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10.1180/mgm.2024.68

Manganonewberyite, $\text{Mn}(\text{PO}_3\text{OH})(\text{H}_2\text{O})_3$, the manganese analogue of newberyite from the Cassagna mine, Italy

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Abstract

The new mineral manganonewberyite (IMA2024-004), $\text{Mn}(\text{PO}_3\text{OH})(\text{H}_2\text{O})_3$, was found underground at the Cassagna mine, Liguria, Italy, where it is a secondary phase formed by the interaction of bat guano with Mn-rich rock. Manganonewberyite occurs with niahite, kutnohorite, sampleite and serrabrancaite on a tinzenite-quartz-braunite matrix. Crystals are prisms and blades, up to about 0.15 mm long, elongated parallel to [001], flattened on {100} and exhibiting the forms {100}, {010} and {111}. Crystals are colourless and transparent, with vitreous lustre and white streak. The mineral is brittle with curved fracture. The Mohs hardness is about 3. Cleavage is perfect on {010}. The density is $2.34(2) \text{ g}\cdot\text{cm}^{-3}$. Optically,

manganonewberyite is biaxial (+) with $\alpha = 1.541(2)$, $\beta = 1.547(2)$ and $\gamma = 1.559(2)$ (white light). The $2V$ is $71.6(3)^\circ$. The optical orientation is $X = \mathbf{a}$, $Y = \mathbf{b}$, $Z = \mathbf{c}$. The empirical formula is $(\text{Mn}_{0.960}\text{Mg}_{0.016}\text{Ca}_{0.015})_{\Sigma 0.991}(\text{H}_{1.02}\text{P}_{1.00}\text{O}_4)(\text{H}_2\text{O})_3$. Manganonewberyite is orthorhombic, space group $Pbca$, with cell parameters: $a = 10.4273(6)$, $b = 10.8755(8)$, $c = 10.2126(4)$ Å, $V = 1158.13(11)$ Å³ and $Z = 8$. The crystal structure ($R_1 = 2.79\%$ for $892 I > 2\sigma_I$ reflections) is the same as that of newberyite with Mn in place of Mg.

Keywords: manganonewberyite; new mineral; newberyite; crystal structure; Raman spectroscopy; Cassagna mine, Liguria, Italy

Introduction

There are about 60 minerals that have been first described from deposits related to bat or bird guano. Considering the contrasting behaviors of bats and birds, it should come as no surprise that bat guano deposits generally occur in enclosed spaces, such as caves and mines, whereas bird guano deposits generally form in exposed areas. Significantly more than half of first descriptions of guano minerals are from bat guano deposits. The earliest recorded of these are nitrocalcite, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and nitromagnesite, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, which were described from the Nicajack Cave in Marion County, Tennessee, USA (Romé de Lisle, 1783). The first new mineral to be described as forming from the reaction of bat excrement in a mine was rowleyite (Kampf *et al.*, 2017) as, up to that point, all bat guano derived minerals had been described from caves. However, it should be noted that rouaite, $\text{Cu}_2(\text{NO}_3)(\text{OH})_3$, discovered in the Roua copper mines, Daluis, France, has been conjectured to have derived its nitrate from guano (Sarp *et al.*, 2001) and this may also be the case for its dimorph gerhardtite, $\text{Cu}_2(\text{NO}_3)(\text{OH})_3$, discovered in the United Verde mine, Jerome, Arizona, USA (Wells and Penfield, 1885).

Newberyite, $\text{Mg}(\text{PO}_3\text{OH})\cdot 3\text{H}_2\text{O}$, was described from bat guano in the Skipton Caves, Victoria, Australia (vom Rath, 1879). Herein, we describe the new mineral manganonewberyite, $\text{Mg}(\text{PO}_3\text{OH})\cdot 3\text{H}_2\text{O}$, the Mn analogue of newberyite, from the Cassagna manganese mine in Liguria, Italy. The new mineral and the name have been approved by the International Mineralogical Association (IMA2024-004; Warr symbol: Mnew). The description is based upon one holotype specimen and one cotype specimen deposited in the collections of the Natural History Museum of Los Angeles County, 900 Exposition Boulevard, Los Angeles, CA 90007, USA, catalogue numbers 76311 and 76312.

