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ALUMOKLYUCHEVSKITE, $K_3Cu_3AlO_2(SO_4)_4$, A NEW OXYSULPHATE OF K, Cu AND Al FROM VOCANIC EXHALATIONS, KAMCHATKA, RUSSIA [1]

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АЛЮМОКЛЮЧЕВСКИТ, $K_3Cu_3AlO_2(SO_4)_4$ – НОВЫЙ ОКСИСУЛЬФАТ K, Cu И Al ИЗ ВУЛКАНИЧЕСКИХ ЭКСГАЛЯЦИЙ КАМЧАТКИ, РОСИЯ

Alumoklyuchevskite $K_3Cu_3AlO_2(SO_4)_4$ is an aluminium analogue of klyuchevskite $K_3C_3Fe^{3+}O_2(SO_4)_4$ (Vergasova e. a., 1989) compare to which the Fe^{3+} position is predominantly occupied by Al. Like klyuchevskite it was found in the volcanic exhalation products on the 2-nd cone of the Northern Breakthrough of the Main Tolbachik fracture eruption (1975—1976) (Main Tolbachik fracture eruption, 1984).

[1] The mineral is approved by the Commission on New Mineral and Mineral Names of the Mineralogical Society of Russia on December 25, 1992, by the Commission on New Mimeral and Mineral Names of the International Mineralogical Association on May 26, 1993.

The appearance of alumoklyuchevskite aggregates (*a*) and single crystals (*b*) (REM-photo; mlt: 70 (*a*) and 800 (*b*).

Внешний вид агрегатов (*а*) и кристаллов (*б*) алюмоключевскита (РЕМ-фото, увеличение 70 (*а*) и 800 (*б*).

The appearance of the mineral is similar to that of klyuchevskite. The mineral differs from the later by the chemical composition, colour, refracitive indices, pleochroism and some other properties. It forms the shaftlike aggregates (fig. *a*) of the long prismatic to needle crystals (fig. *b*). The crystals are up to 1 mm long and < 0.1 mm thick. Alumoklyuchevskite occurs in aggregates with fedotovite, tenorite, in association with langbeinite, lammerite.

The chemical composition obtained as an average of 26 electron microprobe analyses (mas.%): K_2O 18.68 (16.81—19.61), CuO 31.19 (30.04—32.79), Al_2O_3 4.65 (3.69—5.71), F_2O_3 3.70 (2.31—5.23), SO_3 40.70 (39.32—42.00), sum 98.92 (97.57—100.32) (table 1) yields the following formula calculated on the basis of O = 18: $K_{3.07}Cu_{3.04}(Al_{0.71}Fe_{0.36})_{1.07}(S_{3.94}O_{18})$. The empirical formula is $K_3Cu_3AlO_2(SO_4)_4$. Operation conditions were 20 kV, 35 nA sample current. Standards used were dolerophanite Cu_2OSO_4 (Cu,S), synthetic magnesiopherrite $MgFe_2O_4$ (Fe), hanite $ZnAl_2O_4$ (Al), synthetic orthoclase $KAlSi_3O_8$ (K).

In alumoklyuchevskite as compared to klyuchevskite Al predominates over Fe^{3+}. The content of Fe_2O_3 is 7.86 while Al_2O_3 is 1.38 (mas.%) (Gorskaya e. a., 1992). For alumoklyuchevskite we have 3.61 and 4.78 respectavely. Al/Fe ratio for the investigated samples of both minerals varies from 2.51 to 2.56 in klyuchevskite and from 0.26 to 0.88 in

Продолжение рисунка.

alumoklyuchevskite. So we can consider the existance of alumoklyuchevskite—klyuchevskite series.

The composition of the investigated samples doesn't permit to draw the conclusion about the extent of the isomorphic substitution of Fe^{3+}—Al. The members of this series with Fe/Al < 1 are considered as alumoklyuchevskite.

Chemical composition of alumoklyuchevskite calculated from the ideal formula is: K_2O 18.81, CuO 31.77, Al_2O_3 6.79, SO_3 42.63 (mas.%).

X-ray powder diffraction study of alumoklyuchevskite was carried out in Co_{K_α} radiation with internal Ge standard. The indices for powder diffraction data were obtained using unit cell parameters from the X-ray single crystal study.

