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Pattersonite, $PbFe_3(PO_4)_2(OH)_4[(H_2O)_{0.5}(OH)_{0.5}]_2$, a new supergene phosphate mineral: description and crystal structure**

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Abstract: Pattersonite, $PbFe_3(PO_4)_2(OH)_4[(H_2O)_{0.5}(OH)_{0.5}]_2$, is a new supergene lead iron(III) phosphate mineral. It was discovered in a single boulder on the dumps of the Grube Vereinigung, near Eisenbach, Taunus, Hesse, Germany. The mineral forms aggregates of dark yellow, subparallel, pinacoidal plates up to 0.5 mm in size, and is accompanied by goethite, kintoreite and (rare) pyromorphite. Pattersonite is translucent, with a very pale yellow streak and adamantine lustre. It is brittle and shows one poor cleavage of unknown orientation, conchoidal fracture, a Mohs hardness of 4½ (VHN_{25} = 530(80) kg/mm^2), and has D(meas.) > 4.04, D(calc.) 4.17 g/cm^3 (from crystal-structure solution). Optically, it is biaxial negative, with α = 1.86(1), β = 1.917 (calc.), γ = 1.93(1), $2V_\alpha$ = 50(5)°. Dispersion is very strong ($r > v$) and the pleochroism is weak, X = nearly colourless to very pale yellow, Y = pale yellow to yellow, Z = yellow to dark yellow (depending on grain size), with absorption $Z > Y > X$. Orientation (polar coordinates in terms of ϕ and ρ based on (010) = 0°/90°) is X (–113°/85°); Y (155°/70°); Z (–10°/21°). Pattersonite is non-fluorescent.

The mineral is triclinic, space group $P\overline{1}$ (No. 2), with a = 5.309(1), b = 7.211(1), c = 7.349(1) Å, α = 87.74(3), β = 86.38(3), γ = 71.40(3)°, V = 266.06(7) Å^3 (single-crystal data), and Z = 1. Strongest lines in the X-ray powder diffraction pattern are [d in Å (I_{calc}) (hkl)]: 4.848 (100) (110), 6.839 (64) (0–10), 3.547 (57) (1–10), 3.417 (52) (0–20), 3.022 (51) (112), 3.667 (47) (00–2), 2.8339 (45) (11–2). The crystal structure was determined from single-crystal X-ray diffraction data (Mo-$K\alpha$, CCD area detector, $R(F)$ = 5.6 %). The chemical formula obtained, $PbFe_3(PO_4)_2(OH)_4[(H_2O)_{0.5}(OH)_{0.5}]_2$, is in good agreement with quantitative electron microprobe analysis which also indicated negligible amounts of impurity elements. The unique crystal structure consists of an interrupted three-dimensional framework based on intersecting zig-zag chains of corner-sharing FeO_6 octahedra, linked by PO_4 tetrahedra. The [8]-coordinated Pb atom is located within elliptical [100] channels. The asymmetric unit contains one unique Pb, three Fe, one P, seven O (two of which represent OH groups and one a mixed $[(H_2O)_{0.5}(OH)_{0.5}]$ ligand with a calculated bond-valence sum of 0.75 valence units) and 3.5 H atoms. The coordination environment of the Pb^{2+} cation can be described as a monoclinically distorted cuboid; the lone electron pair on the cation is not stereochemically active. Average Pb-O, Fe-O and P-O bond lengths are 2.65, 2.02 and 1.53 Å, respectively. Single-crystal laser-Raman spectroscopy is used to describe the vibrational properties.

The new mineral may be considered a dimorph of kintoreite, ideally $PbFe_3(PO_4)_2(OH,H_2O)_6$, a member of the alunite supergroup. The structure is, however, only remotely similar to that of kintoreite. The apparent rarity of the new mineral suggests it may be metastable with respect to kintoreite. The name honours Arthur Lindo Patterson (1902–1966), innovative crystallographer who devised the well-known Patterson method.

Key-words: pattersonite, new mineral, lead iron phosphate, crystal structure, Taunus.

Introduction

In 1986 the mineral collector Peter Schönig of Niederkassel, Germany, discovered unusual yellow tabular crystals in a boulder from the dumps of a small lead-zinc mine in the Taunus region, Germany. In 2001 and 2005, samples were submitted for analysis to one of the authors (G.B.). Preliminary chemical analyses showed that the mineral was a Pb-Fe-phosphate. A powder X-ray diffraction pattern could not be matched to any known mineral or synthetic compound. Subsequent studies confirmed a new mineral species. The mineral and its name have been approved by the IMA Commission on New Minerals and Mineral Names prior to

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publication (IMA 2005-049). The type specimen has been deposited in the collection of the Natural History Museum, Vienna, Austria.

