



# Pleysteinite, $[(\text{H}_2\text{O})_{0.5}\text{K}_{0.5}]_2\text{Mn}_2\text{Al}_3(\text{PO}_4)_4\text{F}_2(\text{H}_2\text{O})_{10} \cdot 4\text{H}_2\text{O}$ , the Al analogue of benyacarite, from the Hagendorf-Süd pegmatite, Oberpfalz, Bavaria, Germany

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**Abstract.** Pleysteinite,  $[(\text{H}_2\text{O})_{0.5}\text{K}_{0.5}]_2\text{Mn}_2\text{Al}_3(\text{PO}_4)_4\text{F}_2(\text{H}_2\text{O})_{10} \cdot 4\text{H}_2\text{O}$ , is the aluminium analogue of benyacarite, from the Hagendorf-Süd pegmatite, Oberpfalz, Bavaria, Germany. It was found in specimens of altered zwieselite, in association with nordgauite, fluellite, rockbridgeite, pyrite and columbite. Pleysteinite occurs as isolated and small aggregates of colourless, stubby prisms that are typically 10 to 30  $\mu\text{m}$  wide and up to 100  $\mu\text{m}$  long. The crystals are flattened on {010} and bounded by {111}, {100} and {001} planes. The calculated density is 2.34  $\text{g cm}^{-3}$ . Optically, pleysteinite crystals are biaxial (+), with  $\alpha = 1.566(2)$ ,  $\beta = 1.580(2)$ ,  $\gamma = 1.600(2)$  (measured in white light) and  $2V(\text{meas.}) = 80(1)^\circ$ . The empirical formula from electron microprobe analyses and structure refinement is  $[(\text{H}_2\text{O})_{0.50}\text{K}_{0.50}]_2(\text{Mn}_{1.20}\text{Mg}_{0.49}\text{Fe}_{0.27}^{2+}\text{Zn}_{0.05})_{\Sigma 2.01}(\text{Al}_{1.63}\text{Fe}_{0.20}^{3+}\text{Ti}_{0.19}^{4+})_{\Sigma 2.02}(\text{Al}_{0.56}\text{Ti}_{0.44})_{\Sigma 2.02}(\text{PO}_4)_{4.02}[\text{F}_{0.58}\text{O}_{0.31}(\text{OH})_{0.11}]_2(\text{H}_2\text{O})_{10} \cdot 3.92\text{H}_2\text{O}$ . Pleysteinite has orthorhombic symmetry, with space group *Pbca* and unit-cell parameters  $a = 10.4133(8) \text{ \AA}$ ,  $b = 20.5242(17) \text{ \AA}$ ,  $c = 12.2651(13) \text{ \AA}$ ,  $V = 2621.4(4) \text{ \AA}^3$  and  $Z = 4$ . The crystal structure was refined using single-crystal data to  $wR_{\text{obs}} = 0.054$  for 1692 reflections with  $I > 3\sigma(I)$ . The crystal structure contains corner-connected linear trimers of Al-centred octahedra that share corners with  $\text{PO}_4$  tetrahedra to form 10-member rings parallel to (010).  $\text{K}^+$  cations and water molecules are located in the rings. Additional corner-sharing of the  $\text{PO}_4$  tetrahedra with  $\text{Mn}(\text{H}_2\text{O})_4\text{O}_2$  octahedra occurs along [010] to complete the 3D framework structure.

## 1 Introduction

Pleysteinite was found in specimens of altered zwieselite from the Hagendorf-Süd pegmatite mine, Bavaria. The specimens were collected in the 1970s by one of the authors (Erich Keck) from the 64–67 m level of the mine. Energy-dispersive spectroscopic (EDS) analysis of the small prismatic crystals of the mineral indicated that it was most likely the aluminium analogue of the titanium-bearing phosphate mineral benyacarite,

$(\text{H}_2\text{O},\text{K})_2(\text{Mn}^{2+},\text{Fe}^{2+})_2(\text{Fe}^{3+},\text{Ti})_2\text{Ti}(\text{PO}_4)_4(\text{O},\text{F})_2 \cdot 14\text{H}_2\text{O}$  (Demartin et al., 1993, 1997), and this was confirmed from a single-crystal structure determination.

Benyacarite is closely related to two other titanium-bearing phosphate minerals, paulkerrite,  $\text{KTi}(\text{Mg},\text{Mn})_2(\text{Fe}^{3+},\text{Mg},\text{Al},\text{Ti})_2(\text{PO}_4)_4(\text{OH})_3 \cdot 15\text{H}_2\text{O}$  (Peacor et al., 1984) and mantienneite,  $(\text{K}_{0.5}\square_{0.5})\text{Ti}(\text{Mg}_{1.5}\text{Fe}_{0.5}^{3+})_{\Sigma 2}\text{Al}_2(\text{PO}_4)_4(\text{OH})_3 \cdot 15\text{H}_2\text{O}$ ,  $\square = \text{vacancy}$  (Fransolet et al., 1984). Demartin et al. (1993) proposed the general formula

