

# Pseudolyonsite, $\text{Cu}_3(\text{VO}_4)_2$ , a new mineral species from the Tolbachik volcano, Kamchatka Peninsula, Russia

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**Abstract:** Pseudolyonsite, ideally  $\text{Cu}_3(\text{VO}_4)_2$ , is a new mineral from the medium-temperature fumaroles of the New Tolbachik scoria cones, Tolbachik volcano, Kamchatka Peninsula, Russia. It occurs as needles that are 5–20  $\mu\text{m}$  across and up to 0.5 mm in the length, which sometimes produce parallel intergrowths, sprays or openwork clusters up to 2 mm. Associated minerals are: piypite, hematite, magnetite, lyonsite, apthitalite, palmierite, langbeinite, filatovite, lammerite, vergasovaite, rutile and native gold. Pseudolyonsite is dark red with a brownish tint to black, translucent to opaque, with a reddish-brown streak and adamantine to semi-metallic lustre. The mineral is brittle, but thin long needles are flexible. The fracture is conchoidal, and no cleavage was observed. The calculated density is 4.749  $\text{g}/\text{cm}^3$ . In reflected light in air the mineral is grey with a weak bluish tint, non-pleochroic, has distinct anisotropy and ubiquitous red to orange internal reflections. The reflectance values ( $R_1$  and  $R_2$ , %) in air for the four COM wavelengths are, respectively, 17.05, 19.6 (470 nm); 16.1, 18.15 (546 nm); 15.85, 17.7 (589 nm); and 15.55, 17.4 (650 nm). Four electron probe (EDS) analyses produced the following mean values:  $\text{V}_2\text{O}_5$  40.37,  $\text{CuO}$  48.83,  $\text{ZnO}$  7.60,  $\text{MoO}_3$  1.89, and  $\text{SiO}_2$  0.14, total 98.83 wt%, which corresponds, on the basis of 8 O atoms, to  $(\text{Cu}_{2.58}\text{Zn}_{0.44})_{\Sigma 3.02}(\text{V}_{1.88}\text{Mo}_{0.06}\text{Si}_{0.02})_{\Sigma 1.96}\text{O}_8$ . The idealised formula is  $\text{Cu}_3(\text{VO}_4)_2$ . Pseudolyonsite is monoclinic:  $P2_1/c$ ,  $a = 6.2695(4)$ ,  $b = 8.0195(3)$ ,  $c = 6.3620(3)$  Å,  $\beta = 111.96(1)^\circ$ ,  $V = 296.66(3)$  Å<sup>3</sup>,  $Z = 2$ . The strongest powder X-ray diffraction lines [ $d$  in Å ( $hkl$ )] are: 4.70 (60) (110); 3.30 (79) (021, 120); 3.22 (87) (111); 3.18 (34) ( $-121$ ,  $-102$ ); 2.894 (74) (200,  $-211$ ); 2.761 (100) (012); 2.479 (59) ( $-212$ ,  $-122$ ); 2.419 (67) (031, 130). The crystal structure was solved from single-crystal data and refined to  $R = 0.0444$ . Pseudolyonsite is isostructural with synthetic monoclinic  $\text{Cu}_3(\text{VO}_4)_2$ . The crystal structure of pseudolyonsite contains corrugated octahedral layers formed by the chains of edge-shared, distorted Cu(2)-octahedra running along the  $c$  axis and connected to each other by distorted Cu(1)-octahedra. The octahedra of both types contain Cu and subordinate Zn, and they are typically Jahn-Teller-distorted. Adjacent octahedral layers are connected to each other by  $\text{VO}_4$  tetrahedra. Pseudolyonsite is dimorphous with triclinic mcbirneyite. The name pseudolyonsite comes from its close visual similarity to another vanadate mineral, lyonsite,  $\text{Cu}_3\text{Fe}^{3+}_4(\text{VO}_4)_6$ . Both the mineral and its name have been approved by the IMA CNMNC (IMA No. 2009-062).

**Key-words:** pseudolyonsite,  $\text{Cu}_3(\text{VO}_4)_2$ , copper vanadate, new mineral, crystal structure, optical properties, Tolbachik, volcano, fumarole.

## 1. Introduction

Fumaroles on passively degassing volcanoes and cooling scoria cones produce specific mineral associations known as “incrustations” or “sublimates”. The latter term reflects the genesis of fumarole minerals that are deposited directly from the gaseous phase. The volatile transport of metals together with gas-rock interaction, abruptly changing temperature and  $f\text{O}_2$  near the fumarole orifice provide a diversity of mineral species in the sublimates.

The post-eruptive mineral deposition at the New Tolbachik scoria cones (Kamchatka, Russia) is an example of such diversity. Since 1982, 32 new mineral species have

been discovered there; as of 2010, only seven have been found elsewhere. Tolbachik fumarole gases typically contain >99 % air, ~1 % water vapour and less than 0.1 % acid species and trace elements (data by M. Zelenski). The minerals deposited by such gases are mostly oxysalts, including sulphates, selenites, arsenates, molybdates and vanadates.

