



Article

Aleutite $[\text{Cu}_5\text{O}_2](\text{AsO}_4)(\text{VO}_4)\cdot(\text{Cu}_{0.5}\square_{0.5})\text{Cl}$, a new complex salt-inclusion mineral with Cu^{2+} substructure derived from a Kagome-net

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Abstract

Aleutite, ideally $[\text{Cu}_5\text{O}_2](\text{AsO}_4)(\text{VO}_4)\cdot(\text{Cu}_{0.5}\square_{0.5})\text{Cl}$, was found in the Yadovitaya fumarole of the Second scoria cone of the Great Fissure Tolbachik eruption, Kamchatka Peninsula, Russia. Aleutite occurs as individual crystals in the masses of polycrystalline anhydrite. Aleutite is monoclinic, $C2/m$, $a = 18.090(2)$ Å, $b = 6.2284(6)$ Å, $c = 8.2465(9)$ Å, $\beta = 90.597(2)^\circ$, $V = 929.1(2)$ Å³ and $Z = 4$ (from single-crystal X-ray diffraction data). The empirical formula calculated on the basis of $(\text{As} + \text{V} + \text{Mo} + \text{Fe}^{3+}) = 2$ atoms per formula unit is $\text{Cu}_{5.40}\text{Zn}_{0.05}\text{Ca}_{0.01}\text{As}_{1.09}\text{V}_{0.84}\text{Mo}_{0.04}\text{Fe}_{0.03}\text{K}_{0.05}\text{Pb}_{0.02}\text{Rb}_{0.01}\text{Cs}_{0.01}\text{O}_{9.97}\text{Cl}_{1.07}$. The crystal structure was solved by direct methods and refined to an agreement index $R_1 = 0.066$. Aleutite has a new structure type. Aleutite is unique amongst natural and synthetic copper vanadates and arsenates, as it has As^{5+} and V^{5+} cations ordered over two tetrahedral sites. The topology of ${}^\infty[\text{Cu}_5\text{O}_2]^{6+}$ oxocentred bands in aleutite is novel and has not been described before in minerals and synthetic materials. The structural architecture of the ${}^\infty[\text{Cu}_5\text{O}_2]^{6+}$ band in aleutite can be derived from a kagome network and represents a one-dimensional slice from it. In addition, aleutite is an interesting and complex example of a natural salt-inclusion phase.

Keywords: aleutite, new minerals, copper, vanadates, arsenates, kagome nets, salt-inclusion solids, Tolbachik volcano

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Introduction

Anhydrous copper vanadates are abundant minerals in active fumaroles of scoria cones related to the Great Fissure Tolbachik eruption (Pekov *et al.*, 2013; Vergasova and Filatov, 2016). Some of them contain chloride ions: averievite $\text{Cu}_5\text{O}_2(\text{VO}_4)_2\cdot n\text{MX}$ (Vergasova *et al.*, 1998), leningradite $\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$ (Siidra *et al.*, 2007); yaroshevskite $\text{Cu}_9\text{O}_2(\text{VO}_4)_4\text{Cl}_2$ (Pekov *et al.*, 2013) and dokuchaevite $\text{Cu}_8\text{O}_2(\text{VO}_4)_3\text{Cl}_3$ (Siidra *et al.*, 2019). Copper arsenate minerals are also common in high-temperature fumarolic assemblages (Pekov *et al.*, 2018).

Herein we report on the composition, structure and properties of aleutite (Cyrillic = алеутит). The mineral is named for the Aleuts ethnic group who are the original inhabitants living on the Commander Islands, Aleutsky District, Kamchatka Krai. Both the mineral and the mineral name were approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (IMA2018-014, Siidra *et al.*, 2018b). Type material is deposited at the Mineralogical Museum, St. Petersburg State University, St. Petersburg, Russia (catalogue no. 1/19689).

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Occurrence and association

Aleutite occurs as a product of fumarolic activity. It was found in the summer of 2015 in Yadovitaya ('Poisonous') fumarole at the Second scoria cone of the Northern Breakthrough of the Great Fissure Tolbachik Eruption in Kamchatka, Russia. The Second scoria cone is located ~18 km SSW of the active shield volcano Ploskiy Tolbachik (Fedotov and Markhinin, 1983). The temperature of gases at the sampling location was ~300°C. Aleutite could be deposited directly from the gas phase as a volcanic sublimate.

All the samples recovered were packed immediately and isolated to avoid any contact with atmosphere. Aleutite is very rare and closely associates with anhydrite. Other associated minerals are euchlorine, kamchatkite, langbeinite, lyonsite, pseudolyonsite, tenorite and hematite.

General appearance and physical properties

Aleutite occurs as individual crystals in masses of polycrystalline anhydrite (Fig. 1). Aleutite is dark red, with a reddish black streak and close to adamantine lustre. It is brittle with no cleavage observed. Parting was not observed and its fracture is uneven. The density could not be measured due to lack of sufficient material. The calculated density using the empirical formula derived from the analytical data given in Table 1 is 4.887 g cm⁻³.

