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Mineralogy and Genesis of Karites of the Murun Complex

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We studied mineralogy of the karite sample from Murun alkaline complex. Karite belongs to the silexites group and has so far been one of the few rocks of this family whose igneous genesis has not been questioned. The studied rock consists of quartz (73 vol. %), aegirine (4 vol. %), orthoclase (23 vol. %), and a number of accessory minerals, which are typical for fenites (narsarsukite, steacyite-turkestanite, delyite, etc.). Large euhedral quartz crystals with numerous oriented aegirine ingrowths create a formal resemblance to the porphyritic texture of effusive rocks, however, formation conditions of rock-forming minerals correspond to low temperature (<400°C). Possibly the rock was formed during the impregnation of a silica-rich fluid through a grorudite or aegirinite substrate. The study of karite of the Murun complex did not reveal any sign of the igneous genesis of these rocks. It can be concluded that karites, like many other representatives of the silexites family, are not magmatic, but of hydrothermal-metasomatic origin.

Keywords: Murun alkaline complex, silexites, quartz, steaciite, turkestanite, narsarsukite.

Introduction

Karite is a rare and unusual rock, consisting of large quartz crystals with aegirine ingrowths, immersed in a fine-grained mass composed of potassium feldspar, aegirine, and albite. The main distinguishing criteria for these rocks are the extremely high content of SiO_2 (80-92 wt.%) and their structural and textural features, expressed in well-formed large (1-3 mm in diameter) quartz crystals with numerous aegirine ingrowths (Fig. 1). The amount of quartz in the rock reaches 80 vol. %.

For the first time, karites were found by A.E. Gedroits in the alluvium of the Kara River (a tributary of the Shilka River in the Trans-Baikal Territory) and described by A.P. Karpinsky [Karpinsky, 1903]. Later, karites were found in various regions of Eastern Transbaikalia, Yakutia, and the Irkutsk Region [Konev and Feoktistov, 1998]. A.P. Karpinsky (1903) made detailed petrographic descriptions of two samples, and compared them to numerous finds of rocks of the grorudite family, and suggested that karites are a representative of a series of vein rocks tinguaite - grorudite - quartz grorudite - karite, extremely enriched in quartz. Indeed, in many described objects, grorudites, quartz grorudites, and karites are connected by smooth transitions [Konev and Feoktistov, 1998].

Numerous fluid inclusions were found in quartz from quartz grorudites of the Kara River region, which form a single series with karites [Volkova et al., 2016]. They were homogenized into a liquid at 350°C, their salinity corresponds to 4.2 wt.% NaCl equiv., and their density is 0.64 g/cm^3, which corresponds to a pressure of 1.6 kbar [Volkova et al., 2016]. Melt inclusions in quartz grorudites and karites have not been described. The presence of a liquid and relatively low-temperature dense fluid during quartz crystallization in the absence of melt inclusions called into question the magmatic genesis of these rocks.

In this work, we studied the mineral composition of karite and the textural features of quartz. Particular attention was paid to accessory minerals as indicators of mineral formation processes.

Samples and methods

A sample collected by A.A. Konev (Institute of the Earth Crust, Irkutsk) was studied, which is stored in the collection of the Fersman Mineralogical Museum (sample FMM_FN_669). The sample was taken from the karite lens in the grorudite dyke within an eruptive breccia body with grorudite cement. This dyke crosscuts the Archean granite-gneisses and shales and is located approximately 300-400 meters from the contact with the alkaline granitoids of the Kedrovy massif [Konev and Feoktistov, 1998]. Fig. 1 shows a general view of the sample of the studied karite. Numerous quartz crystals are well separated and have a greenish tint due to aegirine ingrowths.

The composition of minerals was determined by energy-dispersive electron probe analysis (Oxford X-MaxN spectrometer with a crystal area of 50 mm^2, mounted on a JEOL IT-500 electron microscope) at the Department of Petrology and Volcanology, Faculty of Geology, Moscow State University. The analysis was carried out at an accelerating voltage of 20 kV and a probe current of 0.7 nA. Natural silicates [Jarosevich et al., 1980] and synthetic metal oxides were used as standards.