The name honours the innovative crystallographer Arthur Lindo Patterson (1902–1966), who developed a method employing a Fourier series to generate a three-dimensional function, the now well-known "Patterson function" in crystal-structure determination. The Patterson method is still currently being developed, with very convincing results (*e.g.* Burla *et al.*, 2007 a, b).

Occurrence and paragenesis

Pattersonite was found in a single, head-sized boulder collected in 1986 on the dumps of the Grube Vereinigung, near Eisenbach, about 5 km N of Bad Camberg, Taunus, Hesse, Germany. The following information on the history and mineralogy of the mine was kindly provided by Mr. Schönig, the finder of the new mineral.

The Grube Vereinigung is a small ancient lead-silver mine, opened in 1586 and closed in 1901. The dumps were rediscovered by mineral collectors in the mid-1970s. The most important primary mineral is silver-bearing galena which occurs in quartz veins hosted by Devonian slates. Siderite also is present as a gangue mineral. The width of the veins ranges between 30 and 50 cm. Secondary minerals reported from the mine include sulphur, covellite, goethite, minium, tenorite, azurite, cerussite (very common), malachite, anglesite, caledonite, devillite, elyite, lanarkite, langite, leadhillite, linarite, susannite, hinsdalite, kintoreite(-corkite?) (exact As:S ratio undetermined), carminite, pyromorphite (very common) and mimetite. Wittern (2001) lists the additional species arsenbrackebuschite, cuprite and pyrolusite.

Pattersonite was found almost exclusively accompanied by yellow crusts and brown acute rhombohedra of kintoreite (possibly with small SO_4 content) on a matrix of mamillary goethite. Very rarely, white pyromorphite is also present on the samples.

Appearance and physical properties

Pattersonite forms small aggregates composed of dark yellow, subparallel plates. Single crystals are rare, indistinctly tabular (pinacoidal) and up to 0.5 mm in size. Observed forms are: {110} (dominant platy form), {100}, {001} and minor {011}, {0–11}, {–101}. In general, all forms are poorly developed (Fig. 1). The crystals are slightly elongated along [001]. The mineral has a strong tendency to form subparallel to rosette-like intergrowths; no twinning features were observed.

Pattersonite is translucent, with a very pale yellow streak and adamantine lustre. It is brittle, shows one poor cleavage of unknown orientation, conchoidal fracture, a Mohs hardness of $4^1/_2$ (based on measured Vickers microindentation hardness VHN_{25} = 530(80) kg/mm^2, from six individual measurements), and has D(meas.) > 4.04, D(calc.) 4.17 g/cm^3 (from crystal-structure solution). Optically, it is biaxial negative, with α = 1.86(1), β = 1.917 (calc.), γ = 1.93(1), $2V_\alpha$ = 50(5)° (indices measured on grain mounts with Cargille liquids; 2V derived from extinction measurements using a spindle stage). Dispersion is very strong ($r > v$) and the pleochroism is weak, X = nearly colourless to very pale yellow, Y = pale yellow to yellow, Z = yellow to dark yellow (depending on grain size), with absorption $Z > Y > X$. Orientation (polar coordinates in terms of ϕ and ρ based on (010) = 0°/90°) is X (−113°/85°); Y (155°/70°); Z (−10°/21°). Pattersonite is non-fluorescent and insoluble in cold 1:1 HCl.

Fig. 1. SEM micrograph of aggregates of subparallel indistinct tabular pattersonite crystals (globular aggregates at bottom and in centre are goethite).

Table 1. Electron microprobe analysis of pattersonite.

	Wt.%	Range	Stand. dev.
PbO	33.10	31.71-34.73	0.66
Fe_2O_3	35.64	35.11-36.48	0.32
P_2O_5	20.73	19.86-21.54	0.34
H_2O_{calc}*	9.32	9.19-9.51	(0.06)
Total	98.79	97.57-100.22	

* The sums were calculated taking into account 5 OH and 1 H_2O pfu (based on the crystal-structure determination).
Notes: CAMECA SX50 instrument used. WDS scans revealed only negligible trace amounts of impurities. Measurement parameters: 15 kV, 10 nA, 8 μm, 20 s on peak, 20 s on background. Number of analyses = 46. Probe standards: analysed mimetite (Pb), synth. andradite (Fe), synth. $AlPO_4$ (P). The empirical formula is $Pb_{1.00}Fe_{3.02}(PO_4)_{1.98}(OH)_{5.12}(H_2O)_{0.94}$ (based on six cations).

