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Polyarsite, $Na_7CaMgCu_2(AsO_4)_4F_2Cl$, a New Mineral with Unique Complex Layers in the Novel-Type Crystal Structure

Igor V. Pekov [1], Natalia V. Zubkova [1,*], Atali A. Agakhanov [2], Dmitry I. Belakovskiy [2], Marina F. Vigasina [1], Vasiliy O. Yapaskurt [1], Sergey N. Britvin [3], Anna G. Turchkova [1], Evgeny G. Sidorov [4,†], Elena S. Zhitova [4] and Dmitry Yu. Pushcharovsky [1]

[1] Faculty of Geology, Lomonosov Moscow State University, Vorobievy Gory, 119991 Moscow, Russia
[2] Fersman Mineralogical Museum, Russian Academy of Sciences, Leninsky Prospekt 18-2, 119071 Moscow, Russia
[3] Department of Crystallography, St. Petersburg State University, University Emb. 7/9, 199034 St. Petersburg, Russia
[4] Institute of Volcanology and Seismology, Far Eastern Branch of Russian Academy of Sciences, Piip Boulevard 9, 683006 Petropavlovsk-Kamchatsky, Russia
* Correspondence: n.v.zubkova@gmail.com
† Deceased 20 March 2021.

Abstract

The new mineral polyarsite, ideally $Na_7CaMgCu_2(AsO_4)_4F_2Cl$, was discovered in high-temperature incrustations of the active Arsenatnaya fumarole at the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption, Tolbachik volcano, Kamchatka, Russia. It is associated with aegirine, sanidine, ferrisanidine, hematite, halite, sylvite, cassiterite, evseevite, axelite, badalovite, johillerite, arsmirandite, aphthitalite, tridymite, potassic-magnesio-fluoro-arfvedsonite and litidionite. Polyarsite forms short-prismatic, equant or tabular crystals up to 0.15 mm across, their clusters up to 0.3 mm in size or crusts up to 0.5 mm across and up to 0.03 mm thick. Polyarsite is transparent, sky-blue to light blue, with vitreous lustre. It is brittle, no cleavage is observed and the fracture is uneven. $D_{calc.}$ = 3.592 g cm^{-3}. Polyarsite is optically biaxial (+), α = 1.624 (4), β = 1.645 (4), γ = 1.682 (4) (589 nm), $2V_{meas.}$ = 70 (10)°. The empirical chemical formula calculated based on 19 O+F+Cl apfu is $Na_{7.04}Ca_{1.00}Mg_{0.92}Cu_{2.06}Fe^{3+}_{0.06}(As_{3.96}S_{0.05})_{\Sigma 4.01}O_{16.28}F_{1.66}Cl_{1.06}$. Polyarsite is monoclinic, space group $I2/m$, a = 8.4323(4), b = 10.0974(4), c = 10.7099(6) Å, β = 90.822(4)°, V = 911.79(8) Å^3 and Z = 2. The crystal structure was determined based on SCXRD data, R = 0.0391. Polyarsite demonstrates a novel structure type. The structure is based on the (1 0 1) heteropolyhedral layers formed by Cu_2O_8Cl dimers built by CuO_4Cl tetragonal pyramids sharing common Cl vertex, AsO_4 tetrahedra and MgO_4F_2 octahedra. Adjacent layers are linked via CaO_8 cubes to form a pseudo-framework which hosts octahedrally coordinated Na cations. Polyarsite was named based on the Greek words πολύς, poly, "many" and due to belonging to arsenates: this arsenate contains many chemical components ordered between different positions in crystal structure.

Keywords: polyarsite; new mineral; chloro-fluoro-arsenate; crystal structure; fumarole sublimate; Tolbachik volcano; Kamchatka

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1. Introduction

In this article, we describe the new mineral species polyarsite, a complex chloro-fluoro-arsenate with the ideal formula $Na_7CaMgCu_2(AsO_4)_4F_2Cl$ and a unique crystal structure.

It was discovered in high-temperature incrustations of the active Arsenatnaya fumarole situated at the summit of the Second scoria cone of the Northern Breakthrough of the Great Tolbachik Fissure Eruption 1975–1976, Tolbachik volcano, Kamchatka peninsula, Far-Eastern Region, Russia (55°41′ N, 160°14′ E, 1200 m asl). The Second scoria cone is a monogenetic volcano *ca*. 300 m high and about 0.1 km^3 in volume formed in 1975 [1] and still, after a half of century, demonstrates strong fumarolic activity. The fumaroles located here belong to the oxidizing type due to the mixing of hot (up to 500 °C) volcanic gas with atmospheric oxygen. Some fumaroles are richly mineralized and show an outstanding mineral diversity and originality [2]. The largest and mineralogically richest of them is Arsenatnaya. This active fumarole was discovered by us in 2012 and soon became famous as one of the world-class mineral localities: at present day, >210 mineral species were identified reliably in its incrustations including 73 IMA-approved new minerals. We named this fumarole for the unusual abundance and diversity of arsenates which belong to the specific genetic type being high-temperature volcanic sublimates: 58 valid arsenate minerals are known here, including 40 new mineral species. The Arsenatnaya fumarole and the mineralization formed in this unique "natural laboratory" were characterized in general in [3–5].