Occurrence

Manganonewberyite was found by one of the authors (FC) in an underground gallery of the Cassagna mine, Graveglia Valley, Ne, Genoa Province, Liguria, Italy ($44^\circ 20' 8''\text{N}$, $9^\circ 28' 31''\text{E}$). The manganese deposit exploited by the Cassagna mine was discovered in 1877, along with several other manganese deposits in the Graveglia Valley. Manganese mining in the mines began in 1881 and operations at the Cassagna mine ended in 1998. The underground workings are extensive and there is a more recent large open pit. The manganese ores (mainly braunite intermixed with quartz) occur in stratiform layers, massive lenses and boudins near the base of the Monte Alpe Chert Formation, which overlies the ophiolitic basement. In the final tectono-metamorphic stage of the formation of these deposits, hydrothermal fluids circulated through systems of extensional fractures resulting in polyphase mineral assemblages.

Manganonewberyite occurs with niahite, kutnohorite, sampleite and serrabrancaite on a tinzenite-quartz-braunite matrix. Considering the mineral association and the fact that bats are plentiful in the gallery in which the material was found, the formation of

manganonewberyite can clearly be attributed to the interaction of bat guano with the Mn-rich rock.

Physical and optical properties

Manganonewberyite crystals are colourless prisms and blades, up to about 0.15 mm long, occurring as individuals and in irregular groupings (Figs. 1 and 2). Crystals are elongated parallel to [001], are more or less flattened on {100} and exhibit the forms {100}, {010} and {111} (Fig. 3). The mineral is transparent and has white streak. The mineral does not fluoresce in long- or short-wave ultraviolet light. The Mohs hardness is about 3 based on scratch tests. Crystals are brittle with curved fracture. Cleavage is perfect on {010}. The density measured by flotation in a mixture of methylene iodide and toluene is $2.34(2) \text{ g}\cdot\text{cm}^{-3}$. The calculated density is $2.337 \text{ g}\cdot\text{cm}^{-3}$ for the empirical formula and $2.351 \text{ g}\cdot\text{cm}^{-3}$ for the ideal formula, in both cases using the single-crystal cell. At room temperature, the mineral is insoluble in H_2O and dissolves easily in dilute HCl.

Optically, manganonewberyite is biaxial (+) with indices of refraction $\alpha = 1.541(2)$, $\beta = 1.547(2)$ and $\gamma = 1.559(2)$ measured in white light. The $2V$ determined from extinction data analysed with EXCALIBRW (Gunter *et al.*, 2004) is $71.6(3)^\circ$; the calculated $2V$ is 71.0° . No dispersion was observed and the optical orientation is $X = \mathbf{a}$, $Y = \mathbf{b}$, $Z = \mathbf{c}$. The mineral is nonpleochroic. The Gladstone-Dale compatibility index (Mandarino, 2007) is 0.007 for the empirical formula and 0.011 for the ideal formula, in both cases in the range of superior compatibility.

Raman spectroscopy

Raman spectroscopy was conducted on a Horiba XploRA PLUS using a 532 nm diode laser, 200 μm slit, 1800 grooves/mm diffraction grating and a $100\times$ (0.9 NA) objective.

Because the mineral is very sensitive to the laser, low power (~2 mW) was used, which provided a very noisy spectrum. The Raman spectrum of manganonewberyite is very similar to that of newberyite (Frost *et al.*, 2011). It is dominated by the stretching and bending vibrations of HPO₄ tetrahedra and O–H stretching vibrations. The spectrum from 3900 to 70 cm⁻¹ shown in Figure 4 includes band assignments based on Frost *et al.* (2011).

Composition

Electron probe microanalyses (EPMA; 7 points) were performed at Caltech on a JXA-iHP200F electron microprobe in WDS mode. Analytical conditions were 15 kV accelerating voltage, 10 nA beam current and 5 μm beam diameter. Insufficient material is available for the determination of H₂O, so it is calculated based on the structure. No beam damage was observed during analyses; however, as is common for highly hydrated minerals, much of the H₂O in manganonewberyite was lost under vacuum. Analysis under milder conditions using EDS under ambient pressure is unlikely to yield accurate results. The loss of H₂O resulted in much higher concentrations for the remaining constituents than are to be expected for the fully hydrated phase; therefore, the other analyzed constituents have been normalized to provide a total of 100% when combined with the calculated H₂O content. Analytical data are given in Table 1. The empirical formula based on 1 P and 7 O *apfu* is (Mn_{0.960}Mg_{0.016}Ca_{0.015})_{Σ0.991}(H_{1.02}P_{1.00}O₄)(H₂O)₃. The simplified formula is (Mn,Mg,Ca)(PO₃OH)(H₂O)₃ and the ideal formula is Mn(PO₃OH)(H₂O)₃, which requires MnO 34.61, P₂O₅ 34.63, H₂O 30.76, total 100 wt%.