Pseudolyonsite,  $\text{Cu}_3(\text{VO}_4)_2$ , which is described in the present paper, is a new copper vanadate from the Tolbachik sublimates. It contains solely the orthovanadate anion  $\text{VO}_4^{3-}$  and thereby differs from the other Tolbachik vanadates with composite anions: coparsite,  $\text{Cu}_4[\text{O}_2\text{Cl}(\text{AsO}_4, \text{VO}_4)]$  (Vergasova *et al.*, 1999); averievite,

$\text{Cu}_6[\text{O}_2\text{Cl}_2(\text{VO}_4)_2] \cdot n(\text{K}, \text{Cs}, \text{Rb})\text{Cl}$  (Vergasova *et al.*, 1998) and leningradite,  $\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$  (Vergasova *et al.*, 1990). The new mineral also differs in chemistry and structure from other natural anhydrous copper vanadates – namely, blossomite,  $\alpha\text{-Cu}_2\text{V}_2\text{O}_7$  (Robinson *et al.*, 1987); ziesite,  $\text{Cu}_2\text{V}_2\text{O}_7$  (Hughes & Birnie, 1980); stoiberite,  $\text{Cu}_5\text{V}_2\text{O}_{10}$  (Birnie & Hughes, 1979); and fingerite,  $\text{Cu}_{11}(\text{VO}_4)_6\text{O}_2$  (Hughes & Hadidiacos, 1985) – all of which are products of volcanic fumarole activity. Pseudolyonsite is dimorphous with mcbirneyite,  $\text{Cu}_3(\text{VO}_4)_2$  (Hughes *et al.*, 1987b) and the natural analogue of synthetic monoclinic  $\text{Cu}_3(\text{VO}_4)_2$ , which was studied by Shannon & Calvo (1972). Pseudolyonsite (Cyrillic: ПСЕВДОЛИОНСИТ) receives its name from its visual similarity with another vanadate mineral, lyonsite,  $\text{Cu}_3\text{Fe}^{3+}_4(\text{VO}_4)_6$  (Hughes *et al.*, 1987a). These two minerals are nearly identical in terms of crystal habit, colour and other physical properties. Lyonsite and pseudolyonsite crystallise under similar conditions, and they occur in the same fumarole at Tolbachik. The type specimen is deposited in the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow (registration no. 3879/1).

## 2. Occurrence, paragenesis and general appearance

Pseudolyonsite was found among other fumarolic minerals in the Yadovitaya (“Poisonous”) fumarole, Second cone, New Tolbachik scoria cones, Kamchatka Peninsula, Far East Asia, Russia. The cones (55°41'N, 160°14'E, 1200 m asl) are monogenetic volcanoes that formed during the Tolbachik Fissure eruption in 1975. A detailed geological description of the site was given by Fedotov & Markhinin (1983). Two of the four cones have a relative height of 300–320 m and a volume of approximately 0.1 km<sup>3</sup>. In 2009, 34 years after the eruption, there were still several gas vents with temperatures of 200–480 °C at the apical parts of the cones. The rocks there are altered by HF- and HCl-rich gases and are often covered by a fluoride-rich crust. Pseudolyonsite, as most other minerals discovered on Tolbachik, occurs in cavities from several centimetres to 1.5 m in size under the surface crust.

Pseudolyonsite is one of the rarest minerals of Tolbachik. It is commonly present as an overgrowth on acicular piypite. Crystals occur as needles that are up to 0.5 mm long and 5–20 µm across. The crystals are separate, or they form parallel intergrowths sprays or openwork clusters up to 1 mm. The mineral's dark red crystals are clearly visible on the overall green background of copper sulphates (Fig. 1). Pseudolyonsite was most likely deposited at a temperature ranging from 200 to 300 °C. The gas composition was close to that of atmospheric air with an admixture of meteoric water vapour and magmatic components, mainly HCl and HF. The sequence of deposition observed in the collected specimens shows that the formation of pseudolyonsite occurred during one of the latest stages. Closely associated minerals are piypite (Vergasova *et al.*, 1984), palmierite, lyonsite and hematite. Pseudolyonsite overgrows aggregates of piypite, but it is rarely overgrown

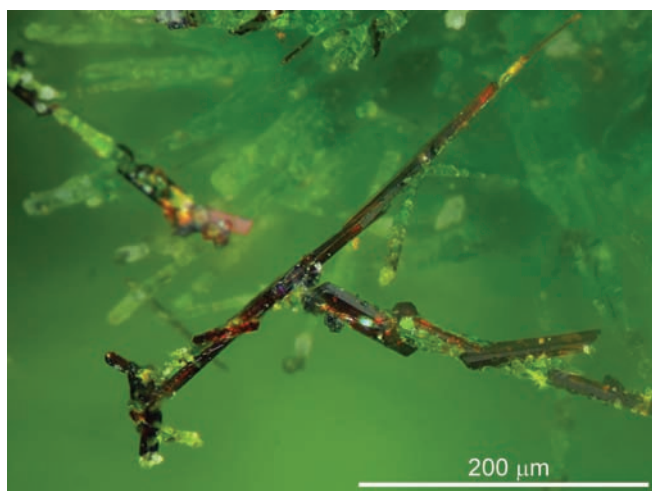


Fig. 1. Openwork cluster of dark-red pseudolyonsite on a green background of piypite crystals. Nikon Eclipse LV100 POL, plane polarised light was used to diminish reflections from the crystal surfaces, multi-shot focus stacking by means of CombineZP software.

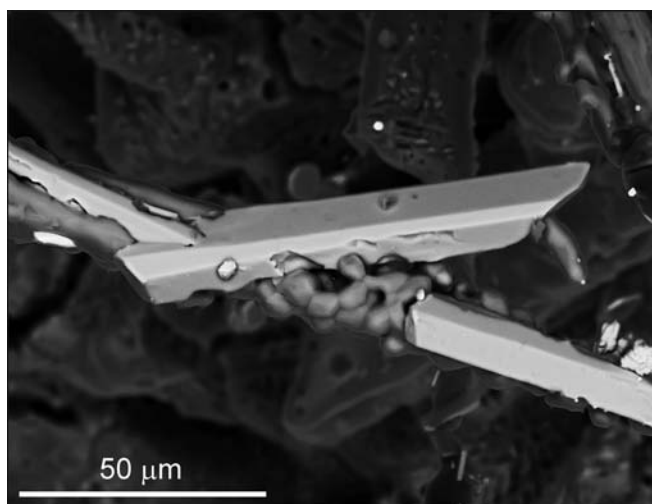


Fig. 2. Well-shaped crystals of pseudolyonsite (light grey) overgrown by piypite (grey) and palmierite (white). Vega Tescan SEM image, mixed SE + BSE detectors.

by minute crystals of piypite, palmierite and hematite (Fig. 2). Other spatially related minerals are magnetite, apthitalite, langbeinite, filatovite (Vergasova *et al.*, 2004), lammerite, vergasovaite (Bykova *et al.*, 1998), rutile and native gold.