Polyarsite is named from the Greek πολύς, *poly*, "many" and due to belonging to *ars*enates: this arsenate mineral contains many chemical components ordered between different positions in crystal structure, namely four species-defining metal cations (Na, Ca, Mg and Cu^{2+}) and two species-defining additional halide anions (F^- and Cl^-). Both the new mineral and its name have been approved by the IMA Commission on New Minerals, Nomenclature and Classification (CNMNC), IMA2019–058. The IMA-accepted symbol is Par. The type material is deposited in the systematic collection of the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, with the catalogue number 96700.

2. Methods

The chemical composition of polyarsite was studied in the Laboratory of Analytical Techniques of High Spatial Resolution, Dept. of Petrology, Moscow State University, using a JEOL JXA 8230 Superprobe instrument (Jeol, Japan). Electron microprobe analyses (EMPA) were carried out in WDS mode (20 kV and 20 nA; the electron beam was 3 μm in diameter). The probe standards used were as follows: albite (Na), wollastonite (Ca), chromite (Mg), Cu (Cu), magnetite (Fe), InAs (As), ZnS (S), fluorophlogopite (F) and atacamite (Cl). Contents of other chemical elements with atomic numbers higher than that of carbon are below their detection limits.

The Raman spectrum of a randomly oriented crystal of polyarsite was obtained using an EnSpectr R532 instrument (Chernogolovka, Russia) at the Dept. of Mineralogy, Lomonosov Moscow State University with a green laser (532 nm) at room temperature. The output power of the laser beam was about 13 mW. The spectrum was processed using the EnSpectr expert mode programme in the range from 100 to 4000 cm^{-1} with the use of a holographic diffraction grating with 1800 lines mm^{-1} and a resolution of 6 cm^{-1}. Acquisition time for a single scan was 2000 ms and the signal was averaged over 2 scans. The diameter of the laser spot on the sample was about 10 μm. The backscattered Raman signal was collected with 40× objective.

The single-crystal X-ray diffraction (XRD) investigation was carried out at Dept. of Crystallography and Crystal Chemistry, Lomonosov Moscow State University. The data were obtained with an Xcalibur S diffractometer equipped with a CCD detector (Oxford Diffraction, Oxford, UK) (Mo$K\alpha$ radiation). Data reduction was performed using CrysAlisPro Version 1.171.39.46 [6]. The crystal structure was solved by direct methods and refined with the use of the SHELX software package (version 2018/3) [7].

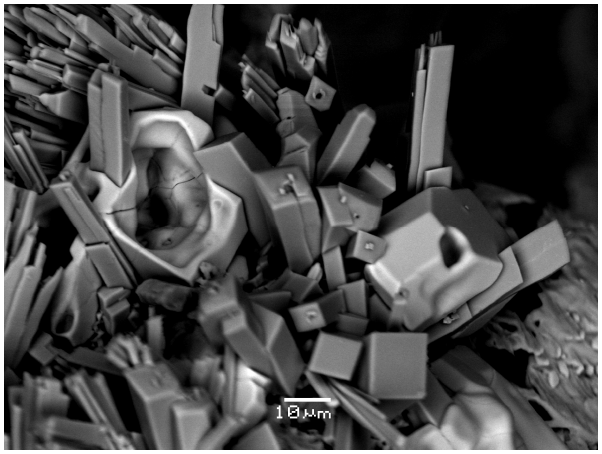
The powder XRD study of polyarsite was carried out at the Centre for X-Ray Diffraction Research of the Science Park of St. Petersburg State University. Diffraction data were collected with a Rigaku R-AXIS Rapid II (Rigaku Corporation, Tokyo, Japan) diffractometer equipped with cylindrical image plate detector using the Debye–Scherrer geometry (d = 127.4 mm). The data were integrated using the software package Osc2Tab [8].

