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MINERALOGICAL AND PETROLOGICAL PECULIARITIES
OF GRORUDITES OF EASTERN AZOV AREA (UKRAINE)

Alkaline granites and their hypabyssal and effusive varieties have a limited distribution on the Ukrainian Shield, unlike other Precambrian platforms and shields. Grorudite dikes in the Eastern Azov region have discrete chemical and mineral composition and are considered as analogues of alkaline granites — pantellerites (high-Ti or aegirine type) or comendites (low-Ti or amphibole type). High-Ti grorudites are highly enriched in incompatible elements (REE, Zr and Nb) in comparison to low-Ti type. As a result of high-Ti grorudite investigation, new for these rocks titanium minerals (titaniferous hematite with high MnO content, minerals of the $FeTiO_3$—$MnTiO_3$—$ZnTiO_3$ series), previously unknown in these rocks Ca-Na-amphiboles, as well as structural relationships between aegirine and alkaline amphibole were revealed. Despite of high or increased content of HFSE in grorudites, information about their accessory minerals is quite restricted. In the aegirine-bearing varieties of grorudites, such rare elements minerals: monazite-(Ce), bastnäsite-(Ce), britholite-like mineral and REE-enriched apatite, zircon, a Na-rich mineral similar to calciocatapleiite, as well as unidentified zirconium minerals and minerals of the aeschynite group were recognized. In amphibole-bearing dikes zircon and Nb-bearing rutile were only found. These minerals are often very small in size, the largest of them can reach 15—20 µm in size; mostly do not exceed 10 µm. It greatly complicates their identification. An interesting and unusual fact is that many of rare minerals, especially bastnäsite-(Ce), aeschynite group minerals and zircon are present as inclusions in titaniferous hematite. It is assumed that a significant part of rare metals isomorphically incorporate to rock-forming minerals (alkaline pyroxenes and amphiboles). Some of rare minerals (especially zirconium ones) are secondary mineral and were formed as a result of replacement of primary Na (eudialyte, catapleiite, hilairite) or Ca (gittinsite, calciocatapleiite) Zr-silicates, which are more typical in peralkaline (agpaitic) rocks. Taking into account the petrological features and the nature of the rare-earth mineralization of grorudites of the Eastern Azov region, there is a reason to believe that such type of mineralization in these rocks occurs in course of differentiation of the initial magmatic melt(s). Such melts are similar to high-Ti basalts (characteristic rocks of this region) of Devonian age. Secondary hydrothermal processes are weakly manifested

in the studied rocks and probably led to substitution of primary accessory minerals. Considering the increased or high concentrations of Nb in high-Ti grorudites and an insignificant amount of Nb-minerals, it is likely that differentiation conditions (low F, high fO$_2$ and hypabyssal conditions of crystallization) did not promote prolonged crystallization with significant accumulation of rare-metal minerals. However, the presence of grorudites with high content of rare metals found in this region increases the prospects for discovery of small alkaline granite intrusions (holocrystalline analogues of grorudites) which may host deposits and/or occurrences of Nb, REE, Zr, Sn, Be.

Keywords: grorudite, alkaline granite, aeschynite-(Ce), zirconium minerals, monazite-(Ce), bastnäsite-(Ce), britholite-like mineral, REE-apatite, Na-rich calciocatapleiite.

Introduction. Among all igneous rocks, alkaline rocks contain the highest concentrations of Zr and other HFSE. The significant resources of these elements are often hosted in alkaline intrusive complexes. So, massifs of alkaline granites or alkaline rocks of syenite-granitic composition host economic or potentially economic HFSE resources in many countries, for instance, the Strange Lake granites (Canada) with rich Zr, Y, REE, Nb mineralization [32, 33, 47], the Khaldzan-Buregtey (Mongolia) deposit in peralkaline granite with large resources of Zr, Nb and REE [25], the Amis complex (Namibia) with Zr, Nb, and REE mineralization [41].

Despite the fact that numerous works dedicated to alkaline granites have been published, the genesis of associated HFSE mineralization is quite often controversial. Most of their HFSE deposits are thought to appear as a result of combination of magmatic and hydrothermal processes, although in some cases one of these processes can be dominant [38].

Unlike other Precambrian platforms and shields, alkaline granites and their hypabyssal or effusive varieties are not common on the Ukrainian Shield. Aegirine and riebeckite in granites are known in the Perga area (Perga granite complex), as well as grorudites in the Eastern Azov region that occur as the dike analogues of pantellerites (high-Ti or aegirine type) and comendites (low-Ti or amphibole type) [7, 12]. Their geological position, chemical composition, mineralogical and geochemical characteristics were considered in details by [5, 7, 8, 12, 14]. Grorudites are the most interesting alkaline rocks in terms of petrological and geochemical aspects and still poorly investigated. Moreover, aegirine and amphibole varieties have different strikes (northwest and sublatitude, respectively). At the same time, aegirine grorudites are usually enriched (as for alkaline granites) in titanium (0.9—1.43% TiO$_2$) and incompatible elements (Zr, Nb, LREE) (Table 1). However, own minerals of these elements have not been discovered so far, and their findings (zircon, rutile, cheralite) have been mentioned only in crushed samples [12]. Partially it is due to rather small size of accessory minerals in these rocks (hundredth, rarely tenth parts of a millimeter). It is possible that during the sample preparation such fine-grained accessory minerals, considering their high density and hardness, were crushed and subsequently lost during washing. Our investigation of aegirine and amphibole grorudites allowed to identify own rare metal minerals, as well as titanium minerals (titaniferous hematite, FeTiO$_3$−MnTiO$_3$−ZnTiO$_3$ series minerals). As for Nb- and Zr-bearing minerals (aeschynite group and Na-enriched calciocatapleiite), they are not fully identified. Also, the new types of Ca-Na-amphiboles as well as previously unknown structural relationships between aegirine and alkaline amphibole have been identified.

Methods. The major element compositions of grorudites samples were determined by standard chemical analysis at the Chemical Laboratory of the M.P. Semenenko Institute of Geochemistry, Mineralogy, and Ore Formation (IGMOF), National Academy of Sciences of Ukraine. Trace and rare earth elements were determined in two samples by inductively coupled plasma-mass spectrometry (*ICP-MS*) at Acme Analytical Laboratories (Vancouver, Canada) using an ELAN 9000 *ICP-MS*; fifteen samples were analyzed by *XRF* at the Chemical Laboratory of the IGMOF of the NAS of Ukraine.

Three samples of grorudites, two of them being high-Ti aegirine type of grorudite and one low-Ti amphibole type, have been studied by *JCXA*-733 (*JEOL*) electron microprobe equipped with three vertical wavelength dispersive spectrometers, in the IGMOF of the NAS of Ukraine. The analytical conditions were as follows: acceleration voltage of 15 kV, beam current 20 nA, and beam diameter of 2 μm; counting times per analysis of 30 s on peak and 10 s on both background positions.

The chemical composition of rare metal minerals was determined using *JSM*-6700*F* field emission scanning electron microscope equipped with *JED*-2300 energy-dispersive spectrometer (*JEOL*) in the IGMOF of the NAS of Ukraine. Operating conditions were as follows: 20 kV accelerating voltage, 1.0 nA beam current, 2 μm beam size and a counting

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time of 90 seconds for one analysis. Pure metals, synthetic compounds and natural minerals were used for calibration. Raw counts were corrected for matrix effects with the ZAF algorithm implemented by JEOL.

Mafic minerals and their textural relationships. As shown by previous authors [12], the most typical mafic minerals in aegirine type grorudites are rare aegirine phenocrysts (up to 1 cm), aegirine microlites in groundmass, and arfvedsonite-riebeckite amphiboles (but rare individual crystals of amphibole similar to richterite were mentioned too); in amphibole type grorudites there are phenocrysts of arfvedsonite-riebeckite am-

phiboles, the groundmass hosts aegirine and Na-amphiboles.

