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# Fluor-elbaite, fluoronatromicrolite and fluorcalciomicrolite from lithium-bearing granite pegmatites of Lipovka (Middle Urals)

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**The relevance of the work** is due to the need to study the mineralogy of lithium-bearing granite pegmatites of Lipovka, a one-of-a-kind facility that gave the world a large amount of crystalline raw materials of colored tourmaline.

**The purpose of the work.** Study of fluorine-containing minerals found in lithium-bearing granite pegmatites of the Lipovskoye vein field (Middle Urals). **Methodology of the research.** Quantitative analysis of the chemical composition of fluorine-containing minerals was performed with CAMECA SX 100 X-ray electron probe microanalyzer. Measurement conditions: accelerating voltage is 15 kV, current strength is 50 nA, electron beam diameter is 2 μm. The intensity was recorded using Kα lines on inclined wave spectrometers with TAP, LPET, and LiF crystal analyzers. To determine fluorine, a separate LPCO crystal analyzer was used. The lithium content in tourmaline was determined using ICP-MS ELAN-9000 mass spectrometer with preliminary dissolution of the frayed samples in heated acids.

**Results.** When studying crystals of dark blue tourmaline, which turned out to be fluor-elbaite in chemical composition, we have found some inclusions of tantaloniobates. According to up-to-date classification, they belong to the microlite group and some of analyzes relate to fluornatromicrolite because fluorine, tantalum and sodium predominate in them in certain positions and part of them belong to fluorcalciomicrolite because calcium, tantalum and fluorine are dominated substances. The fluorine content in these tantaloniobates varies from 1.4 to 1.6 wt.%. In polychrome tourmalines, pink and crimson parts of crystal belong to fluor-elbaite due to the high fluorine content (which varies from 1.2 to 1.7 wt.%).

**Conclusions.** Three new minerals such as fluor-elbaite, fluornatromicrolite and fluorcalciomicrolite have been identified for lithium-bearing granite pegmatites of the Lipovskoye vein field. The last two tantaloniobates were found in the form of small inclusions in crystals of dark blue fluor-elbaite. Tourmaline itself is quite widespread in Lipovka, it composes the intermediate and marginal zones of colored and polychrome tourmaline, and at least fluor-elbaite is found in pink, crimson and dark blue crystals. The find of three fluorine-containing minerals suggests that the fluorine activity was very high at the final stage of the formation of lithium-bearing granite pegmatites of Lipovka.

Keywords: fluor-elbaite, fluornatromicrolite, fluorcalciomicrolite, minerals, lithium-bearing granite pegmatites, Lipovskoye vein field, Middle Urals.

ntroduction

Lipovka mines became famous all over the world thanks to the mining of rubellites. The first find of colored tourmaline in this area dates from the spring of 1900 years[1]. In the pre-revolutionary period, Lipovskoye tourmaline vein was studied by a number of prominent researchers, such as P. L. Dravert (1904), V. I. Vorob`yev (1901–1904), V. I. Vernadsky (1908), K. A. Nenadkevich and V. I. Kryzhanovsky (1911). During the period of 1912–1916 years and later these mines were visited by A. E. Fersman, who left the most detailed surviving evidence of the work carried out here during the first decades [1]. Since 1921 works at the Lipovskoye pink tourmaline deposit have been carried out by "Rayruda". There was a facility in a nearby village – the office directed by G. G. Kitaev, a well-known Ural free miner and a major expert in precious and collectable stones of the Middle Urals (up to 120 people worked in the mine every year). Simultaneously, the prospecting mining of tourmaline has been carried out until the 1930<sup>th</sup> year. Much later, in 1956 years, geologists discovered the Lipovskoye deposit of silicate nickel [2], during the development of which new pegmatite bodies with pink tourmaline were found. The richest color tourmalines turned out to be two pegmatite bodies of the Sherlova mine – Toporkov and Staratel`skaya veins, which were developed at the beginning of the twentieth century. These veins were crossed and explored in 1968–1970 by geologists at the Rezhevskoy Nickel Plant according to the assignment of Glavnikelkobalt company [2]. In 1991 years, a silicate nickel deposit was abandoned and pegmatite open pits were flooded.

Despite the wide distribution of lithium-bearing veins in the given area and their relatively good mineralogical knowledge [1, etc.], it turned out that accessory ore mineralization of lithium-bearing pegmatites is covered fragmentarily and not fully studied. This work presents data about the finding of fluor-elbaite, fluornatromicrolite, and fluorcalciomicrolite in lithium-bearing granite pegmatites of Lipovka that were not previously described here.

# Geological position of the object of research

The granite pegmatites of the Lipovskoye vein field are located in the eastern slope of the Middle Urals (70 km to northeast from Ekaterinburg and in 5 km to the west from the village of Lipovskoye). Pegmatites are limited to a gently sloping synclinal structure sandwiched between three large granite massifs – Murzinsky (from north-west), Aduysky (from south-west) and Sokolovsky (from east). The dominant lithology of synclinal fold is metamorphic rocks of the Proterozoic age, in which various gneisses, schists, and amphibolites predominate [1, 2, etc.]. Separate bodies of serpentinites and marbles are also noted here, which are usually tectonically interspersed with each other in the melange zone. The karst marbles and weathering crusts of serpentinites are associated with famous and developed deposit of nickel-silicate ores. Granite pegmatites are widespread within the Lipovskoye vein field and usually represented by intragranular, lithium-bearing and desilicated types. The age of rare-metal pegmatites inside the granites was determined by us within the range of 266.4 ± 2.6 Ma [3]. The yields of lithium-bearing granite pegmatites with fluorine-containing minerals studied by us are shown on the geological map (Fig. 1).

