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The crystal structure determination and redefinition of matulaite, $Fe^{3+}Al_7(PO_4)_4(PO_3OH)_2(OH)_8(H_2O)_8{\cdot}8H_2O$

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ABSTRACT

Matulaite was first described by Moore and Ito (1980) from the Bachman mine, Hellertown, Northampton County, Pennsylvania, USA. Its ideal formula was reported as $CaAl_{18}(PO_4)_{12}(OH)_{20}{\cdot}28H_2O$, based on wet-chemical analysis. Re-examination of both existing cotype specimens of matulaite revealed no material matching the powder or single-crystal X-ray diffraction data reported for the species. Other samples examined from the type locality, as well as from the LCA pegmatite in North Carolina, USA, and Fumade, Tarn, France, provided material crystallographically consistent with matulaite: $P2_1/n$, a = 10.604(2), b = 16.608(4), c = 20.647(5) Å, β = 98.848(7)° and Z = 4. Electron microprobe and crystal structure analysis of newly studied material from the type locality showed the ideal formula of matulaite to be $Fe^{3+}Al_7(PO_4)_4(PO_3OH)_2(OH)_8(H_2O)_8{\cdot}8H_2O$. The chemical composition reported by Moore and Ito (1980) was most probably determined on a mixture of mostly kobokoboite and afmite, with lesser amounts of crandallite. As there is no matulaite on any of the existing cotype specimens of the species, the two specimens used to obtain the new chemical analyses, powder and single-crystal X-ray diffraction data and the structure determination are designated as neotypes. The neotypes have also been used to obtain crystal morphology and new measurements of the physical and optical properties of the species. The neotypes and new data have been approved by the CNMNC, proposal 11-F. The crystal structure of matulaite contains seven-member chain segments of AlO_6 octahedra decorated by PO_4 tetrahedra. The PO_4 tetrahedra also link to isolated FeO_6 octahedra, resulting in a 'pinwheel' $Fe(PO_4)_6$ group. The linkage of octahedra and tetrahedra defines a thick layer parallel to {001}. The only linkage between layers is via hydrogen bonding to interlayer water molecules.

Keywords: matulaite, kobokoboite, afmite, crystal structure, redefinition, neotype, hydrous aluminium phosphates, Bachman mine, Hellertown, Pennsylvania, USA, Fumade, Tarn, France.

Introduction

Matulaite was first described by Moore and Ito (1980) from the Bachman mine, Hellertown, Northampton County, Pennsylvania, USA (see also Oswald, 1978). Their characterization included powder and single-crystal X-ray diffraction studies, a wet-chemical analysis, and the determination of optical and physical properties; however, they were unable to find a crystal suitable for structure determination. They reported the ideal chemical formula as $CaAl_{18}(PO_4)_{12}(OH)_{20}{\cdot}28H_2O$. Moore and Ito (1980) reported the mineral to occur also at the Rotläufchen iron mine, Waldgirmes, Germany,

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and in the LCA pegmatite, Gaston County, North Carolina, USA. Since that time, matulaite has been reported from several other localities; however, there have been no further published reports of the chemical composition of the mineral.

In the course of our study of the new mineral afmite (Kampf *et al*., 2011) from Fumade, Tarn, France, we encountered an associated mineral (Fig. 1) that provided powder and single-crystal X-ray diffraction results consistent with matulaite; however, chemical analysis showed it to be an Al phosphate with relatively minor Fe, and no Ca. Due to the very small crystal size, we tried to collect structure data using synchrotron radiation. The structure analysis (R_1 = 14%) revealed the essential details of the structure and showed the ideal formula to be $Fe^{3+}Al_7(PO_4)_4(PO_3OH)_2(OH)_8(H_2O)_8{\cdot}8H_2O$. To further clarify the chemistry of matulaite, we set out to investigate type material and additional material from the type locality.

Examination of specimens from the type locality

Moore and Ito (1980) did not specify depositories for matulaite type material; however, we were successful in locating specimens that they deposited as type material in the US National Museum of Natural History (NMNH), Smithsonian Institution (one large and one small piece; catalogue number 137020), and the Natural History Museum, London (catalogue number BM 1984,138). The specimens have prominent coatings and veinlets of thin white tabular crystals in rosette and sheaf-like spherulitic aggregates (Figs 2 and 3). The matrix consists of fractured chert, impregnated with limonitic material. Radial sprays of reddish brown beraunite needles are also in evidence beneath the white coatings on the larger piece of NMNH #137020. In both pieces of the NMNH cotype, there are gouges in the white coatings where material has been removed, presumably for the wet-chemical analysis reported by Moore and Ito (1980).

Unfortunately, detailed study of the white crystalline coatings on both cotypes by powder X-ray diffraction did not reveal any material matching matulaite. Nearly all of the white material proved to be either afmite, $Al_3(OH)_4(H_2O)_3(PO_4)(PO_3OH){\cdot}H_2O$, (Kampf *et al*., 2011) or kobokoboite, $Al_6(PO_4)_4(OH)_6{\cdot}11H_2O$ (Mills *et al*., 2010). In fact, on the smaller piece of NMNH #137020 we found only kobokoboite and on the larger piece we found only afmite coated in places with crandallite, $CaAl_3(PO_4)_2(OH)_5{\cdot}H_2O$.

We next investigated ten specimens labelled "matulaite" from the Bachman mine (or simply

FIG. 1. A scanning electron microscope image of matulaite plates on cacoxenite from Fumade, Tarn, France. Note that these crystals exhibit slightly different morphology to those from the Bachman mine. The forms observed are {001}, {010} and {120}. Image by Vincent Bourgoin and Jean-Claude Boulliard, Association Jean Wyart, Paris.

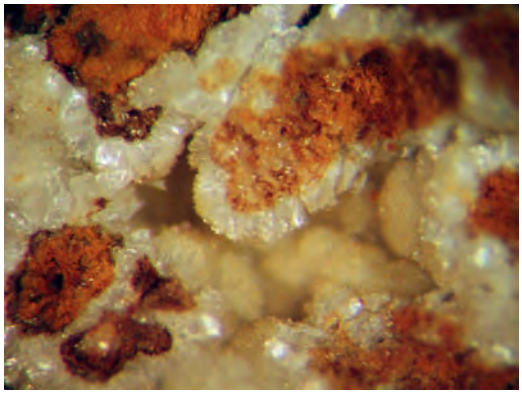

FIG. 2. Kobokoboite plates overgrowing limonitic matrix from the Bachman mine, Hellertown, Pennsylvania, USA. The field of view is 3 mm (NMNH #137020, small piece of the cotype matulaite).

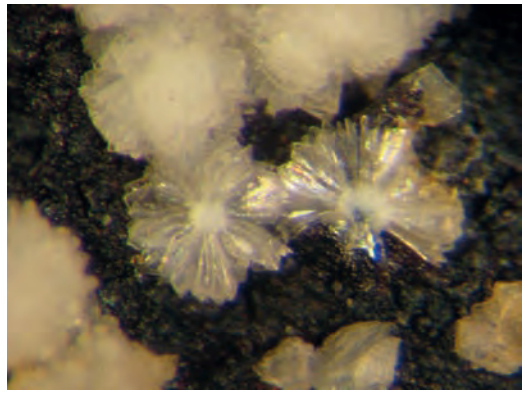

FIG. 4. Radial aggregates of matulaite blades with clusters of diamond-shaped matulaite plates on a dark red-brown goethite crust from the Bachman mine, Hellertown, Pennsylvania, USA. The field of view is 1.5 mm (NHMLAC #28324).

Hellertown) in the collection of the Natural History Museum of Los Angeles County (NHMLAC). Five of these were matulaite, one afmite, two kobokoboite and two crandallite. We also checked three specimens labelled "matulaite" from the LCA pegmatite and determined them all to be matulaite.

One of the Bachman mine matulaite specimens (NHMLAC #28324) provided crystals (Fig. 4) for structure data collection and morphological study (Fig. 5) and material for electron-microprobe analysis. A second specimen (NHMLAC #28323), identical in appearance and provenance, provided material for detailed powder X-ray diffraction analysis (see below). Both specimens are micromounts from the collection of Benjamin J. Chromy, received as a bequest to NHMLAC in 1985.

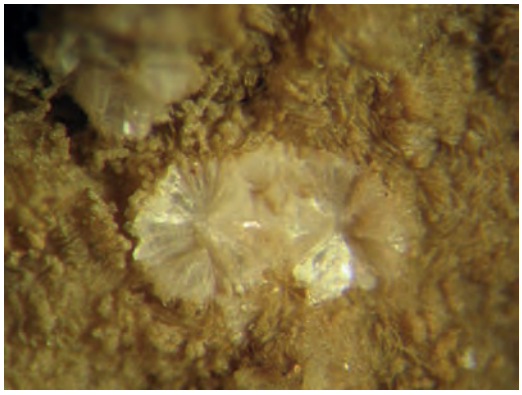

FIG. 3. Radiating aggregates of afmite blades on a thick crust of afmite from the Bachman mine, Hellertown, Pennsylvania, USA. The field of view is 3 mm (NMNH #137020, large piece of the cotype matulaite). Note the buff-coloured surface coating of crandallite.