Low Na_2O (7.0—7.47%) and CaO (0.7—2.7%) content (which are more common for riebeckite) were noticed previously [7] in Na-Ca-amphiboles from amphibole type grorudites. According to the new data, amphibole composition is more diverse, as amphiboles with low (riebeckite 6.2% Na_2O and 2.7% K_2O) and high alkali content (arfvedsonite Na_2O up to 10 and K_2O up to 1.9%) have been identified. The degree of iron oxidation in the riebeckite-arfvedsonite amphiboles is lower than that in the associated aegirine. So, in the riebeckite formula three of the five octahedral cations are

Table 1. **Chemical compositions (wt %) and concentration of some trace elements (ppm, *XRF*) in representative samples of grorudites of Eastern Azov region by [12]**

| Component	High-Ti with aegirine					Low-Ti with amphibole					
	1	2	3	4	5	6	7	8	9	10	11
	87-2	87-2/1	87-2/3	88-2/1	88-2	89-8/1	89-8/2	89-8/3	87-3/2	89-9	89-9/2
SiO_2	73.19	74.2	73.0	71.4	72.8	75.0	74.0	73.95	74.38	74.2	75.8
TiO_2	1.43	1.43	1.43	1.04	1.04	0.34	0.35	0.36	0.3	0.33	0.35
Al_2O_3	7.9	8.1	7.9	9.2	8.6	10.4	10.2	10.0	10.04	10.4	10.6
Fe_2O_3	6.65	5.8	6.2	5.86	6.7	1.9	2.3	2.84	2.01	2.1	1.7
FeO	1.36	1.15	1.22	2.02	1.3	3.6	2.88	2.66	2.87	2.88	2.66
MnO	0.23	0.17	0.2	0.23	0.31	0.11	0.09	0.09	0.15	0.1	0.06
MgO	0.36	0.34	0.32	0.26	0.2	0.02	0.03	—	0.3	—	0.04
CaO	0.35	0.35	0.7	0.45	0.33	0.3	0.4	0.28	0.22	0.22	0.2
ZrO_2	—	—	—	0.19	0.17	0.12	0.11	0.11	—	0.11	0.13
Na_2O	3.84	3.84	3.84	4.32	3.68	4.6	4.2	4.2	4.32	4.2	3.84
K_2O	4.5	4.4	4.5	4.48	4.32	3.2	4.46	4.62	4.86	4.4	4.32
P_2O_5	0.03	0.03	0.11	0.08	0.03	0.03	0.03	0.05	0.05	0.06	0.05
CO_2	0.24	—	—	0.1	0.07	0.14	0.17	0.06	0.21	0.2	0.17
$S\ (SO_3)$	0.02	0.02	0.02	—	—	0.01	0.01	0.02	—	0.05	0.02
H_2O^-	—	—	0.1	0.15	0.4	—	—	—	—	—	—
LOI	0.3	0.32	0.73	—	0.17	0.26	0.45	0.34	0.1	0.32	0.43
Total	*100.4*	*100.2*	*100.27*	*99.8*	*100.12*	*100.03*	*99.68*	*99.58*	*99.81*	*99.57*	*100.37*
(Na + K)/Al	1.43	1.37	1.42	1.3	1.26	1.06	1.16	1.19	1.23	1.13	1.03
Na_2O/K_2O	0.85	0.87	0.85	0.96	0.85	1.44	0.94	0.91	0.89	0.95	0.89
Cr	25	20	20	—	20	22	5	5	10	10	5
Ni	20	20	20	—	20	20	15	15	17	15	15
Li	60	60	250	10	10	40	60	50	15	10	30
Be	4	4	4	4	6	3	3	4	5	2	2
Rb	175	180	205	175	175	90	162	165	144	144	165
Ba	39	54	34	51	74	73	26	40	40	40	90
Sr	45	35	35	10	10	10	40	10	10	10	10
Nb	1218	120	273	420	400	140	112	112	112	125	133
Zr	1557	1588	1445	1494	1580	948	925	887	886	837	1071
Th	15	15	15	25	20	10	10	9	10	10	15
Y	180	180	162	140	207	130	112	103	122	117	140
La	175	119	146	186	235	154	105	63	122	139	45
Ce	320	203	193	279	343	231	156	95	189	229	129
Nd	238	166	155	204	—	184	129	141	140	141	83

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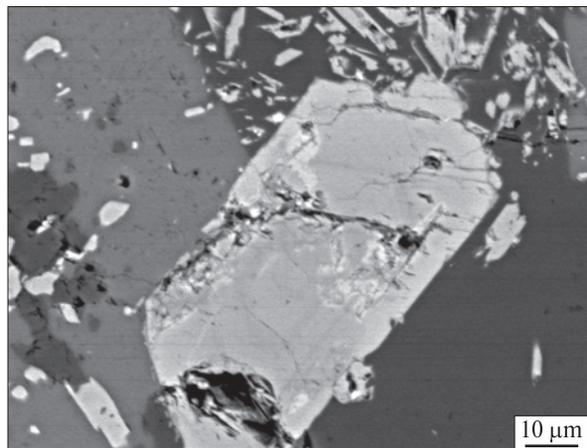
Fig. 1. Amphibole phenocryst with heterogeneous texture and irregular zonality in aegirine grorudite (BSE image). The lighter areas and the central part of the phenocryst are rich in MnO and CaO

Fig. 2. Inclusions and horseshoe-shaped rim of fine-grained amphiboles (Amph) in rounded quartz (Qu)

Fe^{+3}, whereas in arfvedsonite the iron oxidation degree is lower with one Fe^{+3} per formula.

Some amphibole phenocrysts reveal obscure zoning with MgO-rich (up to 8.8%) cores, whereas separate areas have a composition similar to winchite (5.87% CaO, 3.8% Na_2O, 0.8% K_2O, and 5.55% MnO, Table 2, Fig. 1). Small needle-like inclusions of amphibole and its horseshoe-like rim in and around quartz have been analyzed, too (Fig. 2). In contrast to the mentioned above phenocrysts of amphibole, they reveal maximum enrichment in FeO and alkalis, lack of MgO and insignificant CaO content which are typical for arfvedsonite (Table 2, an. 9). Amphibole of richterite composition (5.05% CaO, 7.27% Na_2O,
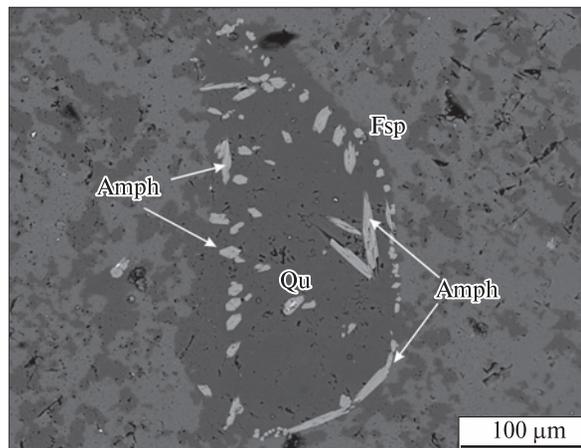
0.29% K_2O and 5.55% MnO) is also presented. Amphiboles of such composition were previously regarded as members of winchite-richterite series and probably were described as richterite [12].

In aegirine type grorudites, enrichment in TiO_2 (1 to 2.2%) and significant range of CaO (0.5 to 4.6%) were revealed in aegirine. Early aegirine phenocrysts contain increased amount of hedenbergite component, whereas iron in aegirines from the groundmass is completely oxidized.

Additionally, unknown textural relationships (intergrowth) of aegirine and alkaline amphibole (Figs. 3, 4) in aegirine grorudites have been revealed. These intergrowths of two minerals have elongated shape (~100 μm) with acute-angled branches where the central part is presented by alkaline amphibole

Table 2. **Chemical compositions of mafic minerals in aegirine grorudites (EDS, wt.%)**

Component	Aegirine				Amphibole					
	1	2	3	4	5	6	7	8	9	10
SiO_2	53.13	53.21	53.72	52.61	54.77	54.78	55.74	50.51	48.95	51.17
TiO_2	4.00	1.37	2.68	1.88	1.98	1.83	0.41	—	2.67	—
Al_2O_3	—	1.55	—	0.63	0.62	0.10	0.20	0.09	0.39	0.34
FeO	27.82	29.12	27.91	29.02	20.04	19.93	21.46	38.53	35.32	37.36
MnO	—	—	—	—	1.66	1.70	5.55	0.44	0.60	—
MgO	—	1.98	—	—	8.64	8.83	6.16	—	—	—
CaO	—	0.82	1.20	0.61	1.11	0.93	5.87	—	1.43	—
Na_2O	15.04	11.96	14.48	15.26	10.08	10.80	3.81	7.42	8.96	8.01
K_2O	—	—	—	—	1.10	1.10	0.81	3.01	1.70	3.12
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

