

On “Birthmarks” in Rare-Metal Granites of the Losevka Pluton, Northern Kazakhstan

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Abstract—The Losevka pluton of rare-metal albite granite, which was explored as a possible source of columbite–zircon–malacon ore, is composed of quartz, sodic plagioclase, potassium feldspar, annite, protolithionite, lepidomelane, and Li-muscovite. The average chemical composition of this rock is as follows, wt %: 74.14 SiO₂, 0.04 TiO₂, 14.07 Al₂O₃, 1.05 Fe₂O₃, 0.78 FeO, 0.15 MnO, 0.09 MgO, 0.47 CaO, 4.65 Na₂O, 4.11 K₂O, and 0.03 P₂O₅. The accessory minerals are zircon, malacon, and cyrtolite (874 ppm); apatite (18 ppm); ilmenite (114 ppm); xenotime and monazite (119 ppm); and Nb-columbite (463 ppm). The black inclusions up to 15 cm in size, which are observed in this granite and called “birthmarks” by local geologists, consist of the same rock-forming minerals as the surrounding granite, but are enriched in MnO, MgO, CaO, TiO₂, and F and depleted in SiO₂ relative to the light granite. The black granite is also distinguished by much higher Sr and Ba contents and lower La, Rb, Y, Nb, REE, Cs, Ta, Th, and U contents. The black color is caused by enrichment in manganese oxides, manganoilmenite, and Mn-annite. All rock-forming minerals are pervaded by thin veinlets of Mn-oxides. In addition, bastnaesite, Y- and Th-fluorides, zircon, and malacon have been identified. Aggregates of black-colored minerals are not the products of the fractionation of the initial magma or immiscibility effects, because the structure of the albite–potassium feldspar–quartz–mica matrix is the same both in black and light granites. The percolation of a deep-sourced fluid enriched in Mn and F into a granitic melt might be a more probable origin.

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In rare-metal albite granite of the Losevka pluton, particularly in its northern part, one can see black patches that reach 10–15 cm across called “birthmarks.” They actually resemble these alien spots contrastingly standing out against the background of light-colored granite (Fig. 1). The black spots are dispersed throughout the pluton. While being weathered, they serve as sources of Mn hydroxides that penetrate for 3–5 cm into the adjacent granite as thin veinlets, so that some geologists inclined to their supergene origin. Because the “birthmarks” occur throughout the pluton and are observed in the cores of deep boreholes, their supergene origin is doubtful, the more so since the granite of the Losevka pluton and country granites of the Balkalshino and Zerenda complexes are low-Mn rocks (Letnikov, 2005) and do not contain melanocratic bodies, which could be found in the Losevka pluton as xenoliths. These observations stimulated us to carry out a detailed investigation of this exotic rock.

The Losevka pluton is a complexly built harpolith that cuts through both biotite granite of the Zerenda Complex and leucogranite of the Balkashino Complex dated at 443 ± 11 (Shatagin, 1994) and 412 ± 6 Ma (Letnikov and Kostitsyn, 2002), respectively. The U–Pb

age of malacon and columbite from the Losevka Granite was estimated at 360 ± 30 Ma (Serykh, 1982). This estimate requires refinement, though the younger age of the Losevka Granite relative to the Zerenda and Balkalshino complexes is not in doubt. In the 1950s, the Losevka pluton was explored as a complex Nb–Zr deposit.



Fig. 1. Sample of black granite.

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Table 1. Chemical composition of granite (major elements), wt %

Component	Losevka granite					Granite of black spots		
	KCh-11	KCh-12	KCh-13	71/2003	LS-20	3/05	67/2003	LS-18
SiO ₂	74.50	72.78	73.10	75.75	76.12	76.58	74.82	74.09
TiO ₂	0.05	0.07	0.06	0.09	0.14	0.11	0.11	0.20
Al ₂ O ₃	12.33	13.65	13.76	13.95	11.78	12.2	12.80	12.27
Fe ₂ O ₃	3.29	2.68	2.19	0.75	0.85	0.33	0.50	0.72
MnO	0.19	0.19	0.18	0.04	0.15	0.33	0.35	0.42
MgO	0.01	0.01	0.01	Tr.	0.10	0.26	0.11	0.19
CaO	0.10	0.06	0.02	Tr.	0.20	0.84	1.07	0.46
Na ₂ O	4.97	5.61	5.64	6.59	4.63	3.48	4.09	4.99
K ₂ O	4.35	4.62	4.59	2.10	3.80	4.72	4.63	4.42
P ₂ O ₅	0.02	0.017	0.01	0.02	0.02	0.01	0.01	0.03
F	–	–	–	0.07	0.12	0.50	0.51	0.15
LOI	–	–	0.09	–	–	–	–	0.71
Total	99.81	99.68	99.66	100.21	99.57	100.5	100.47	99.64

