

МІНЕРАЛОГІЯ, ГЕОХІМІЯ ТА ПЕТРОГРАФІЯ

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PECULIARITIES OF DISTRIBUTION AND COMPOSITION OF BETAFITE FROM DIFFERENT FORMATIONS OF THE ALDAN SHIELD (SAKHA-YAKUTIA)

Світлій памяті Юрія Капустіна присвячується!

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Character of Nb and Ta distribution in the different geological formations of the Aldan Shield are given in this article. To get idea about betafite from different endogenic etalon formations the authors analyzed its well known locations in the pegmatites, skarns, carbonatites, metasomatites and late veins segregations. Geological setting and mineralogical composition of the apatite-bearing rocks from the Aldan Shield are described, and the most significant in scale metamorphosed carbonate and silicate varieties among them have been distinguished. Apatite mineralization in magnesium skarns and metasomatites is developed locally.

Titanite and betafite are the main concentrators of Nb and Ta and apatite is typical accompanying mineral in the studied rocks. Betafite was detected in the pegmatite bodies from magnesium skarns and metasomatites of the Shield with irregular distribution within rocks rich and poor in apatite, but was not found in the most developed apatite-carbonate rocks which are regarded as ores of the Seligdar type, so it cannot be mineralogical indicator for this type of ores.

Late carbonate generations are significantly enriched in light carbon and oxygen isotopes in contrast to positive $\delta^{13}\text{C}$ values in apatite-carbonate bodies of the Seligdar deposit and its family and the highest $\delta^{18}\text{O}$ values. We used these indicators to distinguish origin of the rocks with various carbonate generations, which have different amounts of betafite. Appearance of betafite is determined by primary composition of the initial rocks. Chemical composition of betafites from the skarns and metasomatites is similar, but with local variations. The most significant feature of the mineral composition is very low Ta content. Titanite is characterized by variable amounts of Nb and Ta in scale of sectors as well as within separate grains.

Keywords: betafite, titanite, Nb and Ta, metamorphic apatite-carbonate ores, Aldan Shield, pegmatites, metasomatites, skarns, carbonatites, C-O isotopes

Introduction and statement of the problem. Betafite is rich in Ti member ($2\text{Ti} \geq \text{Nb} + \text{Ta}$) of the pyrochlore group (Christy and Atencio, 2013; Hogarth, 1977), which was firstly discovered in pegmatites from the Betafo area, Madagascar (Turner, 1928). Later betafite finds were described in granite pegmatites and skarns of the Kragero, Norway, and Bancroft, Canada, (Bjorlykke, 1937; Hogarth, 1959; Hogarth, 1977), carbonatites, alkaline rocks, and young pegmatites (Kapustin, 1971; Lents and Suzuki, 2001; Pieczka, 2010) in various regions. Lately, betafite has been determined in the modern active volcanoes areas of Italia (Camara et al., 2004). Betafite is currently becoming interesting from mineralogical point of view, as a phase with wide substitutions of Ti, Ta, Nb, Ca, U etc. in the mineral structure and important indicator of different petrologic processes, and from industrial one as a mineral, which is bearing significant elements for modern technique and high technology (Lumpkin et al., 2001).

The discovery of the Seligdar apatite deposit in the Precambrian rocks of the Aldan Shield (Bulakh et al., 1990) has stimulated here scientific investigations of apatite-bearing formations. Apatite-carbonate mineralization at the Aldan Shield was earlier known after different geological mapping and exploration works and rich in apatite Precambrian rocks were described within metamorphic sequences of the Shield (Fig. 1) as the conformable bedding of apatite-bearing and host gneisses, crystalline schists, calc-silicate rocks and marbles (Vinogradov et al., 1975). Their regional distribution and geological position is confirmed by the lithological control of apatite-carbonate mineralization (Bulakh et al., 1990; Vinogradov et al., 1975; Guliy and Wada, 2003).

In opposite to these data betafite finds in various apatite-bearing metasomatites from the manifestations of the Nimnry River basin as well as presence of Nb and Ta in phlogopite of the Seligdar deposit, some authors used to state (Entin et al., 1987; Entin et al., 1989) an indicator role of betafite-apatite association for apatite-bearing ores of the Seligdar type and its carbonatite origin.

We initiated our investigation of betafite distribution in the Precambrian rocks of the Aldan Shield, and peculiarities of the mineral composition from different formations of the Shield, to determine its origin and estimate possible betafite role as carbonatite indicator for the Seligdar apatite-carbonate ores type.

Analysis of latest investigations. Detailed geological exploration works at the Seligdar apatite deposit were accompanied by prospecting and assessment of analogous objects in other sectors of the Aldan Shield (see fig. 1). Due to these efforts, geologists of the Yakutskgeologiya Industrial Geological Enterprise discovered and evaluated apatite deposits in basins of the Bol'shoi Nimnry, Yllymakh, and Timpton rivers (Bulakh et al., 1990; Guliy and Wada, 2004), which are located at the southern end of the apatite-bearing zone (see fig. 1). Major ore bodies consist of apatite-bearing carbonate and silicate rocks that are similar to earlier studied rocks in the Central Aldan deposits (Bulakh et al., 1990).

Idea about mantle carbonatite nature of the apatite-bearing ores of the Seligdar firstly appeared because of formal main similarity of carbonate-bearing mineral associations of the rocks and carbonatites (Kapustin, 1971; Mineev et al., 1978; Entin et al., 1987) and later modified to mantle-crust carbonatite origin under influence of folding structure of the deposit (Bulakh et al., 1990) with intercalations of apatite-bearing rocks and hosting gneisses and crystalline schists of the Fedorovskaya Formation within limits of ore bodies, the evidences on the metasedimentary carbon and oxygen isotopic composition of carbonates from apatite-carbonate ores (Guliy and Wada, 2003; Guliy and Wada, 2004), difference in REE and Sr enrichment of apatite from carbonatite, ultrabasic and alkaline rocks (Kapustin, 1971; Mineev et al., 1978; Pushkarev et al., 1989; Guliy et al., 2017).

