

Original paper

A novel sheet topology in the structure of kamitugaite, $\text{PbAl}[(\text{UO}_2)_5(\text{PO}_4)_{2.38}(\text{AsO}_4)_{0.62}\text{O}_2(\text{OH})_2](\text{H}_2\text{O})_{11.5}$

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Kamitugaite is a rare supergene uranyl phosphate of aluminum and lead occurring at the Kobokobo pegmatite in the Sud-Kivu Province, Democratic Republic of Congo; its structure has remained unknown until now. Based on single-crystal X-ray diffraction data carried out on the type specimen of kamitugaite (no. 13986, Royal Museum for Central Africa, Tervuren), it is triclinic, space group $P\bar{1}$, with $a = 9.0296(8)$, $b = 10.9557(8)$, $c = 15.8249(15)$ Å, $\alpha = 89.585(7)^\circ$, $\beta = 85.349(8)^\circ$, $\gamma = 84.251(7)^\circ$, $V = 1552.5(2)$ Å³ and $Z = 2$. The structure was refined from diffraction data to $R = 0.1074$ for 2697 unique observed reflections. The structure of kamitugaite is based upon infinite sheets of uranyl and phosphate polyhedra, stacked perpendicular to c ; these sheets result from edge-sharing of UO_7 and UO_8 bipyramids, forming chains approximately parallel to b , which are linked by $(\text{P,As})\text{O}_4$ tetrahedra. Such a sheet has not been observed in minerals or synthetic compounds and is related to the phosphuranylite topology; the ring symbol is $6^15^43^34$. There are two distinct interlayer complexes in kamitugaite: one involving Pb^{2+} and H_2O groups and another involving octahedrally coordinated Al^{3+} and isolated H_2O groups. Adjacent sheets are linked a) through the $\text{Pb}^{2+}\text{--O}$ and H-bonds, and b) *via* H-bonds only in case of the interlayer with Al, the bonding differences being largely attributable to the very different stereochemistry of Pb^{2+} compared to Al^{3+} . The unique combination of these two elements is probably a key reason for the scarcity of kamitugaite.

Keywords: kamitugaite, uranyl phosphate, crystal structure, topology

Received: 6 October, 2017; **accepted:** 8 December, 2017; **handling editor:** J. Sejkora

The online version of this article (doi: 10.3190/jgeosci.246) contains supplementary electronic material.

1. Introduction

Uranyl phosphates and arsenates are environmentally important minerals resulting from hydration–oxidation weathering of primary U minerals, mainly uraninite. They are common constituents of the oxidized parts of U deposits worldwide (Finch and Murakami 1999; Krivovichev and Plášil 2013). Generally, due to their low solubility products, they often occur in the very leached parts of the deposit, *i.e.*, on outcrops, thus being an important control of U mobility (see, *e.g.*, Göb et al. 2013).

The Kobokobo pegmatite in the Sud-Kivu Province (western Democratic Republic of Congo, Africa) (Safiannikoff and Van Wambeke 1967; Van Wambeke 1987) is one of the most interesting mineralogical localities in the World, largely due to occurrences of rare uranium and thorium phosphates within the U-bearing quartz–albite–muscovite pegmatite. This pegmatite is a type-locality for twelve actinide-bearing phosphates, most of which contain Al (Tab. 1). Although several crystal-structure studies have been conducted, structures of many of the Kobokobo type minerals remain unknown. Results of a study on the particularly interesting structure of kamitugaite are presented in this paper.

2. Sample

The crystal of kamitugaite investigated by single-crystal X-ray diffraction originates from the type specimen of this mineral preserved in the collection of the Royal Museum for Central Africa in Tervuren (Belgium); specimen n° RGM13986. It contains yellow to amber prismatic kamitugaite (Fig. 1) along with yellow lath-like phuralumite, yellow micaceous mundite, yellow prismatic upalite and metatorbernite.

3. Single-crystal X-ray crystallography

3.1. Experimental

A prismatic crystal of kamitugaite, with dimensions $0.054 \times 0.014 \times 0.008$ mm, was selected for the diffraction experiment on a Rigaku SuperNova diffractometer equipped with Atlas S2 CCD detector and mirror-monochromatized MoK_α radiation provided by the microfocus X-ray tube. A sphere of three-dimensional intensity data was collected using frame widths of 1.0° in ω , with 400 seconds counting per frame. Diffraction data were processed using the CrysAlis software (Rigaku



Fig. 1 Crystalline crusts composed of prismatic kamitugaite crystals growing in a fissure. Kobokobo pegmatite, specimen no. RMG13986, Royal Museum for Central Africa, Tervuren, Belgium. Width of photograph is 10 mm (photo by E. Van Der Meersche).