Raman spectra were obtained using a JY Horiba XPloRA confocal Raman microscope (Department of Petrology and Volcanology, Faculty of Geology, Moscow State University) equipped with two lasers (532 and 785 nm) based on an Olympus BX41 polarizing microscope. The operating temperature of the CCD (IVAC Andor CCD) detector is -51°C, cooling is carried out using Peltier elements. The spectra were accumulated under excitation with a laser with a wavelength of 532 nm and a power of 25 mW (12 mW measured on the sample surface), a 100x objective (spatial resolution <1 μm), a spectrometer slit size was 100 μm, and a confocal hole was 300 μm. The survey was carried out in the range from 200 to 4000 cm^{-1} using a 1800T spectral grating (1800 lines per mm). The spectra were accumulated on the polished surface of the crystals in an arbitrary orientation. The accumulation time for each spectrum window was 60 sec (3 times 20 sec) in the mode of automatic window gluing with an overlap of 100 lines. The primary processing of the spectra was carried out in the LabSpec program, ver. 5.78.24.

Results

The rock-forming minerals in the studied sample are quartz, aegirine, and potassium feldspar. The modal composition of the rock was determined using the mass balance for all petrogenic components. The bulk analysis of the sample is given in [Konev, Feoktistov, 1998]. The composition of quartz was taken as 100% SiO_2, and for aegirine and potassium feldspar, averaged values were taken from 10 analyses for each mineral. The sum of the squared deviations of the measured and calculated compositions was less than 0.14. Volumetric contents were calculated taking into account the density of quartz (2.65 g/cm^3), aegirine (3.6 g/cm^3), and orthoclase (2.56 g/cm^3). The studied sample contains quartz (73 vol.%), aegirine (4 vol.%), potassium feldspar (23 vol.%), as well as accessory narsarsukite, delyite, turkestanite, grayite, vanadium-bearing rutile, magnetite, and others.

Quartz forms regular crystals (1-2 mm in diameter) with hexagonal sections. Quartz occurs only in large crystals and is absent in the rock matrix. All sections are isometric and, as noted by previous researchers [Karpinsky, 1903; Konev and Feoktistov, 1998] correspond to the bipyramidal crystal habit. The edges are clear, without bay-like outlines, which are typical for quartz of effusive and subvolcanic rocks.

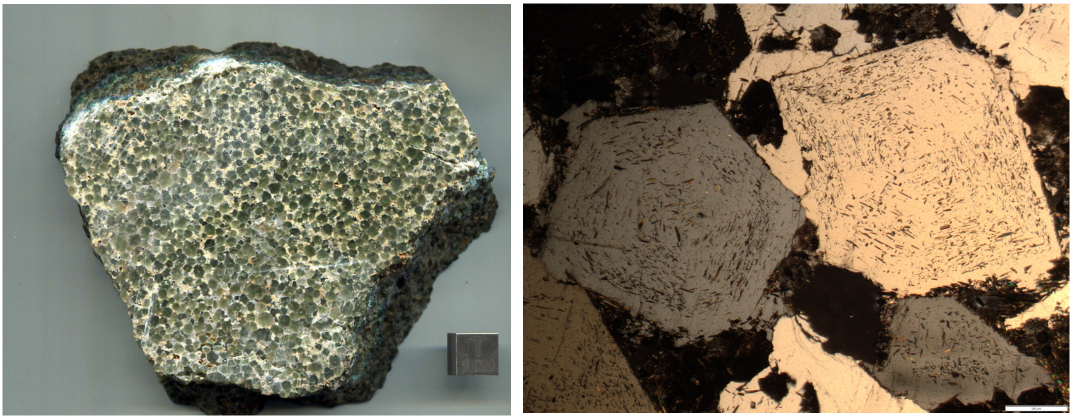

Fig. 1. General view of karite. On the left is the scanned surface of the sample, the face of the scale cube is 1 cm; on the right is a photograph of the thin section made in crossed polarizers, the scale bar corresponds to 0.5 mm.