Despite the transparency of aleutite, its optical properties had to be investigated in reflected light because of the high values of

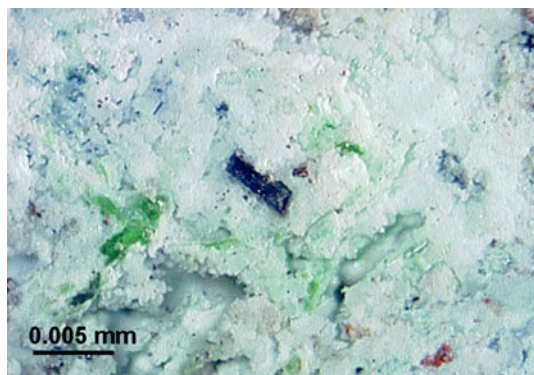


Fig. 1. Aleutite dark-red prismatic crystal associated closely with anhydrite (white) and euchlorine (green).

refractive indices, typical of arsenates and vanadates. Reflectance measurements were made using a SiC standard in air in the range 400–700 nm (Table 2). In reflected light, aleutite is grey with a yellowish tint. It is non-pleochroic, with abundant, brown–red internal reflections and a weak bireflectance. The measured anisotropy is $\Delta R_{589} = 0.35\%$.

Composition

Three crystals ($60 \mu\text{m} \times 15 \mu\text{m} \times 10 \mu\text{m}$) of aleutite checked previously by single-crystal X-ray diffraction were mounted in epoxy resin and polished with oil suspension. Six spot analyses on the grains were obtained using a JEOL Superprobe 733 scanning electron microscope equipped with an Oxford Instruments INCA Energy Dispersive Spectrometer. The electron beam accelerating voltage was 20 kV, and electron beam current 2 nA, measured with a Faraday cup. X-ray acquisition live-time was 30 s. System calibration was performed on Ni. A defocused beam ($5 \mu\text{m}$) was used for analyses. X-ray matrix correction was carried out automatically by the Oxford Instruments INCA version of the Pouchou and Pichoir (XPP) routine. No other elements with $Z > 9$ other than those reported in Table 1 were detected. The empirical formula calculated on the basis of $(\text{As} + \text{V} + \text{Mo} + \text{Fe}^{3+}) = 2$ atoms per formula unit is $\text{Cu}_{5.40}\text{Zn}_{0.05}\text{Ca}_{0.01}\text{As}_{1.09}\text{V}_{0.84}\text{Mo}_{0.04}\text{Fe}_{0.03}\text{K}_{0.05}\text{Pb}_{0.02}\text{Rb}_{0.01}\text{Cs}_{0.01}\text{O}_{9.97}\text{Cl}_{1.07}$ or $(\text{Cu}_{4.94}\text{Zn}_{0.05}\text{Ca}_{0.01})_{\Sigma 5.00}\text{O}_{2.11}[(\text{As}_{0.54}\text{V}_{0.42}\text{Mo}_{0.02}\text{Fe}_{0.02})_{\Sigma 1.00}\text{O}_{\Sigma 3.93}]_2(\text{Cu}_{0.46}\text{K}_{0.05}\text{Pb}_{0.02}\text{Rb}_{0.01}\text{Cs}_{0.01})_{\Sigma 0.55}\text{Cl}_{1.07}$.

Table 1. Composition (EPMA, wt.%) of the studied aleutite.

Constituent	Mean	Range	S.D.	Probe standard
MoO ₃	0.83	0.62–1.02	0.15	CaMoO ₄
As ₂ O ₅	18.33	17.77–19.83	0.51	InAs
V ₂ O ₅	11.13	10.56–11.85	0.33	V metal
Fe ₂ O ₃	0.36	0.23–0.41	0.05	Omphacite USNM 110607
CuO	62.73	61.79–63.54	0.50	Cu metal
ZnO	0.60	0.39–0.77	0.11	Zn metal
PbO	0.75	0.59–0.98	0.11	PbTiO ₃
CaO	0.10	0.00–0.22	0.07	Anorthite USNM 137041
K ₂ O	0.35	0.24–0.47	0.07	Microcline USNM 143966
Cs ₂ O	0.16	0.05–0.31	0.08	Cs ₂ Nb ₄ O ₁₁
Rb ₂ O	0.18	0.09–0.27	0.05	Rb ₂ Nb ₄ O ₁₁
Cl	5.54	5.40–5.78	0.10	Atacamite
–Cl = O	1.25			
Total	99.81	100.02–101.83		

S.D. – standard deviation

Table 2. Reflectance values for aleutite (SiC standard in air).

λ (nm)	R_{max} (%)	R_{min} (%)	λ (nm)	R_{max} (%)	R_{min} (%)
400	15.10	14.71	560	13.06	12.69
420	14.80	14.45	580	12.81	12.47
440	14.51	14.14	589	12.70	12.35
460	14.25	13.92	600	12.58	12.22
470	14.30	13.79	620	12.36	12.00
480	14.00	13.65	640	12.13	11.80
500	13.74	13.41	650	12.03	11.70
520	13.54	13.18	660	11.92	11.59
540	13.28	12.94	680	11.70	11.38
546	13.23	12.88	700	11.47	11.15

The reference wavelengths required by the Commission on Ore Mineralogy are given in bold.

Taking into account structural data, the simplified formula is $[\text{Cu}_5\text{O}_2](\text{AsO}_4)(\text{VO}_4) \cdot (\text{Cu}_{0.5}\square_{0.5})\text{Cl}$. Aleutite is soluble in hot H₂O.