N o t e. 1 — a small inclusion in titaniferous hematite; 2 — a small inclusion in titaniferous hematite with rounded zircon grains (Fig. 5, *c*); 3 — a small aegirine overgrowing (replacement ?) of amphibole (Fig. 4); 4 — the same (Fig. 3); 5, 6 — the central part of amphibole grain with heterogeneous texture (Fig. 1); 7 — lighter area of the same crystal; 8, 10 — earlier grains of amphibole that are overgrown (or replaced) by aegirine (Figs. 3 and 4, respectively); 9 — small amphibole grain that occur as small inclusions and horseshoe-shaped rim around the "large" quartz grain (Fig. 2).
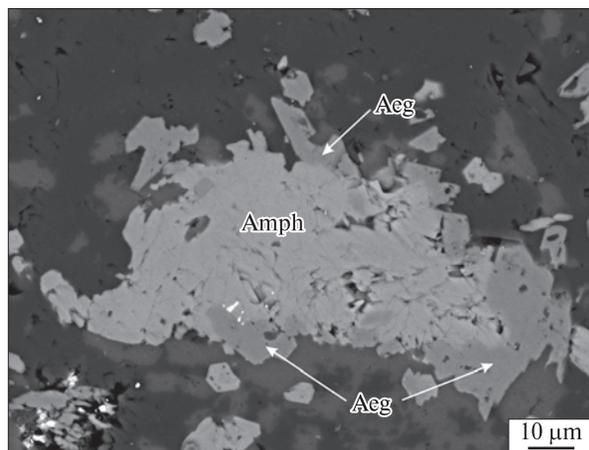
Fig. 3. Amphibole grain (Amph) with irregular aegirine rim (Aeg)

Fig. 4. Textural relationships between arfvedsonite (Amph) and aegirine (Aeg) in aegirine grorudite

whereas periphery part by interrupted aegirine rim. It seems that aegirine develops (partial replacement or overgrowth) after primary arfvedsonite (Table 2). Content and degree of Fe oxidation may explain the complex textural relationships between Na-Ca-amphiboles and aegirine (aegirine rims around amphibole grains, Figs. 3, 4). Similar replacement of Na-Ca-amphibole by aegirine was observed in alkaline granites of the Strange Lake, which was explained by liberation of aqueous fluid at the final stages of crystallization with its subsequent interaction with the rocks [36]. In addition, some amphiboles of grorudites, especially Ca-Na-varieties, are rich in MgO, which may be due to the early amphibole crystallization from the less differentiated melt compared to late aegirine in the groundmass.

Titanium minerals. Previous investigations [7] did not reveal any significant amount of titanium minerals, the presence of which could explain the high titanium content (up to 1.43% TiO_2) in aegirine grorudites. Rare ilmenite and rutile were mentioned, and presence of hematite with high Ti con-
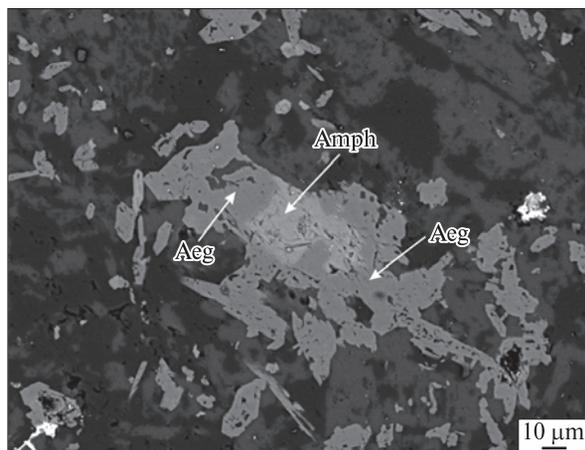
tent was assumed. It is possible that grorudites, as it is common for many pantellerites, also contain aenigmatite, since high concentration of TiO_2 (up to 6.3 wt %) was found in some aegirine [12]. Numerous titaniferous hematite crystals bearing up to 7.3% TiO_2 (rarely up to 22.6%), mineral similar to ilmenorutile and minerals of the $FeTiO_3$–$MnTiO_3$–$ZnTiO_3$ series were detected in aegirine grorudites. High content of TiO_2 in hematite indicates high temperature of crystallization. Rare inclusions of ilmenite ($FeTiO_3$–$MnTiO_3$–$ZnTiO_3$ series) in hematite probably indicate the beginning of decomposition of solid solution.

Titaniferous hematite often forms grains of uncertain shape sized up to 0.1 mm, rarely with fuzzy outer margins. All analyzed hematite grains are rich in MnO up to 6% (Table 3). In addition, these hematite grains host unusual and surprisingly frequent microscopic inclusions of aegirine, zircon, rare earth fluorocarbonates and, presumably, a mineral of aeschynite group (Fig. 5). Besides mentioned above inclusions, some hematite crystals host areas (inclusions or exsolution) of intermediate

Table 3. **Chemical composition of titanium minerals in aegirine grorudites (EDS, wt.%)**

| Component	Titaniferous hematite				Pseudo-brookite		Mn-Zn-Ilmenite		Rutile						
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
TiO_2	6.79	17.25	16.95	22.63	66.37	69.84	51.74	50.86	98.56	94.3	94.69	94.1	92.2	92.3	92.37
FeO	93.21	76.76	79.01	72.67	18.04	19.69	32.20	32.04	1.44	1.68	2.25	2.87	1.05	1.03	1.13
MnO	—	5.99	4.04	4.70	4.65	3.21	10.67	11.61	—	—	—	—	—	—	—
ZnO	—	—	—	—	6.57	5.28	4.47	4.01	—	—	—	—	—	—	—
Nb_2O_5	—	—	—	—	—	—	0.91	1.49	—	3.99	3.06	3.05	6.76	6.65	6.5
WO_3	—	—	—	—	4.37	1.97	—	—	—	—	—	—	—	—	—
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100	100
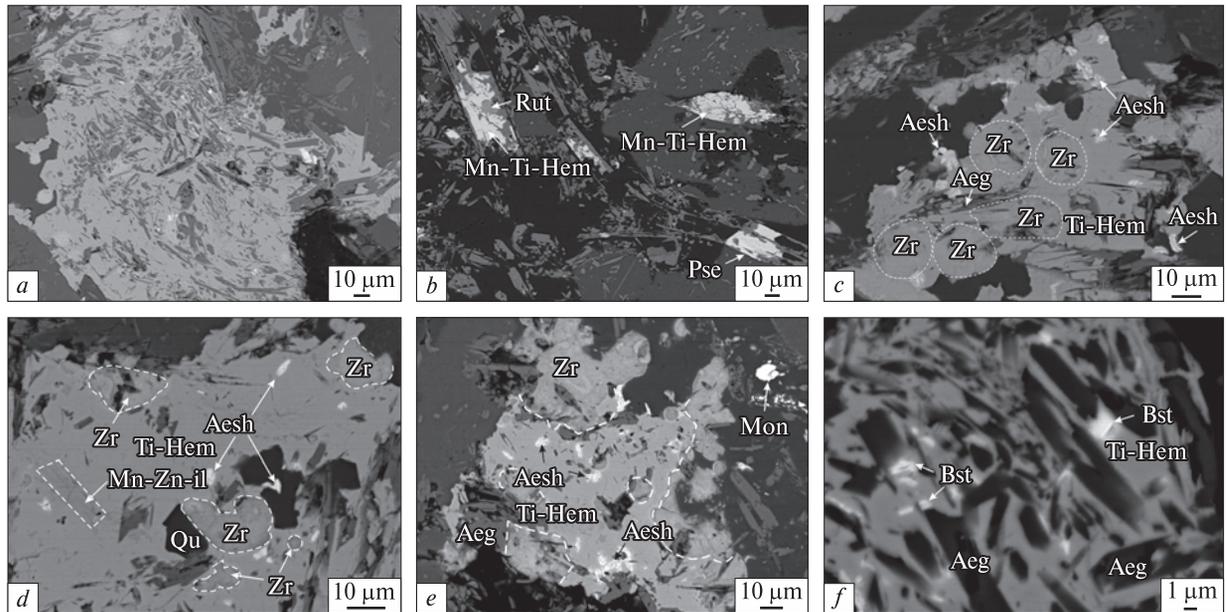
Fig. 5. Titaniferous hematite with numerous inclusions of other minerals in aegirine grorudites (BSE image). *a*) the segregation of titaniferous hematite grains with frequent inclusions of other minerals among which needle-like or prismatic aegirine and rare earth minerals (lighter parts) prevail; *b*) grains of different titanium minerals in the fine-grained groundmass. *Symbols*: Mn-Ti-Hem-titaniferous hematite with high content of manganese (up to 6% MnO, Table 3), Pse — pseudobrookite with high content of Zn, Mn and W (Table 3), Rut — rutile; *c*) grain of titaniferous hematite with numerous rounded zircon inclusions (Zr), small isometric inclusions of aeschynite group (Aesh) minerals and aegirine (Aeg); *d*) a part of titaniferous hematite (Ti-Hem) grain containing rounded zircon inclusions (hardly differ from general background of the site) and angular or irregular aegirine inclusions, Zn- and Mn-rich ilmenite (Mn-Zn-Il), small irregular or isometric inclusions of aeschynite group mineral and quartz (Qu); *e*) irregularly shaped titaniferous hematite with irregular or rounded zircon inclusions which are presumably at grain margin. Also, isometric or elongated inclusions of aeschynite group minerals and needle-like and prismatic aegirines are present. At the peripheral part of image isometric grain of monazite (Mon) is observed; *f*) the magnified fragment of titaniferous hematite grain with numerous inclusions aegirine and bastnäsite (Bst). The white dashed lines indicate the boundaries of the rounded zircon grains

chemical composition containing 23—25 mol. % $MnTiO_3$ and 7—8 mol. % $ZnTiO_3$, with increased content of Nb_2O_5 (0.9—1.49%) (Fig. 5).

