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Cuprokalininite, $CuCr_2S_4$, a New Sulfospinel from Metamorphic Rocks of the Sludyanka Complex, South Baikal Region[1]

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Abstract—Cuprokalininite as an accessory mineral has been found in Cr–V-bearing quartz–diopside metamorphic rock of the Sludyanka Complex, South Baikal region, Russia. This mineral is named as Cu analogue of kalininite ($ZnCr_2S_4$), is associated with quartz, Cr–V- bearing tremolite and mica, calcite, diopside–kosmochlor, goldmanite–uvarovite, dravite–chromdravite, Cr–V spinellide, karelianite–eskolaite, V-bearing titanite, pyrite, and plagioclase. Cuprokalininite forms euhedral microcrystals up to 0.05–0.20 mm in size, of octahedral and cuboctahedral habit with faces *o* {111} and *a* {100}, and polysynthetic and simple twinning along the {111}. Cleavage and parting were not observed. The mineral is black with a dark bronze tint, black streak, and metallic luster. The microhardness (*VHN*) is 356–458 (loadings are 20 and 30 g), 396 kgf/mm^2, on average. The Mohs hardness is 4.5–5.0, $d_{calc} = 4.16(2)$. In reflected light, the mineral is pale-cream-colored, without anisotropy; reflectance values (λ, nm–*R*, %): 400–34.3, 420–34.1, 440–33.9, 460–33.7, 480–33.5, 500–33.2, 520–33.0, 540–32.8, 560–32.3, 580–32.2, 600–31.9, 620–31.6, 640–31.2, 660–30.9, 680–30.6, 700–30.4. Cubic, space group $Fd\bar{3}m$, $Z = 8$; unit cell parameter $a = 9.814(2)$ Å, $V = 945.2(4)$ Å^3. The strongest lines of the X-ray powder diffraction pattern [*d*, Å (*I*) (*hkl*)]: 3.44 (6)(220), 2.94 (10)(311), 2.44 (6)(400), 1.884 (9)(511, 333), 1.731 (10)(440), 1.133 (6)(751, 555), 1.098 (6)(840), 1.030 (6)(931), 1.002 (10)(844). Chemical composition (mean of 202 microprobe analyses of 11 grains, wt %): Cu 21.03, Fe 0.47, Zn 0.17, Cr 29.01, V 5.85, As 0.21, Sb 0.08, S 43.25; the total is 100.07. The empirical formula calculated on the basis of seven ions is $(Cu_{0.98}Fe_{0.02}Zn_{0.01})_{1.01}(Cr_{1.65}V_{0.34}As_{0.01})_{2.00}S_{3.99}$. The type material has been deposited at the Fersman Mineralogical Museum of the Russian Academy of Sciences, Moscow, Russia.

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INTRODUCTION

Two new sulfospinels, kalininite $ZnCr_2S_4$ and florensovite $Cu(Cr_{1.5}Sb_{0.5})_2S_4$, making up continuous isomorphic series were discovered in rocks of the Sludyanka Complex, South Baikal region in the 1980s (Reznitsky, Sklyarov and Ushchapovskaya, 1985; Reznitsky et al., 1989). These were the first chromium sulfospinels found in terrestrial rocks. Now, they are being supplemented by a new sulfospinel, a natural analogue of copper thiochromate, $CuCr_2S_4$. The new mineral was named cuprokalininite as a copper analogue of kalininite. The $CuCr_2S_4$ compound was repeatedly synthesized; its properties have been studied in detail (see final section of this paper).

OCCURRENCE AND PHYSICAL PROPERTIES

Cr–V mineralization is related to the specific group of quartz–diopside rocks traditionally recognized in the Slyudyanka Complex. They were repeatedly characterized earlier, when new and rare Cr and V minerals (pyroxenes, micas, spinels, tourmalines, and simple oxides) were found therein. The most complete characterization of the Cr–V-bearing quartz–diopside rocks was given in monographs on the Sludyanka Complex and new and rare minerals of East Siberia (Vasil'ev et al., 1981; Konev et al., 2001). The sample containing cuprokalininite (PR-78) is a typical rock variety of the group consisting of alternating rough bands and lenses (3–4 cm) of pale gray quartz and pale green fine-grained (sugarlike) diopside. Cr and V minerals including cuprokalininite occur (mostly in accessory amounts) as disseminated inclusions in quartz.

