Original paper

New crystallographic data and formula revision of phuralumite, $Al_2[(UO_2)_3(PO_4)_2O(OH)](OH)_3(H_2O)_9$

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The crystal structure of phuralumite, $Al_2[(UO_2)_3(PO_4)_2O(OH)](OH)_3(H_2O)_9$, from the Kobokobo pegmatite (Kivu, Democratic Republic of Congo), was refined from single crystal X-ray diffraction data. Four samples have been investigated in this study, and the crystal structure was refined to R_1 = 0.0566, 0.0544, 0.0661 and 0.0353, for 5739, 5953, 6007 and 5793 unique observed reflections, for the samples VC2048, VC2048, VC2054 and VC2055, respectively. Phuralumite is monoclinic, space group $P2_1/n$, a = 9.4407(3), b = 20.8596(8), c = 13.4326(4) Å, β = 107.905(4)°, V = 2517.40(17) Å^3, and Z = 4 (sample VC2048). The structure consists of $[(UO_2)_3(PO_4)_2O(OH)]^{3-}$ layers, parallel to (010), which are connected by Al^{3+} ions and H_2O molecules. The uranyl phosphate sheets show the phosphuranylite anion topology, while the Al^{3+} ions occur in 5- and 6-fold coordination and are connected together to form $Al_4O_4(OH)_6(H_2O)_4$ clusters. The crystallographic data obtained from the four structural models converge and confirm the previously determined structure for phuralumite. However, these new data also show some discrepancies in the bond-valence analysis, especially in the assignment of the OH^- groups and water molecules. As a consequence of this study, the structural formula of phuralumite, previously reported as $Al_2[(UO_2)_3(PO_4)_2(OH)_2](OH)_4(H_2O)_{10}$, must be modified to $Al_2[(UO_2)_3(PO_4)_2O(OH)](OH)_3(H_2O)_9$.

Keywords: phuralumite, crystal structure, aluminium, uranyl phosphate, Kobokobo, formula revision
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1. Introduction

Uranyl phosphates and arsenates constitute the most diverse group of uranyl minerals, with more than eighty species described to date. The reason of this abundance is the wide distribution of phosphorus in many kinds of geological environments, and especially in the oxidation zones of uranium deposits (Finch and Murakami 1999; Krivovichev and Plášil 2013). One of the most remarkable occurrences of uranyl phosphates is the uraniferous quartz–albite–muscovite pegmatite of Kobokobo, situated in the region of Kivu in the western Democratic Republic of Congo (DRC). This pegmatite is the type-locality for twelve actinides- and aluminium-bearing phosphates: althupite, eylettersite, kamitugaite, metavanmeersscheite, moreautite, mundite, phuralumite, ranunculite, threadgoldite, triangulite, upalite and vanmeersscheite.

Phuralumite, $Al_2[(UO_2)_3(PO_4)_2(OH)_2](OH)_4(H_2O)_{10}$, was originally described from the Kobokobo pegmatite by Deliens and Piret (1979), and is associated with meta-autunite, $Ca[(UO_2)(PO_4)]_2(H_2O)_6$, phosphuranylite, $CaK(H_3O)_3(UO_2)[(UO_2)_3(PO_4)_2O_2]_2(H_2O)_8$, and ranunculite, $Al(UO_2)(PO_3OH)(OH)_3(H_2O)_4$. Piret et al. (1979) solved the structure of phuralumite and confirmed the chemical composition previously obtained from electron-microprobe analyses by Deliens and Piret (1979). Phuralumite is monoclinic, $P2_1/a$, Z = 4, a = 13.836(6), b = 20.918(6), c = 9.428 (3) Å, β = 112.44(3)°. The structure is based on sheets showing the composition $[(UO_2)_3(PO_4)_2(OH)_2]^{2-}$, similar to those observed in the minerals of the phosphuranylite group (Krivovichev and Plášil 2013). These minerals are characterized by a U:P (or U:As) ratio of 3:2, and occur under slightly alkaline conditions (pH *c.* 7.5–8.5) in the end of the acidic stage of the development of oxidation zones (Chernikov 1981; Plášil et al. 2009; Krivovichev and Plášil 2013; Plášil 2014). Note that in addition to phosphates and arsenates, five uranyl selenites are structurally related to the phosphuranylite group: guilleminite $Ba(UO_2)_3(SeO_3)_2O_2(H_2O)_3$ (Cooper and Hawthorne 1995), piretite $Ca(UO_2)_3(SeO_3)_2(OH)_4(H_2O)_4$ (Vochten et al. 1996), haynesite $(UO_2)_3(SeO_3)_2(OH)_2(H_2O)_5$ (Čejka et al. 1999), marthozite $Cu(UO_2)_3(SeO_3)_2O_2(H_2O)_8$ (Cooper and Hawthorne 2001) and larisaite $Na(H_3O)(UO_2)_3(SeO_3)_2O_2(H_2O)_4$ (Chukanov et al. 2004).

During our reinvestigation of uranyl minerals from the Kobokobo pegmatite, several samples of phuralumite have been studied (Dal Bo 2016). The new crystallographic data obtained on these samples show some discrepancy with those reported by Piret et al. (1979), and prompt us to publish new single-crystal X-ray diffraction data in order to revise the formula of phuralumite.

