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PETROLOGICAL FEATURES OF ACID PLUTONIC ROCKS OF THE OSNYTSKYI COMPLEX (VOLYNSKYI MEGABLOCK OF THE UKRAINIAN SHIELD)

The Osnytskyi complex, located within the Volynskyi megablock of the Ukrainian Shield, is represented by gabbro-diorite-granodiorite-granite series and is a plutonic part of the Klesivsko-Osnytska volcanic-plutonic association. Granitoid rocks of the Osnytskyi complex form a single formation of granites, which have a common spatial and structural origin. There are such types of granites as leptite-like, fine-grained, inequigranular-medium-grained, coarse-grained, etc.

Petrographic, mineralogical and petrochemical studies of Osnytski inequigranular porphyraceous granites have been performed. Rock-forming (potassium feldspar, plagioclase, quartz, biotite and hornblende), accessory (zircon, apatite, titanite), ore (magnetite, ilmenite, pyrite) and secondary (epidote, sericite, chlorite, siderite, bastnäsite) minerals were identified and described. Biotite chemically corresponds to siderophyllite of magmatic origin (calcareous-alkaline orogenic complexes). Crystallization of the granites took place under conditions of low acidity at a temperature of ~ 760 °C and a sufficiently high pressure.

Key words: granitoids, Osnytskyi complex, rock-forming, accessory, ore and secondary minerals, biotite, formation conditions, Volynskyi megablock, Ukrainian Shield.

Introduction. The Osnytskyi complex, developed within the Osnytska and Novohrad-Volynska structural zones of the Volynskyi megablock (Ukrainian Shield), is represented by gabbro-diorite-granodiorite-granite series of rocks and is a plutonic part of the Klesivsko-Osnytska volcanic-plutonic association (Fig. 1). In the Osnytska zone, the rocks of the complex comprise a large Rokytnianskyi massif (covering an area of up to 1,000 km^2) and several smaller massifs, which are confined to the so-called Volyno-Poliskyi (Osnytsko-Mikashevytskyi) belt on the border of the Ukrainian Shield and the Belarusian Crystal Massif. In the Novohrad-Volynska zone, the Osnytskyi complex is represented by relatively small (up to 20 km^2) rare massifs (Shepetivskyi, Mukharivskyi, Tokarivskyi, etc.), which form branches from the belt.

Various researchers distinguish from three to five age generations of rocks of the Osnytskyi complex: gabbro, gabbro-diorites; diorites, monzodiorites, subalkaline quartz diorites; granodiorites, quartz monzonites; granites, granodiorites; leucocratic granites [20]. The Mukharivskyi and Tokarivskyi massifs are composed exclusively of granites, and the Smoldyrivskyi and Shepetivskyi ones – of granodiorites and diorites.

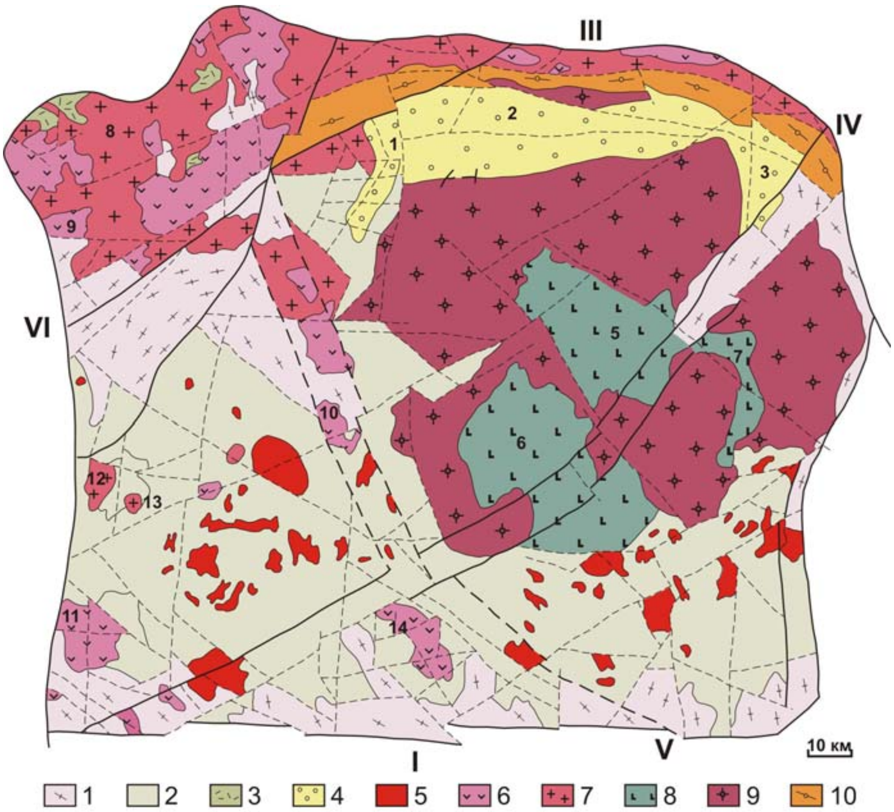


Fig. 1. Geological structure of the Volynskyi megablock (North-Western region) of the Ukrainian Shield: *1* – plutono-metamorphic complexes; *2* – Teterivska series; *3* – Klesivska series; *4* – Ovrutska series; *5* – double mica granites of the Kirovohrad-Zhytomyrskyi complex; Osnytskyi complex: *6* – diorites, granodiorites; *7* – granites; Korostenskyi complex: *8* – gabbro-anorthosites; *9* – rapakivi and rapakivi-like granites; *10* – granites of the Perzhanskyi complex. Main faults: I – Andrushivskyi; II – Brusylivskyi; III – Prypiatskyi; IV – Teterivskyi; V – Tsentralnyi; VI – Sushchano-Perzhanskyi. Numbers on the map: 1 – Bilokorovytska structure; 2 – Ovrutska structure; 3 – Vilchanska structure; 4–14 – massifs: 4 – Perzhanskyi, 5 – Chopovytskyi, 6 – Volodarsk-Volynskyi, 7 – Fedorivskyi, 8 – Rokytnianskyi, 9 – Vyryvskyi, 10 – Barashivskyi, 11 – Shepetivskyi, 12 – Mukharivskyi, 13 – Tokarivskyi, 14 – Bukynskyi.

To the history of the study of the Osnytskyi complex. Osnytskyi granite complex was identified by L. Tkachuk [17]. Various aspects of geology, petrology, mineralogy, etc. of these granites have been studied by such scientists as P. Veremiev, V. Verkhohliad, A. Khatuntseva, O. Matkovskyi, M. Shcherbak, I. Shcherbakov, V. Skobelev, K. Sveshnikov, K. Yesypchuk, O. Zinchenko and many other geologists [1–3, 6, 7, 9–12, 15, 16, 18–20, etc.]. They significantly supplemented the works of geologists of the older generation (V. Laskarev, S. Małkowski, P. Radzishewski, K. Smulikowski, Yu. Tokarski, P. Tutkovskyi, etc.) with the data of modern analytical research [20].

In [13], ultrametamorphic and igneous formations were distinguished within the Osnytskyi complex. The group of ultrametamorphic rocks includes Vyryvski diorites and granodiorites and plagioclase, plagioclase-microcline and essentially microcline granites, which are the products of granitization of the Klesivska series volcanites – diabases, diabasic and trachyandesitic porphyrites, dacite- and quarz-porphyries, leptites. The group of igneous formations includes diorites, granodiorites, and granites, which have intrusive relationships with the rocks of the Klesivska and Teterivska series, as well as with granitoids of the first group.