X-ray crystallography and structure refinement

X-ray powder diffraction data were recorded using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromatized MoK α radiation. A Gandolfi-like

motion on the φ and ω axes was used to randomize the sample. Observed d -values and intensities were derived by profile fitting using JADE Pro software (Materials Data, Inc.). The powder data are presented in Table 2. The unit-cell parameters refined from the powder data using JADE Pro with whole-pattern fitting (space group $Pbca$) are $a = 10.430(8)$, $b = 10.875(8)$, $c = 10.210(7)$ Å, $V = 1158.1(15)$ Å³.

Single-crystal X-ray studies were done on the same diffractometer and radiation noted above. The Rigaku CrystalClear software package was used for processing the structure data, including the application of an empirical absorption correction using the multi-scan method with ABSCOR (Higashi, 2001). The structure was solved using the intrinsic-phasing algorithm of SHELXT (Sheldrick, 2015a). SHELXL-2016 (Sheldrick, 2015b) was used for the refinement of the structure. After the solution of the structure, atom positions were transformed to correspond to those reported for the structure of synthetic $\text{Mn}(\text{PO}_3\text{OH})(\text{H}_2\text{O})_3$ (Cudennec *et al.*, 1989). The occupancy of the Mn site refined to 0.971(3), which is consistent with the site also containing small amounts of Mg and Ca, as suggested by the EPMA. Difference Fourier syntheses located all H atom positions, which were then refined with soft restraints of 0.82(3) Å on the O–H distances and 1.30(3) Å on the H₂O H–H distances. The U_{eq} of the H atom of the (PO₃OH) group set to $\times 1.5$ that of its donor O atom. The U_{eq} of each H atom of the H₂O groups was set to $\times 1.2$ that of its donor O atom. In the final refinement, the Mn site was modelled with Mg and Ca contents corresponding to the EPMA and with the Mn occupancy refined, yielding $(\text{Mn}_{0.952(3)}\text{Mg}_{0.016}\text{Ca}_{0.015})_{\Sigma 0.983}$. Data collection and refinement details are given in Table 3, atom coordinates and displacement parameters in Table 4, selected bond distances in Table 5 and a bond valence analysis in Table 6.

Discussion

Manganonewberyite is isostructural with newberyite (Abbona *et al.*, 1979; Bartl *et al.*, 1983) and, as noted above, corresponds to a known synthetic phase (Cudennec *et al.*, 1989). The $\text{MnO}_3(\text{H}_2\text{O})_3$ octahedra and $\text{PO}_3(\text{OH})$ share their O vertices forming a sheet of alternating octahedra and tetrahedra parallel to $\{010\}$ (Fig. 5). Successive sheets are linked in the $[010]$ direction only by hydrogen bonds (Fig. 6).

The hydrogen positions determined for manganonewberyite are comparable to those reported for the structure of newberyite by both Abbona *et al.* (1979) (based on X-ray diffraction data) and Bartl *et al.* (1983) (based on neutron diffraction data). The hydrogen bonds from OH, OW1 and OW2 are straightforward; however, those from OW3 are more complex. (Note that the earlier studies use different atom labelling.) Abbona *et al.* (1979) propose a single hydrogen bond from H3A to OW2 and a bifurcated hydrogen bond from H3B to OW1 and OW2. On the other hand, Bartl *et al.* (1983) interpret what they refer to as “pseudo-bifurcated” hydrogen bonds from H3A to OW2 and O1 and from H3B to OW1 and OW2, the second bond in each case being longer and weaker. The hydrogen bonds proposed herein are the same as those proposed by Bartl *et al.* (1983). Hydrogen-bond contributions are included in the bond-valence analysis in Table 6. Although the bond-valence sum (BVS) for O1 is somewhat low (1.85 *vu*), other O sites (O, OH and OW) have very reasonable BVS values, providing further support for the proposed hydrogen-bonding scheme.