Chemical composition

The chemical composition of pattersonite was determined by a combination of quantitative electron microprobe analysis and crystal structure determination. A direct determination of the water content was not possible due to the meagre amount of material. The analytical data, presented in Table 1 along with measurement parameters used, led to the

empirical formula $Pb_{1.00}Fe_{3.02}(PO_4)_{1.98}(OH)_{5.12}(H_2O)_{0.94}$ (based on six cations). This formula is in good agreement with the formula obtained from the structure solution (see below).

X-ray diffraction

X-ray powder diffraction

X-ray diffraction analysis of powdered pattersonite was carried out with CuK_α radiation, using a Siemens D500 diffractometer (2θ range 10–60°; step size 0.01°, counting time per step 47 s). The indexed powder diffraction data, given in Table 2, show very good agreement with a theoretical powder pattern calculated from the refined structure model (see below). The refined unit-cell parameters, a = 5.307(1), b = 7.209(1), c = 7.349(1) Å, α = 87.75(2), β = 86.36(2), γ = 71.42(1)°, V = 265.9(1) Å^3, are in excellent agreement with those obtained from the single-crystal study (see below).

Single-crystal structure determination

Several small crystal fragments from the type specimen were mounted on a Nonius KappaCCD diffractometer equipped with a 300 μm diameter capillary-optics collimator to provide increased resolution. Preliminary investigations evidenced a strong tendency to form subparallel intergrowths, but gave an unambiguous triclinic unit cell bearing no relation to any known mineral or synthetic compound. Intensity data were collected at 293 K from the most suitable fragment (see Table 3 for details). No systematic absences were observed, and structure factor statistics indicated a centrosymmetric atomic arrangement. The structure was solved (by the Patterson method) and refined in $P\overline{1}$ using SHELXS97 and SHELXL97, respectively (Sheldrick, 1997 a, b). An anisotropic refinement of all non-oxygen atoms led to $R(F)$ = 5.6 % (see Table 3 for further details). The imperfect quality of the crystal fragment and the presence of a strong absorber (Pb) precluded the experimental location of H atoms and an anisotropic refinement of the oxygen atoms [although the latter was possible and led to $R(F)$ = 4.6 %, it resulted in a somewhat unrealistic and similarly elongated shape and orientation of the displacement ellipsoid of all oxygen atoms, and also led to relatively large peaks in the final difference-Fourier map (Table 3)].

The atomic coordinates were normalised using the programme STRUCTURE TIDY (Gelato & Parthé, 1987). The O2 and Ow7 sites were subsequently shifted to symmetry-equivalent positions in order to obtain a connected set of atoms. The final positional and displacement parameters are given in Table 4, and selected bond lengths are listed in Table 5. A bond-valence analysis is presented in Table 6. A list of observed and calculated structure factors can be obtained from the first author.

Crystal structure and topology

Cation coordination and structure connectivity

Pattersonite has a unique framework structure (Fig. 2, 3). The asymmetric unit contains one Pb, three Fe, one P, seven O and 3.5 H atoms. Two of the O atoms represent OH groups, and one a mixed $[(H_2O)_{0.5}(OH)_{0.5}]$ ligand with a calculated bond-valence sum of 0.75 valence units (v.u.). The Pb and Fe atoms are all in special positions while the remaining atoms all occupy general positions. No significant deviation from unit occupancy was observed for any of the non-H atoms.

The three Fe sites are octahedrally coordinated by O atoms. All iron is ferric as shown by bond-valence calculations (Table 6), only minor distortion of the three FeO_6 octahedra, and average Fe-O bond lengths of 2.01 to 2.03 Å (Table 5). The ferric nature of the Fe sites is also in agreement with the conditions of formation of pattersonite (supergene mineral formed in an oxidative environment). The P atoms form fairly regular PO_4 tetrahedra with an average P-O bond length of 1.53 Å and individual bond lengths spanning from 1.526(9) to 1.539(9) Å (Table 5).

The Pb^{2+} cation has eight O neighbours within 2.8 Å; further O atoms are too remote to be considered as ligands (> 3.3 Å). The individual Pb-O bond lengths cover a fairly narrow range from 2.567(8) to 2.772(10) Å, with a mean Pb-O bond length of 2.65 Å. The coordination environment of the Pb^{2+} cation can be described as a monoclinically distorted cuboid (Fig. 4). The lone electron pair on the cation is not stereochemically active, in agreement with the minor bond-length distortion of the PbO_8 polyhedron.

The connectivity in pattersonite is characterised by an interrupted three-dimensional framework of FeO_6 octahedra sharing corners with neighbouring FeO_6 octahedra and PO_4 tetrahedra, as demonstrated in views along the a and c axes (Fig. 2, 3). The [8]-coordinated Pb atom is located within elliptical [100] channels (Fig. 2).