The authors of [5] questioned the ultrametamorphic origin of the Osnytski granites. First of all, these granites are not associated with migmatites, as is the case with all ultrametamorphic granitoids. Studies of the peculiarities of contacts between rocks, in particular, the presence of endocontact varieties of subvolcanic appearance, gave grounds to consider all age generations of the complex intrusive formations. The close spatial connection with volcanites, the predominant confinement of granites and granodiorites to volcanic fields of different composition made it possible to treat these rocks as a single volcanic-plutonic association. According to [6, 7, 15], the complex has a significantly magmatic nature; plutonic and volcanic rocks form a single comagmatic series in its composition.

On the Map of Geological Formations of the Precambrian of the Ukrainian Shield [8], the rocks of the Osnytskyi complex are divided into diorite-granodiorite and subalkaline granite formations.

The following values of the radiological age of these granitoids are given: 2.02–1.96 billion years [19], 1,995 ± 15 million years [5], 1,970 ± 20 million years [3].

Research methods. The complex of performed works included geological observations of rocks in outcrops and laboratory studies (petrographic, mineralogical, petrochemical, etc.). We studied the mineral composition and structural and textural features of rocks in thin sections under the МИН-5 polarising light microscope. Microanalytical studies of granitoids' polished samples were performed in the laboratory of the Faculty of Physics of Ivan Franko National University of Lviv using a scanning electron microscope РЕММА-102-02 (Sumy), equipped with energy-dispersive analyzer "EDAR". The parameters of the analysis are as follows: accelerating voltage – 20 kV, probe current – 1 nA, probe diameter – 0.1 μm. The brand of the standard used to calibrate the device is НЭРМА. ГЕО1.25.10.74 ГТ; manufacturer – "Geotechnology" (Ukraine). The following standards were used to calibrate individual elements: Na – albite; Mg – periclase; Al, Si, Ca – anorthite; P – fluorine-apatite; S – pyrite; K – microcline; Ti – macedonite; Cr – eskolaite; Mn – manganite; Fe – hematite; As – GaAs (synthetic); Ba – barite; Sc, Co, Ni, Cu, Zr, Ag, Au are pure elements. "Magallanes 3.2" software was used to process the obtained data.

Material composition of granitoids of the Osnytskyi complex. Granitoid rocks form a single formation of granites that have a common spatial and structural origin. Spatially and genetically, this formation associates with gabbro-diorite-granodiorite formation [4]. The variety of granites is revealed, first of all, in their appearance. Massive medium-grained rocks predominate, fine-grained ones are of limited development, and coarse-grained ones are less common. The rocks usually contain a small amount of porphyraceous feldspar grains. One of the most characteristic macroscopic features of Osnytski granites is purple-grey rounded grains of quartz. Rocks are relatively depleted of accessory minerals [10], most of which are magnetite, zircon, apatite and pyrite.

We identified several varieties of granitoids during the study of their samples.

Osnytski granodiorites (Fig. 2, *a*) are characterized by the fact that the total content of feldspars in them exceeds 60 %, and plagioclase significantly predominates over potassium feldspar.

Leptite-like granites (see Fig. 2, *b*) are slightly common rocks of light pink, brownish-pink colour with a massive, sometimes spotted or eutaxitic structure. They are quite similar to leptites, geochemically and petrochemically related to them, but have a coarser structure.

Fine-grained granites (see Fig. 2, *c*) quite often form large inhomogeneous fields, which contain small bodies of fine-medium-grained granodiorites, gabbro and leptite-like granites; they are often fixed in the form of border strips along the contact with coarse-grained Osnytski granites and granodiorites and plagiomigmatites of the Sheremetivskyi complex. Contacts of fine-grained granites with leptite-like and medium-coarse-grained differences in most cases are indistinct, and with rocks of the diorite-granodiorite series – clear. The colour of the rock is pinkish-grey, pink. The texture is hypidiomorphic, rarely aplitic, there are areas of poikilitic one; also the texture is massive, sometimes directive. The average mineral composition of granites is as follows, %: potassium feldspar – 48, plagioclase – 28, quartz – 20, biotite – 4, single grains of muscovite and epidote.

a *b* *c*

Fig. 2. Granitoid rocks of the Osnytskyi complex:
a – Osnytskyi granodiorite; *b* – leptite-like granite;
c – fine-grained granite.

Inequigranular-medium-grained granites (Fig. 3, *a*) are most common among granitoids. They often form inhomogeneous fields, which contain bodies of granodiorites, leptite-like granites, diorites and gabbroids, and they also form bands around the bodies of typical coarse-grained granites. Macroscopically the rocks are massive, occasionally porphyraceous. Their colour varies from grey, in places dark grey, through pinkish-grey to pinkish of varying saturation and greyish-white. The texture of rocks is hypidiomorphic and granitic, occasionally porphyroid. The mineral composition is as follows, %: feldspars – 55–60, quartz – 25–30, biotite – 3–8, hornblende – 1; accessory minerals – apatite, zircon, titanite, magnetite, ilmenite, rutile, very rarely fluorite; secondary minerals – epidote, chlorite, sericite and calcite.

Coarse-grained granites (see Fig. 3, *b*), available throughout the Osnytskyi block, form massifs and bodies of various shapes and sizes; the largest of them were mapped by geologists in the area of the settlements of Koroshchyno, Snovydovychi, Klesiv, Vyry, and Selyshche. In the east and northeast of the Osnytskyi block, they are in contact with granodiorites, in the south – with medium-fine-grained granites and diorites, in the north-western part – with leptites, leptite-like and fine-grained granites, and occasionally with andesitic porphyrites. Massifs are often heterogeneous, contain small xenoliths and in some places – larger outliers of granodiorites, leptite-like granites, and rocks of the Klesivska series. Macroscopically, the rocks are reddish-pink, pink and light grey, with a massive, sometimes porphyraceous texture, with evenly distributed individual grains or nest-like secretions of purple quartz. The rocks also have hypidiomorphic-grained structure, in broken down varieties – blastocataclastic.

a

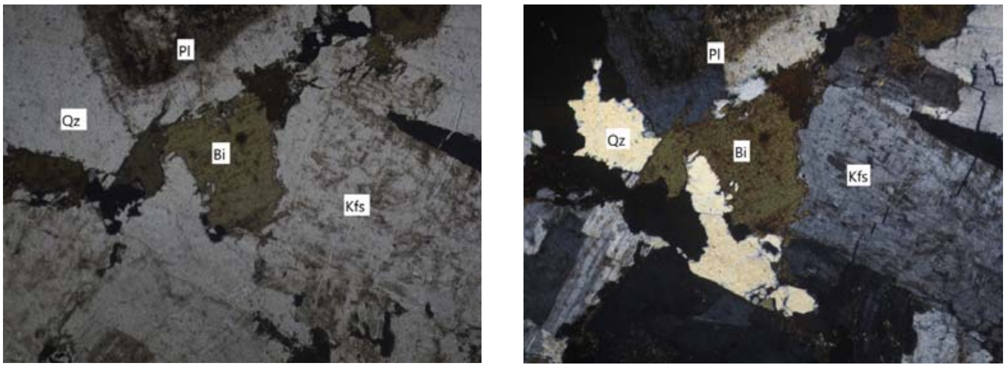
b

Fig. 3. Inequigranular-medium-grained (*a*) and coarse-grained granite (*b*) of the Osnytskyi complex.

Results of petrographic research. We examined different features of inequigranular porphyraceous granites (Fig. 4). Rock-forming minerals in them are represented by potassium feldspar, plagioclase, quartz, biotite and hornblende, accessory – by zircon, apatite, titanite, ore mineral, and secondary – by epidote, sericite, chlorite and others.