The unit-cell parameters, densities and optical properties of newberyite and manganonewberyite are compared in Table 7. The unit-cell volume of manganonewberyite is about 6% greater than that of newberyite, a difference that is entirely attributable to the Mn–O vs Mg–O bond lengths. The expansion of the cell in going from newberyite to manganonewberyite is fairly uniform in that the *a*, *b* and *c* cell parameters each increase by about 2%. In a study of synthetic compounds with the newberyite structure, Antraptseva *et al.* (2021) showed that a complete solid solution exists between $\text{Mg}(\text{PO}_3\text{OH})(\text{H}_2\text{O})_3$ and

$\text{Mn}(\text{PO}_3\text{OH})(\text{H}_2\text{O})_3$ and that the increase in the each of the individual cell lengths is linear. They also reported linear increases in the α and γ indices of refraction. (They did not report data on β .) Their values of α and γ for the $\text{Mg}(\text{PO}_3\text{OH})(\text{H}_2\text{O})_3$ and $\text{Mn}(\text{PO}_3\text{OH})(\text{H}_2\text{O})_3$ endmembers are very close to those for newberyite and manganonewberyite, respectively (Table 7).

Acknowledgements

Two anonymous reviewers and Structures Editor Peter Leverett are thanked for their constructive comments on the manuscript. A portion of this study was funded by the John Jago Trelawney Endowment to the Mineral Sciences Department of the Natural History Museum of Los Angeles County.

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FIGURE CAPTIONS

Figure 1. Manganonewberyite prism with blue sampleite on holotype specimen #65733. The field of view is 0.38 mm across.

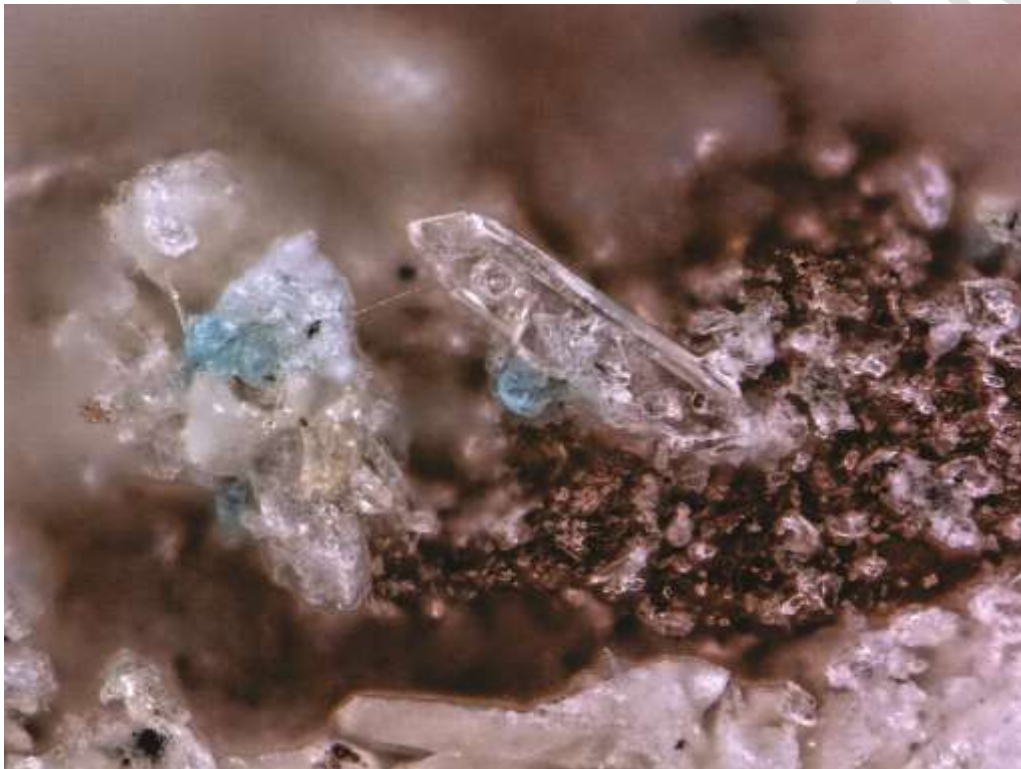


Figure 2. Intergrown colorless blades of manganonewberyite, with cream-coloured niahite and blue sampleite on holotype specimen #65733. The field of view is 0.68 mm across.



Figure 3. Crystal drawings of manganonewberyite prism (left) and blade (right), clinographic projections.

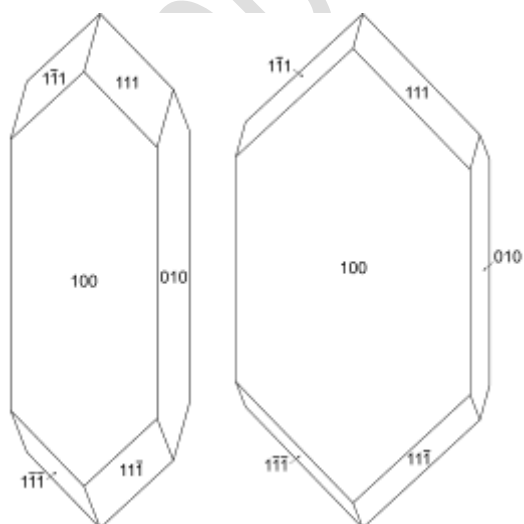


Figure 4. Baseline-corrected Raman spectrum of manganonewberyite recorded with a 532 nm laser.

