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Rare and New Minerals of the Tashelga-Maizaskaya Zone of Gornaya Shoriya, Their Peculiarities and Nature

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Rare and new minerals (tashelgite, mukhinite, hibonite, goldmanite and others) discovered in the process of geological studies of the 20th and the 21st centuries in the carbonate stratum of the Tashelga polymetamorphic complex (R_3-Rz_3ts) composing the graben-syncline structure within the Kuznetsk-Alatau shear zone in Gornaya Shoriya are described. It is shown that the unique mineralization of skarnoids, calciphyres and metasomatites of the district is preconditioned by the processes of metamorphism and further metasomatosis of original carbonate marine sediments contaminated by laterite metabasite weathering products. The impact of the basic rock chemistry on the whole further polychronic endogenous rock mineralization is traced even in such relatively closed systems of the zone as granite pegmatites.

Keywords: Gornaya Shoriya, Tashelga-Maizaskaya zone, tashelgite, mukhinite, fe-hibonite, goldmanite.

The Tashelga-Maizaskaya zone located in the south of the Kemerovo Region (Fig. 1) was attracting the attention of researchers for a long period of time with wide development of ore mineralization of different types and presence of extremely rare and even endemic species in the latter. Two new minerals – mukhinite and tashelgite and rare minerals – hibonite and goldmanite were discovered here in the 20th and the 21st centuries within a relatively limited area. Our work is aimed at characteristic of these phases and explanation of the reasons for their occurrence.

According to the latest data, the Tashelga-Maizaskaya zone occupying the basin of the Tashelga River and spatially coinciding with the same–name graben-syncline joint structure 30x6km in size, is allogenic in relation to the surrounding rocks and represents an independent microlithon participating in the construction of the Kuznetsk-Alatau shear zone [1]. The structure is composed of carbonate strata of the Tashelga polymetamorphic complex (R_3-Rz_3ts) including calcite and dolomite marbles

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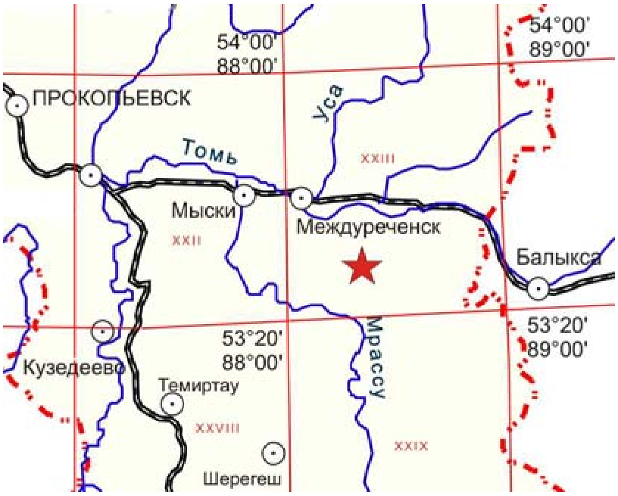

Fig. 1. Sketch map of the Tashelga-Maizaskaya zone location

with subordinated amphibolites, quartzites and crystalline slates. The mineralization discovered to date is developed in carbonate rocks only. The impact of their material composition, as will be shown below, is traced to this or that extent in the nature of the whole further endogenous polychromic and polygenic mineralization and in many ways defines its uniqueness.

Hibonite was the first rare mineral discovered in this zone. Its spectacular black-brown tabular crystals up to 3cm across in calcite marbles of the Tashelga River estuary were discovered in 1938 by the professor of the Tomsk Polytechnic Institute K.V. Radugin. He passed the fining to the department mineralogists, and further crystal studies were conducted by A.M. Kuzmin. The latter determined the composition of the mineral, its physical properties, carried out goniometric measurements, studied the paragenesis and finally referred it incorrectly to hegbomite [2, 3]. The error was detected by T.A. Yakovlevskaya in the process of materials generalization for preparation of the reference book “Minerals”. The mineral gained its current name only after her publications [4]. Unfortunately, the native priority in mineral discovery was already lost then because the similar Gornaya Shoriya mineral phase called hibonite was discovered and described by foreign researchers in marbled limestones of Madagascar [5].