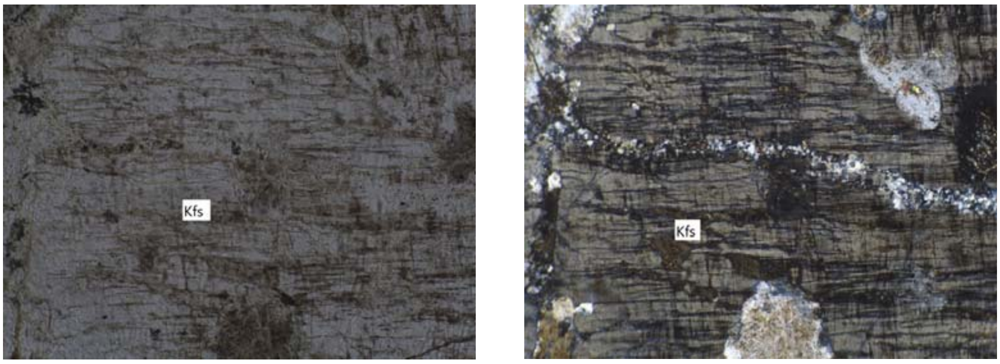
Potassium feldspar (35–40 %) forms large grains over 2 mm in size, sometimes up to 8 mm, prismatic, tabular, without shagreen surface and relief. Here and there cleavage is well defined. Mineral has low colours of first-order interference – grey, light grey; $n_g - n_p = 0.005$–0.007. K-spar is presented by microcline-perthite (Fig. 5). There are microcline lattice and regular ingrowths of albite-oligoclase (perthites), which were formed in different ways. Some ingrowths form clearly demarcated prismatic crystals, sometimes with polysynthetic twinning, and in other cases perthites have a crinkled, jet-like shape. Pelitization (formation of secondary clay minerals) is intensively developed on microcline-perthite, which causes the appearance of brown colour on the surface of K-spar. Silicification is found in the fractures of some grains.

Plagioclase (20–25%) forms elongated prismatic grains up to 1 mm in size, without shagreen surface and relief (Fig. 6). Grains are colourless, light grey colours of the first-order interference are visible under cross polarised light, $n_g - n_p = 0.007$–0.008.



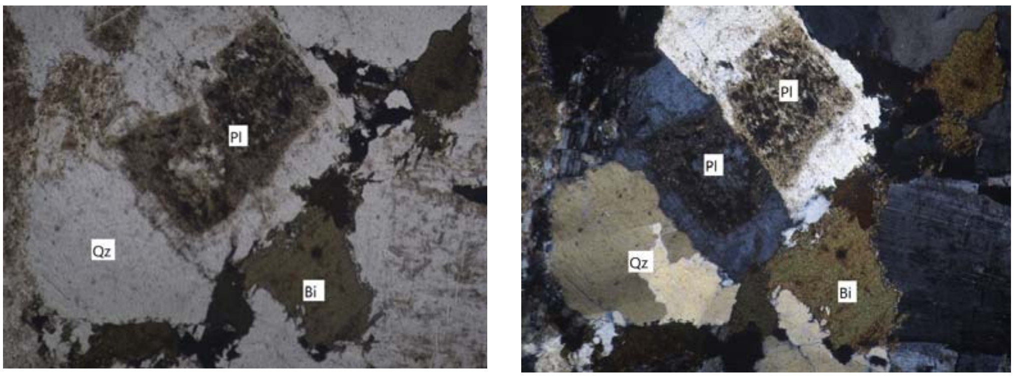
a *b*

Fig. 4. Granitic texture of the Osnytskiy granite, field of view – 2 mm:
a – plane-polarised light (PPL); *b* – cross-polarised light (XPL); Bi – biotite; Kfs – potassium feldspar; Qz – quartz; Pl – plagioclase.



a *b*

Fig. 5. Microcline-perthite in Osnytskiy granite, field of view – 2 mm:
a – PPL; *b* – XPL.



a *b*

Fig. 6. Plagioclase in Osnytskiy granite, field of view – 2 mm:
a – PPL; *b* – XPL.

Polysynthetic twinning is well defined (narrow twins). Sericite develops on acid plagioclase. Some grains have a zoned structure: saussurite (a mixture of secondary carbonates, clay minerals, etc.) develops in the central part of the grains, enriched with an anorthite component.

Quartz (25–30 %) in Osnytski granites was formed later than other rock-forming minerals, so it forms xenomorphic, irregular grains. Two generations of the mineral have been identified: the first is round and elongated weakly fractured grains about 2 mm long, and the second is intensely fractured grains 0.4–0.8 mm in size (Fig. 6). Grains are colourless, without relief and shagreen. Under XPL, we see grey and white colours of interference, $n_g – n_p$ = 0.009. All grains have undulating in blocks extinction.

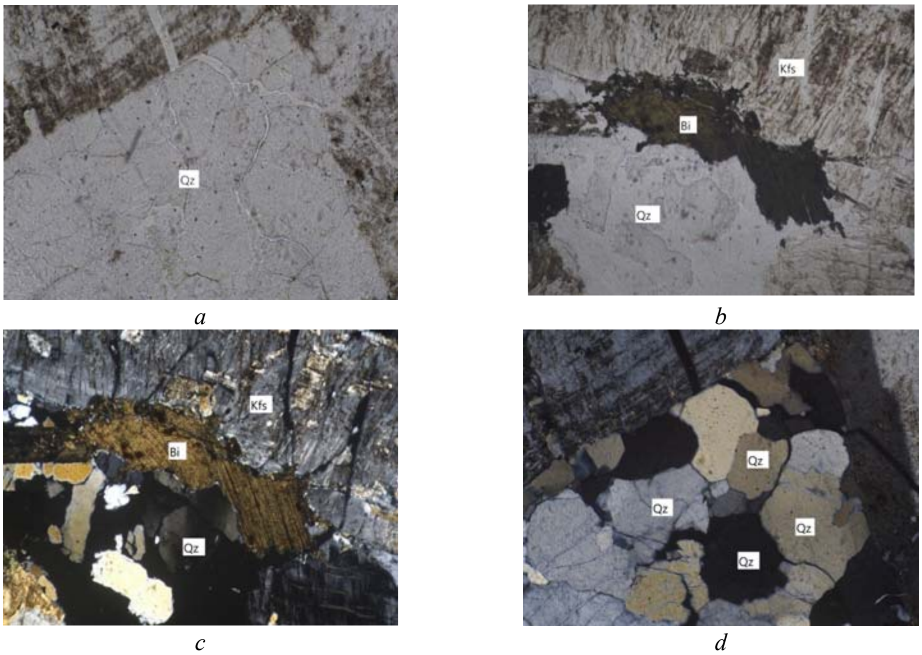


Fig. 6. Quartz in Osnytskiy granite, field of view – 2 mm:
a, b – first generation; *c*, *d* – second generation; *a*, *c* – PPL; *b*, *d* – XPL.

Biotite (5–10 %) is the main femic mineral of inequigranular granites. It is represented in thin sections by prismatic, tabular grains up to 0.8 mm in size (Fig. 7). Grains have shagreen surface and positive relief, the scheme of pleochroism is biotitic – from dark brown, almost black to light yellow-brown. Fractures of perfect cleavage are thin and long; in sections where biotite, due to its plasticity, has tortuous contours, the cleavage lines repeat this tortuosity. Under cross polarised light, the interference colours are masked by an intense dark brown colour. The third-order interference colours were detected by the method of coloured stripes, $n_g – n_p$ = 0.040–0.045. Extinction is straight, optic sign of elongation is positive. The inclusions of zircon (several in one grain) can be seen in almost all sections of biotite, and pleochroic halo have been formed around these inclusions. Also biotite contains inclusions of apatite, titanite, ilmenite and magnetite. Secondary chlorite develops in some grains along the cleavage fractures.