Zig-zag chains of corner-sharing FeO_6 octahedra represent the dominant structural elements. These chains extend along both the b axis (sequence ...-Fe1-Fe3-Fe1-Fe3-...) and the c axis (sequence ...-Fe1-Fe2-Fe1-Fe2-...). PO_4 tetrahedra link the octahedral chains along [110]. A 'layered' character of the polyhedral connectivity is evident in views along [001] (Fig. 3) and [–110] (not shown): (110) layers of FeO_6 octahedra alternate with layers of PO_4 tetrahedra. A noteworthy feature is also a [100] chain formed by $Fe3O_6$ octahedra bridged by PO_4 tetrahedra. This octahedral-tetrahedral chain has the topology of the so-called kröhnkite chain, a widespread structural unit in oxysalts; representatives of the kröhnkite chain form a large family of closely related natural and synthetic compounds (Fleck *et al.*, 2002; Fleck & Kolitsch, 2003; Kolitsch & Fleck, 2005, 2006).

OH groups, water molecules and hydrogen bonding

The O atoms Oh5 and Oh6 represent OH groups, as clearly demonstrated by their bond-valence sums of 1.02 v.u. and

Table 2. X-ray powder diffraction data for pattersonite.

d_{meas} (Å)	d_{calc} (Å)	I_{meas}	I_{calc}	*hkl*
7.345	7.333	11	24	00-1
6.839	6.832	22	**64**	0-10
-	5.049	-	2	0-1-1
-	5.023	-	1	100
4.948	4.949	18	31	0-11
4.848	4.846	100	**100**	110
4.252*	4.252	[8]*	8	101
4.173	4.172	21	26	111
4.045	4.044	13	19	10-1
3.924	3.925	4	4	11-1
3.667	3.666	47	47	00-2
3.547	3.546	44	**57**	1-10
3.417	3.416	34	**52**	0-20
3.364*	3.364	[6]*	6	120
3.257	3.258	2	3	0-1-2
-	3.204	-	1	0-12
3.158	3.158	11	15	1-1-1
3.124	3.124	14	20	121
-	3.120	-	1	0-2-1
3.073	3.073	14	19	0-21
3.041	3.041	21	18	102
3.022	3.022	38	**51**	112
-	2.9946	-	1	12-1
2.8894	2.8881	27	13	10-2
2.8339	2.8348	52	45	11-2
2.6443	2.6445	14	12	210
2.5844	2.5847	14	19	1-12
2.5503	2.5506	1	2	122
2.5402	2.5405	2 *b*	3	211
2.5242	2.5246	4	10	0-2-2
2.5134	2.5143	40 *b*	21	1-1-2
	2.5123		25	200
-	2.4823	-	6	1-20
2.4746	2.4745	11	13	0-22
2.4440	2.4442	11	6	00-3
-	2.4379	-	2	21-1
2.4229	2.4231	13 *b*	9	220
2.4166	2.4164		5	201
-	2.4129	-	6	12-2
2.3764	2.3766	19	26	130
-	2.3598	-	4	1-21
2.3422	2.3426	10 *b*	6	1-2-1
-	2.3378	-	6	20-1
2.3152	2.3161	8	8	0-1-3
-	2.2923	-	3	131
2.2864	2.2868	[14]* *b*	5	0-13
	2.2772		5	0-30
2.2564	2.2566	8	6	22-1
2.2425	2.2429	[7]* *b*	5	113
2.2303	2.2306		5	13-1
2.2133	2.2136	3	5	212
2.1870	2.1872	2	2	0-3-1
-	2.1624	-	1	0-31
2.1521	2.1526	3	2	10-3
2.1267	2.1262	[8]*	12	202
2.0867	2.0861	21*b*	15	222
-	2.0831	-	7	2-11
-	2.0819	-	3	21-2
-	2.0671	-	2	1-22
-	2.0440	-	3	1-2-2
2.0386	2.0389	10*b*	3	1-13
	2.0389		1	2-1-1
	2.0375		11	132
-	2.0320	-	1	123
2.0220	2.0218	13	15	20-2
2.0065	2.0069	4	5	0-2-3
1.9963	1.9967	5*b*	4	231
-	1.9869	-	1	1-1-3
-	1.9691	-	2	0-23
1.9620	1.9625	9	10	22-2
1.9550	1.9533	12*b*	10	13-2
-	1.9521	-	5	0-3-2
1.9341	1.9340	3	3	23-1
1.9265	1.9267	4	3	12-3
-	1.9172	-	2	0-32
1.8855	1.8858	2	3	2-12
1.8638	1.8637	14	13	1-30
-	1.8556	-	1	213
1.8330	1.8331	22*b*	12	00-4
-	1.8307	-	2	232
-	1.8215	-	1	2-1-2
-	1.8078	-	1	1-31
1.8045	1.8047	-	1	1-3-1
-	1.8009	-	1	203
-	1.8003	-	2	140
-	1.7808	-	1	223
-	1.7794	-	1	0-1-4
1.7725	1.7729	5	6	2-20
-	1.7650	-	1	141
-	1.7616	-	3	0-14
1.7600	1.7604	8	6	310
1.7529	1.7532	12	9	114
-	1.7528	-	1	104
-	1.7525	-	4	1-23
-	1.7445	-	1	133
-	1.7407	-	1	21-3
-	1.7382	-	1	23-2
1.7361	1.7369	3*b*	1	320
-	1.7360	-	1	311
-	1.7340	-	1	2-21
1.7150	1.7155	4	3	321
-	1.7122	-	1	2-2-1
1.7071	1.7080	5*b*	7	0-40
-	1.7068	-	1	20-3
-	1.6885	-	1	31-1
-	1.6827	-	2	0-3-3
-	1.6823	-	4	240
1.6788	1.6790	7*b*	5	11-4
1.6739	1.6742	3	1	300
-	1.6707	-	1	0-4-1
-	1.6660	-	2	32-1
1.6635	1.6640	4*b*	4	1-32
-	1.6597	-	1	241
-	1.6587	-	4	1-3-2
-	1.6564	-	1	0-41
-	1.6496	-	1	0-33
-	1.6484	-	1	124
1.6470	1.6473	4	5	1-14
-	1.6457	-	1	2-13
-	1.6288	-	5	0-2-4
1.6272	1.6263	11	10	312
-	1.6205	-	1	24-1
1.6160	1.6157	12	7	330
-	1.6151	-	1	233
-	1.6136	-	1	30-1
1.6133	1.6135	17*b*	7	2-22
-	1.6109	-	1	322
-	1.6106	-	7	1-1-4
1.6022	1.6026	8*b*	7	0-24
-	1.5999	-	1	331
-	1.5916	-	1	14-2
-	1.5824	-	1	2-1-3
1.5789	1.5790	5*b*	7	2-2-2
1.5614	1.5619	8*b*	10	242
-	1.5599	-	6	0-4-2
-	1.5547	-	1	302
-	1.5539	-	1	214
1.5501	1.5505	3	5	31-2