3. Results

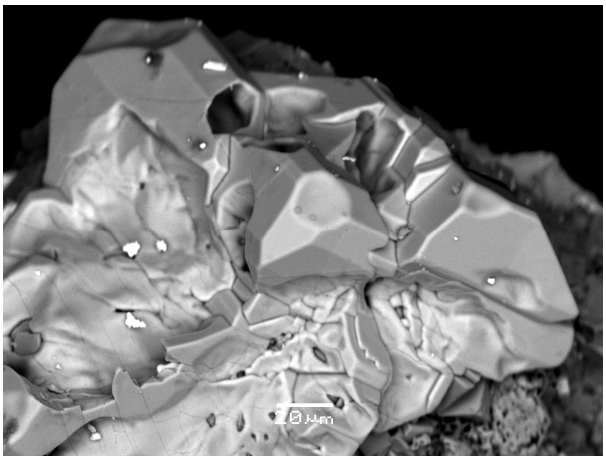
3.1. Occurrence and General Appearance

Polyarsite belongs to the rarest minerals in incrustations of the Arsenatnaya fumarole. The specimens in which it was discovered were collected by us in July 2018 from the intermediate zone of Arsenatnaya, about 1.5 m below the surface. The temperatures measured with the use of a chromel-alumel thermocouple in these pockets immediately after the opening were 300–350 °C. The minerals associated with polyarsite are aegirine, sanidine, ferrisanidine, hematite, halite, sylvite, cassiterite, evseevite, axelite, badalovite, johillerite, arsmirandite, aphthitalite, tridymite, potassic-magnesio-fluoro-arfvedsonite and litidionite.

Polyarsite forms short-prismatic, equant or tabular crystals up to 0.15 mm across, well-shaped (Figure 1a,b) or, more typically, crude, distorted. Sometimes they are combined in clusters (Figures 1b and 2) up to 0.3 mm in size. Some crystals of the mineral are skeletal (Figure 1a). Most commonly, polyarsite occurs as small (up to 0.5 mm across and up to 0.03 mm in thickness) crusts which overgrow aegirine, hematite, sanidine (Figures 1c and 2) or badalovite.

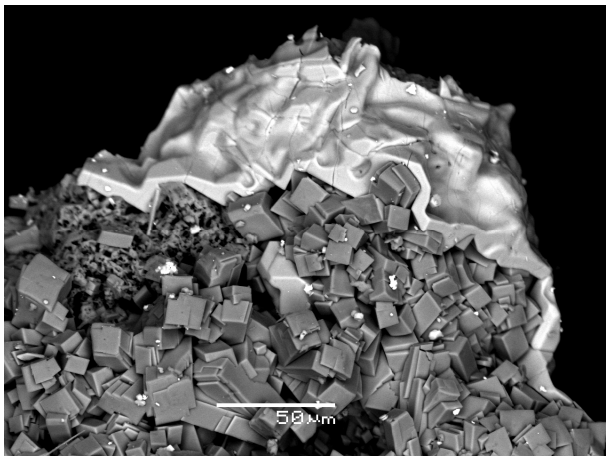


(**a**)



(**b**)

Figure 1. *Cont.*



(**c**)

Figure 1. Morphology of polyarsite: (**a**) two skeletal crystals (light grey) on aggregate of well-formed aegirine crystals; (**b**) crust composed by well-shaped and distorted, crude crystals; (**c**) crust on aegirine crystal crust with separate tiny cassiterite grains (bright white). SEM images, BSE mode. FOV width (mm): (**a**) 0.13; (**b**) 0.21; (**c**) 0.24.

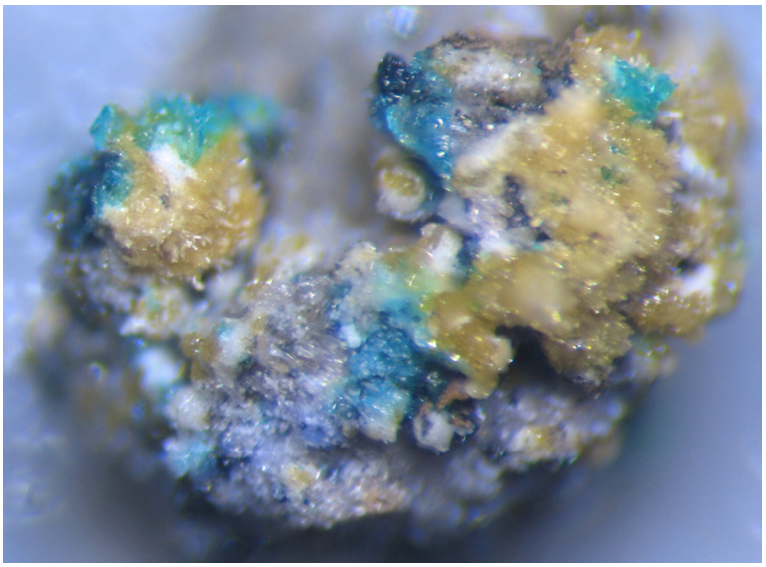


Figure 2. Blue crude crystals, crystal clusters and crusts of polyarsite with yellow aegirine, colourless to white tridymite and sanidine and black hematite. FOV width: 1.7 mm. Photo: I.V. Pekov and A.V. Kasatkin.

3.2. Physical Properties and Optical Data

Polyarsite is sky-blue to light blue. Its streak is white streak and lustre is vitreous. The mineral is transparent. It is brittle, with no cleavage or parting and the fracture is uneven. The calculated density, using the program MINCALC recommended by the IMA CNMNC (based on the empirical formula and unit cell volume obtained from SCXRD data), is 3.592 g cm^{-3}.