X-ray crystallography

Experiment

Powder X-ray diffraction data were collected using a Rigaku R-Axis Rapid II single-crystal diffractometer equipped with a cylindrical image plate detector using Debye–Sherrer geometry (with $d = 127.4$ mm) (CoK α radiation) at the Department of Crystallography, St. Petersburg State University, Russia after crushing the crystal fragments used for the single-crystal analysis. Data (in Å) are given in Table 3. Unit-cell parameters refined from the powder data are as follows: monoclinic, space

Table 3. Powder X-ray diffraction data (d in Å) for aleutite.

l_{meas}	l_{calc}	d_{meas}	d_{calc}	$h k l$
25	45	5.8759	5.8891	1 1 0
46	9	4.7957	4.7847	1 1 1
9	58	4.5360	4.5223	4 0 0
4	14	4.3215	4.3322	3 1 0
7	2	3.3808	3.3829	$\bar{1}$ 1 2
29	33	3.3960	3.3722	1 1 2
48	39	2.9848	3.1284	5 1 0
4	3	2.9798	2.9755	30 1 2
74	62	2.9337	2.9337	5 1 1
31	9	2.9134	2.9134	0 2 1
36	84	2.8251	2.8221	6 0 1
20	100	2.7459	2.7487	0 0 3
30	42	2.5674	2.5649	4 2 0
5	2	2.4929	2.4940	$\bar{1}$ 1 3
9	20	2.4948	2.4814	5 1 2
100	24	2.4490	2.4458	6 0 2
8	36	2.3941	2.3924	2 2 2
4	10	2.3546	2.3598	$\bar{4}$ 0 3
16	4	2.3366	2.3381	4 0 3
1	10	2.0576	2.0572	7 1 2
23	3	2.0174	2.0208	6 0 3
25	10	2.0139	2.0127	$\bar{2}$ 2 3
2	5	1.9869	1.9914	3 0 2
6	6	1.9468	1.9478	$\bar{1}$ 1 4
3	8	1.8549	1.8561	3 1 4
3	3	1.7385	1.7374	8 0 3
3	1	1.7209	1.7190	0 2 4
7	10	1.6835	1.6862	2 2 4
6	3	1.6621	1.6672	8 2 2
2	3	1.6616	1.6629	$\bar{1}$ 0 2
3	1	1.6257	1.6255	$\bar{2}$ 0 5
6	5	1.5886	1.5901	$\bar{7}$ 3 1
24	4	1.5665	1.5677	$\bar{7}$ 1 4

Table 4. Crystallographic data and refinement parameters for aleutite

Crystal data	
Ideal formula	[Cu ₅ O ₂](AsO ₄)(VO ₄)·(Cu _{0.5} □ _{0.5})Cl
Crystal size (mm)	0.07 × 0.07 × 0.20
Crystal system, space group	Monoclinic, C2/m
Temperature (K)	296
a, b, c (Å)	18.090(2), 6.2284(6), 8.2465(9)
β (°)	90.597(2)
V (Å ³)	929.1(2)
Z	4
Calculated density (g·cm ⁻³)	4.774
μ (mm ⁻¹)	16.131
Data collection	
Instrument	Bruker Apex 2 Duo
Radiation type, wavelength (Å)	MoKα, 0.71073
θ range (°)	2.252–27.982
No. of measured, independent and observed [F _o ≥ 4σ _F] reflections	2642, 826, 618
R _{int}	0.051
Range of h, k, l	−23 ≤ h ≤ 23, −8 ≤ k ≤ 6, −10 ≤ l ≤ 10
Refinement	
R ₁ [F > 4σ(F)], wR ₂ [F > 4σ(F)]	0.066, 0.163
R ₁ all, wR ₂ all	0.082, 0.172
GoF	1.046
Weighting coefficients a, b	0.10000, 0.000
No. refined parameters	111
No. of restraints	12
Largest diff. peak and hole (e ⁻ Å ⁻³)	3.388, −1.908

group C2/m, a = 18.0788(9) Å, b = 6.2270(5) Å, c = 8.2445(3) Å, β = 90.56(4)°, V = 928.09(7) Å³ and Z = 4.

A dark-red prismatic crystal fragment of aleutite was mounted on a thin glass fibre for X-ray diffraction analysis using a Bruker APEX II DUO X-ray diffractometer with a micro-focus X-ray tube operated with MoKα radiation at 50 kV and 40 mA. The data were integrated and corrected for absorption using a multi scan type model implemented in the Bruker programs APEX and SADABS (Bruker-AXS, 2014). More than a hemisphere of X-ray diffraction data was collected. The structure was solved by direct methods and successfully refined with the use of the SHELX software package (Sheldrick, 2015). The refinement in the C2/m space group converged to R₁ = 0.066 (Table 4). The structure was refined as a 2-component twin (twin ratio

0.955:0.045). The final atomic coordinates and anisotropic displacement parameters are given in Table 5, and selected interatomic distances in Table 6. The crystallographic information files have been deposited with the Principal Editor of *Mineralogical Magazine* and are available as Supplementary material (see below).

Cation coordination

The crystal structure of aleutite contains four symmetrically independent Cu sites occupied by Cu²⁺ cations with different coordination environments (Fig. 2). The Cu1 site is coordinated by four O atoms to form an almost planar CuO₄ square that is complemented by an apical Cl⁻ anion and one O²⁻ anion. As a result, an elongated CuO₄OCl octahedron is formed. The Cu2, Cu3 and Cu4 sites are coordinated by five oxygen atoms each and as a result Cu2O₅ regular trigonal bipyramid and strongly distorted Cu3O₅ and Cu4O₅ tetragonal pyramids are formed.