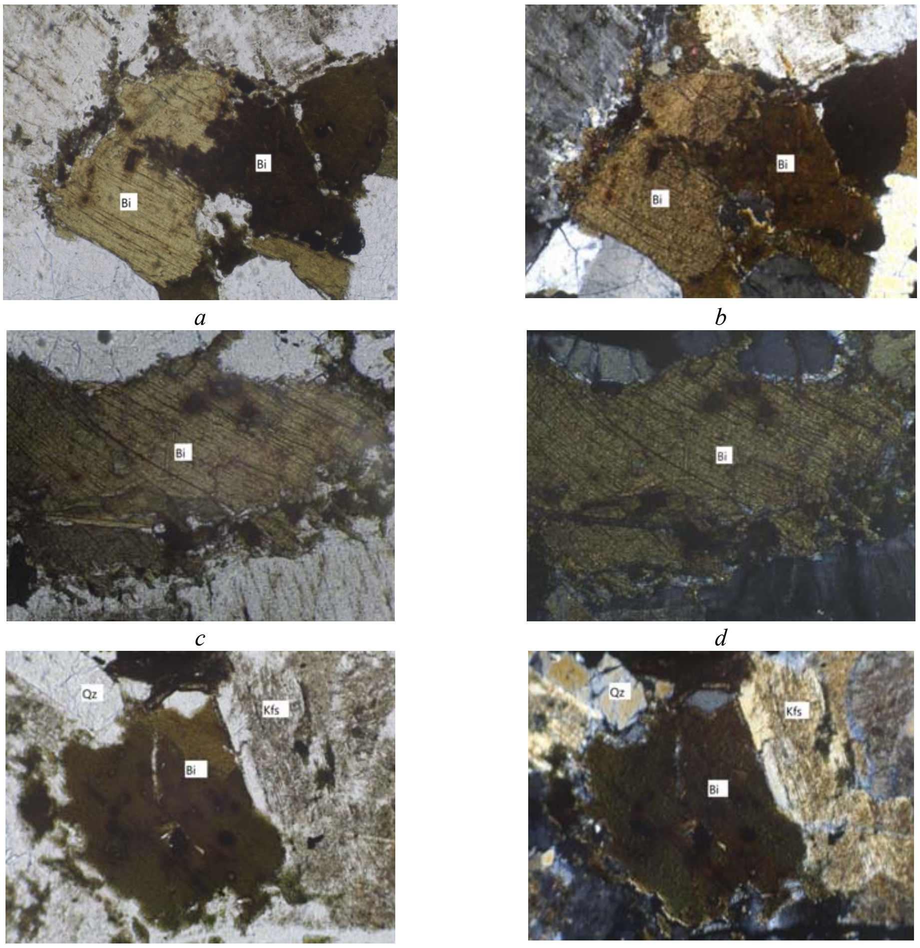


Fig. 7. Biotite in Osnytskiy granite, field of view – 2 mm:
a, *c*, *e* – PPL; *b*, *d*, *f* – XPL.

The content of *hornblende*, which is limited in Osnytski granites, is 1–2 %. In thin sections, mineral has an elongated prismatic shape, dark green colour, shagreen surface and positive relief (Fig. 8). Scheme of pleochroism is biotitic – from dark green to yellow-green. Between crossed polarisers, interference colours are masked due to intense colour of mineral. It is determined that these are second-order green colours, $n_g - n_p$ = 0.017–0.026, extinction is oblique, extinction angle –s 12 °, optic sign of elongation is positive.

Zircon in thin sections has an elongated-prismatic, sometimes rounded shape, a clear shagreen surface and positive relief. Grains (0.1–0.3 mm) are colourless. Under cross polarised light, we see high crimson and green colours of third-order interference, $n_g - n_p$ = 0.045–0.050, extinction is straight, optic sign of elongation – positive. Usually zircon forms inclusions in biotite with the formation of pleochroic halo (Fig. 9).

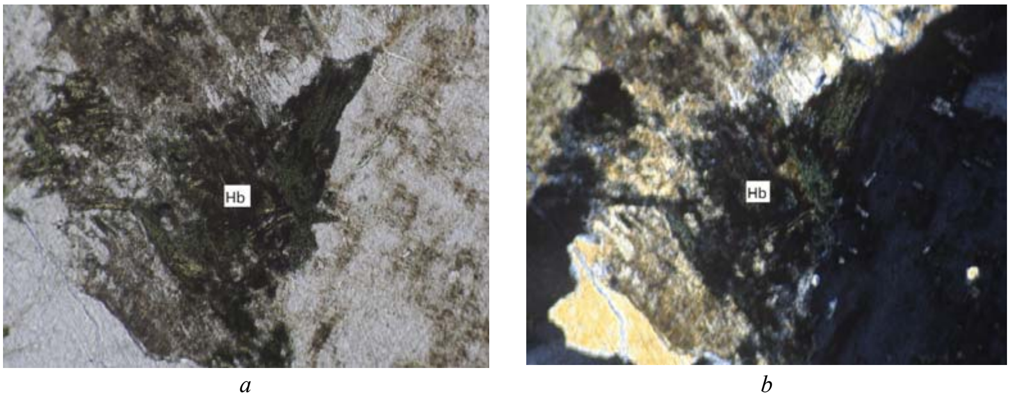


Fig. 8. Hornblende (Hb) in Osnytskiy granite, field of view – 2 mm:
a – PPL; *b* – XPL.

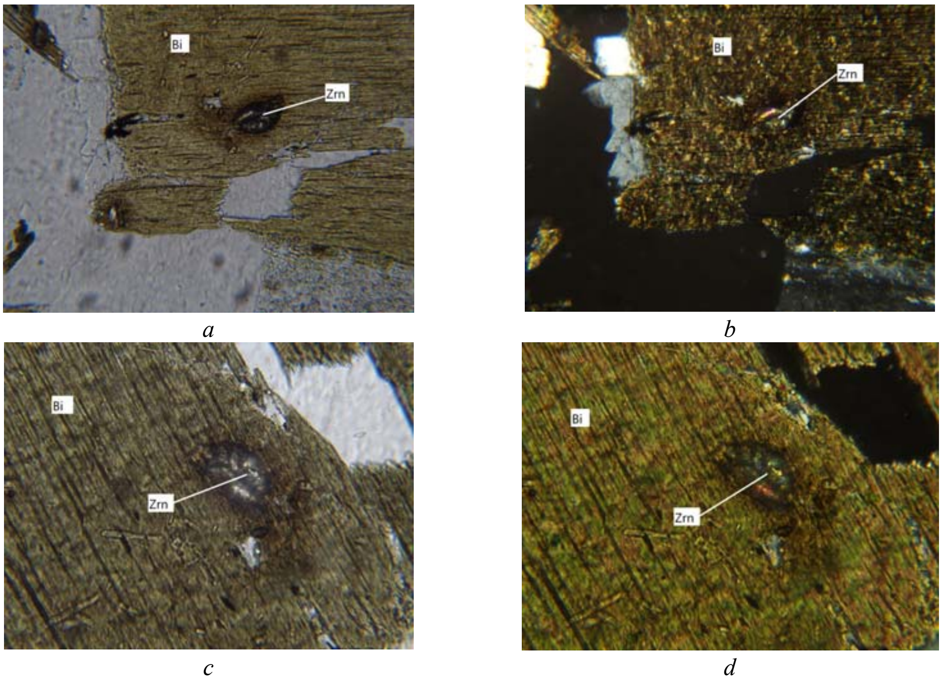


Fig. 9. Zircon (Zrn) in Osnytskiy granite:
a – PPL; *b* – XPL (field of view – 5 mm); *c* – PPL; *d* – XPL (field of view – 10 mm).