Pinpointing unresolved issues. The most exotic hypotheses of apatite-carbonate rocks origin have given place to better documented models about the primary fold structure and metamorphogenic nature of the deposit (Bulakh et

al., 1990; Guliy and Wada, 2003; Guliy and Wada, 2004). At the same time, information on betafite finds in some "typical manifestation" (Entin et al., 1989, p. 83) or "studied character sector" (Entin et al., 1987, p. 948), without any indication of locality, with apatite-bearing rocks were involved to assert genetic relationships between the Seligdar deposit and carbonatites. After these researches there are no clear evidences about genetic relations of betafite and apatite-carbonate rocks of the Aldan Shield, in general, and the phosphate ores of the Seligdar deposit, in particular.

Carbonatites and genetically related alkaline rocks are regarded as mantle differentials and it determinates their specific composition and origin (Kapustin, 1971), but betafite presence in various environment situations itself can't be suggested meaning on its origin. So, it is necessary to search for paragenetic associations of betafite and carbonate to determine peculiarities of the primary betafite.

Setting objectives. This paper presents results of the systematic search of betafite peculiarities from various endogenic complexes to determine its origin in apatite-bearing formations of the Aldan Shield. We attempt to trace genetic links between the betafite finds and hosting its primary and

metasomatic rocks, to estimate the role of parent's sources of the mineral, and to outline conditions of the formation and preservation of initial rocks.

Research part and findings validated.

1. Geological setting and main rocks types.

Structural situation, shape of the ore bodies, analogous apatite-carbonate composition of the ores are common features of all apatite deposits of the Aldan Shield, but a big variation in thicknesses and lengths is different for the most deposits. The most significant dimensions are typical for the Seligdar deposits where total thickness of the intercalated apatite-calcites rocks and host gneisses and crystalline schist in limits of industrial counter is about 1000 m.

The most variable dimensions of the apatite-bearing rocks are typical for deposits in basins of the Bol'shoi Nimnyr, and the Yllymakh rivers. Besides its features among these deposits there are sharp compositional variations of apatite-bearing rocks (Tab. 1). Deposits on this territory are represented by small in size ore bodies, often they are like veins in shape, and some of them are rich in quartz (Bulakh et al., 1990; Guliy and Wada, 2004).

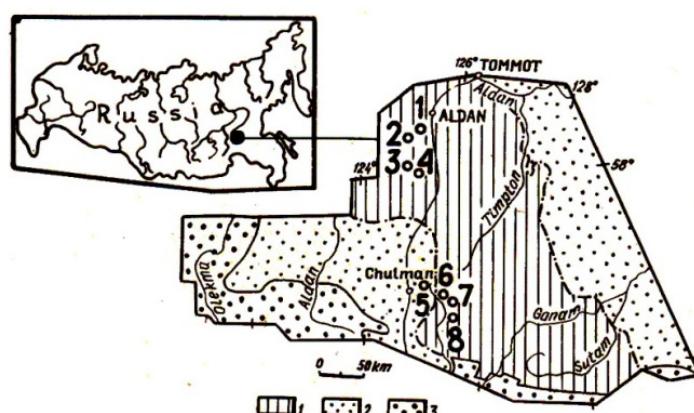


Fig. 1. Location scheme of apatite deposits of the Aldan Shield.

Location: 1- Seligdar, 2- Niryandzha, 3- Dorozhniy, 4- Mustolaakh, 5- Ust'Chul'man, 6- Levyi Byrnyi, 7- Birkeen, 8- Chukurdun. (1) – high-grade metamorphism, (2) – transitional metamorphic facies, (3) – relatively low-grade metamorphism (Kitsul et al., 1979)

Table 1

Mineral composition of the apatite-bearing rocks from sectors of the Bolshoi Nimnyr River basin

Sector	Rocks	№ samples	Minerals (vol. %)						Sum
			apa-tite	Dolomite	calcite	quartz	chlorite	hematite	
Dorozhniy	Apatite-carbonate	к. 1	8,7	84,0	-	-	7,3	-	100,0
		к. 2	22,5	58,0	-	4,0	14,0	1,5	100,0
	Trubka	12	1,2	74,0	10,0	9,8	5,0	-	100,0
		14	5,2	56,1	18,1	8,3	11,3	1,0	100,0
Osenniy List	Apatite-quartz	16	0,5	-	-	93,5	6,0	-	100,0
		3	1,0	-	-	98,0	1,0	-	100,0

These characteristic deposits in this area are similar to numerous vein-types metasomatite deposits rich in rare, rare earth and radioactive elements (Goroshko et al., 1975; Radkov et al., 2015). Quartz, carbonates, apatite, chlorite are main minerals in these deposits and betafite, titanite, sulfides, zircon were determined as accessory phases (Bulakh et al., 1990). All vein-types metasomatite deposits are connected to late stages of tectonic-magmatic activation of the Aldan Shield and also related to faults zones (Radkov et al., 2015).

Local distribution and small in scale are apatite-bearing formations which are connected to the magnesium skarn deposits (Bulakh et al., 1990). It bears similarity to calc-silicate rocks, which are developed together with apatite-bearing

rocks and obligated to the presence of phosphorus and favorable physic-chemical environments for the precipitation of the protophosphate sediment in paleobasins elsewhere.