2017). A spherical absorption correction combined with empirical scaling was applied in Jana2006 (Petříček et al. 2014).

3.2. Structure solution and refinement

The structure was solved by the charge-flipping algorithm in SHELXT (Sheldrick 2015). The structure subsequently was refined by the full-matrix least-squares with the Jana2006 program (Petříček et al. 2014) based on F^2 . Atoms that were not found by the initial solution were later located by difference-Fourier syntheses. Uranium, P, As, Al and Pb atoms, were refined with anisotropic atomic displacement parameters (ADP). Hydrogen atoms could not be located.

Careful inspection of the diffraction frames revealed the presence of additional reflections that result from the split crystal; therefore, it was treated as a twin in the refinement. Metrics of the kamitugaite cell suggest that it could be a twin by reticular merohedry; twin operation by the matrix $(-1\ 0\ 7; -1\ 0\ 0; 0\ -1\ 0)$; however, the twin fraction obtained from the refinement was very low (~ 0.007) with no impact on refinement. Final cycles converged to $R = 0.1074$ and $wR = 0.2539$ for 2697 observed reflections with goodness of fit (GOF) of 1.81 (Tab. 1). The relatively low quality of the refinement is mainly due to poorly fitted absorption effects. Several O atoms (O1, O2, O7, O8) within the sheet were restrained to have the same displacement parameters, because of the tendency of some of them

Tab. 1 Actinide-bearing minerals discovered from the Kobokobo pegmatite

	Chemical formula	Structure determined by	Primary reference
<i>U minerals</i>			
Kamitugaite	$\text{PbAl}[(\text{UO}_2)_5(\text{PO}_4)_3\text{O}_2(\text{OH})_2](\text{H}_2\text{O})_{11.5}$	this work	Deliens and Piret (1984)
Metavanmeersscheite	$\text{U}^{6+}(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_6(\text{H}_2\text{O})_2$		Piret and Deliens (1982)
Moreauite	$\text{Al}_3(\text{UO}_2)(\text{PO}_4)_3(\text{OH})_2(\text{H}_2\text{O})_{13}$		Deliens and Piret (1985a)
Mundite	$\text{Al}(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_3(\text{H}_2\text{O})_{5.5}$		Deliens and Piret (1981)
Phuralumite	$\text{Al}_2[(\text{UO}_2)_3(\text{PO}_4)_2\text{O}(\text{OH})](\text{OH})_3 \cdot 9\text{H}_2\text{O}$	Dal Bo et al. (2017b)	Deliens and Piret (1979a)
Ranunculite	$\text{Al}(\text{UO}_2)(\text{PO}_3\text{OH})(\text{OH})_3(\text{H}_2\text{O})_4$		Deliens and Piret (1979c)
Threadgoldite	$\text{Al}(\text{UO}_2)_2(\text{PO}_4)(\text{OH})(\text{H}_2\text{O})_8$	Khosrawan-Sazedj (1982)	Deliens and Piret (1979b)
Triangulite	$\text{Al}_3(\text{UO}_2)_4(\text{PO}_4)_4(\text{OH})_5(\text{H}_2\text{O})_5$		Deliens and Piret (1982)
Upalite	$\text{Al}[(\text{UO}_2)_3(\text{PO}_4)_2\text{O}(\text{OH})](\text{H}_2\text{O})_7$	Piret and Declercq (1983)	Deliens and Piret (1979a)
Vanmeersscheite	$\text{U}^{6+}(\text{UO}_2)_3(\text{PO}_4)_2(\text{OH})_6(\text{H}_2\text{O})_4$	Piret and Deliens (1982)	Piret and Deliens (1982)
Furongite*	$\text{Al}_4[(\text{UO}_2)_4(\text{PO}_4)_6](\text{OH})_2(\text{H}_2\text{O})_{19.5}$	Dal Bo et al. (2017a)	Hunan Team (1976)
<i>Th minerals</i>			
Althupite	$\text{AlTh}(\text{UO}_2)_7(\text{PO}_4)_4\text{O}_2(\text{OH})_5(\text{H}_2\text{O})_{15}$	Piret and Deliens (1987)	Piret and Deliens (1987)
Eylettersite	$\text{Th}_{0.75}\text{Al}_3(\text{PO}_4)_2(\text{OH})_6$		Van Wambeke (1972)