Titanite in thin sections is represented by relatively large (up to 0.8 mm) diamond-shaped grains (Fig. 10), also forms inclusions in biotite in the form of rounded and shapeless grains up to 0.3 mm. Due to the high refractive index, the mineral has an intense shagreen surface, so it is brownish in plane-polarised light. Under cross polarised light, it has the highest – nacreous colours of interference, which are masked by its intense colour.

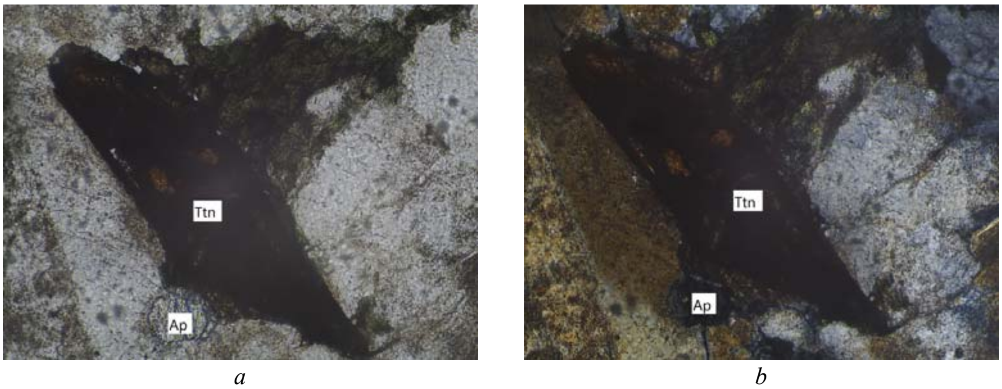


Fig. 10. Titanite (Ttn) and apatite (Ap) in Osnytskiy granite, field of view – 2 mm:
a – PPL; *b* – XPL.

Apatite in thin sections forms colourless prismatic grains or hexagonal and rounded sections (up to 0.2 mm) with a well-defined shagreen surface and a positive relief (see Fig. 10). Under XPL, it has dark grey interference colours of the first order, $n_g - n_p = 0.005$, extinction is straight, optic sign of elongation – negative. Most often, apatite grains are grouped near biotite or form inclusions in it.

Ore minerals are most common among the minerals available in accessory quantities. Some of them have a clear rectangular shape, while others form shapeless aggregates. The size varies from 0.05 to 0.30 mm. Ore minerals are most often concentrated near biotite grains, although they also occur in K-spar and plagioclase grains. Microprobe analysis determined that magnetite, ilmenite and pyrite are among the ore minerals.

The order of minerals' formation in the rock is as follows: the first – well-developed elongated-prismatic grains of acid plagioclases, later – tabular and lamellar crystals of biotite and elongated grains of potassium feldspar, the latter xenomorphic grains of quartz formed.

Microanalytical studies of Osnytski granites. According to the results of microprobe analysis, the mineral composition of granites is as follows: feldspars, quartz, biotite, carbonate, chlorite, accessory minerals are zircon, apatite, titanite, ore minerals – magnetite, ilmenite and pyrite. The groundmass of the rock is composed of alkaline feldspars and plagioclases (Fig. 11).

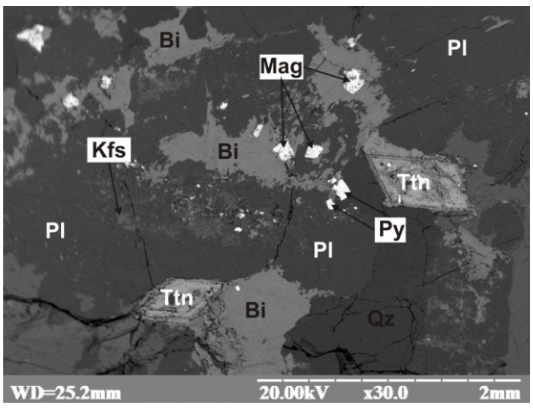


Fig. 11. Plagioclase (Pl), alkaline feldspar (Kfs), biotite (Bi), quartz (Qz), titanite (Ttn), magnetite (Mag) and pyrite (Py) in the granite of the Osnytskyi complex. BSE image.

The chemical composition of *plagioclase* varies from albite to oligoclase (Table 1). The general crystal chemical formula of plagioclase is as follows:

$$(Na_{0.73–0.92}Ca_{0.01–0.18}K_{0.01–0.02})_{0.92–0.97}[Si_{2.78–2.96}Al_{1.03–1.35}O_{10}].$$

Crystal chemical formula of *alkaline feldspars* (see Table 1) is as follows:

$$(K_{0.89–0.96}Na_{0.07–0.11}Ca_{0.00–0.02})_{1.02–1.07}[Si_{2.90–2.95}Al_{1.04–1.06}O_{8}].$$

Table 1

Chemical composition (wt. %) and formula coefficients of feldspars

Compo-nents	Sample number							
	1	*10*	*12*	*22*	*3*	*8*	*11*	*23*
SiO_2	63.52	60.75	59.17	63.17	62.36	67.00	63.50	67.30
TiO_2	0.00	0.00	0.53	0.33	0.01	0.00	0.12	0.14
Al_2O_3	19.37	18.40	18.43	19.14	23.73	19.80	23.27	20.19
FeO	0.00	0.22	0.00	0.05	0.00	0.61	0.00	0.00
MnO	0.00	0.05	0.00	0.05	0.00	0.12	0.00	0.00
MgO	0.00	0.67	0.69	0.49	0.39	0.53	0.19	0.64
CaO	0.00	0.64	0.27	0.57	3.69	0.26	3.63	0.65
Na_2O	0.91	1.14	0.77	1.17	8.40	10.91	8.81	10.90
K_2O	16.20	15.17	14.89	15.04	0.23	0.16	0.29	0.18
Total	100.00	97.05	94.73	100.00	98.81	99.38	99.80	100.00
Formula coefficients								
Si	2.95	2.92	2.90	2.92	2.78	2.96	2.80	2.94
Al	1.06	1.04	1.06	1.04	1.25	1.03	1.21	1.04
Total	4.00	3.96	3.96	3.97	4.03	3.98	4.01	3.99
Na	0.08	0.11	0.07	0.11	0.73	0.93	0.75	0.92
K	0.96	0.93	0.93	0.89	0.01	0.01	0.02	0.01
Ca	0.00	0.03	0.01	0.03	0.18	0.01	0.17	0.03
Total	1.04	1.07	1.02	1.02	0.92	0.95	0.94	0.97
Minals								
X(Ab)Kfs	0.08	0.10	0.07	0.10	0.79	0.98	0.80	0.96
X(An)Kfs	0.00	0.03	0.01	0.03	0.19	0.01	0.18	0.03
X(Or)Kfs	0.92	0.87	0.91	0.87	0.01	0.01	0.02	0.01

In the three-component Albite–Orthoclase–Anorthite diagram (Fig. 12), the figurative points of the analyzed feldspars composition are located in the fields of albite, oligoclase, and K-spar.