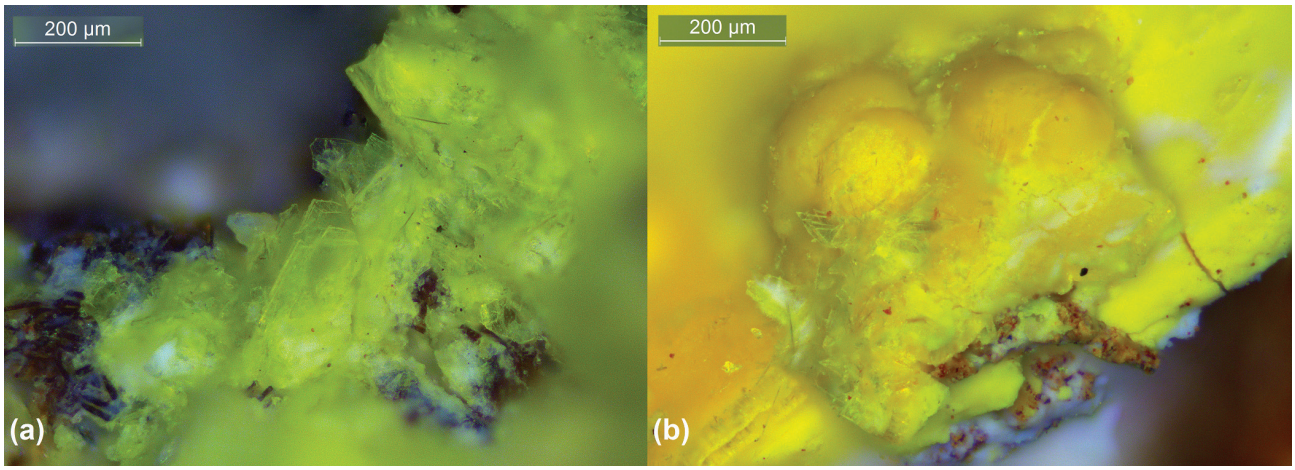

Fig. 1 Intergrowth of phuralumite prismatic crystals (**a**) and view of the close association between phuralumite and the nodules of ranunculite (**b**). Sample VC2055; photographs by R. Warin.

2. Sample description

Four samples from the Kobokobo pegmatite (VC2040, VC2048, VC2054 and VC2055) containing phuralumite crystals have been investigated. Phuralumite occurs as flattened and irregular monoclinic lemon-yellow prisms, commonly in subparallel or random intergrowths (Fig. 1). The crystals can reach up to 0.25 mm in length. In the present case, phuralumite is observed in close association with gold-yellow nodules of ranunculite. These samples belong to the collection of the Musée National d'Histoire Naturelle du Luxembourg.

3. Chemical composition

Energy-dispersive X-ray spectroscopy (EDS) was used to confirm the chemical composition of phuralumite. The

Tab. 1 Crystallographic data and refinement details for phuralumite samples

Sample	VC2040	VC2048	VC2054	VC2055
Ideal structural formula		$Al_2[(UO_2)_3(PO_4)_2O(OH)](OH)_3(H_2O)_9$		
a (Å)	9.4280(3)	9.4407(3)	9.4423(5)	9.4467(2)
b	20.8445(5)	20.8596(8)	20.8723(9)	20.9023(6)
c	13.4207(4)	13.4326(6)	13.4307(6)	13.4396(3)
β (°)	107.962(3)	107.905(4)	107.862(5)	107.944(3)
V (Å³)	2508.92(12)	2517.40(17)	2519.3(5)	2524.68(11)
Space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/n$
Z	4	4	4	4
Calculated density (g.cm^{-3})	3.394	3.383	3.380	3.373
Absorption coefficient (mm^{-1})	19.621	19.555	19.540	19.498
F(000)	2272	2408	2272	2272
Radiation (Å)	MoK_α, 0.71073	MoK_α, 0.71073	MoK_α, 0.71073	MoK_α, 0.71073
Crystal size (mm)	0.12 × 0.11 × 0.08	0.13 × 0.07 × 0.03	0.16 × 0.13 × 0.06	0.19 × 0.04 × 0.02
Temperature (K)	293	293	293	293
θ range (°)	2.33 to 28.47	2.32 to 28.18	2.34 to 27.21	2.45 to 28.84
Reflection range	$-12 \le h \le 11$ $-28 \le k \le 25$ $-17 \le l \le 14$	$-12 \le h \le 12$ $-27 \le k \le 27$ $-17 \le l \le 16$	$-12 \le h \le 12$ $-28 \le k \le 27$ $-17 \le l \le 17$	$-12 \le h \le 12$ $-27 \le k \le 26$ $-17 \le l \le 17$
Total no. of reflections	11860	19906	23278	13308
Unique reflections	5739	5953	6007	5793
Observed reflections, $\|Fo\| \ge 4\sigma F$	4268	3911	3937	4665
Refined parameters	314	314	304	329
R_1, $\|Fo\| \ge 4\sigma F$	0.0566	0.0544	0.0661	0.0353
R_1, all data	0.0831	0.1035	0.1148	0.0522
wR_2 (F^2), all data	0.1454	0.1379	0.1655	0.0835
GOF obs/all	1.07, 1.07	1.04, 1.04	1.04, 1.04	1.02, 1.02
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e/Å³)	5.00, –2.64	2.64, –2.27	3.37, –3.95	2.08, –2.06

crystals were mounted on adhesive carbon tape, carbon-coated, and then analysed by an environmental scanning electron microscope (FEX XL30 ESEM-FEG) working in high vacuum mode, using 15 kV accelerating potential. In all analysed crystals the only chemical elements detected are U, P, Al and O (Fig. 2). Samples VC2048, VC2054 and VC2055 also revealed a small amount of Si; however, the presence of this element in the crystal structure of phuralumite is not supported by the crystallographic data. The absence of As is consistent with the geological environment (pegmatite) in which this element is usually very scarce. Presence of fluorine was carefully checked and this chemical element remains absent. No other elements, especially those prone to substitute for Al, were detected.

4. X-ray crystallography and structure determination

4.1. Single-crystal X-ray diffraction and structure solution

Single-crystal X-ray study of phuralumite was carried out with an Rigaku Xcalibur four-circle diffractometer (kappa geometry), using MoK_α radiation (λ = 0.71073 Å, 40 kV, 40 mA), and equipped with an EOS CCD area detector, on crystal fragments from four different samples VC2040, VC2048, VC2054 and VC2055.