(H<sub>2</sub>O, K)<sub>2</sub>TiM<sub>1</sub>M<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>(O,F)<sub>2</sub> · 14H<sub>2</sub>O for these minerals, which are distinguished by the dominant cations at the *M1* and *M2* sites: Mn<sup>2+</sup> and Fe<sup>3+</sup> in benyacarite, Mg and Fe<sup>3+</sup> in paulkerrite and Mg and Al in mantienneite. A proposal for a paulkerrite group, based on the first-described member, has been submitted to the International Mineralogical Association (IMA) Commission on New Minerals, Nomenclature and Classification (CNMNC). Pleysteinite is the fourth member of the group, with dominant Mn<sup>2+</sup> at the *M1* site and dominant Al at the *M2* and Ti sites. Full characterisation of the mineral led to its approval as a new species by the IMA CNMNC, proposal IMA2022-077. The name is for Pleystein, a municipality in Bavaria located 18 km east of Weiden in the Oberpfalz. The Hagendorf-Süd pegmatite that provided the specimens of pleysteinite is situated near the municipal area of Pleystein. The holotype specimen is housed in the collections of the Mineralogical State Collection Munich (SNSB), with registration number MSM 38032. A cotypic used for optical characterisation and the powder diffraction pattern is housed in the mineralogical collections of the Natural History Museum of Los Angeles County, catalogue number 76271.

## 2 Occurrence and associated minerals

The holotype specimen, Hag500, containing pleysteinite crystals on altered zwieselite (Fig. 1) comes from the Hagendorf-Süd pegmatite, Oberpfalz, Bavaria, Germany (49°39'1" N, 12°27'35" E). The zwieselite specimens are bleached to a very light maroon colour and contain many vugs up to some millimetres in diameter. The fine-grained zwieselite is very soft and sometimes shows a silky lustre. The larger holes contain rockbridgeite, Fe<sup>2+</sup>Fe<sup>3+</sup>(PO<sub>4</sub>)<sub>3</sub>(OH)<sub>5</sub>, and crystals of fluellite, Al<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>F<sub>2</sub>OH · 7H<sub>2</sub>O, up to 1 mm. The smaller vugs contain silky needles of white nordgauite, MnAl<sub>2</sub>(PO<sub>4</sub>)<sub>2</sub>(F,OH)<sub>2</sub> · 5H<sub>2</sub>O, and are lined with colourless equant crystals of pleysteinite up to 0.1 mm. Nordgauite is younger than pleysteinite. Embedded and sometimes protruding into vugs are cubes of pyrite and tiny tabular crystals of columbite which are older than the zwieselite.

## 3 Physical and optical properties

Pleysteinite forms isolated and small aggregates of colourless, stubby prisms on fine-grained zwieselite (Fig. 1). The crystals are typically 10 to 30 μm wide and up to 100 μm long and often display pyramidal terminations (Fig. 2). A feature of the crystals is that they readily cleave into thin tablets parallel to {010} in a vacuum due to dehydration (Fig. 3). The crystals are flattened on {010} and bounded by {111}, {100} and {001} planes (Fig. 2). The calculated density, for the empirical formula and single-crystal unit-cell volume, is 2.34 g cm<sup>-3</sup>.

**Table 1.** Analytical data (wt %) for pleysteinite.

Constituent	Mean	Range	SD	Standard
K <sub>2</sub> O	5.20	4.78–5.54	0.25	Adularite
MnO	9.26	7.97–10.81	1.00	MnSiO <sub>3</sub>
ZnO	0.41	0.23–0.80	0.18	Phosphophyllite
MgO	2.13	1.28–3.19	0.59	Spinel
Al <sub>2</sub> O <sub>3</sub>	12.14	11.09–13.02	0.61	Berlinite
FeO (total)	(3.69)	2.31–5.18	0.94	Hematite
FeO	2.14			
Fe <sub>2</sub> O <sub>3</sub>	1.72			
TiO <sub>2</sub>	5.47	4.98–6.60	0.61	Rutile
P <sub>2</sub> O <sub>5</sub>	31.07	29.45–33.55	1.50	Berlinite
F	2.41	2.04–2.96	0.30	Fluorite
H <sub>2</sub> O*	29.50			
-O≡F	-1.01			
Total	100.44			

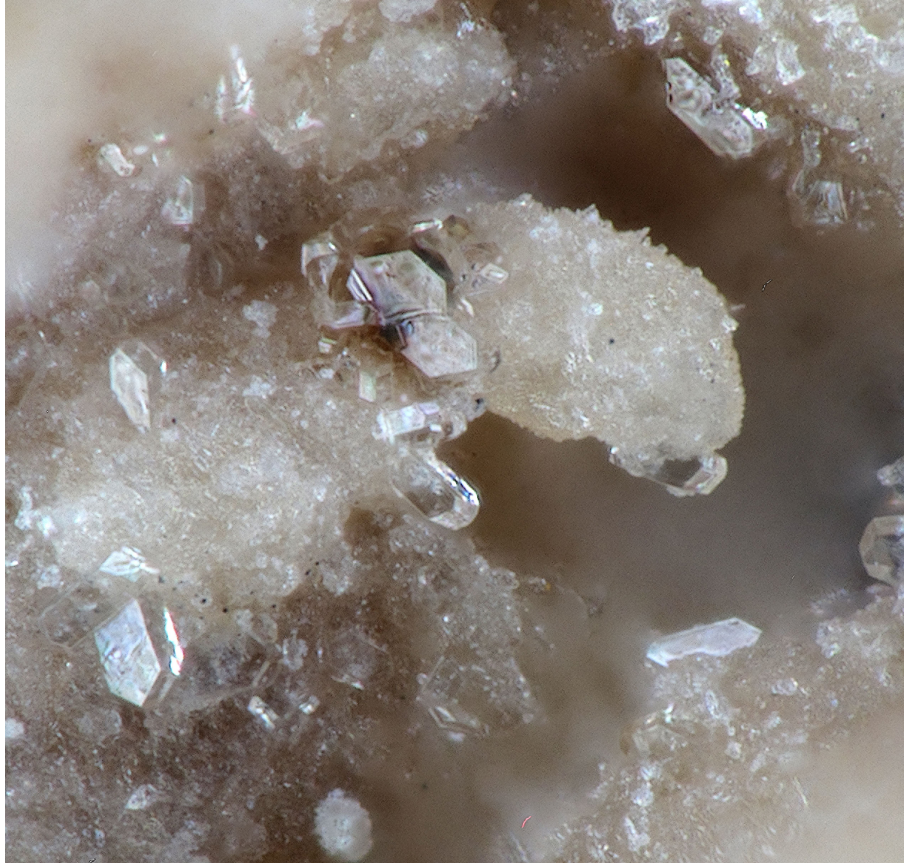
\* Based on the structural formula.