Polyarsite is optically biaxial (+), α = 1.624 (4), β = 1.645 (4), γ = 1.682 (4) (589 nm), $2V$ (meas.) = 70 (10)° and $2V$ (calc.) = 75°. Dispersion of optical axes is weak, $r > v$. Pleochroism is distinct: Z (turquoise-blue) > Y (light turquoise-blue) > X (pale bluish to colourless).

3.3. Raman Spectroscopy

Bands in the Raman spectrum of polyarsite (Figure 3) are assigned according to [9]. Bands between 930 and 760 cm^{-1} correspond to As^{5+}–O stretching vibrations of the groups $[AsO_4]^{3-}$. Bands lower than 550 cm^{-1} are assigned to bending vibrations of AsO_4 tetrahedra, stretching vibrations of Cu^{2+}–O, Mg–O, Ca–O and Na–O and lattice modes. No bands with frequencies > 930 cm^{-1} that indicates that groups with O–H, C–H, C–O, N–H, N–O and B–O bonds are absent in polyarsite.

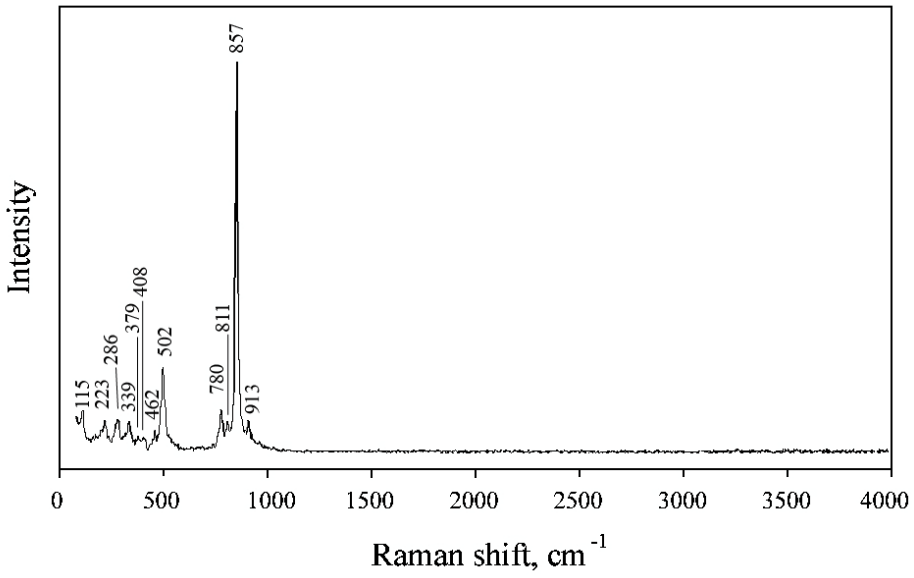


Figure 3. The Raman spectrum of polyarsite.

3.4. Chemical Composition

The chemical data for polyarsite in wt.% are reported in Table 1.

Table 1. Chemical composition (in wt.%) of polyarsite.

Constituent	Mean *	Range	SD
Na_2O	22.32	21.45–23.29	0.58
CaO	5.74	5.20–6.15	0.29
MgO	3.81	3.11–4.60	0.51
CuO	16.80	15.83–17.26	0.58
Fe_2O_3 **	0.45	0.08–0.79	0.26
As_2O_5	46.54	45.89–47.12	0.48
SO_3	0.44	0.06–0.69	0.20
F	3.23	3,01–3.49	0.16
Cl	3.85	3.77–3.98	0.09
–O=(F,Cl)	−2.23		
Total	100.95		

* Averaged for eight spot analyses. ** Trivalent state of minor Fe in polyarsite is suggested due to strongly oxidizing mineral formation conditions: all iron minerals in the Arsenatnaya fumarole contain only Fe^{3+} [4]. SD—standard deviation.

The empirical formula calculated on the basis of 19 (O+F+Cl) atoms per formula unit (*apfu*) is $Na_{7.04}Ca_{1.00}Mg_{0.92}Cu_{2.06}Fe^{3+}_{0.06}(As_{3.96}S_{0.05})_{\Sigma 4.01}O_{16.28}F_{1.66}Cl_{1.06}$.

The ideal formula is $Na_7CaMgCu_2(AsO_4)_4F_2Cl$ which requires Na_2O 22.1, CaO 5.7, MgO 4.1, CuO 16.2, As_2O_5 46.9, F 3.9, Cl 3.6, –O=(F,Cl) −2.5, total 100 wt.%.

A low value of the Gladstone–Dale compatibility index [10] confirms the correctness of the obtained data: $1 - (K_p/K_c) = -0.030$ (rated as excellent).

3.5. X-Ray Crystallography and Crystal Structure Determination

The XRD data of polyarsite obtained from powder sample (for Co*K*α) are given in Table 2. Unit cell parameters refined from the powder data are as follows: a = 8.436(2), b = 10.097(3), c = 10.717(4) Å, β = 90.86(2)° and V = 912.8(8) Å^3.