Biotite forms lamellar grains up to 2 mm in size (Fig. 13, *a*), often containing inclusions of magnetite, zircon and apatite (see Fig. 13, *b*). The crystal chemical formula of biotite according to the results of microanalytical studies (Table 2) is as follows:

$$(K_{0.96–1.01}Na_{0.00–0.11}Ca_{0.01–0.04})_{0.99–1.11}(Fe^{2+}_{1.42–1.59}Mg_{1.08–1.17}Al_{0.20–0.36}Ti_{0.12–0.14}Mn_{0.00–0.05})_{3.00–3.14} \cdot$$
$$\cdot (OH)_2[Si_{2.69–2.76}Al_{1.10–1.14}Ti_{0.12–0.17}O_{10}].$$

We analyzed one grain of *hornblende*, the chemical composition of which is as follows, wt. %: SiO_2 – 45.30; TiO_2 – 1.43; Al_2O_3 – 8.04; FeO – 17.58; MnO – 0.39; MgO – 11.66; CaO – 11.54; Na_2O – 1.02; K_2O – 0.82. The crystal chemical formula of hornblende is as follows:

$$(K_{0.16}Na_{0.12})_{0.29}(Ca_{1.84}Na_{0.16})_{2.00}(Mg_{2.58}Fe^{2+}_{1.54}Fe^{3+}_{0.58}Ti_{0.16}Al_{0.14}Mn_{0.05})_{5.05}(OH)_2[Si_{6.72}Al_{1.27}O_{22}].$$

Zircon grains 10–50 µm in size are most often isometric, sometimes prismatic, and contained in titanite (Fig. 14, *a*). The chemical composition of zircon according to microprobe analysis is as follows, wt. %: ZrO – 58.35; SiO_2 – 17.85; FeO – 2.48; CaO – 1.85; Al_2O_3 – 1.55. Crystallochemical formula of zircon – $Zr_{1.14}[Si_{0.72}Al_{0.07}O_4]$.

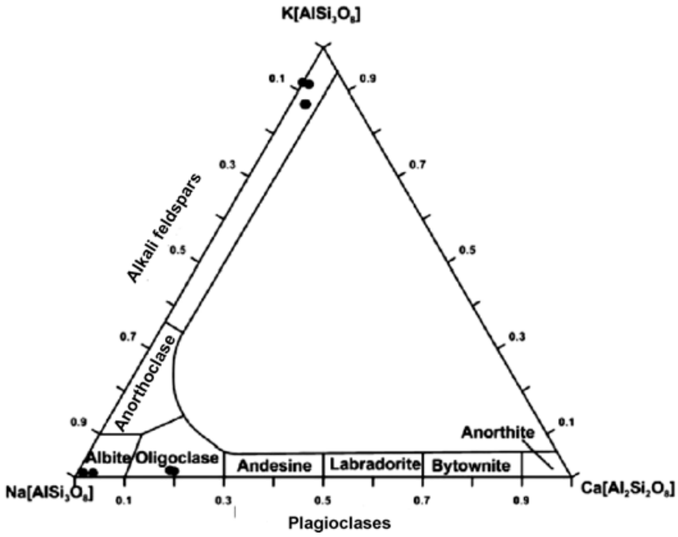


Fig. 12. Variations in the chemical composition of feldspars on the triangular diagram $Na[AlSi_3O_8]$–$K[AlSi_3O_8]$–$Ca[Al_2Si_2O_8]$.

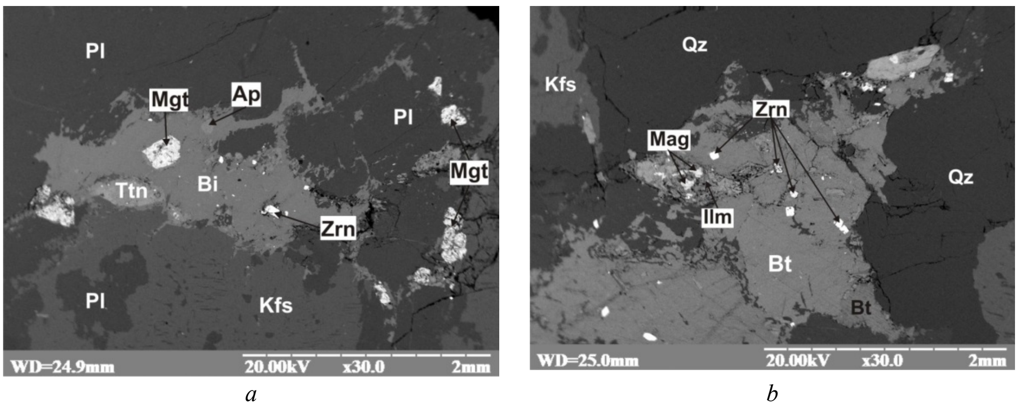


Fig. 13. Biotite in feldspar aggregate, BSE image.

Minerals: *a* – Bi – biotite, Mgt – magnetite, Zrn – zircon, Ap – apatite; *b* – Bt – biotite, Mag – magnetite, Ilm – ilmenite.

Titanite forms diamond-shaped grains up to 1 mm in size, most of which have undergone alterations. In the relic grains of titanite, there are inclusions of zircon, bastnäsite, quartz (see Fig. 14, *a*) and ilmenite and magnetite (see Fig. 14, *b*). The crystal chemical formula of titanite, according to the results of microprobe analysis (Table 3), is as follows:

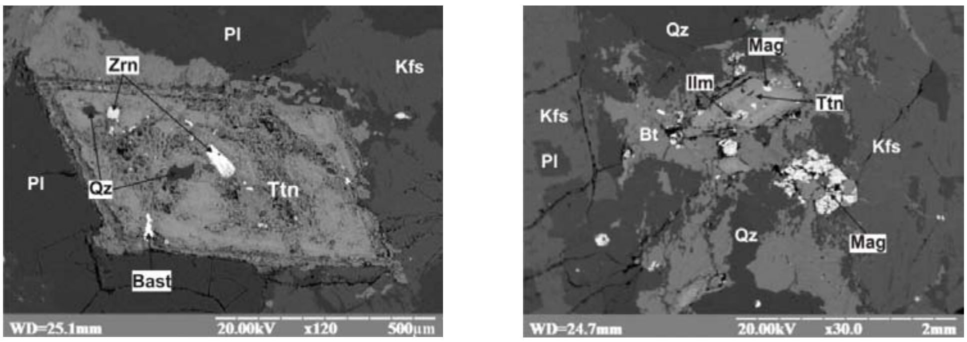
$$(Ca_{0.95–0.98}Mg_{0.02–0.04}Mn_{0.00–0.01})_{0.99–1.01}(Ti_{0.79–0.91}Al_{0.12–0.22})O[SiO_4].$$

Magnetite is represented by isometric grains up to 1 mm in size (see Figs. 11, 13–15). The chemical composition of the mineral is as follows, wt. %: Fe_2O_3 – 61.65; FeO – 26.5; Al_2O_3 – 1.05; MgO – 0.70; CaO – 0.17; Na_2O – 0.17; TiO_2 – 0.16. Crystal chemical formula of magnetite is $(Fe^{2+}_{0.91}Mg_{0.04})_{0.95}(Fe^{3+}_{1.90}Al_{0.05})_{1.96}O_4$.

Table 2

Chemical composition (wt. %) and formula coefficients of biotite

Compo-nents	Sample number								
	4	*5*	*19*	*20*	*24*	*26*	*27*	*28*	*29*
SiO_2	35.61	36.30	35.20	36.09	34.88	34.95	35.31	34.30	34.16
TiO_2	2.20	2.07	2.32	2.41	2.96	2.42	2.33	2.34	2.62
Al_2O_3	15.25	16.62	14.98	15.56	14.88	14.23	14.12	14.19	14.05
FeO	23.07	22.40	22.89	23.18	24.58	23.07	23.72	22.63	23.46
MnO	0.35	0.25	0.00	0.00	0.41	0.82	0.53	0.02	0.38
MgO	10.21	9.56	9.61	9.82	9.80	9.27	9.46	9.26	9.52
CaO	0.27	0.31	0.52	0.18	0.33	0.39	0.28	0.29	0.42
Na_2O	0.11	0.03	0.04	0.35	0.16	0.59	0.75	0.07	0.25
K_2O	10.22	9.90	10.01	10.07	9.17	9.83	9.65	9.80	9.13
Total	97.30	97.43	95.57	97.65	97.19	95.56	96.15	92.90	93.99
Formula coefficients									
Si	2.74	2.75	2.75	2.75	2.69	2.75	2.76	2.76	2.73
Al	1.14	1.13	1.12	1.11	1.13	1.11	1.10	1.10	1.11
Ti	0.13	0.12	0.14	0.14	0.17	0.14	0.14	0.14	0.16
Total	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Al	0.24	0.36	0.26	0.29	0.22	0.21	0.20	0.25	0.21
Ti	0.13	0.12	0.14	0.14	0.17	0.14	0.14	0.14	0.16
Fe^{2+}	1.48	1.42	1.50	1.48	1.59	1.52	1.55	1.52	1.57
Mg	1.17	1.08	1.12	1.12	1.13	1.09	1.10	1.11	1.13
Mn	0.02	0.02	0.00	0.00	0.03	0.05	0.04	0.00	0.03
Total	3.04	3.00	3.01	3.02	3.14	3.01	3.03	3.03	3.09
Ca	0.02	0.03	0.04	0.01	0.03	0.03	0.02	0.03	0.04
Na	0.02	0.00	0.01	0.05	0.02	0.09	0.11	0.01	0.04
K	1.00	0.96	1.00	0.98	0.90	0.99	0.96	1.01	0.93
Total	1.04	0.99	1.05	1.05	0.96	1.11	1.10	1.04	1.00