*originally described from Hunan province, China; from Kobokobo reported by Deliens and Piret (1985a)

to have non-positive definite atomic displacement parameters (most probably due to poor absorption correction). Details of the data collection and miscellaneous crystallographic and structure refinement parameters are listed in Tab. 1. Final atom coordinates and displacement parameters are given in Tabs 2 and 3. Bond-valence sums were calculated by the DIST option in Jana2006 using the parameters given by Burns et al. (1997) and Gagné and Hawthorne (2015). Selected bond distances are given in Tab. 4. The CIF file, also containing a block with the reflections, is deposited at the Journal's webpage www.jgeosci.org.

4. Results – crystal structure

There are five U, three P/As, one Pb, one Al and thirty-eight O sites in the structure of kamitugaite. There are four U sites (U1 to U4), occupied by U⁶⁺ and coordinated by seven ligands, and a single U5 site, coordinated by eight ligands in a hexagonal bipyramid. Three tetrahedrally coordinated cation sites are filled dominantly by P⁵⁺. However, one site (As1/P1) was found to be occupied predominantly by As⁵⁺ over P⁵⁺. Interlayer cations, Al³⁺ and Pb²⁺, are coordinated by six and nine ligands, respectively.

The UO₇ pentagonal bipyramids form dimers by edge-sharing, which in turn share edges with UO₈ hexagonal bipyramids resulting in fragments (Fig. 2) of the well-known phosphuranylite topology (Burns 2005). In kamitugaite, however, these fragments are linked by edge-sharing of two UO₇ bipyramids, resulting in infinite chains along [010] (Fig. 3). The O sites shared by two bipyramids are OH groups (Tab. 3). Adjacent chains of U-polyhedra are connected through corner-sharing (As1/P1) and edge-sharing (P2, P3) tetrahedra, yielding a [(UO₂)₅(PO₄)₃O₂(OH)₂]⁵⁻ sheet parallel to {001} (Fig. 3). There are two different intersheet regions in kamitugaite

Tab. 2 Crystallographic data and refinement details for kamitugaite

Crystal data	
Structure formula	PbAl[(UO ₂) ₅ (PO ₄) _{2.38} (AsO ₄) _{0.62} O ₂ (OH) ₂](H ₂ O) _{11.5}
Crystal system	triclinic
Space group	<i>P</i> -1
Unit-cell parameters: <i>a</i> , <i>b</i> , <i>c</i> [Å]	9.0296(8), 10.9557(8), 15.8249(15)
α , β , γ [°]	89.585(7), 85.349(8), 84.251(7)
Unit-cell volume [Å ³]	1552.5(2)
<i>Z</i>	2
Calculated density [g/cm ³]	4.639 (for above-mentioned formula)
Crystal size [mm]	0.054 × 0.014 × 0.008
<i>F</i> ₀₀₀	1822
Data collection	
Diffractometer	Rigaku SuperNova with Atlas S2 detector
Temperature [K]	295
Radiation, wavelength [Å]	MoK α , 0.71073 (50 kV, 30 mA)
θ range for data collection [°]	3.42–29.58
Limiting Miller indices	<i>h</i> = -11 → 11, <i>k</i> = -13 → 12, <i>l</i> = -14 → 20
Axis, frame width (°), time per frame (s)	ω , 1, 400
Total reflections collected	11435
Unique reflections	4721
Unique observed reflections, criterion	2697, [<i>I</i> > 3 σ (<i>I</i>)]
Absorption coefficient [mm ⁻¹], type	32.32; Spherical + empirical
<i>T</i> _{min} / <i>T</i> _{max}	0.022/0.046
<i>R</i> _{int}	0.076
Structure refinement by Jana2006	
Number of refined parameters, restraints, constraints	222, 10, 12
<i>R</i> , <i>wR</i> (obs)	0.1074, 0.2538
<i>R</i> , <i>wR</i> (all)	0.1511, 0.2751
GOF obs/all	1.81, 1.48
Weighting scheme, weights	σ , $w = 1/(\sigma^2(I) + 0.0081000002I^2)$
Largest diffraction peak and hole (e ⁻ /Å ³)	12.25 (1.51 Å to O9, -6.22)
Twin matrix; volume fractions	$\begin{pmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ -0.281 & 0.006 & 1 \end{pmatrix}$, 0.647(5)/0.353(5)