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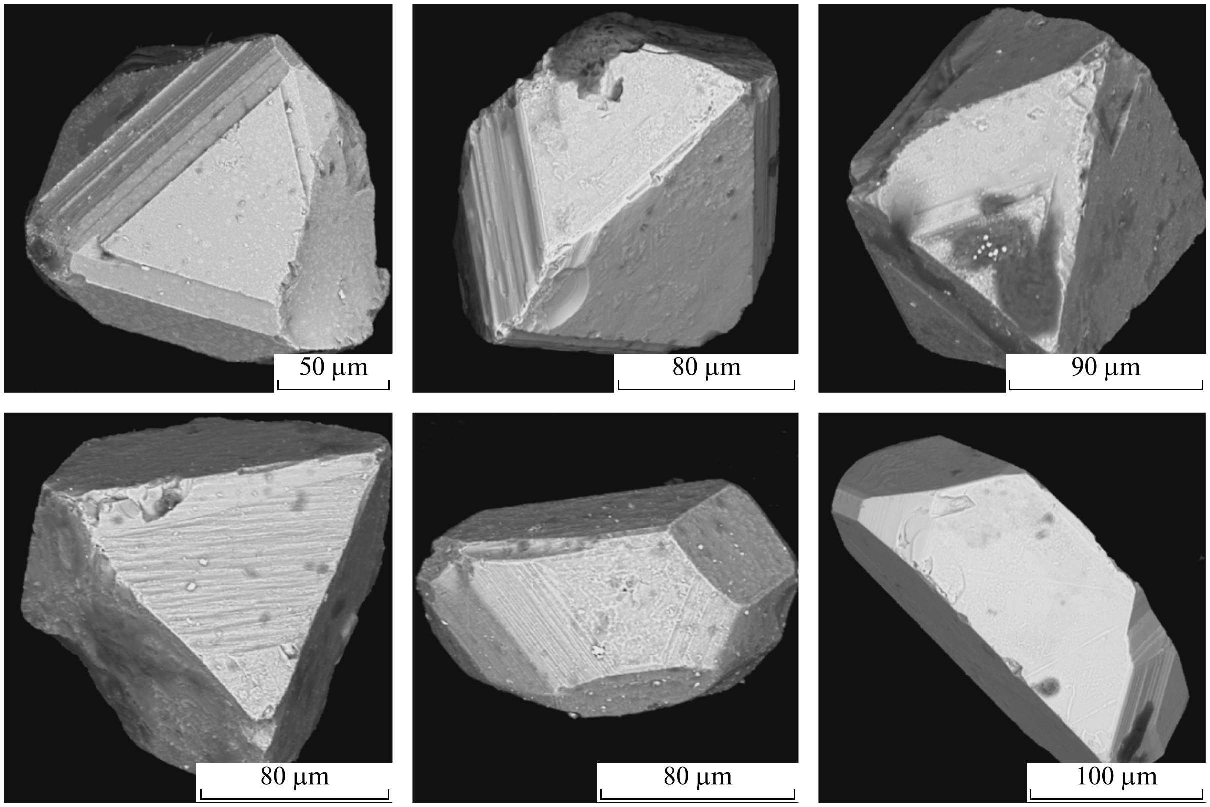

Fig. 1. Cuprokalininite microcrystals. SEM images.

Cuprokalininite was identified and studied in preparations of ore minerals preliminarily separated with an electromagnet and heavy liquids; the ore minerals were examined on a SEM/EDS. More than 30 microcrystals of the mineral were picked out from the sample. The identified grains were prepared for the further investigation. In addition to rock-forming quartz, Cr–V-bearing diopside, minor calcite, and Cr–V-bearing tremolite, cuprokalininite is associated with natalyite–kosmochlor, goldmanite–uvarovite, Cr–V spinellide, tourmaline, mica, karelianite–escolaite, V-bearing titanite, pyrite, and plagioclase, which are incorporated into quartz as inclusions and small clusters.

Cuprokalininite occurs as euhedral octahedral or cuboctahedral microcrystals ranging from 40–50 to 150–200 μm in size with the {111} and {110} faces (Fig. 1) frequently with distinct growth steps (Fig. 2). Polysynthetic twins {111} are typical; traces of composition planes are observed on the faces of each microcrystal. Occasionally, simple twinning by the spinel law is identified (Fig. 3). The morphology of cuprokalininite grains drastically differs from that of other sulfospinels, kalininite and florensovite, which occur as anhedral inclusions devoid of any faces (Reznitsky, Sklyarov and Ushchapovskaya, 1985; Reznitsky et al., 1989). No cleavage was revealed.