a *b*

Fig. 14. Relict grains of titanite with inclusions of zircon, bastnäsite (Bast) and quartz (*a*) and with inclusions of magnetite and ilmenite (*b*). BSE image.

Ilmenite in the relict grain of titanite (see Fig. 14, *b*) has a size of about 0.2 mm and such chemical composition, wt. %: TiO_2 – 48.81; FeO – 42.54; MnO – 6.66; Al_2O_3 – 0.75; MgO – 0.24; SiO_2 – 0.24; CaO – 0.09. The crystal chemical formula of ilmenite is as follows:

$$(Fe^{2+}_{0.91}Mg_{0.01})_{0.92}(Ti_{0.94}Al_{0.02})_{0.96}O_2.$$

Table 3

Chemical composition (wt. %) and formula coefficients of titanite

Components	Sample number			
	6	*7*	*9*	*17*
SiO_2	29.77	27.58	27.94	28.10
TiO_2	32.97	34.80	29.37	32.37
Al_2O_3	5.05	2.94	5.42	2.86
FeO	1.77	2.57	1.31	1.98
MnO	0.22	0.01	0.00	0.23
MgO	0.32	0.41	0.57	0.76
CaO	27.42	26.03	25.35	24.72
Na_2O	0.12	0.00	0.54	0.02
K_2O	0.13	0.00	0.00	0.00
Total	97.77	94.35	90.5	91.03
Formula coefficients				
Ca	0.98	0.97	0.98	0.95
Mn	0.01	0.00	0.00	0.01
Mg	0.02	0.02	0.03	0.04
Total	1.00	0.99	1.01	1.00
Ti	0.83	0.91	0.79	0.87
Al	0.20	0.12	0.23	0.12
Total	1.03	1.03	1.02	0.99
Si	0.99	0.96	1.00	1.01

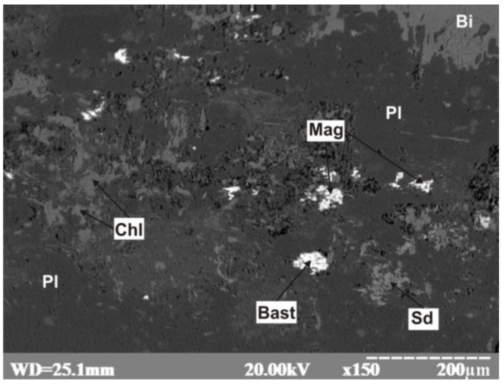


Fig 15. Bastnäsite, siderite (Sd), chlorite (Chl), magnetite, biotite and plagioclase in Osnytskyi granite. BSE image.

Based on the determined chemical composition of *chlorite* (FeO – 32.4; SiO_2 – 23.00; Al_2O_3 – 17.83; MgO – 8.57; MnO – 1.00; TiO – 0.40; CaO – 0.32; Na_2O – 0.22; K_2O – 0.08 wt. %) we calculated its crystallochemical formula:

$$(Fe^{2+}_{3.18}Mg_{1.50}Al_{1.19}Mn_{0.10}Ca_{0.04})_{6.00}(OH)_8[Si_{2.70}Al_{1.27}Ti_{0.04}O_{10}].$$

The analyzed carbonates, according to the results of microanalytical studies, are represented by siderite and bastnäsite (see Figs. 14, 15). Siderite has such chemical composition, wt. %: FeO – 45.16–52.60; CaO – 3.90–4.40; MnO – 1.04–2.95; MgO – 0.54–2.09; SiO_2 – 0.50–1.11; Al_2O_3 – 0.59–0.87; TiO_2 – 0.17; Na_2O – 0.13. The crystal chemical formula of siderite is as follows: $(Fe^{2+}_{0.76–0.87}Ca_{0.08–0.09}Mg_{0.02–0.06}Mn_{0.02–0.06})_{0.96–0.98}[CO_3]$.

Bastnäsite forms irregularly shaped grains about 40 microns in size. In general, it is a characteristic mineral of hydrothermal deposits associated with alkaline rocks and carbonatites. The secondary formation of bastnäsite is probably due to the destruction of rare earth silicates. According to the chemical composition of bastnäsite (Ce_2O_3 – 26.78; La_2O_3 – 16.89; Nd_2O_3 – 6.27; CaO – 4.13; SiO_2 – 1.53 wt. %), its crystal chemical formula is as follows:

$$(Ce_{0.32}Ca_{0.29}La_{0.21}Nd_{0.07}Si_{0.10})F[CO_3].$$

Conditions for the formation of the Osnytskyi complex granitoids. For reliable petrological reconstructions it is necessary to take into account not only the chemical composition of the rock in general, but also the peculiarities of the rock-forming and accessory minerals composition. For most granitoids, the only available (and best studied) representative of magnesium-ferrous silicates is biotite. According to statistical studies of biotite from granitoids of different genesis, the closest correlations between the content of oxides of the same name in biotite and rock are characteristic of unaltered intrusive rocks. In the case of metamorphogenic-metasomatic granitization and changes in the composition of parent rocks, the biotite–rock bond weakens. This leads to the conclusion about the "inertness" of the biotite composition transformation, i.e. its chemical composition depend on physicochemical crystallization conditions and composition of parent rocks. That is why biotite is widely used for correlation and delimitation of igneous rocks, determination of temperature conditions, elucidation of acidity–alkalinity and genesis of rocks and reproduction of geodynamic conditions of rocks' formation. The composition of biotite is also considered an indicator of the granitoids ore-bearing capacity.

Actually biotite is interpreted as a series of trioctahedral mica (dark and lithium-free) between the annite $KFe^{2+}{}_3[AlSi_3O10](OH)_2$–phlogopite $KMg_3[AlSi_3O_{10}](OH)_2$ and siderophyllite $KFe^{2+}{}_2Al[Al_2Si_2O_{10}](OH)_2$–eastonite $KMg_2Al[Al_2Si_2O_{10}](OH)_2$. In the classical Foster diagram [23] (Fig. 16, *a*), the figurative points of biotite from granites of the Osnytskyi complex fall into the field of ferrous biotite, and in the classification diagram Fe/(Fe+Mg)–Al^{IV} of F. Yavuz [29] (see Fig. 16, *b*) – in the field of siderophyllite. The magmatic origin of biotite from investigated granites is confirmed by the diagram MgO–FeO_{total}–Al_2O_3 of A. Neiva [28], on which the fields of magmatic and metamorphogenic-metasomatic biotite are highlighted (see Fig. 16, *c*).