## 3. Physical and optical properties

Pseudolyonsite is dark red with a brownish tint. Thick needles or parallel intergrowths may be black. The mineral is translucent to opaque, has a reddish-brown streak and has an adamantine to semi-metallic lustre. Pseudolyonsite

is brittle, but thin long needles are flexible and elastic. The fracture is conchoidal, and no cleavage has been observed. The density has not been measured because of the small size of the crystals. The calculated density (from the empirical formula and single-crystal X-ray data) is 4.749 g/cm<sup>3</sup>. The Mohs hardness is 2–3.

Under the microscope in reflected light, pseudolyonsite is grey with a weak bluish tint. Pleochroism is not observed, and the bireflectance is weak. The mineral has strong red internal reflections. The anisotropy is distinct, however, in case of thin needles it is barely observable because of strong internal reflections. The reflectance was measured in air with an MSPH-21 microspectrophotometer (LOMO, Russia), which was equipped with an R928 Hamamatsu photomultiplier tube. Measurements were performed for specimen and standard (SiC, Zeiss 545) under the same conditions in air with a  $\times 40$  objective and with the effective numerical aperture reduced to 0.35. The diameter of the measured area was 3  $\mu\text{m}$ . The bandwidth of the grating monochromator was set to 12 nm, and the intensity data were collected at an interval of 20 nm from 400 to 700 nm. The reflectance values (%) for R<sub>1</sub> and R<sub>2</sub> are reported in Table 1. For comparison, the reflectance values for mcbirneyite, Cu<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub>, and lyonsite, Cu<sub>3</sub>Fe<sub>4</sub>(VO<sub>4</sub>)<sub>6</sub>, are also given. The air reflectance spectra of pseudolyonsite, mcbirneyite and lyonsite are shown in Fig. 3. The spectra of pseudolyonsite are clearly different

Table 1. Reflectance data (%) for pseudolyonsite, lyonsite and mcbirneyite.

$\lambda$ , nm	Pseudolyonsite <sup>a</sup>		Lyonsite <sup>b</sup>		Mcbirneyite <sup>c</sup>
	R <sub>1</sub>	R <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>	R'
400	19	21.75			
420	18.55	21.1			
440	17.9	20.55			
460	17.25	19.95			
470 (COM)	17.05	19.6			
480	16.9	19.3	17.5	23.1	18.5
500	16.6	18.9			
520	16.35	18.5			
540	16.15	18.25			
546 (COM)	16.1	18.15	16.6	22.3	17.5
560	16	17.95			
580	15.9	17.75			
589 (COM)	15.85	17.7			18.7
591			14.7	20.7	
600	15.8	17.6			
620	15.7	17.45			
640	15.6	17.4			
644			14.4	18.8	
650 (COM)	15.55	17.4			20.6
660	15.5	17.4			
680	15.5	17.4			
700	15.5	17.4			

<sup>a</sup>This work.

<sup>b</sup>Hughes *et al.* (1987a).

<sup>c</sup>Hughes *et al.* (1987b).

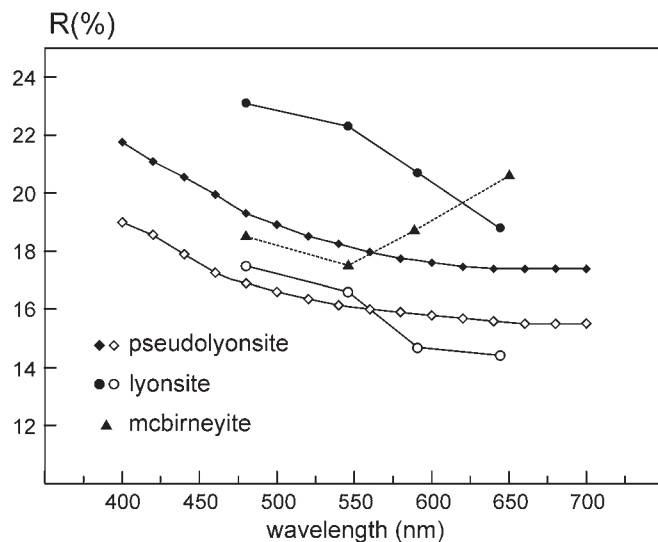


Fig. 3. Air reflectance spectra of pseudolyonsite, mcbirneyite and lyonsite. Open symbols refer to R<sub>1</sub>, filled symbols refer to R<sub>2</sub>. Only a single value of R' for each wavelength is available for the spectrum of mcbirneyite.

Table 2. CIE colour values for pseudolyonsite.

	Illuminant C (6774 K)		Illuminant A (2856 K)	
	R <sub>1</sub>	R <sub>2</sub>	R <sub>1</sub>	R <sub>2</sub>
x	0.301	0.299	0.440	0.438
y	0.305	0.303	0.404	0.403
Y, %	16.1	18.1	16.0	17.9
$\lambda_d$ , nm	474	475	485	486
P <sub>e</sub> , %	4.6	5.7	1.9	2.5

from those of mcbirneyite and lyonsite, both in reflectance and dispersion values.