Nonetheless, the mineral turned out to be extremely rare in nature, especially in such large and well-formed crystals. Furthermore, the Tashelga variety is noticeably enriched with ferric iron and is a ferriferous mineral variety as compared to all other known findings representing practically ironless hibonite varieties (Table 1).

We found out that the intensive black-brown colour of the Gornaya Shoriya hibonite is defined by iron ions forming a part of the mineral [6]. The analysis of the optical absorption spectrum received (Fig. 2) shows that there are both bi- and trivalent iron ions simultaneously present in Fe-hibonite. The first ones are detected on the basis of intensive absorption belts 1800, 2070, 2400 Nm in the IR spectrum zones and are associated with electronic transitions from the $^5E(D)$ level to the orbital triplet $^5T_2(D)$ level split down by the crystalline field into three sublevels in Fe^{2+} ions occupying the tetrahedral site in the mineral structure ($Dq=485cm^{-1}$). The remaining insignificant part of Fe^{2+} ions fills the octahedral

Table 1. Chemical composition of Fe-hibonite (mass %)

Components	1	2	3	4	5
SiO_2	4.44	1.03	0.72	0.53	0.42
TiO_2	5.15	5.10	5.79	5.82	6.23
Al_2O_2	66.16	73.67	72.51	74.97	73.69
Fe_2O_3	11.54	9.90	10.57	9.96*	10.05*
FeO	-	0.35	-	-	-
MgO	0.93	1.59	1.38	1.62	1.15
MnO	0.54	-	0.16	0.12	-
CaO	10.47	8.67	8.47	7.94	9.01
nnn	1.16	-	ND	ND	ND
Sum	100.39	100.31	99.60	100.96	100.55

Note: 1 – analyst I.P. Onyfriyenok [2]; 2 – analyst N.A. Stukalova [9]; 3 – microprobe MAR-2 IZK SB of the USSR AS, average for 5 points, analyst T.I. Medvedyeva; 4 – microprobe MAR -3 SB of the USSR AS, analyst N.S. Karmanov; 5 – microprobe CAMEBAX, IGEM, microprobe G.N. Muravitskaya. * – iron re-calculated for Fe_2O_3.

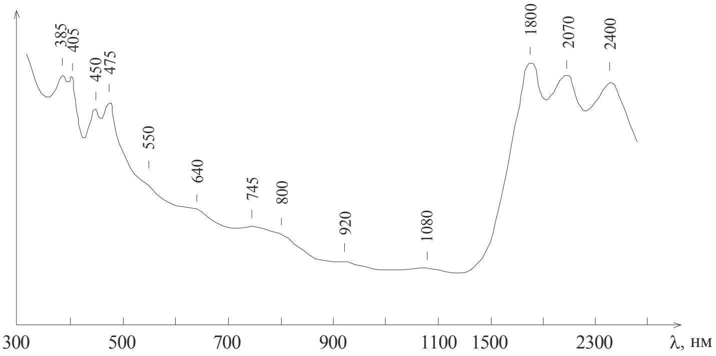

Fig. 2. Fe-hibonite optical absorption spectrum

cavities of the structure. This occurs in the form of weak absorption belts in the 920-1080Nm zone of the spectrum, corresponding to $^5T_2(D) \rightarrow {}^5E(D)$ transitions (Fig. 2 and 3).