structure, one at *z* ~ 0 and second at *z* ~ 0.5. These two intersheet regions accommodate cations with very different stereochemistries. The first complex involves octahedrally coordinated Al³⁺ site, in the form of a regular octahedron, by the two O atoms from the P2 and P3 tetrahedra (within the same sheet) and four H₂O groups. The second intersheet region features a Pb²⁺ cation surrounded by nine ligands (Tab. 5), including four O_{Uranyl} atoms from adjacent sheets and five H₂O groups (two of them occupy symmetrically related O38 sites). The slight asymmetry of the Pb²⁺ coordination environment suggests that the 6s² lone-electron pair can be stereoactive in kamitugaite. There are additional four independent O sites (O25, O32, O31 and a half-occupied O35) in both intersheet regions occupied by H₂O that are not linked directly to any metal cation. To sum up, adjacent structure

Tab. 3 Atom coordinates, occupational and displacement parameters and bond-valence sums (in valence units) for the crystal structure of kamitugaite

Atom	Occupancy	x/a	y/b	z/c	U_{eq}	BV
U1		-0.0348(2)	0.39108(16)	0.26031(12)	0.0172(6)	5.89(13)
U2		0.5529(2)	0.51275(17)	0.28474(12)	0.0177(6)	5.78(18)
U3		1.1353(2)	-0.01012(17)	0.28366(12)	0.0170(6)	5.87(12)
U4		0.7277(2)	0.10699(16)	0.25875(12)	0.0169(6)	5.99(13)
U5		-0.1524(2)	0.75100(17)	0.24676(12)	0.0187(6)	6.13(11)
As1/P1	0.62(4)/0.38(4)	0.3474(8)	0.2498(6)	0.2752(4)	0.014(2)*	5.5(3)
P2		0.5033(15)	0.8479(11)	0.2154(8)	0.016(3)*	5.3(3)
P3		0.2009(15)	0.6552(11)	0.2177(8)	0.016(3)*	6.0(4)
Al1		0.377(2)	0.7491(15)	0.0476(11)	0.028(5)	2.82(15)
Pb1		0.7225(3)	0.8886(2)	0.50280(17)	0.0364(8)	2.28(15)
O1#		0.900(4)	-0.046(3)	0.266(2)	0.017(3)*	1.98(5)
O2#		0.588(4)	0.721(3)	0.244(2)	0.017(3)*	1.99(10)
O3		0.721(5)	0.327(3)	0.299(2)	0.031(9)*	1.29(6)
O4		0.790(4)	0.556(3)	0.258(2)	0.014(7)*	1.91(8)
O5		0.704(6)	0.670(4)	0.513(3)	0.041(11)*	0.41(4)
O6		0.215(4)	0.310(3)	0.219(2)	0.022(8)*	1.77(10)
O7#		0.642(4)	-0.077(3)	0.214(2)	0.017(3)*	1.98(12)
O8#		0.393(4)	0.362(3)	0.334(2)	0.017(3)*	1.70(10)
O9		0.390(4)	0.889(3)	0.280(2)	0.017(7)*	2.08(15)
O10		-0.070(4)	0.365(3)	0.1534(11)	0.019(7)*	1.74(7)
O11		0.787(5)	0.144(3)	0.1516(12)	0.034(10)*	1.73(7)
O12		0.664(4)	0.074(3)	0.3657(11)	0.025(8)*	1.82(7)
O13		0.540(5)	0.624(3)	0.044(2)	0.025(8)*	0.50(5)
O14		0.556(4)	0.553(3)	0.397(2)	0.018(7)*	1.55(11)
O15		0.196(6)	0.862(4)	0.042(3)	0.040(11)*	0.44(6)
O16		0.995(6)	0.814(4)	0.513(3)	0.040(11)*	0.32(4)
O17		1.167(4)	0.031(3)	0.1748(10)	0.015(7)*	1.74(4)
O18		-0.182(5)	0.761(4)	0.3600(9)	0.036(10)*	1.93(5)
O19		0.000(4)	0.406(3)	0.3686(11)	0.020(7)*	1.74(7)
O20		0.491(4)	0.186(3)	0.212(2)	0.017(3)*	1.62(9)
O21		0.266(7)	0.661(5)	0.140(3)	0.063(15)*	2.5(3)
O22		-0.135(6)	0.744(4)	0.1341(9)	0.039(10)*	1.76(5)
O23		1.103(4)	-0.042(3)	0.3952(9)	0.017(7)*	1.72(6)
O24		0.546(4)	0.458(3)	0.179(2)	0.015(7)*	1.79(6)
O25		0.652(5)	0.312(3)	0.477(2)	0.032(9)*	0.00
O26		0.786(4)	0.110(3)	0.493(2)	0.018(7)*	0.31(2)
O27		0.286(5)	0.662(3)	-0.038(2)	0.033(10)*	0.45(5)
O28		0.272(4)	0.151(3)	0.343(2)	0.016(7)*	1.90(9)
O29		0.446(6)	0.837(4)	0.131(3)	0.048(12)*	2.1(2)
O30		0.484(6)	0.843(4)	-0.041(3)	0.049(12)*	0.41(5)
O31		0.228(8)	1.104(5)	0.008(4)	0.070(16)*	0.00
O32		0.872(6)	0.392(4)	0.569(3)	0.042(11)*	0.00
O33		0.303(5)	0.617(4)	0.285(3)	0.034(10)*	1.83(17)
O34		0.074(6)	0.577(4)	0.224(3)	0.044(11)*	2.14(19)
O35	0.5	0.773(9)	0.667(6)	-0.046(4)	0.022(16)*	0.00
O36		0.961(4)	0.170(3)	0.303(2)	0.022(8)*	1.28(5)
O37		0.1140(17)	0.782(3)	0.250(3)	0.053(13)*	1.99(10)
O38		0.548(6)	0.117(4)	0.548(3)	0.044(11)*	0.40(3)