The colour values (Table 2) for pseudolyonsite were calculated for the CIE standard illuminants C (6774 K) and A (2856 K) by means of the computer MicroMin System (Boldyreva *et al.*, 2009). The dominant wavelengths in reflected light for R<sub>1</sub> $\lambda_d$  and R<sub>2</sub> $\lambda_d$  (for CIE illuminant C) are 474 and 475 nm, respectively, that determine the blue tint of the grey (Y = 16.1–18.1 %) mineral. Colour values for illuminant A demonstrate lower saturation (P<sub>e</sub> = 1.9–2.5 %) of greenish-blue ( $\lambda_d$  = 485–486 nm) tint of the mineral.

#### 4. Chemical composition

Crystals of pseudolyonsite were studied with a Tescan Vega II XMU scanning electron microscope equipped with Inca Energy and Inca Wave microanalysis systems (IEM RAS, Chernogolovka, Russia) at 20 kV and 0.5 nA. The diameter of the beam was 0.26  $\mu\text{m}$ , and the counting time was 180 s. The following standards were used: Cu (metal 99.999 %), Zn (metal 99.9 %), V (metal 99.9 %) and

Table 3. Chemical composition (wt%) of pseudolyonsite.

No.	V <sub>2</sub> O <sub>5</sub>	CuO	ZnO	MoO <sub>3</sub>	SiO <sub>2</sub> <sup>a</sup>	Total
1	40.79	51.76	4.87	1.98	0.56	99.95
2	40.27	47.09	9.00	1.65	0.00	98.01
3	40.24	48.23	9.36	2.13	0.00	99.95
4	40.18	48.24	7.19	1.80	0.00	97.42
Mean	40.37	48.83	7.6	1.89	0.14	98.83
Minimum	40.18	47.09	4.87	1.65	0	97.42
Maximum	40.79	51.76	9.36	2.13	0.56	99.95
SD	0.28	2.03	2.06	0.21	0.28	1.31

<sup>a</sup>Si content possibly derived from silica pollution of the analysed material.

Mo (metal 99.8 %). The average chemical composition is shown in Table 3.

The empirical formula of pseudolyonsite was calculated on the basis of eight oxygen atoms per formula unit (apfu). In addition to the major, species-defining constituents Cu (2.34–2.75 apfu) and V (1.78–1.96 apfu), pseudolyonsite contains Zn (up to 0.59 apfu), Mo (0.04–0.07 apfu) and, possibly, Si (up to 0.12 apfu; the possibility that the Si content was caused by silica pollution was not excluded). Unlike lyonsite, this new mineral does not contain Fe in detectable amounts. The average empirical formula for pseudolyonsite is  $(\text{Cu}_{2.58}\text{Zn}_{0.44})_{\Sigma 3.02}(\text{V}_{1.88}\text{Mo}_{0.06}\text{Si}_{0.02})_{\Sigma 1.96}\text{O}_8$ . The idealised formula is  $\text{Cu}_3(\text{VO}_4)_2$ , which requires CuO 56.75 and V<sub>2</sub>O<sub>5</sub> 43.25, total 100.00 wt%.

## 5. X-ray crystallography and crystal structure

A 0.05 × 0.06 × 0.35-mm pseudolyonsite crystal was used for structure determination at room temperature with an Xcalibur S diffractometer equipped with a CCD detector. A total of 7679 reflections were obtained within a  $\theta$  range of 3.50 to 32.58°. The diffraction intensities were integrated using the CrysAlis software (Oxford Diffraction, 2006). The data were corrected for Lorentz and polarisation effects; the absorption correction was applied according to the shape of the crystal. A monoclinic unit cell was revealed with the following values:  $a = 6.2695(4)$ ,  $b = 8.0195(3)$ ,  $c = 6.3620(3)$  Å,  $\beta = 111.96(1)^\circ$ . Space group  $P2_1/c$  was determined on the basis of the systematic absences. The crystal structure of the pseudolyonsite was solved through direct methods and was refined anisotropically using the SHELX software package (Sheldrick, 1997, 2008) to  $R = 0.0444$  for 707 unique reflections with  $I > 2\sigma(I)$ . The refinement indicated the following structural formula for the mineral:  $(\text{Cu}_{0.88}\text{Zn}_{0.12})(\text{Cu}_{0.88}\text{Zn}_{0.12})_2(\text{V}_{0.975}\text{Mo}_{0.02})\text{O}_4$ . The refinement of the electron content of the sites and the analysis of the interatomic distances in the corresponding polyhedra showed a random distribution of Cu and Zn in two crystallographically nonequivalent positions. A small amount of Mo was added to the V site according to the chemical composition data. The occupancy coefficients of all cations were fixed in the final stages of the refinement.

Table 4. Crystal data, data collection information and refinement details for pseudolyonsite.