Fe^{3+} ions occupy octahedral sites in the Fe-hibonite structure. In the optical spectrum strong absorption belts in the ultra-violet zone (385-405 Nm) correspond to them. These are associated with transfer to high excitation levels of $D(^4E^4T_2)$ therms weaker in intensity 450, 475, 640 and 800 Nm, corresponding to sixtet-quartet transitions from the $^6A_1(S)$ position to the $^4A_1{}^4E(G)$, $^4T_2(G)$ and $^4T_1(G)^4$ positions forbidden by spins. Splitting of the $\rightarrow A_1{}^4E(G)$ transition belt into two components is observed. This is evidently associated with reduction of the local structure symmetry as a result of Fe^{3+}- octahedral distortion. Finally, a weak wide belt in the 745Nm zone occurred in the Fe-hibonite absorption spectrum testifies to presence of a small amount of exchange-coupled pairs Fe^{2+}_{VI} -Fe^{3+}_{VI} in the mineral.

The results received agree well with the following ideas: spinel block packages containing both Al-octahedra and Mg-Fe-tetrahedra are present in the hibonite structure in addition to plane-coupled

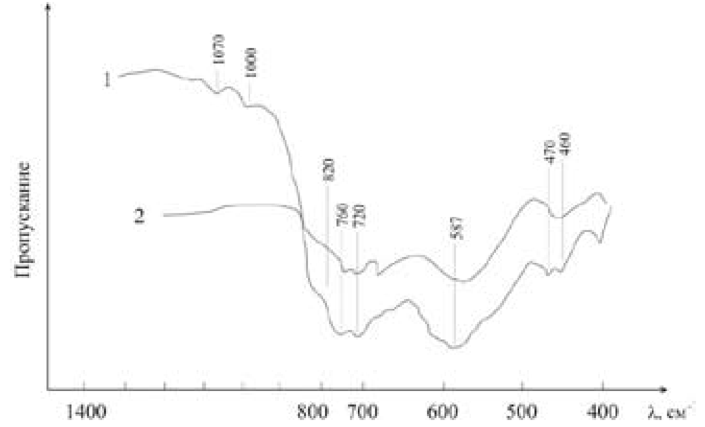

Fig. 3. Fe-hibonite infra-red spectra

Fe-octahedra pairs (corundum-hematite) [7]. Unfortunately, it is impossible to reliably evaluate the Fe^{2+} and Fe^{3+} correlation in the Gornaya Shoriya Fe-hibonite on the basis of the optical spectroscopy data. According to the published chemical analyses [5], Fe^{3+} noticeably prevails in the mineral. This is also confirmed by the IR-spectrum of Fe-hibonite received by us (Fig. 3), in which a strong absorption belt is present in the zone of the characteristic frequency of Fe^{3+} ions being in the octahedral site (460 cm^{-1}).

The first endemic of the Tashelga-Maizaskaya zone – a complex Ca, Al, Mg and Fe oxide tashelgite was discovered in the association with Fe-hibonite. Its history started in the middle of the previous century when V.I. Nefedev received the specimens with pseudohegbomite from Tomsk. He described a potentially new mineral species in addition to already known phases in the course of study of their mineral paragenesis. He called it lodochnikovite [8, 9]. However, the quantitative chemical composition, the crystalline texture, thermic, spectroscopic and other important characteristics of this mineral were not defined at that time. Consequently, lodochnikovite did not receive an independent status. Only a half a century later the former lodochnikovite was approved by the Commission on New Minerals, Nomenclature and Classification of the International Mineralogical Association (5th of June 2010, IMA 2010-017) as a new mineral species and received the other name – tashelgite associated with the place of its finding. It became possible only after repeated detail study carried out by the authors of this work together with the group of colleagues. The detail description of tashelgite was published in [10]. It was found out that it does not have close analogues in the mineral reign and represents a new structural type. The uniqueness of the tashelgite structure (Fig. 4) is as follows: it contains functionally different Al atoms with three coordination types – octahedral, tetrahedral and diorthogroups [11]. According to this, the crystallochemical formula of the mineral will look as follows (Z= 4): $Ca_2 Mg_2{}^{IV} Fe^{(2+)N}_2$ $[Al^{VI}_{14} O_{31}(OH)][Al^{IV}_2 O][Al^{IV}][Al^{IV}(OH)]$. Here Roman figures mean the atom coordination, and square brackets mean Al-octahedra belts, inter-layer Al-diorthogroups and inter-layer Al-tetrahedra of two types – without OH-groups and hydrated. The OH-groups are identified on the basis of the local basicity balance. The idealized tashelgite formula looks as follows: $CaMgFe^{2+}Al_9O_{16}(OH)$. The following composition (mass. %) corresponds to it: CaO 8.82, MgO 6.34, FeO 11.29, Al_2O_3 72.13, H_2O 1.42, sum 100.00. The real one is given in Table 2.