2. Sampling and analytical methods.

2.1. Material studied.

We collected diverse data on distribution of betafite in different endogenic formations, its connection to various mineral associations, distinguished features of the mineral for separate and individual petrologic regimes, based on early published information from scientific works as well as using our own materials.

During field surveys we observed drilling cores after prospecting works by geologists of the Yakutskgeologiya Industrial Geological Enterprise, quarries of the magnesium skarn deposits, and outcrops within area of the apatite-bearing

rocks distribution to get information about betafite presence at the various formations of the Aldan Shield and its location and composition peculiarities.

2.2. Analytical methods.

Beside routine geological investigations we carried out petrographic studying of thin sections to determine crystallization ordering for minerals of apatite-bearing rocks and its hosting gneisses, schists, marbles, magmatites, skarns, pegmatites, metasomatites etc., which are typical for the Aldan Shield region.

A set of different in size samples we used to find and determinate peculiarities of betafite and other accessory phases among the apatite-carbonate ores. We also studied samples with different weights from a couple of kilograms up to 40 tons (Bulakh *et al.*, 1990), which have been prepared for technological testing to determine the quality of the ores as well as discover accompanied minerals, including betafite.

Microbeam analyses of betafite, titanite, apatite and other associated minerals grains were carried out using a SX50, Cameca according to routine procedure. Involved instruments include facilities of the Geological Survey of Canada and Carlton University (Ottawa, Canada), Mekhanobr-Analit and PGO Sevzapgeologia (St.-Petersburg, Russia). We analyzed chemical composition of separate phases as well as components variations within grains. Set of the betafite and titanite grains were used to determine its inner heterogeneity and distribution of Nb and Ta in co-existing phases.

The oxygen and carbon isotopic compositions of carbonates from the typical apatite-carbonate ores, as well as from late carbonate veins, metasomatites, and skarns, were analyzed in the Laboratory of Stable Isotopes (Institute of the Lithosphere of Marginal Seas, Moscow). The relative difference in oxygen and carbon isotope ratios in CO_2 (gas) was measured on a Varian MAT-250 mass spectrometer. The accuracy of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ measurement in samples was $\pm 0.1\text{\textperthousand}$ and $\pm 0.2\text{\textperthousand}$ respectively. The Craig correction was taken into consideration for the determination of $\delta^{13}\text{C}_{\text{sample}}$ (PDB) and $\delta^{18}\text{O}_{\text{sample}}$ (SMOW). To determine metasomatic alteration of initial rocks and nature of new formed carbonates we used the diagram of $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ according to procedure described early for different carbonate rocks of the Aldan Shield (Guliy and Wada, 2003; Guliy and Wada, 2004).

3. Obtained results and discussion.

3.1. Character of betafite distribution in the endogenic formations.

The first most famous locations of betafite are known (Turner, 1928) from the Madagascar pegmatites. The big in size and weight betafite crystals are located in zones formed essentially of quartz and altered biotite with orthite, tourmaline and traces of former beryl crystals. A number of pegmatite locations near Kragero (Norway) with betafite had been described (Bjorlykke, 1937) to give a mineralogical description of the objects mined many years before. The pegmatite dikes at the Tangen feldspar quarry are surrounded by amphibolites and chiefly composed of cleavelandite and quartz, but sometimes with numerous irregular patches of microcline. Betafite in these dikes is associated with noted (Bjorlykke, 1937) microcline, quartz, oligoclase, cleavelandite, tourmaline, topaz, magnetite, hematite, apatite, yttriotitanite, orthite, alvite, thorite, columbite, and phenacite. Within pegmatites betafite crystals occur both in microcline and cleavelandite. The last has been stained red around the nodules of betafite. To distinguish pegmatites in different parts of Norway there was used (Bjorlykke, 1937; Pršek *et al.*, 2010) the plenitude of Ca as indicated by the presence of calcite, rare minerals, hellandite, titanite, and betafite.

Similar betafite occurrences connected to pegmatites had been described (Hogarth, 1959; Lents and Suzuki,

2001) in the Bancroft Region, Ontario, Canada, due to feldspar mining and prospecting for uranium in Canada. D. Hogarth essentially expanded a number of betafite-bearing rocks and added (Hogarth, 1959) to previously known pegmatites also granite-syenite, irregular carbonate bodies, calcite-fluorite-apatite veins, radioactive breccias and carbonatites, which are developed in some adjacent parts of the Ontario and Quebec Provinces. Calcite-fluorite-apatite veins cut granite pegmatites and hornblende gneisses, and they are traced by betafite crystals in association with apatite, calcite and mica. More significant betafite concentration is described (Hogarth, 1959) in apatite-rich portions in the Basin carbonate body, which is regarded as a carbonatite or as a mineralized lens of the Grenville limestone.

Clastic structures north of Meach Lake were previously described (Hogarth, 1959) as conglomerates or explosive breccia, and the rocks are distributed irregular, showing independence from primary substratum. Calcite, apatite and biotite are common matrix minerals with significant variations of its amounts from occurrence to occurrence. Apatite occurs as rounded prisms which are often fractured near betafite. Betafite crystals look fresh, but the matrixes of breccia are rich in limonite or hematite dust and are light brown in color.

Numerous amphibole veins hold small amounts of biotite, quartz, apatite and pyrite. Thin sections showed minor hematite, titanite, calcite, pyroxene, zircon and plagioclase. Betafite occurs as small rounded octahedral and is most common where apatite is abundant.

The vein carbonate is notably impure. The minerals include apatite, pyrite, pale amphibole and phlogopite, with rare quartz, betafite, zircon, magnetite and feldspar. The betafite was observed in the apatite-rich zone and was localized along strike fractures near the hanging-wall of the carbonate body. Grains usually show numerous inclusions of apatite and calcite. Hematite often rims the grains.