#### Methods of research

Quantitative analysis of the chemical composition of fluorine-containing minerals was performed with CAMECA SX 100 electron probe microanalyzer (Zavaritsky Institute of Geology and Geochemistry of the Ural Branch of the Russian Academy of Sciences, analyst is V. V. Khiller). The polished sections were made from fragments of colored tourmaline crystals and then they were sprayed with a thin layer of carbon. Measurement conditions: accelerating voltage is 15 kV, current strength is 50 nA,

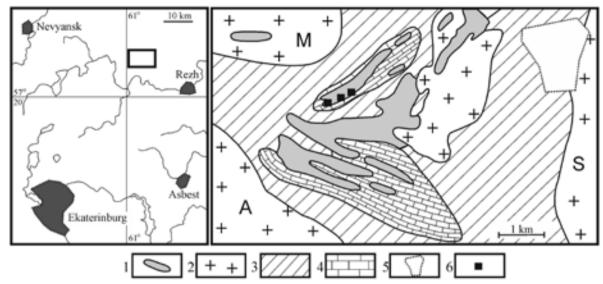


Figure 1. Geologic pattern of the Lipovskoye vein field (according to [3]). 1 – serpentinites; 2 – granites (A – Aduysky massif, M – Murzinsky massif, S – Sokolovsky massif); 3 – gneiss; 4 – marble; 5 – contours of Lipovskoye village; 6 – lithium-bearing granite pegmatites outcrops. Рисунок 1. Геологическая схема Липовского жильного поля (дано по [3]). 1 – серпентиниты; 2 – граниты (А – Адуйский массив, М – Мурзинский массив, С – Соколовский массив); 3 – гнейсы; 4 – мраморы; 5 – контуры села Липовское; 6 – выходы литиеносных гранитных пегматитов.

electron beam diameter is 2  $\mu$ m. Standard samples: fluorphlogopite for F and Mg, andradite for Si, Fe, Ca and O, tantalite for Ta, columbite for Nb, orthoclase for Al, jadeite for Na, rutile for Ti, eskolaite for Cr, rhodonite for Mn, uraninite for U, Th, Pb, bismuthinite for Bi. The intensity was recorded using K $\alpha$  lines on inclined wave spectrometers (40 X-ray angle) with TAP analyzer crystals (for Na, Mg, Al, Si), LPET (Ca, Ti, Cr) and LiF (Mn, Fe and other). To determine fluorine, a separate LPC0 crystal analyzer was used. When performing a quantitative analysis, the time of measuring the intensity at the peak was twice as high as the background measurement time.

The lithium content in tourmaline was determined using ICP-MS ELAN-9000 mass spectrometer with preliminary dissolution of the frayed samples in heated acids (the analysts are N. N. Adamovich, N. V. Cherednichenko). From each color zone of the crystal, a monofraction of tourmaline was isolated for analysis.

### Research results and their discussion

Fluornatromicrolite and fluorcalciomicrolite. According to literary sources [1], a number of tantaloniobates as ore minerals are characteristic for lithium-bearing contaminated granite pegmatites of Lipovka – columbite-(Mn), stibiocolumbite, stibiotantalite, bismutotantalite, plumbomicrolite, bismutomicrolite, uranmicrolite and microlite. Moreover, the last two minerals were also noted in silica-depleted pegmatites as substitution products of primary tantalite-(Mn) in association with other tantaloniobates and magnesiotantalite [4]. Previously, we studied tantaloniobates in contaminated pegmatites and found tantalite-(Mn) not mentioned earlier in them [5].

Unfortunately, the classification of the microlite-group [6, 7], as well as other tantaloniobates, has now become much more complicated, primarily due to the expansion of the crystal chemical position in the area of anions with respect to oxygen, fluorine, OH

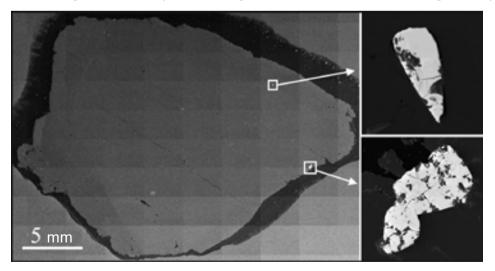


Figure 2. Fluor-elbaite crystal with microlite inclusions (their enlarged images are shown on the right). Cross tourmaline crystal, polished thin section. BSE-image, CAMECA SX 100 microanalyzer. The photo of tourmaline was made by the mosaic method, by way of "gluing" pictures with each other.