Formula	$(\text{Cu}_{0.88}\text{Zn}_{0.12})(\text{Cu}_{0.88}\text{Zn}_{0.12})_2$ $[(\text{V}_{0.97}\text{Mo}_{0.02})\text{O}_4]_2$
Formula weight	422.45
Crystal system, space group, Z	Monoclinic, $P2_1/c$ ; 2
Unit-cell dimensions (Å, °)	$a = 6.2695(4)$ , $b = 8.0195(3)$ , $c = 6.3620(3)$ $\beta = 111.96(1)$
V (Å <sup>3</sup> )	296.66(3)
Density (calculated) (g/cm <sup>3</sup> )	4.729
$\mu$ (mm <sup>-1</sup> )	13.790
$F(000)$	396
Crystal dimensions (mm)	$0.06 \times 0.05 \times 0.35$
Diffractometer	Xcalibur S CCD
Temperature (K)	293
Radiation and wavelength (Å)	MoK $\alpha$ ; 0.71073
$h, k, l$ ranges	$-9 \leq h \leq 9$ , $-11 \leq k \leq 12$ , $-9 \leq l \leq 9$
Total reflections measured	7679
Unique reflections	1037 ( $R_{\text{int}} = 0.0916$ )
Unique reflections with $I > 2\sigma(I)$	707
Refinement on	$F^2$
Number of parameters refined	61
$R_1^a$ for $I > 2\sigma(I)$	0.0444
$wR_2^b$ for all data	0.0749
Goof	0.983
$\Delta\rho_{\text{min}}/\Delta\rho_{\text{max}}$ (e/Å <sup>3</sup> )	-0.935/1.087

$$^a R_1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|}$$

$$^b wR_2 = \left[ \frac{\sum [w(F_o^2 - F_c^2)^2]}{\sum [w(F_o^2)^2]} \right]^{1/2}; w = \frac{1}{[\sigma^2(F_o^2) + (0.0292P)^2 + 0.000P]}$$

$$P = \frac{\max(0 \text{ or } F_o^2) + 2F_c^2}{3}$$

Details of the single-crystal X-ray data collection and the structure refinement of the pseudolyonsite are given in Table 4.

The final atom coordinates and displacement parameters are given in Table 5, and interatomic distances are given in Table 6.

The X-ray powder diffraction pattern of pseudolyonsite (Table 7) was determined using a 57.3-mm Debye-Scherrer camera (Ni-filtered CuK $\alpha$  radiation). Several closely adjacent lines (doublets and triplets) were unresolved in the obtained pattern. Indexing of the reflections was performed based on the structural data (see below). The monoclinic unit-cell dimensions of the pseudolyonsite refined from the powder data are:  $a = 6.239(5)$ ,  $b = 7.984(3)$ ,  $c = 6.364(6)$  Å,  $\beta = 111.92(6)^\circ$  and  $V = 294.1(5)$  Å<sup>3</sup>.

Pseudolyonsite is isostructural with a synthetic monoclinic  $\text{Cu}_3(\text{VO}_4)_2$  (Shannon & Calvo, 1972). Its crystal structure (Fig. 4a) is formed by chains of edge-sharing distorted octahedra involving Cu(2) running along the  $c$  axis and connected to each other by distorted octahedra involving Cu(1). The octahedra of both types contain Cu and subordinate Zn. The corrugated octahedral layers (Fig. 4b)



Table 5. Atom coordinates and displacement parameters (Å<sup>2</sup>) for pseudolyonsite.

Atom (position)	x	y	z	U <sub>eq</sub>
V [= V <sub>0.97</sub> Mo <sub>0.02</sub> ]	0.24993(14)	0.61919(11)	0.14155(14)	0.00670(18)
Cu(1) [= Cu <sub>0.88</sub> Zn <sub>0.12</sub> ]	0.0	0.0	0.0	0.0115(2)
Cu(2) [= Cu <sub>0.88</sub> Zn <sub>0.12</sub> ]	0.26769(11)	0.24606(9)	0.39505(11)	0.01039(16)
O(1)	0.0137(6)	0.7611(5)	0.0335(6)	0.0097(7)
O(2)	0.2309(7)	0.4935(5)	0.3565(6)	0.0109(7)
O(3)	0.5030(6)	0.7266(4)	0.2401(6)	0.0097(8)
O(4)	0.7534(7)	0.5004(5)	0.0738(6)	0.0107(7)

Table 6. Interatomic distances (Å) in pseudolyonsite.

V – O(4) 1.666(4)	Cu(2) – O(3) 1.938(4)
– O(3) 1.705(4)	– O(1) 1.983(4)
– O(2) 1.738(4)	– O(4) 1.989(4)
– O(1) 1.789(4)	– O(2) 2.002(4)
	– O(3) 2.238(3)
Cu(1) – O(1) 1.926(4) × 2	– O(1) 2.637(4)
– O(2) 1.980(3) × 2	
– O(4) 2.570(4) × 2	

Table 7. X-ray powder diffraction data for pseudolyonsite.

I <sub>meas</sub>	d <sub>meas</sub> , Å	I <sub>calc</sub>	d <sub>calc</sub> , Å	hkl
26	5.88	21	5.815	100
60	4.70	33	4.707	110
79	3.30	27, 26	3.316, 3.301	021, 120
87	3.22	61	3.233	111
34	3.18	16, 2	3.183, 3.149	–121, –102
25	2.957	10, 4	2.950, 2.931	002, –112
74	2.894	33, 36	2.907, 2.899	200, –211
100	2.761	100	2.769	012
9	2.628	4, 4	2.651, 2.617	121, –202
59	2.479	59, 14	2.488, 2.476	–212, –122
67	2.419	16, 65	2.434, 2.429	031, 130
14	2.367	13, 3, 7	2.381, 2.376, 2.354	–131, 022, 220
22	2.303	27	2.306	102
16	2.194	19, 3	2.202, 2.192	211, –222
15	2.006	21	2.005	040
29	1.992	24, 4, 4	1.999, 1.989, 1.981	122, 221, 032
7	1.720	14	1.725	212
11	1.683	13	1.691	–142
7	1.652	4, 8, 3	1.661, 1.658, 1.646	–133, 042, 113
6	1.614	7	1.617	222
9	1.603	9, 3	1.610, 1.600	–233, –323
14	1.567	26	1.574	–204
12	1.561	16	1.569	330
8	1.539	14, 8	1.546, 1.534	150, –151
9	1.518	15	1.526	–412
21	1.507	48	1.513	142
6	1.477	3, 7	1.475, 1.468	004, –124
9	1.448	20, 4, 2,	1.454, 1.450, 1.448,	400, –422, –421,
		3	1.444	–314
17	1.408	41, 2, 2	1.416, 1.414, 1.409	–342, 331, 052