Chemistry

Chemical analyses (19) were conducted using a Cameca SX100 electron microprobe (EMP) in the Mineralogy Department at the Natural History Museum, London operating in wavelength-dispersive spectrometry (WDS) mode at 20 kV, 10 nA with a 20 μm beam diameter. The small amount of material available did not allow direct determination of H_2O, so it was calculated by stoichiometry from the results of the crystal structure analysis. Rapid loss of H_2O from

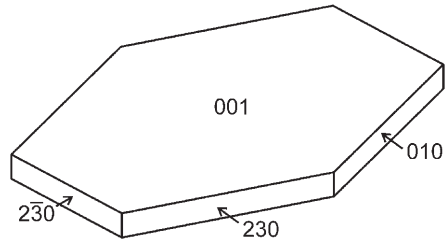

FIG. 5. Crystal drawing of matulaite from the Bachman mine (clinographic projection).

TABLE 1. Chemical analytical data (19 analyses) for matulaite from probe mount BM 2011,100, made from NHMLAC 28324.

Constituent	Wt.%	Range	SD	Probe standard	Number of ions*
Fe_2O_3	7.25	5.00–8.84	1.14	Fayalite	1.078
Al_2O_3	29.69	27.11–32.12	1.52	Corundum	6.915
P_2O_5	35.52	33.25–38.12	1.32	Scandium phosphate	5.943
SiO_2	0.39	0.27–0.57	0.09	Wollastonite	0.077
$H_2O^{\dagger}$	31.86				41.998
Total	104.71				56.011

* Based on 48 oxygen atoms.
† Based on the structure.

TABLE 2. X-ray powder diffraction data for matulaite.

Moore and Ito (1980)		This study		Calculated from structure data		
I_{obs}	d_{obs}	I_{obs}	d_{obs}	d_{calc}	I_{calc}	$h\ k\ l$
100	9.96	100	10.2307	10.2007	100	0 0 2
10	8.45	7	8.6068	8.5443	4	$\bar{1}$ 1 1
40	6.37	8	6.4255	6.3791	7	$\bar{1}$ 2 1
20	6.02	7	6.0825	6.0355	3	1 2 1
30	4.83	10	4.8785	4.8948	2	1 3 0
				4.8656	4	0 3 2
40	4.42	9	4.4428	4.4516	5	$\bar{2}$ 2 1
		11	4.3297	4.3417	2	$\bar{2}$ 1 3
				4.2943	2	1 3 2
20	4.23	2	4.2287	4.2176	3	2 2 1
				3.9551	3	$\bar{2}$ 2 3
30	3.79	7	3.8062	3.8326	2	$\bar{1}$ 4 1
				3.8052	2	2 3 0
30	3.66	16	3.7114	3.7511	2	0 3 4
				3.7032	3	$\bar{2}$ 3 2
				3.6798	2	$\bar{1}$ 4 2
				3.6621	5	0 2 5
10	3.51	3	3.5681	3.5443	1	1 4 2
				3.5437	1	0 4 3
				3.5356	2	1 1 5
10	3.40	7	3.4184	3.4415	2	2 3 2
				3.4112	1	1 3 4
				3.4002	3	0 0 6
				3.3173	3	1 2 5
20	3.24	12	3.2540	3.2569	3	$\bar{3}$ 1 3
				3.2276	1	$\bar{2}$ 3 4
				3.2200	4	0 4 4
30	3.07	15	3.0870	3.1070	1	1 5 1
				3.1031	1	3 1 2
				3.0838	4	$\bar{3}$ 2 3
				3.0764	1	$\bar{2}$ 0 6
				3.0603	1	$\bar{3}$ 1 4

TABLE 2 (*contd*.).

Moore and Ito (1980)		This study		Calculated from structure data		
I_{obs}	d_{obs}	I_{obs}	d_{obs}	d_{calc}	I_{calc}	$h\ k\ l$
				3.0177	4	2 4 2
				2.9539	3	3 3 0
				2.9414	1	$\bar{3}$ 3 2
				2.9229	2	$\bar{1}$ 5 3
20	2.927	30	2.9220	2.9154	2	$\bar{3}$ 2 4
				2.9102	2	0 4 5
20	2.878			2.8974	3	0 3 6
10	2.805			2.8318	3	2 4 3
				2.7680	1	0 6 0
				2.7623	1	3 2 3
20	2.728	7	2.7329	2.7601	1	$\bar{1}$ 2 7
				2.7436	2	3 3 2
				2.7221	1	$\bar{3}$ 2 5
10	2.661			2.6707	1	2 0 6
				2.4196	2	$\bar{2}$ 6 2
40	2.395	8	2.4143	2.4090	1	$\bar{1}$ 6 4
				2.4054	4	2 3 6
10	2.293	4	2.3066	2.3109	2	0 7 2
20	2.222	5	2.2425	2.2491	2	$\bar{4}$ 0 6
				2.2402	1	0 7 3
10	2.135	5	2.1817	2.1886	1	$\bar{2}$ 1 9
				2.1868	1	0 2 9
10	2.088			2.0998	2	$\bar{4}$ 1 7
				2.0489	1	4 1 5
20	2.043	15	2.0394	2.0381	1	$\bar{4}$ 5 3
				2.0324	1	$\bar{1}$ 8 1
20	2.021			2.0222	1	4 5 1
				1.9939	1	$\bar{2}$ 1 10
				1.9911	1	$\bar{3}$ 2 9
10	1.971	2	1.9837	1.9855	1	0 8 3
				1.9781	1	$\bar{5}$ 3 2
20	1.915	4	1.9255	1.9245	1	$\bar{5}$ 3 4
10	1.867					
10	1.833					
20	1.799	3	1.8108	1.8165	1	$\bar{4}$ 2 9
10	1.731	1	1.7421	1.7961	1	$\bar{2}$ 2 11
		1	1.7142	1.7077	1	2 8 5
10	1.657	3	1.6638	1.6683	1	$\bar{6}$ 2 5
				1.6654	1	6 3 0
				1.6221	1	2 9 4
30	1.613	4	1.6181	1.6177	1	$\bar{4}$ 8 3
				1.6138	1	$\bar{4}$ 6 8
10	1.576	9	1.5835	1.5635	1	$\bar{4}$ 8 5
10	1.546	2	1.5469	1.5492	1	4 8 3
10	1.493	3	1.4997	1.4987	1	$\bar{6}$ 3 8
10	1.470	7	1.4770	1.4761	1	$\bar{4}$ 6 10
		2	1.4501	1.4493	1	4 6 8
10	1.408	2	1.4102			
30	1.321	3	1.3240	1.3251	1	$\bar{8}$ 0 2

exposure to the vacuum of the EMP chamber and induced heating from the electron beam led to high analytical totals. The amount of H_2O was initially assumed by difference in order to give a better PAP matrix correction and was subsequently recalculated. Trace amounts of Na, Ca, Cr, S and Cl were indicated, but they are at or below the detection limits of the instrument. No other elements were detected. Analytical data are given in Table 1.

The empirical formula, based on 48 oxygen atoms, is $(Fe^{3+}_{1.08}Al_{6.92})_{\Sigma 8.00}(P_{5.94}Si_{0.08})_{\Sigma 6.02}O_{22}(OH)_{10}(H_2O)_{16}$. The ideal structure-based formula is $Fe^{3+}Al_7(PO_4)_4(PO_3OH)_2(OH)_8(H_2O)_8{\cdot}8H_2O$, which requires Fe_2O_3 6.43, Al_2O_3 28.76, P_2O_5 34.32, H_2O 30.49, total 100.00%.

X-ray crystallography and structure determination

Powder and single-crystal X-ray studies were conducted using a Rigaku R-Axis Rapid II curved-imaging-plate microdiffractometer, with monochromatic Mo$K\alpha$ radiation, in the Department of Mineral Sciences of the Natural History Museum of Los Angeles County. For the powder diffraction study, the observed *d* spacings and intensities were derived by profile fitting using *JADE 9.3* software. The powder data presented in Table 2 are in good agreement with the pattern calculated from the structure and with the powder data reported by Moore and Ito (1980). The powder patterns of matulaite, afmite and kobokoboite are compared graphically in Fig. 6.

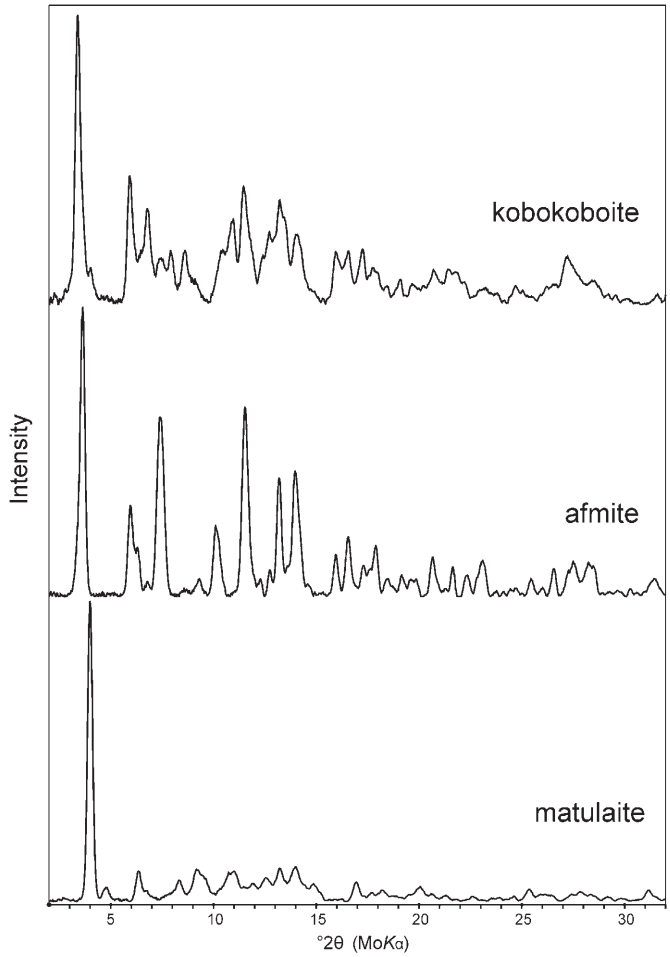

FIG. 6. Comparison of the powder X-ray diffraction patterns of kobokoboite, afmite and matulaite.