Рисунок 2. Включения микролита в матрице фтор-эльбаита. Поперечный кристалл турмалина, полированный шлиф. BSE-изображение, микроанализатор CAMECA SX 100. Фото турмалина сделано методом мозаики, путем «склеивания» картинок друг с другом.

group, water, and vacancy. All this implies more detailed studies of the mineral and, according to the results of microprobe analysis (which cannot diagnose water, oxygen or a vacancy) it is extremely difficult to determine the microlite to a mineral type. Currently, only fluornatromicrolite is officially and reliably determined from the sodium differences of microlite [8], the remaining four mineral species remain unknown. Among the calcic microlites, only fluorcalciomicrolite [9] and oxycalciomicrolite [7] were found; the other three mineral species are also unknown. The previously described microlite finds within the Lipovskoye vein field [10, 11] remained undetermined to the mineral form for various reasons (within the framework of the current classification).

When studying the cross and long sections of crystals of dark blue, almost black, tourmaline, which turned out to be fluor-elbaite in chemical composition, we found numerous inclusions of tantaloniobates. They form weakly elongated and rounded grains up to 200–250  $\mu$ m in size (Fig. 2). According to the microprobe analysis (Table 1), inclusions differ in a quite stable chemical composition and are confidently determined as tantaloniobates from the microlite-group. Among the essential impurities in grains one can find uranium (UO<sub>2</sub> up to 14.5 wt.%), niobium (Nb<sub>2</sub>O<sub>5</sub> up to 2.7 wt.%), titanium (TiO<sub>2</sub> up to 2.6 wt.%), lead (PbO up to 1 wt.%) and bismuth (Bi<sub>2</sub>O<sub>3</sub> up to 0.7 wt%). The total amount of compounds is characterized by a slight shortage, which is quite typical for tantaloniobates. Against the background of significant impurities of uranium, the mineral could fall under partial metamictization.

The crystallochemical microlite recalculation shows that the "A" position in the mineral has a slight drawback, and the "B" position, on the contrary, has an excess, which is possibly associated with inclusion of water into the "A" position. The recalculation shows that the amount of uranium varies from 0.32 to 0.35 f. units, i. e. no more than 17.5% of the uranium microlite minal. The ratio of calcium and sodium in tantaloniobates varies slightly, and in one analysis (an. 4), according to crystallochemical recalculation, calcium prevails over sodium. The same applies to fluorine: in almost all analyzes (an. 1-4) it prevails in the so-called "Y" position (i. e., fills it) of a flawless microlite, which means that the prefix "fluorine" should be applied to them. In two other analyzes, fluorine is already below the 50% threshold.

Therefore, using the current classification of the microlite-group [6, 7], it can be assumed that the first three analyzes (an. 1–3) relate to fluornatromicrolite because fluorine, tantalum and sodium prevail in certain positions in them. The fourth analysis (an. 4) relates to fluorcalciomycrolite because it is dominated by calcium, tantalum and fluorine. The remaining two analyzes correspond exactly to sodium microlites, since sodium and tantalum are dominated substances. Moreover, the amount of fluorine in these analyzes is below the threshold value; therefore, this mineral phase can be hydronatromicrolite, oxinatromicrolite, hydroxynatromicrolite or kenonatromicrolite, i.e. a new mineral that is not recorded yet. What particular mineral it is we will determine further. The task is facilitated by the fact that these two analyzes were performed for the smallest inclusion of tantaloniobate (in Fig. 2, it is located on top), which means that it will be possible to conduct an X-ray diffraction study of the grain.

Interestingly, when studying Lipovka microlites, no significant fluorine concentrations were observed in them [1, 10, 11], although various associations and paragenesis of the mineral were considered. Apparently, fluorine accumulates in tantaloniobates (and in other minerals as well) at the final crystallization stage of lithium-bearing granite pegmatite.

Fluor-elbaite. It is a recently discovered mineral specimen from the tourmaline supergroup [12, 13], but it has not yet been determined in the Lipovka pegmatites, although the existence of fluorelbaite has long been assumed by us [14, 15]. At the same

Table 1.Chemical composition (in wt.%) of microlite inclusions from fluor-elbaite crystals. Таблица 1. Химический состав (в мас.%) включений микролита из кристаллов фтор-эльбаита.