The following indicators were calculated for biotite:

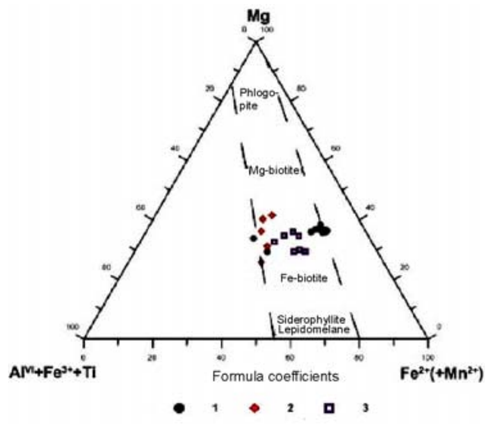
K_{Al} = [Al:(Al+Mg+Fe+Si)]·100 % is 21.38–22.71 (average value – 22.23);

f = [Fe:(Fe+Mg)]·100 % – from 57.68 to 64.53 (average – 61.46);

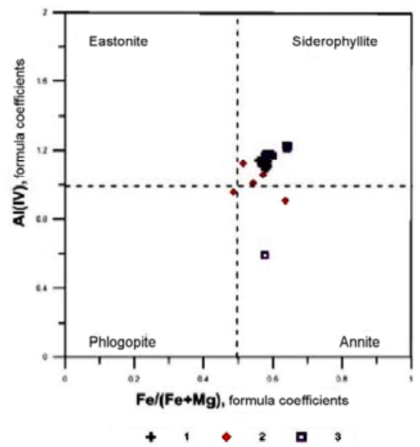
K_{Ti} = [Ti:(Ti+Mn+Fe+Mg)]·100 % – from 3.57 to 6.37 (average – 5.17).

The influence of temperature and pressure, at which granitoids have been crystallized, affects in some way all the main chemical parameters of biotite. For the relative (qualitative) assessment of the *PT*-conditions of mica crystallization, not the total aluminosity of biotite is important, but the distribution of Al in the tetrahedral and octahedral positions in the mineral structure. Indicative properties of aluminium are based in this case on the following crystal chemical postulates: increasing pressure promotes the entry of Al into octahedral coordination; increasing the temperature promotes the replacement of silicium in the tetrahedron. The biotite of the Osnytskyi complex granites contains a sufficiently large amount of Al in the octahedral position, which indicates the crystallization of granites under conditions of sufficiently high pressure.

Oxygen fugacity which is a measure of the redox state of the rock formation environment is also important. The presence of typical paragenesis of magnetite–titanite in the studied granites already indicates higher oxygen fugacity during rock crystallization. The consequence



a



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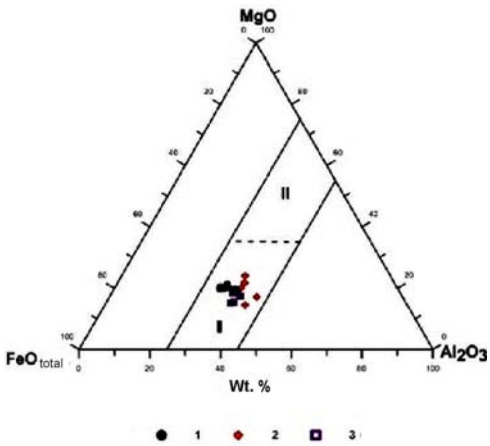

c

Fig. 16. The position of the figurative points of the biotite composition on different diagrams:

a – diagram of M. Foster for trioctahedral mica [23]; *b* – classification diagram of F. Yavuz [29]; *c* – diagram of A. Neiva [28] (fields on the diagram: I – magmatic, II – metamorphogenic-metasomatic biotite); *1–3* – composition of biotite according to our data (*1*), [20] (*2*) and [1] (*3*).

of this is a lower content of Ti in the biotite of Osnytski granites, compared to other complexes of the Volynskyi megablock, where the leading accessory mineral is ilmenite. The authors of [1] to determine the temperature of biotite formation used diagram of the stability of the solid solution of phlogopite–annite in the coordinates "temperature–oxygen fugacity" (Wones, Eugster, 1965). According to their data, the granites of the Osnytskyi complex were formed under conditions of low acidity at a temperature of 760 °C.

We used two-feldspar, chlorite, and magnetite-ilmenite geothermometers to determine the temperature of mineral formation and later alterations of the Osnytskyi complex granites. According to two-feldspar geothermometer, based on experimentally obtained formulas [24, 25] we determined that the temperature of mineral formation ranged from 647 to 324 °C, and according to the graphical method [14] it differs slightly – 525–450 °C.

The presence of syngenetic growths of ilmenite and magnetite made it possible to calculate the temperature of mineral formation using a magnetite-ilmenite geothermometer. According to [27], the temperature of 694–574 °C was determined based on the chemical composition of ilmenite and magnetite.

The authors of [22] found a positive correlation between the amount of Al in the quadratic coordination in the structure of chlorite and the crystallization temperature. According to [26], the amount of Al in the quadratic coordination in chlorite increases with increasing Fe/(Fe+Mg), i.e. the amount of Fe and Mg depends on temperature. Using the data of the microprobe study of chlorite from Osnytski granites, we calculated that according to the chlorite geothermometer the temperature of mineral formation was 337.7 °C.

To elucidate the geodynamic conditions for the formation of plutonic rocks, A. Abdel-Rahman [21] proposed various binary and triangular diagrams with defined fields, using a database of hundreds of biotite analyzes from around the world. Biotite fields of anorogenic alkaline complexes, alumina complexes (including *S*-type) and calcareous-alkaline orogenic complexes were isolated. In the diagrams of A. Abdel-Rahman FeO_{total}–MgO–Al_2O_3 and FeO_{total}–Al_2O_3, the figurative points of the studied biotite composition fall into the fields of calcareous-alkaline orogenic complexes.

Thus, the main features of the chemical composition of the granitoids of the Osnytskyi complex are as follows: subalkaline tendency of differentiation of magmatic melts; slightly increased basicity; fairly high alumina and the degree of oxidation of iron, which increases with increasing content of SiO_2 and alkalis; increased potassium content compared to sodium (with the exception of coarse-grained granites, in which the difference between K and Na content is insignificant).

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ПЕТРОЛОГІЧНІ ОСОБЛИВОСТІ КИСЛИХ ПЛУТОНІЧНИХ ПОРІД ОСНИЦЬКОГО КОМПЛЕКСУ (ВОЛИНСЬКИЙ МЕГАБЛОК УКРАЇНСЬКОГО ЩИТА)

Осницький комплекс, поширений у межах Волинського мегаблока Українського щита, представлений габро-діорит-гранодіорит-гранітною серією порід і є плутонічною частиною клесівсько-осницької вулкано-плутонічної асоціації. Гранітоїдні породи осницького комплексу утворюють єдину формацію гранітів, які мають спільне просторове і структурне походження. Наявні такі різновиди гранітів, як лептитоподібні, дрібнозернисті, нерівномірно-середньозернисті, крупнозернисті та ін.

Виконано петрографічні й мінералогічні дослідження осницьких нерівномірнозернистих порфіроподібних гранітів. Визначено й описано породоутворювальні (калієвий польовий шпат, плагіоклаз, кварц, біотит, рогова обманка), акцесорні (циркон, апатит, титаніт), рудні (магнетит, ільменіт, пірит) і вторинні (епідот, серицит, хлорит, сидерит, бастнезит) мінерали. Біотит за хімічними особливостями відповідає сидерофіліту магматичного походження (вапнисто-лужні орогенні комплекси). Кристалізація гранітів осницького комплексу відбувалася за умов низької кислотності за температури близько 760 °C і достатньо високого тиску.

Ключові слова: гранітоїди, осницький комплекс, породоутворювальні, акцесорні, рудні і вторинні мінерали, біотит, умови кристалізації, Волинський мегаблок, Український щит.