There are two tetrahedral sites coordinated by four O anions each (Fig. 2, Table 6). The As1 site is occupied predominantly by As⁵⁺ cations, whereas the V1 site is occupied mostly by V⁵⁺ cations (Table 5). The <As1–O> distance of 1.693 Å correlates well with the <As⁵⁺–O> value of 1.685 Å reported in Majzlan *et al.* (2014). The <V1–O> distance in the structure of aleutite demonstrates value of 1.716 Å, which is in a good agreement with the <V⁵⁺–O> distance of 1.721 Å reported for vanadates by Gopal and Calvo (1973). Note, AsO₄ tetrahedra in the structure of aleutite are very regular and undistorted, whereas VO₄ show a significant degree of distortion. The Baur (1974) distortion index in aleutite for AsO₄ is 0.0015 and 0.025 for VO₄.

There is one mixed and partially occupied M1 site in the structure of aleutite. The occupancy of this site refined using the atomic scattering factors of Cu is 0.45(1). The M1-site coordination is strongly distorted (Fig. 2) with four M1–O bonds and two M1–Cl bonds demonstrating similar bond-length values. Chemical analysis reveals a number of additional monovalent (K, Rb and Cs) and divalent (Pb) cations in aleutite, probably concentrated in the M1 site. The similar substitutions were reported previously in averievite (Vergasova *et al.*, 1998; Krivovichev *et al.*, 2015). On the final stages of the crystal structure refinement occupancy of the M1 site was fixed in agreement with microprobe data. The M1–M1 short distance of 2.67 Å along

Table 5. Coordinates, isotropic and anisotropic displacement parameters (Å²) of atoms in aleutite.

Atom	Site	x	y	z	U _{eq}	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
As1*	4i	0.1296(1)	½	−0.0155(3)	0.0101(8)	0.012(1)	0.011(1)	0.006(1)	0	−0.0029(7)	0
V1**	4i	0.1790(2)	0	0.6612(4)	0.010(1)	0.015(2)	0.011(2)	0.004(1)	0	−0.002(1)	0
Cu1	8j	0.1191(1)	0.2577(3)	0.3537(2)	0.0121(5)	0.017(9)	0.013(9)	0.007(9)	0.0002(6)	−0.0033(7)	0.0057(6)
Cu2	4i	0.3201(2)	½	−0.0851(3)	0.0161(7)	0.024(1)	0.021(2)	0.003(1)	0	−0.0054(9)	0
Cu3	4i	0.0483(2)	½	−0.3692(4)	0.062(2)	0.008(1)	0.173(5)	0.004(1)	0	−0.004(1)	0
Cu4	4i	0.2183(1)	½	−0.3664(3)	0.0193(7)	0.009(1)	0.044(2)	0.005(1)	0	−0.0050(8)	0
O1	4i	0.0577(7)	½	0.398(2)	0.010(3)	0.007(4)	0.018(5)	0.004(4)	0	−0.002(4)	0
O2	4i	0.1762(7)	0	0.320(2)	0.008(3)	0.013(6)	0.006(6)	0.006(6)	0	0.000(5)	0
O3	8j	0.1387(6)	0.242(2)	0.595(1)	0.011(2)	0.017(5)	0.011(5)	0.006(4)	−0.002(4)	−0.003(4)	0.000(3)
O4	4i	0.0531(9)	½	−0.137(2)	0.041(6)	0.015(8)	0.102(2)	0.007(8)	0	0.000(7)	0
O5	4i	0.2310(7)	½	0.400(2)	0.011(3)	0.010(4)	0.013(5)	0.009(5)	0	−0.005(4)	0
O6	4i	0.2058(8)	½	−0.132(2)	0.016(3)	0.015(7)	0.031(9)	0.002(6)	0	−0.004(5)	0
O7	4i	0.3161(9)	½	0.141(2)	0.020(3)	0.032(9)	0.013(8)	0.017(8)	0	−0.011(6)	0
O8	8j	0.1269(8)	0.285(2)	0.110(1)	0.022(3)	0.036(7)	0.016(5)	0.015(5)	0.000(5)	0.003(5)	0.012(5)
Cl1	4i	−0.0009(5)	0	0.734(3)	0.142(9)	0.024(4)	0.031(4)	0.37(3)	0	0.058(1)	0
M1***	4g	0	0.214(2)	0	0.070(3)	0.028(4)	0.141(10)	0.042(5)	0	0.004(4)	0

*As_{0.82(3)}V_{0.18(3)}; **V_{0.81(3)}As_{0.19(3)}; ***fixed in agreement with microprobe data Cu_{0.46}Pb_{0.02}(K,Rb,Cs)_{0.04}.

Table 6. Selected interatomic distances (Å) in aleutite.