The Rigaku *CrystalClear* software package was used for processing the structure data, including the application of an empirical absorption correction. The *SHELX-97* software package (Sheldrick, 2008) was used for the solution (*SHELXS*) and refinement (*SHELXL*) of the structure. Direct methods revealed all of the cation sites and most of the oxygen sites. The remaining oxygen sites were located using difference Fourier syntheses.

One of the octahedrally coordinated cation sites has significantly longer bonds to oxygen atoms and a higher scattering power than the others and therefore, Fe was assigned to this site. Although the EMP data are consistent with full occupancy of this site by Fe, the structure refinement indicated occupancy by 71% Fe and 29% Al. It may be that some Fe is distributed among some of the Al sites. The Al2 and Al6 sites have slightly longer bond lengths and might, therefore, be the best candidates. Attempts to refine all of the Al sites with joint occupancy by Al and Fe, resulted in full occupancies by Al for all sites except Al6 and Al7 sites, which refined to Al:Fe occupancies of 0.956:0.044(17) and 0.949:0.051(18), respectively; however, R_1 did not improve and the displacement parameters for two O atoms went slightly non-positive definite. Consequently, in the final refinement, the Al6 and Al7 sites were assigned full occupancy by Al. A second possibility is that the structure crystal may contain less than the ideal amount of Fe. Nevertheless, the dominance of Fe at the Fe site and Al at the other octahedrally coordinated sites is clear and unambiguous.

Subsequent difference Fourier syntheses located all of the H-atom sites associated with

TABLE 3. Data collection and structure refinement details for matulaite.

Diffractometer	Rigaku R-Axis Rapid II
X-ray radiation/power	Mo$K\alpha$ (λ = 0.71075 Å)/50 kV, 40 mA
Temperature	298(2) K
Structural Formula	$(Fe^{3+}_{0.71}Al_{0.29})Al_7(PO_4)_4(PO_3OH)_2(OH)_8(H_2O)_8{\cdot}8H_2O$
Space group	$P2_1/n$
Unit-cell dimensions	a = 10.604(2) Å
	b = 16.608(4) Å
	c = 20.647(5) Å
	β = 98.848(7)º
Z	4
Volume	3592.8(13) Å^3
Density (for above formula)	2.279 g cm^{-3}
Absorption coefficient	0.912 mm^{-1}
F(000)	2517
Crystal size	220 × 80 × 10 μm
θ range	3.13 to 17.20º
Index ranges	$-8 \leqslant h \leqslant 8$, $-13 \leqslant k \leqslant 13$, $-17 \leqslant l \leqslant 17$
Reflections collected/unique	16,863/2130 [R_{int} = 0.13]
Reflections with $F_o > 4\sigma F$	1523
Completeness to θ = 17.20º	98.1%
Max. and min. transmission	0.9909 and 0.8245
Refinement method	Full-matrix least-squares on F^2
Parameters refined	686
Restraints	58
GoF	1.094
Final R indices [$F_o > 4\sigma F$]	R_1 = 0.0667, wR_2 = 0.1718
R indices (all data)	R_1 = 0.0945, wR_2 = 0.1957
Largest diff. peak/hole	+0.52 / −0.46 e A^{-3}

$R_{int} = \Sigma|F_o^2 - F_o^2(mean)|/\Sigma[F_o^2]$.
GoF = $S = \{S[w(F_o^2-F_c^2)^2]/(n-p)\}^{1/2}$.
$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$.
$wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ where a is 0.140, b is 4.500 and P is $[2F_c^2 + \text{Max}(F_o^2,0)]/3$.

TABLE 4. Final atom coordinates and displacement parameters (Å^2) for matulaite.

	x/*a*	*y*/*b*	*z*/*c*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Fe*	0.5012(3)	0.84428(16)	0.24566(13)	0.0372(17)	0.030(3)	0.025(2)	0.059(3)	−0.0004(16)	0.0158(16)	−0.0006(16)
Al1	0.3876(5)	0.0873(3)	0.3597(3)	0.0383(17)	0.026(4)	0.028(4)	0.062(4)	−0.002(3)	0.011(3)	−0.007(3)
Al2	0.2319(5)	0.0902(3)	0.2028(2)	0.0353(17)	0.024(4)	0.033(4)	0.050(4)	0.004(3)	0.009(3)	−0.007(3)
Al3	0.1005(5)	0.9439(3)	0.1514(3)	0.0448(18)	0.040(4)	0.038(4)	0.060(4)	0.004(3)	0.017(3)	−0.001(3)
Al4	−0.0023(5)	0.8432(3)	0.2441(3)	0.0442(18)	0.036(4)	0.030(4)	0.071(4)	0.001(3)	0.021(3)	0.000(3)
Al5	0.8992(5)	0.7481(3)	0.3413(3)	0.0419(18)	0.036(4)	0.031(4)	0.059(4)	−0.010(3)	0.008(3)	−0.002(3)
Al6	0.7292(5)	0.0974(3)	0.2053(2)	0.0334(16)	0.028(4)	0.020(4)	0.056(4)	0.001(3)	0.019(3)	−0.002(3)
Al7	0.6080(5)	0.5915(3)	0.1391(3)	0.0387(18)	0.027(4)	0.029(4)	0.065(4)	0.000(3)	0.021(3)	0.001(3)
P1	0.3633(5)	0.6817(3)	0.1786(2)	0.0410(16)	0.031(4)	0.039(5)	0.057(4)	0.002(3)	0.021(3)	0.000(3)
P2	0.6361(5)	0.0028(3)	0.3210(3)	0.0445(17)	0.033(4)	0.031(4)	0.072(4)	0.000(3)	0.015(4)	0.001(3)
P3	0.2521(5)	0.9354(3)	0.2955(2)	0.0438(17)	0.038(4)	0.041(4)	0.055(4)	−0.002(3)	0.015(3)	−0.008(4)
P4	0.7467(5)	0.7492(3)	0.1964(2)	0.0397(16)	0.034(4)	0.035(4)	0.053(4)	−0.006(3)	0.016(3)	−0.003(4)
P5	0.6318(5)	0.7209(3)	0.3690(3)	0.0436(17)	0.031(4)	0.039(5)	0.062(4)	0.002(3)	0.012(3)	0.001(3)
P6	0.3725(5)	0.9736(3)	0.1266(3)	0.0434(17)	0.036(4)	0.038(4)	0.060(4)	−0.002(3)	0.019(3)	0.002(3)
O1	0.3686(10)	0.7705(6)	0.1970(5)	0.041(3)	0.044(9)	0.001(8)	0.077(9)	0.003(6)	0.004(6)	0.007(6)
O2	0.4709(10)	0.6614(6)	0.1386(5)	0.044(3)	0.035(9)	0.029(8)	0.069(8)	−0.005(6)	0.016(7)	−0.008(6)
O3	0.3784(10)	0.6267(6)	0.2398(5)	0.038(3)	0.037(8)	0.047(8)	0.032(7)	0.006(6)	0.013(6)	−0.011(6)
O4	0.2331(10)	0.6645(6)	0.1354(5)	0.037(3)	0.030(9)	0.027(8)	0.055(8)	−0.002(5)	0.013(7)	−0.002(6)
O5	0.6341(9)	0.9159(6)	0.2977(5)	0.037(3)	0.029(8)	0.028(9)	0.055(8)	−0.002(6)	0.006(6)	−0.006(6)
O6	0.7643(10)	0.0173(6)	0.3651(5)	0.040(3)	0.033(9)	0.031(8)	0.054(8)	0.003(6)	0.004(7)	0.005(6)
O7	0.6205(10)	0.0618(7)	0.2631(5)	0.044(3)	0.037(8)	0.039(8)	0.057(8)	0.015(7)	0.007(6)	0.012(6)
O8	0.5281(10)	0.0186(6)	0.3613(5)	0.045(3)	0.018(8)	0.037(8)	0.080(9)	0.012(6)	0.014(7)	0.001(6)
O9	0.3699(10)	0.8847(7)	0.2948(5)	0.044(3)	0.015(8)	0.056(9)	0.067(9)	0.001(6)	0.021(6)	0.006(7)
O10	0.2708(10)	0.9990(6)	0.3492(5)	0.040(3)	0.038(8)	0.033(8)	0.050(8)	−0.003(7)	0.012(6)	−0.004(6)
O11	0.1342(10)	0.8855(7)	0.3046(5)	0.045(3)	0.040(9)	0.050(9)	0.048(8)	−0.007(6)	0.017(6)	−0.009(7)
O12	0.2200(10)	0.9788(6)	0.2285(5)	0.039(3)	0.034(8)	0.027(8)	0.061(9)	−0.005(7)	0.023(6)	−0.012(6)
O13	0.8613(10)	0.7966(6)	0.1844(5)	0.048(3)	0.038(9)	0.031(8)	0.080(9)	0.009(6)	0.020(7)	−0.014(7)
O14	0.6300(11)	0.8041(6)	0.1957(5)	0.047(3)	0.047(9)	0.024(8)	0.078(9)	−0.003(6)	0.031(7)	0.007(7)
O15	0.7227(10)	0.6816(7)	0.1450(5)	0.046(3)	0.035(8)	0.040(9)	0.067(8)	−0.004(7)	0.016(6)	−0.014(6)
O16	0.7807(10)	0.7094(6)	0.2660(5)	0.044(3)	0.045(8)	0.045(9)	0.042(8)	0.003(6)	0.005(6)	−0.008(7)
O17	0.5406(10)	0.7605(6)	0.3166(5)	0.041(3)	0.028(8)	0.017(7)	0.078(9)	0.006(6)	0.011(7)	0.003(6)
O18	0.7611(11)	0.7638(6)	0.3867(5)	0.042(3)	0.036(9)	0.019(7)	0.073(9)	−0.006(6)	0.019(6)	0.000(6)
O19	0.6514(10)	0.6320(6)	0.3513(5)	0.041(3)	0.045(9)	0.000(8)	0.081(9)	0.001(6)	0.026(6)	0.002(6)
OH20	0.5710(10)	0.7251(7)	0.4327(6)	0.043(3)	0.032(9)	0.036(9)	0.068(9)	−0.002(6)	0.025(8)	−0.001(7)
H20	0.497(8)	0.706(9)	0.442(7)	0.052						
O21	0.4658(11)	0.9275(7)	0.1770(6)	0.048(3)	0.048(9)	0.031(8)	0.065(9)	−0.012(7)	0.010(7)	0.004(7)
O22	0.3512(10)	0.0605(7)	0.1473(5)	0.044(3)	0.043(9)	0.034(9)	0.060(8)	−0.001(6)	0.017(6)	0.011(6)