Isolated small (20 μm) grains of titanium mineral very similar by Ti/Fe ratio to pseudobrookite were also found in the groundmass. This mineral has high content of ZnO (5—7%), MnO (3—5%) and WO_3 (up to 4.4%). It differs from the common ilmenorutile by the lack of Nb.

Hence, all detected titanium minerals in grorudites are rich in Mn, Zn and partly Nb, that is common for minerals of alkaline rocks and fenites of this region (the Dmytrivka open pit). Both aegirine- and amphibole-bearing grorudites host rutile which contains up to 6.6% Nb_2O_5. Taking into account that aegirine is the most abundant mafic mineral in the rock and it is rich in titanium (up to 4.26% TiO_2), it must be considered as important titanium mineral too.

Increased MnO and ZnO content in the mineral of ilmenite-pyrophanite series as well as in some amphiboles is a typical feature of minerals from agpaitic rocks and is related to the so-called Zn-Mn-trend of their evolution. Such enriched in Zn and Mn minerals (Zn-kupletskite, hendricksite, serandite, Mn-taramite, Mn-annite, pyrophanite, ecandrewsite) have been described in various rocks of the Oktyabrsky massif and alkaline metasomatites of the Eastern Azov region [2].

Accessory minerals. As was noted in previous publications [7, 12], grorudites of high-Ti aegirine type are richer in REE, Zr, Nb than the low-Ti ones (Table 1). It is also reflected in the amount of accessory minerals in these rocks. An aeschynite group mineral, Na-enriched calciocatapleiite, monazite-(Ce), bastnäsite-(Ce), britholite-like mineral, rare-earth apatite, zircon and unidentified Zr mineral were observed in high-Ti aegirine grorudites. Furthermore, zircon and Nb-bearing rutile were found only in amphibole grorudites. All these minerals are very small in size, the largest of them reaching 15—20 μm (rarely up to 50 μm), but most of them do not exceed 10 μm (commonly 5—6 μm) (Figs. 5, 6). Most grains or inclusions of these
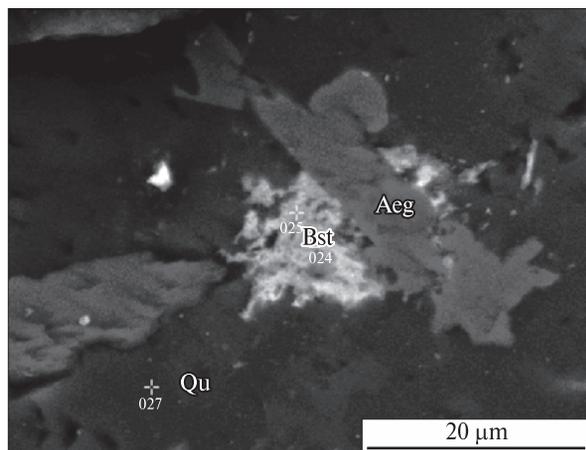
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Fig. 6. Intergrowth of small fibrous bastnäsite-(Ce) (Bst) with aegirine (Aeg)

Fig. 8. Fine-grained inclusions of rare earth F-carbonate (F-Car) in the central part of the prismatic aegirine (Aeg)

Fig. 7. Anhedral bastnäsite-(Ce) (Bst) grains in association with alkaline amphibole (Amph)

Fig. 9. A part of titaniferous hematite (Ti-Hem) grain with abundant fine and elongated inclusions of bastnäsite-(Ce) (Bst)

minerals are completely unhedral, and only some of their sections appear tetrahedrally or prismatic. Rare-earth fluorocarbonates mainly bastnäsite-(Ce), rarely parisite-(Ce) are the most common rare earth minerals; other minerals are monazite-(Ce), rare britholite-like mineral and rare earth apatite (Table 4).

Bastnäsite-(Ce) often forms small intergranular grains, the largest of which does not exceed 5 μm (Figs. 6, 7); rarely do they occur as inclusions in the central parts of aegirine grains (Fig. 8). Quite often numerous of bastnäsite-(Ce) inclusions in association with rare parisite-(Ce) are observed in titaniferous hematite (Figs. 5, *f*; 9). Due the tiny size of these inclusions the high content of some components (Si, Fe) is probably caused by capture from the host mineral. As it is common for the studied grorudites, LREE predominate in bastnäsite-(Ce) composition, while Y_2O_3 content is low (0.6—
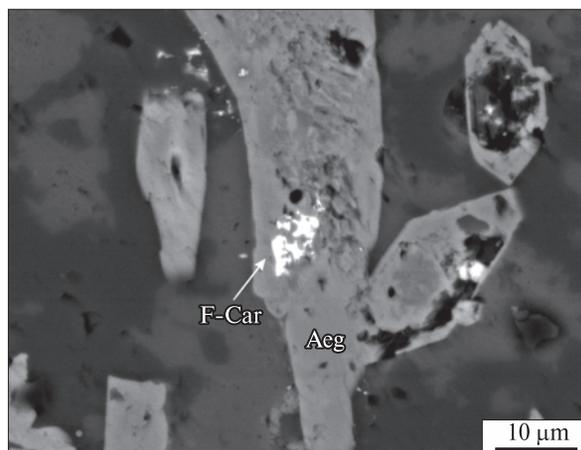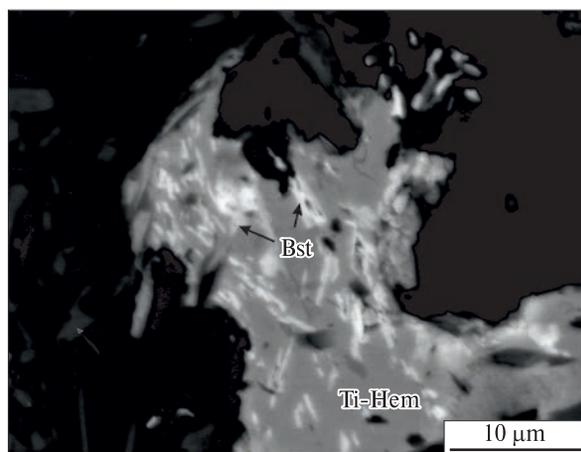
1.2 wt%, Table 4, an. 1—3). Yttrium minerals have not been found in grorudites.

The second most common rare earth mineral is *monazite-(Ce)* which often occurs as isolated small (10—15 μm) prismatic grains and sometimes in aggregates. These small grains of monazite-(Ce) seem to be intergrowths with bastnäsite-(Ce) and possibly britholite-(Ce) (according to the presence of SiO_2) (Table 4). Larger monazite grains possess increased CaO content (up to 4.9%), rarely PbO (2.1%) or ThO_2 (up to 4.5%). These chemical characteristics of Ca-bearing monazite-(Ce) are very similar to cheralite that was mentioned previously [12].