The sector zoning is noticeable in some quartz crystals (Fig. 2), which is emphasized by the non-simultaneous extinction of crystals in crossed polarizers, the inhomogeneous distribution of aegirine ingrowths, and outgrowths of individual sectors beyond the contours of an ideal crystal.

Quartz crystals do not show any signs of cathodoluminescence, the content of Al and Ti is below the detection limits (0.04 and 0.03 wt.%, respectively). Fluid inclusions (up to 20 µm in diameter) similar to those described in [Volkova et al., 2016] were found in quartz crystals. No melt inclusions were found in the studied thin sections.

Aegirine is represented by small (up to 200 µm) elongated prismatic crystals, most of which form ingrowths in quartz, but also occur as clusters in the intergranular space (Fig. 3). There is no clear correlation between grain size, their position with respect to the center of quartz crystals, and their compositions; however, the largest grains (about 200 µm) are more often found in the intergranular space or in the marginal parts of quartz grains. The composition of aegirine varies within a very narrow range - $Aeg_{(80.3\text{-}84.0)}Di_{(6.8\text{-}9.0)}Hed_{(9.5\text{-}16.8)}$. The average composition of 15 analyzes calculated for 4 cations corresponds to the crystal-chemical formula $(Na_{0.93}Ca_{0.06})_{0.99}(Fe^{3+}{}_{0.71}Fe^{2+}{}_{0.10}Mg_{0.08}Ti_{0.08}Al_{0.01}V_{0.01}Mn_{0.01})_{1.00}[Si_{2.01}O_6]$. The aegirine of the studied karite contains stable impurities of TiO_2 (2.2–3.7 wt %), Al_2O_3 (0.14–0.39 wt %), V_2O_3 (0.13–0.26 wt %), and MnO (0.20–0.48 wt %) (Table 1).

Potassium feldspar is also homogeneous in composition. It contains 96-99% orthoclase and 1-4% albite endmembers. The iron content is up to 0.36 wt. % Fe_2O_3, and the calcium content in all analyses is below the detection limit (Table 1).

Fig. 4 shows representative Raman spectra of rock-forming minerals. The spectrum of quartz corresponds to α-quartz, potassium feldspar - to orthoclase.

Among the accessory minerals, the most common is the mineral of the steacyite group, which forms small (5–10 µm) well-formed grains uniformly distributed in quartz crystals (Fig. 5a). Analyzes of this mineral and other accessory silicates are given in the Supplementary materials to the article (https://fmm.ru/Journal/NDM57_2023_eng). The general formula of steacyite group minerals can be represented as $AB_2(K1\text{-}x\square x)Si_8O_{20}{}^*nH_2O$, where *A* polyhedra are occupied by Th, U, and REE, *B* polyhedra by Na, Ca, and other divalent cations, and water can be present in zeolite-like channels (Kaneva et al., 2023). The Raman spectra did not reveal vibrations in the range of 3200-3600 cm^{-1}, which could indicate the presence of water, so we consider this mineral to be anhydrous. The formula normalized to 8 silicon atoms can be represented as $(Th_{0.78\text{-}0.92}U_{0.05\text{-}0.08}\mathit{REE}_{0.07\text{-}0.12})_{0.95\text{-}1.10}(Na_{0.76\text{-}1.0}Ca_{0.88\text{-}1.02})_{1.64\text{-}2.03}(K_{0.87\text{-}1.0}\square_{0\text{-}0.13})Si_8O_{20}$. The Ca/Na ratio of the mineral varies from 0.98 to 1.31, which is intermediate between steacyite ($K_{0.3}(Na,Ca)_2ThSi_8O_{20}$) and turkestanite $(K,\square)(Ca,Na)_2ThSi_8O_{20} \cdot nH_2O$. At the same time, there is much more potassium (0.87-1.00 f.u. in terms of 8 silicon atoms) than indicated in the formula of steacyite.