O23	0.2430(10)	0.9307(7)	0.1086(5)	0.045(3)	0.029(9)	0.046(9)	0.064(8)	−0.001(6)	0.018(6)	0.001(7)
OH24	0.4341(12)	0.9799(7)	0.0634(6)	0.057(4)	0.053(10)	0.049(10)	0.074(10)	−0.011(7)	0.028(8)	0.010(7)
H24	0.497(12)	0.952(10)	0.050(8)	0.068						
OH25	0.3766(10)	0.1063(6)	0.2680(5)	0.040(3)	0.039(8)	0.010(7)	0.071(9)	0.003(6)	0.010(7)	−0.010(6)
H25	0.405(14)	0.156(4)	0.263(7)	0.048						
OH26	0.0935(11)	0.0554(7)	0.1400(5)	0.045(3)	0.053(9)	0.035(9)	0.051(8)	−0.007(7)	0.019(7)	−0.010(7)
H26	0.105(15)	0.052(10)	0.098(3)	0.054						
OH27	−0.0349(10)	0.9436(7)	0.2045(6)	0.049(4)	0.019(8)	0.032(8)	0.103(10)	0.042(7)	0.027(7)	0.006(7)
H27	−0.115(7)	0.926(10)	0.207(8)	0.059						
OH28	1.0297(10)	0.7445(6)	0.2869(5)	0.041(3)	0.023(8)	0.034(9)	0.063(9)	0.001(6)	−0.008(6)	0.004(6)
H28	1.079(13)	0.704(7)	0.306(7)	0.050						
OH29	0.6264(10)	0.5779(6)	0.2317(6)	0.043(3)	0.031(9)	0.021(8)	0.082(9)	−0.001(6)	0.023(7)	0.004(6)
H29	0.559(10)	0.606(9)	0.239(7)	0.052						
OH30	−0.1037(11)	0.8554(6)	0.3109(5)	0.042(3)	0.045(9)	0.022(8)	0.061(8)	−0.001(6)	0.013(7)	−0.001(6)
H30	−0.165(12)	0.893(7)	0.296(7)	0.050						
OH31	0.9029(11)	0.6380(7)	0.3564(6)	0.045(3)	0.038(9)	0.031(10)	0.068(9)	0.008(6)	0.014(7)	−0.011(6)
H31	0.975(9)	0.609(9)	0.363(8)	0.054						
OH32	0.1051(10)	0.8351(7)	0.1783(5)	0.037(3)	0.021(8)	0.045(9)	0.053(8)	0.001(6)	0.030(6)	−0.004(6)
H32	0.176(9)	0.809(8)	0.169(7)	0.044						
OW33	0.5830(12)	0.5976(7)	0.0447(5)	0.049(3)	0.044(10)	0.042(9)	0.060(9)	−0.009(7)	0.008(7)	−0.006(6)
H33A	0.636(11)	0.626(8)	0.022(5)	0.059						
H33B	0.529(11)	0.571(8)	0.014(5)	0.059						
OW34	0.4867(11)	0.5005(7)	0.1236(6)	0.048(3)	0.043(9)	0.033(9)	0.070(10)	0.013(6)	0.018(7)	−0.004(7)
H34A	0.409(6)	0.478(8)	0.127(7)	0.057						
H34B	0.545(8)	0.471(8)	0.150(6)	0.057						
OW35	0.5149(11)	0.1740(7)	0.3832(7)	0.057(4)	0.039(9)	0.040(9)	0.096(10)	−0.025(8)	0.028(8)	−0.012(7)
H35A	0.594(7)	0.169(8)	0.373(8)	0.068						
H35B	0.494(13)	0.226(3)	0.381(8)	0.068						
OW36	0.2286(12)	0.2019(7)	0.1676(6)	0.050(3)	0.051(10)	0.045(9)	0.057(9)	0.002(7)	0.012(7)	0.013(7)
H36A	0.150(7)	0.207(7)	0.145(7)	0.061						
H36B	0.247(13)	0.149(3)	0.171(9)	0.061						
OW37	1.0154(12)	0.7719(8)	0.4166(6)	0.056(4)	0.060(10)	0.036(10)	0.073(10)	0.006(7)	0.012(8)	−0.003(7)
H37A	1.068(14)	0.814(7)	0.425(6)	0.068						
H37B	1.017(15)	0.745(8)	0.454(4)	0.068						
OW38	−0.0100(13)	0.9234(7)	0.0741(6)	0.060(4)	0.064(10)	0.032(9)	0.082(10)	−0.002(7)	0.005(8)	0.003(8)
H38A	−0.031(17)	0.968(5)	0.051(6)	0.072						
H38B	−0.007(17)	0.882(5)	0.048(5)	0.072						
OW39	0.3895(11)	0.0707(6)	0.4530(5)	0.045(3)	0.049(9)	0.028(8)	0.059(9)	−0.015(6)	0.012(6)	−0.005(7)
H39A	0.450(11)	0.083(7)	0.487(5)	0.054						
H39B	0.400(13)	0.018(3)	0.444(6)	0.054						
OW40	0.7240(12)	0.9903(6)	0.1641(6)	0.050(4)	0.044(10)	0.021(8)	0.090(10)	−0.006(7)	0.024(8)	0.004(7)
H40A	0.656(9)	0.961(7)	0.173(8)	0.060						

TABLE 4 (*contd.*)

	x/a	*y/b*	*z/c*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
H40B	0.776(10)	0.955(6)	0.148(8)	0.060						
OW41	0.7157(13)	0.7145(8)	0.5412(7)	0.073(4)	0.079(12)	0.060(11)	0.087(11)	0.002(8)	0.035(9)	0.001(9)
H41A	0.693(14)	0.736(11)	0.578(5)	0.088						
H41B	0.797(7)	0.730(12)	0.540(8)	0.088						
OW42	0.8197(12)	0.9077(8)	0.4752(6)	0.066(4)	0.044(9)	0.078(11)	0.086(10)	0.013(9)	0.036(8)	0.007(8)
H42A	0.736(5)	0.912(11)	0.478(6)	0.080						
H42B	0.826(13)	0.915(11)	0.432(3)	0.080						
OW43	0.5305(11)	0.1139(9)	0.5613(6)	0.067(4)	0.047(9)	0.078(11)	0.077(10)	0.007(8)	0.017(8)	0.009(9)
H43A	0.538(13)	0.099(11)	0.604(3)	0.080						
H43B	0.611(7)	0.126(11)	0.554(7)	0.080						
OW44	0.7394(14)	0.6636(9)	−0.0272(6)	0.081(4)	0.068(11)	0.088(12)	0.088(11)	0.016(8)	0.018(9)	0.019(9)
H44A	0.741(19)	0.671(9)	−0.070(3)	0.097						
H44B	0.77(2)	0.614(5)	−0.016(7)	0.097						
OW45	0.9833(18)	0.7215(8)	0.5366(9)	0.098(5)	0.124(14)	0.057(11)	0.121(14)	−0.015(10)	0.038(13)	−0.030(10)
H45A	1.047(12)	0.685(9)	0.545(11)	0.118						
H45B	0.911(9)	0.695(10)	0.522(11)	0.118						
OW46	−0.1771(14)	0.0363(9)	0.0331(7)	0.085(5)	0.086(12)	0.072(12)	0.093(12)	0.012(8)	0.000(9)	0.004(10)
H46A	−0.261(6)	0.038(13)	0.039(8)	0.102						
H46B	−0.176(15)	0.062(11)	−0.007(5)	0.102						
OW47	−0.1552(16)	0.8153(10)	−0.0063(7)	0.092(5)	0.080(13)	0.075(12)	0.111(12)	−0.019(9)	−0.010(10)	−0.020(10)
H47A	−0.19(2)	0.863(7)	0.004(8)	0.110						
H47B	−0.13(2)	0.788(9)	0.031(5)	0.110						
OW48	0.352(2)	0.0974(9)	−0.0218(9)	0.113(6)	0.123(15)	0.089(13)	0.126(14)	0.003(10)	0.020(14)	0.029(12)
H48A	0.34(3)	0.074(11)	−0.062(4)	0.135						
H48B	0.38(2)	0.057(9)	0.008(7)	0.135						

* The Fe site refines to 0.71(2) Fe and 0.29(2) Al.

the OH and H_2O groups. This, coupled with bond valence analysis, allowed the unambiguous assignment of all OH and H_2O in the structure.