Nº	1	2	3	4	5	6				
Ta <sub>2</sub> O <sub>5</sub>	63.72	66.18	65.87	65.80	66.15	66.14				
$Nb_2O_5$	2.43	2.67	2.48	2.61	2.37	2.35				
ThO <sub>2</sub>	0.26	0.14	0.17	0.19	0.41	0.04				
$UO_2$	14.10	14.46	14.21	13.89	13.99	14.38				
SiO <sub>2</sub>	0.33	0.32	0.34	0.29	0.31	0.31				
TiO <sub>2</sub>	2.52	2.62	1.81	2.28	2.01	1.97				
$Bi_2O_3$	0.70	0.52	0.59	0.63	0.66	0.69				
PbO	1.13	1.13	0.98	1.01	0.97	0.93				
FeO	_	_	0.18	0.11	_	0.05				
CaO	5.62	6.17	6.04	6.24	5.98	5.72				
MnO	_	0.01	0.06	_	0.09	0.01				
Na <sub>2</sub> O	3.97	3.74	3.75	3.36	4.06	3.25				
F	1.68	1.79	1.53	1.42	1.27	1.01				
2F≣O	-0.71	-0.75	-0.64	-0.60	-0.53	-0.42				
Total	95.75	99.00	97.37	97.22	97.74	96.45				
		Crys	tallochemical formul	las .						
1	$(Na_{0.82}Ca_{0.64}U_{0.33}Pb_{0.03}Bi_{0.02}Th_{0.01})_{1.85}(Ta_{1.83}Ti_{0.20}Nb_{0.12})_{2.15}O_{6}(F_{0.62}X_{0.38})$									
2	$(Na_{0.76}Ca_{0.68}U_{0.33}Pb_{0.03}Bi_{0.01})_{1.81}(Ta_{1.86}Ti_{0.20}Nb_{0.13})_{2.19}O_{6}(F_{0.65}X_{0.35})$									
3	$(Na_{0.76}Ca_{0.68}U_{0.33}Pb_{0.03}Bi_{0.02}Fe_{0.02}Mn_{0.01})_{1.85}(Ta_{1.89}Ti_{0.14}Nb_{0.12})_{2.15}O_6(F_{0.57}X_{0.43})$									
4	$(Ca_{0.71}Na_{0.69}U_{0.33}Pb_{0.03}Bi_{0.02}Fe_{0.01}Th_{0.01})_{1.80}(Ta_{1.90}Ti_{0.18}Nb_{0.12})_{2.20}O_{6}(F_{0.53}X_{0.47})$									
5	$(Na_{0.82}Ca_{0.66}U_{0.32}Pb_{0.03}Bi_{0.02}Th_{0.01}Mn_{0.01})_{1.87}(Ta_{1.86}Ti_{0.16}Nb_{0.11})_{2.13}O_{6}(F_{0.47}X_{0.53})$									
	$(Na_{0.82}Ca_{0.66}O_{0.32}, D_{0.03}D_{0.02}, I_{0.01}NII_{0.01}/_{1.87}(Ia_{1.86}, Io_{0.16}ND_{0.11}/_{2.13}O_{6}(Io_{0.47}N_{0.53})$ $(Na_{0.69}Ca_{0.67}U_{0.35}Pb_{0.03}Bi_{0.02}Fe_{0.01})_{1.77}(Ta_{1.96}Ti_{0.16}Nb_{0.11})_{2.23}O_{6}(F_{0.49}X_{0.60})$									
6		(Na <sub>0.69</sub> Ca <sub>0.67</sub>	,U <sub>0.35</sub> Pb <sub>0.03</sub> Bl <sub>0.02</sub> Fe <sub>0.01</sub> ,	) <sub>1.77</sub> ( 1a <sub>1.96</sub> 11 <sub>0.16</sub> IND <sub>0.11</sub> ) <sub>2.</sub>	$_{23}$ $\cup_{6}$ ( $\Gamma_{0.40}$ $\wedge_{0.60}$ )					

Note: The analyses were made using CAMECA SX 100 (The Zavaritsky Institute of Geology and Geochemistry of the Ural Branch of RAS, Ekaterinburg, analyst V. V. Khiller); an. 1–3 – fluornatromicrolite, an. 4 – fluorcalciomycrolite, an. 5–6 – natromicrolite is undefined yet; X in the formulas is either O, OH, H<sub>2</sub>O or a vacancy.

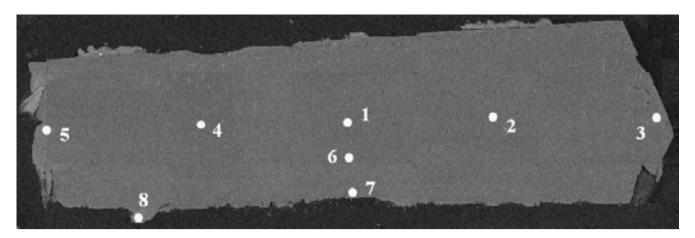


Figure 3. Long section of a polychrome tourmaline crystal, about 2 cm long. Image in BSE mode, CAMECA SX 100. Analyses 2–3 – crimson zone, an. 1, 6–7 – pink zone, an. 4–5, 8 – greenish zone.

Рисунок 3. Продольный срез кристалла полихромного турмалина, длина около 2 см. Снимок в BSE-режиме, CAMECA SX 100. Анализы 2–3 – малиновая зона, ан. 1, 6–7 – розовая зона, ан. 4–5, 8 – зеленоватая зона.

time, its fluorine–free analogue, elbaite, is quite often found within the Lipovskoye vein field. It was described in all lithium-bearing pegmatites of the object [1, 14 etc.], where it is a common mineral in association with potassium feldspar, albite and lepidolite.

The chemical composition of the colored tourmalines of Lipovka has been studied quite well; they are mainly represented by elbaite (colored differences) and rarely rossmanite (colorless differences). The first data on the composition of non–ferrous tourmaline were presented recently [16], as well as some works were published on the chemistry and zoning of lithium borosilicates [1, 17]. We have studied the chemical composition of polychrome tourmaline from the "German" lithium—bearing pegmatite vein (Table 2). For this purpose, a rubellite crystal was selected with a rough cross-banded zonality (in long section) from the crimson color (top of the crystal) through the pink center to a pale green base. In the individual in the cross section, concentric zoning with a greenish core and a pink rim is noted. The long section of the crystal and the location of the microprobe analysis points are shown in Fig. 3.