The *britholite-like mineral* (Table 4) as most other accessory minerals occurs as rare small grains reaching 5—10 μm in size, which are often located at the marginal parts of aegirine crystals or very close to them. These grains are heterogeneous
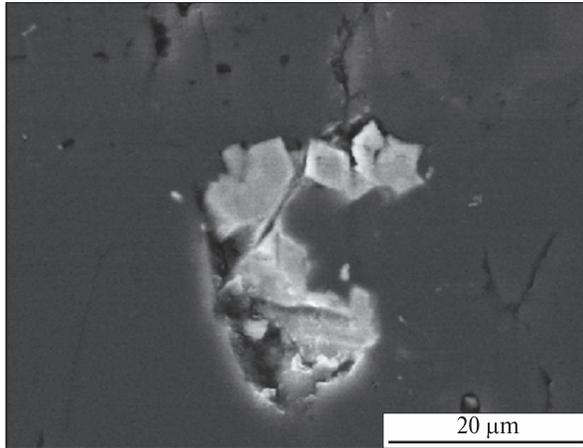
Fig. 10. Accumulation of small diamond-shaped zircon crystals possibly formed by replacement of primary Ca-Na-zirconosilicates

Fig. 11. Intergrowth of high-Y zircon (Zr) with aegirine (Aeg)

and likely form thin ingrowths with bastnäsite-(Ce) or, more likely, with monazite since high concentrations of phosphorus (up to 1.65% P_2O_5) and Pb (up to 1.1% PbO) were observed in some analyzes. As mentioned above, an increased content of PbO was recorded in some analyzes of monazite-(Ce). The britholite-like mineral has a slightly lower concentration of CaO (2.69—3.95%) and LREE substantially prevail over HREE.
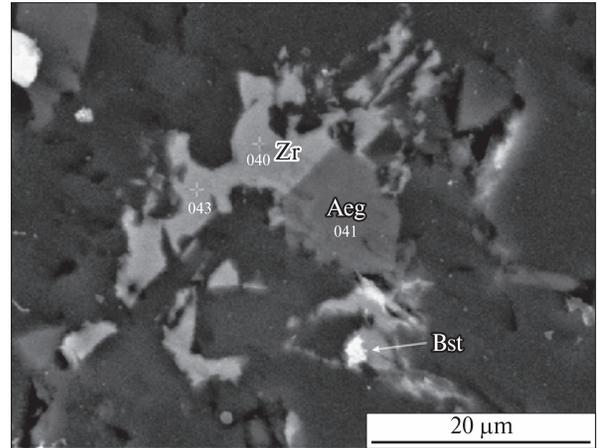
REE apatite is extremely rare in the investigated grorudites because of their low CaO (0.2—0.4 wt %, up to 1.7 wt % in one sample) and P_2O_5 (0.03—0.09 wt %) content. Only one heterogeneous irreular grain, 6×10 μm in size, has been discovered. Considering the high REE concentration, it is possible that it consists of tiny intergrowths of apatite with bastnäsite. However, the matrix of this grain has high CaO (29.43 wt %) and P_2O_5 (36.57 wt %) contents, and we consider this

Table 4. **Chemical composition of accessory rare metal minerals (WDS + EDS, wt.%)**

Compo-nent	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
SiO_2	10.08	—	—	13.17	14.34	11.34	6.01	34.28	36.56	42.89	37.37	39.14	37.13	32.84	36.24	30.71
Al_2O_3	1.62	—	—	0.89	3.16	1.45	1.29	2.13	3.30	4.23	1.28	0.94	2.78	0.98	3.88	3.05
FeO	4.05	—	—	4.92	1.41	3.21	0.69	3.56	2.21	9.9	8.8	15.52	1.2	1.87	1.85	5.05
CaO	2.77	5.48	5.44	4.93	3.18	3.95	29.4	1.07	2.55	0.71	1.82	1.47	0.85	1.08	0.83	1.29
K_2O	0.24	—	—	—	—	—	0.21	—	—	—	—	0.16	—	—	1.99	1.35
P_2O_5	—	—	—	24.39	0.02	1.65	36.57	—	—	—	—	—	—	—	—	—
F	—	3.79	4.55	—	—	—	—	—	—	—	—	—	—	—	—	—
PbO_2	0.77	—	—	2.09	—	1.11	—	0.6	0.85	0.24	—	1.89	—	—	0.7	0.25
Y_2O_3	0.55	—	—	—	0.45	0.57	0.47	1.47	1.81	1.53	2.10	1.24	7.80	8.40	2.25	1.90
La_2O_3	13.07	19.77	19.19	9.48	12.15	12.89	4.52	—	0.17	0.24	—	0.19	—	—	0.12	1.75
Ce_2O_3	24.92	44.55	44.07	21.52	27.1	27.38	14.37	0.15	0.17	0.65	—	0.89	—	—	0.45	3.69
Pr_2O_3	2.38	8.5	8.91	1.79	2.72	2.51	1.01	—	—	—	—	—	—	—	—	—
Nd_2O_3	9.47	17.95	17.8	8.12	9.92	9.91	6.03	—	—	—	0.01	0.63	—	—	0.20	1.35
Gd_2O_3	1.33	—	—	0.65	0.87	0.91	0.29	—	—	—	—	—	—	—	—	—
Dy_2O_3	0.35	—	—	0.14	0.36	—	0.12	—	—	—	—	—	—	—	—	—
Th_2O_3	0.11	—	—	1.94	0.58	0.75	0.18	—	—	—	—	—	—	—	0.72	0.44
UO_2	0.51	—	—	1.39	0.31	1.33	0.53	1.83	1.5	2.28	2.31	0.74	—	—	—	0.26
ZrO_2	—	—	—	—	—	—	—	50.8	40.29	32.36	33.57	38.62	50.23	54.84	38.14	35.93
Nb_2O_5	—	—	—	—	—	—	—	0.37	1.15	0.65	0.87	0.92	—	—	1.40	1.62
Total	72.21	100*	100*	97.38	76.55	78.96	101.73	96.3	90.56	95.67	88.14	102.4	99.99	100.00	88.78	88.64

N o t e. * — total is presented as 100%. 1—3 — bastnäsite-(Ce); 4 — monazite-(Ce), 1.94% SO_3 is included in the total; 5, 6 — britholite-like mineral; 7 — rare earth apatite; 8—12 — zircon; 13, 14 — Y-enriched zircons; 15, 16 — unidentified zirconium minerals rich in Y and Nb.

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grain as apatite (Table 4) with a high REE content (26.3 wt % total REE) and significant predominance of LREE (14.37 wt % of Ce_2O_3). The high content of REE, as well as the increased concentrations of radioactive elements, may also indicate partial capture of other minerals, like bastnäsite-(Ce) or monazite-(Ce) by the microprobe beam.

Zirconium minerals are zircon, Na-enriched calciocatapleiite and rarely an unidentified zirconium mineral (36—38 wt % ZrO_2, Table 4) with increased content of Nb_2O_5, Y_2O_3, UO_2, in some analyzes REE.

Zircon forms small grains of irregular shape, rarely there are aggregates (Fig. 10) and numerous small rounded inclusions in titaniferous hematite. These inclusions hardly distinguishable from the titaniferous hematite matrix in *BSE*-images (Fig. 5, c—e). In some grains of hematite such inclusions can occupy a considerable part of the mineral-matrix (Fig. 5, c). Some zircon grains contain up to 8.4 wt % Y_2O_3 (Fig. 11).

In one aegirine grorudite sample, a mineral containing Zr, Ca and Na was discovered. By the chemical composition it is close to minerals of the *calciocatapleiite* ($CaZr(Si_3O_9) \cdot 2H_2O$) — catapleiite ($Na_2Zr(Si_3O_9) \cdot 2H_2O$) series (Fig. 12). A general formula is $Na_xCa_{1-0.5x}Zr(Si_3O_9) \cdot 2H_2O$, where x can reach a maximum of 2 (i.e. catapleiite). Possible minerals are hilairite ($Na_2Zr[SiO_3]_3 \cdot 3H_2O$),
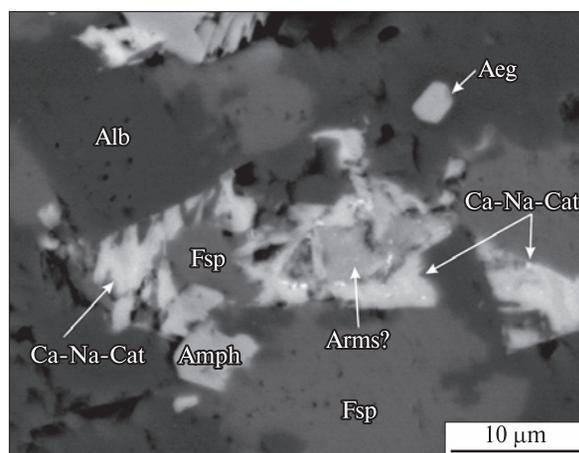

Fig. 12. An aggregate of Ca-Na-Zr-silicates of catapleiitegroup (Ca-Na-Cat) and armstrongite (Arms ?) in albite (Alb)-microcline (Fsp) groundmass

calciohilairite ($CaZr[SiO_3]_3 \cdot 3H_2O$), gaidonnayite ($Na_2Zr[SiO_3]_3 \cdot 2H_2O$), keldyshite ($Na, H)_2ZrSi_2O_7$) or parakeldyshite ($Na_2ZrSi_2O_7$). This catapleiite mineral requires more accurate investigation together with evaluation of its water content.