Visually and under a binocular microscope, cuprokalininite is black with a weak dark bronze tint; powder is black; luster is close to metallic; fracture is uneven. The mineral is very brittle. The microhardness was measured with a UI PMT-3 microhardness tester; loading was 20 and 30 g, but even in this case, most indentations were accompanied by microcracks. The obtained $VHN = 356–458$ kgf/mm^2, 396 on average (eight indentations in six grains), corresponding to a Mohs hardness of 4.5–5.0, should be regarded as approximate. The X-ray density of cuprokalininite is 4.16(2).

The new mineral is separated into an electromagnetic fraction by magnetic separators at a weak current intensity, attracted by the strong faces of a Sochnev magnet, and insoluble in HCl.

In polished sections, in reflected light, the mineral is pale cream in color, isotropic, and without internal reflections. The reflectance is given in Table 1. As seen from Table 1 and Fig. 4, the mineral is characterized by normal dispersion of reflectance with slope of the R curve toward long-wavelength region. The reflectance of sulfospinels of the kalininite–florensovite series was measured under the same conditions for comparison. The arcuate spectral curve of kalininite with a positive extremum and a maximum in the region of 520–540 nm

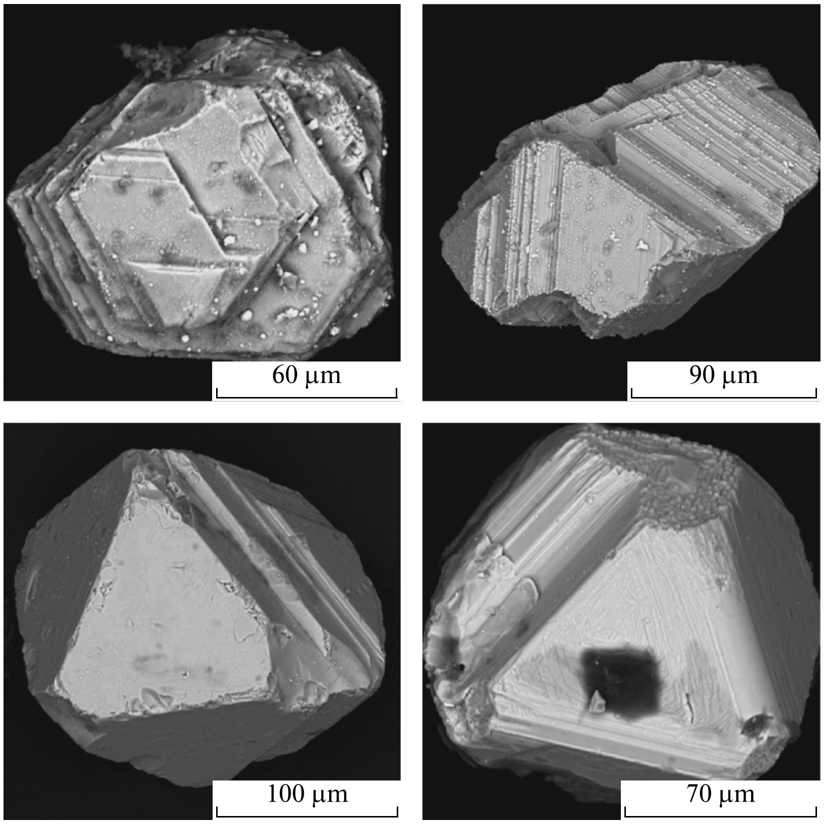

Fig. 2. Growth surface of cuprokalininite. SEM images.

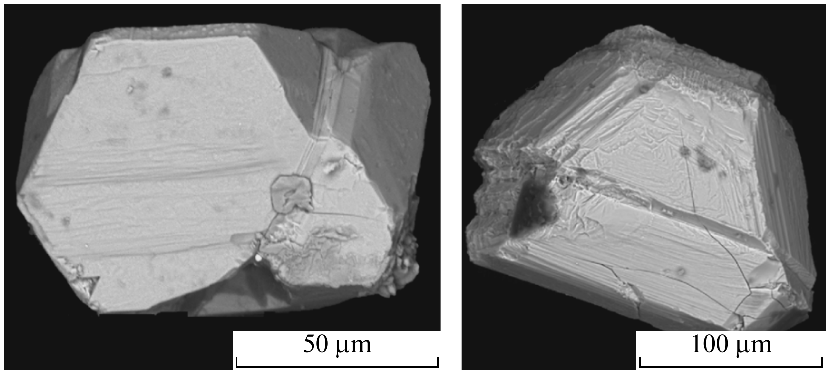

Fig. 3. Cuprokalininite twins. SEM images.