Details of the data collection and the final structure refinement are provided in Table 3, final atom coordinates and displacement parameters in Table 4, selected interatomic distances in Table 5, hydrogen bond distances and angles and bond valence contributions in Table 6 and a bond-valence analysis in Table 7.

Description of the structure

The crystal structure of matulaite (Fig. 7) contains seven-member chain segments of AlO_6 octahedra. The central part of the chain segments consist of five AlO_6 octahedra linked to each other by shared edges. The chain segments are completed by corner-linked AlO_6 octahedra at each end and are decorated by PO_4 tetrahedra, producing a contorted vermiform configuration (Fig. 8). The PO_4 tetrahedra also link to isolated FeO_6 octahedra such that each FeO_6 octahedron shares each of its six vertices with PO_4 tetrahedra, resulting in a 'pinwheel' $Fe(PO_4)_6$ group (Fig. 7*b*). Two of the six independent PO_4 tetrahedra have an unshared corner, which is an OH group. The linkage of octahedra and tetrahedra described above defines a thick layer parallel to {001}. The only linkage between

TABLE 5. Selected interatomic bond distances (Å) in matulaite.

Fe–O14	1.952(11)	Al1–O4	1.825(12)	Al2–O3	1.887(11)
Fe–O9	1.963(11)	Al1–O8	1.873(12)	Al2–OH26	1.894(12)
Fe–O21	1.974(12)	Al1–OH25	1.905(12)	Al2–OH25	1.899(12)
Fe–O1	2.013(11)	Al1–O10	1.910(12)	Al2–O22	1.899(12)
Fe–O17	2.016(11)	Al1–OW39	1.943(13)	Al2–O12	1.934(12)
Fe–O5	2.022(11)	Al1–OW35	1.983(12)	Al2–OW36	1.991(13)
<Fe–O>	**1.990**	**<Al–O>**	**1.907**	**<Al–O>**	**1.917**
Al3–OW38	1.860(13)	Al4–OH27	1.867(12)	Al5–OH31	1.855(13)
Al3–OH26	1.867(12)	Al4–OH28	1.868(12)	Al5–OW37	1.872(12)
Al3–O23	1.876(12)	Al4–OH30	1.886(12)	Al5–O18	1.873(12)
Al3–OH32	1.890(12)	Al4–O11	1.895(12)	Al5–OH30	1.889(12)
Al3–OH27	1.936(12)	Al4–OH32	1.906(11)	Al5–OH28	1.913(13)
Al3–O12	1.965(12)	Al4–O13	1.913(12)	Al5–O16	1.952(12)
<Al–O>	**1.899**	**<Al–O>**	**1.889**	**<Al–O>**	**1.892**
Al6–OH31	1.869(12)	Al7–O6	1.843(12)		
Al6–O7	1.877(12)	Al7–O2	1.859(12)		
Al6–OH29	1.877(13)	Al7–OH29	1.905(13)		
Al6–O19	1.938(12)	Al7–O15	1.922(12)		
Al6–O16	1.960(12)	Al7–OW33	1.929(12)		
Al6–OW40	1.968(12)	Al7–OW34	1.978(13)		
<Al–O>	**1.915**	**<Al–O>**	**1.906**		
P1–O1	1.521(11)	P2–O5	1.520(11)	P3–O9	1.508(11)
P1–O2	1.545(11)	P2–O6	1.535(11)	P3–O10	1.523(11)
P1–O3	1.547(11)	P2–O7	1.536(11)	P3–O11	1.536(11)
P1–O4	1.551(11)	P2–O8	1.538(11)	P3–O12	1.550(12)
<P–O>	**1.541**	**<P–O>**	**1.532**	**<P–O>**	**1.529**
P4–O13	1.501(11)	P5–O17	1.489(11)	P6–O21	1.526(12)
P4–O14	1.534(11)	P5–O18	1.539(11)	P6–O22	1.532(12)
P4–O15	1.539(12)	P5–O19	1.542(11)	P6–O23	1.541(12)
P4–O16	1.571(11)	P5–OH20	1.553(12)	P6–OH24	1.551(13)
<P–O>	**1.536**	**<P–O>**	**1.531**	**<P–O>**	**1.538**

TABLE 6. Hydrogen bond lengths (Å), angles (º) and bond-valence contributions (vu) in matulaite.

O_D–H···O_A	O_D–H	H···O_A	O_D–O_A	∠O_D–H–O_A	BV
OH20–H20···OW47	0.90(4)	2.09(7)	2.95(2)	161(15)	0.11
OH24–H24···OW48	0.90(4)	1.96(5)	2.85(2)	173(18)	0.14
OH25–H25···OH28	0.90(4)	1.98(7)	2.809(15)	154(13)	0.13
OH26–H26···none	0.90(4)				0.00
OH27–H27···O13	0.90(4)	2.21(15)	2.683(15)	112(12)	0.09
OH28–H28···OW36	0.91(3)	2.02(13)	2.686(15)	129(13)	0.12
OH29–H29···O3	0.89(3)	1.94(8)	2.782(15)	156(16)	0.14
OH30–H30···O5	0.91(3)	2.18(11)	2.928(15)	139(14)	0.09
OH31–H31···O22	0.90(4)	2.05(6)	2.919(16)	163(15)	0.11
OH32–H32···O1	0.91(4)	2.14(8)	2.963(15)	151(13)	0.10
OW33–H33A···OW44	0.91(3)	1.72(5)	2.629(19)	171(15)	0.21
OW33–H33B···OW42	0.90(3)	2.27(12)	2.937(17)	131(14)	0.08
OW34–H34A···O10 (½)	0.92(3)	2.07(9)	2.870(15)	145(13)	0.11 (½)
OW34–H34A···O11 (½)	0.92(3)	2.17(10)	2.841(15)	129(9)	0.09 (½)
OW34–H34B···OH30	0.90(3)	2.14(9)	2.942(15)	148(12)	0.10
OW35–H35A···O15	0.90(3)	2.05(5)	2.931(16)	168(13)	0.11
OW35–H35B···OH32	0.89(3)	2.34(9)	3.146(17)	149(15)	0.07
OW36–H36A···O17	0.90(3)	2.45(13)	3.080(16)	127(13)	0.06
OW36–H36B···O22	0.90(3)	1.95(10)	2.747(16)	147(17)	0.14
OW37–H37A···OW44	0.90(4)	1.96(11)	2.700(18)	138(14)	0.14
OW37–H37B···OW45	0.90(3)	1.83(8)	2.69(2)	159(17)	0.17
OW38–H38A···OW46	0.90(3)	1.91(12)	2.629(19)	136(16)	0.15
OW38–H38B···OW47	0.88(3)	2.10(14)	2.750(19)	130(15)	0.10
OW39–H39A···OW43	0.90(3)	1.71(5)	2.592(16)	166(15)	0.22
OW39–H39B···OW43	0.90(3)	2.33(5)	3.208(18)	167(10)	0.07
OW40–H40A···O21	0.91(3)	2.11(6)	2.980(16)	161(13)	0.10
OW40–H40B···OH27	0.91(3)	2.17(14)	2.679(16)	115(12)	0.09
OW41–H41A···O4	0.91(3)	2.04(12)	2.783(16)	139(14)	0.11
OW41–H41B···OW45	0.90(4)	1.99(8)	2.86(2)	160(19)	0.13
OW42–H42A···OW39	0.90(3)	2.11(8)	2.873(17)	142(12)	0.10
OW42–H42B···O6	0.91(3)	2.22(14)	2.901(16)	131(14)	0.09
OW43–H43A···O8	0.91(3)	2.23(14)	2.844(17)	125(14)	0.08
OW43–H43B···OW44	0.91(4)	1.87(4)	2.768(19)	169(14)	0.16
OW44–H44A···O11	0.89(3)	2.83(13)	3.575(17)	142(16)	0.03
OW44–H44B···none	0.89(3)				0.00
OW45–H45A···OW48	0.91(4)	1.91(11)	2.75(3)	153(20)	0.15
OW45–H45B···OW41	0.90(4)	2.20(15)	2.86(2)	130(17)	0.09
OW46–H46A···OH24	0.92(4)	2.59(16)	3.130(18)	118(13)	0.05
OW46–H46B···O23	0.92(3)	2.12(11)	2.952(18)	149(17)	0.10
OW47–H47A···OW48	0.90(3)	1.94(16)	2.68(2)	137(21)	0.14
OW47–H47B···OW35	0.90(3)	2.75(6)	3.608(19)	159(15)	0.03
OW48–H48A···OW40	0.91(4)	2.37(7)	3.27(2)	167(24)	0.07
OW48–H48B···OH24	0.91(4)	1.77(4)	2.68(2)	177(25)	0.20

Hydrogen-bond strengths are based on H···O bond lengths, from Brown and Altermatt (1985); however, because X-ray diffraction locates the centroid of the electron density rather than the position of the nucleus, the determined H atom positions are too close to the donor atom by about 0.05 Å. Consequently, the H···O bond lengths are too long and the corresponding bond-valence contributions are roughly 10% too low.