Furthermore it is observed in aggregates or intergrowth with Ca-Na-Zr-silicate, in which Zr : Si ratio is about 1 : 6, and the sum (p.f.u.) of Ca + + Na is 1.15 (Ca 0.77 and Na 0.34). Such Na-rich calciocatapleiite forms small individual grains (<10 μm) of irregular shape or their segregation in albite-feldspar groundmass. This mineral is

Table 5. **Composition of Ca-Na-Zr-silicates and aeschynite group minerals (EDS, wt.%)**

Component	Ca-Na-Zr-sillicates			Aeschynite group					
	1	2	3	4	5	6	7	8	9
SiO_2	52.35	53.27	67.75	8.51	17.26	—	7.28	7.86	2.37
TiO_2	1.01	0.88	—	43.1	41.08	43.63	44.26	47	45.01
ZrO_2	29.83	28.76	18.04	—	—	—	—	—	—
Al_2O_3	0.98	0.47	2.37	—	—	—	—	—	—
FeO	1.38	1.05	2.23	4.21	3.59	15.35	16.39	14.57	18.55
CaO	11.47	12.23	7.45	1.48	1.01	—	1.24	1.87	—
Na_2O	2.99	3.33	1.81	—	—	—	—	—	—
Y_2O_3	—	—	—	—	—	5.44	—	—	—
Ce_2O_3	—	—	—	16.83	12.67	—	—	—	14.1
Nd_2O_3	—	—	—	17.52	16.35	14.6	20.32	20.32	15.61
Gd_2O_3	—	—	—	—	—	5.05	4.10	—	—
ThO_2	—	—	—	—	—	8.47	—	—	—
Nb_2O_5	—	—	—	8.35	8.04	4.98	6.42	8.38	4.36
Ta_2O_5	—	—	—	—	—	2.48	—	—	—
Total	100	100	100	100	100	100	100	100	100

N o t e. 1, 2 — isolated grains of Na-enriched Ca-catapleiite; 3 — a mineral similar to armstrongite (Fig. 12); 4—9 — small inclusions in titaniferous hematite grains.

characterized by moderate Na_2O and the highest CaO content in comparison with other, even rock-forming, minerals. The mineral of such composition is inherent for agpaitic rocks and, in our opinion, it belongs to a primary zirconium mineral of grorudites. The Ca-Na-Zr-silicate in association with calciocatapleiite usually occupies the central part of aggregate, periphery of which is replaced by calciocatapleiite (Fig. 12). According to the formulae units of Ca + Na, Zr, and Si (calculation on the base of 9 cations), this Ca-Na-Zr-silicate is very similar to armstrongite $(CaZr[Si_6O_{15}]3H_2O)$.

As to the third zirconium mineral, it could not be analyzed accurately considering its extremely small size (up to 10 μm) and it needs to be studied further. According to the available analyses (Table 4), Si prevails over Zr + Y + Nb with a ratio of 1.4:1 to 2.2:1 in this mineral. The mineral could be classified as hagatalite (due to a high content of Nb, Y, sometimes REE, U), although the predominance of Si over Zr approximates it to gittinsite with low CaO content.

Apparently, Zr-minerals, at least a part of them, replaced primary Na-(eudialite, catapleiite, hilairite) or Ca-(gittinsite, armstrongite) Zr-silicates, which are typical for alkali-saturated rocks. Na-enriched calciocatapleiite could be one of them. For example, eudialite had been previously assumed as primary minerals in mariupolites of the Oktyabrsky massif [11], and later it was confirmed in agpaitic phonolites [10]. In recent studies [9] catapleiite relics were also found in bipyramidal zircon crystals in mariupolites. It is possible that monazite-(Ce) and bastnäsite-(Ce) in grorudites is consequence of replacement of britholite and/or aeschynite.

Niobium minerals. Although Nb concentration in aegirine grorudites is quite high (110—486 ppm by *XRF*, and up to 1218 ppm in one analysis), Nb minerals in these rocks have been unknown until now. We found a single Ti-REE-Nb-oxide, which most likely corresponds to a mineral of the aeschynite group, as small (~5 μm) inclusions in titaniferous hematite or in its marginal parts, rarely in the groundmass (Fig. 5, *c—e*). It is associated with zircon and REE-carbonate and has up to 8.35 wt % Nb_2O_5 (Table 5). REE (Ce_2O_3 and Nd_2O_3 being the more common) contents are in the order of 30 wt %. The (REE + Ca):(Ti + Nb) ratio in this minerals is close to 1:2 and quite similar to the minerals of aeschynite group. The high Fe content in some analyses is an artifact caused by

overlapping analyses with host titaniferous hematite; FeO content in the mineral located outside of hematite does not exceed 4 wt. % which is common for aeschynite [6].

An increased Nb content was recorded in a mineral of ilmenite-pyrophanite series in aegirine grorudite. In contrast, in the sample of amphibole grorudite with medium Nb concentration (88 ppm by *ICP-MS* or 133 ppm by *XRF*), only rutile with 6.76% Nb_2O_5 was found (Table 3). Such rutile occurs as inclusions in hematite (up to 3.82% TiO_2) or is present among quartz. It is possible that a significant or even prevailing part of Nb is isomorphically scattered in other minerals, such as in the unidentified Zr-mineral.

A possible relationship of trace-element minerals and titaniferous hematite. To the best of our knowledge, these unusual exsolution (?) textures of rare minerals in titaniferous hematite have not been found in other alkaline granite complexes. Therefore, all our further arguments regarding the possible origin of the close association (intergrowth, inclusions) of HFSE-mineralization with titaniferous hematite in grorudites are based mainly on the crystallization conditions of hematite and experimental studies of trace elements' distribution in silicate melts. As noted above, titaniferous hematite grains are usually anhedral and often contain numerous small inclusions of needle-like aegirine and HFSE-minerals. We take this as an argument for late crystallization, possibly from the residual and low-Ti and Fe-rich melt (or individual melt droplets) close in composition to hematite. Assuming such a residual melt, the redistribution of a number of trace elements into this melt is also quite probable. The experimental data of [28] can partly support this model. According to these authors, partition coefficients of trace-elements in the Fe_2SiO_4–Fe_3O_4–$KAlSi_2O_6$–SiO_2, Fe_3O_4–$KAlSi_2O_6$–SiO_2, Fe_3O_4–Fe_2O_3–$KAlSi_2O_6$–SiO_2, Fe_3O_4–Fe_2O_3–$KAlSi_2O_6$–SiO_2–$Ca_{0.5}Na_{0.5}Al_{1.5}Si_{2.5}O_8$ systems (in the presence of H_2O or other elements such as P, S, F or Cl) indicate strong preference of HFSE and REE for the Fe-rich melt, in contrast to anhydrous melts of similar composition (regardless of fO_2). This data is consistent with the results of the earlier experimental work [34, 45] related to the trace element partitioning between immiscible silicate liquids where trace elements were concentrated in Fe-rich melts. In Ti-rich systems, enriched in REE, Y, Sr and Nb, at 1200 and 1250 °C and P = 2 kbar in the presence of aqueous or alkaline fluid the melt also splits into two phases, an aluminosilicate
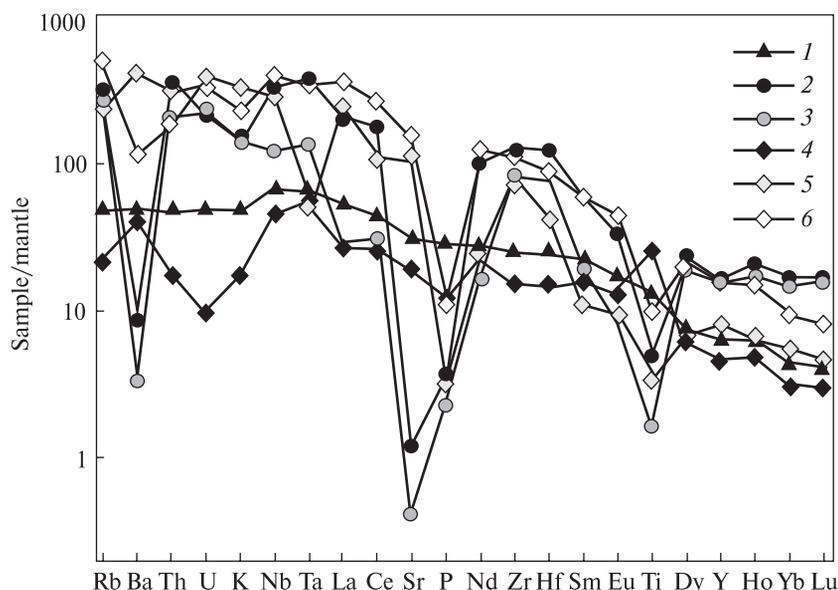
Fig. 13. Primitive mantle normalized trace element diagrams for Devoniand rocks of the Azov region. *Legend*: *1* — OIB by [44]; *2, 3* — high-Ti and low-Ti grorudites, respectively; *4* — gabbro of the Pokrovo-Kyriyivo complex; *5, 6* — nepheline syenites of this complex

matrix and droplets enriched in Ti, REE, Y, Sr, and Nb [43]. Thus, in the Ti-silicate systems liquid immiscibility also leads to a significant enrichment in rare components, including Zr, in the Ti-rich melt phase. As the temperature decreased, HFSE were expelled from titaniferous hematite with subsequent crystallization of their own minerals.