Table 2. Powder X-ray diffraction data (d in Å) of polyarsite.

I_{obs}	d_{obs}	I_{calc} *	d_{calc} **	*hkl*
12	7.35	6	7.347	011
42	**6.66**	35	6.672	−101
15	6.48	9	6.472	110
98	**5.357**	67	5.354	002
5	5.054	3	5.049	020
48	**4.218**	34	4.216	200
10	4.148	8	4.148	−112
6	4.004	2	4.005	121
23	3.673	17, 2	3.673, 3.672	022, −211
20	3.365	8, 9	3.365, 3.335	013, −202
49	**3.304**	35, 7	3.304, 3.289	−103, 202
24	3.237	24	3.236	220
68	**3.127**	58	3.126	130
61	**2.783**	68	2.783	−222
100	**2.757**	9, 100, 13	2.765, 2.756, 2.745	−123, 222, 123
54	**2.704**	1, 7, 31	2.709, 2.708, 2.706	301, 310, −132
61	**2.679**	13, 32	2.693, 2.677	132, 004
7	2.614	3	2.613	213
12	2.550	12	2.549	231
17	2.525	15	2.524	040
6	2.484	4	2.484	−114
14	2.431	13	2.430	−312
7	2.402	2, 4	2.403, 2.400	312, −321
3	2.358	2	2.357	141
3	2.276	2	2.275	−204
2	2.246	2	2.245	204
2	2.225	1	2.224	−303
2	2.193	2	2.193	303
5	2.126	5	2.127	−233
12	2.108	13	2.108	400
4	2.084	3	2.083	−105
5	2.069	5	2.069	105
6	2.052	5	2.052	224
6	2.003	1, 0.5, 2	2.006, 2.003, 1.998	−143, 242, 143
12	1.965	9	1.964	150
6	1.925	5	1.926	−125
9	1.917	5, 5	1.917, 1.914	−314, 125
4	1.892	4	1.891	314
10	1.851	7, 1	1.853, 1.847	−341, 341
37	1.837	7, 32, 11	1.842, 1.837, 1.836	152, 044, −422
10	1.821	10	1.821	422
2	1.797	1, 0.5	1.797, 1.794	−413, 251
2	1.777	2	1.776	413
4	1.759	3	1.758	431
13	1.716	1, 16	1.716, 1.715	116, −305
4	1.692	3, 1	1.692, 1.690	305, −244
8	1.684	5	1.683	060
6	1.668	1, 5	1.669, 1.668	−343, −235
22	1.642	11, 16	1.645, 1.640	404, 350
3	1.625	0.5, 3	1.626, 1.624	−253, −325
2	1.605	1, 0.5	1.605, 1.604	062, 325
10	1.581	4, 1, 4, 6	1.585, 1.582, 1.581, 1.579	−521, 512, 154, 521
8	1.572	8, 2	1.572, 1.570	−352, −226
10	1.565	11	1.564	352

Table 2. *Cont.*

I_{obs}	d_{obs}	I_{calc} *	d_{calc} **	*hkl*
16	1.556	17, 2	1.556, 1.554	226, −442
2	1.534	2	1.533	−503
5	1.508	3, 4	1.509, 1.508	−107, 530
5	1.499	1, 1, 4	1.501, 1.500, 1.498	107, −316, 262
8	1.469	6, 7	1.469, 1.467	055, −523
4	1.457	2	1.456	−532
11	1.446	4, 5, 5, 3	1.447, 1.446, 1.446, 1.443	−451, 532, −127, 451
4	1.421	3, 3	1.422, 1.419	170, −345
6	1.406	0.5, 5	1.405, 1.405	345, 600
7	1.393	7, 1, 3	1.393, 1.392, 1.392	354, −541, −255

* For the calculated pattern only reflections with intensities ≥0.5 are given. ** For the unit-cell parameters obtained from single-crystal data. The strongest reflections are marked with bold type.

Crystal data, data collection information and structure refinement details for polyarsite are reported in Table 3. Coordinates and equivalent thermal displacement parameters of atoms are given in Table 4, selected interatomic distances in Table 5 and bond valence calculations in Table 6.

Table 3. Crystal data, data collection information and single-crystal structure refinement details for polyarsite.