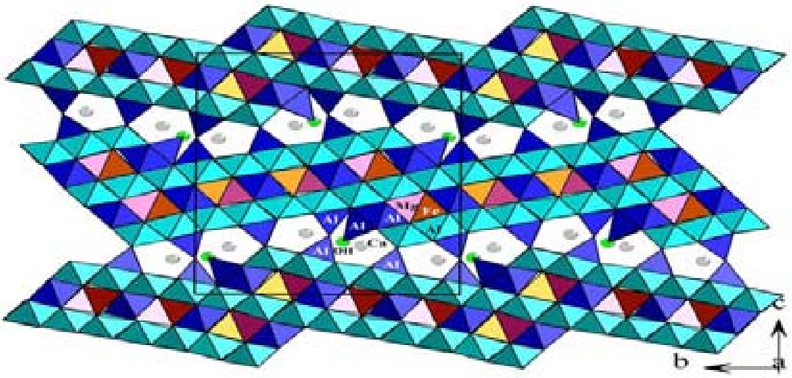

Fig. 4. Crystalline texture of tashelgite: general view, projection *bc* [10]

Table 2. Chemical composition of tashelgite (mass. %)

Components	Content, mass. %	Content Range	References
CaO	7.98	7.75 – 8.33	
MgO	6.75	6.51 – 7.09	
MnO	0.45	0.26 – 0.59	Mn
FeO*	11.32	12.09 – 12.84**	Fe_2O_3
Fe_2O_3**	1.40		
Al_2O_3	70.70	70.10 – 71.61	Fe_2O_3
H_2O***	1.8		
Sum	100.40		

Note: * – the content of total iron re-calculated for FeO makes 12.58%; the division of FeO and Fe_2O_3 was made with the use of the intensity of J(FeKβ_5 / J(FeKβ_1) lines in the X-ray iron radiation spectrum; ** – re-calculated from the total FeO content; *** – on the basis of the thermogravimetry data as loss on ignition up to 1000° C in vacuum.

The sizes of tashelgite inclusions are much smaller than that of Fe-hibonite, making shares of mm and first mm. The mineral usually forms long prismatic needlelike slightly flattened crystals stretched along Axis a (Fig. 5). Almost all of them are polysinthetically twinned along (001) and, as a result, bear coarse longitudinal combination hatching. The main simple forms are {001} and {010}. In addition to crystals, diverse columnar inclusions (up to 1cm across) of fibrous-diverse and radial columnar structure are found.

The colour of individual grains varies from blue-green to colourless and white. The luster is vitreous. Cleavage and jointing are lacking. The tashelgite hardness is very close to Fe-hibonite hardness and makes 7.5 as per the Mohs scale.

The mineral is found in the same association as Fe-hibonite. It includes Fe-hibonite, grossular, vesuvian, magnetite, hercynite and leucosapphire, the typochemical peculiarities of which were described by us earlier [2]. The analysis of the sequence of these minerals formation shows that Fe-hibonite was the first one to crystallize, then grossular, vesuvian of the first generation, magnetite, hercynite and vesuvian of the second generation occurred, and leucosapphire and tashelgite completed