* atoms refined with isotropic displacement parameters; # atoms restricted to have same displacement parameters;

 BV – sum of bond-valences (in valence units)**Tab. 4** Anisotropic displacement parameters for the crystal structure of kamitugaite

Atom	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
U1	0.0109(9)	0.0129(9)	0.0284(11)	-0.0037(7)	-0.0028(8)	-0.0007(7)
U2	0.0117(9)	0.0169(9)	0.0248(10)	-0.0034(7)	-0.0011(8)	-0.0007(7)
U3	0.0106(9)	0.0155(9)	0.0256(10)	-0.0033(7)	-0.0021(8)	-0.0023(7)
U4	0.0131(9)	0.0120(9)	0.0263(11)	-0.0034(7)	-0.0024(8)	-0.0007(7)
U5	0.0131(9)	0.0167(9)	0.0274(11)	-0.0055(7)	-0.0031(8)	-0.0013(8)
Pb1	0.0359(14)	0.0339(12)	0.0408(14)	-0.0053(10)	-0.0087(11)	-0.0003(10)
Al1	0.034(10)	0.017(7)	0.033(9)	-0.005(7)	-0.005(8)	-0.003(7)

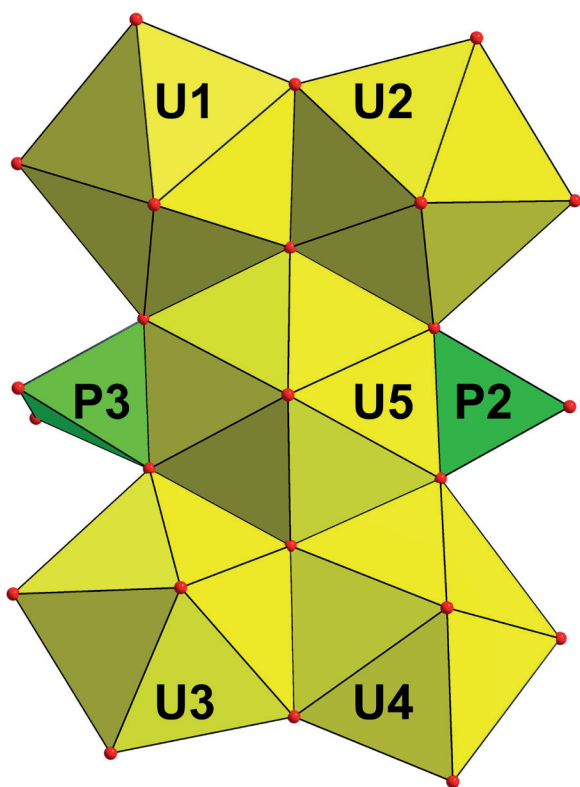


Fig. 2 Fundamental building block in the structural sheet of kamitugaite (U polyhedra yellow, PO₄ green).

units are linked either by Pb–O bonds (+hydrogen bonds), or through hydrogen bond only (in case of intersheet region with Al) (Fig. 4).