Note: Automated X-ray powder diffractometer; Cu$K\alpha$ radiation.
Indexing based on structure refinement; only reflections with $I_{calc} \geq 1$ are listed.
* Overlap with internal standard (synth. quartz). *b* = broad reflection.

Table 3. Crystal data, data collection information and refinement details for pattersonite.

Crystal data	
Formula	$PbFe_3(PO_4)_2(OH)_4[(H_2O)_{0.5}(OH)_{0.5}]_2$
Formula weight	667.74
Space group, Z	$P\bar{1}$ (No. 2), 1
a, b, c (Å)	5.309(1), 7.211(1), 7.349(1)
α, β, γ (°)	87.74(3), 86.38(3), 71.40(3)
V (Å^3)	266.06(7)
$F(000)$, ρ_{calc} (g·cm^{-3})	309, 4.167
μ (mm^{-1})	20.164
Absorption correction	multi-scan*
Crystal dimensions (mm)	0.03 × 0.05 × 0.08
Data collection and refinement	
Diffractometer	Nonius KappaCCD system
λ (Mo-$K\alpha$) (Å), T (K)	0.71073, 293
Crystal-detector distance (mm)	30
Rotation axis, width (°)	φ, ω, 1.0
Total no. of frames	956
Collect. time per frame (s)	50
Collection mode, $2\theta_{max}$ (°)	sphere, 65
h, k, l ranges	–8 → 8, –10 → 10, –11 → 11
Total reflections measured	3523
Unique reflections	1898 (R_{int} = 4.38 %)
Refinement on	F^2
$R1(F)$, $wR2_{all}(F^2)$**	5.58 %, 14.06 %
'Observed' refls.	1868 [$F_o > 4\sigma(F_o)$]
Extinct. coefficient	0.007(2)
No. of refined parameters	63
GooF	1.285
$(\Delta/\sigma)_{max}$	0.000
$\Delta\rho_{min}, \Delta\rho_{max}$ (e/Å^3)	–3.01, 4.57

Note: Unit-cell parameters were refined from 1821 recorded reflections.
Scattering factors for neutral atoms were employed in the refinement.
* Otwinowski & Minor (1997); Otwinowski *et al*. (2003).
** $w = 1/[\sigma^2(F_o^2) + (0.04P)^2 + 8.5P]$; $P = ([\text{max of } (0 \text{ or } F_o^2)] + 2F_c^2)/3$.