Formula	$Na_7CaMgCu_2(AsO_4)_4F_2Cl$
Formula weight	981.53
Temperature, K	293(2)
Radiation and wavelength, Å	Mo$K\alpha$; 0.71073
Crystal system, space group, Z	Monoclinic, $I2/m$, 2
Unit cell dimensions, Å/°	a = 8.4323(4) b = 10.0974(4), β = 90.822(4) c = 10.7099(6)
V, Å^3	911.79(8)
Absorption coefficient μ, mm^{-1}	10.267
F_{000}	924
Crystal size, mm	0.03 × 0.09 × 0.11
Diffractometer	Xcalibur S CCD
θ range for data collection, °/collection mode	2.77–28.28/full sphere
Index ranges	$-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $-14 \leq l \leq 14$
Reflections collected	7603
Independent reflections	1200 (R_{int} = 0.0569)
Independent reflections with $I > 2\sigma(I)$	1125
Data reduction	CrysAlisPro, Agilent Technologies, v. 1.171.37.35 [6]
Absorption correction	Gaussian
Structure solution	direct methods
Refinement method	full-matrix least-squares on F^2
Number of refined parameters	89
Final R indices [$I > 2\sigma(I)$]	$R1$ = 0.0391, w$R2$ = 0.0754
R indices (all data)	$R1$ = 0.0454, w$R2$ = 0.0769
GoF	1.247
Largest diff. peak and hole, e/Å^3	1.03 and −1.46

Table 4. Coordinates and equivalent displacement parameters (U_{eq}, in Å^2) of atoms and site multiplicities (Q) for polyarsite.

Site	x	y	z	U_{eq}	Q
Na(1)	0.2058(4)	½	0.7532(3)	0.0164(6)	4
Na(2)	0.1959(3)	0.7497(2)	0.5112(2)	0.0187(5)	8
Na(3)	0	½	0	0.0153(9)	2

Table 4. *Cont.*

Site	*x*	*y*	*z*	U_{eq}	*Q*
Mg	0	0	½	0.0043(6)	2
Ca	0	0	0	0.0085(4)	2
Cu	0.17576(10)	½	0.27884(8)	0.00693(19)	4
As	0.02510(6)	0.79403(5)	0.22226(4)	0.00457(14)	8
O(1)	0.0319(4)	0.6285(3)	0.1996(3)	0.0097(7)	8
O(2)	0.4844(4)	0.6614(4)	0.1278(3)	0.0109(7)	8
O(3)	0.6323(4)	0.6490(3)	0.3587(3)	0.0092(7)	8
O(4)	0.1830(4)	0.8646(3)	0.1513(3)	0.0088(7)	8
Cl	0	½	½	0.0171(5)	2
F	0.2672(5)	½	−0.0299(4)	0.0148(9)	4

Table 5. Selected interatomic distances (Å) in the structure of polyarsite.

As–O(2) 1.670(3)	Na(1)–O(3) 2.369(4) × 2
- O(3) 1.677(3)	- F 2.372(5)
- O(1) 1.690(3)	- O(1) 2.446(4) × 2
- O(4) 1.699(3)	- Cl 3.199(3)
Cu–O(4) 1.955(3) × 2	Na(2)–O(3) 2.240(4)
- O(1) 1.961(3) × 2	- O(2) 2.296(4)
- Cl 2.8121(9)	- O(4) 2.336(4)
	- O(2) 2.369(4)
Mg–F 1.984(4) × 2	- F 2.554(3)
- O(2) 2.134(3) × 4	- Cl 3.015(3)
Ca–O(3) 2.418(3) × 4	Na(3)–F 2.280(4) × 2
- O(4) 2.608(3) × 4	- O(1) 2.512(3) × 4

Table 6. Bond valence calculations for polyarsite.

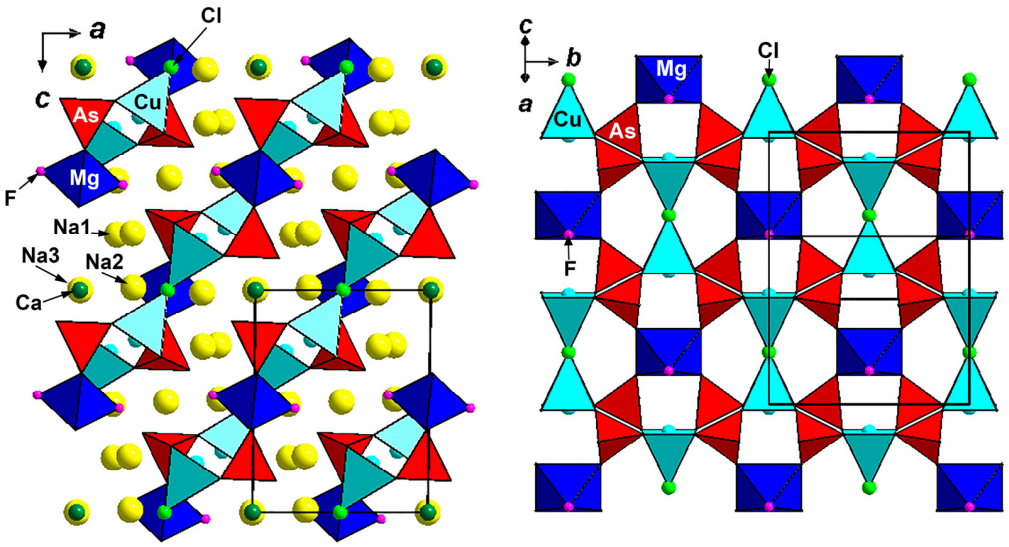
	Na(1)	Na(2)	Na(3)	Mg	Ca	Cu	As	∑
O(1)	$0.17^{\times 2\downarrow}$		$0.14^{\times 4\downarrow}$			$0.46^{\times 2\downarrow}$	1.24	2.01
O(2)		0.24 0.20		$0.31^{\times 4\downarrow}$			1.31	2.06
O(3)	$0.20^{\times 2\downarrow}$	0.27			$0.29^{\times 4\downarrow}$		1.28	2.04
O(4)		0.22			$0.18^{\times 4\downarrow}$	$0.47^{\times 2\downarrow}$	1.21	2.08
Cl	$0.06^{\times 2\rightarrow}$	$0.10^{\times 4\rightarrow}$				$0.11^{\times 2\rightarrow}$		0.74
F	0.15	$0.09^{\times 2\rightarrow}$	$0.20^{\times 2\downarrow}$	$0.34^{\times 2\downarrow}$				0.87
∑	0.95	1.12	0.96	1.92	1.88	1.97	5.04	