There are two main kinds of carbonatites, early and late (Kapustin, 1971). Early carbonatites (sevites) form a big in thickness monolithic stocks (up to 5 km in diameter), systems of conic-ring-shaped or linear cutting veins (up to 10 km in length) with sharp contact. These veins have regular composition and texture, without visible zonation, in boarder parts are represented by eruptive breccia, and often contain xenoliths of hosting rocks. Within contacts, in narrow zone (from 0.1 up to 1.0 m), all hosting rocks are altered with new-formed of phlogopite (biotite), pyroxene, and apatite. Pyrochlore, gatchetolite, baddeleite, calcirtite or zircon are accessory minerals of sevites. High contents of Ti, REE (mainly Ce series), Nb, Sr (typically from 0.1 up to 1.0 %), and Ta, U, Th (less than 0.1 %) are typical for these rocks.

Early carbonatites have systems of features which are typical for intrusive (or effusive-volcanogenic) rocks, but intensive magnesium-alkaline metasomatism of hosting rocks is permanently connected to its. With big in scale concentrations and regular enrichment by apatite, grade of P_2O_5 everywhere is up to 3-7 wt.%. Minerals of Nb and baddeleite are associated with apatite in all massive (Kapustin, 1971).

Late carbonatites are multistage and they form series of linear veins, small stocks, sometimes with clear symmetric zonation, mineralized brecciated zones with intensive metasomatism of hosting rocks. Brecciated cavity-druse crustification and vein structures are typical for the late carbonatite. Besides extremely irregular, often zoned structure of its bodies, late carbonatites are everywhere enriched by Sr, Ba, REE, with amount commonly more than 1-5 %. But these carbonatites don't contain their own Nb concentrations, and only in some places of ankerite development within hosting earlier pyrochlore-bearing carbonatites, where pyrochlore

and gatchetolite are fully replaced by columbite, Nb concentrations are increasing (equal or higher than 1%). In structure, composition and character of near vein alteration late carbonatites are similar to hydrothermal sulfide-carbonate veins and, probably, were formed under circulation of hydrothermal solutions, which are retained after crystallization of earlier carbonates.

3.2. *Ta and Nb distribution and its concentrators in the hosting rocks of the Aldan Shield.*

Results of Ta and Nb distributions in different formations of the Aldan Shield geologists used to create indicators for exploration of rare, radioactive elements and precise metals (Goroshko et al., 1975; Radkov et al., 2015). According to previous explorations at the Aldan Shield, relatively high Nb and Ta concentrations dominantly form only geochemical anomalies which are connected to pegmatite veins and metasomatites reworking after tectonic-magmatic activation of the Precambrian basement. Some of them are located at the western and southern borders of the Shield and to the eastern areas from the rich in apatite deposits zone (see fig. 1). In most cases the Nb and Ta manifestations were discovered during mapping and explorations of uranium mineralization.

At the Central Aldan Nb and Ta mineralization is related to alkaline granites (Radkov et al., 2015) where numbered quartz-feldspar veins are developed in linear zones of hydrothermal altered rocks after primary metamorphic rocks of the Fedorov Formation. The last rocks are often red in color due to hematite pigmentation. Veins pegmatites which are located within the magnesium skarns deposits have commonly simple composition.

Beside Nb and Ta anomalies, vein pegmatites, alkaline granites and metasomatites in this part of the Shield are rich in uranium, phosphorus, and some associated rare and rare earth elements mineralization. Therefore, this area was under exploration and small in scale uranium deposit Osenenny List (near Dorozhnyi and Mustolaakh deposits, see fig. 1) has been established (Radkov et al., 2015). Here, phosphorus-rare metals – uranium mineralization is located within carbonate – quartz – epidote – chlorite metasomatites and breccia which are connected to linear zones with thicknesses up to a few dozen meters. Gneisses and crystalline schists of the Fedorov Formation are hosting rocks for developed zones. Uraninite, coffinite, betafite associated with apatite, pyrite, titanite and fine grained hematite are common minerals in the ore aggregates. Typical limits of the Nb concentrations are from 0,11 up to 0,72% Nb₂O₅, under phosphorus amounts from 0,05 up to 7,72% P₂O₅.

For these ore concentrations have been noted (Radkov et al., 2015) age formation from 650 up to 1420 m.y. We obtained (Pushkarev et al., 1989) the united Pb – Pb isochrones with 1854 ± 7 m.y. for apatite from the apatite-carbonate ores of the Seligdar, Mustolaakh, Niryandzha deposits and this date is older.

At the Seligdar deposit Nb concentrations (from 0.002 up to 0.06 % of Nb) have been reported to have phlogopite from near ore magnesium skarns, which are represented by diopside, pargasite-diopside, pargasite and diopside-plagioclase rocks. Relatively similar levels of Nb (from 0.03 up to 0.05 % Nb) are given (Entin et al., 1987) for the Elkonka and Emeldzhakskarn deposits and barite-hematite-quartz ores of the Hematitovoe deposit. Within basin of the Bolshoi Nimnyr River (see fig. 1), where metasomatites with rare metals and uranium mineralization, noted above, are developed, the analogous Nb concentrations have been suggested for the metasomatites from the Saap-Kyuel, Kaplia, Dorozhnyi sectors. Information on Ta concentrations and finds of betafite for this area from the authors was absent, but later on they published articles (Entin et al.,

1987; Entin et al., 1989) with description of betafite in apatite-bearing ores of the Seligdar type. However, in these cited articles any suggestion from which place authors collected betafite is absent. There is not also any mention on betafite presence in the apatite-carbonate ores of the Seligdar deposit.