Narsarsukite crystals have a rectangular shape (Fig. 5b), size from 10 to 200 µm, and correspond to the formula $(Na_{3.48\text{-}388}K_{0.06\text{-}0.1})_{3.56\text{-}3.94}(Ti_{1.46\text{-}1.50}Fe_{0.34\text{-}0.42}Al_{0.04\text{-}0.06}Zr_{0.02\text{-}0.1})_{1.97\text{-}1.99}[Si_8O_{20}](O,OH,F_{0.42\text{-}0.5})_2$. Rutile ($TiO_2$) forms acicular aggregates, which are most often confined to the boundaries between quartz and potassium feldspar or are located inside quartz crystals (Fig. 5b). Inside quartz, rutile is encountered only in polymineral aggregates with potassium feldspar and other accessory minerals (magnetite, narsarsukite, mottramite, dalyite). Magnetite forms octahedral crystals from 20 to 60 µm in diameter (Fig. 5b, 5d). Dalyite ($K_{2\text{-}2.02}(Zr_{0.94\text{-}0.99}Ti_{0\text{-}0.04})_{0.98\text{-}1.0}Si_6O_{15}$) forms

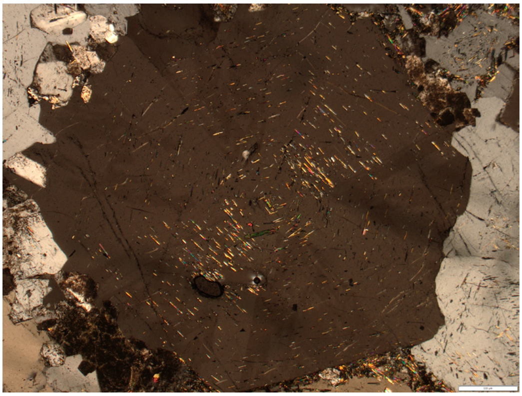

Fig. 2. Sector zoning of a quartz crystal in karite. The sectoral distribution of aegirine ingrowths in the quartz crystal is clearly visible. Photograph in transmitted polarized light, crossed polarizers. Sample FMM_FN_669.

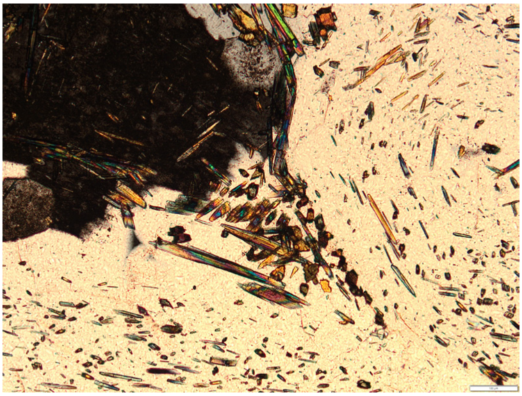

Fig. 3. Aegirine ingrowths in quartz and in the intergranular space in the karite. Photo is in transmitted polarized light, crossed polarizers. sample FMM_FN_669. Scale bar - 100 µm.

elongated grains from 10 to 600 μm confined to the boundaries of quartz grains (Fig. 5c). Mottramite ($PbCu[VO_4](OH)$) forms precipitates up to 10-15 μm in areas of accumulation of other accessory minerals. All these minerals were previously described in the rocks of the Murun massif [Konev et al. 1996].

Rutile, narsarsukite, and dalyite were confirmed by Raman spectroscopy (Fig. 6). The remaining accessory minerals either turned out to be in segregations unsuitable for obtaining a good quality Raman spectrum (small size, high reflection, luminescence) on an instrument available to us, or the spectra of the studied minerals suitable for comparison are absent in the reference spectrum databases (grayite, steacyite, turkestanite).