Optically, pleysteinite crystals are biaxial (+), with  $\alpha = 1.566(2)$ ,  $\beta = 1.580(2)$ ,  $\gamma = 1.600(2)$  (measured in white light). The measured  $2V$  from extinction data analysed with EXCALIBR (Gunter et al., 2004) is 80(1)°, and the calculated  $2V$  is 80.7°. Dispersion and pleochroism were not observed. The optical orientation is  $X = c$ ,  $Y = b$ ,  $Z = a$ . The Gladstone–Dale compatibility index (Mandarino, 1981) is -0.019 (superior) based on the empirical formula and the calculated density.

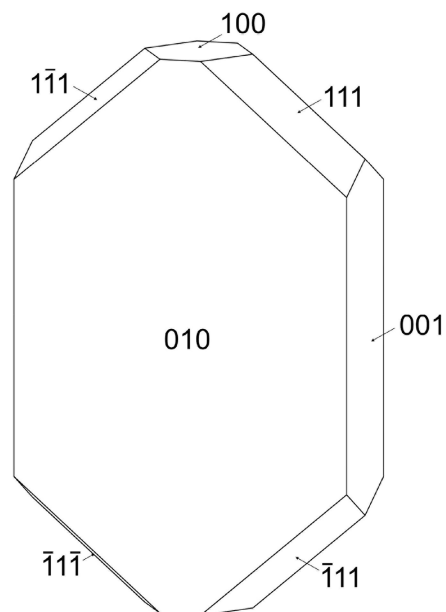
## 4 Chemical composition

Crystals of pleysteinite were analysed using wavelength-dispersive spectrometry on a JEOL JXA-8500F Hyperprobe operated at an accelerating voltage of 15 kV and a beam current of 2.2 nA. The beam was defocused to 10 μm. Analytical results (average of analyses on seven crystals) are given in Table 1. There was insufficient material for direct determination of H<sub>2</sub>O, so it was based upon the crystal structure analysis. The atomic proportions, normalised to 33 anions and with Fe<sup>2+</sup>/Fe<sup>3+</sup> based on the crystal structure ((Fe<sup>2+</sup> with other divalent cations at the *M1* site and remaining iron as Fe<sup>3+</sup> at the *M2* site), are K<sub>1.00</sub>Mn<sub>1.20</sub>Mg<sub>0.49</sub>Fe<sub>0.27</sub><sup>2+</sup>Zn<sub>0.05</sub>Al<sub>2.19</sub>Fe<sub>0.20</sub><sup>3+</sup>Ti<sub>0.63</sub><sup>4+</sup>P<sub>4.02</sub>F<sub>1.16</sub>O<sub>31.84</sub>H<sub>30.06</sub>.

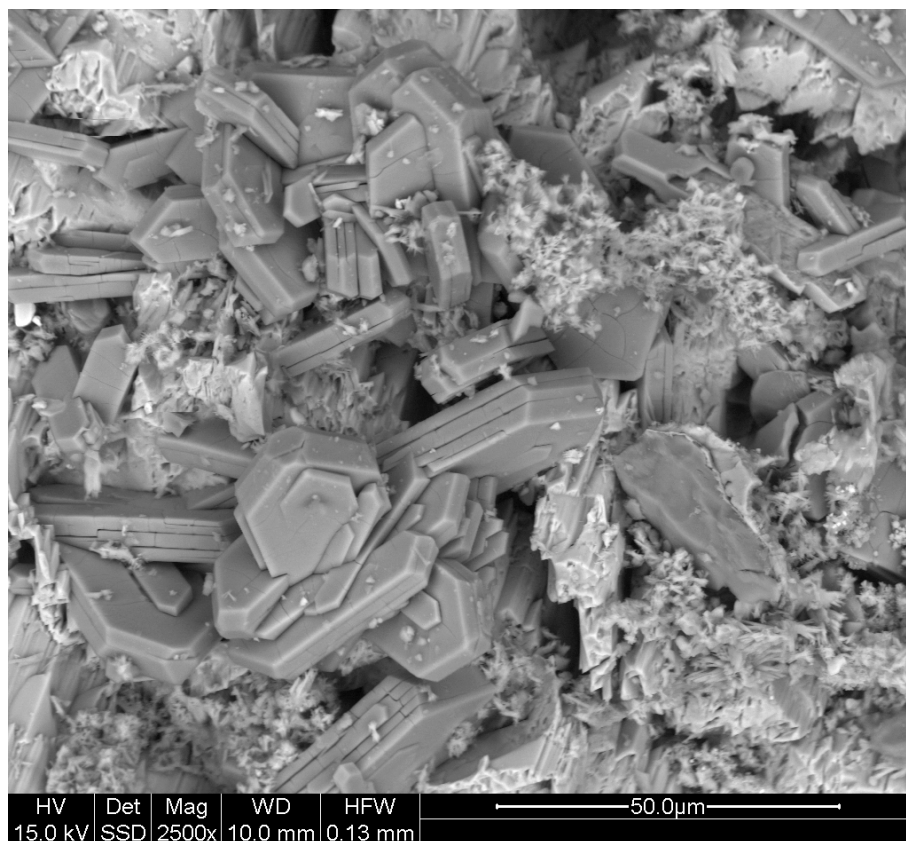
The empirical formula is calculated based on the crystal structure, with divalent cations located at *M1* and with the site assignment at *M3* from the site occupancy refinement, and the remaining small cations from the EMP analyses located at *M2*: [(H<sub>2</sub>O)<sub>0.5</sub>K<sub>0.5</sub>]<sub>2</sub><sup>M1</sup>(Mn<sub>1.20</sub>Mg<sub>0.49</sub>Fe<sub>0.27</sub><sup>2+</sup>Zn<sub>0.05</sub>)<sub>Σ2.01</sub><sup>M2</sup>(Al<sub>1.63</sub>Fe<sub>0.20</sub><sup>3+</sup>Ti<sub>0.19</sub><sup>4+</sup>)<sub>Σ2.02</sub><sup>M3</sup>(Al<sub>0.56</sub>Ti<sub>0.44</sub><sup>4+</sup>)(PO<sub>4</sub>)<sub>4.02</sub>[F<sub>0.58</sub>O<sub>0.31</sub>(OH)<sub>0.11</sub>]<sub>2</sub>(H<sub>2</sub>O)<sub>10</sub> · 3.92H<sub>2</sub>O.