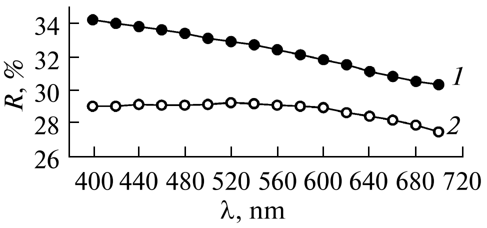

Fig. 4. Reflectance spectra of cuprokalininite (*1*) and florensovite (*2*).

given in the description of the mineral has been confirmed. The curve of reflectance dispersion flattens with increasing Cu and Sb contents, and for the $Cu_{0.85}Zn_{0.15}$ grain, i.e., containing 85 mol % of florensovite, is close to neutral and becomes normal in the long-wavelength region (Fig. 4). The reflectance of florensovite is appreciably lower than that of cuprokalininite. Thus, the earlier data (Reznitsky et al., 1989) on reflectance of florensovite turned out inaccurate (apparently because of low-quality standards and tester) and should be corrected.

Table 1. Reflectance (*R*, %) of cuprokalininite and florensovite

Mineral	*R* for different wavelengths (nm)							
	400	420	440	460	480	500	520	540
Cuprokalininite	34.30	34.10	33.90	33.70	33.50	33.20	33.00	32.80
Florensovite	29.10	29.10	29.20	29.15	29.15	29.20	29.30	29.25
Mineral	*R* for different wavelengths (nm)							
	560	580	600	620	640	660	680	700
Cuprokalininite	32.50	32.20	31.90	31.60	31.20	30.90	30.60	30.40
Florensovite	29.15	29.10	29.00	28.70	28.50	28.25	27.95	27.55

Note: A MSF-21 microspectrophotometer was used; the slit of the monochromator is 0.4 mm (degree of monochromatism is 12–15 nm), the beam diameter is 0.1 mm (the diameter of the measured area is 4.8 μm). Recording is automatic with a measurement step of 20 nm. The standard is SiC (Reflectionsstandardt 474251, no. 545, Germany).

X-RAY CRYSTALLOGRAPHY

X-ray single crystal study of cuporokalininite was unsuccessful. Even visually ideal octahedral microcrystals of the mineral are in fact polysynthetic twins. Therefore, only an X-ray powder diffraction study has been performed. Three microcrystals, which had earlier been examined with the SEM/EDS, were investigated. In total, their composition was sufficiently close to the average composition of cuprokalininite. The X-ray powder diffraction data are given in Table 2. The X-ray powder diffraction pattern is similar to that of synthetic $CuCr_2S_4$ except for five weak reflections, which were not identified for cuprokalininite. Similarly to synthetic $CuCr_2S_4$, space group $Fd\bar{3}m$ is assigned to cuprokalininite, $Z = 8$. In determining the unit cell dimensions ($a = 9.814(2)$ Å), the following reflections were used: 731, 800, 822, 751, 840, 664, 931, and 844; when calculated from all reflections, the result is identical ($a = 9.813$ Å). The available published unit cell dimensions of $CuCr_2S_4$ range from 9.810 to 9.822 Å probably depending on the synthesis conditions. The unit cell dimensions reported by Raccah, Bouchard, and Wold (1966) and Tret'yakov et al. (1973) are consistent with those of cuprokalininite.

CHEMICAL COMPOSITION

The chemical composition of cuprokalininite was determined on a Superprobe JXA-820 Jeol electron microprobe, operating at an accelerating voltage of 20 kV, a current of 20 nA, a beam diameter of 1 μm; analyst L.F. Suvorova. The following standards were used: chalcopyrite (Cu, Fe, S), sphalerite (Zn), arsenopyrite (As), chalcostibite (Sb), pyrite (S), Cr_2O_3 (Cr), and V_2O_5 (V). To verify the data, one grain (03-Z-10-12) was examined with a CAMECA SX-100 electron microprobe at Warsaw University, operating at 15 kV, 20 nA, and a beam diameter 1–2 μm; analyst P. Dzerzanovsky. The following standards were used: GaAs (As), galena (S), Cr_2O_3 (Cr), GaSb (Sb), V_2O_5 (V), chalcopyrite (Cu, Fe), and sphalerite (Zn).