Discussion

The origin of rocks extremely enriched in quartz has been debatable for more than a century. Initially, quartz cores of pegmatites, as well as quartz dykes and

Table 1. Composition of rock-forming minerals in the karite of the Murun Complex

Oxide	1	2	3	4	5	6	7	8	9	10	11	12
SiO_2	52.12	52.21	52.08	52.32	51.93	52.49	52.21	51.56	52.17	52.37	64.54	64.54
TiO_2	2.76	2.31	2.94	2.91	2.48	2.68	3.00	2.78	3.64	2.71	–	–
Al_2O_3	0.19	0.34	0.14	0.36	0.36	0.33	0.32	0.33	0.34	0.39	18.42	18.80
FeO	4.34	4.20	3.49	4.09	3.97	3.25	4.10	3.43	6.00	3.52	–	–
Fe_2O_3	24.84	25.45	24.48	25.10	26.11	27.15	25.69	26.31	22.32	26.53	0.47	0.07
MnO	0.24	0.18	0.48	0.23	0.20	0.25	0.22	0.21	0.26	0.22	0.06	b.d.l.
MgO	1.41	1.16	1.75	1.24	1.11	1.26	1.27	1.33	1.21	1.24	b.d.l.	b.d.l.
CaO	1.47	1.45	1.45	1.22	1.22	1.40	1.25	1.30	1.46	1.15	b.d.l.	0.07
Na_2O	12.04	12.12	12.07	12.31	12.21	12.43	12.28	12.18	11.94	12.43	0.42	0.07
K_2O	–	–	–	–	–	–	–	–	–	–	16.48	17.13
V_2O_3	0.19	0.23	0.08	0.19	0.16	0.18	0.14	0.17	0.26	0.13	–	–
Total	99.60	99.65	98.96	99.97	99.75	101.42	100.48	99.60	99.61	100.69	100.40	100.68
Mg#	36.68	32.98	47.20	35.06	33.28	40.89	35.57	40.88	26.43	38.59		
Aeg	80.29	81.76	80.89	81.91	82.64	83.99	81.73	82.96	77.23	83.42		
Di	7.23	6.02	9.02	6.34	5.78	6.55	6.50	6.97	6.02	6.40		
Hed	12.48	12.23	10.09	11.75	11.58	9.46	11.77	10.07	16.75	10.18		

All analyzes are given in wt.%. 1-10 - aegirine; 1-5 - ingrowths in quartz, 6-8 - grains in the matrix, 9-10 - ingrowths in potassium feldspar; 11-12 - potassium feldspar. Dashes - not determined, b.d.l. - concentrations below the detection limit. FeO and Fe2O3 for aegirine were calculated from the oxygen balance. Magnesian content ($Mg\#=100*Mg/(Mg+Fe^{2+})$) and endmembers (Aeg+Di+Hed=100 mol %) were calculated for aegirine only.

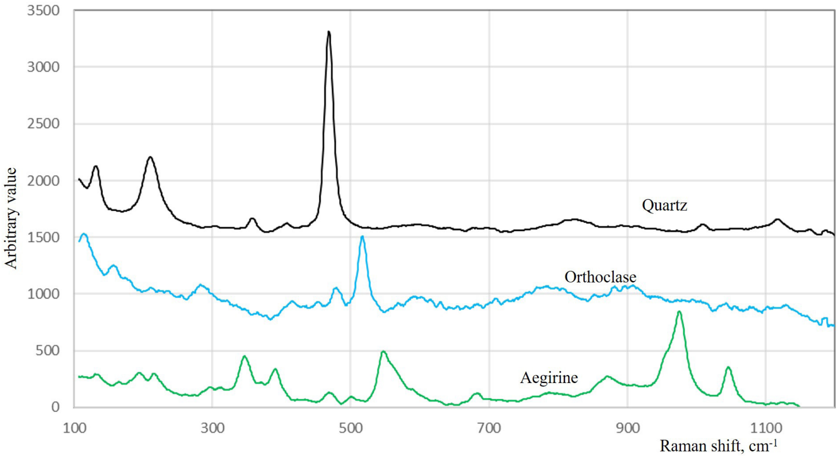

Fig. 4. Raman spectra of rock-forming minerals in the karite. Sample FMM_FN_669.