**Figure 1.** Pleysteinite crystals on fine-grained zwieselite. Field of view is 0.5 mm. Photo by Christian Rewitzer.



**Figure 2.** Pleysteinite crystal (photo Christian Rewitzer) with crystal drawing (clinographic projection in nonstandard orientation, a vertical) showing face indexing.



**Figure 3.** Back-scattered electron image of pleysteinite crystals, showing dehydration cleavage in the vacuum of the electron microscope.

The simplified formula is  $[(\text{H}_2\text{O})_{0.5}\text{K}_{0.5}]_2(\text{Mn}, \text{Mg}, \text{Fe}^{2+}, \text{Zn})_2(\text{Al}, \text{Fe}^{3+}, \text{Ti}^{4+})_2(\text{Al}, \text{Ti}^{4+})(\text{PO}_4)_4(\text{F}, \text{O}, \text{OH})_2(\text{H}_2\text{O})_{10} \cdot 4\text{H}_2\text{O}$ .

The ideal formula is  $[(\text{H}_2\text{O})_{0.5}\text{K}_{0.5}]_2\text{Mn}_2\text{Al}_3(\text{PO}_4)_4\text{F}_2(\text{H}_2\text{O})_{10} \cdot 4\text{H}_2\text{O}$ , which requires  $\text{K}_2\text{O}$  5.13,  $\text{MnO}$  15.46,  $\text{Al}_2\text{O}_3$  16.66,  $\text{P}_2\text{O}_5$  30.93,  $\text{F}$  4.14,  $\text{H}_2\text{O}$  29.42,  $-\text{O}\equiv\text{F}$  -1.74, total 100 wt%. Note that the  $\cdot 14\text{H}_2\text{O}$  in the Demartin et al. (1993) general formula has been separated into  $(\text{H}_2\text{O})_{10}$  coordinated at the *M1* and *M2* sites and  $\cdot 4\text{H}_2\text{O}$  molecules occupying cavities, to better reflect the crystal structure.

## 5 Raman spectroscopy

Raman spectroscopy was conducted on a Horiba XploRA PLUS spectrometer using a 532 nm diode laser, 100  $\mu\text{m}$  slit and 1800  $\text{g mm}^{-1}$  diffraction grating and a 100 $\times$  (0.9 NA) objective. The spectrum is shown in Fig. 4. The O–H stretch region has a broad peak that can be assigned to H-bonded water, with a maximum at 3335  $\text{cm}^{-1}$  and a shoulder at 3115  $\text{cm}^{-1}$ . A sharp shoulder at 3560  $\text{cm}^{-1}$  is most likely due to hydroxyls. The H–O–H bending mode region for water has a peak at 1665  $\text{cm}^{-1}$ . The P–O stretching region has strong sharp peaks at 960 and 1015  $\text{cm}^{-1}$  and a weaker peak at 1130  $\text{cm}^{-1}$  with a shoulder at 1095  $\text{cm}^{-1}$ . The two