Previously we suggested betafite finds in the late metasomatic rocks of the Trubka, Dorozhnyi, Kaplia etc. manifestations within basin of the Bolshoi Nimnyr River (Bulakh et al., 1990). These rocks are rich in quartz, epidote, chlorite, and apatite and in fact they are hosting Nb, Ta and uranium mineralization. We also detected permanent Nb and Ta presence in the titanite from the apatite-diopside rocks of the Bish deposit, which is located to the south from the southern apatite deposits (see fig. 1) and have relatively high abundances of Nb and Ta (up to 0,17% Nb₂O₅ and 4,40 % Ta₂O₅). Similar in mineral composition rich in titanite apatite-diopside rocks and metasomatites with the high levels of Nb (up to 0,35 % Nb₂O₅) and Ta (up to 1,71 % Ta₂O₅) are developed in the Bolshoi Nimnyr River basin. Significant Nb and Ta concentrations (up to 0,16 % Nb₂O₅ and 1,49 % Ta₂O₅) we determined in titanite from feldspar rocks of the Seligdar deposit. Due to additional research of the titanite homogeneity we observed inverse ratio in Nb and Ta distributions in cores and rims of the separate titanite crystals.

Extremely high Nb/Ta ratios (up to 239) described (Chen Y.-X. and Zheng Y.-F., 2015) for metamorphic titanite from ultrahigh-pressure metagranite in the Sulu orogen, CPR. The increase of Nb/Ta ratios for the metamorphic titanite is associated more with a decrease of Ta than an increase of Nb, suggesting the control of fluid composition on the titanite Nb/Ta ratios. Taking into account a wide betafite development after rich in titanite rocks in the Bolshoi Nimnyr River basin with intensive brecciation of the initial rocks we can regard the titanite as a precursor of betafite according to the described substitutional scheme (Minerals, 1967; Minerals, 1968) without any relations to carbonatites.

3.3. *Chemical composition of betafite*

We studied betafite from the Emeldzhak deposit which has up to 6.49 % of Ta₂O₅ and 9.6 – 11.4 % of CaO under ratios Nb₂O₅/Ta₂O₅ = 6 – 8 and Nb₂O₅/TiO₂ = 2.7 – 3.5 (tab. 2). After calculations of the results of this mineral (№ 5 in the table 2) with the typical formula we obtained final form: (Ca_{1.00} U⁴⁺_{0.32} Na_{0.29} TR_{0.06} Th_{0.03})_{1.70} (Nb_{1.15} Ti_{0.77} Ta_{0.08})_{2.0}O_{6.00} [F_{0.72}(OH)_{0.28}]_{1.00} x 0.95H₂O. Betafite from the Emeldzhak is characterized by clear high Nb amount and low concentrations of Ti and U.

Aldan's betafite is sharply distinguished from gatchetolite from carbonatites in composition. The latter contains 8–25 % of Ta₂O₅ under ratios Nb₂O₅/Ta₂O₅ = 3 – 5 and Nb₂O₅/TiO₂ = 3 – 8 with U₃O₈ up to 20 % and CaO ≤ 14 %. There is a direct positive correlation between Ta and U concentrations in the betafite. Gatchetolite is found only in the early calcite carbonatites and during its dolomitization the mineral is replaced by pyrochlore with high Nb amount (U < 1 %). Gatchetolite and pyrochlore are replaced by columbite during ankeritization.

Betafite from the quartz-chlorite diafiorites of the Dorozhnyi deposit (Guly et al., 2017) contains unusually low Ta concentration (tab. 3) with ratio Nb₂O₅/Ta₂O₅ > 300, while Ta₂O₅ amount for majority samples of this mineral is 3–10 %, with minimal concentration in 0.54 % (Minerals, 1967), and ratio Nb₂O₅/Ta₂O₅ is typically within limits of 10–30 (maximum 80). Concentration of TiO₂ and ratio Nb₂O₅/TiO₂ in the mineral is common for betafite. Judging by the Ti content, in the Aldan betafite should be about 20 % of UO₂ (this component didn't determine in the analysis and, possibly, it was included to "other").

Table 2

Chemical analyses of betafite from magnesia skarns of the Aldan Shield (number 4–7) and the Near Baikal region

Components	Number of analysis			
	5	6	7	16
Nb ₂ O ₅	35.27	34.50	57.64	36.64
Ta ₂ O ₅	4.32	5.49	2.75	3.95
TiO ₂	12.84	13.73	3.17	13.46
ThO ₂	2.00	2.15	0.46	1.90
U ₃ O ₈	19.50	21.11	3.11	20.90
TR ₂ O ₃	2.11	1.80	2.68	2.78
FeO	2.73	2.36	-	2.64
MnO	-	9.61	-	0.71
CaO	12.42	0.10	-	9.76
(Sr,Ba)O	0.22	2.60	-	0.17
PbO	1.67	1.60	-	1.90
Na ₂ O	1.85	-	-	0.81
H ₂ O	3.80	-	-	3.90
F	2.93	-	-	2.05
O=F ₂	1.20	-	-	0.84
Σ	100.46	-	-	100.73

Note. Analyses 5–7 – skarns of the Emeldzhak deposit. Analytic – G.V. Lyubomilova. Analysis 16 – skarns of the Slyudianka deposit. Analytic – T.A. Kapitonova. n.d. – not detected.