The X-ray powder diffraction patterns of klyuchevskite and alumoklyuchevskite are very similar, especially for the most strong reflections (table 2) of alumoklyuchevskite (*I—d—hkl*): 84—9.15—002, 100—9.04—200, 52—7.20—$\bar{2}$02, 37—3.781—204, 33—3.757—402, 21—2.786—$\bar{6}$04. The unit cell parameters calculated by LS method are appeared to be closely allied for the both minerals (table 3), although the volume of alumoklyuchevskite's unit cell is about 4% over that of klyuchevskite due to the parameter $b = 5.139$ Å (table 3).

The mineral is transparent, dark-green in colour. Strongly pleochroic: Z — dark-green, Y — greyish-green, X — dirty-green. The refractive indices of

Table 1

The chemical analyses data for alumoklyuchevskite (mas.%)

N	K_2O	CuO	Fe_2O_3	Al_2O_3	SO_3	Sum	Fe/Al
1	16.81	32.22	3.95	4.71	41.42	99.11	0.54
2	17.57	31.32	4.14	4.13	40.41	97.57	0.64
3	16.78	32.52	3.46	5.28	41.91	99.95	0.42
4	16.85	32.79	3.97	4.79	41.92	100.32	0.53
5	17.50	31.58	2.31	5.64	42.26	99.29	0.26
6	17.17	31.84	3.03	5.71	41.40	99.15	0.34
7	18.23	31.56	3.00	5.15	42.00	99.94	0.37
8	18.92	31.10	4.11	4.42	40.57	99.13	0.59
9	19.20	30.94	5.10	3.69	41.11	100.04	0.88
10	18.50	30.73	3.81	4.74	40.15	97.94	0.51
11	19.49	30.81	3.14	4.76	39.59	97.79	0.42
12	19.41	30.04	3.74	4.46	40.58	98.23	0.54
13	19.46	30.50	3.42	4.65	40.05	98.08	0.47
14	19.05	30.70	3.93	4.47	40.31	98.47	0.56
15	19.15	30.67	4.33	4.38	40.58	99.11	0.63
16	19.16	30.42	3.80	4.57	40.95	98.90	0.53
17	19.61	31.13	3.68	4.45	40.51	99.38	0.53
18	19.24	30.68	3.20	4.63	40.57	98.33	0.44
19	19.29	30.76	3.67	4.59	40.18	99.48	0.51
20	19.44	30.99	2.89	4.80	40.57	98.69	0.38
21	19.51	31.24	2.92	4.75	40.54	98.95	0.39
22	18.98	30.67	5.23	4.01	40.41	99.31	0.83
23	19.06	31.20	4.36	4.19	40.09	98.89	0.66
24	19.05	31.32	4.50	4.42	40.56	99.86	0.65
25	19.06	31.98	3.21	4.88	40.30	99.34	0.42
26	19.16	31.44	3.28	4.70	39.32	97.90	0.47
Average:	18.68	31.19	3.70	4.65	40.70	98.92	0.51

alumoklyuchevskite are less than that of klyuchevskite (table 3) due to the low value of specific refraction for Al_2O_3 (0.242) as compared to that for Fe_2O_3 (0.315) (Mandarino J. A., 1976).

Z is parallel to b axis. Y and X are in the perpendicular plane. It was impossible to determine the orientation of the Y and X owing to the small size of the crystals. $2V$ angle was not measured for this reason too.

Alumoklyuchevskite's crystals are streched along the b axis (up to 1 mm long) and practically isometric in the perpendicular section (< 0.1 mm thick). The crystals have perfect cleavage along ($h0l$).

Hardness is $H = 42$ kgs/mm^2 (Mohs—2.3). The density of alumoklyuchevskite measured in the hard liquid (Klerichy liquid + water) is 3.1 g/cm^3, calculate — 2.95 (5) g/cm^3.

The optical and physical constants, X-ray data, chemical composition of alumoklyuchevskite and klyuchevskite show that they are related minerals. Isovalent isomorphism Fe^{3+}—Al in alumoklyuchevskite—klyuchevskite series occurs.