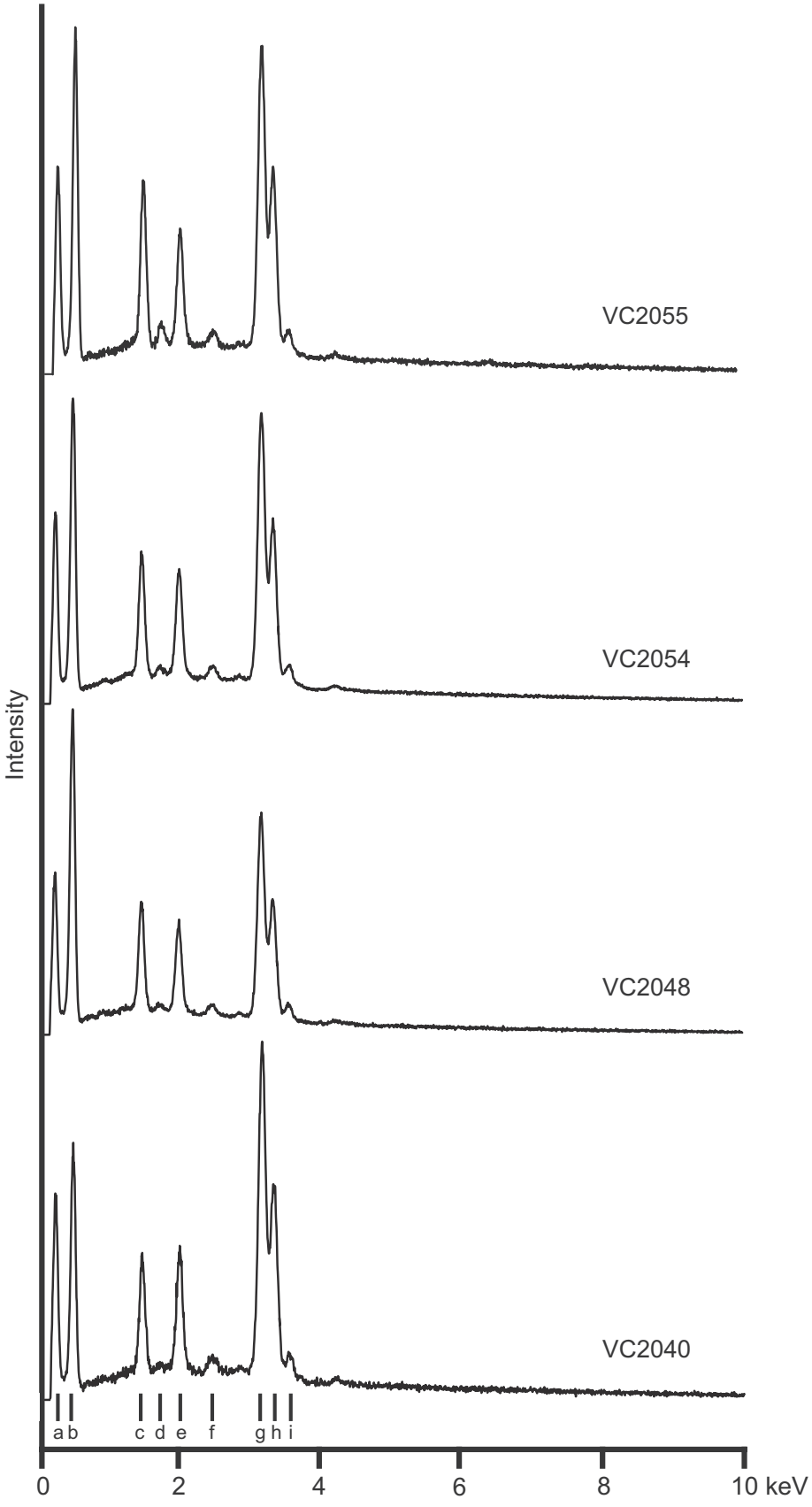

Fig. 2 Energy-dispersive X-ray emission spectra of furongite. The labelled peaks correspond to the following lines: a – CK_α; b – OK_α; c – AlK_α; d – SiK_α; e – PK_α; f – UM_ζ; g – UM_α; h – UM_β; i – UM_γ.

Tab. 2 Atom coordinates and displacement parameters (Å²) for the crystal structure of phuralumite (sample VC2048)