Table 3

Chemical composition of betafite from apatite-bearing rocks of the Bolshoi Nimnry River basin (wt. %)

Components	Number of sample			
	1	2	3	4
Nb ₂ O ₅	30.39	31.20	30.62	40.45
Ta ₂ O ₅	0.10	N.d.	N.d.	-
TiO ₂	14.92	15.17	16.32	13.91
ZrO ₂	1.52	N.d.	N.d.	-
SiO ₂	3.06	2.73	1.25	-
TR ₂ O ₃	0.23	0.23	0.73	24.03
Al ₂ O ₃	0.32	0.44	0.14	-
FeO	2.86	2.99	2.65	-
MnO	0.18	0.14	0.15	-
CaO	19.15	19.53	19.88	20.52
PbO	0.39	0.43	0.49	-
Na ₂ O	0.62	0.82	0.55	-
I.o.v	22.19	22.37	23.56	-
Sum	96.54	96.15	96.34	98.91

Note. Samples 1–3 – (Entin et al., 1987; Entin et al., 1989). Analytic – V.F. Makhotko, 4 – authors data. Analytic – O.A. Yakovleva.

There is an unusually high level of CaO concentrations (up to 19 %), although it is commonly around 3 – 9 % (maximum up to 11.54 % (Minerals, 1967). Calculation of data № 1–3 from table 3 (Entin et al., 1987) on typical betafite-pyrochlore formula (Ca, U)₂ (Nb, Ti)₂O₆ Fe nH₂O the formulas of analyzed samples (№ 1–3) led to the next form: (Ca_{1.7}Na_{0.1}Fe²⁺_{0.2})_{2.0} (Nb_{1.1}Ti_{0.9})_{2.0}O_{6.7} nH₂O. According to the chemical analysis and our results the mineral contains about 20% UO₂, and thus its final formula should be more complicated: (Ca_{1.7}U⁴⁺_{0.4}Na_{0.1}Fe²⁺_{0.2})_{2.4} (Nb_{1.1}Ti_{0.9})_{2.0}O_{7.3} nH₂O (there is a possibility of presence in the mineral about 2–3 % of F). These formulas show clear overstating of the cations amounts (most likely Ca) up to 7–10 mass %. For all minerals of the pyrochlore group and especially for betafite there is a typical deficit of cations in Ca group (formula coefficient of this group is commonly less than 2 (1.2–1.7).

To generalized collected and authors' data on chemical composition of the betafite from different geological formations of the Aldan Shield (table 2 and 3) we used triangle diagram of Ti – Nb – Ta (fig. 2) which takes into account role of the main classification constituents of the pyrochlore group (Hogarth, 1977). Additional betafite compositions for carbonatites, pegmatites and skarns are plotted from data in (Minerals, 1967; Minerals, 1968; Sakharova, 1955).

On the diagram the figurative points of betafite from the apatite-bearing rocks are located on or near the Ti – Nb line. They are concentrated very close to the line between betafite and pyrochlore fields, but in general are determined as betafites. Compositional data for other genetic types of the

rocks used to draw the diagram are much more variable and are not located in some limited fields. From the noted configurations we can assume specific composition of betafite from the apatite-bearing rocks which is far from common for carbonatite data.

3.4. Isotope signatures in carbonates of the region

In the δ¹³C – δ¹⁸O coordinates the isotopic compositions of carbonates from layered apatite-carbonate rocks of all apatite deposits yield a scatter of δ¹⁸O values from +18.0 up to +21.6 ‰, SMOW without any depending from apatite resources. The studied carbonates are characterized by positive δ¹³C values in sheeted apatite-carbonate bodies of the Seligdar deposit and its family (up to +4.4 ‰, PDB) and negative values in late spatially associated veinlet and isolated pockets (δ¹³C values from -0.7 up to -5.2 ‰, PDB).

Late carbonates from veinlets and pocket-like aggregates are significantly enriched in light carbon isotope (lowest δ¹³C value is -5.2 ‰, PDB for carbonate of the Khayumkan sector).

Carbonate from skarns of the Emeldzhak deposit is depleted in ¹³C and ¹⁸O (up to δ¹³C = -6.6 ‰, PDB, and δ¹⁸O = +13.5 ‰, SMOW). Similar depleted ¹³C values we determined for carbonates from the calciphyres and marble (up to δ¹³C = -3.8 ‰, PDB), but carbonates from the Ariabilovka, Sivagli, Mariika deposits are enriched in ¹⁸O (δ¹⁸O vary from +20.3 up to +21.6 ‰, SMOW) and analogous to ¹⁸O values in carbonates from the apatite-carbonate rocks of the Shield (Gulyi and Wada, 2004).

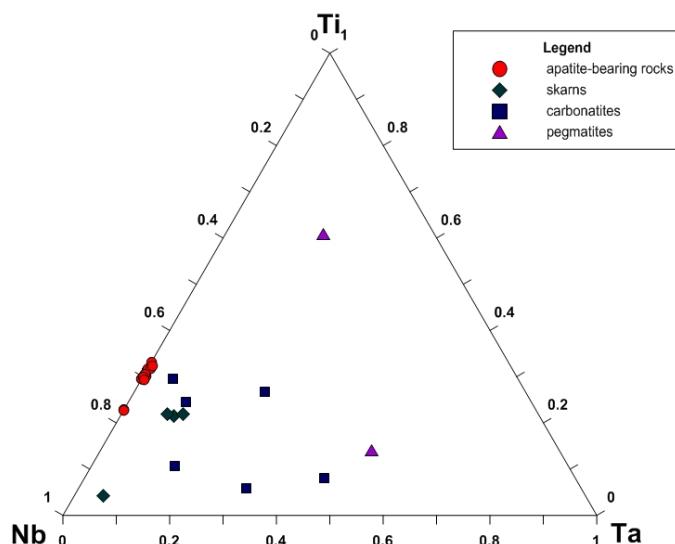


Fig. 2. The triangle diagram of Ti - Nb - Ta for betafite from different geological formations of the Aldan Shield and elsewhere (Minerals, 1967; Minerals, 1968; Sakharova, 1955)

4. Discussion of the results and conclusions.

Betafite polygenetic origin is well known and its finds were described in fenites, albitites, "apogranites", alkaline metasomatites and nepheline syenites. But the most significant typical betafite finds are in granite pegmatites of Norway, Madagascar, Finland, Karelia, and Kola Peninsula, South-Western areas of the Near Baikal and syenite pegmatites of the Urals (Minerals, 1967; Minerals, 1968). According to comparison of betafite from different geological locations similarities of betafite from the Aldan samples and granite pegmatites of the Urals and Norway were established as well as sharp difference from gatchetolite from carbonatites.