The intrusion is characterized by a cupola-like morphology with its apical portion composed of albite granite affected by metasomatic albitization and enriched in columbite and malacon. Stockscheiders that occur in the frontal contact zone (Marin and Efros, 1968) are bodies of pegmatoid quartz–feldspar, often amazonite-bearing rocks up to 0.5–1.2 m thick associated with pegmatite bodies 10 × 6 m in size with distinctly delineated quartz cores and banded quartz–feldspar aggregates containing columbite and malacon. The albite granite with economic Nb–Zr ore mineralization occupies the contact zone and at a distance from the contact grades into porphyritic albite leucogranite with subeconomic Nb–Zr ore, which, in turn, gives way to the barren albitized granite porphyry (Letnikov, 2000).

The upper portion of the pluton is composed of white lepidomelane–protolithionite albite granite with characteristic spots of pealike quartz grains. This granite grades with the depth into inequigranular granite with a prevalence of magmatic albite and poorly developed metasomatic albitization. Granites are cut by dikes of the same composition; the country rocks are albitized and greisenized in narrow contact zones.

The Losevka rare-metal granite consists (vol %, averaged estimates) of quartz (32.4), plagioclase (39.4), potassium feldspar (26.0), and mica (2.2). The maximum microcline (10–45 mol % of albite and 55–90% of orthoclase end members) is predominant. Plagioclase corresponds to albite–oligoclase in composition. Micras are identified as protolithionite, Li-muscovite, and less abundant Li-phengite-muscovite and lepidomelane. The average chemical composition of this rock is as follows (Letnikov, 2005), wt %: 74.14 SiO₂, 0.04 TiO₂, 14.07 Al₂O₃, 1.05 Fe₂O₃, 0.78 FeO, 0.15 MnO, 0.09 MgO, 0.47 CaO, 4.65 Na₂O, 4.11 K₂O, and 0.03 P₂O₅; Na₂O/K₂O = 1.13, (Na₂O + K₂O)/Al₂O₃ = 0.62.

The accessory minerals are zircon, malacon, and cyrtolite (874 ppm); apatite (18 ppm); ilmenite (114 ppm); xenotime and monazite (119 ppm); and columbite (463 ppm) (Krasil'nikova, 1969). Thus, the rock may be defined as an ultrasilicic alkali leucogranite with low contents of melanocratic components.

Let us examine the compositional difference between the black “birthmarks” and the background albite leucogranite.

The chemical compositions of the Losevka granites are shown in Table 1. Samples KCh-12 and KCh-13 characterize an ore-bearing variety mostly enriched in Nb and Zr, while samples KCh-11, 71/2003 and LS-20 contain less columbite and zircon (Nb and Zr, respectively). The ore-bearing granite contain less SiO₂ and is enriched in Al₂O₃, CaO, K₂O, and (except sample 71/2003) Na₂O. Variable alkali metal contents emphasize a nonuniform development of late- and postmagmatic alkaline metasomatism. The concentrations of the other components do not reveal a significant difference between ore-bearing and barren granites.

Granite in black inclusions is enriched in MnO, MgO, CaO, F, and partly TiO₂ with a tendency toward decreasing Na₂O and total Fe in the form of Fe₂O₃ (Table 1). The maximum Fe₂O₃ content is typical of the ore with the highest columbite grade. Let us compare samples LS-18 (black granite) and LS-20 (light granite) taken 10 cm apart from the boundary with a black spot (Table 1). The black granite contains 2.5 wt % SiO₂ less, but is enriched in TiO₂, Al₂O₃, MnO, MgO, CaO, Na₂O, and K₂O in comparison with the light granite; the difference in MnO, MgO, CaO, and F is most contrasting. The difference in trace element contents (ICP-MS) is still sharper (Table 2). A comparison of three groups of granites—high-grade ore (samples KCh-12, KCh-3),

Table 2. Chemical composition of granite (trace elements), ppm (ICP-MS results)