The structural formula of kamitugaite obtained from the results of the structure refinement is $\text{Pb}(\text{H}_2\text{O})_4\text{Al}(\text{H}_2\text{O})_4[(\text{UO}_2)_5(\text{PO}_4)_{2.38}(\text{AsO}_4)_{0.62}\text{O}_2(\text{OH})_2](\text{H}_2\text{O})_{3.5}$, $Z = 2$.

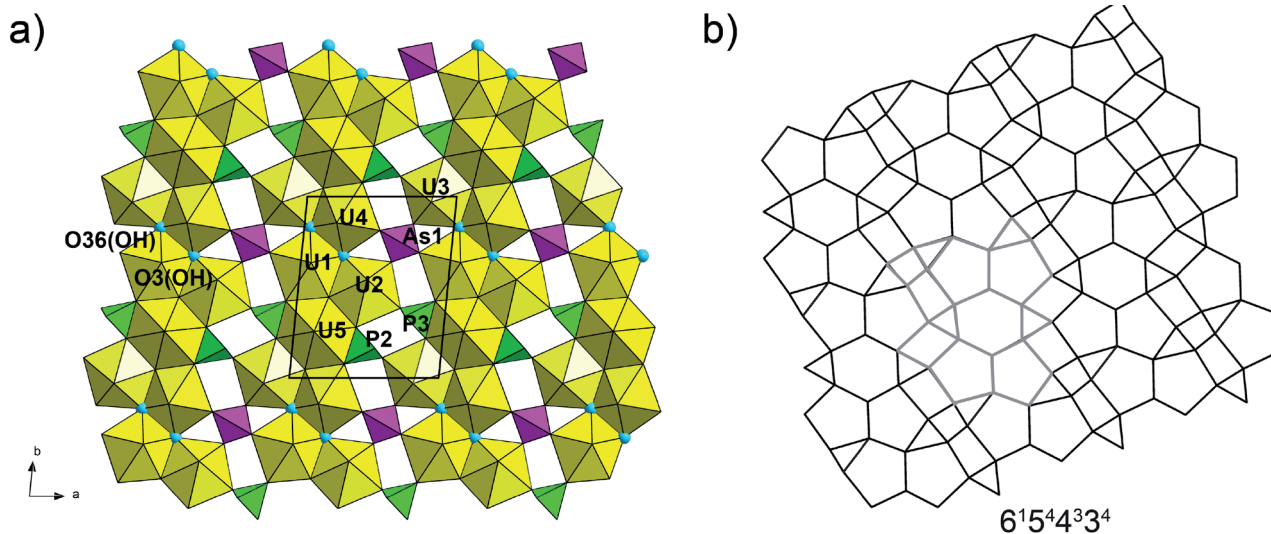


Fig. 3 Structural unit in kamitugaite. **a** – Uranyl phosphate–arsenate sheet composed of infinite chains built up from phosphuranylite-like fragments that are linked *via* edge- and vertex-sharing AsO₄ and PO₄ tetrahedra. The OH groups are represented by blue spheres. Unit cell edges outlined by black lines. **b** – Corresponding uranyl-anion topology with the ring symbol (particular part shaded in grey).

5. Discussion and conclusions

5.1. Sheet topology

The uranyl–phosphate sheet found in kamitugaite represents a novel topological type with some similarities to phosphuranylite anion topology. The basic module within the sheet is the phosphuranylite-like $(\text{UO}_8)(\text{UO}_7)_4(\text{TO}_4)_2$ module. However, in kamitugaite there is an additional *T*-site linking adjacent uranyl–phosphate chains together by sharing all vertices. The proportion U:*T* in kamitugaite is 5:3 while in phosphuranylite it is 3:2 (within the sheet). This results in the sheet composed of triangles, squares, pentagons and hexagons (*TrSqPtHx* sheet) of the new topology that has not been observed either in minerals or synthetic compounds (Burns 2005; Lussier et al. 2016); the sheet is characterized by the ring symbol $6^15^43^34$ (Fig. 4; following Krivovichev 2009).

Both P2 and P3 tetrahedra share three of their vertices with the U–P chains, leaving the third vertex not linked within the sheet (Fig. 3). This may result in the possibility of orientational stereoisomerism within the sheet (Krivovichev 2009, 2010). Although, in kamitugaite the vertices are not free since they are linked to the Al site.