are connected to each other by VO<sub>4</sub> tetrahedra. Both types of Cu octahedra are typically Jahn-Teller-distorted with four shorter and two longer Cu–O bonds (Table 6). This distortion leads to a reduction of the symmetry to monoclinic in comparison with other closely related synthetic vanadates with the general formula M<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> (M = Mg, Ni, Co, Zn). In these compounds, the M octahedra are relatively undistorted and, as a result, the symmetry is orthorhombic, with the space group *Cmca* (Gopal & Calvo, 1971; Krishnamachari & Calvo, 1971; Sauerbrei *et al.*, 1973). Mcbirneyite, a triclinic (sp. gr. *P-1*) natural modification of Cu<sub>3</sub>(VO<sub>4</sub>)<sub>2</sub> found in fumarolic sublimates of the Izalco volcano, El Salvador (Hughes *et al.*, 1987b) and its synthetic analogue have a different structure (Coing-Boyat, 1982). In this structure, the Cu<sup>2+</sup> cations also occupy two sites but, unlike pseudolyonsite, they are 4- and 5-coordinated (Fig. 4c). As a result, the X-ray powder diffraction patterns and the optical data for pseudolyonsite and mcbirneyite differ greatly.

## 6. Discussion: genetic features of fumarolic vanadates

Fumarole incrustations are a plentiful source of new minerals. Most quiescently degassing volcanoes emit water-rich gas with high sulphur and halogen content and low oxygen fugacity. Near the fumarole orifice, the gas cools and undergoes partial oxidation. Host rocks around the fumarole not only serve as a substrate for mineral deposition from gas but are also a subject for gas-rock interaction. A direct precipitation of minerals from the gas together with the gas-rock interaction provide a specific mineral association that generally comprises sulphides (including sulphosalts) of As, Cd, Pb, Bi, Fe together with sulphates and halides of NH<sub>4</sub>, Na, K, Mg, Ca, Al and Fe. Different forms of silica and native sulphur are also common, especially at low-end temperatures.

When volcanic activity ceases, the temperature of fumarole gases gradually decreases with a consequent diminution of mineral diversity around the fumaroles. In some cases, however, ambient air penetrates into a conduit system along with falling gas pressure. This action can ultimately change the mineral associations found around and inside the fumaroles. Examples of mineral parageneses associated with partially oxidised fumarolic gases are Colima

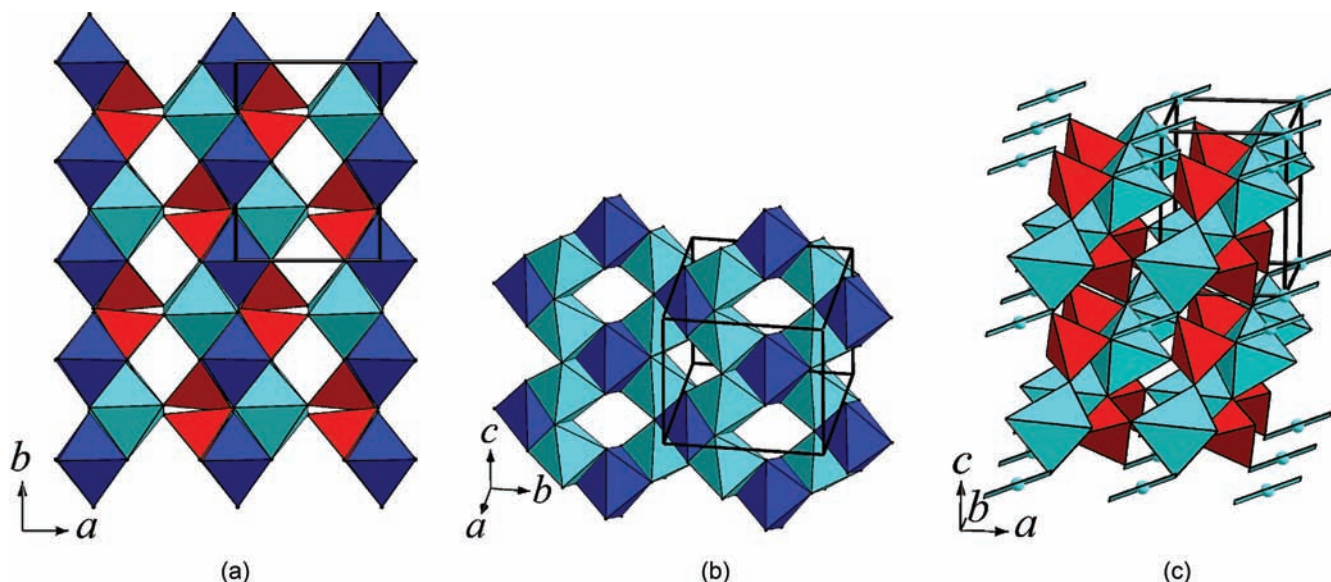


Fig. 4. Crystal structure of pseudolyonsite (*a* – general view, *b* – octahedral motif: our data) and synthetic analogue of mcbirneyite (*c*: Coing-Boyat, 1982). For pseudolyonsite, the Cu(1) octahedra are dark-blue, and the Cu(2) octahedra are turquoise-blue; for mcbirneyite, the Cu positions are turquoise-blue; the  $\text{VO}_4$  tetrahedra are red for both minerals.