Component	Rare-metal granite				Granite of black spots	
	KCh-11	KCh-12	KCh-13	LS-20	3/05	LS-18
Ga	64	75	84	25.70	15.95	9.37
Rb	1090	1872	2378	1032.4	1140.75	557.57
Sr	5	12	3	16.63	55.72	33.93
Y	75	113	84	118.00	43.24	33.08
Zr	253	1164	1467	327	95.51	556.96
Nb	487	862	973	72.59	48.75	26.50
Cs	9.3	13.3	12.3	8.37	1.16	6.49
Ba	10.5	12.1	10.6	95.52	53.94	68.15
La	39	40	27	43.57	72.37	16.77
Ce	68	95	86	117.75	115.50	29.02
Pr	5.9	9	9	13.17	9.06	3.23
Nd	12.7	19.3	19.3	28.06	20.95	7.47
Sm	2.2	3.7	3.7	6.89	3.0	1.56
Eu	0.071	0.08	0.08	0.23	0.21	0.16
Gd	3.2	5.1	4.6	6.74	2.77	2.04
Tb	0.74	1.30	1.11	1.46	0.71	0.37
Dy	6.0	10.6	9.6	11.39	4.91	3.71
Ho	1.72	3.1	2.9	3.07	1.29	0.96
Er	6.8	13.1	12.7	13.02	5.40	4.03
Tm	1.20	2.6	2.6	2.01	1.02	0.65
Yb	9.7	21	23	13.37	7.92	4.47
LU	1.59	3.5	3.9	2.35	1.04	0.73
Hf	14.9	61	98	12.97	4.15	13.04
Ta	20	31	90	6.59	2.14	1.66
Th	88	277	284	34.90	44.45	12.58
U	38	96	186	25.26	6.80	4.52

barren granite (samples KCh-11, LS-20), and granite of black spots—demonstrates the following features:

(1) Granite with high Nb and Zr contents is enriched in La, Rb, Y, Cs, Gd, Lu, Hf, Ta, Th, and U relative to black granite, but markedly depleted in Sr and Ba.

(2) Black granite is enriched in Sr and Ba in line with enrichment in MnO, CaO, and MgO (Table 1) and contains much less Nb, Ta, U, and Th. Sample 3/05 additionally contains (ppm) 1.14 Cr, 0.58 Co, 4.5 Ni, 3.62 Cu, and 128.3 Zn.

These differences are especially contrasting, when black granite (sample LS-18) is compared with adjoining light granite (sample LS-20) enriched in La, Rb, Y, Nb (but not Zr), Cs, REE, Ta, Th, and U. Thus, two trends of geochemical specialization are outlined for granitic rocks contrasting in color and petrography. This implies that local enrichment of black granite in Mn, Ca, and Mg occurred at the magmatic or late magmatic stages. The results of SEM and microprobe

examination of the rocks at the Geological Institute, Siberian Branch of the Russian Academy of Sciences, Ulan-Ude (MAR-3 microprobe, analyst N.S. Karmanov) support this conclusion.

Figure 2 demonstrates a large zircon crystal ($300 \times 200 \mu\text{m}$) with small thorite inclusions. At the boundary with albite, zircon is overgrown with magnetite. Albite is crossed by small veinlets of Mn-oxides (Fig. 3). Albite contains bastnaesite grains $30 \times 10 \mu\text{m}$ in size (Fig. 3) associated with malacon ($5 \times 5 \mu\text{m}$). Large segregations of Mn-oxides ($\sim 60 \mu\text{m}$) incorporated into albite contain manganoilmenite grains $20\text{--}40 \mu\text{m}$ in size. Small ($\sim 10 \mu\text{m}$) bastnaesite grains and still smaller (up to $5 \mu\text{m}$) malacon crystals are contained in a large zircon crystal ($80 \times 100 \mu\text{m}$) (Fig. 4). A magnetite crystal up to $30 \mu\text{m}$ in size is intergrown with zircon. Numerous elongated grains of Mn-oxide ($\sim 50 \mu\text{m}$) and Th- and Y-fluorides were detected in large magnetite grains. Judging from their relationships, they were formed during the crystallization of magnetite. In one

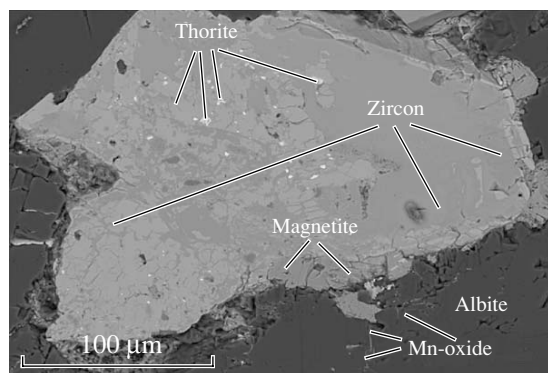


Fig. 2. Small thorite inclusions in a large zircon crystal ($300 \times 200 \mu\text{m}$). Zircon intergrown with magnetite; Mn-oxide occurs as veinlets in albite.