strong peaks correspond to antisymmetric stretching modes, and the weaker peaks correspond to symmetric P–O stretching modes. Bending modes of the  $(\text{PO}_4)^{3-}$  groups are manifested by two bands centred at 610 and 460  $\text{cm}^{-1}$ . Peaks at lower wavenumbers are related to lattice vibrations. A strong peak at 850  $\text{cm}^{-1}$  with a shoulder at 780  $\text{cm}^{-1}$  is an interesting feature of the spectrum. A tentative assignment is to stretching vibrations for short *M*–(O,F) bonds that occur in linear trimers of corner-connected octahedra *M2*–*M3*–*M2* in the structure (Fig. 5). The potassium titanyl phosphate,  $\text{KTiOPO}_4$ , has chains of corner-connected octahedra with short (1.81–1.83 Å) Ti–O bonds, and the Raman spectrum has an intense band at 770  $\text{cm}^{-1}$  that has been assigned to the symmetric Ti–O stretching vibration (Tu et al., 1996). Strong Raman bands in the range 800 to 900  $\text{cm}^{-1}$  have been reported and assigned to Ti–O stretch vibrations for several potassium titanates, which have corner-connected  $\text{TiO}_6$  octahedra involving short ( $\sim 1.8$  Å) bridging Ti–O bonds (Bamberger et al., 1990). The *M2* site in pleysteinite similarly has the *M2* atom displaced from the centre of the octahedron towards the corner-sharing anion with the *M3* octahedron giving a short (1.825 Å) *M2*–(O,F) bond.

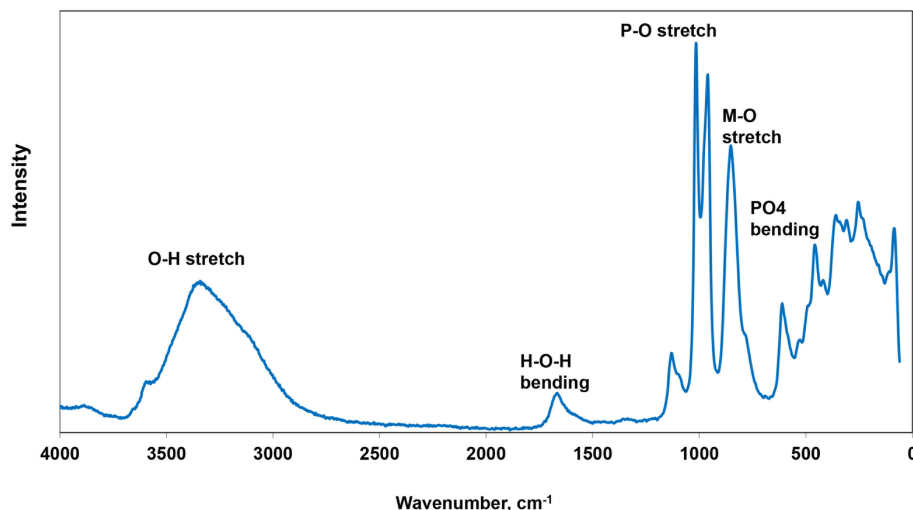


Figure 4. Raman spectrum for pleysteinite.

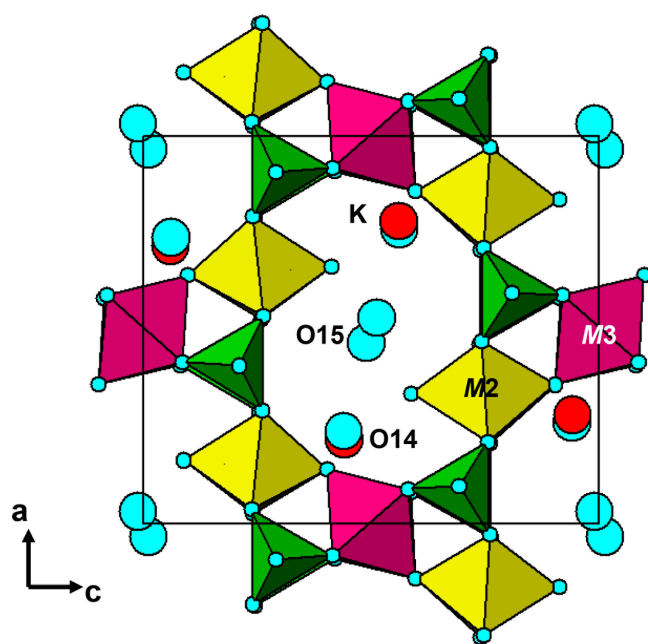


Figure 5. {010} slice of the pleysteinite structure.

## 6 Crystallography

X-ray powder diffraction data were recorded using a Rigaku R-Axis Rapid II curved imaging plate microdiffractometer with monochromatised Mo  $K\alpha$  radiation. A Gandolfi-like motion on the  $\phi$  and  $\omega$  axes was used to randomise the sample. Observed  $d$  values and intensities were derived by profile fitting using JADE Pro software (Materials Data, Inc.). Data are given in Table 2. Refined orthorhombic unit-cell parameters (space group  $Pbca$  (#61)) are  $a = 10.407(4)$  Å,  $b =$

$20.557(8)$  Å,  $c = 12.247(5)$  Å,  $V = 2619.9(7)$  Å<sup>3</sup> and  $Z = 4$ .

Single-crystal diffraction data were collected at room temperature using a Rigaku Oxford Diffraction Supernova four-circle diffractometer equipped with an Atlas CCD detector and using Mo $K\alpha$  radiation ( $\lambda = 0.71073$  Å). Refined unit-cell parameters and other data collection details are given in Table 3.

### Structure refinement

A structural model was obtained in space group  $Pbca$  using SHELXT (Sheldrick, 2015). It was found to be the same as that reported for benyacarite (Demartin et al., 1993). The scattering curve for Mn was used to represent (Mn + Mg + Fe + Zn) at the  $M1$  site, and Fe and Al were located at the  $M2$  site with their occupancies refined. The K + O (for H<sub>2</sub>O) occupancies at the K site were also refined. The mean bond distance for the Ti site ( $\equiv M3$ ) was found to be only 1.91 Å, which is too short for Ti<sup>4+</sup>-O (expected 1.96 Å from bond valence sum (BVS) for an ideal octahedron), and the isotropic displacement parameter was elevated ( $U = 0.03$ ), suggesting replacement by a lighter cation. Al was added to the  $M3$  site and the occupancies of Al/Ti refined, giving dominant Al in the site [Al<sub>0.56(1)</sub>Ti<sub>0.44(1)</sub>].