In total, 202 high-quality analyses of 11 microcrystals were obtained (Table 3). As seen from the results, in addition to the major components, Cu, Cr, and S, the mineral contains a significant amount of V (maximum 9.09 wt %, or 0.526 apfu); some grains contain a significant admixture of Fe (up to 1.82 wt %, or 0.096 apfu), and less abundant As (up to 1.16 wt %, or 0.046 apfu) and Zn (up to 0.80 wt %, or 0.036 apfu). The Sb concentration is insignificant; the contents of other components are below the detection limit. It is noteworthy that in contrast to other Cr and V minerals from Slyudyanka metamorphic rocks (and metamorphic rocks as a whole) characterized by wide compositional variations within single micrograins, the composition of cuprokalininite is rather stable. The difference in the content of minor components between different microcrystals is significant, although all grains were selected from one sample. The empirical formula of cuprokalininite is $(Cu_{0.98}Fe_{0.02}Zn_{0.01})_{1.01}(Cr_{1.65}V_{0.34}As_{0.01})_{2.00}S_{3.99}$; the ideal formula is $CuCr_2S_4$. The theoretical composition is as follows, wt %: 21.48 Cu, 35.16 Cr, and 43.36 S.

We draw attention to the fact that S content in most compositions is slightly below the theoretical level, although measurements were repeatedly duplicated and S was measured using varied standards. Nonstoichiometric compositions $CuCr_2S_{4-\sigma}$, where σ reached 0.16, were also established for synthetic $CuCr_2S_4$ (Tret'yakov et al., 1973). The S-deficient phases were formed either due to substantial deficiency in chalcogen in the system or at an elevated synthesis temperature. The latter is consistent with the probable formation conditions of cuprokalininite (see below).

DISCUSSION

The composition of cuprokalininite is close to that of florensovite $CuCr_{1.5}Sb_{0.5}S_4$ discovered earlier. In

Table 2. X-ray powder diffraction data on cuprokalininite

Cuprokalininite				$CuCr_2S_4$ (PDF 03-065-4606)		Florensovite (Reznitsky et al., 1989)	
I	d_{meas}, Å	d_{calc}, Å	*hkl*	*I*	*d* (Å)	*I*	*d* (Å)
—	—	—	111	110	5.66	4	5.78
6	3.44	3.47	220	373	3.468	5	3.53
10	2.94	2.96	311	999	2.958	10	3.01
1	2.82	2.83	222	29	2.832	—	—
6	2.44	2.45	400	50	2.452	8	2.50
—	—	—	331	4	2.250	—	—
4	1.997	2.00	422	112	2.002	4	2.04
9	1.884	1.889	511,333	374	1.888	8	1.923
10	1.731	1.735	440	712	1.734	10	1.768
—	—	—	531	10	1.658	—	—
1	1.552	1.552	620	35	1.551	1 dif	1.582
2	1.497	1.497	533	76	1.496	4	1.525
—	—	—	622	5	1.479	—	—
2	1.416	1.417	444	63	1.416	4	1.444
—	—	—	711	12	1.374	1 dif	1.401
2	1.312	1.312	642	40	1.312	3	1.336
5	1.277	1.278	731, 553	93	1.277	6	1.302
5	1.227	1.227	800	73	1.226	4	1.250
—	—	—	733	4	1.198	—	—
1	1.155	1.157	822,660	17	1.156	1	1.178
6	1.133	1.133	751, 555	55	1.133	5	1.156
6	1.098	1.097	840	61	1.097	5	1.119
—	—	—	911	5	1.077	—	—
1	1.045	1.046	664	4	1.046	1 dif	1.066
6	1.030	1.029	931	43	1.028	5	1.050
10	1.002	1.002	844	121	1.001	8	1.021
Unit cell dimension							
$a = 9.814(2)$ Å $V = 945.2(4)$ Å^3				$a = 9.810$ Å		$a = 10.005(6)$ Å	

Note: X-ray powder diffraction data were collected with a RKD-53.7 mm camera, $d_{sample} = 0.3$ mm, FeK_α radiation (β lines are omitted). Because of the extremely small size, the sample was rolled up in a ball of rubber adhesive; the sample was analyzed without an internal standard. Film loading is asymmetric. Analyst Z.F. Ushchapovskaya; dif is diffuse reflection.

addition to the difference in chemical composition and unit cell dimensions, the synthetic counterparts of these minerals differ in the valence formula (valence of Cr) and related physical properties.