There has been shown clear difference between apatite-carbonate rocks of the Seligdar type and any kind of carbonatites. The apatite-carbonate rocks differ from sevites by dolomite composition, absence of silicates (diopside, eugenerite, phlogopite, gastinsite, montichellite) which are typical for carbonatites, and magnetite, baddeleite, Nb minerals, absence of indicator for carbonatites fenitization and near-contact alkaline-magnesium metasomatism (with new-formed phlogopite, pyroxene, and olivine), and extremely low levels of Sr, REE, Nb, Ta, Zr, Ti. In contrast to the late carbonatites, the Seligdar apatite-carbonate ores are not completely composed of Sr, Ba, REE and Ti minerals, and sulfides, and are characterized by extremely low concentrations of Sr, Ba, REE, Ti, Fe (II), S, F, and absence of multi-stages features as well as a low temperature magnesium-ferruginous metasomatism in surrounding rocks.

Absence of alkaline rocks and alkaline metasomatites at the Seligdar deposits as well as concordant bedding of the apatite-bearing and associated rocks with rich in Cl and SO₃ apatite under extremely low levels of Sr and REE are evidences on the primary sedimentary origin of the mineralization.

There has also been shown distinctive difference between minerals from the Seligdar apatite deposit with well-studied minerals of carbonatites. Seligdar's dolomite contains significant admixtures of Fe₂O₃ (including of fine dispersions of hematite) with extremely low amount of Fe (II), and apatite is characterized by high concentrations of Fe₂O₃, SiO₂, Cl, and SO₃. Both minerals are poor in Sr, Ba, and REE (up to 0.1%).

Fluorapatite with 50 % of hydroxylapatite mineral and trifling (less than 0.1%) amounts of Cl and SO₃ with constant high Sr and REE (mainly Ce series) is typical for carbonatites

(Kapustin, 1971). Calcite from earlier carbonatites is also enriched by Sr and REE, and ferrodolomite – ankerite from late carbonatites is relatively barren of these elements, but enriched by FeO (up to 5%) under absence of Fe₂O₃. Comparison of REE ratios in apatite from the Seligdar deposit and other deposit has shown its relative similarity (Minerals, 1968; Guliy et al., 2017).

At the same time apatite from the Seligdar deposit and Nimnyr's manifestations is practically identical to apatite from quartzites, calciphyres and phlogopite-bearing metasomatites (magnesial skarns and veins) of the Slyudianka and Emeldzhak deposits after composition, although apatite from the Emeldzhak deposit is enriched in REE. High amounts of Cl and SO₃ are typical for apatite from metasedimentary and metasomatic-metamorphic formations, with ratio F/Cl equal 0.5–1.0 and F/SO₃ from 3 up to 7.

Isotopic investigations of carbonates of all genetic types from the Aldan Shield showed (Guliy and Wada, 2003; Guliy and Wada, 2004) that apatite-carbonate rocks differ from other carbonate rocks, particularly Ca – Mg metasomatites, skarns and carbonatites, in carbon and oxygen isotopic compositions. Isotopic data indicate clear difference in nature of carbonate materials from the apatite-carbonate rocks of the Seligdar and allied apatite deposits and late metasomatites which are locally developed in the basin of the Bolshoi Nimnyr River within area with apatite-carbonate primary sedimentary rocks. Peculiarities of the C and O isotope compositions of the different genetic types of carbonate rocks at the Aldan Shield and determined specific rich in heavy carbon and oxygen isotopes carbonates for the apatite-carbonate rocks as signatures of a primary sedimentary protolith are in accordance with isotopic models proposed (Lents and Suzuki, 2001) for carbonate family rocks similar in geological position and origin at the Canadian Shield.

Apatite-bearing manifestations of the Aldan Shield which are regarded now as the 'Seligdar type' have heterogeneous origin. Besides dolomite layers within the deposits there are primary quartzite, quartz and quartz-chlorite metasomatites with poor in apatite mineralization, and probably primary apatite-bearing calciphyres. Betafite finds within late diafiorites which are located far from the Seligdar deposits cannot be indicator of its carbonatites origin of the apatite-bearing rocks. In addition to this fact, composition of the betafite without Ta from the diafiorites sharply differs from gatchetolite from carbonatites, which is commonly enriched by Ta, and is closely similar to betafite from granite pegmatites.

In fact, betafite was found in metasomatites and brecias, which are developed in breaking zones of gneisses, quartzites, and possibly quartz-carbonate rocks with apatite. Taking into account relatively high temperature conditions of betafite formation in intrusive rocks during magmatic or high temperature pneumatolite stage, the mineral can be relic in origin in the quartz-chlorite diafiorites. In rock blocks with cataclastic textures betafite is evidently detrital in origin. The mineral grains together with rounded or angular quartz and apatite are cemented by late quartz, epidote, carbonate and chlorite aggregates.