Refinement with anisotropic displacement parameters for all atoms in JANA2006 (Petříček et al., 2014) converged at  $wR_{\text{obs}} = 0.054$  for 1692 reflections with  $I > 3\sigma(I)$ . Unambiguous location of H atoms in correct configurations for H<sub>2</sub>O molecules in difference Fourier maps was not achieved. Partial H positions have been previously reported for benyacarite (Demartin et al., 1993). Details of the data collection and refinement are given in Table 3. The refined coordinates, equivalent isotropic displacement parameters and bond valence sum (BVS) values (Gagné and Hawthorne, 2015) from

**Table 2.** Powder X-ray diffraction data ( $d$  in Å) for pleysteinite ( $I_{\text{calc}} > 1.5$ ).

$I_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{calc}}$	$hkl$	$I_{\text{obs}}$	$d_{\text{obs}}$	$d_{\text{calc}}$	$I_{\text{calc}}$	$hkl$
49	10.29	10.2621	39	0 2 0			2.1546	2	2 8 2
65	7.41	7.4037	56	1 1 1			2.1108	2	2 3 5
100	6.13	6.1326	100	0 0 2			2.0910	3	2 6 4
43	5.20	5.2843	2	1 0 2	12	2.061	2.0716	3	4 6 0
		5.2066	21	2 0 0			2.0592	3	2 9 1
		5.1823	7	1 3 1			2.0442	7	0 0 6
		5.1311	10	0 4 0	7	2.005	1.9845	5	4 0 4
17	4.67	4.6980	3	1 2 2	29	1.9666	1.9627	15	4 6 2
		4.6671	2	2 1 1			1.9555	3	3 8 2
		4.6432	7	2 2 0			1.9366	2	5 2 2
33	3.944	3.9691	9	2 0 2	12	1.9183	1.9226	2	4 7 1
		3.9353	3	0 4 2			1.9132	2	1 10 2
		3.9253	17	2 3 1			1.9076	2	3 6 4
59	3.699	3.7418	5	1 1 3	5	1.8888	1.8990	5	0 4 6
		3.7018	39	2 2 2			1.8709	8	2 2 6
		3.6546	8	2 4 0	11	1.8542	1.8509	5	4 4 4
7	3.424	3.4207	5	0 6 0			1.8482	4	5 1 3
		3.3257	3	1 3 3	14	1.8317	1.8406	2	2 8 4
69	3.122	3.1176	48	2 5 1			1.8231	6	2 10 2
34	3.050	3.0663	20	0 0 4			1.7841	2	2 4 6
		3.0208	11	3 0 2	11	1.7647	1.7694	3	2 7 5
15	3.004	3.0014	2	3 3 1			1.7614	5	3 0 6
		2.9874	11	0 6 2			1.7576	2	4 7 3
21	2.941	2.9414	15	1 0 4			1.7547	2	0 6 6
		2.9379	2	0 2 4	17	1.7146	1.7166	4	4 6 4
		2.9101	3	2 3 3			1.7104	9	0 12 0
76	2.867	2.8978	4	3 2 2			1.6989	2	4 9 1
		2.8589	30	2 6 0			1.6819	2	5 7 1
21	2.804	2.8276	8	1 2 4	11	1.6652	1.6660	2	3 4 6
		2.7908	12	1 5 3			1.6628	6	2 6 6
37	2.606	2.6421	6	2 0 4	19	1.6467	1.6552	2	2 1 7
		2.6032	16	3 4 2			1.6483	2	6 2 2
		2.5912	11	2 6 2			1.6475	3	0 12 2
9	2.567	2.5587	3	2 2 4			1.6440	7	6 4 0
		2.5518	6	1 4 4	8	1.6236	1.6249	2	2 12 0
24	2.526	2.5272	8	4 1 1			1.6138	2	2 3 7
10	2.490	2.5011	11	2 7 1			1.6118	3	4 10 0
		2.4679	4	3 3 3	15	1.5928	1.5925	2	1 5 7
		2.3668	2	0 8 2			1.5880	9	6 4 2
7	2.349	2.3490	2	2 4 4			1.5818	2	4 9 3
		2.3336	4	4 2 2	9	1.5601	1.5588	6	4 10 2
17	2.308	2.3079	6	1 8 2			1.5477	2	6 6 0
		2.2980	4	3 0 4			1.5465	2	5 3 5
		2.2832	3	0 6 4			1.5249	2	4 7 5
19	2.172	2.1835	2	4 1 3	6	1.5083	1.5104	2	6 0 4
		2.1712	7	4 4 2			1.5051	3	4 11 1
		2.1640	2	4 5 1			1.4937	2	0 12 4