Discussion. *Grorudite origin.* Many authors considered that silica-oversaturated agpaitic rocks originated due to the crustal contamination of mantle-derived, silica-undersaturated alkaline magmas [21, 30]. Primary silica-undersaturated alkaline melts occur as a result of partial melting of metasomatically enriched mantle under relatively dry and reducing conditions [16, 26].

Low-degree partial melting of mantle gives rise to alkali and often silica-undersaturated parent magmas, and already at the stage of melt generation the conditions for HFSE enrichment were favorable. During evolution, these melts achieve a significant enrichment in volatile components (Cl and F) and alkali metals (Na and K), that considerably decreases the solidus temperatures and allows such melts to differentiate down to unusually low temperatures (~400 °C according to [29, 39]) before expelling fluid. It is considered that high concentrations of alkalis and fluorine increase the solubility of HFSE as well as higher proportion of non-bridging oxygen allows concentrating HFSE. So, the high concentrations of volatile components in highly evolved peralkaline magmas lead to high concentrations of highly incompatible elements.

Considering the Devonian age of grorudites, there is a reason to believe them to be the derivatives
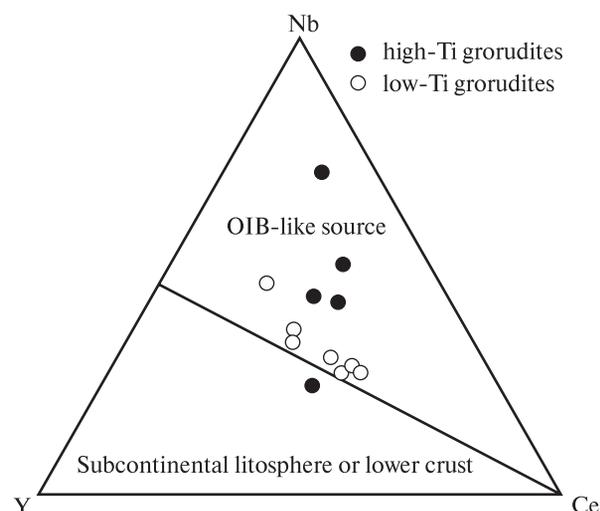

Fig. 14. Triangular Y-Nb-Ce diagram for distinguishing of different types of A-type granites [20]

of primary subalkaline basalts similar to initial melts of the Pokrovo-Kyriyivo complex [7]. High agpaitic index and low #Mg also point to highly evolved composition of grorudites. This assumption is confirmed by high, as for granites, concentrations of Ti, Cr, V, Ni, possibly inherited from the primary basic melts. This caused crystallization of titaniferous hematite, ilmenite and rutile as well as aegirine with increased TiO_2 content in aegirine grorudites. Samples of high-Ti and low-Ti grorudites show slightly fractionated REE patterns and moderate Eu/Eu^* ratios (($La/Yb)_n$ 11.5 and 1.7; Eu/Eu^* 0.77 and 0.46 respectively). Primitive mantle-normalized spider-diagrams for both types of grorudites are highly enriched in trace elements compared with those of OIB and gabbro of the
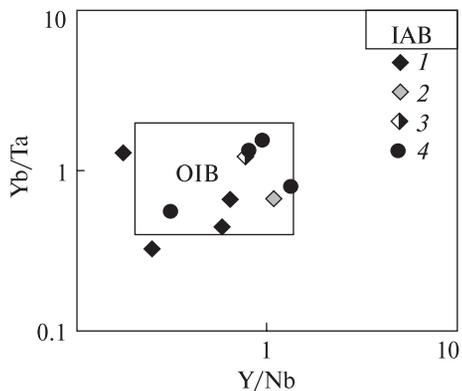
Fig. 15. Yb / Ta vs. Y/Nb in various A-type granitoid suites [20]. OIB — the oceanic-island basalt; IAB — island-arc basalts. *Legend*: *1* — basic and syenitic rocks from the Pokrovo-Kyriyivo complex; *2*, *3* — essexites of the Zirka and Prymorskyi massifs respectively; *4* — grorudites

Pokrovo-Kyriyivo complex but similar to those of nepheline syenites from this complex (Fig. 13). The deep negative anomalies of Ba, Sr, P and Ti and enrichment by other incompatible elements are consisted with generation of alkali granitic melts during fractionation of mantle derived basaltic melts. Moreover, high- and low-Ti grorudites fall into the upper A1 field in the Nb-Y-Ce diagram (Fig. 14) [20], implying a source for these granites was similar to that of oceanic-island basalts. Their position within OIB field in another diagram (Fig. 15) also confirms a common source for Devonian primary basalts and grorudites of the Azov region, as well as for gabbro and essexites from other Devonian massifs of this region.

Differentiation of such primary basaltic melt at the final stages could have led to the appearance of silica-oversaturated agpaitic residual liquids of granitic composition, similar to grorudites [7].

***Possible processes of HFSE concentration.** Hydrothermal processes.* Many researchers believe that hydrothermal processes have played a significant role in the Zr-Nb-Y-REE mineralization in alkaline granitic rocks [3, 36, 37] since there is a lot of evidences that HFSE are mobile in hydrothermal systems. An occurrence of HFSE minerals (e. g., bastnäsite and baddeleyite) in fluid inclusions is also used as a direct evidence of HFSE migration in hydrothermal fluids [27, 35]. The geochemical and mineralogical data indicate that the alterations of agpaitic acidic rocks results in the significant Ca, F and HFSE enrichment, hematitization and silicification. Furthermore, according to the experimental data [48], Zr and Nb solubility in the hydrothermal systems is quite low, and that Ta is

even less soluble than Nb in aqueous fluid. However, solubility and hydrothermal transfer of Ta and Nb, as well as Zr, are significantly increased by temperature and F (or Cl^-, CO_3^{2-}, PO_4^{2-}) in the solution [1, 48].

Triggers for different ore-forming processes in alkali acidic rocks are not yet fully understood. For instance, the Zr, Nb, REE and Y enrichment in agpaitic granites of the Khaldzan deposit (Mongolia) is considered as a result of magmatic fractionation [25] or as a result of intensive secondary alteration [3, 4].

The absence or insignificant effect of hydrothermal alterations of grorudites is indicated by the only minor development of aegirine after amphibole, restricted appearance of rare-earth F-carbonates, rather high Nb/Ta ratio (~15), low concentration (ppm) of Li (<60, rarely 250), Sn (8—12), Cs (0.2—0.3) and W (0.9—1.2) and increased concentration of Rb (90—205), as well as by low (in available chemical analyses) concentration of volatile components (H_2O, Cl, F and CO_2). Mentioned incompatible elements have a strong affinity for magmatic fluids, so their enrichment is commonly used as a marker of a magmatic-hydrothermal alteration of granites [15]. The high Nb/Ta and Zr/Hf ratios have been proposed as the markers of magmatic-hydrothermal interactions. In the investigated grorudites the Zr/Hf ratio is uniform (~38) whereas in the granites enriched by Sn, Li, W, Nb and Ta this ratio is typically <25. It is possible that the low content of volatiles, especially F, may indicate quite dry conditions during crystallization or early volatile expulsion from the residual melt at hypabyssal conditions. That may explain the absence or insignificant occurrence of secondary HFSE mineralization or immobility of these elements after the crystallization. Considering the high HFSE concentrations, it is more possible that grorudites have originated due to the primary magmatic differentiation. Processes of hydrothermal alteration did not affect significantly the studied rocks and resulted mainly in the partial replacement of the primary accessory minerals. We assume that crystallization of large bodies or intrusions of grorudites (agpaitic alkaline granites) took place at more fluid-saturated conditions, which facilitated prolonged melt differentiation; the influence of post-magmatic fluids on the concentration and migration of HFSE was more significant. Hence, large volumes of HFSE could have concentrated in such bodies of holocrystalline alkaline granites during the melt crystallization

with subsequent separation of the volatile-enriched fluids. This process could promote the more effective redistribution and accumulation of HFSE minerals in the apical parts or contact zones of the intrusions.