Betafite is a sporadic mineral in the high metamorphosed Aldan granite-gneisses and associated granite and pegmatite bodies. At the Emeldzhak phlogopite deposit in the quartz-feldspar lensed in shape pegmatites within gneisses we found rare small (up to 2 mm) betafite and pyrochlore grains in association with crystals of accessory titanite, magnetite and zircon which intergrowth to foggy quartz in the center of pegmatoids lenses.

Genetically indeterminate finds of betafite in metasomatic altered cataclasites far from the Seligdar deposit cannot be determined as genetic types of the deposit. Thus, the Seligdars' carbonates, taking into account structures, composition amounts and REE ratios cannot be compared to any well-known kinds of carbonatites. Finally, apatite compositions from the Seligdar deposit are evidences for clear determination of the deposit as sedimentary-metamorphic formation with some metasomatic secondary alterations (Bulakh et al., 1990; Kapustin, 1971; Gulyi et al., 2017).

Determination of the Seligdar' rocks as a special "crust carbonatites" has not any sense due to absence of descriptions of these carbonatites. Finally, there are not any evidences to regard betafite with basite and gabbro-anorthozite intrusives (Entin et al., 1987), due to absence of betafite in these rocks and extremely low levels of Nb, Ta, U, TR. There is not any evidences to distinguish "formation of the crust carbonatites" similar to the Seligdar kind of rocks, due to the typically mantle origin of alkaline rocks and carbonatites, which have specific combination of the geological and geochemical indicators features, suggestion on their mantle nature.

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ОСОБЛИВОСТІ РОЗПОДІЛУ ТА СКЛАДУ БЕТАФІТУ З РІЗНОМАНІТНИХ ФОРМАЦІЙ АЛДАНСЬКОГО ЩИТА (САХА-ЯКУТІЯ)

Описано характер розподілу Nb і Ta у різних геологічних формaciях Алданського щита. Проаналізовано бетафіт етапонних ендогенних комплексів із відомих об'єктів, пов'язаних із пегматитами, скарнами, карбонатитами, метасоматитами та пізніми жильними утвореннями. Описано структурне положення та мінеральний склад апатитоносних порід Алданського щита і встановлено найбільш масивні метаморфізовані карбонатні та силікатні різновиди серед них. Апатитова мінералізація у магнезіальніх скарнах і метасоматитах розвивається локально.

Головними концентраторами Nb і Ta є бетафіт та титаніт, з якими постійно зустрічається апатит. Бетафіт є звичним у пегматитах поширеніх у магнезіальніх скарнах та метасоматитах щита, але він не виявлені у представницьких апатит-карбонатних породах – рудах селігдарського типу, отже, не може служити індикатором цього типу руд.

Пізні генерації карбонатів сумістю збагачені легкими ізотопами вуглецю і кисню, на відміну від позитивних значень $\delta^{13}\text{C}$ в апатит-карбонатних тілах Селігдарського родовища і споріднених об'єктів та найвищих значень $\delta^{18}\text{O}$. Ці індикатори застосували, щоб відрізняти відмінні за генезисом карбонатні породи, що містять різну кількість бетафіту, появя якого визначається первинним складом вихідних порід. Хімічний склад бетафіту із скарнів та метасоматитів подібний, але виявлено локальні варіації окремих компонентів. Найважливішою рисовою хімічного складу мінералу є дуже низький вміст Ta. У той же час титаніту властиві перемінні кількості Nb і Ta як у межах різних ділянок, так і в окремих частинах зерен титаніту.

Ключові слова: бетафіт, титаніт, Nb і Ta, метаморфічні апатит-карбонатні руди, Алданський щит, пегматити, метасоматити, скарни, карбонатити, С-О ізотопи.

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ОСОБЕННОСТИ РАСПРЕДЕЛЕНИЯ И СОСТАВА БЕТАФИТА ИЗ РАЗЛИЧНЫХ ФОРМАЦИЙ АЛДАНСКОГО ЩИТА (САХА-ЯКУТИЯ)

Описан характер распределения Nb и Ta в разных геологических формаций Алданского щита. Проанализирован бетафит эпапонных эндогенных комплексов из известных объектов, связанных с пегматитами, скарнами, карбонатитами, метасоматитами и поздними жильными образованиями. Описано структурное положение и минеральный состав апатитоносных пород Алданского щита и выявлены наиболее массивные метаморфизованные карбонатные и силикатные разновидности среди них. Апатитовая минерализация в магнезиальных скарнах и метасоматитах развивается локально.

Главными концентраторами Nb и Ta является бетафит и титанит, с которыми постоянно встречается апатит. Бетафит обычен в пегматитах, распространенных в магнезиальных скарнах и метасоматитах щита, но не обнаружен в представительских апатит-карбонатных породах – рудах селигдарского типа, следовательно, не может служить индикатором этого типа руд.

Поздние генерации карбонатов существенно обогащены легкими изотопами углерода и кислорода, в отличие от положительных значений $\delta^{13}\text{C}$ в апатит-карбонатных телах Селигдарского месторождения и родственных ему объектов и наибольших значений $\delta^{18}\text{O}$. Мы использовали эти индикаторы для выделения различных по генезису карбонатных пород, которые содержат разное количество бетафита, появление которого определяется первичным составом исходных пород. Химический состав бетафита из скарнов и метасоматитов близок, но наблюдаются локальные вариации отдельных компонентов при крайне низком содержании Ta. Для титанита свойственны переменные количества Nb и Ta как в пределах разных участков, так и в отдельных частях зерен титанита.

Ключевые слова: бетафит, титанит, Nb и Ta, метаморфические апатит-карбонатные руды, Алданский щит, пегматиты, метасоматиты, скарны, карбонатиты, С-О изотопы