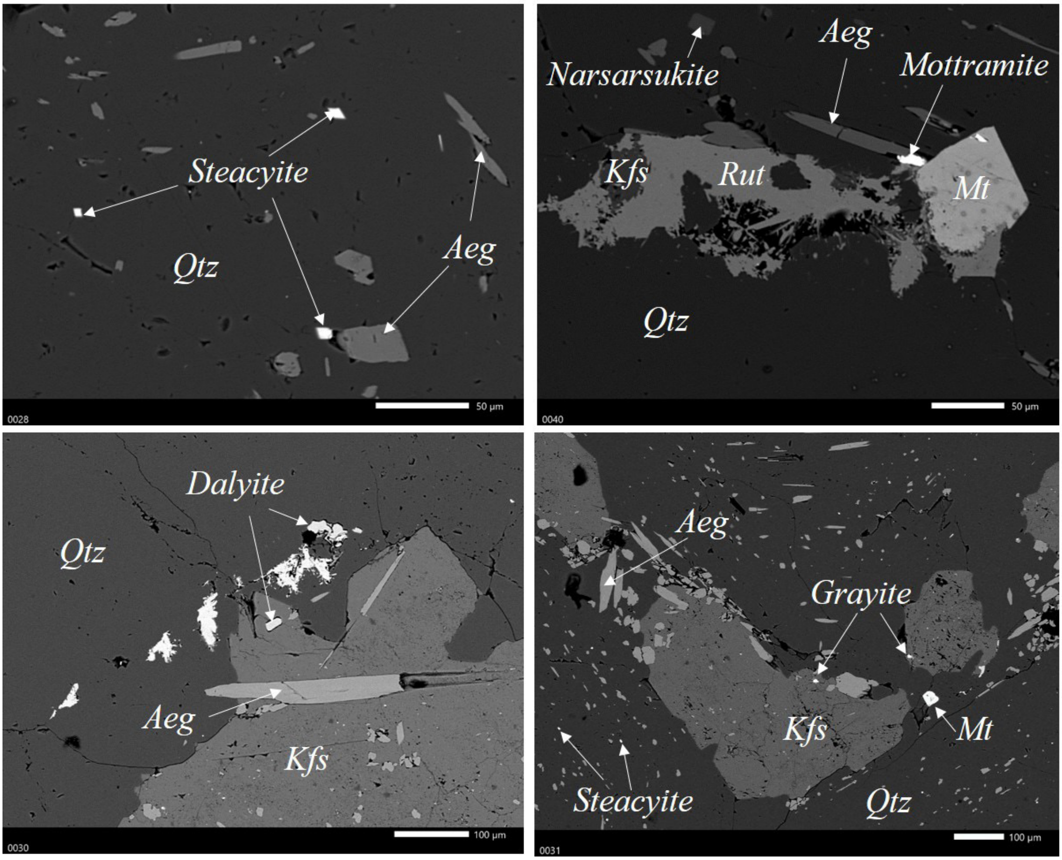

Fig. 5. BSE images of accessory minerals in the studied karite (Sample FMM_FN_669). The names of rare accessory minerals are fully signed. Qtz - quartz, Aeg - aegirine, Kfs - potassium feldspar, Mt - magnetite.