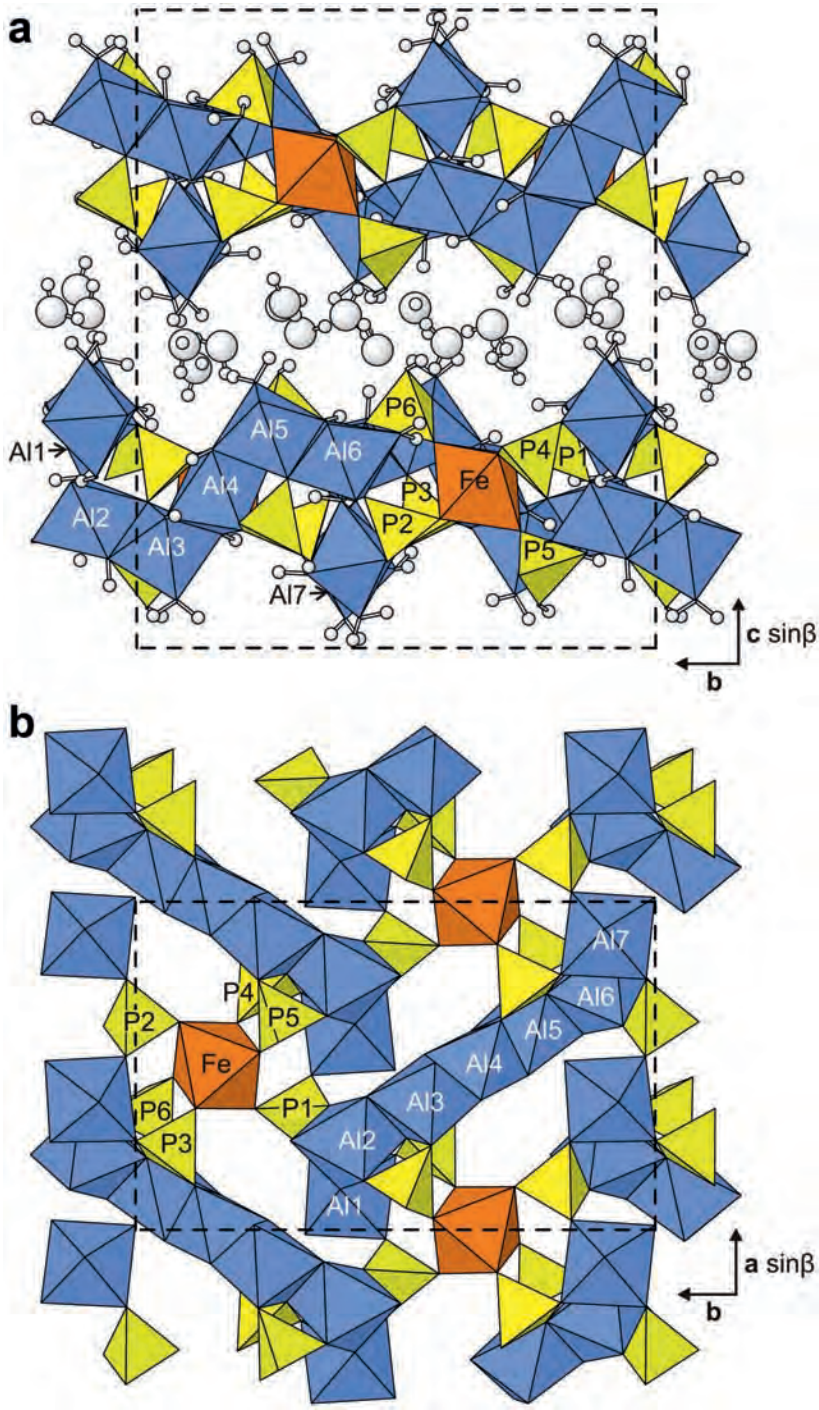

FIG. 7. Crystal structure of matulaite: (*a*) view down *a* showing the thick layers of octahedra and tetrahedra on edge with interlayer H_2O molecules between (oxygen atoms are shown as large white spheres and hydrogen atoms as small white spheres); (*b*) view down *c* showing the linkage of octahedra and tetrahedra in a single layer.

TABLE 7. Bond-valence analysis for matulaite.

	Fe	Al1	Al2	Al3	Al4	Al5	Al6	Al7	P1	P2	P3	P4	P5	P6	Hydrogen bonds	Σ
O1	0.46								1.25						0.10	1.81
O2								0.57	1.17							1.74
O3			0.53						1.17						0.14	1.83
O4		0.62							1.15						0.11	1.89
O5	0.45									1.25					0.09	1.79
O6								0.60		1.21						1.80
O7							0.54			1.20						1.74
O8		0.55								1.20					0.08	1.82
O9	0.53										1.30					1.83
O10		0.50									1.24				0.06	1.80
O11					0.52						1.20				0.05	1.76
O12			0.47	0.43							1.16					2.05
O13					0.49							1.32			0.09	1.90
O14	0.55											1.21				1.76
O15								0.48				1.19			0.11	1.78
O16						0.44	0.43					1.09				1.97
O17	0.46												1.36		0.06	1.88
O18						0.55							1.19			1.74
O19							0.46						1.18			1.64
OH20													1.15		−0.10	1.04
O21	0.51													1.23	0.10	1.84
O22			0.51											1.21	0.11, 0.14	1.98
O23				0.54										1.19	0.10	1.83
OH24														1.15	−0.14, 0.05, 0.20	1.26
OH25		0.50	0.51												−0.13	0.88
OH26			0.52	0.56												1.08
OH27				0.46	0.56										−0.09, 0.09	1.02
OH28					0.56	0.49									−0.12, 0.13	1.06
OH29							0.54	0.50							−0.14	0.91
OH30					0.53	0.53									−0.09, 0.10	1.07
OH31						0.58	0.55								−0.11	1.02
OH32				0.52	0.50										−0.10, 0.07	1.00
OW33								0.47							−0.21, −0.08	0.18
OW34								0.41							−0.10, −0.10	0.21
OW35		0.41													−0.11, −0.07, 0.03	0.26
OW36			0.40												−0.06, −0.14, 0.12	0.32
OW37						0.55									−0.14, −0.17	0.24

OW38			0.57									−0.15, −0.10			0.32
OW39		0.45										−0.22, −0.07			0.16
OW40						0.42						−0.10, −0.09, 0.07			0.30
OW41												−0.11, −0.13, 0.09			−0.15
OW42												−0.10, −0.09, 0.08			−0.11
OW43												−0.08, −0.16, 0.22, 0.07			0.05
OW44												−0.03, 0.21, 0.14, 0.16			0.48
OW45												−0.15, −0.09, 0.17, 0.13			0.06
OW46												−0.05, −0.10, 0.15			0.00
OW47												−0.14, −0.03, 0.11, 0.10			0.04
OW48												−0.07, −0.20, 0.14, 0.15, 0.14			0.16
Σ	2.96	3.04	2.93	3.09	3.16	3.14	2.96	3.03	4.74	4.86	4.90	4.81	4.89	4.79	

Values are expressed in valence units (vu).
All non-hydrogen bond strengths are from Brese and O'Keeffe (1991).

layers is via hydrogen bonding to interlayer H_2O molecules.

The structure of matulaite is unique, but has some similarities to that of afmite. Both structures are based upon thick layers of linked octahedra and tetrahedra, with the only linkage between layers being via hydrogen bonding to interlayer H_2O molecules. Both structures contain normal and acid phosphate groups. Both structures have edge-sharing and corner-sharing linkages between AlO_6 octahedra. A significant contrast is seen in the topology of the successive linkage between the AlO_6 octahedra (Fig. 8). The structure of afmite contains infinite chains of AlO_6 octahedra that are made up of dimers of edge-sharing octahedra alternating with individual octahedra linked to the dimers by corner sharing.

Conclusions

Examination of both existing cotype specimens of matulaite revealed no material matching the powder or single-crystal X-ray diffraction data reported by Moore and Ito (1980). Other samples examined from the type locality, and from the LCA pegmatite in North Carolina, USA, and Fumade, Tarn, France, provided material that is crystallographically consistent with the description of matulaite by Moore and Ito (1980).

Electron-microprobe and crystal-structure analysis of newly studied material from the type locality (NHMLAC #28324) showed the ideal formula of matulaite to be $Fe^{3+}Al_7(PO_4)_4(PO_3OH)_2(OH)_8(H_2O)_8{\cdot}8H_2O$. The chemical composition reported by Moore and Ito (1980) was probably determined using material removed from the two pieces of the cotype specimen (NMNH #137020), which was actually a mixture of mostly kobokoboite and afmite, with lesser amounts of crandallite.