Magmatic processes. The importance of magmatic processes for the HFSE enrichment and subsequent formation of the economical deposits follows from the melt inclusions studies. Unfortunately, such studies are not carried out for grorudites of the Azov region. Studies from other complexes, however, indicate that HFSE concentration in alkaline felsic magmas is higher than in other types of felsic melts and in some cases can reach the percentage level. For example, Zr, Nb and REE concentrations reach 2.7, 0.6 and 0.3 wt % correspondingly in melt inclusions in agpaitic granite of the Khaldzan-Buregtey massif [25]. Similar concentrations of these metals are recorded in melt inclusions in agpaitic granites of the Amis complex [42]. According to experimental studies, the solubility of Zr in metaluminous and plumasite granitic melts is below 100 ppm [23, 46], whereas in agpaitic melts it often exceeds 1 wt % [24, 31]. Moreover, the increased agpaitic index of the melt, and high alkali and fluorine concentrations facilitate solubility of HFSE due to the formation of alkaline-silicate and/or alkaline-fluoride compounds and increased proportion of non-bridging oxygen (comparing to metaluminous and peraluminous melts) that allows to increase concentration of HFSE [17, 19, 40, 46]. Therefore, the residual aluminosilicate melts from the crystallization differentiation of the primary magmas are enriched in Nb, Ta and probably Zr, Y and REE. Expectedly, their subsequent crystallization (after expelling of fluid phase) is accompanied by a rich gangue mineralization. Experimental data regarding Nb and Ta partition between aqueous F-fluids and aluminosilicate melt at high temperature (900—1200 °C) [17] indicates that these elements are partitioned mainly into the alkaline aluminosilicate melt. Similar results regarding Ta and Nb partition between peralkaline granitic melt and F-alkaline fluids were obtained by [22]. Therefore, considering increased or high Nb concentrations in grorudites, the PT-conditions of differentiation (e. g., low F concentration, high fO_2 and short crystallization term) probably did not facilitate appearance and subsequent accumulation of Nb minerals. Taking into account these data, as well as 1) the very low #Mg and high agpaitic index of grorudites, 2) the increased concentration of

HFSE and REE, but low Sr and Ba, and 3) the moderate Eu* (0.46—0.77) anomalies, accumulation of trace elements as a consequence of their concentration in the residual fractions of differentiated mafic and alkaline-mafic initial melts is most likely.

Conclusions. 1. The mafic minerals of high-Ti (aegirine-bearing) grorudites of the Azov region, especially amphiboles, appear to be more diverse in chemical composition than previously thought. During the early stage of their evolution the phenocrysts of Ca-Na- and alkali amphiboles crystallized first. With increasing alkalinity and oxygen fugacity aegirine became more stable during the evolution.

2. The aegirine grorudite are more enriched in incompatible elements and consequently contains more abundant gangue mineralization compared with the amphibole type. In polished section significant part of rare-metal mineralization is spatially related to the titaniferous hematite, the main ore mineral of the aegirine-type grorudites. Probably, the close association of these minerals is a consequence of HFSE and REEs concentration in the residual iron-enriched melt phase. The latter could be formed as a result of liquid immiscibility between alkali silicate and Ti-Fe-rich melt at high alkalinity and volatile-rich fluids, which contribute to the partitioning of HFSE and REEs into the Ti-Fe-rich melt.

3. Taking into account the revealed peculiarities of gangue mineralization and some geochemical features of grorudites, these rocks crystallized without significant influence of hydrothermal alteration. The latter is observed only as partial replacement of primary accessory Na-Ca-Zr-silicates and the appearance of secondary fluoro-carbonates.

4. Considering their Devonian age, grorudites' mineralogical composition and incompatible element concentration indicate that these rocks belong to A-type granites, which are genetically related to primary subalkaline basaltic magmas similar to initial melts of the Pokrovo-Kyriyivo complex and other gabbro-syenitic massifs of the Eastern Azov region.

5. Further mineralogical and geochemical studies of grorudites of the Eastern Azov region are related not only with petrological and mineralogical importance but have also significant practical implications. Small intrusions of alkaline granites (holocrystalline analogues of grorudites, i. e. pantellerites and commendites), that potentially

can be discovered in this region, may host occurrences or deposits of Nb, REE, Zr, Sn, and Be, like the Perga granites (Ukrainian Shield) or the Katugino deposit (Aldan Shield, Russia). Small massifs or intrusions of alkaline granites in the Eastern Azov region could easily be missed during geological mapping or prospecting, because coarse-grained grorudites in the central parts of some dikes (for example Talova ravine) are macroscopically almost indistinguishable from the host granites.

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МІНЕРАЛОГО-ПЕТРОЛОГІЧНІ ОСОБЛИВОСТІ ГРОРУДИТІВ СХІДНОГО ПРИАЗОВ'Я (УКРАЇНА)

У межах Українського щита лужні граніти та їхні гіпабісальні й ефузивні аналоги поширені обмежено. У Східному Приазов'ї відомі дайкові аналоги лужних гранітів (грорудити), які є дискретними за хімічним та мінеральним складом і розглядаються як аналоги пантелеритів (егіринові високотитанисті) або комендитів (амфіболові низькотитанисті). Високотитанисті егіринові грорудити інтенсивніше збагачені некогерентними рідкісними елементами (*REE*, Zr, Nb) порівняно з низькотитанистими різновидами. У результаті останніх досліджень виявлено нові для цих порід мінерали титану (титанистий гематит із підвищеним вмістом MnO, різновиди серії $FeTiO_3$—$MnTiO_3$—$ZnTiO_3$), невідомі раніше в цих породах Ca-Na-амфіболи, а також структурні взаємовідношення егірину та лужного амфіболу. Незважаючи на високий або підвищений вміст *HFSE* в грорудитах, інформації про власні мінерали-концентратори цих елементів майже не було. В егіринових різновидах нами виявлено і проаналізовано мінерали рідкісних елементів — монацит-(Се), бастнезит-(Се), бритолітоподібний мінерал та рідкісноземельний апатит, циркон, Ca-Na-катаплеїт, а також остаточно недіагностовані мінерали цирконію та мінерал групи ешиніту. В амфіболовому грорудиті із акцесорних мінералів виявлено лише циркон і ніобійвмісний рутил. Згадані мінерали часто мають дуже дрібні розміри, найбільші з них можуть досягати 15—20 µm, більшість не перевищує 10 µm, що значно ускладнює їх остаточну діагностику. Цікавим і досить незвичним виявилося те, що значна частина рідкісних мінералів, особливо бастнезит-(Се), мінерал типу ешиніту, циркон, утворюють включення у більших зернах титанистого гематиту. Припускається, що значна частина рідкісних металів може ізоморфно входити до складу породоутворювальних мінералів (лужних піроксенів та амфіболів), а циркон та інші недіагностовані мінерали Zr (принаймні їхня частина) є вторинними і утворилися за рахунок первинних натрієвих (евдіаліт, катаплеїт, ілерит) або кальцієвих (гітинсит, кальціокатаплеїт) цирконосилікатів, характерних для перенасичених лугами (агпаїтових) порід. Зважаючи на петрологічні особливості та характер рідкісноземельної мінералізації грорудитів Приазов'я, є підстави вважати, що рідкіснометалева мінералізація в цих породах є наслідком диференціації вихідних магматичних розплавів, які за складом подібні до титанистих базальтів (характерних порід цього району). Вторинні гідротермальні процеси слабко проявлялися у досліджуваних породах і призводять переважно до заміщення первинних акцесорних мінералів. Ураховуючи підвищену або високу концентрацію Nb у високотитанистих грорудитах і незначну кількість Nb-мінералів, ймовірно, що фізико-хімічні параметри диференціації магматичних розплавів (низька концентрація F, висока fO_2 і гіпабісальні умови формування) не сприяли повній розкристалізації та накопиченню рідкіснометалевої мінералізації. Проте наявність грорудитів із високим вмістом рідкісних металів у цьому регіоні вказує на перспективи виявлення невеликих масивів подібних лужних гранітів (розкристалізованих аналогів грорудитів), з якими можуть бути пов'язані родовища та/або прояви Nb, *REE*, Zr, Sn, Be.

Ключові слова: грорудит, лужний граніт, ешиніт-(Се), цирконієві мінерали, монацит-(Се), бастнезит-(Се), бритолітоподібний мінерал, *REE*-апатит, Na-збагачений кальціокатаплеїт.