Atom	*x/a*	*y/b*	*z/c*	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Al1	0.0526(6)	0.6120(2)	0.4328(4)	0.0225(12)	0.027(3)	0.022(3)	0.020(3)	0.004(2)	0.009(2)	0.001(2)
Al2	0.1633(6)	0.4903(3)	0.5490(4)	0.0289(13)	0.024(3)	0.023(3)	0.040(3)	0.004(3)	0.010(3)	0.002(2)
U1	1.23243(6)	0.72697(3)	–0.14555(4)	0.01664(16)	0.0121(3)	0.0255(4)	0.0124(3)	–0.0003(2)	0.0039(2)	–0.0012(2)
U2	0.90906(7)	0.71891(3)	–0.03206(4)	0.01673(16)	0.0126(3)	0.0251(4)	0.0131(3)	0.0001(2)	0.0047(2)	–0.0003(2)
U3	0.32937(7)	0.73958(3)	0.17254(4)	0.01768(16)	0.0134(3)	0.0258(4)	0.0139(3)	–0.0009(3)	0.0043(2)	–0.0006(3)
P1	0.5874(5)	0.7575(2)	0.0603(3)	0.0170(9)	0.014(2)	0.026(2)	0.012(2)	–0.0015(17)	0.0043(17)	0.0007(17)
P2	0.0598(5)	0.7186(2)	0.2707(3)	0.0170(9)	0.012(2)	0.026(2)	0.014(2)	0.0008(17)	0.0050(17)	0.0008(17)
O1	1.2204(13)	0.08086(5)	–0.1224(8)	0.027(3)	0.028(7)	0.034(7)	0.014(6)	0.003(5)	0.001(5)	–0.002(6)
O2	1.2497(13)	0.6440 (6)	–0.1677(8)	0.030(3)	0.039(8)	0.035(8)	0.023(7)	0.000(5)	0.020(6)	0.001(6)
O3	0.9390(12)	0.8023(6)	–0.0170(9)	0.029(3)	0.019(7)	0.045(8)	0.023(6)	–0.002(6)	0.007(5)	0.012(6)
O4	0.8757(12)	0.6354(5)	–0.0442(9)	0.025(3)	0.019(7)	0.027(7)	0.031(7)	0.000(5)	0.011(6)	–0.009(5)
O5	0.3773(13)	0.6600(6)	0.02146(8)	0.029(3)	0.024(7)	0.047(8)	0.017(6)	–0.001(5)	0.007(5)	0.009(6)
O6	0.2751(12)	0.8173(5)	0.1225(9)	0.027(3)	0.022(7)	0.039(8)	0.020(6)	–0.001(5)	0.009(5)	0.000(6)
O7	0.0466(12)	0.7105(5)	0.1545(8)	0.021(3)	0.013(6)	0.041(8)	0.008(5)	0.007(5)	0.000(5)	0.001(5)
O8	0.9815(12)	0.7196(5)	–0.1788(8)	0.024(3)	0.014(6)	0.039(7)	0.019(6)	0.005(5)	0.007(5)	–0.011(5)
O9	0.5997(12)	0.7561(5)	0.1767(8)	0.022(3)	0.018(6)	0.038(7)	0.011(6)	0.005(5)	0.005(5)	0.002(5)
O10 (OH)	1.1706(11)	0.6942(5)	0.0092(8)	0.021(3)	0.009(6)	0.038(7)	0.018(6)	–0.002(5)	0.008(5)	0.001(5)
O11	0.4372(12)	0.7240(5)	0.0114(8)	0.024(3)	0.020(6)	0.030(7)	0.022(6)	0.004(5)	0.006(5)	–0.001(5)
O12	–0.0674(12)	0.7583(5)	0.2865(8)	0.022(3)	0.017(6)	0.025(7)	0.025(6)	0.001(5)	0.010(5)	0.005(5)
O13	0.2100(12)	0.7555(5)	0.3133(8)	0.022(3)	0.018(6)	0.030(7)	0.021(6)	–0.007(5)	0.009(5)	–0.010(5)
O14	0.0714(15)	0.6523(6)	0.3225(9)	0.037(3)	0.057(10)	0.030(8)	0.033(7)	0.002(6)	0.030(7)	–0.006(6)
O15	0.7146(12)	0.7220(6)	0.0388(8)	0.026(3)	0.011(6)	0.051(8)	0.018(6)	0.001(5)	0.006(5)	–0.002(5)
O16	0.5779(13)	0.8267(5)	0.0240(8)	0.028(3)	0.039(8)	0.023(7)	0.021(6)	0.003(5)	0.008(6)	0.001(6)
O17 (OH)	–0.1192(12)	0.5722(5)	0.3670(9)	0.028(3)	0.016(7)	0.026(7)	0.044(8)	0.002(6)	0.014(6)	–0.005(5)
O18 (OH)	0.2003(12)	0.5543(5)	0.4623(9)	0.026(3)	0.020(7)	0.026(7)	0.036(7)	0.008(6)	0.013(6)	–0.002(5)
O19 (H_2O)	0.3064(13)	0.5243(6)	0.6660(9)	0.038(3)	0.027(8)	0.039(8)	0.037(8)	0.003(6)	–0.007(6)	–0.010(6)
O20 (H_2O)	0.3057(14)	0.4357(6)	0.5133(11)	0.042(4)	0.039(9)	0.024(7)	0.069(10)	0.003(7)	0.026(8)	0.005(6)
O21 (OH)	0.0032(12)	0.5479(5)	0.5521(9)	0.028(3)	0.018(7)	0.026(7)	0.040(7)	–0.010(6)	0.008(6)	–0.008(5)
O22 (H_2O)	–0.0291(17)	0.5713(7)	0.7440(11)	0.057(4)	0.070(12)	0.055(10)	0.047(9)	–0.004(8)	0.018(9)	–0.006(8)
O23 (H_2O)	0.4514(15)	0.6309(6)	0.6717(10)	0.039(3)	0.047(9)	0.030(8)	0.046(8)	–0.004(6)	0.023(7)	–0.006(6)
O24 (H_2O)	0.5874(14)	0.4422(6)	0.6348(10)	0.044(4)	0.028(8)	0.055(10)	0.054(9)	0.013(7)	0.022(7)	0.018(7)
O25 (H_2O)	1.204(2)	0.5631(8)	0.0388(14)	0.083(6)	0.087(16)	0.063(13)	0.092(14)	–0.004(10)	0.020(12)	0.010 (10)
O26 (H_2O)	0.687(2)	0.5459(12)	0.7646(17)	0.135(9)	0.048(14)	0.24(3)	0.113(18)	–0.048(18)	0.020(13)	0.022(16)
O27*† (H_2O)	0.262(4)	0.3977(16)	0.842(2)	0.073(10)	–	–	–	–	–	–
O28*† (H_2O)	0.469(4)	0.4730(19)	0.853(3)	0.101(13)	–	–	–	–	–	–
O29*† (H_2O)	0.440(4)	0.4153(18)	1.038(3)	0.088(12)	–	–	–	–	–	–
O30*† (H_2O)	0.037(3)	0.4689(15)	0.873(2)	0.062(9)	–	–	–	–	–	–

* occupancy factor constrained to 0.5; † atom refined with isotropic atomic displacement parameter