Table 2. Chemical composition (in wt.%) of tourmaline (longitudinal cut of crystal). Таблица 2. Химический состав (в мас.%) турмалина (продольный срез кристалла).

•		, 31		-1	,							
Nº	1	2	3	4	5	6	7	8				
SiO <sub>2</sub>	39.01	38.76	38.96	38.56	38.90	38.70	38.88	39.51				
TiO <sub>2</sub>	_	0.06	0.04	_	0.04	0.04	_	0.06				
$Al_2O_3$	40.05	40.35	41.24	43.32	43.46	40.75	40.04	42.20				
$Cr_2O_3$	_	_	0.01	_	_	_	_	0.04				
FeO	0.59	0.25	0.10	_	0.02	0.52	0.45	0.05				
MnO	1.76	1.55	0.61	0.12	0.02	1.45	1.90	0.27				
MgO	_	0.01	-	_	0.01	_	_	_				
CaO	0.60	0.70	0.54	0.32	0.04	0.46	0.63	0.13				
Na <sub>2</sub> O	2.17	2.07	2.16	1.73	1.78	2.12	2.13	1.94				
$K_2O$	0.01	0.02	0.01	0.01	0.01	0.01	0.01	0.01				
Cs <sub>2</sub> O	_	_	_	0.08	_	0.01	_	0.02				
Li <sub>2</sub> O*	1.46	1.51	1.51	1.35	1.35	1.46	1.46	1.46				
F	1.20	1.26	1.66	0.67	0.67	1.22	1.20	0.77				
O≡F <sub>2</sub>	-0.51	-0.53	-0.70	-0.28	-0.28	-0.51	-0.51	-0.32				
Total	86.34	86.01	86.14	85.88	86.02	86.23	86.19	86.14				
1		(N	<i>Crystalloc</i> la <sub>0.65</sub> Ca <sub>0.10</sub> ) <sub>0.75</sub> (Al <sub>1</sub>	<i>hemical formul</i> <sub>.73</sub> Li <sub>0.95</sub> Mn <sub>0.24</sub> Fe		3O <sub>3</sub> ) <sub>3</sub> (OH <sub>3.29</sub> F <sub>0.71</sub>	<sub>1</sub> ) <sub>4</sub>					
2		$(Na_{0.62Ca_{0.12}})_{0.74}(Al_{1.76Li_{0.99}Mn_{0.21}Fe_{0.03}Ti_{0.01}})_3Al_6[Si_6O_{18]}(BO_3)_3(OH_{3.25F_{0.75}})_4$										
3		$(Na_{0.64Ca_{0.09}})_{0.73}(AI_{1.91Li_{1.00}Mn_{0.08}Fe_{0.01}})_3AI_6[Si_6O_{18](BO_3)_3}(OH_{3.29F_{0.98}})_4$										
4	$(Na_{0.52Ca_{0.05}})_{0.57}(Al_{2.13Li_{0.84}Mn_{0.02}Cs_{0.01}})_3Al_{6[Si_{6}O_{18}]}(BO_{3})_3(OH_{3.60F_{0.40}})_4$											
5	$(Na_{0.53}Ca_{0.01})_{0.54}(AI_{2.16}Li_{0.84})_3AI_{6}[Si_{6}O_{18}](BO_{3})_3(OH_{3.60}F_{0.40})_4$											
6	$(Na_{0.64Ca_{0.08}})_{0.72}(AI_{1.77Li_{0.94}Mn_{0.20}Fe_{0.07}})_3AI_6[Si_6O_{18](BO_3)_3}(OH_{3.27F_{0.73}})_4$											
7		$(Na_{0.64Ca_{0.10}})_{0.74}(AI_{1.72Li_{0.96}Mn_{0.26}Fe_{0.06}})_3AI_6[Si_6O_{18]}(BO_3)_3(OH_{3.29F_{0.71}})_4$										
8	$(Na_{0.57Ca_{0.02}})_{0.59}(Al_{2.00Li_{0.95}Mn_{0.04}Fe_{0.01}})_3Al_6[Si_6O_{18]}(BO_3)_3(OH_{3.57F_{0.43}})_4$											

Note: The Zavaritsky Institute of Geology and Geochemistry of the Ural Branch of RAS, Ekaterinburg, analyst V. V. Khiller; \* – lithium was determined by the ICP–MS method in ppm and converted into oxides. An. 1–3, 6, 7 – fluor-elbaite, an. 4, 5, 8 – elbaite.

According to the microprobe profiling (Fig. 3), we can say that the visual color of tourmaline is in good agreement with changes in the chemical composition. Pink and crimson zones of borosilicate are enriched with manganese, iron, calcium, sodium and fluorine; greenish zones are vice versa and they contain a little more alumina. The lithium content in each color zone was determined by the ICP-MS method (green zone – 6298 ppm, pink – 6776 ppm, crimson – 7022 ppm) and, when converted to oxide, they correlated quite well with previously published results. For example, in an earlier work [16], the amount of Li O for mixed-colored elbaites is given from 1.1 to 1.6 wt.%. Based on our crystallochemical calculations, the pink and crimson parts of crystal due to the high fluorine content (it varies from 1.2 to 1.7 wt.%) belong to fluor-elbaite; the greenish zone is elbaite with a high rossmanite. It follows that in the lithium-bearing pegmatite veins of Lipovka, along with the well-known tourmalines - elbaite and rossmanite - fluor-elbaite is also widespread. It is possible that fluor-elbaite is the main tourmaline of these pegmatites. Currently, we have analyzed in detail three crystals of colored lithium-containing tourmaline (dark blue, pink and crimson) and it turned out that the core in them is composed of elbaite (rarely rossmanite), and the intermediate zone and border - fluor-elbaite, i. e. up to 2/3 of the crystal volume.