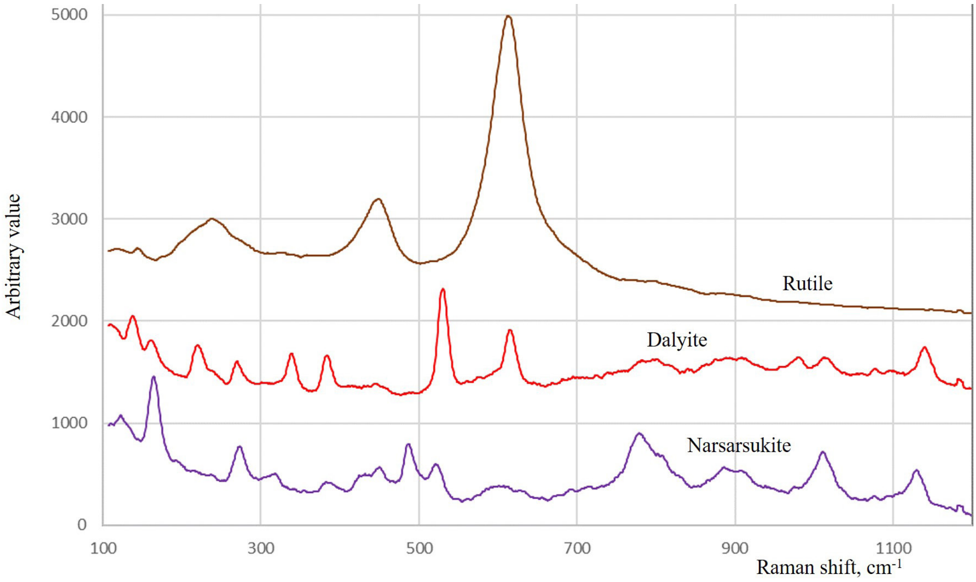

Fig. 6. Raman spectra of accessory minerals in the karite. Sample FMM_FN_669.

veins, were considered as igneous rocks. For such quartz rocks (>60 vol.% quartz), the name silexite was proposed [Miller, 1919]. A. Holmes proposed the term quartzolite for rocks containing more than 90% quartz [Holmes, 1928]. A. Johannsen in his classification [Johannsen, 1920] described in detail the family of silexites, which included esmeraldite (quartz-muscovite rock), tarantulites and orthotarantulites (rocks transitional between leucocratic alaskites and pure quartz), tourmalite (tourmaline-quartz rock), topazite (topaz-quartz rock), as well as greisens and beresites. For some of these rocks, enrichment in quartz was proved, which occurred due to metasomatism at the postmagmatic stage [Johannsen, 1920], while the other part turned out to be metasomatic rocks close to greisen.

Until now, karite has been one of the few rocks of this family whose igneous genesis has not been questioned [Karpinsky, 1903; Konev, Feoktistov, 1998, etc.]. Indeed, the texture of karites is very similar to the porphyritic or series-porphyritic structure of effusive rocks. However, a detailed study of the rock family reveals a significant number of features that make it possible to assert that this similarity is only superficial.

The place where karites were found is located outside the Kedrovy massif, approximately 300-400 meters from the contact with granosyenites. The host rocks are fenitized Archean granite-gneisses and shales [Konev and Feoktistov, 1998], as well as black shales (siltstones, dolomites) [Dumanska-Slowik et al., 2022]. In the same northern contact zone of the Kedrovy massif, dianites (richterite metasomatites), numerous quartz veins with anatase mineralization, veins with lithium-beryllium mineralization, etc. have been described. Karites themselves do not form an separated geological body, forming separate lenses in grorudites [Konev, Feoktistov, 1998]. If karites belonged to the magmatic stage of the formation of the Murun complex, then they should have traces of postmagmatic stages of mineral formation, which are recorded in all rocks of this zone. However, no processes superimposed on the quartz-kfsh-aegirine paragenesis were noted in karite. Consequently, this paragenesis itself was formed at a relatively late (low-temperature) stage in the evolution of the Murun alkaline complex and did not undergo significant changes after that. Within the sample, no zoning is observed, and we are unable to study the contacts of karite and host grorudite in order to determine the type of their relationship. Gradual transitions between grorudite and karite are noted [Konev and Feoktistov, 1998], which may serve as an indirect sign of metasomatic zoning.

Quartz in the studied karite has characteristic features (sharp edges, sector structure, aegirine ingrowths), which were not described in any effusive rock known to the authors. Quartz phenocrysts in effusive rocks usually have a rounded shape, gulf-like outlines, and numerous melt inclusions [Plechov, 2014; Barbee et al., 2020]. The sectoral zoning has been described in quartz during hydrothermal synthesis and rapid growth from colloidal solutions [Chernov and Khadzhi, 1968]. In natural quartz, the sectoral distribution of actinolite and hematite inclusions is described for quartz in pegmatites and hydrothermal veins [Jiang et al., 2022]. The sectoral structure of crystals is considered a reliable criterion for the primary growth of the low-temperature trigonal modification of quartz [Lemmlein, 1948]. The absence of melt inclusions and the relative abundance of fluid inclusions also argue against the magmatic origin of these quartz crystals.