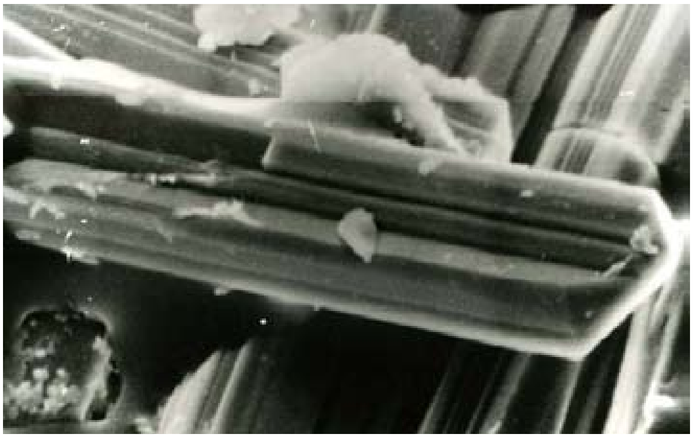

Fig. 5. Long-prismatic tashelgite crystals. SEM image. Field width – 30 micron

mineral formation. The latter grows not only over but partially in vesuvian-2 and hercynite, and also forms isolated crystal phenocrysts in massive calcite. Later, magnetite inclusions and one perovskite grain were discovered in tashelgite with the help of a microprobe.

When examining the above-given paragenesis, it is easy to find out that CaO, Al_2O_3, FeO, TiO_2, SiO_2 and MgO are species-forming components in the sequence of reduction of the value and the frequency of occurrence in minerals. Only calcium is indisputably autochthonous because it determines the composition of marbles. The rest of them require supply and, meanwhile, they are mostly exceptionally low-mobile elements. The latter circumstance makes the idea of the mineral association belongingness to typical calcareous skarns very unlikely [2, 3]. The geological position of occurrence surely contradicts to that as well.

Alongside with that, the confideness of the mineralization zone to the contact of migmatized amphibolites and migmatites of the Konzhinsky complex with marbles definitely indicates their genetic connection with migmatization events, i.e. belongingness to skarnoids. A.I. Letuvninkas was the first one to pay attention to this [13]. Simultaneously he thought that all mineral parageneses of the zone were formed metasomatically and admitted large-scale supply of aluminum, iron and titanium to marbles by acidic solutions rich in volatiles, coming from the amphibolite migmatization zone.

Consequently, the structure of the mineralization zone should be described in detail because it makes this point of view doubtful. According to the undestroyed exploratory trenches and rare natural outcrops, this zone has a near-meridional strike conformable with the strike of surrounding rocks. Massive pyroxene-garnet skarn is developed in its western contact where marbles join directly migmatized amphibolites and migmatites. It consists of an intermediate in composition diopside-hedenbergite and grossular with relatively high iron content (25-30 % of andradite minal). Garnet is subordinated in general. In addition, meionite is present as a secondary mineral, and hydroxylapatite and rutile are present in accessory quantities. The skarnoid association is gradually replaced in the eastern direction by white grainy marble. The latter becomes more fine-grained and gains a typical grey and grey-bluish colour with the distance from the contact. Dispersed Fe-hibonite, vesuvian, subordinated grossular dissemination occurs in it, and marble transfers to typical calciphyre with dotted belt-like mineralization stressing the primary stratification of carbonate sediments which were contaminated some time by the silicate material and oxides resistant to element weathering (Al, Fe^{3+}, Ti). Concretions and small lenses (up to 5-10cm) of silicate minerals (vesuvian plus grossular) and dominating Fe-hibonite occur in the eastern contour of the zone in calciphyres. A continuous belt of sites with varying Fe-hibonite content (above 50 % of the volume), with varying vesuvian, grossular, hercynite, magnetite, corundum, perovskite and tashelgite (found only here) content is traced at the contour eastern flank. The eastern limb of the zone is cut by a tectonic fault.