In general, the find of three fluorine-containing minerals (tourmaline and inclusions in it) suggests that fluorine activity was very high at the final stage of the formation of lithium-bearing granite pegmatites of Lipovka. This is confirmed by the host lepidolite in tourmaline (in composition it occupies an intermediate position between polylithionite and trilithionite), as well as the minerals associated with paragenesis – topaz and fluorapatite.

### Conclusions

Thus, in the course of the study, three new minerals for lithium-bearing granite pegmatites of the Lipovskoye vein field - fluor-elbaite, fluornatromicrolite and fluorcalciomicrolite - were determined. The last two tantaloniobates were found in the form of small inclusions in crystals of dark blue fluor-elbaite. Tourmaline itself is quite widespread in Lipovka, it composes the intermediate and marginal zones of colored and polychrome tourmaline, and at least fluor-elbaite is found in pink, raspberry and dark blue crystals. The find of three fluorine-containing minerals (tourmaline and inclusions in it) suggests that fluorine activity was very high at the final stage of the formation of lithium-bearing granite pegmatites of Lipovka.

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- 1. Pekov I. V., Memetova L. R. 2008, Mineraly granitnykh pegmatitov Lipovki, Sredniy Ural [Minerals of granite pegmatites of Lipovka, Middle Urals]. In the world of minerals. Mineralogical almanac, no. 13, P. 7-44. (In Russ.)
- 2. Emlin E. F., Vakhrusheva N. V., Kaynov V. I. 2002, Samotsvetnaya polosa Urala [Precious band of the Urals], Rezhevskoy State natural and mineralogical sanctuary. Guide. Ekaterinburg; Rezh, 156 p.

  3. Khiller V. V., Erokhin Yu. V., Zakharov A. V., Ivanov K. S. 2014, Th–U–Pb dating of granite pegmatites from the Lipovskoye ore field (Urals) for
- three minerals. Doklady Akademii nauk [Doklady Earth Sciences], vol. 455, no. 2, P. 323-326. (In Russ.)
- 4. Pekov I. V., Yakubovich O. V., Shcherbachev D. K., Kononkova N. N. 2003, Magnesiotantalite (Mg, Fe) (Ta, Nb)  $_{2}O_{6}$  is a new mineral of the colombite-tantalite group from silica-depleted granite pegmatites of Lipovka (Middle Urals). Zapiski RMO (Proceedings of the Russian Mineralogical Society), no. 2, P. 49-59. (In Russ.)
- 5. Erokhin Yu. V., Zakharov A. V. 2013, Manganotantalit i bismutotantalit iz kontaminirovannykh pegmatitov Lipovskogo zhil'nogo polya (Sredniy Ural) [Manganotantalite and bismuthotantalite from contaminated pegmatites of the Lipovskoye vein field (Middle Urals)]. 14th All-Russian scientific readings in memory of the Ilmen mineralogist V. O. Polyakov. Miass, P. 25-29. (In Russ.)
- 6. Atencio D., Andrade M. B., Christy A. G., Giere R., Kartashov P. M. 2010, The pyrochlore supergroup of minerals: nomenclature. Canadian Mineralogist, vol. 48, P. 673-698.
- 7. Christy A. G., Atencio D. 2013, Clarification of status of species in the pyrochlore supergroup. Mineralogical Magazine, vol. 77, P. 13–20. https://doi.org/10.1180/minmag.2013.077.1.02
- 8. Witzke T., Steins M., Doering T., Schuckmann W., Wegner R., Pöllmann H. 2011, Fluornatromicrolite, (Na,Ca, Bi), Ta,O,F, a new mineral species from Quixaba, Paraíba, Brazil. Canadian Mineralogist, Vol. 49. P. 1105–1110. https://doi.org/10.3749/canmin.49.4.1105
- 9. Andrade M. B., Atencio D., Persiano A. I. C., Ellena J. 2013, Fluorcalciomicrolite, (Ca,Na,□), Ta,O,F, a new microlite-group mineral from Volta Grande pegmatite, Nazareno, Minas Gerais, Brazil. *Mineralogical Magazine*, vol. 77, issue 7, P. 2989–2996. https://doi.org/10.1180/minmag.2013.077.7.08 10. Zakharov A. V., Erokhin Yu. V. 2015, About the mineralogy of tantaloniobates in contaminated pegmatites of Lipovka (Middle Urals). Vestnik Ural'skogo otdeleniya RMO [Bulletin of the Ural branch of the Russian Mineralogical Society]. Ekaterinburg, no. 12, P. 46-53. (In Russ.)
- 11. Zakharov A. V., Erokhin Yu. V. 2015, Mikrolit i svyazannyye s nim stibiotantalit i bismutotantalit iz kontaminirovannykh pegmatitov Lipovskogo zhil'nogo polya (Sredniy Ural) [Microlite and associated stibiotantalite and bismuthotantalite from contaminated pegmatites of the Lipovskoye vein field (Middle Urals)]. 16th All-Russian scientific readings in memory of the Ilmen mineralogist V. O. Polyakov. Miass, P. 23–29. (In Russ.)
- 12. Bosi F., Andreozzi G. B., Skogby H., Lussier A. J., Abdu Y. A., Hawthorne F. C. 2013, Fluor-elbaite, Na(Li, Al, Al, Al, Al, Ola, OH), F, a new mineral species of the tourmaline supergroup. American Mineralogist, vol. 98, P. 297-303.
- 13. Henry D. J., Novák M., Hawthorne F. C., Ertl A., Dutrow B. L., Uher P., Pezzotta F. 2011, Nomenclature of the tourmaline-supergroup minerals. American Mineralogist, vol. 96, P. 895-913. https://doi.org/10.2138/am.2011.3636
- 14. Erokhin Yu. V., Zakharov A. V. 2011, Polikhromnyye turmaliny i lepidolit iz redkometal'nykh granitnykh pegmatitov Lipovskogo zhil'nogo polya (Sredniy Ural) [Polychrome tourmaline and lepidolite from rare-metal granite pegmatites of the Lipovskoye vein field (Middle Urals)]. Yearbook-2010. Proceedings of the Zavaritsky Institute of Geology and Geochemistry of the Ural Branch of the Russian Academy of Sciences. Issue 158. P. 135–139. (In Russ.) 15. Khiller V. V. 2015, Determination of boron and oxygen in tourmaline by X-ray microprobe analysis. Vestnik Ural'skogo otdeleniya RMO [Bulletin of the Ural branch of the Russian Mineralogical Society], no. 12, P. 128–135. (*İn Russ*.)
  16. Serdyuchenko D. P., Bolshakova T. N., Cherepivskaya G. E. 1984, Tourmalines from pegmatites and granites of Lipovka in the Urals. *Zapiski*
- RMO (Proceedings of the Russian Mineralogical Society), part 113, issue 4, P. 478–485. (In Russ.)
- 17. Memetova L. R., Pekov I. V., Bryzgalov I. A. 2005, Khimicheskiy sostav i zonal'nost' turmalinov v redkometall'no-samotsvetnykh pegmatitakh Lipovki, Sredniy Ural [Chemical composition and zoning of tourmaline in rare-metal semiprecious pegmatites of Lipovka, Middle Urals]. Materials of the V International Symposium called "Mineralogical Museums", P 151–153. (In Russ.)