**Table 3.** Crystal data and structure refinement for pleysteinite.

Ideal formula	$[(\text{H}_2\text{O})_{0.5}\text{K}_{0.5}]_2\text{Mn}_2\text{Al}_3(\text{PO}_4)_4\text{F}_2(\text{H}_2\text{O})_{10} \cdot 4\text{H}_2\text{O}$
Formula weight	917.8
Temperature	294 K
Wavelength	0.71073 Å
Space group	<i>Pbca</i> (#61)
Unit-cell dimensions	$a = 10.4133(8)$ Å $b = 20.5242(17)$ Å $c = 12.2651(14)$ Å
Volume	2621.4(4) Å <sup>3</sup>
Z	4
Absorption correction	Gaussian, $\mu = 1.91 \text{ mm}^{-1}$
Crystal size	0.031 × 0.074 × 0.110 mm <sup>3</sup>
Theta range for data collection	2.75 to 30.19°.
Index ranges	$-9 \leq h \leq 13$ , $-26 \leq k \leq 23$ , $-11 \leq l \leq 16$
Reflections collected	18 163
Independent reflections	3310
Reflections with $I_o > 3\sigma(I)$	1692
Refinement method	Full-matrix least squares on <i>F</i>
Data/restraints/parameters	3310/0/199
Final <i>R</i> indices [ $I > 3\sigma(I)$ ]	$R_{\text{obs}} = 0.054$ , $wR_{\text{obs}} = 0.054$
<i>R</i> indices (all data)	$R_{\text{obs}} = 0.114$ , $wR_{\text{obs}} = 0.068$
Largest diff. peak and hole	0.93 and $-0.86 \text{ e Å}^{-3}$

**Table 4.** Atom coordinates, equivalent isotropic displacement parameters (Å<sup>2</sup>) and bond-valence sums (BVSs) for pleysteinite.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>	BVS
M1	0.49486(8)	0.74656(4)	0.24312(7)	0.0202(3)	2.05
M2	0.66101(10)	0.50287(6)	0.74560(9)	0.0140(4)	3.01
M3	0.5	0.5	0.5	0.0155(6)	3.52
P1	0.90897(12)	0.59393(7)	0.80267(11)	0.0123(4)	5.11
P2	0.58548(12)	0.58881(7)	0.29706(12)	0.0140(4)	5.03
K/O	0.71780(19)	0.85351(11)	0.05950(18)	0.0322(9)	0.85
F	0.6415(3)	0.50294(16)	0.5977(2)	0.0210(10)	1.22
O1	0.9028(3)	0.66716(19)	0.8080(3)	0.0199(13)	1.73
O2	1.0279(3)	0.57076(19)	0.7410(3)	0.0193(13)	1.73
O3	0.9099(3)	0.56638(18)	0.9198(3)	0.0152(12)	1.81
O4	0.7881(3)	0.56986(19)	0.7447(3)	0.0172(12)	1.94
O5	0.5921(3)	0.66266(18)	0.2901(3)	0.0203(13)	1.71
O6	0.4631(3)	0.56527(18)	0.2370(3)	0.0145(12)	1.73
O7	0.5820(3)	0.56560(19)	0.4144(3)	0.0197(13)	1.92
O8	0.7071(3)	0.56232(19)	0.2400(3)	0.0202(13)	1.74
O9	0.3455(4)	0.6849(2)	0.1774(4)	0.0298(15)	0.34
O10	0.5823(4)	0.7409(2)	0.0779(3)	0.0258(14)	0.48
O11	0.6447(3)	0.80717(20)	0.3119(4)	0.0288(15)	0.33
O12	0.4009(4)	0.7516(2)	0.4054(4)	0.0298(15)	0.42
O13	0.6639(3)	0.5027(2)	0.9123(3)	0.0242(13)	0.37
O14	0.2614(4)	0.6400(2)	0.4407(4)	0.0333(16)	0.00
O15	0.5328(4)	0.4084(2)	1.0119(4)	0.0453(19)	0.12

Site scattering: M1 = 0.950(4)Mn; M2 = 0.685(6)Al+0.315Fe; M3 = 0.56(1)Al + 0.44Ti;  
K/O = 0.473(9)K + 0.527O.

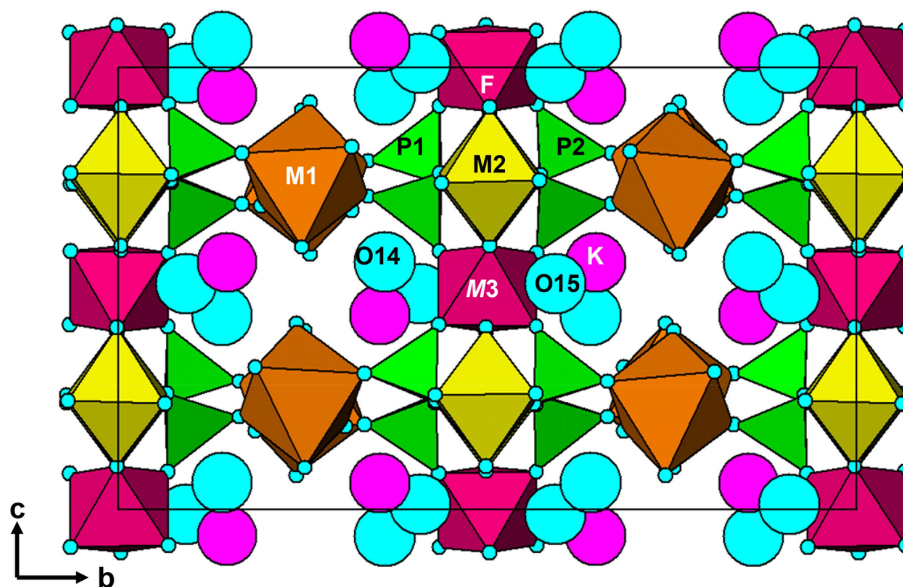


Figure 6. [100] projection of the structure of pleysteinite, made using ATOMS (Dowty, 2006).

the single-crystal refinement are reported in Table 4. Selected interatomic distances are reported in Table 5. Although the H atoms were not located, the BVS values in Table 4 show clearly the presence of seven independent H<sub>2</sub>O molecules, O9 to O15. An indication of H<sub>2</sub>O at the K/O site was obtained by pairs of weak peaks in a difference Fourier map at 0.8 Å from the central atom and making a H–O–H angle of 100°.