The identified pattern of construction of the described mineralized zone testifies to its possible formation by means of supply of chemical components (Mg, Fe, Si and partially Al) from the side of Konzhinsky amphibolites suffering migmatization. It occurs from the western side only, in the immediate contact with alumosilicate rocks. Nonetheless, this zone does not contain Fe-hibonite at all. It is impossible to explain the occurrence of the dispersed Fe-hibonite dissemination in calcite marbles far away from the linear zone of contact skarnoids in this way. The nature of mineral distribution in calciphyres and their concentration in the form of large conformable lenses and belts in marble at a significant distance from the contact with the migmatization zone (tens of meters) testify to the only possible way of occurrence of such accumulations. They occur in the process of re-crystallization of laterite-like sediments in particular which some time contaminated the limestones of the carbonate cover inside the ocean uplift composed of metabasites of the MORB type (Konzhinsky amphibolitic complex). As for the metamorphism period, it corresponds to the Riphean age – T = 694±43 mln. years ago according to the recent data [14]. The level of rock transformation corresponded at that time to the transient facies from the green schist to the epidote-amphibolitic one in the low and moderate pressure zones (T=490-570ºC, P=2-4 Kbar). Later, repeated tectonic strata processing occurred together with regional heating and metamorphism, especially during the period of formation of the Kuznetsk-Alatau shear zone. At that time metamorphism reached the amphibolitic stage with migmatization and anatexis occurrence. At the same time the Tashelga polymetamorphic series was formed and the rocks contacting it were transformed. This was repeated metamorphism for them. It led to occurrence of contact skarnoids and re-crystallization of earlier occurred metamorphic mineral parageneses, including hibonite ones. The occurrence of the zone endemic – tashelgite in the composition of the hibonite association is probably associated with this stage.

Calciphyres with metamorphic mineral parageneses are developed in the Tashelga-Mayzaskaya zone and outside the occurrence described above. Nonetheless, they are different in composition there. The most interesting ones are revealed in the basin of the right tributary of the Tashelga River – the Mramorny creek, near the same-name iron-ore deposit where dispersed dotted dissemination of fine (1-3mm) irregular in shape pink-lilac semi-transparent corundum grains is observed, accompanied by black-green phlogopite, dark and emerald-green muscovite, graphite and sulfides (pyrite, pyrrhotite) in small and middle-grained calcite marbles. The discovered mineralization emphasizes the primary marble stratification, sometimes forming lens-shaped (up to 20x50cm) accumulations consisting of small-grained aggregates of the same mineral phases. The grains of all minerals have a “melted” view with rounded peaks and edges of coarsely cut crystals. This indicates nonequilibrium growth conditions. The chemical composition of mica and corundum of this association defined with the help of a microprobe is given in Table 3.

Quite low chrome concentrations in pink corundum and especially emerald-green muscovite draw attention. This muscovite is simultaneously rich in V_2O_3 (0.85 mass %) and thus is not fuchsite

Table 3. Chemical composition of calciphyre minerals (mass. %) in the area of the Mramorny Creek

Components	1	2	3	4	5
SiO_2	-	34.73	43.43	37.49	36.50
TiO_2	0.02	1.26	1.34	-	-
Al_2O_2	99.34	21.17	36.28	3.98	21.81
Cr_2O_3	0.21	0.34	0.08	0.20	0.28
V_2O_3	0.18	0.02	0.85	21.87	11.29
Fe_2O_3	-	-	-	2.48	1.31
FeO	0.17	10.46	1.15	4.00	-
MnO	0.05	0.72	0.03	-	-
MgO	0.00	16.21	0.82	0.09	-
CaO	-	-	-	30.45	22.23
Na_2O	-	0.40	0.64	-	-
K_2O	-	10.23	10.66	-	-
H_2O^+	-	ND	ND	-	1.76
F	-	2.12	0.92	-	-
Sum	99.97	97.66	96.2	100.56	95.18

Note: 1 – pink-lilac corundum; 2 – phlogopite; 3 – emerald-green muscovite; 4 – emerald-green goldmanite [17]; 5 – vanadium epidote – mukhinite [18].

frequently accompanying noble corundum in ruby-bearing calciphyres [15, 16] but muscovite rich in roscoelite minal. In this context we have to recall two more rare minerals of the Tashelga-Mayzaskaya zone – goldmanite and mukhinite.