Chalcogenides of transitional metals had been studied in detail for a long time in the physics and chemistry of solids, because of the wide range and close interrelations of the optical, magnetic, and electric properties (ferri-, ferro-, and antiferromagnetics, semiconductors, metals, and superconductors). Sulfospinel $CuCr_2S_4$ differs from other thiochromates in the unusual combination of ferromagnetism and *p*-type metal conductivity, which served as the basis for two models of zoned structures known as the Lotgering and Goodenough models.

According to Lotgering (1962, 1964) and Lotgering and Van Stapele (1967), the properties of $CuCr_2S_4$ can be explained if half of the Cr ions in octahedra are $3d^2$ tetravalent and half are trivalent in the $3d^3$ configuration: $Cu^+[Cr^{3+}\ Cr^{4+}]S_4^{2-}$. Goodenough (1967, 1969) proposed a model with valence formula Cu^{2+} $Cr_2^{3+}S_4^{2-}$, supposing that Cr^{4+} and Cu^+ cannot coexist because of sharp difference in ionization potential.

Table 3. Chemical composition (wt %) of cuprokalininite

Compo-nent	99T2-15-27		08R1-13-16		08R1-12-13		08R2-1-1		08R2-2-1		03Z-10-12	
	range	average (22)	range	average (20)	range	average (17)	range	average (4)	range	average (5)	range	average (9)
Cu	21.15–21.83	21.51	19.77–20.57	20.23	20.46–21.20	20.86	20.59–20.70	20.65	21.30–21.56	21.45	20.97–21.84	21.44
Fe	0.17–0.23	0.21	0.84–1.07	0.94	0.73–0.90	0.80	0.26–0.34	0.31	0.03–0.07	0.05	0.32–0.45	0.37
Zn	0.00–0.10	0.04	0.28–0.43	0.33	0.06–0.14	0.10	0.43–0.48	0.46	0.17–0.23	0.19	0.00–0.11	0.04
Cr	26.28–27.05	26.63	31.13–31.93	31.59	31.73–32.49	32.16	30.04–30.50	30.32	27.14–27.64	27.46	29.14–30.29	29.61
V	8.17–8.85	8.53	2.65–3.05	2.82	2.70–3.05	2.87	3.87–4.06	3.95	7.46–7.89	7.67	4.93–5.50	5.09
As	0.00	0.00	0.97–1.16	1.02	0.00–0.14	0.07	0.46–0.53	0.49	0.00	0.00	0.02–0.07	0.04
Sb	0.00	0.00	0.12–0.25	0.17	0.09–0.20	0.16	0.19–0.24	0.21	0.00	0.00	0.00–0.06	0.02
S	42.71–43.66	43.17	42.75–3.50	43.04	42.61–3.99	43.09	43.23–43.43	43.32	42.63–43.95	43.42	42.92–3.48	43.23
Total	99.51–100.53	100.09	99.49–100.67	100.13	99.53–100.59	100.12	99.40–99.85	99.70	99.52–100.76	100.25	99.46–100.16	99.82
Atoms per formula unit (calculated on the basis of 7 ions)												
Cu	42.71–3.66	1.000	0.926–0.959	0.944	0.946–0.987	0.972	0.962–0.967	0.965	0.986–1.006	0.995	0.974–1.018	1.000
Fe	99.510–100.53	0.011	0.045–0.057	0.050	0.039–0.048	0.042	0.014–0.018	0.016	0.002–0.004	0.003	0.017–0.024	0.019
Zn	0.000–0.005	0.002	0.013–0.020	0.015	0.003–0.006	0.005	0.020–0.022	0.021	0.008–0.010	0.009	0.000–0.005	0.001
Cu + Fe + Zn	0.993–1.029	1.013	0.990–1.028	1.009	0.992–1.032	1.019	1.000–1.003	1.002	0.996–1.019	1.007	0.993–1.038	1.020
Cr	1.491–1.534	1.513	1.775–1.827	1.802	1.793–1.852	1.831	1.719–1.742	1.732	1.532–1.576	1.557	1.659–1.719	1.687
V	0.477–0.513	0.495	0.154–0.177	0.164	0.157–0.176	0.167	0.225–0.236	0.230	0.429–0.456	0.444	0.286–0.320	0.296
As	–	–	0.038–0.046	0.041	0.000–0.005	0.003	0.018–0.021	0.019	–	–	0.001–0.003	0.001
Sb	–	–	0.003–0.006	0.004	0.002–0.005	0.004	0.005–0.006	0.005	–	–	0.000–0.001	0.000
Cr + V + As + Sb	1.992–2.029	2.008	1.984–2.032	2.011	1.977–2.022	2.004	1.973–1.996	1.986	1.982–2.022	2.001	1.972–2.006	1.985
S	3.957–4.008	3.979	3.959–4.015	3.981	3.958–4.031	3.977	4.001–4.024	4.012	3.959–4.013	3.992	3.983–4.011	3.995