volcano (Mexico) and Izalco volcano (El Salvador). The latter volcano has provided a rare vanadium mineralisation. Eight new vanadium minerals have been discovered in fumarolic sublimate at the Izalco volcano soon after the cessation of its eruptive activity in 1958. Four of these minerals belong to the  $\text{CuO-V}_2\text{O}_5$  system: stoiberite ( $\text{Cu}_5\text{V}_2\text{O}_{10}$ , Birnie & Hughes, 1979), ziesite ( $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ , Hughes & Birnie, 1980), fingerite ( $\text{Cu}_{11}(\text{VO}_4)_6\text{O}_2$ , Hughes & Hadidiacos, 1985), and mcbirneyite ( $\text{Cu}_3(\text{VO}_4)_2$ , Hughes *et al.*, 1987b). Hughes & Stoiber (1985) proposed that the V-rich sublimate formed around the fumarole vents from a mixture of air and vanadium-bearing gas, which was presumably exsolved from basaltic magma. Hughes & Birnie (1980) estimated the temperature of the mineral genesis of ziesite and fingerite on the basis of the phase relations in the synthetic system  $\text{CuO-V}_2\text{O}_5$  (Brisi & Molinari, 1958) and the intergrowth between these two minerals. However, the calculated temperature (760 °C) was considerably higher than the measured temperatures (200–300 °C).

The fumaroles of the New Tolbachik volcanoes demonstrate another case of mineral deposition from oxygen-rich gases. The Tolbachik scoria cones resemble the Izalco volcano, as the formation of sublimate at both sites occurred in the post-eruptive stage of volcanic activity. Unlike Izalco, the Tolbachik sublimate consist of different oxysalts, including vanadates, arsenates, selenites, molybdates and numerous sulphates. Halides, oxyhalides and oxides are also present, and Na, K, Fe, Cu and Zn appear to be the main cations. (Although many papers are devoted to the individual mineral phases found on Tolbachik, there is currently no summary review of the mineral forming processes of the site). Specific elemental and chemical compositions can account for some distinctive features of the Tolbachik fumaroles. The gases here

are almost pure atmospheric air, which infiltrates through loose scoria, is heated inside and discharges at the apical parts of the cones. This “volcanic air” contains some meteoric water vapour (~1 vol%) and less than 0.1 vol% HF and HCl. Such gas with high  $f\text{O}_2$  in general turns anion-forming elements with variable valencies (S, Mo, V, As) to their highest oxidation state. There are two exceptions to this rule. Selenium occurs at Tolbachik only as selenites, and vanadium in paufferite  $\text{VOSO}_4$  is in oxidation state 4+.

Another question is the source of elements. It could be assumed that acids enter the gas from cooling scoria and, consequently, that trace elements are extracted from the scoria and are volatilised due to the overall high content of HCl in the gas. In this case, the gas could interact with a large amount of porous basalt to provide high concentrations of metals sufficient for the deposition of minerals. Although the basaltic scoria at the New Tolbachik cones contains 260 ppm V and 155 ppm Cu (data by M. Zelenski) that are close to average for Earth’s basalts, the sublimate here are enriched with copper and vanadium. The list of Tolbachik fumarole minerals includes eight vanadium species. Three of these minerals have also been found at Izalco (shcherbinaite,  $\text{V}_2\text{O}_5$ , mcbirneyite,  $\text{Cu}_3(\text{VO}_4)_2$ , and lyonsite,  $\text{Cu}_3\text{Fe}_4(\text{VO}_4)_6$ ). The other five minerals are still endemic to Tolbachik: averievite,  $\text{Cu}_6[\text{O}_2\text{Cl}_2(\text{VO}_4)_2] \cdot n(\text{K,Cs,Rb})\text{Cl}$ ; leningradite,  $\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$ ; coparsite,  $\text{Cu}_4[\text{O}_2\text{Cl}(\text{AsO}_4, \text{VO}_4)]$ ; paufferite  $\text{VOSO}_4$  (Krivovichev *et al.*, 2007); and pseudolyonsite,  $\text{Cu}_3(\text{VO}_4)_2$ .

The exact temperature of deposition remains obscure because the process could have occurred at any time after the eruption ceased. Nevertheless, the spatial relations between the minerals show that the deposition probably occurred at the latest stages, when the temperature did not exceed 300 °C. The case of Tolbachik shows that

mineral deposition from highly oxidised gases not only forms specific mineral associations but can also produce sublimates that are even more fertile than those formed from common reducing volcanic gases.