As1–O8	1.69(1) ×2	Cu3–O4	1.92(2)
As1–O6	1.69(1)	Cu3–O1	1.93(1)
As1–O4	1.70(2)	Cu3–O1	1.93(1)
<As1–O>	1.69	Cu3–O3	2.31(1) ×2
V1–O7	1.64(2)	Cu4–O5	1.94(1)
V1–O5	1.71(1)	Cu4–O2	1.94(1)
V1–O3	1.76(1) ×2	Cu4–O6	1.95(1)
<V1–O>	1.72	Cu4–O3	2.18(1) ×2
Cu1–O1	1.911(8)	M1–O4	2.32(1) ×2
Cu1–O2	1.930(7)	M1–O8	2.50(1) ×2
Cu1–O3	2.02(1)	M1–Cl1	2.56(2) ×2
Cu1–O8	2.02(1)		
Cu1–O5	2.55(1)	O1–Cu1	1.911(8) ×2
Cu1–Cl1	2.76(1)	O1–Cu3	1.93(1)
		O1–Cu3	1.93(1)
		<O1–Cu>	1.920
Cu2–O7	1.86(1)	O2–Cu1	1.930(7) ×2
Cu2–O2	1.94(1)	O2–Cu2	1.94(1)
Cu2–O8	2.03(1) ×2	O2–Cu4	1.94(1)
Cu2–O6	2.10(2)	<O2–Cu>	1.937

[010] is in agreement with the partial occupancy of the M1 site. We note large U^{22} values for the M1, Cu3 and O4 atoms indicating positional disorder along [010] and an even larger U^{33} value for Cl1 suggesting significant disorder of this atom along [001]. There is a possibility of significant ionic mobility with increasing temperature in the voids of the metal oxide framework, which might act as an ‘electron reservoir’.

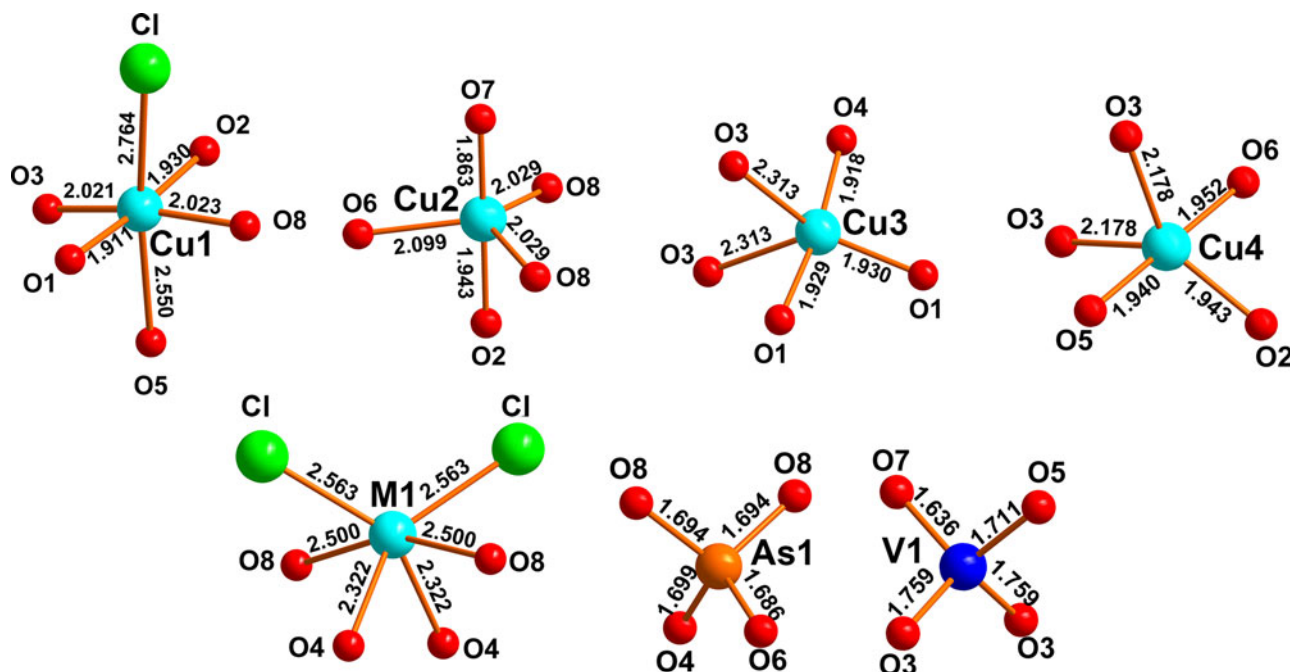
Oxygen atoms O3, O4, O5, O6, O7 and O8 are strongly bonded in tetrahedral AsO_4^{3-} and VO_4^{3-} groups. We may term them as O_t . ‘Additional’ oxygen atoms O1 and O2 are bonded exclusively to Cu^{2+} cations and can be designated as O_a . Cu^{2+} – O_a bonds are in the range of 1.911(8)–1.94(1) Å, whereas Cu^{2+} – O_t range from

1.86(2) to 2.55(1) Å (Table 6). Because of the variability of the coordination polyhedra around Cu^{2+} cations and the strength of the Cu – O_a bonds compared to the weaker Cu – O_t and especially Cu –Cl bonds, one can describe the Cu –oxide substructure of aleutite in terms of oxocentred OCu_4^{2+} tetrahedra.