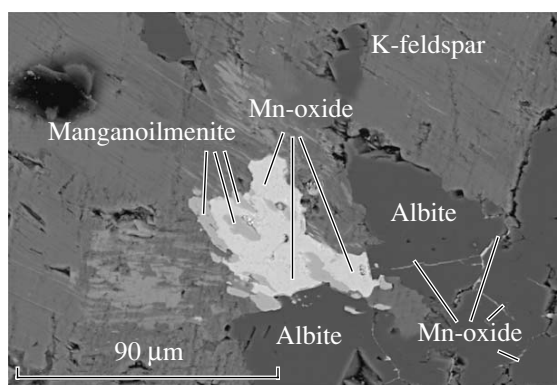


Fig. 3. A large segregation of Mn-oxides with manganoilmenite inclusions.

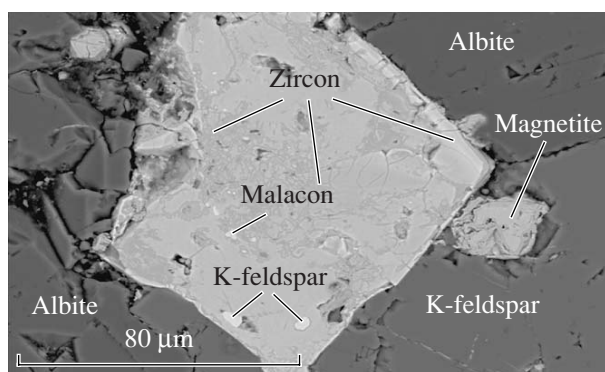


Fig. 4. Small bastnaesite and malacon inclusions in a zircon crystal.

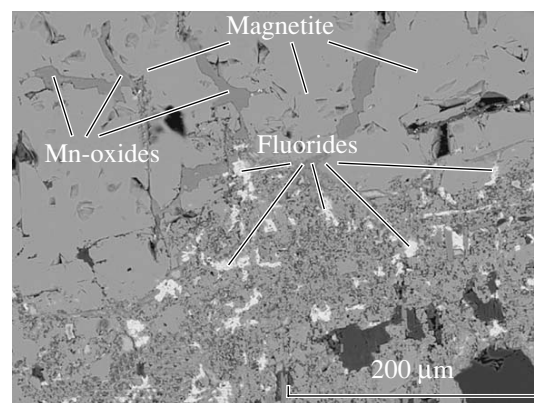


Fig. 5. Veinlets of Mn-oxides and Th- and Y-fluorides in magnetite.

case, the Th- and Y-fluorides are arranged as a band $\sim 100 \mu\text{m}$ in size along the margin of a large ($0.7\text{--}1.0 \text{ mm}$) magnetite crystal; numerous individuals of Mn-oxides within this crystal resemble an exsolution structure (Fig. 5). The large Mn-annite crystals host manganoilmenite crystals up to $20\text{--}40 \mu\text{m}$ in size (Fig. 6). In addition to small veinlets that cross albite, Mn-oxides make up larger (up to $20\text{--}30 \mu\text{m}$) segregations. The intergrowths of large (up to $50 \mu\text{m}$) bastnaesite grains and a malacon crystal ($1\text{--}5 \mu\text{m}$) are noted within albite (Fig. 7).

The following relationships between the minerals are visually established in the black spots under an electron microscope:

(i) Feldspars entrain zircon crystals with inclusions of malacon, bastnaesite, and thorite; zircon–magnetite intergrowths are noted.

(ii) Mn-oxides occur as inclusions and small veinlets in the crystals of albite, potassium feldspar, and magnetite; manganoilmenite occurs within Mn-oxide grains and along the cleavage planes in annite.

(iii) Bastnaesite and malacon grains are incorporated into albite.

(iv) The marginal zone of the zircon crystal at the contact with magnetite contains up to 11 wt % HfO_2 .

(v) Small grains of Th- and Y-fluorides are observed in magnetite together with veinlets and grains of Mn-oxides.