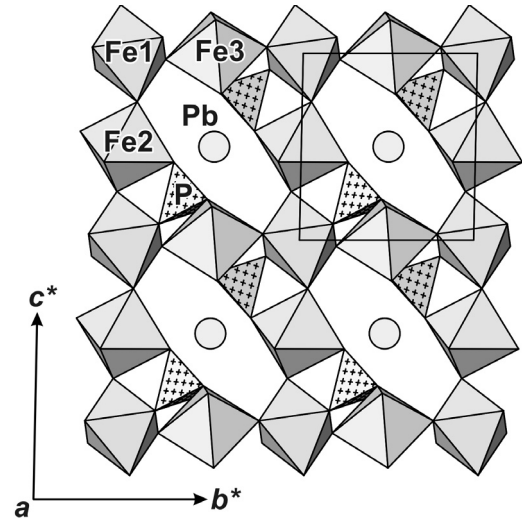

Fig. 2. View of pattersonite along the *a*-axis. Note the interlinked chains of corner-sharing FeO_6 octahedra, the linking PO_4 tetrahedra and the Pb atoms within the elliptical [100] channels. All drawings were done with ATOMS (Shape Software, 1999).

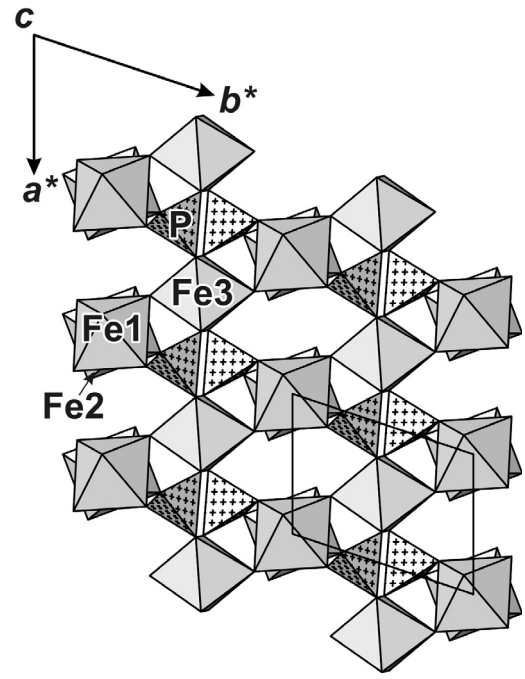

Fig. 3. View of pattersonite along the *c*-axis. Note the kröhnkite-type [100] chain formed by $Fe3O_6$ octahedra bridged by PO_4 tetrahedra. Such chains are the fundamental building unit in a large family of closely related natural and synthetic compounds (Fleck *et al*., 2002; Fleck & Kolitsch, 2003; Kolitsch & Fleck, 2005, 2006).

0.98 v.u., respectively (Table 6). The Ow7 site is noteworthy because it must be occupied by a 50:50 mixture of H_2O and OH in order to achieve a charge-balanced formula [note that Ow7 is located in a general position but the two cations to which it is bonded (Pb, Fe2) are both in special positions]. A calculated bond-valence sum of 0.75 v.u. for Ow7 (Table 6) confirms the inferred occupancy; this sum is intermediate between the bond-valence sums commonly calculated for the oxygen atoms of water molecules (0.00 to about 0.40 v.u.) and the oxygen atoms of hydroxyl groups (1.00 to about 1.40 v.u.).

Probable hydrogen bonds all have donor-acceptor distances > 2.7 Å and therefore have to be considered as weak bonds. The Oh6 group probably donates a hydrogen bond to the O1 atom (Oh6···O1 = 2.71 Å), thus reinforcing the framework along the *a*-axis. The O1 atom is the most undersaturated of all O atoms (1.83 v.u., Table 6). In contrast, the Ow7 site seems to be involved in only very weak hydrogen bonding to O4 (Ow7···O4 = 3.27 Å) and O2 (Ow7···O2 = 3.31 Å). The extremely weak hydrogen bonds donated by the Oh5 group are most likely accepted by the O2 and O3 atoms, both located at distances > 3.4 Å, respectively; these bonds cross the side part of the elliptical void occupied by the Pb atom.

Table 4. Fractional atomic coordinates and displacement parameters (Å^2) for pattersonite.