Structure description

O1Cu_4 and O2Cu_4 tetrahedra have shared Cu – Cu edges and corners thus forming ${}^1_\infty[\text{Cu}_5\text{O}_2]^{6+}$ bands (Fig. 3a). These bands grow parallel to the b axis. In order to describe the linkage of oxocentred tetrahedra with each other, connectivity diagrams (Siidra *et al.*, 2008) depicted in Fig. 3a can be used. Each diagram represents a view from above onto a regular tetrahedron resting on one of its triangular faces. The following graphical indicators are used: (1) a corner shared with an adjacent tetrahedron is designated by a circle; (2) a shared edge is designated by a bold line. Identical or chiral diagrams are called equivalent. Thus the topology of ${}^1_\infty[\text{Cu}_5\text{O}_2]^{6+}$ bands is novel and has not been described before in minerals and synthetic materials. ${}^1_\infty[\text{Cu}_9\text{Pb}_2\text{O}_4]^{14+}$ bands described previously in the structures of complex synthetic oxyhalide selenites (Kovrugin *et al.*, 2015; Siidra *et al.*, 2018a) contain only corner sharing between the neighbouring OCu_4 tetrahedra. However, ${}^1_\infty[\text{Cu}_5\text{O}_2]^{6+}$ bands in aleutite can be cut from the ${}^2_\infty[\text{Cu}_6\text{Pb}_3\text{O}_4]^{10+}$ layers described in $[\text{Cu}_6^{2+}\text{Pb}_3\text{O}_4](\text{Cu}^+\text{Pb}_{1.27}\text{Br}_{3.54})(\text{SeO}_3)_4\text{Br}_2$ (Siidra *et al.*, 2018a).

The structural architecture of the oxocentred ${}^1_\infty[\text{Cu}_5\text{O}_2]^{6+}$ band in aleutite can be derived from a kagome (Mekata, 2003) network and represents a one-dimensional (Fig. 3b) slice from it (Fig. 3c). The kagome fragment in aleutite is formed by Cu1 – Cu1 – Cu2 and Cu1 – Cu1 – Cu3 triangles. Cu2 – Cu2 – Cu3 triangles are capped by additional Cu4 atoms above or below triangular faces, whereas Cu1 – Cu1 – Cu3 triangles are complemented by additional Cu3 atoms. It is of interest to consider the Cu – Cu distances of tetrahedral edges in Cu_4 tetrahedra depicted in Fig. 3d.