Tab.3 Selected interatomic in the structure of phuralumite

	VC2040	VC2048	VC2054	VC2055
U1–O1	1.740(12)	1.740(11)	1.751(13)	1.759(7)
U1–O2	1.770(10)	1.772(12)	1.757(11)	1.765(7)
U1–O8	2.282(9)	2.277(10)	2.267(13)	2.273(5)
U1–O9	2.330(10)	2.357(10)	2.356(11)	2.360(6)
U1–O10	2.420(9)	2.425(9)	2.409(12)	2.416(6)
U1–O11	2.377(11)	2.383(11)	2.395(11)	2.380(6)
U1–O12	2.341(10)	2.358(10)	2.345(14)	2.355(6)
<U1–O_{Ur}>	1.75	1.76	1.75	1.76
<U1–O_{eq}>	2.35	2.36	2.35	2.36
U2–O3	1.809(12)	1.765(12)	1.772(12)	1.777(7)
U2–O4	1.771(11)	1.769(11)	1.749(12)	1.787(7)
U2–O7	2.451(11)	2.449(10)	2.464(12)	2.458(6)
U2–O8	2.264(9)	2.277(10)	2.301(13)	2.260(5)
U2–O10	2.406(10)	2.414(10)	2.425(12)	2.416(6)
U2–O13	2.396(10)	2.393(11)	2.410(11)	2.399(6)
U2–O15	2.325(10)	2.314(10)	2.340(15)	2.328(6)
<U2–O_{Ur}>	1.79	1.77	1.76	1.78
<U2–O_{eq}>	2.37	2.37	2.39	2.37
U3–O5	1.780(11)	1.767(12)	1.768(12)	1.767(7)
U3–O6	1.780(11)	1.769(11)	1.760(12)	1.773(7)
U3–O7	2.662(10)	2.675(10)	2.686(14)	2.668(6)
U3–O8	2.225(10)	2.238(11)	2.223(11)	2.246(6)
U3–O9	2.559(9)	2.559(10)	2.556(13)	2.555(6)
U3–O10	2.432(10)	2.436(11)	2.412(11)	2.430(6)
U3–O11	2.693(10)	2.680(10)	2.665(13)	2.685(6)
U3–O13	2.523(10)	2.505(9)	2.532(13)	2.505(6)
<U3–O_{Ur}>	1.78	1.77	1.76	1.77
<U3–O_{eq}>	2.52	2.52	2.51	2.51
P1–O9	1.560(10)	1.533(10)	1.542(12)	1.525(6)
P1–O11	1.509(10)	1.536(12)	1.519(13)	1.532(7)
P1–O15	1.496(12)	1.512(11)	1.486(14)	1.508(7)
P1–O16	1.516(11)	1.518(12)	1.497(12)	1.516(7)
<P1–O>	1.52	1.52	1.51	1.52
P2–O7	1.532(11)	1.536(10)	1.531(12)	1.531(6)
P2–O12	1.531(11)	1.526(11)	1.523(14)	1.521(6)
P2–O13	1.533(10)	1.560(11)	1.535(13)	1.549(6)
P2–O14	1.527(10)	1.536(12)	1.513(12)	1.527(7)
<P2–O>	1.53	1.54	1.53	1.53
Al1–O14	1.778(11)	1.760(12)	1.795(13)	1.782(7)
Al1–O16	1.736(11)	1.735(12)	1.756(12)	1.745(7)
Al1–O17	1.780(11)	1.795(12)	1.793(14)	1.788(7)
Al1–O18	1.766(11)	1.792(12)	1.771(14)	1.786(7)
Al1–O21	2.205(11)	2.244(12)	2.238(14)	2.195(7)
<Al1–O>	1.85	1.86	1.87	1.86
Al2–O17	1.860(11)	1.854(12)	1.855(13)	1.855(7)
Al2–O18	1.876(11)	1.872(11)	1.879(14)	1.866(7)
Al2–O19	1.858(12)	1.869(13)	1.875(14)	1.884(8)
Al2–O20	1.914(12)	1.932(13)	1.928(15)	1.937(8)
Al2–O21	1.913(12)	1.907(12)	1.917(13)	1.920(7)
Al2–O21^{i}	1.945(11)	1.941(12)	1.931(14)	1.946(7)
<Al2–O>	1.89	1.90	1.90	1.90

Symmetry code: (i) –x; 1–y; 1–z

Tab. 4 The O···O separation distances found in the structure of phuralumite (sample VC2048)

O1–OH17^{i}	2.94(2)
O1–H_2O20^{ii}	3.07(2)
O2–H_2O22^{iii}	2.95(2)
O2–H_2O23^{iii}	3.29(1)
O2–H_2O29^{iv}	3.18(4)
O3–H_2O23^{v}	2.87(2)
O3–H_2O24^{ii}	3.30(2)
O4–H_2O26^{vii}	3.21(1)
O4–H_2O29^{vi}	3.18(5)
O4–H_2O30^{vi}	3.10(3)
O5–H_2O24^{vi}	2.88(2)
O5–H_2O25^{viii}	3.15(2)
O6–H_2O20^{ix}	3.02(2)
O6–H_2O22^{v}	3.10(2)
O8–H_2O22^{iii}	3.26(2)
OH10– H_2O25	2.77(2)
O11– H_2O29^{vi}	3.28(4)
O12– H_2O23^{x}	2.81(2)
O14–OH17	2.65(2)
O14–OH18	2.79(2)
O15–H_2O27^{vi}	2.95(4)
O15–H_2O29^{vi}	3.24(4)
O16–OH18^{v}	2.96(1)
O16–OH21^{v}	2.76(1)
OH17–OH18	2.91(1)
OH17–H_2O19^{xi}	2.63(2)
OH17–H_2O20^{xi}	2.73(1)
OH17–OH21^{xi}	2.81(1)
OH17–OH21	2.45(2)
OH17–H_2O27^{xi}	2.76(3)
OH18–H_2O19	2.69(2)
OH18–H_2O20	2.68(2)
OH18–OH21	2.51(1)
OH18–OH21^{xi}	2.83(2)
OH18–H_2O24^{vi}	2.71(1)
$OH_2$19–H_2O20	2.77(8)
$OH_2$19–OH21	2.84(1)
$OH_2$19–H_2O23	2.60(2)
$OH_2$19–H_2O24	3.29(2)
$OH_2$19–H_2O28	2.70(4)
$OH_2$20–OH21^{xi}	2.79(2)
$OH_2$20–H_2O24	2.68(1)
OH21–OH21^{xi}	2.42(1)
OH21–H_2O22	2.73(2)
OH22–H_2O26^{viii}	2.82(4)
$OH_2$22–H_2O30	2.69(3)
$OH_2$23–H_2O26	2.78(3)
$OH_2$24–H_2O26	2.79(3)
$OH_2$25–H_2O28^{iv}	3.09(4)
$OH_2$25–H_2O30^{vi}	2.93(4)
$OH_2$25–H_2O30^{xii}	3.07(3)
$OH_2$26–H_2O28^{iv}	3.10(5)
$OH_2$27–H_2O28	2.48(6)
$OH_2$27–H_2O29	2.69(5)
$OH_2$27–H_2O30	2.74(5)
$OH_2$28–H_2O29^{xiii}	2.76(6)
$OH_2$28–H_2O29	2.86(5)