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# Фтор-эльбаит, фторнатромикролит и фторкальциомикролит из литиеносных гранитных пегматитов Липовки (Средний Урал)

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**Актуальность работы** обусловлена необходимостью изучения минералогии литиеносных гранитных пегматитов Липовки, уникального объекта, давшего миру большое количество кристаллосырья цветного турмалина.

**Шель работы:** исследование фторсодержащих минералов, обнаруженных в литиеносных гранитных пегматитах Липовского жильного поля (Средний Урал).

**Методология исследования:** количественный анализ химического состава фторсодержащих минералов выполнен на рентгеноспектральном электронно-зондовом микроанализаторе CAMECA SX 100. Условия измерения: ускоряющее напряжение 15 кВ, сила тока 50 нА, диаметр пучка 2 мкм. Регистрация интенсивности проводилось по Кα-линиям на наклонных волновых спектрометрах с кристаллами-анализаторами ТАР, LPET и LiF. Для определения фтора использовался отдельный кристалл-анализатор LPCO. Содержание лития в турмалине было установлено на масс-спектрометре ICP-MS ELAN-9000 с предварительным растворением истертых проб в нагретых кислотах.

Результаты. При изучении кристаллов темно-синего турмалина, который по химическому составу оказался фтор-эльбаитом, нами обнаружены включения танталониобатов. Согласно современной классификации, они принадлежат группе микролита, и часть анализов относится к фторнатромикролиту, так как в них в определенных позициях преобладают фтор, тантал и натрий, а часть относится к фторкальциомикролиту, так как в них преобладают кальций, тантал и фтор. Содержание фтора в этих танталониобатах варьирует от 1,4 до 1,6 мас.%. В полихромных турмалинах, розовая и малиновая части кристалла, благодаря высокому содержанию фтора, который варьирует от 1,2 до 1,7 мас.%, относятся к фтор-эльбаиту. Выводы. Установлено три новых минерала для литиеносных гранитных пегматитов Липовского жильного поля – фтор-эльбаит, фторнатромикролит и фторкальциомикролит. Последние два танталониобата были обнаружены в виде мелких включений в кристаллах темно-синего фтор-эльбаита. Сам турмалин достаточно широко распространен на Липовке, он слагает промежуточные и краевые зоны цветных и полихромных турмалинов, по крайней мере, фтор-эльбаит установлен в розовых, малиновых и темно-синих кристаллах. Находка трех фторсодержащих минералов говорит о том, что на заключительной стадии формирования литиеносных гранитных пегматитов Липовки активность фтора была очень высокой.

**Ключевые слова:** фтор-эльбаит, фторнатромикролит, фторкальциомикролит, минералы, литиеносные гранитные пегматиты, Липовское жильное поле, Средний Урал.