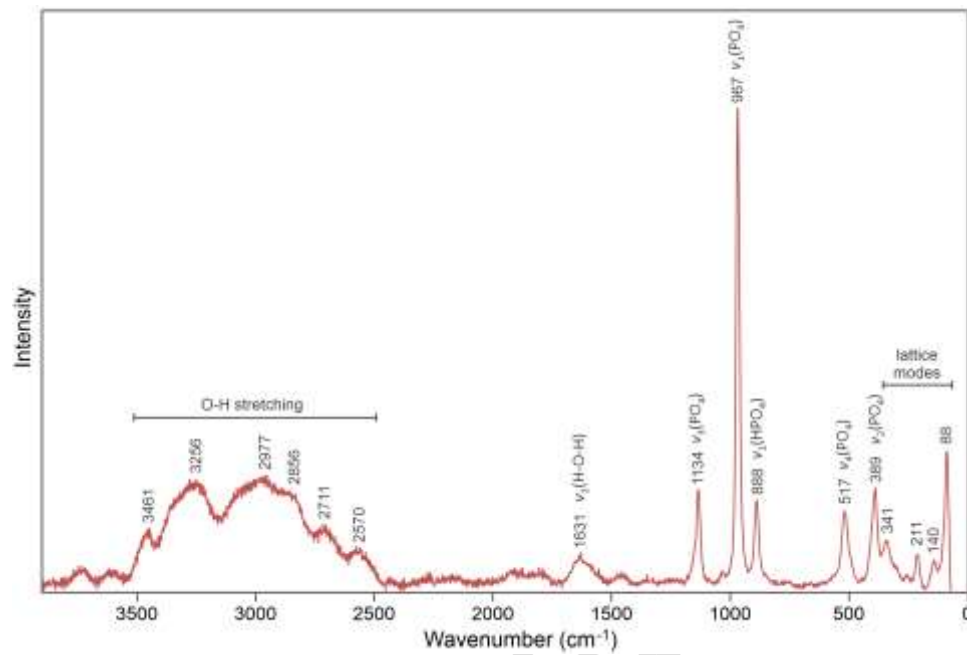


Figure 5. Sheet composed of $\text{MnO}_3(\text{H}_2\text{O})_3$ octahedra and $\text{PO}_3(\text{OH})$ tetrahedra in the structure of manganonewberyite. The unit cell outline is shown with dashed lines.

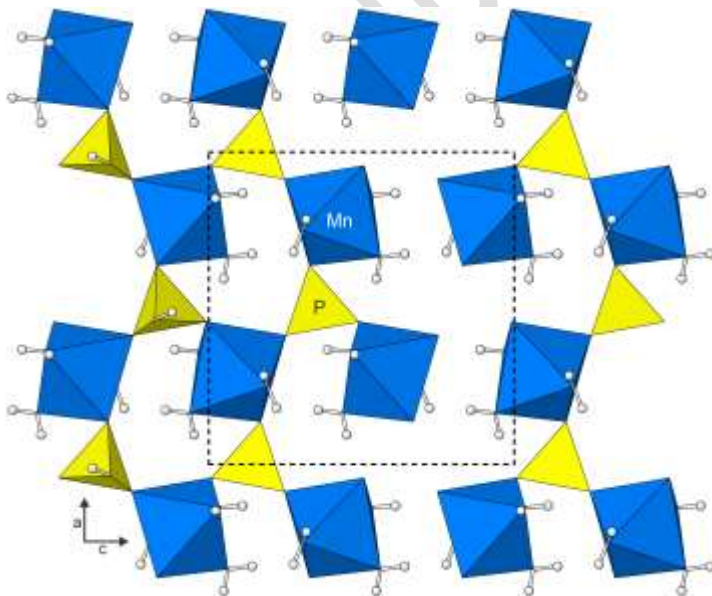


Figure 6. Stacking of polyhedral layers in the structure of manganonewberyite. The hydrogen bonds are shown in red. The unit cell outline is shown with dashed lines.