Symmetry codes: (i) 3/2+x, 3/2–y, –1/2+z; (ii) 3/2–x, 1/2+y, 1/2–z; (iii) 1+x, y, –1+z; (iv) 2–x, 1–y, 1–z; (v) 1/2+x, 3/2–y, –1/2+z; (vi) 1–x, 1–y, 1–z; (vii) x, y, –1+z; (viii) –1+x, y, z; (ix) 1/2–x, 1/2+y, 1/2–z; (x) –1/2+x, 3/2–y, –1/2+z; (xi) –x, 1–y, 1–z; (xii) –1+x, y, 1+z; (xiii) 1–x, 1–y, 2–z

The crystallographic data and the refinement details on these phuralumite crystals are reported in the Tab. 1. The data were corrected for Lorentz, polarization and absorption effects, the latter with an empirical method using the SCALE3 ABSPACK scaling algorithm included in the CrysAlisRED software package (Agilent Technologies 2012). The crystal structures were solved by direct methods and subsequently refined using SHELXS and SHELXL software (Sheldrick 2008). The reflection conditions and statistics clearly indicate the $P2_1/n$ space group, consistent with the $P2_1/a$ space group previously reported by Piret et al. (1979) (transformation matrix [101/010/–100]). Scattering curves for neutral atoms and anomalous dispersion correction were taken from Wilson (1992).

The structure of phuralumite was solved by direct methods and was refined successfully on the basis of F^2 for all unique data in space group $P2_1/n$. Structure models including anisotropic displacement parameters for all non-H atoms converged and gave an agreement index ($R1$) of 5.66 %, 5.44 %, 6.61 % and 3.53 % calculated for the 4268, 3911, 3937 and 4665 observed unique reflections ($|F_o| \geq 4\sigma_F$) (VC2040, VC2048, VC2054 and VC2055, respectively). The relative occupancy of the Al and P sites was freely refined in order to detect some cationic substitutions. The relative occupancies of all Al and P sites stay very close to unity, and therefore these Al and P sites were considered as fully occupied. This observation is consistent with the cationic content of the phuralumite samples VC2040, as confirmed by EDS analyses**.** The presence of Si in phuralumite samples VC2048, VC2054 and VC2055 is not supported by the relative occupancy of the P sites. The occupancy factor of the O27 to O30 sites, which are occupied by water molecules, has been set to 0.5 in order to keep their isotropic atom displacement parameters at acceptable values. Final atom coordinates, isotropic atom displacement parameters and site occupancies, are given in Tab. 2 for sample VC2048, and selected interatomic distances are reported in Tabs 3 and 4. Bond-valence sums (BVS) were calculated with the parameters of Brown and Altermatt (1985) for Al and P, and those of Burns et al. (1997) for U^{6+} (Tab. 5). Final atom coordinates, as well as the bond-valence tables for samples VC2040, VC2054 and VC2055, are provided as electronic supplementary materials 1–6.