## 7 Discussion

The structure comprises [100] chains of alternating corner-connected M<sub>2</sub>O<sub>4</sub>F(H<sub>2</sub>O) octahedra and PO<sub>4</sub> tetrahedra that are connected along [001] by corner-sharing with M<sub>3</sub>O<sub>4</sub>F<sub>2</sub> octahedra into (010) layers shown in Fig. 5. The corner-connected polyhedra form 10-member rings that are occupied by K<sup>+</sup> ions and water molecules, O14 and O15. These layers are interconnected into a 3D framework structure *via* corner sharing of the PO<sub>4</sub> tetrahedra with M<sub>1</sub>O<sub>2</sub>(H<sub>2</sub>O)<sub>4</sub> octahedra, shown in Fig. 6. The K site contains approximately equal amounts of K<sup>+</sup> ions and H<sub>2</sub>O molecules, as found also for benyacarite (Demartin et al., 1993). The K<sup>+</sup>/H<sub>2</sub>O coordination is irregular, with six distances in the range 2.72 to 3.09 Å (Table 5) and two longer distances at ~3.3 Å.

Pleysteinite is isostructural with benyacarite (Demartin et al., 1993). The published orthorhombic unit-cell parameters for paulkerrite and mantienneite suggest that these two minerals also have the same crystal structure as benyacarite. Demartin et al. (1997) proposed a general formula for the three minerals, (H<sub>2</sub>O,K)<sub>2</sub>TiM<sub>1</sub>M<sub>2</sub>(PO<sub>4</sub>)<sub>4</sub>(O,F)<sub>2</sub> · 14H<sub>2</sub>O, with divalent cations, Mn<sup>2+</sup> and Mg<sup>2+</sup> at the M<sub>1</sub> site and trivalent cations, Fe<sup>3+</sup> and Al<sup>3+</sup> at the M<sub>2</sub> site. All three miner-

Table 5. Polyhedral bond lengths [Å] for pleysteinite.

P1–O1	1.506(4)	P2–O5	1.520(4)
P1–O2	1.527(4)	P2–O6	1.549(3)
P1–O3	1.544(4)	P2–O7	1.517(4)
P1–O4	1.528(4)	P2–O8	1.546(4)
<b>avg</b>	<b>1.532</b>	<b>avg</b>	<b>1.533</b>
M1–O1	2.109(4)	K–F	3.088(4)
M1–O5	2.079(4)	K–O4	2.858(4)
M1–O9	2.162(4)	K–O7	2.863(5)
M1–O10	2.224(4)	K–O10	2.717(5)
M1–O11	2.166(4)	K–O12	2.863(5)
M1–O12	2.220(4)	K–O15	2.890(5)
<b>avg</b>	<b>2.160</b>	<b>avg</b>	<b>2.880</b>
M2–F	1.825(3)	M3–F (x2)	1.900(3)
M2–O2	1.972(4)	M3–O3 (x2)	1.925(4)
M2–O4	1.909(4)	M3–O7 (x2)	1.909(4)
M2–O6	1.916(4)	<b>avg</b>	<b>1.911</b>
M2–O8	1.918(4)		
M2–O13	2.045(4)		
<b>avg</b>	<b>1.931</b>		

als have approximately one Ti<sup>4+</sup> cation per formula unit, and this was allocated to the special site (1/2, 1/2, 0) in *Pbca* in the refinement of benyacarite. Our refinement of the pleysteinite crystal structure, however, shows that Al, rather than Ti, is dominant at the Ti site, and the Ti is partitioned between the Ti and M<sub>2</sub> sites. On this basis the formula proposed by Demartin et al. (1997) needs modifying to replace the Ti site with a more general M<sub>3</sub> site. We have also separated the ·14H<sub>2</sub>O in the Demartin formula into (H<sub>2</sub>O)<sub>10</sub> coordinated at the M<sub>1</sub> and M<sub>2</sub> sites and ·4H<sub>2</sub>O molecules occupying cavities, to better reflect the crystal structure. The resulting



formula is  $A_2M_1M_2M_3(PO_4)_4X_2(H_2O)_{10} \cdot 4H_2O$ , where  $A = K, H_2O$  and  $X = O, F, OH$ .

*Data availability.* Crystallographic data for pleysteinite are available in the Supplement.

*Supplement.* The supplement related to this article is available online at: <https://doi.org/10.5194/ejm-35-189-2023-supplement>.

*Author contributions.* IEG oversaw the research and wrote the paper. EK was responsible for the field collection of the specimen. RH and CR obtained preliminary EDS analyses, and CR obtained optical images of the specimen. WGM assisted in the diffraction data analysis. CMM conducted the EMP analyses. ARK measured the optical properties, Raman spectrum, PXRD and crystal morphology. RWG collected the single-crystal diffraction data, and CD prepared polished mounts of the specimen for EMP analyses.

*Competing interests.* The contact author has declared that none of the authors has any competing interests.

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