In light of our failure to confirm the existence of matulaite on either of the extant cotype specimens, the specimens NHMLAC #28323 and #28324 are now designated as the neotypes for the species, together with the probe mount made from NHMLAC #28324, now accessioned as BM 2011,100 (probe block ref no. P17365), which is deposited in the Natural History Museum, London. The designation of these neotype specimens and the changes to the ideal formula have been approved by the International Mineralogical Association (IMA) Commission on New Minerals, Nomenclature and Classification (CNMNC), proposal 11-F. We have redetermined

TABLE 8. Comparison of selected descriptive data for matulaite, afmite and kobokoboite.

	Matulaite Moore and Ito (1980)	Matulaite This study	Afmite Kampf *et al.* (2011)	Kobokoboite Mills*et al.* (2010)
Ideal formula	$CaAl_{18}(PO_4)_{12}(OH)_{20}{\cdot}8H_2O$	$Fe^{3+}Al_7(PO_4)_4(PO_3OH)_2(OH)_8(H_2O)_8{\cdot}8H_2O$	$Al_3(OH)_4(H_2O)_3(PO_4)(PO_3OH){\cdot}H_2O$	$Al_6(PO_4)_4(OH)_6{\cdot}11H_2O$
Chemical composition (ideal formula)				
CaO (wt.%)	2.23			
Fe_2O_3 (wt.%)		6.43		
Al_2O_3 (wt.%)	36.56	28.76	37.12	36.33
P_2O_5 (wt.%)	33.93	34.32	34.45	33.71
H_2O (wt.%)	27.28	30.49	28.42	29.96
Crystallography*				
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$	$P1$ or $P\bar{1}$
a (Å)	20.4	10.604(2)	7.386(3)	7.460(1)
b (Å)	16.7	16.608(4)	7.716(3)	7.737(1)
c (Å)	10.6	20.647(5)	11.345(4)	12.385(5)
α (°)	90	90	99.773(5)	102.79(2)
β (°)	98.2	98.848(7)	91.141(6)	90.20(3)
γ (°)	90	90	115.58(5)	116.33(2)
V (Å^3)	3574	3592.8(13)	571.6(3)	620.6(3)
Z	2	4	2	1
Optics				
Optical class	Biaxial (−)	Biaxial (−)	Biaxial (+)	Biaxial (−)
α	−	1.535(2)[§]	1.554(1)	~1.550
β	1.576(2)	1.563(1)	1.558(1)	1.558(2)
γ	1.582(2)	1.579(1)	1.566(1)	1.562(2)
$2V_{meas}$ (°)	~60	73(2)	70(5)	large, 60−80
Dispersion	$r < v$, strong	none observed	none observed	none observed
Orientation	$Y = b$, $Z \wedge c = 8°$	$Y = b$, $Z \wedge a = 8°$	$Y \approx a$, $Z \wedge b = 55°$	$X \approx b$
Physical properties				
Colour/streak	colourless/white	colourless/white	colourless/white	colourless/white
Lustre	pearly	vitreous	pearly	pearly
Hardness	1	1½	1½	2
Fracture	−	irregular	irregular	irregular
Tenacity	slightly flexible	very slightly flexible	flexible, but not elastic	brittle
Cleavage	{100}, perfect	{001}, perfect	{001} perfect, {010} and {1$\bar{1}$0} good	none observed
D_{meas} (g cm^{-3})	2.330	2.27(3)	2.39(3)	2.21(3)
D_{calc} (g cm^{-3})[†]	2.333	2.294	2.394	2.287

* Our cell for matulaite has a and c transformed relative to the cell reported by Moore and Ito (1980).
[§] Due to the unfavourable orientation, α could not be measured. It is calculated from β, γ and 2V.
[†] Calculated densities are based on ideal formulae.

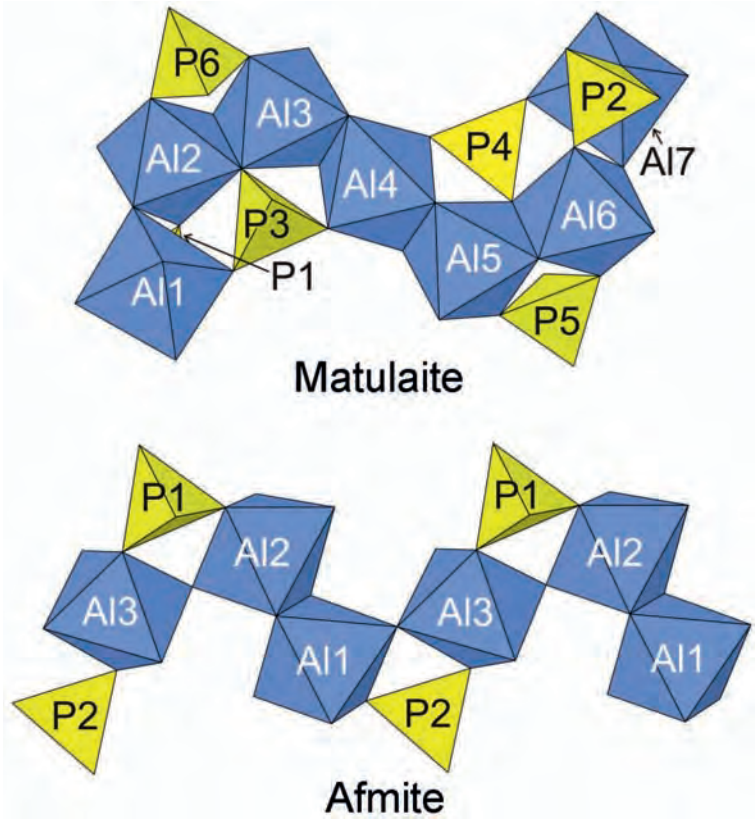

FIG. 8. Chain segment in matulaite compared with the chain in afmite.

the physical and optical properties of matulaite from crystals from these specimens. Table 8 compares the formulae, ideal chemical compositions, unit-cell data, optical properties and physical properties of matulaite, afmite and kobokoboite.

Matulaite, afmite and kobokoboite all occur in aggregates of thin colourless to white plates with relatively similar morphologies (Figs 1–5). Powder X-ray diffraction can definitively discriminate between the three and the presence of significant Fe (measured by semi-quantitative EDS) can readily distinguish matulaite from afmite and kobokoboite. However, matulaite can usually be visually distinguished by careful examination. Afmite and kobokoboite both tend to occur as more or less warped plates with distinctly pearly lustre, whereas matulaite plates are generally quite flat and exhibit vitreous rather than pearly lustre. Matulaite cleaves very easily on {001}, yielding transparent plates with lustrous cleavage surfaces. In radial aggregates, matulaite blades exhibit distinctive tapering toward the centres of the aggregates.