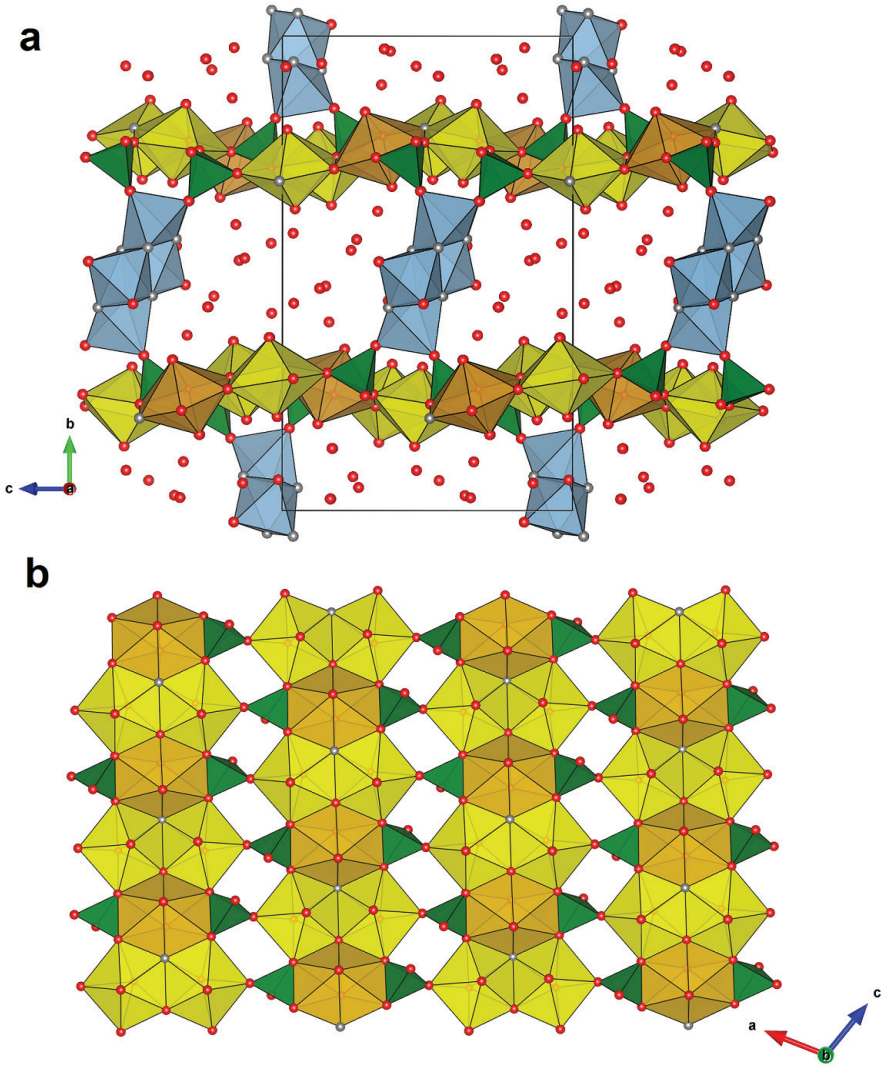

Fig. 3 General view of the structure of phuralumite (**a**) and view of one isolated uranyl phosphate sheet running parallel to (010) (**b**). UO_7 are yellow, UO_8 orange, Al octahedra blue, hydroxyl groups grey and oxygen atoms and water molecules red. Unit-cell edges are outlined by the solid black line. (VESTA 3 software; Momma and Izumi 2011).

4.2. Description of the crystal structure

The crystal structure of phuralumite contains three symmetrically independent U^{6+} cations which are forming typical nearly linear UO_2^{2+} uranyl ions (*Ur*). U1 and U2 are coordinated by five additional oxygen atoms located at the equatorial vertices of the uranyl ions to form the $UrO_4(OH)$ pentagonal bipyramids. The $<U–O_{Ur}>$ and $<U–O_{eq}>$ (*eq* = equatorial) mean

bond lengths vary between 1.76 and 1.79 Å, and between 2.35 and 2.39 Å, respectively (Tab. 3). U3 is coordinated by six additional oxygen atoms located at the equatorial vertices of the uranyl ion to form $UrO_5(OH)$ hexagonal bipyramids. The <U–O_{Ur}> and <U–O_{eq}> mean bond lengths are 1.77–1.78 Å, and 2.51 Å, respectively. These values closely match the typical bond lengths reported by Burns et al. (1997) for UO_7 and UO_8 polyhedra. Two P^{5+} cations are also occurring in the structure as PO_4 tetrahedra. The <P–O> mean bond lengths vary between 1.51 and 1.54 Å. The UrO_5 pentagonal bipyramids formed dimer by edge-sharing, which are then sharing edges with UrO_6 hexagonal bipyramids to form chains. Adjacent chains are connected together by corner- and edge-sharing PO_4 tetrahedra, yielding a $[(UO_2)_3(PO_4)_2O(OH)]^{3-}$ sheet parallel to (101) (Fig. 3). Two independent Al^{3+} cations are occurring in 5-fold coordination (Al1) and in octahedral coordination (Al2). Al1 form a trigonal bipyramid characterized by four Al–ϕ (ϕ = O^{2-}, OH^- and H_2O) bond lengths of 1.76–1.77 Å, and one longer Al–ϕ bond length of 2.20–2.24 Å. Four $Al1O_2(OH)_3$ and $Al2(OH)_4(H_2O)_2$ are connected by edge-sharing to form $Al_4O_4(OH)_6(H_2O)_4$ clusters, which are linked to free apical oxygen atoms of the PO_4 tetrahedra (Fig. 4). Finally, the interlayer of the structure contains eight isolated water molecules, four of which have a site occupation constrained to 0.5. The structural formula of phuralumite obtained from the refinement is $Al_2[(UO_2)_3(PO_4)_2O(OH)](OH)_3(H_2O)_9$.

Tab. 5 The bond-valence analysis for phuralumite (sample VC2048)

	Al1	Al2	U1	U2	U3	P1	P2	Σ	Species
O1			1.819					1.82	O
O2			1.708					1.71	O
O3				1.732				1.73	O
O4				1.718				1.72	O
O5					1.722			1.72	O
O6					1.715			1.72	O
O7				0.453	0.286		1.245	1.98	O
O8			0.635	0.635	0.679			1.95	O
O9			0.542		0.360	1.255		2.16	O
O10			0.475	0.485	0.459			1.42	OH
O11			0.515		0.283	1.245		2.04	O
O12			0.541				1.279	1.82	O
O13				0.505	0.401		1.167	2.07	O
O14	0.685						1.245	1.93	O
O15				0.590		1.328		1.92	O
O16	0.733					1.307		2.04	O
O17	0.623	0.531						1.15	OH
O18	0.628	0.505						1.13	OH
O19		0.510						0.51	H_2O
O20		0.430						0.43	H_2O
O21	0.185	0.460 0.420						1.07	OH
O22								0.00	H_2O
O23								0.00	H_2O
O24								0.00	H_2O
O25								0.00	H_2O
O26								0.00	H_2O
O27								0.00	H_2O
O28								0.00	H_2O
O29								0.00	H_2O
O30								0.00	H_2O
Σ	2.85	2.86	6.23	6.12	5.90	5.13	4.93		

5. Discussion

The general features of the phuralumite structure reported in this work are identical to those observed by Piret et al. (1979). The sheets of uranyl polyhedra and phosphate tetrahedra show the phosphuranylite anion topology, characterized by triangles, squares, pentagons and hexagons (Burns 2005). However, close examination of the bond-valence tables obtained in the present study indicates some discrepancies in the assignment of the O^{2-} atoms, OH^- groups and H_2O molecules. In their later publication about the crystal structure of upalite, Piret and Declercq (1983) reported the formula of phuralumite as $Al_2[(UO_2)_3(PO_4)_2O(OH)](OH)_3(H_2O)_{11}$. It is important to note that the current bond-valence parameters for U^{6+} were not available to Piret et al. (1979) and Piret and Declercq (1983), and therefore this may have contributed to their assignments of O atoms that we believe were incorrect in some cases.