Bond-valence parameters are taken from [11] for As-O, Cu-O, Mg-O, Ca-O and Na-O and from [12] for Cu-Cl, Mg-F, Na-F and Na-Cl.

4. Discussion

Polyarsite is unique in terms of crystal structure: its structure type is novel. The structure of polyarsite (Figure 4a) is based on the (1 0 1) heteropolyhedral layers formed by CuO_4Cl elongated tetragonal pyramids, AsO_4 tetrahedra and MgO_4F_2 octahedra (Figure 4b). According to [13], five-fold coordinated Cu^{2+} ions preferably occupy an apically strongly elongated square pyramids, whereas electrostatic calculations slightly favour an elongated trigonal bipyramid compared with a compressed square pyramid. Two CuO_4Cl pyramids share common Cl vertex to form Cu_2O_8Cl dimer which shares all eight oxygen vertices with eight AsO_4 tetrahedra. Each As-centred tetrahedron is linked via two oxygen vertices with Cu-centred polyhedra belonging to adjacent dimers and one vertex with

Mg-centred octahedron. MgO_4F_2 octahedra share all oxygen vertices with AsO_4 tetrahedra. Adjacent Cu-Mg-As-O-F-Cl layers are linked via CaO_8 cubes to form a pseudo-framework in which each CaO_8 cube shares four common edges with four As-centred tetrahedra (two tetrahedra belonging to one layer and two of the neighbouring one) and two edges with CuO_4Cl tetragonal pyramids from adjacent layers (Figure 5).



(**a**) (**b**)

Figure 4. The crystal structure of polyarsite projected along the *b* axis (**a**) and heteropolyhedral layer in this structure (**b**). The unit cell is outlined.

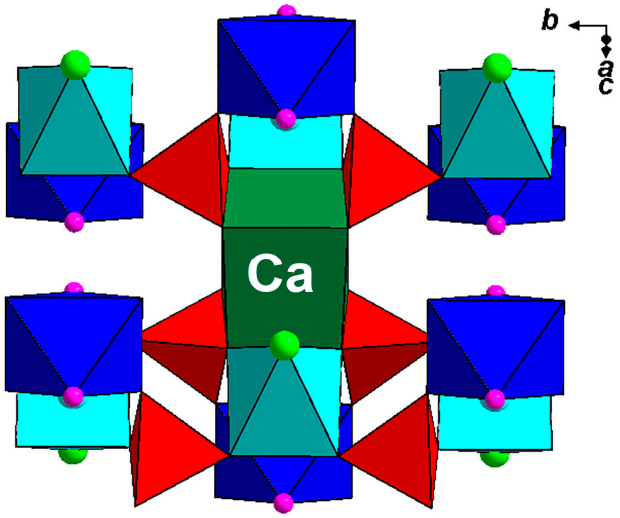


Figure 5. The location of the CaO_8 cube, sharing common edges with AsO_4 tetrahedra and CuO_4Cl tetragonal pyramids, between adjacent Cu-Mg-As-O-F-Cl layers in the structure of polyarsite. For legend see Figure 4.

Three crystallographically non-equivalent octahedrally coordinated Na sites are localized in cavities of the pseudo-framework. The Na(1) sites centre strongly distorted $Na(1)O_4FCl$ octahedra, located in the [0 1 0] channels inside the pseudo-framework; these octahedra share common Cl vertices and form isolated from each other dimers $[Na_2O_8F_2Cl]$ (Figure 6a). The Na(2) sites are located between F^- anions and occupy distorted $Na(2)O_4FCl$ octahedra connected with each other via common Cl–O(2)–O(2) faces forming dimers. Two adjacent dimers share common Cl vertex to form four-polyhedral cluster. These clusters are linked via common F vertices forming ribbons $[Na_4O_{12}F_2Cl]^{\infty}$ running along the *b*

axis (Figure 6b). Na(3)-centred octahedra $Na(3)O_4F_2$ isolated from each other are located between CaO_8 cubes (Figure 6c). The structural fragments built by Na-centred octahedra share edges and faces and form a complicated cationic motif (Figure 6d).