#### ЛИТЕРАТУРА

- 1. Пеков И. В., Меметова Л. Р. Минералы гранитных пегматитов Липовки, Средний Урал // В мире минералов. Минералогический альманах. 2008. № 13. С. 7–44.
- 2. Емлин Э. Ф., Вахрушева Н. В., Кайнов В. И. Самоцветная полоса Урала: Режевской государственный природно-минералогический заказник: путеводитель. Екатеринбург; Реж, 2002. 156 с.
- 3. Хиллер В. В., Ерохин Ю. В., Захаров А. В., Иванов К. С. Th–U–Pb-датирование гранитных пегматитов Липовского рудного поля (Урал) по трем минералам // ДАН. 2014. Т. 455, № 2. С. 216–219.
- 4. Пеков И. В., Якубович О. В., Щербачев Д. К., Кононкова Н. Н. Магнезиотанталит (Mg, Fe)(Та, Nb)<sub>2</sub>O<sub>6</sub> новый минерал группы колумбитатанталита из десилицированных гранитных пегматитов Липовки (Средний Урал) // Записки ВМО. 2003. № 2. С. 49–59.
- 5. Ерохин Ю. В., Захаров А. В. Манганотанталит и бисмутотанталит из контаминированных пегматитов Липовского жильного поля (Средний Урал) // XIV Всерос. науч. чтения памяти ильменского минералога В. О. Полякова. Миасс: Ин-т минералогии УрО РАН, 2013. С. 25–29. 6. Atencio D., Andrade M. B., Christy A. G., Giere R., Kartashov P. M. The pyrochlore supergroup of minerals: nomenclature // Canadian Mineralogist. 2010. Vol. 48. P. 673–698.
- 7. Christy A. G., Atencio D. Clarification of status of species in the pyrochlore supergroup // Mineralogical Magazine. 2013. Vol. 77. P. 13–20. https://doi.org/10.1180/minmag.2013.077.1.02
- 8. Witzke T., Steins M., Doering T., Schuckmann W., Wegner R., Pöllmann H. Fluornatromicrolite, (Na,Ca, Bi)<sub>2</sub>Ta<sub>2</sub>O<sub>6</sub>F, a new mineral species from Quixaba, Paraíba, Brazil // Canadian Mineralogist. 2011. Vol. 49. P. 1105–1110. https://doi.org/10.3749/canmin.49.4.1105
- 9. Andrade M. B., Atencio D., Persiano A. I. C., Ellena J. Fluorcalciomicrolite, (Ca,Na,□), Ta,O,F, a new microlite-group mineral from Volta Grande pegmatite, Nazareno, Minas Gerais, Brazil. *Mineralogical Magazine*, 2013. Vol. 77, issue 7. P. 2989–2996. https://doi.org/10.1180/minmag.2013.077.7.08 10. Захаров А. В., Ерохин Ю. В. К минералогии танталониобатов в контаминированных пегматитах Липовки (Средний Урал) // Вестник УрО РМО. 2015. № 12. С. 46–53.
- 11. Захаров А. В., Ерохин Ю. В. Микролит и связанные с ним стибиотанталит и бисмутотанталит из контаминированных пегматитов Липовского жильного поля (Средний Урал) // XVI Всерос. науч. чтения памяти ильменского минералога В. О. Полякова. Миасс: Интинералогии УрО РАН, 2015. С. 23–29.
- 12. Bosi F., Andreozzi G. B., Skogby H., Lussier A. J., Abdu Y. A., Hawthorne F. C. Fluor-elbaite, Na(Li<sub>1.5</sub>Al<sub>1.5</sub>)Al<sub>6</sub>(Si<sub>6</sub>O<sub>18</sub>)(BO<sub>3</sub>)<sub>3</sub>(OH)<sub>3</sub>F, a new mineral species of the tourmaline supergroup // American Mineralogist. 2013. Vol. 98. P. 297–303.
- 13. Henry D. J., Novák M., Hawthorne F. C., Ertl A., Dutrow B. L., Uher P., Pezzotta F. Nomenclature of the tourmaline-supergroup minerals // American Mineralogist. 2011. Vol. 96. P. 895–913. https://doi.org/10.2138/am.2011.3636
- 14. Ерохин Ю. В., Захаров А. В. Полихромные турмалины и лепидолит из редкометалльных гранитных пегматитов Липовского жильного поля (Средний Урал) // Ежегодник-2010: труды ИГГ УрО РАН. 2011. Вып. 158. С. 135–139.
- 15. Хиллер В. В. Определение бора и кислорода в турмалинах методом рентгеноспектрального микрозондового анализа // Вестник УрО РМО. 2015. № 12. С. 128–135.
- 16. Сердюченко Д. П., Большакова Т. Н., Черепивская Г. Е. Турмалины из пегматитов и гранитов Липовки на Урале // Записки ВМО. 1984. Ч. 113. Вып. 4. С. 478–485.
- 17. Меметова Л. Р., Пеков И. В., Брызгалов И. А. Химический состав и зональность турмалинов в редкометалльно-самоцветных пегматитах Липовки, Средний Урал // Минералогические музеи: материалы V Междунар. симпоз. СПбГУ, 2005. С. 151–153.

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