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## References

- Birnie, R.W. & Hughes, J.M. (1979): Stoiberite,  $\text{Cu}_5\text{V}_2\text{O}_{10}$ , a new copper vanadate from Izalco volcano, El Salvador, Central America. *Am. Mineral.*, **64**, 941–944.
- Boldyreva, M.M., Kiselev, D.A., Romanovsky, J.V. (2009): MicroMin, a computer information system for identification of ore minerals and calculation of their colour values. SPbSU, St. Petersburg, 40 p. (in Russian).
- Brisi, C. & Molinari, A. (1958): Il sistema ossido ramicoanidride vanadica. *Ann. Chim.*, **48**, 263–269.
- Bykova, E.Y., Berlepsch, P., Kartashov, P.M., Brugger, J., Armbruster, T., Criddle, A.J. (1998): Vergasovaite  $\text{Cu}_3\text{O}[(\text{Mo}, \text{S})\text{O}_4][\text{SO}_4]$ , a new copper-oxy-molybdate-sulfate from Kamchatka. *Schweiz. Mineralog. Petrogr. Mitt.*, **78**, 479–488.
- Coing-Boyat, J. (1982): Structure de la variété ordinaire, triclinique, de l'orthovanadate de cuivre(II),  $\text{Cu}_3(\text{VO}_4)_2$ . *Acta Cryst.*, **B38**, 1546–1548.
- Fedotov, S.A. & Markhinin, Y.K., eds. (1983): The great Tolbachik fissure eruption. Cambridge University Press, New York, 341 p.
- Gopal, R. & Calvo, C. (1971): Crystal structure of  $\alpha\text{-Zn}_3(\text{VO}_4)_2$ . *Can. J. Chem.*, **49**, 3056–3059.
- Hughes, J.M. & Birnie, R.W. (1980): Ziesite,  $\beta\text{-Cu}_2\text{V}_2\text{O}_7$ , a new copper vanadate and fumarole temperature indicator. *Am. Mineral.*, **65**, 1146–1149.
- Hughes, J.M. & Hadidiacos, C.G. (1985): Fingerite,  $\text{Cu}_{11}\text{O}_2(\text{VO}_4)_6$ , a new vanadium sublimate from Izalco volcano, El Salvador: descriptive mineralogy. *Am. Mineral.*, **70**, 193–196.
- Hughes, J.M. & Stoiber, R.E. (1985): Vanadium sublimates from the fumaroles of Izalco volcano, El Salvador. *J. Volc. Geoth. Res.*, **24**, 283–291.
- Hughes, J.M., Starkey, S.J., Malinconico, M.L., Malinconico, L.L. (1987a): Lyonsite,  $\text{Cu}_3^{2+}\text{Fe}_4^{3+}(\text{VO}_4)_6^{3-}$ , a new fumarolic sublimate from Izalco volcano, El Salvador: descriptive mineralogy and crystal structure. *Am. Mineral.*, **72**, 1000–1005.
- Hughes, J.M., Christian, B.S., Finger, L.W., Malinconico, L.L. (1987b): Mcbirneyite,  $\text{Cu}_3(\text{VO}_4)_2$ , a new sublimate mineral from the fumaroles of Izalco Volcano, El Salvador. *J. Volc. Geoth. Res.*, **33**, 183–190.
- Krishnamachari, N. & Calvo, C. (1971): Refinement of the structure of  $\text{Mg}_3(\text{VO}_4)_2$ . *Can. J. Chem.*, **49**, 1629–1637.
- Krivovichev, S.V., Vergasova, L.P., Britvin, S.N., Filatov, S.K., Kahlenberg, V., Ananiev, V.V. (2007): Pauflerite,  $\beta\text{-VO}(\text{SO}_4)$ , a new mineral from the Tolbachik volcano, Kamchatka Peninsula, Russia. *Can. Mineral.*, **45**, 921–927.
- Oxford Diffraction. (2006): CrysAlis Software Package, Oxford Diffraction, Oxfordshire, UK.
- Robinson, P.D., Hughes, J.M., Malinconico, M.L. (1987): Blossite,  $\alpha\text{-Cu}_2[\text{V}_2\text{O}_7]$ , a new fumarolic sublimate from Izalco volcano, El Salvador. *Am. Mineral.*, **72**, 397–400.
- Sauerbrei, E.E., Faggiani, R., Calvo, C. (1973): Refinement of the crystal structures of  $\text{CoV}_2\text{O}_8$  and  $\text{NiV}_2\text{O}_8$ . *Acta Cryst.*, **B29**, 2304–2306.
- Shannon, R.D. & Calvo, C. (1972): Crystal structure of a new form of  $\text{Cu}_3\text{V}_2\text{O}_8$ . *Can. J. Chem.*, **50**, 3944–3949.
- Sheldrick, G.M. (1997): SHELXS-97, a program for the solution of crystal structures. University of Göttingen, Göttingen, Germany.
- (2008): A short history of SHELX. *Acta Crystallogr.*, **A64**, 112–122.
- Vergasova, L.P., Filatov, S.K., Serafimova, Y.K., Starova, G.L. (1984): Piypite,  $\text{K}_2\text{Cu}_2\text{O}(\text{SO}_4)_2$ , a new mineral of volcanic sublimates. *Dokl. Akad. Nauk SSSR*, **275**, 714–717 (in Russian).
- Vergasova, L.P., Filatov, S.K., Semenova, T.F., Ananiev, V.V. (1990): Leningradite  $\text{PbCu}_3(\text{VO}_4)_2\text{Cl}_2$  – a new mineral from volcanic sublimates. *Dokl. Akad. Nauk SSSR*, **310**, 1434–1437.
- Vergasova, L.P., Starova, G.L., Filatov, S.K., Ananiev, V.V. (1998): Averievite  $\text{Cu}_5(\text{VO}_4)_2\text{O}_2 \cdot n\text{MX}$ : a new mineral of volcanic exhalations. *Dokl. Akad. Nauk SSSR*, **359**, 804–807.
- Vergasova, L.P., Starova, G.L., Krivovichev, S.V., Filatov, S.K., Ananiev, V.V. (1999): Coparsite,  $\text{Cu}_4\text{O}_2[(\text{As}, \text{V})\text{O}_4]\text{Cl}$ , a new mineral species from the Tolbachik volcano, Kamchatka Peninsula, Russia. *Can. Mineral.*, **37**, 911–914.
- Vergasova, L.P., Krivovichev, S.V., Britvin, S.N., Burns, P.C., Ananiev, V.V. (2004): Filatovite,  $\text{K}[(\text{Al}, \text{Zn})_2(\text{As}, \text{Si})_2\text{O}_8]$ , a new mineral species from the Tolbachik volcano, Kamchatka peninsula, Russia. *Eur. J. Mineral.*, **16**, 533–536.

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