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H24 H 0.497(12) 0.952(10) 0.050(8) 0.068 Uiso 1 1 d D . .
OH25 O 0.3766(10) 1.1063(6) 0.2680(5) 0.040(3) Uani 1 1 d D . .
H25 H 0.405(14) 1.156(4) 0.263(7) 0.048 Uiso 1 1 d D . .
OH26 O 0.0935(11) 1.0554(7) 0.1400(5) 0.045(3) Uani 1 1 d D . .
H26 H 0.105(15) 1.052(10) 0.098(3) 0.054 Uiso 1 1 d D . .
OH27 O -0.0349(10) 0.9436(7) 0.2045(6) 0.049(4) Uani 1 1 d D . .
H27 H -0.115(7) 0.926(10) 0.207(8) 0.059 Uiso 1 1 d D . .
OH28 O 1.0297(10) 0.7445(6) 0.2869(5) 0.041(3) Uani 1 1 d D . .
H28 H 1.079(13) 0.704(7) 0.306(7) 0.050 Uiso 1 1 d D . .
OH29 O 0.6264(10) 0.5779(6) 0.2317(6) 0.043(3) Uani 1 1 d D . .
H29 H 0.559(10) 0.606(9) 0.239(7) 0.052 Uiso 1 1 d D . .
OH30 O -0.1037(11) 0.8554(6) 0.3109(5) 0.042(3) Uani 1 1 d D . .
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H30 H -0.165(12) 0.893(7) 0.296(7) 0.050 Uiso 1 1 d D . .
OH31 O 0.9029(11) 0.6380(7) 0.3564(6) 0.045(3) Uani 1 1 d D . .
H31 H 0.975(9) 0.609(9) 0.363(8) 0.054 Uiso 1 1 d D . .
OH32 O 0.1051(10) 0.8351(7) 0.1783(5) 0.037(3) Uani 1 1 d D . .
H32 H 0.176(9) 0.809(8) 0.169(7) 0.044 Uiso 1 1 d D . .
OW33 O 0.5830(12) 0.5976(7) 0.0447(5) 0.049(3) Uani 1 1 d D . .
H33A H 0.636(11) 0.626(8) 0.022(5) 0.059 Uiso 1 1 d D . .
H33B H 0.529(11) 0.571(8) 0.014(5) 0.059 Uiso 1 1 d D . .
OW34 O 0.4867(11) 0.5005(7) 0.1236(6) 0.048(3) Uani 1 1 d D . .
H34A H 0.409(6) 0.478(8) 0.127(7) 0.057 Uiso 1 1 d D . .
H34B H 0.545(8) 0.471(8) 0.150(6) 0.057 Uiso 1 1 d D . .
OW35 O 0.5149(11) 1.1740(7) 0.3832(7) 0.057(4) Uani 1 1 d D . .
H35A H 0.594(7) 1.169(8) 0.373(8) 0.068 Uiso 1 1 d D . .
H35B H 0.494(13) 1.226(3) 0.381(8) 0.068 Uiso 1 1 d D . .
OW36 O 0.2286(12) 1.2019(7) 0.1676(6) 0.050(3) Uani 1 1 d D . .
H36A H 0.150(7) 1.207(7) 0.145(7) 0.061 Uiso 1 1 d D . .
H36B H 0.247(13) 1.149(3) 0.171(9) 0.061 Uiso 1 1 d D . .
OW37 O 1.0154(12) 0.7719(8) 0.4166(6) 0.056(4) Uani 1 1 d D . .
H37A H 1.068(14) 0.814(7) 0.425(6) 0.068 Uiso 1 1 d D . .
H37B H 1.017(15) 0.745(8) 0.454(4) 0.068 Uiso 1 1 d D . .
OW38 O -0.0100(13) 0.9234(7) 0.0741(6) 0.060(4) Uani 1 1 d D . .
H38A H -0.031(17) 0.968(5) 0.051(6) 0.072 Uiso 1 1 d D . .
H38B H -0.007(17) 0.882(5) 0.048(5) 0.072 Uiso 1 1 d D . .
OW39 O 0.3895(11) 1.0707(6) 0.4530(5) 0.045(3) Uani 1 1 d D . .
H39A H 0.450(11) 1.083(7) 0.487(5) 0.054 Uiso 1 1 d D . .
H39B H 0.400(13) 1.018(3) 0.444(6) 0.054 Uiso 1 1 d D . .
OW40 O 0.7240(12) 0.9903(6) 0.1641(6) 0.050(4) Uani 1 1 d D . .
H40A H 0.656(9) 0.961(7) 0.173(8) 0.060 Uiso 1 1 d D . .
H40B H 0.776(10) 0.955(6) 0.148(8) 0.060 Uiso 1 1 d D . .
OW41 O 0.7157(13) 0.7145(8) 0.5412(7) 0.073(4) Uani 1 1 d D . .
H41A H 0.693(14) 0.736(11) 0.578(5) 0.088 Uiso 1 1 d D . .
H41B H 0.797(7) 0.730(12) 0.540(8) 0.088 Uiso 1 1 d D . .
OW42 O 0.8197(12) 0.9077(8) 0.4752(6) 0.066(4) Uani 1 1 d D . .
H42A H 0.736(5) 0.912(11) 0.478(6) 0.080 Uiso 1 1 d D . .
H42B H 0.826(13) 0.915(11) 0.432(3) 0.080 Uiso 1 1 d D . .
OW43 O 0.5305(11) 1.1139(9) 0.5613(6) 0.067(4) Uani 1 1 d D . .
H43A H 0.538(13) 1.099(11) 0.604(3) 0.080 Uiso 1 1 d D . .
H43B H 0.611(7) 1.126(11) 0.554(7) 0.080 Uiso 1 1 d D . .
OW44 O 0.7394(14) 0.6636(9) -0.0272(6) 0.081(4) Uani 1 1 d D . .
H44A H 0.741(19) 0.671(9) -0.070(3) 0.097 Uiso 1 1 d D . .
H44B H 0.77(2) 0.614(5) -0.016(7) 0.097 Uiso 1 1 d D . .
OW45 O 0.9833(18) 0.7215(8) 0.5366(9) 0.098(5) Uani 1 1 d D . .
H45A H 1.047(12) 0.685(9) 0.545(11) 0.118 Uiso 1 1 d D . .
H45B H 0.911(9) 0.695(10) 0.522(11) 0.118 Uiso 1 1 d D . .
OW46 O -0.1771(14) 1.0363(9) 0.0331(7) 0.085(5) Uani 1 1 d D . .
H46A H -0.261(6) 1.038(13) 0.039(8) 0.102 Uiso 1 1 d D . .
H46B H -0.176(15) 1.062(11) -0.007(5) 0.102 Uiso 1 1 d D . .
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H47B H -0.13(2) 0.788(9) 0.031(5) 0.110 Uiso 1 1 d D . .
OW48 O 0.352(2) 1.0974(9) -0.0218(9) 0.113(6) Uani 1 1 d D . .
H48A H 0.34(3) 1.074(11) -0.062(4) 0.135 Uiso 1 1 d D . .
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O6 0.033(9) 0.031(8) 0.054(8) 0.003(6) 0.004(7) 0.005(6)
O7 0.037(8) 0.039(8) 0.057(8) 0.015(7) 0.007(6) 0.012(6)
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OH24 0.053(10) 0.049(10) 0.074(10) -0.011(7) 0.028(8) 0.010(7)
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OH26 0.053(9) 0.035(9) 0.051(8) -0.007(7) 0.019(7) -0.010(7)
OH27 0.019(8) 0.032(8) 0.103(10) 0.042(7) 0.027(7) 0.006(7)
OH28 0.023(8) 0.034(9) 0.063(9) 0.001(6) -0.008(6) 0.004(6)
OH29 0.031(9) 0.021(8) 0.082(9) -0.001(6) 0.023(7) 0.004(6)
OH30 0.045(9) 0.022(8) 0.061(8) -0.001(6) 0.013(7) -0.001(6)
OH31 0.038(9) 0.031(10) 0.068(9) 0.008(6) 0.014(7) -0.011(6)
```

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OW33 0.044(10) 0.042(9) 0.060(9) -0.009(7) 0.008(7) -0.006(6)
OW34 0.043(9) 0.033(9) 0.070(10) 0.013(6) 0.018(7) -0.004(7)
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OW36 0.051(10) 0.045(9) 0.057(9) 0.002(7) 0.012(7) 0.013(7)
OW37 0.060(10) 0.036(10) 0.073(10) 0.006(7) 0.012(8) -0.003(7)
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OW41 0.079(12) 0.060(11) 0.087(11) 0.002(8) 0.035(9) 0.001(9)
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OW46 0.086(12) 0.072(12) 0.093(12) 0.012(8) 0.000(9) 0.004(10)
OW47 0.080(13) 0.075(12) 0.111(12) -0.019(9) -0.010(10) -0.020(10)
OW48 0.123(15) 0.089(13) 0.126(14) 0.003(10) 0.020(14) 0.029(12)

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 All esds (except the esd in the dihedral angle between two l.s. planes)
 are estimated using the full covariance matrix.  The cell esds are taken
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 and torsion angles; correlations between esds in cell parameters are
only
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(isotropic)
 treatment of cell esds is used for estimating esds involving l.s.
planes.
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OH28 Al4 H27 151.9(19) 1_455 . ?
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Al3 Al4 H27 66(3) . . ?
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OH31 Al5 O18 93.0(5) . . ?
OW37 Al5 O18 91.2(6) . . ?
OH31 Al5 OH30 170.2(6) . 1_655 ?
OW37 Al5 OH30 93.0(6) . 1_655 ?
O18 Al5 OH30 93.5(5) . 1_655 ?
OH31 Al5 OH28 93.9(5) . . ?
OW37 Al5 OH28 92.9(6) . . ?
O18 Al5 OH28 171.7(5) . . ?
OH30 Al5 OH28 79.1(5) 1_655 . ?
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O7 Al6 O19 177.1(6) . 2_655 ?
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O16 Al6 OW40 171.4(6) 2_655 . ?
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P1 O4 Al1 131.9(7) . 2_545 ?
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P3 O12 Al3 127.7(6) . . ?
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P6 O23 Al3 125.8(7) . . ?
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loop_
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OH25 H25 OH28  0.90(4) 1.98(7) 2.809(15) 154(13) 2_655
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OW34 H34B OH30  0.90(3) 2.14(9) 2.942(15) 148(12) 2_545
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OW36 H36A O17  0.90(3) 2.45(13) 3.080(16) 127(13) 2
OW36 H36B O22  0.90(3) 1.95(10) 2.747(16) 147(17) .
OW37 H37A OW44  0.90(4) 1.96(11) 2.700(18) 138(14) 4_676
OW37 H37B OW45  0.90(3) 1.83(8) 2.69(2) 159(17) .
OW38 H38A OW46  0.90(3) 1.91(12) 2.629(19) 136(16) .
OW38 H38B OW47  0.88(3) 2.10(14) 2.750(19) 130(15) .
OW39 H39A OW43  0.90(3) 1.71(5) 2.592(16) 166(15) .
OW39 H39B OW43  0.90(3) 2.33(5) 3.208(18) 167(10) 3_676
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OW46 H46B O23  0.92(3) 2.12(11) 2.952(18) 149(17) 3_575
OW47 H47A OW48  0.90(3) 1.94(16) 2.68(2) 137(21) 3_575
OW47 H47B OW35  0.90(3) 2.75(6) 3.608(19) 159(15) 2_545
OW48 H48A OW40  0.91(4) 2.37(7) 3.27(2) 167(24) 3_675
OW48 H48B OH24  0.91(4) 1.77(4) 2.68(2) 177(25) .

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