**Fig. 2.** Coordination of atoms in aleutite.

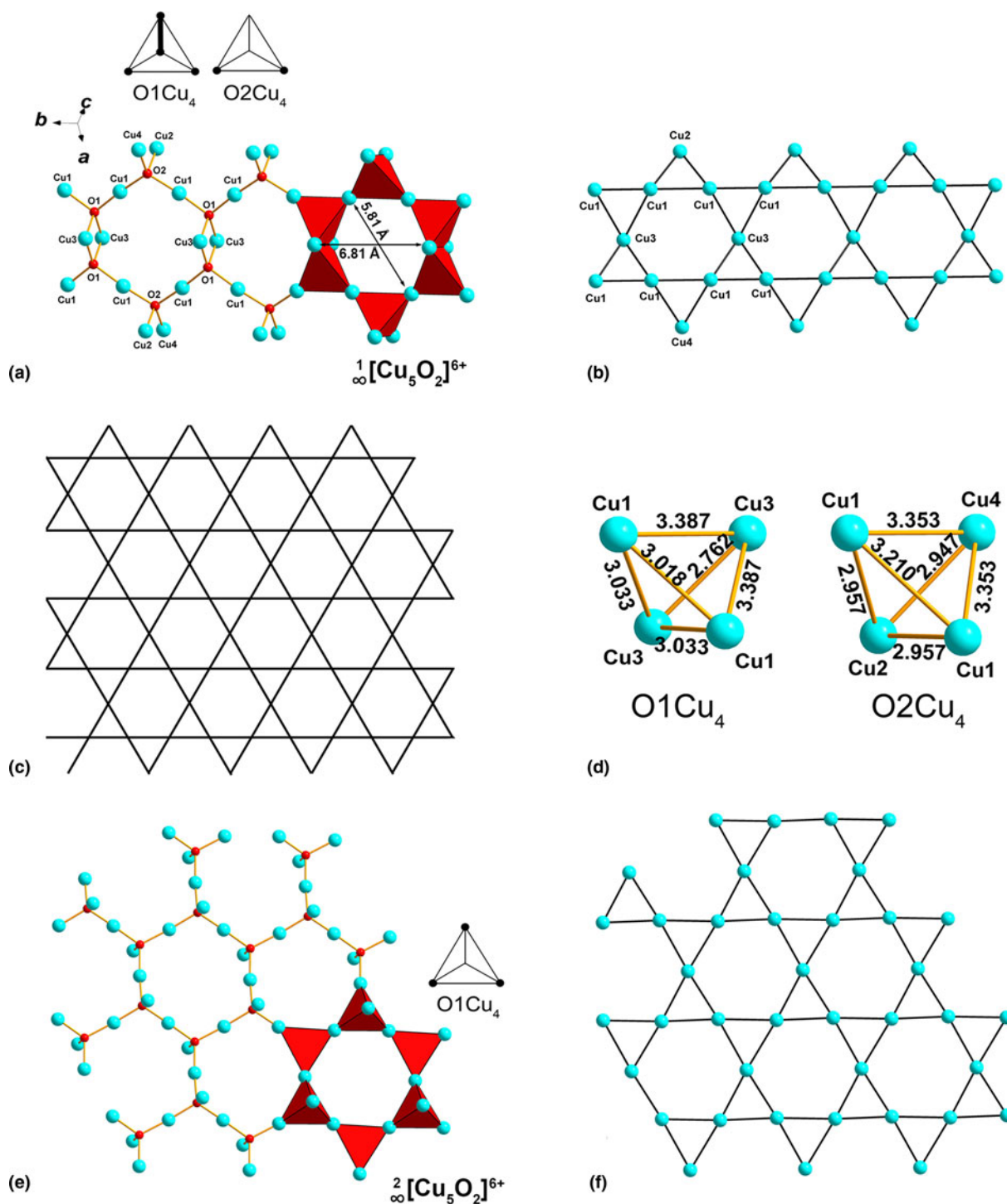


Fig. 3. (a) Ball-and-stick and polyhedral representation of $[\text{Cu}_5\text{O}_2]^{6+}$ oxocentred bands elongated along the b axis and connectivity diagrams for O1Cu_4 and O2Cu_4 oxocentred tetrahedra. (b) One-dimensional kagome-like fragment in aleutite, formed by Cu1-Cu1-Cu2 and Cu1-Cu1-Cu3 triangles. Cu2-Cu2-Cu3 triangles are complemented by additional Cu4 atoms above or below triangular faces, whereas Cu1-Cu1-Cu3 triangles are complemented by additional Cu3 atoms. (c) An ideal kagome network. (d) Cu-Cu distances in two symmetrically independent OCu_4 tetrahedra. (e) $[\text{Cu}_5\text{O}_2]^{6+}$ layers in the structure of averievite and connectivity diagrams for O1Cu_4 tetrahedra. (f) Kagome sheets in averievite.

The $\text{Cu3}\cdots\text{Cu3}$ edge in the O1Cu_4 tetrahedron has a length of 2.762 Å, whereas two $\text{Cu3}\cdots\text{Cu1}$ and one $\text{Cu1}\cdots\text{Cu1}$ have almost identical edges of ~ 3 Å. The two other $\text{Cu3}\cdots\text{Cu1}$ edges have significantly longer but identical values of 3.387 Å. The similar distribution of $\text{Cu}\cdots\text{Cu}$ distances is observed for O2Cu_4 tetrahedron. $\text{Cu4}\cdots\text{Cu2}$ and two $\text{Cu2}\cdots\text{Cu1}$ edges are ~ 3 Å long. The

$\text{Cu1}\cdots\text{Cu1}$ edge is 3.210 Å and two $\text{Cu1}\cdots\text{Cu4}$ are each 3.353 Å long.

AsO_4 and VO_4 tetrahedra are attached to OCu_4 tetrahedra in face-to-face fashion (Krivovichev *et al.*, 2013) thus providing the assemblage of the bands into a porous $\{^3_\infty[\text{Cu}_5\text{O}_2]\}(\text{AsO}_4)(\text{VO}_4)^0$ electroneutral framework shown in Fig. 4a,b. A two-dimensional