Atom	x	y	z	U_{eq}/U_{iso}
Pb	0.5	0.5	0.5	0.01253(18)
Fe1	0.0	0.0	0.0	0.0170(4)
Fe2	0.0	0.0	0.5	0.0230(5)
Fe3	0.5	0.5	0.0	0.0148(4)
P	0.0503(5)	0.3543(5)	0.2244(4)	0.0218(6)
O1	0.1548(17)	0.1912(13)	0.0863(11)	0.0212(15)
O2	–0.2259(19)	0.4935(14)	0.1806(13)	0.0271(18)
O3	0.2545(16)	0.4655(12)	0.2197(11)	0.0202(15)
O4	0.0199(19)	0.2705(14)	0.4171(13)	0.0270(18)
Oh5	0.1134(16)	0.0530(12)	0.7402(11)	0.0195(14)
Oh6	0.3606(16)	0.7889(12)	0.0331(11)	0.0196(14)
Ow7*	–0.388(2)	0.1309(18)	0.5814(16)	0.041(2)

Note: Oxygen atoms were refined isotropically. Oxygen atoms of hydroxyl groups are designated as Oh, those of water molecules as Ow.
$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \mathbf{a}_j$ (Fischer & Tillmanns, 1988).
* Mixed $[(H_2O)_{0.5}(OH)_{0.5}]$ position (see text).

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Pb	0.0125(2)	0.0115(2)	0.0117(2)	–0.00024(15)	–0.00072(15)	–0.00119(16)
Fe1	0.0109(8)	0.0309(11)	0.0126(8)	–0.0129(8)	0.0040(6)	–0.0108(8)
Fe2	0.0364(13)	0.0382(13)	0.0087(8)	–0.0057(8)	0.0072(8)	–0.0329(11)
Fe3	0.0085(8)	0.0288(11)	0.0096(8)	–0.0064(7)	0.0011(6)	–0.0091(7)
P	0.0145(12)	0.0432(18)	0.0155(12)	–0.0159(12)	0.0082(9)	–0.0201(12)

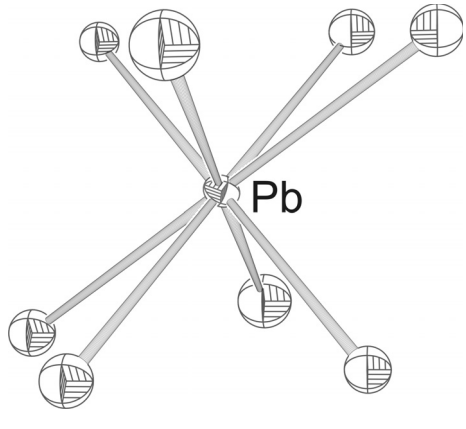

Fig. 4. Stereochemistry of the Pb^{2+} cation in pattersonite (ORTEP-3 for Windows drawing; Farrugia, 1997). The arrangement of the oxygen ligands demonstrates that the lone electron pair on the Pb^{2+} cation is not stereochemically active.

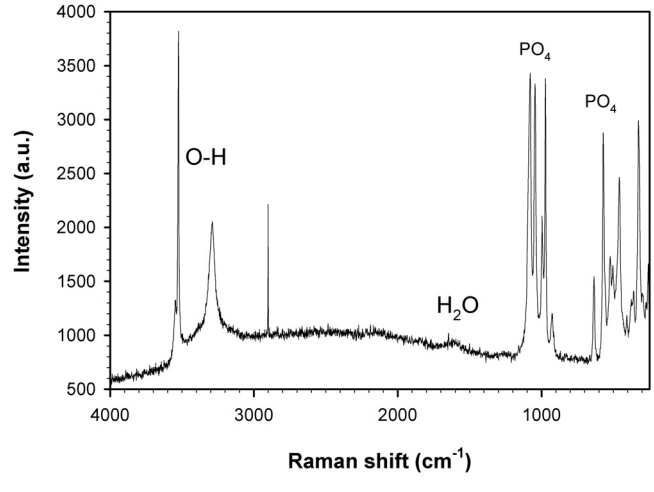

Fig. 5. Representative laser-Raman spectrum of a pattersonite fragment (see text for band positions and tentative interpretation; note: the very sharp "peak" at ~ 2900 cm^{-1} is an artefact).