The first one of them is calcium-vanadium garnet and the second one is vanadium epidote. They were discovered in the second half of the 20th century in metamorphosed carbonate rocks of the Mramorny deposit. Mukhinite was discovered here for the first time as a new mineral species [18], and goldmanite was found in the deposit first time for the USSR [17]. Both minerals are found in the same paragenesis and are in close aggregation forming fine grains and hypidiomorphic crystals from shares of mm to 3 mm in size in a thin veinlet (up to 1 cm) together with later sulfides – pyrite, pyrrhotite, sphalerite and galenite. Mukhinite individuals have a thick black colour, at the background of which emerald-green transparent grains of vanadium garnet are very contrast. They have all advantages of a true gem. It was noted that this epigenetic mineralization is confined to the calcite marble zone highly enriched with emerald-green vanadium-bearing muscovite. It evidently became a source for this element for its own minerals in the course of the metamorphogenic-hydrothermal process.

It should be noted here that classic tsavorite deposits (of vanadium-bearing grossular) in the Mozambique mobile belt of Eastern Africa similar in the geological position (contact of marble strata with graphitized crystalline slate and gneiss), according to foreign researchers, were formed in the process of regional carbonate-clastic strata metamorphism reaching the level of the amphibolitic facies [19]. Basic carbonate sediments some time contaminated with stable weathering products of alumosilicate rocks surrounding sedimentation basins served as the sources for vanadium and other elements xenogenic to marbles.

The above-described examples of the mineralization in carbonate rocks of the Tashelga complex demonstrate the cases of direct impact of the basic sedimentary rock composition peculiarities on the nature of metamorphogenic parageneses occurred later, because the components some time contaminating the sediment are transformed into independent mineral phases in the process of re-crystallization. Then they can partially dissolve and re-deposit at the following metamorphism stages or in the process of metasomatosis, forming new mineral species. The system generally remains open, and the specifics of its phasal composition is defined by low-mobile and inert chemical elements Si, Fe, V, Ti and, of course, Al. However, the observations show that this impact is also traced in a weakened form in other even relatively closed endogenic geological systems of the zone, for example granite pegmatites. They are significantly younger than metamorphogenic and metasomatic rocks, bedding in them in the form of conformable – cross-cutting vein bodies. In the earliest barren veins the impact of surrounding marbles leads to occurrence of rare diopside crystals in vein contacts. No xenogenic minerals are formed in later spodumen pegmatites, and rock-forming albite-oligoclase is developed instead of albite regular for them. A visible share of grossular minal occurs in the almandine-spessartine accessory garnet. The indicated facts testify to the occurred assimilation of calcium of the marbles hosting veins with basic pegmatite melts.

In the conclusion it should be stressed that the rare natural mineralization identified in the Tashelga-Maizaskaya zone, in addition to the scientific interest, is definitely of practical value as well, primarily as the source of unique collection material and, probably, extremely deficient gems.

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Редкие и новые минералы ташелгино-майзаской зоны Горной Шории, их особенности и природа

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Рассмотрены редкие и новые минералы (ташелгит, мухинит, хибонит, голдманит и др.), обнаруженные в ходе геологических исследований XX и XXI веков в карбонатной толще Ташелгинского полиметаморфического комплекса (R3-Rz3ts), слагающего грабен–синклинальную структуру в пределах Кузнецко-Алатаусской сдвиговой зоны Горной Шории. Показано, что уникальная минерализация скарноидов, кальцифиров и метасоматитов района обусловлена процессами метаморфизма и последующего метасоматоза исходных карбонатных морских осадков, загрязненных латеритными продуктами выветривания метабазитов. Установлено влияние химизма исходных пород на всю последующую полихронную эндогенную минерализацию, даже в таких относительно замкнутых системах, каковыми являются гранитные пегматиты района.

Ключевые слова: Горная Шория, Талшелгино-Майзаская зона, ташелгит, мухинит, Fe-хибонит, голдманит.