5.2. A comparison with the original description

The unit cell reported in the original paper by Deliens and Piret (1984) describing kamitugaite as a new mineral is very similar to that found by the current single-crystal X-ray study; the only difference is in the unit cell set-

Tab. 5 Selected interatomic distances in the crystal structure of kamitugaite

U1–O10	1.783(19)	U2–O14	1.84(3)	U3–O17	1.783(18)
U1–O19	1.785(19)	U2–O24	1.79(3)	U3–O23	1.802(16)
U1–O3 ⁱ	2.41(4)	U2–O2	2.41(3)	U3–O1	2.24(4)
U1–O4 ⁱ	2.28(3)	U2–O3	2.43(4)	U3–O9 ⁱⁱ	2.45(3)
U1–O6	2.38(3)	U2–O4	2.25(4)	U3–O28 ⁱⁱⁱ	2.48(4)
U1–O34	2.39(5)	U2–O8	2.39(4)	U3–O36	2.40(3)
U1–O36 ⁱ	2.51(3)	U2–O33	2.42(4)	U3–O37 ⁱⁱ	2.37(3)
<U1–O _{lr} >	1.78	<U2–O _{lr} >	1.82	<U3–O _{lr} >	1.79
<U1–O _{eq} >	2.39	<U2–O _{eq} >	2.38	<U3–O _{eq} >	2.39
U4–O11	1.79(2)	U5–O18	1.792(15)		
U4–O12	1.793(19)	U5–O22	1.779(14)		
U4–O1	2.19(3)	U5–O1 ^{iv}	2.34(3)		
U4–O3	2.49(3)	U5–O2 ⁱ	2.40(4)		
U4–O7	2.36(3)	U5–O4 ⁱ	2.25(3)		
U4–O20	2.40(4)	U5–O7 ^{iv}	2.59(3)		
U4–O36	2.44(4)	U5–O34	2.66(5)		
<U4–O _{lr} >	1.79	U5–O37	2.47(2)		
<U4–O _{eq} >	2.38	<U5–O _{lr} >	1.79		
		<U5–O _{eq} >	2.45		
As1–O6	1.63(4)	P2–O2	1.60(3)	P3–O21	1.32(5)
As1–O8	1.65(3)	P2–O7 ^v	1.57(4)	P3–O33	1.50(5)
As1–O20	1.67(3)	P2–O9	1.42(3)	P3–O34	1.49(5)
As1–O28	1.67(3)	P2–O29	1.48(5)	P3–O37	1.59(3)
<As1–O>	1.66	<P2–O>	1.52	<P3–O>	1.48
Al1–O13	1.90(4)	Pb1–O5	2.42(4)		
Al1–O15	1.96(5)	Pb1–O12 ^v	3.00(3)		
Al1–O21	1.99(6)	Pb1–O16	2.53(5)		
Al1–O27	1.95(4)	Pb1–O18 ⁱⁱⁱ	2.71(3)		
Al1–O29	1.82(5)	Pb1–O23 ^{vi}	2.98(3)		
Al1–O30	1.98(5)	Pb1–O26 ^v	2.55(3)		
<Al1–O>	1.93	Pb1–O28 ^{vii}	2.48(3)		
		Pb1–O38 ^v	2.88(4)		
		Pb1–O38 ^{vii}	2.64(5)		
		<Pb1–O>	2.69		

Symmetry codes: (i) $x-1, y, z$; (ii) $x+1, y-1, z$; (iii) $x+1, y, z$; (iv) $x-1, y+1, z$; (v) $x, y+1, z$; (vi) $-x+2, -y+1, -z+1$; (vii) $-x+1, -y+1, -z+1$; (viii) $-x+1, -y+1, -z$; (ix) $x, y-1, z$; (x) $-x, -y+1, -z$; (xi) $-x+1, -y, -z+1$; (xii) $-x, -y+2, -z$; (xiii) $-x+2, -y, -z+1$; (xiv) $-x+1, -y+2, -z$.

ting. The chemical composition given in the original description differs in the total amount of H₂O, giving 14 H₂O (= 9.5 H₂O + 9 OH); however, H₂O content was not determined directly, but by difference. The current structure study reliably indicates 11.5 H₂O + 2 OH in total (including one half-occupied H₂O site). Notably, kamitugaite was described as an As-containing (Deliens and Piret 1984, 1985b) species. As indicated by the current structure study, As is predominant at one of the tetrahedral sites only (As1 site; with the mean bond length of 1.66 Å). Based on the site-scattering refinement, the As content is equal to 0.64 As *pfu*, which is even higher than reported in the original paper.