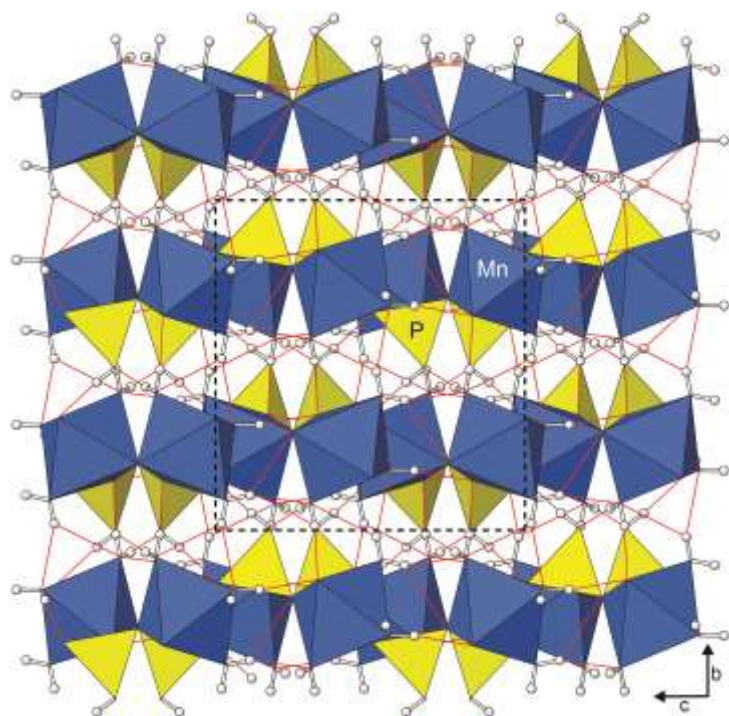


Table 1. Compositional data in wt% for manganonewberyite.

Constituent	Mean	Range	S.D.	Standard	Normalized
MnO	42.00	41.19–42.40	0.42	Mn ₂ SiO ₄	33.41
CaO	0.50	0.30–1.15	0.27	apatite	0.40
MgO	0.40	0.08–1.14	0.38	forsterite	0.32
P ₂ O ₅	43.74	43.53–43.94	0.17	apatite	34.83
H ₂ O*					31.04
Total					100.00

* Based on the structure, i.e., P = 1 and O = 7 *apfu*

Table 2. Powder X-ray diffraction data (d in Å) for manganonewberyite. Only calculated lines with $I > 4.5$ are listed.

I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl	I_{obs}	d_{obs}	d_{calc}	I_{calc}	hkl
44	6.049	6.059	55	1 1 1	29	2.112	2.113	26	2 2 4
78	5.425	5.438	100	0 2 0			2.082	9	1 4 3
82	4.767	[4.800	58	0 2 1	16	2.017	[2.022	16	3 1 4
		4.701	50	2 1 0			2.007	11	2 5 0
86	4.590	4.586	82	1 0 2	22	1.966	[1.975	11	3 4 2
29	4.199	4.226	9	1 1 2			1.965	20	1 5 2
52	3.743	[3.763	36	2 2 0			1.934	7	4 2 3
		3.722	27	0 2 2	20	1.917	[1.925	14	3 2 4
		3.648	13	2 0 2			1.913	8	5 2 1
100	3.517	[3.531	59	2 2 1			1.901	10	5 1 2
		3.506	64	1 2 2	16	1.829	1.832	24	1 4 4
		3.459	6	2 1 2			1.824	5	4 0 4
		3.247	10	1 3 1	19	1.794	[1.799	16	4 1 4
55	3.143	3.149	55	3 1 1			1.790	15	3 3 4
33	3.092	3.102	56	1 1 3	5	1.748	1.753	12	2 4 4
9	3.011	3.030	12	2 2 2	34	1.712	[1.716	13	6 1 0
		2.976	6	2 3 0			1.712	17	2 6 0
46	2.864	[2.873	34	3 0 2	11	1.696	[1.704	18	5 3 2
		2.844	36	1 3 2			1.686	16	1 6 2
60	2.782	2.778	74	3 1 2	13	1.675	1.670	14	4 5 0
		2.757	8	2 1 3			1.634	6	6 2 1
28	2.621	2.627	34	0 4 1			1.629	9	4 3 4
		2.571	5	2 3 2	28	1.625	[1.624	12	0 2 6
6	2.548	2.548	10	1 4 1			1.618	14	2 0 6
		2.460	9	4 1 1	16	1.597	1.598	17	5 1 4
41	2.425	[2.436	14	3 3 1			1.567	5	6 3 0
		2.411	41	2 4 0			1.551	6	2 2 6
9	2.335	2.339	19	1 4 2			1.520	5	1 7 1
		2.271	6	4 1 2	9	1.481	[1.489	5	2 7 0
35	2.253	2.256	35	1 2 4			1.478	8	2 3 6
		2.241	5	2 3 3	18	1.442	1.444	22	5 5 2
		2.220	5	3 2 3			1.424	6	6 1 4
8	2.169	2.180	11	2 4 2	15	1.418	[1.418	10	7 1 2
		2.135	11	4 2 2			1.413	6	4 1 6