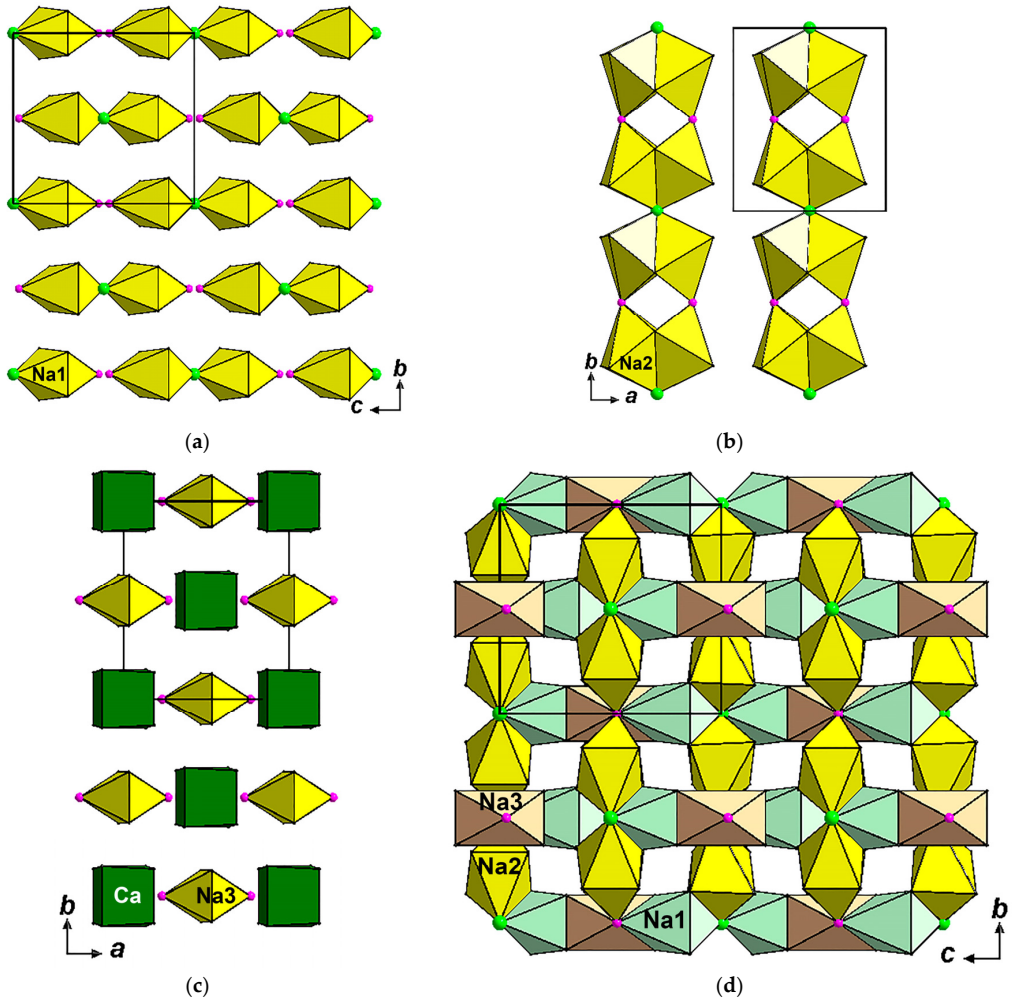


Figure 6. Arrangement of Na-centred octahedra in the crystal structure of polyarsite: Na(1)-centred octahedra (**a**), Na(2)-centred octahedra (**b**), Na(3)-centred octahedra with CaO_8 cubes (**c**) and the motif formed by all Na-centred octahedra (**d**).

Only two arsenate minerals with both species-defining F and Cl are known, namely axelite $Na_{14}Cu_7(AsO_4)_8F_2Cl_2$ [14] and lehmannite $Na_{18}Cu_{12}TiO_8(AsO_4)_8FCl_5$ [15,16]. These fluoro-chloro-arsenates were recently discovered in the same Arsenatnaya fumarole and both are Na- and Cu-rich, like polyarsite $Na_7CaMgCu_2(AsO_4)_4F_2Cl$; however, they strongly differ from polyarsite and from one another in chemistry and crystal structure.

This mineral association forms at temperatures not lower than 350 °C. Polyarsite can be deposited directly from fumarole gas as a volcanic sublimate, but we assume that it is more likely to be formed as a result of the interaction of hot gas with basaltic scoria, which could be the source of Ca and Mg that demonstrate in fumarolic systems very low volatility at temperatures up to 500 °C [17].

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