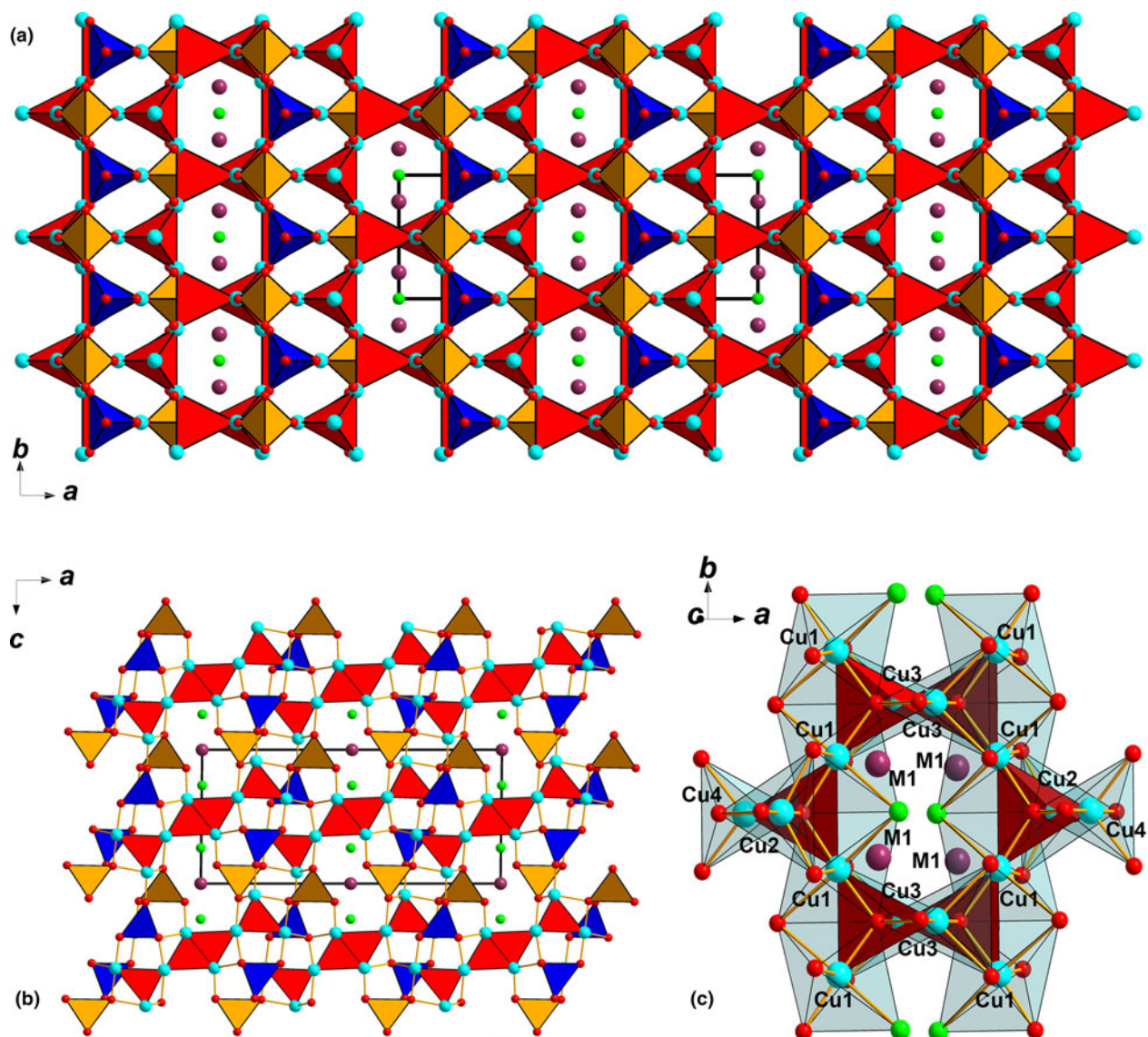


Fig. 4. General projection of the crystal structure of aleutite (a) along the *c* axis and (b) along the *b* axis. The tetrahedral framework is formed by OCu_4 (red), VO_4 (blue) and ASO_4 (orange) tetrahedra. Channels ($\sim 5.81 \text{ \AA} \times 6.81 \text{ \AA}$) in the framework are filled by the different metals occupying the mixed *M1* site (violet balls) and chloride ions (green balls). (c) A segment of the crystal structure of aleutite showing the complex arrangement of Cu-centred polyhedra (light blue) and six-membered rings formed by the corner and edge-sharing OCu_4 tetrahedra (red).

system of channels with dimensions $\sim 5.81 \times 6.81 \text{ \AA}$ is occupied by metal–chloride species. Thus aleutite can be classified as a new mesoporous material.

Discussion

Aleutite is a new structure type. Chemically aleutite is an As, V-analogue of averievite (Table 7). Aleutite is also chemically related to coparsite (Starova *et al.*, 1998). No synthetic compounds directly related to aleutite are known to date.

The structure of aleutite is completely different from averievite (Starova *et al.*, 1997; Vergasova *et al.*, 1998; Krivovichev *et al.*, 2015). Six-membered rings in aleutite (Fig. 4c) are formed by both corner-sharing and edge-sharing OCu_4 tetrahedra. OCu_4 oxocentred tetrahedra via common corners only form ${}_{\infty}[\text{Cu}_5\text{O}_2]^{6+}$ layers in averievite (Fig. 3e). Kagome-net derived layers (Fig. 3f) in synthetic averievite have outstanding magnetic properties described recently (Botana *et al.*, 2018).

It is common for copper vanadate minerals of fumarolic origin to have a significant amount of arsenic substitution. Aleutite is unique amongst copper vanadates, as it has As^{5+} and V^{5+} cations ordered over two tetrahedral sites. Vasilseverginite $\text{Cu}_9\text{O}_4(\text{AsO}_4)_2(\text{SO}_4)_2$ (Pekov *et al.*, 2015) is the only other known example of arsenates of fumarolic origin with segregation of tetrahedrally coordinated As^{5+} and S^{6+} cations.

The framework in aleutite has large elliptical channels occupied by the complex mixed cationic *M* sites and Cl^- anions. This type of structural architecture in aleutite is similar to that observed in leningradite $\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$ (Siidra *et al.*, 2007). The composition of mixed and partially occupied *M* sites in aleutite is somewhat similar to averievite (Vergasova *et al.*, 1998). However, the amount of alkali metals is significantly less in aleutite. The strong distortion of the *M* sites coordination environments in aleutite in comparison with averievite can be probably explained by the presence of Pb^{2+} cations with a stereochemically active lone electron pair in the former. A similar phenomenon is observed in the alunite-supergroup

Table 7. Crystal chemical data of aleutite, averievite (Krivovichev *et al.*, 2015) and coparsite (Starova *et al.*, 1998).

Mineral	Aleutite	Averievite	Coparsite
Formula	[Cu ₅ O ₂] (AsO ₄)(VO ₄) (Cu _{0.5} □ _{0.5})Cl	[Cu ₅ O ₂] (VO ₄) _n MCl _x	[Cu ₄ O ₂] ((As,V)O ₄)Cl
Crystal system	Monoclinic	Trigonal	Orthorhombic
Space group	C2/m	P3m1	Pbcm
a (Å)	18.090(2)	6.3778(2)	5.440(1)
b (Å)	6.2284(6)		11.154(2)
c (Å)	8.2465(9)	8.3966(3)	10.333(2)
β (°)	90.597(2)		
V (Å ³)	929.1(2)	295.79(2)	627.0(3)
Z	4	1	4

minerals. Pb has strongly distorted coordination environments in the structure of plumbogummite because of the presence of a stereochemically active 6s² lone electron pair (Mills *et al.*, 2009), but K is symmetrically coordinated in the structure of jarosite (Mills *et al.*, 2013). One symmetrically independent but disordered *M* site is observed in the structure of aleutite in contrast to two *M* sites in averievite (Krivovichev *et al.*, 2015). The 'host-guest' character of the aleutite structure may be the result of its formation from volcanic gases. The metal oxide species tend to organise in such a structure that allows inclusion of various metal chloride species into a basic oxide matrix.

Aleutite is also an interesting and complex example of a natural salt-inclusion phase. Such synthetic materials consisting of a covalent metal oxide framework containing voids filled by the simple ionic salt species have received considerable attention in the field of materials science and inorganic chemistry (Huang *et al.*, 1999; Ulutagay *et al.*, 1998; Huang *et al.*, 2001).

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