Table 3. Data collection and structure refinement details for manganonewberyite.

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation / source	MoK α ($\lambda = 0.71075 \text{ \AA}$)
Temperature	293(2)
Formula from SREF	(Mn _{0.952(3)} Mg _{0.016} Ca _{0.015}) Σ _{0.983} (PO ₃ OH)(H ₂ O) ₃
Space group	<i>Pbca</i> (#61)
Unit-cell dimensions	$a = 10.4273(6) \text{ \AA}$ $b = 10.8755(8) \text{ \AA}$ $c = 10.2126(4) \text{ \AA}$
<i>V</i>	1158.13(11) \AA^3
<i>Z</i>	8
Density (for above formula)	2.332 g cm ⁻³
Absorption coefficient	2.445 mm ⁻¹
<i>F</i> (000)	818.3
Crystal size	150 × 45 × 35 μm
θ range	3.36 to 25.02°
Index ranges	-12 ≤ <i>h</i> ≤ 12, -11 ≤ <i>k</i> ≤ 12, -11 ≤ <i>l</i> ≤ 12
Reflections collected/unique	8345/1021; $R_{\text{int}} = 0.047$
Reflections with $I > 2\sigma_I$	892
Completeness to $\theta = 25.02^\circ$	99.7%
Refinement method	Full-matrix least-squares on F^2
Parameter/restraints	104/10
GoF	1.113
Final <i>R</i> indices [$I > 2\sigma_I$]	$R_1 = 0.0279$, $wR_2 = 0.0653$
<i>R</i> indices (all data)	$R_1 = 0.0329$, $wR_2 = 0.0686$
Largest diff. peak/hole	+0.38/-0.40 e \AA^{-3}

$R_{\text{int}} = \Sigma|F_o^2 - F_o^2(\text{mean})|/\Sigma[F_o^2]$. GoF = $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$. $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
 $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where *a* is 0.0308, *b* is 1.3868 and *P* is $[2F_c^2 + \text{Max}(F_o^2, 0)]/3$.

Table 4. Atom coordinates and displacement parameters (\AA^2) for manganonewberyite.

	x/a	y/b	z/c	U_{eq}		
Mn*	0.29911(4)	0.24720(4)	0.08828(4)	0.01451(19)		
P	-0.00750(7)	0.13223(7)	0.15083(7)	0.0141(2)		
O1	-0.0869(2)	0.20143(19)	0.2478(2)	0.0235(5)		
O2	-0.04329(18)	0.15942(19)	0.00812(18)	0.0189(5)		
O3	0.13663(18)	0.14987(19)	0.17004(18)	0.0190(5)		
OH	-0.0360(2)	-0.0095(2)	0.1765(2)	0.0221(5)		
H	-0.013(3)	-0.051(3)	0.117(3)	0.033		
OW1	0.1637(2)	0.3182(2)	-0.0621(2)	0.0285(6)		
H1A	0.175(3)	0.319(4)	-0.143(2)	0.034		
H1B	0.094(3)	0.289(3)	-0.050(3)	0.034		
OW2	0.2497(2)	0.4191(2)	0.1928(2)	0.0278(6)		
H2A	0.285(3)	0.487(3)	0.179(3)	0.033		
H2B	0.181(2)	0.434(3)	0.226(3)	0.033		
OW3	0.3615(3)	0.0909(2)	-0.0352(2)	0.0368(7)		
H3A	0.356(4)	0.106(3)	-0.112(2)	0.044		
H3B	0.349(4)	0.020(2)	-0.020(3)	0.044		
	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Mn	0.0130(3)	0.0167(3)	0.0139(3)	0.00221(18)	-0.00005(17)	-0.00108(18)
P	0.0126(4)	0.0165(4)	0.0131(4)	-0.0004(3)	0.0012(3)	0.0006(3)
O1	0.0233(12)	0.0270(12)	0.0204(11)	-0.0043(9)	0.0061(9)	0.0042(9)
O2	0.0197(11)	0.0236(12)	0.0133(11)	-0.0009(8)	-0.0017(8)	0.0032(9)
O3	0.0154(11)	0.0224(12)	0.0193(11)	0.0026(8)	-0.0023(8)	-0.0023(9)
OH	0.0261(12)	0.0190(12)	0.0212(11)	-0.0022(9)	0.0066(9)	-0.0024(10)
OW1	0.0198(12)	0.0466(16)	0.0191(11)	0.0088(11)	-0.0003(9)	-0.0074(11)
OW2	0.0207(12)	0.0208(13)	0.0419(14)	-0.0035(11)	0.0120(11)	-0.0012(10)
OW3	0.0627(18)	0.0237(13)	0.0240(13)	-0.0003(11)	0.0047(12)	-0.0003(13)