First of all, Piret et al. (1979) reported in their bond-valence table sixteen O^{2-} atoms, four OH^- groups and ten H_2O groups, as well as the general formula $Al_2[(UO_2)_3(PO_4)_2(OH)_2](OH)_4(H_2O)_{10}$, which is not in agreement with their bond-valence analysis (six OH^- groups instead of four, and fourteen O^{2-} atoms instead of sixteen). Minerals of the phosphuranylite group are characterized by sheet of general composition $[(UO_2)_3(TO_4)_2(X)_2]$, where T = P or As and X = O^{2-} or OH^- (Krivovichev and Plášil 2013). The anionic X sites

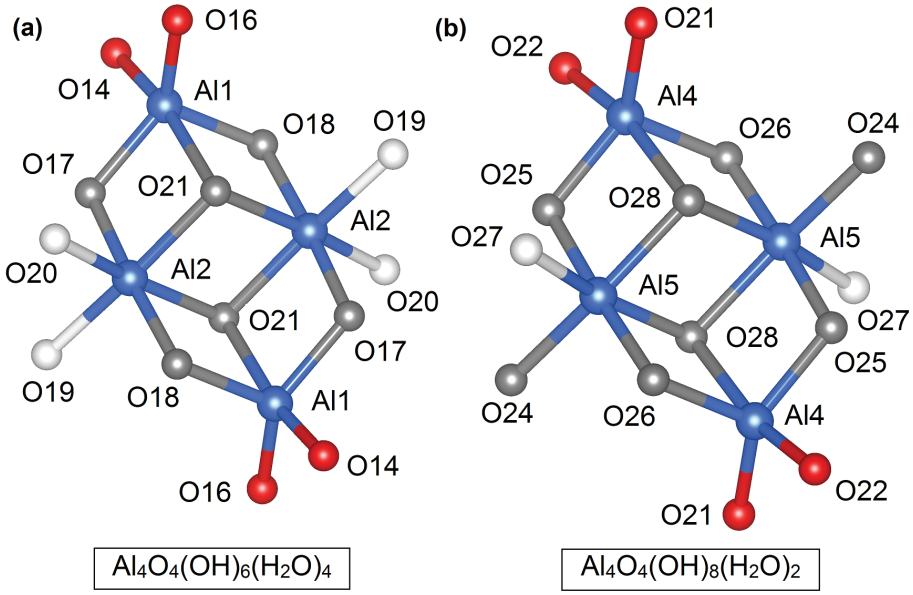

Fig. 4 Detailed view of the Al cluster occurring in the structure of phuralumite according to the present study (**a**) and Piret et al. (1979) (**b**). Oxygen atoms are red, hydroxyl groups grey and water molecules white.

(O8 and O10, this study; O14 and O17, Piret et al. 1979) have the particularity to be only connected to the uranyl polyhedra, and are occupied in the case of phuralumite by O^{2-} atoms (O8) and by OH group (O10). This assignment is supported by the bond-valence sums for O8 and OH10: 1.95 and 1.42 *v. u.*, respectively (*v. u.*: valence unit) (Tab. 5). The O–O distances indicate that O8 is surrounded by H_2O22 at 3.263 Å, limiting the interaction between these two atoms, while the OH10 is closely surrounded by H_2O22 at 2.77 Å, indicating the presence of a O10–H···H_2O22 bond (Tab. 4). Furthermore, the U–O8 bond lengths (2.280, 2.273 and 2.238 Å), which are shorter than the U–OH10 bond lengths (2.427, 2.410 and 2.434 Å) (Tab. 3, sample VC2048), are also an indicator of a different coordination environment around the O8 and H_2O10 atoms. It results that the sheets in the phuralumite structure have the composition $[(UO_2)_3(PO_4)_2O(OH)]^{3-}$, identical to that found in upalite, $Al[(UO_2)_3(PO_4)_2O(OH)](H_2O)_7$ (Piret and Declercq 1983) and françoisite-(Nd), $Nd[(UO_2)_3(PO_4)_2O(OH)](H_2O)_6$ (Piret et al. 1988). The distinction of the O^{2-} and OH^- atoms located on the *X* sites can be achieved in the same manner in the structure of upalite and françoisite-(Nd).

Taking a closer look at the bond-valence table indicates also that the Al atoms are coordinated by three OH^- groups (O17, O18 and O21), while Piret et al. (1979) reported four OH^- groups (O24, O25, O26 and O28), despite the fact that BVS for the O24 is very low for hydroxyl group (0.53 *v. u.*). Hence, the interlayer Al-cluster reported in this work, $Al_4O_4(OH)_6(H_2O)_4$, differs in composition from the $Al_4O_4(OH)_8(H_2O)_2$ cluster described by Piret et al. (1979) (Fig. 4).

Finally, in all the refined structural models presented in the current work, ten of the sites assigned as O atoms correspond to H_2O molecules, four of which have site occupancy constrained to 0.5, given a total of eight H_2O molecules per formula unit. In their structural model, Piret et al. (1979) reported ten sites occupied by water molecules; however, three of them (O35, O36 and O37) have very high thermal parameters, indicating a partial occupancy or a wrong assignment. The number of eight water molecules per unit formula stays consistent with the chemical data provided by Deliens and Piret (1979). All these new crystallographic data indicate that the formula of phuralumite, previously reported as $Al_2[(UO_2)_3(PO_4)_2(OH)_2](OH)_4(H_2O)_{10}$, must be modified to $Al_2[(UO_2)_3(PO_4)_2O(OH)](OH)_3(H_2O)_9$.

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