Table 3. (Contd.)

Component	09R2-1		09R2-2		09R2-3		09R2-4		09R2-5		Average of 11 grains
	range	average (43)	range	average (26)	range	average (8)	range	average (27)	range	average (21)	
Cu	20.57–21.90	21.47	21.23–21.99	21.57	20.62–21.16	20.95	20.20–21.22	20.90	19.97–20.60	20.31	21.03
Fe	0.06–0.15	0.10	0.02–0.09	0.06	0.29–0.39	0.36	0.23–0.37	0.29	1.51–1.82	1.70	0.47
Zn	0.00–0.08	0.05	0.03–0.10	0.06	0.06–0.10	0.08	0.38–0.80	0.48	0.04–0.10	0.06	0.17
Cr	26.79–28.36	27.59	25.97–26.71	26.35	27.42–28.27	27.94	30.17–31.32	30.79	28.25–29.29	28.64	29.01
V	6.99–7.84	7.53	8.42–9.09	8.78	6.78–7.42	7.05	3.70–4.07	3.90	5.88–6.33	6.11	5.85
As	0.00–0.03	0.00	0.00–0.02	0.01	0.00–0.03	0.02	0.40–0.54	0.47	0.00–0.05	0.01	0.21
Sb	0.00–0.05	0.02	0.00–0.06	0.02	0.00–0.04	0.02	0.11–0.27	0.17	0.00–0.08	0.02	0.08
S	42.74–44.00	43.28	42.85–3.74	43.27	43.15–4.00	43.56	42.68–3.48	43.11	42.75–3.90	43.21	43.25
Total	99.44–100.75	100.03	99.53–100.96	100.09	99.51–100.39	99.95	99.40–100.80	100.11	99.50–100.53	100.04	100.07
Atoms per formula unit (calculated on the basis of 7 ions)											
Cu	0.960–1.022	0.998	0.986–1.016	1.003	0.963–0.984	0.973	0.940–0.990	0.975	0.925–0.958	0.944	0.979
Fe	0.003–0.008	0.005	0.001–0.005	0.003	0.015–0.021	0.019	0.012–0.020	0.016	0.080–0.096	0.090	0.025
Zn	0.000–0.004	0.002	0.001–0.004	0.003	0.003–0.005	0.004	0.017–0.036	0.022	0.002–0.005	0.003	0.008
Cu + Fe + Zn	0.966–1.029	1.006	0.989–1.023	1.009	0.987–1.004	0.995	0.993–1.027	1.012	1.018–1.052	1.037	1.011
Cr	1.516–1.604	1.568	1.477–1.521	1.497	1.562–1.606	1.586	1.721–1.779	1.755	1.609–1.659	1.627	1.650
V	0.406–0.454	0.437	0.487–0.526	0.509	0.391–0.432	0.409	0.216–0.237	0.227	0.341–0.367	0.354	0.340
As	0.000–0.001	–	0.000–0.001	0.000	0.000–0.001	–	0.016–0.022	0.019	0.000–0.002	–	0.008
Sb	0.000–0.001	–	0.000–0.001	0.000	0.000–0.001	–	0.003–0.007	0.004	0.000–0.002	–	0.002
Cr + V + As + Sb	1.962–2.045	2.005	1.987–2.027	2.006	1.973–2.020	1.995	1.966–2.029	2.004	1.957–2.022	1.982	2.000
S	3.956–4.032	3.989	3.960–4.014	3.986	3.983–4.033	4.010	3.962–4.015	3.984	3.960–4.018	3.981	3.989