Thus, SEM images display products of the contemporaneous nonequilibrium crystallizations of feldspars, micas, Mn and Fe oxides, Th- and Y-fluorides, zircon, malacon, and bastnaesite. All of these minerals are dispersed through albite–potassium feldspar matrix. The microprobe results indicate that a great mass of manganese was involved in the crystallization (Table 3). Above all else, Mn is contained in the major rock-forming minerals—albite, potassium feldspar, Mn-annite, and manganoilmenite. The formation of annite instead of biotite is controlled by a low Mg content in the melt (Table 1) with the replacement of Mg with Mn in the annite lattice and the occurrence of Mn and Fe in manganoilmenite. The medium of crystallization was also enriched in F that is detected in annite, Th- and Y-fluorides, bastnaesite, malacon, and thorite. Mn-oxides contain Ca, Na, K, Sr, and Zn as admixtures. Small ($\sim 20 \mu\text{m}$) grains of Th- and Y-fluorides captured by

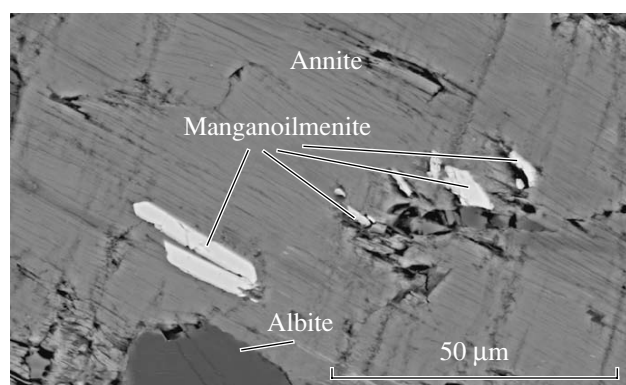


Fig. 6. Manganoilmenite crystals in Mn-annite.

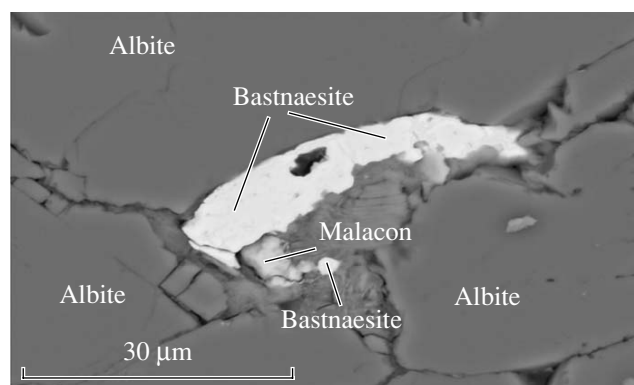


Fig. 7. Intergrowth of bastnaesite and malacon in albite.

magnetite contain more than 1 wt % Ca, Fe, Si, Sr, Ce, La, Nd, Y, Pb, and 0.88 wt % Mn. The nonequilibrium character of the crystallization is emphasized by the nonuniform distribution of trace elements in the same phases. For example, up to 11.05 wt % HfO₂ were

detected in zircon along with some amount of Fe, whereas small malacon grains within large zircon crystals in association with bastnaesite are enriched in Fe, Mn, Ca, Y, Th, U, F in the absence of Hf (Table 3). The Zn content in Mn-oxides and manganoilmenite is note-

Table 3. Chemical composition of minerals, wt % (microprobe results)

Oxide	Albite	K-feldspar	Annite	Magnetite	Mn-oxide	Th-fluoride	Zircon	Bastnaesite	Manganoilmenite	Manganoilmenite	Malacon	Malacon	Thorite
SiO ₂	67.74	65.1	40.26	0.51	0.71	1.02	33.72	0.99	0.76	0.96	19.04	19.1	17.87
TiO ₂			1.94						59.86	52.78			
Al ₂ O ₃	18.79	18.14	8.63							0.45	2.47		
FeO	0.58	0.49	25.58	94.18		2.97	0.63		24.8	19.31		0.44	0.98
MnO	1.33	0.15	5.95		75.6	0.88			16.27	26.1	0.58		
CaO	0.03		0.03		0.3	9.82					1.17	1.02	0.83
Na ₂ O	11.76	0.26	0.21		0.93								
K ₂ O	0.11	16.43	9.46		3.69					0.35			
SrO					0.58	1.13							
ZnO					2.27				2.49	1.49			
Ce ₂ O ₃						2.18		41.17			1.37		
La ₂ O ₃						1.08		16.3			0.62		
Pr ₂ O ₃								2.86					
Nd ₂ O ₃						1.79		8.04					
Y ₂ O ₃						4.06					4.44	1.34	1.73
ThO ₂						62.01					16.81	31.83	42.67
UO ₂											1.33	26.86	21.03
ZrO ₂							58.07				29.99	11.62	3.48
HfO ₂							11.05						0.92
PbO						1.03							
Nb ₂ O ₃										1.99			
P ₂ O ₅													1.21
F			5.32			10.01		8.24			2.7	0.87	1.3
Total	100.36	100.59	101.92	94.69	84.1	97.92	103.47	77.59	104.18	103.44	80.53	93.08	92.02

