–O9 distances to increase Si–Si separation. In a previous study on Mn-bearing vesuvianites, which now have also to be considered manganvesuvianites, Armbruster and Gnos (2000b) noticed tetrahedral vacancies on the orthosilicate groups associated with increased Si–O distances. This unusual behaviour was interpreted as an indication of a hydrogarnet-like substitution in vesuvianite. Evidence of a hydrogarnet-like substitution in vesuvianite has also been reported by Henmi *et al.* (1994). The present structure refinement of manganvesuvianite did not show this hydrogarnet-like substitution. Average Si1–O and Si2–O distances (1.639–1.646 Å) are in the same range as found for many vesuvianites in

the literature (see Fig. 6 of Groat *et al.*, 1992a) and tetrahedral vacancies could also not be identified. The $Y3A,B$ octahedra accept about twice as much Mn as the $Y2A,B$ octahedra (Table 3). In addition, mean $Y3A,B-O$ distances are slightly longer than $Y2A,B-O$ distances (Table 4). The mean $Y3A-O$ distance is significantly longer than the corresponding $Y3B-O$ distance. As shown by neutron diffraction of a $P4/n$ vesuvianite of the approximate composition $Ca_{19}Mg_2Al_{10}Fe^{3+}Si_{18}O_{69}(OH)_9$ (Pavese *et al.*, 1998) the $Y3$ sites are also the preferred positions for octahedral Mg^{2+} . Because Al and Mg have very similar scattering power for X-rays these elements cannot be distinguished in routine structure refinements. The larger size of $Y3A$ compared to $Y3B$ (Table 4) may be interpreted by incorporation of divalent cations (mainly Mg with minor Mn^{2+}) on $Y3A$. The $Y'1A$ and $Y'1B$ sites are partially occupied (67.2(8) and 32.8%, respectively) by Mn^{3+} leading to a characteristic Jahn-Teller distortion for the $Y'1A$ site with $Mn^{3+}-O$ distances of 1.975(4) Å forming the base and 2.125(7) Å forming the height of the square pyramid.

Tweddillite

General aspects of epidote-group crystal chemistry

The crystal structure of monoclinic epidote-group minerals (space group $P2_1/m$) comprises di- (Si_2O_7) and ortho-silicate (SiO_4) units linked to two kinds of chains (parallel to the b axis) built by

edge-sharing octahedra. One chain consists of $M2$ octahedra while the other chain comprises $M1$ octahedra with $M3$ octahedra attached on alternate sides along its length. An OH-group is bonded to $M2$ octahedra. This arrangement gives rise to two types of cavities, a smaller one named $A1$, occupied by Ca and Mn^{2+} (nine-coordinated by oxygen), and a larger one named $A2$, occupied by Ca, Sr, Pb and REE (ten-coordinated by oxygen). Table 5 lists the chemical characteristics of all minerals in this group. If we exclude the REE^{3+} members of the epidote-group, substitution of octahedral Al by Fe^{3+} , Mn^{3+} , V^{3+} occurs preferentially on $M3$. An exception is the new mineral tweddillite with (Mn^{3+}, Fe^{3+}) on $M3$ and $M1$.

Name and definition

The name is in honour of the first curator of the Museum of the Geological Survey at Pretoria, Republic of South Africa, Samuel Milbourn Tweddill FGS, who ran the Museum from 1897 to 1916.

Tweddillite is an epidote-group mineral; closely related to strontioepimontite, but normalized to 8 cations, tweddillite has $Mn^{3+} + Fe^{3+} > 1.5$ p.f.u. and $Mn^{3+} > Fe^{3+}$. Tweddillite is the first epidote-group mineral that has in its end-member composition 2 ($Mn^{3+} + Fe^{3+}$) p.f.u. ($Mn^{3+} + Fe^{3+}$) occupy the $M1$ and $M3$ sites whereas $M2$ is occupied by Al. The simplified formula is $CaSr(Mn^{3+}, Fe^{3+})_2Al[Si_3O_{12}](OH)$.

TABLE 5. Cation distribution and O4 occupancy in monoclinic epidote-group minerals (space group $P2_1/m$).

Name	A1	A2	M1	M2	M3	O4
Clinozoïste	Ca	Ca	Al	Al	Al	O
Epidote	Ca	Ca	Al	Al	Fe^{3+}	O
Mukhinite	Ca	Ca	Al	Al	V^{3+}	O
Hancockite	Ca	Pb	Al	Al	Fe^{3+}	O
Piemontite	Ca	Ca	Al	Al	Mn^{3+}	O
Strontioepimontite	Ca	Sr	Al	Al	Mn^{3+}	O
Tweddillite	Ca	Sr	Mn^{3+}	Al	Mn^{3+}	O
<i>REE</i> -bearing minerals of the epidote-group						
Dissakisite	Ca	REE^{3+}	Al	Al	Mg	O
Allanite	Ca	REE^{3+}	Al	Al	Fe^{3+}	O
Androsite	Mn^{2+}, Ca	REE^{3+}	Mn^{3+}	Al	Mn^{2+}	O
Khrstovite	Ca	REE^{3+}	Mg	Al	Mn^{2+}	F
Dollascite	Ca	REE^{3+}	Mg	Al	Mg	F