Raman spectroscopy

Laser-Raman spectra of crystal fragments of pattersonite were recorded in the range from 4000 to 200 cm^{-1} with a Renishaw M1000 MicroRaman Imaging System using a laser wavelength of 633 nm and excitation through a Leica DMLM optical microscope (unpolarised laser light, 180° backscatter mode, spectral resolution ± 2 cm^{-1}, minimum lateral resolution ~ 2 μm, random sample orientation). The fragments were stable under the laser beam. A representative spectrum (Fig. 5) shows bands (strong ones are underlined; sh = shoulder, b = broad) due to OH stretching vibrations (at 3547, <u>3526</u>, 3291 b cm^{-1}), H-O-H bending vibrations of water molecules (~ 1610 b cm^{-1}) and vibrations of the PO_4 tetrahedra (ν_1 and ν_3: <u>1084</u> (slightly asymmetric), <u>1046</u>, 996, <u>973</u>, 927 cm^{-1}). The region below 650 cm^{-1} comprises partially overlapped bands assigned to the ν_4 (and ν_2) vibrations of the PO_4 tetrahedra, vibrations of the Fe- and Pb-centred polyhedra, and lattice modes (636, <u>571</u>, 523, 504, <u>460</u>, 407, ~ 377, 360, <u>325</u>, ~ 296, ~ 273, 259 cm^{-1}). The positions of the OH bands agree well with those expected from O···O donor-acceptor

Table 5. Selected bond distances (Å) for the coordination polyhedra in pattersonite.

Pb–O3 (2×)	2.567(8)	P–O1	1.526(9)
–Ow7 (2×)	2.589(12)	–O2	1.535(10)
–O2 (2×)	2.676(9)	–O4	1.537(10)
–O4 (2×)	2.772(10)	–O3	1.539(9)
<Pb–O>	2.65	<P–O>	1.534
Fe1–O1 (×2)	1.958(8)	Fe2–Oh5 (×2)	1.989(8)
–Oh5 (×2)	2.025(8)	–Ow7 (×2)	2.035(12)
–Oh6 (×2)	2.052(8)	–O4 (×2)	2.054(10)
<Fe2–O>	2.012	<Fe2–O>	2.026
Fe3–Oh6 (×2)	1.995(8)		
–O2 (×2)	2.019(9)		
–O3 (×2)	2.068(8)		
<Fe3–O>	2.017		

Table 6. Bond-valence analysis for pattersonite.

	Pb	Fe1	Fe2	Fe3	P	Sum
O1		$0.584^{\downarrow\times2}$			1.235	1.82
O2	$0.233^{\downarrow\times2}$			$0.495^{\downarrow\times2}$	1.205	1.93
O3	$0.292^{\downarrow\times2}$			$0.434^{\downarrow\times2}$	1.192	1.92
O4	$0.192^{\downarrow\times2}$		$0.450^{\downarrow\times2}$		1.199	1.84
Oh5		$0.487^{\downarrow\times2}$	$0.537^{\downarrow\times2}$			1.02
Oh6		$0.453^{\downarrow\times2}$		$0.528^{\downarrow\times2}$		0.98
Ow7*	$0.279^{\downarrow\times2}$		$0.474^{\downarrow\times2}$			0.75*
Sum	1.99	3.05	2.92	2.91	4.83	

Note: Bond-valence parameters used are from Brese & O'Keeffe (1991) (P-O, Fe-O) and Krivovichev & Brown (2001) (Pb-O).
* Mixed $[(H_2O)_{0.5}(OH)_{0.5}]$ position (see text).

distances (see correlation curve established by Libowitzky, 1999).

Relation to other species

Pattersonite can be considered a polymorph of kintoreite, $PbFe_3(PO_4)_2(OH,H_2O)_6$ (ideally $PbFe_3(PO_4)_2(OH)_5(H_2O)$; Pring *et al*., 1995; Kharisun *et al.*, 1997), a Pb-Fe^{3+}-phosphate end-member in the alunite supergroup (rhombohedral). The crystal structures of pattersonite and kintoreite are only weakly related to each other. Crystal morphologies and X-ray powder diffraction patterns of both minerals are very different. The apparent rarity of the new mineral suggests it may be metastable with respect to kintoreite. It is pointed out that the density of pattersonite is also lower than that of kintoreite. The mixed $[(H_2O)_{0.5}(OH)_{0.5}]$ site in the structure (Ow7) may be a "weak element" of the atomic arrangement.

Few other lead oxysalt minerals also contain sites occupied by a 50:50 mixture of H_2O and OH. An example is the arsenate tsumcorite $Pb(Zn,Fe^{3+})_2(AsO_4)_2(OH,H_2O)_2$ (Tillmanns & Gebert, 1973) and isotypic members of the tsumcorite group.

The only other natural Pb-Fe^{3+}-phosphate known is drugmanite, $Pb_2(Fe_{0.78},Al_{0.22})H(PO_4)_2(OH)_2$ (Van Tassel *et al*., 1979; King & Sengier-Roberts, 1988) which has a much higher Pb:Fe ratio and contains kröhnkite-type octahedral-tetrahedral chains (*cf*. Fleck *et al*., 2002).

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