worthy; in other phases, Zn is absent (Table 3). REE are established in small grains of Th- and Y-fluorides, in bastnaesite, and partly (La, Ce) in malacon, while Y, Th, and U accumulated in malacon and thorite (Table 3). The Hf content in thorite is as high as 0.92 wt %. Nb-columbite is a typical mineral of albite granite, whereas, in black spots, Nb was detected only in manganoilmenite (1.99 wt %), thus emphasizing once again the compositional difference between light and black granite varieties. The data presented above lead us to the suggestion that the crystallization of an albite granitic melt was predated by the injection of a deep fluid enriched in Mn, Ca, Mg, and F. This fluid was enriched in Sr, Ba, partly La, and Ce and appreciably depleted in Ga, Y, Nb, Cs, Ta, Th, and U. The REE total of albite granite (average of four samples presented in Table 2) is 213.56 ppm, whereas black granite contains 162.65 ppm REE in total.

Thus, the granite inclusions colored in black owing to the occurrence of Mn-oxides cannot be the products of magma fractionation or the effects of immiscibility, because the matrix of albite, potassium feldspar, quartz, and mica is the same in both cases. It seems more plausible that an alien fluid enriched in Mn and F was injected into the granitic melt from a deep-seated source having provided a geochemical difference in light and black granites. The Nb–Zr–REE type of the Losevka granite indicates that this fluid could be related to a deep alkaline ultramafic melt. The injection of such a fluid resulted in the uniform, laminar, and spotty distribution of black granite.

The chemical composition of minerals from black granite (Table 3) reveals a number of anomalies. For example, the MnO content in two samples of manganoilmenite reaches 16.27 and 26.1 wt %. While, in the first case, the composition of the mineral fits manganoilmenite (Betekhtin, 1950), the second composition is more suited to pyrophanite (MnTiO_3) (Deer et al., 1962). In comparison with manganoilmenite, the mineral contains less Fe (24.8–19.31 wt %) and is enriched in MnO and TiO_2 (up to 59.86 and 52.78 wt %), whereas the TiO_2 content in pyrophanite does not exceed 46.23 wt % (Deer et al., 1966).

The elevated Fe and Mn contents in feldspars are caused by the Fe incorporation into the crystal lattice and the penetration of Mn along the grain boundaries and cleavage planes at the stage of crystallization. The problem concerning the absence of Mn in magnetite remains open. The Mn content in annite from black granite is as high as almost 6 wt %, and this mineral may be defined as Mn-annite with an anomalously high F content (5.32 wt %). The segregations of Mn oxides contain up to 75.6 wt % MnO and are characterized by elevated Zn, K, and Sr contents (Table 3). The Th-fluoride contains up to 62 wt % Th and ~10 wt % F plus a high Y content (~4 wt %) and admixtures of Fe, Ca, Sr, Ce, La, and Nd in contrast to bastnaesite that contains only REE with a prevalence of La and Ce and subordinate amounts of Pr and Nd; the F content is 8.24 wt %.

It is noteworthy that Th-fluoride is enriched in Mn. Thorite, in addition to high Th and U concentrations, contains Zr, Hf, Nb, F, and Y in considerable amounts.

The composition of zircon is close to the stoichiometry of this mineral with an anomalous HfO_2 content of 11 wt % in one case. At the same time, malacon contains less SiO_2 , and Al, Fe, Mn, Ca, Ce, La, and F are detected therein. The ZrO_2 contents in malacon are a few times lower in comparison with zircon and Th prevails over U. It is probable that a wide range of admixtures in malacon is caused by its metamict state.

The results of microprobe determinations (Table 3) confirm the conclusion on the nonequilibrium crystallization of many accessory minerals under the effect of fluorine fluid with a high Mn content on the granitic matrix. The black-colored variety of granite is a product of such an effect.

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