The mineral is covered by the white powder if it is exposed to the open air about a week, that is probably connected with the hidratation process.

The mineral is named alumoklyuchevskite due to the chemical and structural relation to klyuchevskite. Type mineral is preserved in Mineralogical museum of Saint-Petersburg Mining Institute.

Table 2

X-ray powder diffraction data for alumoklyuchevskite and klyuchevskite

Alumoklyuchevskite			Klyuchevskite (Vergasova e. a., 1989)		
I/I_0	d_{meas}, Å	d_{calc}, Å	hkl	I/I_0	d_{meas}, Å
12	11.72	11.71	101	10	11.73
84	9.15	9.15	002	95	9.17
100	9.04	9.02	200	100	9.03
				6	8.53*
				2	7.63*
52	7.20	7.20	$\bar{2}02$	35	7.20
				2	6.60*
6	6.16	6.17	$\bar{1}03$	5	6.17
10	6.09	6.09	$\bar{3}01$	8	6.09
8	5.85	5.86	202	7	5.86
12	5.40	5.40	301	10	5.40
1	4.568	4.575	004	6	4.569
15	4.509	4.510	400	25	4.502
8	4.469	4.462	$\bar{2}04$		
				3	4.398*
8	3.908	3.906	310		
		3.904	303	8	3.905
3	3.874*				
37	3.781	3.782	204		
33	3.757	3.754	402	55	3.762
			$\bar{5}01$	23	3.678
4	3.592	3.597	$\bar{4}04$	3	3.594
2	3.560*				
4	3.495*				
10	3.447	3.453	105	20	3.453
15	3.416	3.411	501	28	3.409
2	3.336*				
5	3.176	3.176	$\bar{4}13$		
4	3.127*				
8	3.077	3.077	$\bar{3}18$		
		3.086	$\bar{2}06$	6	3.084
8	3.046	3.050	006	6	3.046
			$\bar{6}02$		
			600	2	3.010
			510	3	2.918
			$\bar{4}06$		
11	2.813	2.805	$\bar{6}04$	15	2.780
21	2.786	2.786	206		
6	2.740	2.726	$\bar{6}13$		
2	2.552	2.555	512	8	2.651
			$\bar{7}01$	7	2.624
			116	2	2.509
			022	2	2.470
			505	5	2.344
6	2.340	2.343	604	3	2.311
4	2.308	2.307	514		
		2.312	008	3	2.287
4	2.288	2.288	800	2	2.253
			613	2	2.234
			703	3	2.215
		2.125	224		
3	2.126	2.122	$\bar{1}18$		
			422	3	2.062
4	2.122	2.120	$\bar{1}25$		
		2.118	$\bar{6}08$	2	2.028
8	2.028	2.030	$\bar{6}17$		
		2.028			

* — probably the oxysulphate of Cu, K, Fe^{3+}.

Table 3

Comparison of some properties for alumoklyuchevskite and klyuchevskite

Character	Alumoklyuchevskite	Klyuchevskite (Vergasova e. a., 1989)	Character	Alumoklyu-chevskite	Klyuchevskite (Vergasova e. a., 1989)
Crystal chemical formula	$K_3Cu_3AlO_2(SO_4)_4$	$K_3Cu_3Fe^{3+}O_2(SO_4)_4$	N_g	1.641 (1)	1.680 (1)
			N_m	1.548 (1)	1.550 (1)
System	monoclinic	monoclinic	N_p	1.542 (1)	1.549 (1)
Space group	12	12	N_g-N_p	0.099	0.131
a, Å	18.423 (5)	18.405 (7)	$2V^0_{calc}$	30	11
b, Å	5.139 (1)	4.940 (2)	Pleochroism		
c, Å	18.690 (7)	18.667 (7)	Z	dark-green	dark-olives
β, °	101.72 (2)	101.50 (5)	Y	greyish-green	green
V, Å^3	1732 (1)	1663 (2)	X	light-green	olives
Z	4	4	D_{meas}, g/cm^3	3.1 (1)	3.10 (5)
D_x, g/cm^3	2.95 (5)	2.98	H (Mohs)	2.3	2.7
			Colour	dark-green (bright-green in thin sections)	dirty-green (with brown shadow)

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