Aegirine contains 92-94% Na and only 5-7% Ca in the *M1* cation position, which is not typical for clinopyroxene of the magmatic stage. Significant differences between the composition of ingrowths and aegirine in the rock matrix were not found. Potassium feldspar contains 97-99% orthoclase end-member, which also indicates a low temperature of formation. The K-feldspar grains do not have perthites or other features indicative of an initially higher temperature. The formation temperature of K-feldspar can only be estimated approximately since there is no albite in the rock. A small amount of albite end-member in the presence of sodium in the mineral-forming medium indicates a crystallization temperature of less than 300-400 ℃ [Parson and Lee, 2009]. We assume that aegirine was formed together with K-feldspar earlier than quartz. During the growth of quartz crystals, aegirine was partially sorbed on the surface of growing crystals (and then formed oriented ingrowths), and partially pushed into the intergranular space.

Karite contains a set of accessory minerals, which was described in near-contact metasomatic rocks of the Little Murun massif and other alkaline massifs. Narsarsukite, steacyite, and dalyite are described in charoitites and other rocks of the fenitization zone of the Little Murun massif [Konev et al., 1996]. Aegirine-albite-quartz-narsarsukite metasomatites are well known in the fenitized near-contact part of the Lovozero massif on Mount Flora [Kartashov, 1994; Pekov, 2001]. Dalyite is also described in the fenitized rocks of the Lovozero massif of Mount Kitknyun [Ivanyuk et al., 2006]. These minerals can be used as an indicator of the processes of fenitization, which takes place with an excess of silica.

Karites could have been formed in the fenitization zone of the Kedrovy massif due to the impregnation of an earlier substrate with a fluid rich in silica. Grorudites (aegirine microgranites) or aegirinites, which are widely distributed within the Murun complex, could be such substrates. Under the influence of fluid, the original rock was completely recrystallized and a low-temperature paragenesis of quartz-aegirine-potassium feldspar was formed with an accompanying set of accessory minerals. The subject of discussion is the composition and state of the fluid, which could cause such changes. In our opinion, it could be a colloidal solution that can easily penetrate the pores of the rock and cause the rock to recrystallize at a relatively low temperature. Such colloidal solutions are common in nature [Chukhrov, 1955] and stabilize in an alkaline medium. They can transfer up to 3.2 wt. % SiO_2, remaining in a colloidal state. Under laboratory conditions, large crystals of various substances are grown from colloidal solutions [Moreno, Mendoza, 2015 and references therein]. An alternative option would be to treat the rock with a gas saturated with silica. The growth of cristobalite from the gas phase has been described on the extrusive domes of many volcanoes [e.g., Ivanova et al., 2018 and references therein]. A significant role in the crystallization of quartz have been played by the effects that occur at the solution-vapor interface in a thermogradient system [Alekseev, Medvedeva, 2018], assuming the existence of a heterophase fluid at the stage of karite formation.

“Mokrushites” described in the near-contact zone of Murzinka pegmatites (Northern Urals) can be similar in genesis [Ivanov, 1999]. These rocks, as well as karites, are composed of quartz crystals (about 2 mm in diameter), but the rock matrix is composed of albite, and does not contain a K-feldspar.

The authors plan further study of quartz-bearing rocks of the Murun complex (grorudites, charoitites, etc.). It would be interesting to compare these rocks with the grorudites and karites of the Kara River valley, where the karites were first described. A detailed study of the ontogeny of quartz and fluid inclusions in it can contribute to the restoring of a more complete picture of the genesis of these unusual rocks. It remains unclear why quartz forms only large crystals in the rock and is absent in the form of small grains.

Conclusions

Karites of the Murun complex are composed of quartz-aegirine-orthoclase assemblage and contain steacyite, dalyite, narsarsukite, rutile, grayite, mottramite and magnetite as accessory minerals. This assemblage corresponds to low-temperature formation conditions (<400℃). It is possible that the rock was formed during the development of a silica-rich fluid of a grorudite or aegirinite substrate. The study of karite of the Murun complex did not reveal any sign of the igneous genesis of these rocks. It can be concluded that the karites of the Murun complex, like many other representatives of the silexite family, are not igneous, but hydrothermal-metasomatic in nature.

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