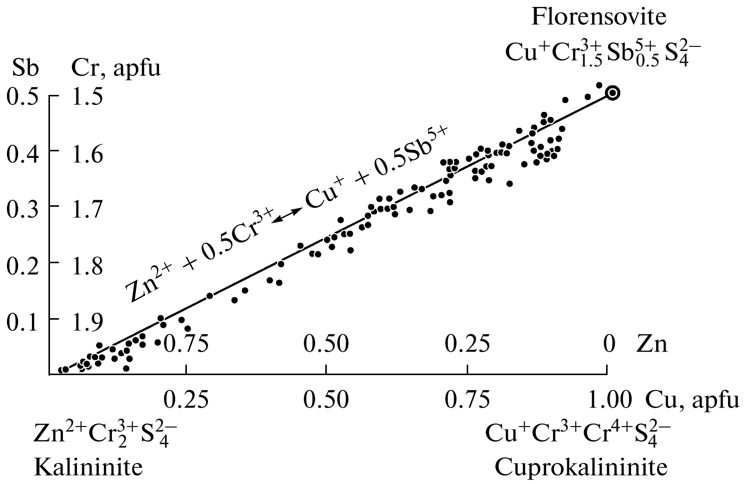

Fig. 5. Relationships between kalininite, florensovite, and cuprokalinite

After experiments and discussion for a decade and half, it has been established that both models and intermediate phases $Cu^{2+}_{1-x}(Cu^{2+} \to Cu^+)_x[(Cr^{3+} \to Cr^{4+})_xCr^{3+}_{2-x}]S^{2-}_4$, $0 \le x \le 1$ can exist depending on the P–T conditions. At ambient and high temperature, the phase with heterovalent Cr and Cu^+ is stable. The drop in temperature down to 60–62 K leads to the electron phase transition with change in valence and redistribution of electrons between Cu and Cr; the pure Goodenough phase is apparently achieved only close to 0 K (Kovtun, Kalinnikov, and Shemyakov, 1977, 1978; Ovchinnikov, 1979; Val'kov and Ovchinnikov, 1980). It has also been shown that the diminished unit cell dimensions (9.810–9.822 Å), within which cuprokalininite falls, correspond to the Lotgering phase, i.e., to the valence formula $Cu^+Cr^{3+}Cr^{4+}S^{2-}_4$ (Ballal and Mande, 1976; Hill, Craig, and Gibbs, 1979). In principle, this should follows from difference in effective ion radii of Cr^{4+}_{VI} and Cr^{3+}_{VI} (0.55 and 0.615 Å, respectively).

No compounds containing Cr and Sb were known when florensovite had been discovered. According to the scheme of chemical substitution in the florensovite–kalininite continuous solid solution series, we established the formula of the mineral and proposed the valence formula Cu^+ $[Cr^{3+}_{1.5}S^{5+}_{0.5}]S^{2-}_4$ (Reznitsky et al., 1989). Florensovite was synthesized eight years later, the valence formula was confirmed, and it was established that the compound $CuCr_{1.5}Sb_{0.5}S_4$ was an antiferromagnetic–semiconductor (Warczewski et al., 1997). The intermediate phases $CuCr_{1.5}Sb_{0.5}S_4$–$ZnCr_2S_4$ were synthesized eight years later; i.e., the existence of stable solid solutions found in the natural material was confirmed (Reznitsky et al., 1989; Zajdel et al., 2005). At the same time, $CuCr_2S_4$ as a metallic spinel does not form stable solid solutions with thioshromate semiconductors, in particular, with $ZnCr_2S_4$ (Lutz and Okonska-Koziowska, 1982). No indications of miscibility between kalininite and cuprokalininite were found. Thus, kalininite and cuprokalininite correspond to different types of thiospinels, which confirms their attribution to different mineral species. The relationship is shown in Fig. 5.

Quartz–diopside Cr–V-bearing rocks containing cuprokalininite are considered to be siliceous–carbonate sediments metamorphosed under conditions of high-temperature (~800°C) subfacies of granulite facies. The mode of occurrence of cuprokalininite in the rock assumes its formation at the prograde stage, i.e., its syngranulite origin. This assumption is consistent with the synthesis conditions of $CuCr_2S_4$ at a temperature reaching 750°C (Tret'yakov et al., 1973; Ballal and Mande, 1976).

The type samples of cuprokalininite were deposited at the Fersman Mineralogical Museum, Russian Academy of Sciences, Moscow (registration no. 3886/1–3). These are five polished grains (09R2-1-5 in Table 3), which are part of the holotype (chemical composition and physical properties), six single crystals identified with an electron microscope (cotype), and a sample of the host rock. All grains were separated from one sample.

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