* Occupancy: Mn_{0.952(3)}Mg_{0.016}Ca_{0.015}

Table 5. Selected interatomic distances (Å) and angles (°) in manganonewberyite.

Mn–O1	2.113(2)	P–O1	1.494(2)	
Mn–O3	2.165(2)	P–O3	1.528(2)	
Mn–O2	2.1682(19)	P–O2	1.5333(19)	
Mn–OW2	2.214(2)	P–OH	1.592(2)	
Mn–OW3	2.214(2)	<P–O>	1.537	
Mn–OW1	2.224(2)			
<Mn–O>	2.183			
<i>Hydrogen bonds</i>				
<i>D–H...A</i>	<i>D–H</i>	<i>H...A</i>	<i>D...A</i>	< <i>DHA</i>
OH–H...O2	0.80(2)	1.83(2)	2.626(3)	174(4)
OW1–H1A...O3	0.83(2)	1.98(3)	2.772(3)	159(3)
OW1–H1B...O2	0.80(2)	2.09(2)	2.856(3)	158(4)
OW2–H2A...O3	0.84(2)	1.95(2)	2.785(3)	173(3)
OW2–H2B...OH	0.81(2)	1.91(2)	2.711(3)	169(3)
OW3–H3A...O1 ($\times\frac{1}{2}$)	0.80(2)	2.58(3)	3.179(3)	132(3)
OW3–H3A...OW2 ($\times\frac{1}{2}$)	0.80(2)	2.30(3)	3.015(3)	149(4)
OW3–H3B...OW1 ($\times\frac{1}{2}$)	0.80(2)	2.24(3)	2.990(3)	157(4)
OW3–H3B...OW2 ($\times\frac{1}{2}$)	0.80(2)	2.64(3)	3.202(3)	128(4)

Table 6. Bond valences (in valence units) for manganonewberyite.

	Mn	P	H	H1A	H1B	H2A	H2B	H3A	H3B	Σ_{anion}
O1	0.41	1.39						0.05		1.85
O2	0.36	1.26	0.27		0.17					2.05
O3	0.36	1.27		0.19		0.19				2.02
OH		1.08	0.73				0.22			2.04
OW1	0.31			0.81	0.83				0.07	2.02
OW2	0.32					0.81	0.78	0.06	0.05	2.02
OW3	0.32							0.89	0.88	2.09
Σ_{cation}	2.08	5.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	

The bond valences for the Mn site is based on full occupancy by Mn. Bond–valence parameters are from Gagné and Hawthorne (2015). Hydrogen–bond strengths are based on O–O distances according to the relation of Ferraris and Ivaldi (1988).

Table 7. Comparison of selected data for newberyite and manganonewberyite.

	Newberyite	Manganonewberyite
Ideal formula	Mg(PO ₃ OH)(H ₂ O) ₃	Mn(PO ₃ OH)(H ₂ O) ₃
Space group	<i>Pbca</i>	<i>Pbca</i>
<i>a</i> (Å)	10.203(3)	10.4273(6)
<i>b</i> (Å)	10.678(4)	10.8755(8)
<i>c</i> (Å)	10.015(3)	10.2126(4)
<i>V</i> (Å ³)	1091.1(6)	1158.13(11)
<i>Z</i>	8	8
Density (g/cm ³)	2.10	2.34(2)
Optical data	Biaxial (+)	Biaxial (+)
α	1.514(3)	1.541(2)
β	1.517(3)	1.547(2)
γ	1.533(3)	1.559(2)
$2V(^{\circ})$	44.8	71.6
References	Bartl <i>et al.</i> , 1983 Palache <i>et al.</i> , 1951	current study

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