5.3. The occurrence of kamitugaite

Kamitugaite has been reliably confirmed only from the type locality, the Kobokobo pegmatite. At Ko-

bokobo, kamitugaite is one of the two minerals that contain essential Pb, the other being dumontite, Pb₂(UO₂)₃(PO₄)₂(OH)₄·3H₂O. The unique combination of elements in kamitugaite most probably contributes to its scarcity; no other known mineral contains essential Pb, Al and U, let alone P and As. The source of the Pb is unknown; no primary Pb-bearing minerals have been observed in the Kobokobo pegmatite. Most likely radiogenic lead, otherwise rather immobile, was mobilized from weathered uraninite by alteration solutions.

Acknowledgements. We thank Florias Mees (Royal Museum for Central Africa, Tervuren, Belgium) for his kind cooperation in the sample preparation and for valuable comments. Eddy Van Der Meersche (Gent, Belgium) is acknowledged for microphotography. Comments by Sergey Krivovichev and Anthony Kampf helped improving quality of the earlier version of the manuscript. This re-

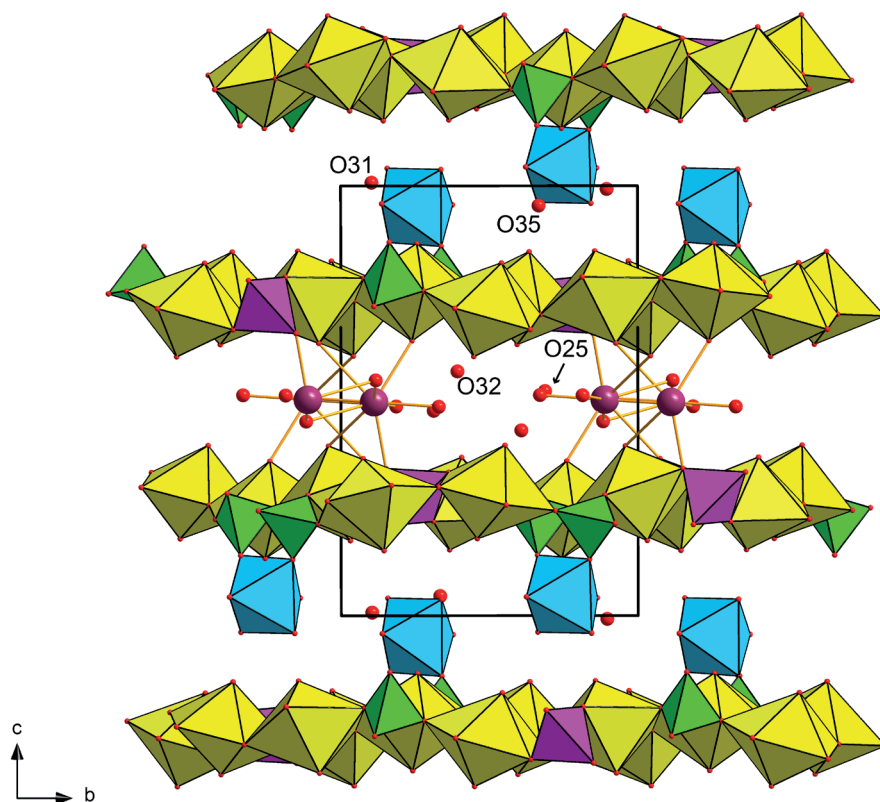


Fig. 4 Crystal structure of kamitugaite viewed down [100]. Uranyl phosphate–arsenate sheets alternate two types of intersheet region: those occupied by Pb^{2+} cation (in plum color, ball-and-stick model) and molecular H_2O , and those occupied by Al^{3+} -octahedra (cyan) and a molecular H_2O . Water molecules that are not linked directly to metal cations are labeled. Other colors follow the scheme from Fig. 3. Unit-cell edges outlined by black lines.

search was supported through the project No. 17-09161S of the Grant agency of the Czech Republic.

Electronic supplementary material. Supplementary crystallographic data for this paper (a CIF file) are available online at the Journal website (<http://dx.doi.org/10.3190/jgeosci.246>).

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