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PUMPELLYITE FROM METABASALTS OF THE UKRAINIAN CARPATHIANS

In general, the pumpellyite series (hydrous silicates of Ca and Al) includes such mineral species as pumpellyite-(Al), pumpellyite-(Fe^{2+}), pumpellyite-(Fe^{3+}), pumpellyite-(Mg), and pumpellyite-(Mn). We studied pumpellyite from the Mesozoic metabasalts of the Ukrainian Carpathians in order to recreatethe facies conditions of mineral formation. The studied rocks are metabasalts of the Rakhivsko-Chyvchynskyi and Uholskyi magmatic complexes, which were studied using mineralogical, petrographical and petrogeochemical methods. In the rocks of the Rakhivsko-Chyvchynskyi complex, two morphological varieties of pumpellyite-(Fe) were found, while in the Uholskyi complex an intermediate mineral species between pumpellyite-(Al) and pumpellyite-(Fe^{2+}) was found. The temperature of mineralization during the formation of pumpellyite-containing parageneses was determined: according to ternary feldspar geothermometry — 260 and 310 °C and according to chlorite geothermometry — from 170 to 320 °C. On the PT-diagram for metamorphic facies, the mineral paragenesis of both studied magmatic complexes fall into the field of prehnite-pumpellyite facies. The absence of clear pumpellyite-actinolite subfacies associations indicates that the pressure in the mineral formation system did not exceed 300 MPa.

Keywords: *pumpellyite, metabasalt, conditions of mineral formation, mineralogical geothermometer, Mesozoic, Ukrainian Carpathians.*

Introduction. Pumpellyite is a hydrous silicate of calcium and aluminium with the general formula $Ca_2XY_2(Si_2O_7)(SiO_4)(OH,O)_2 \times H_2O$, where X is Mg, Fe^{2+}, Mn^{2+}, Fe^{3+}, Al, and Y — Al, Fe^{3+}, Mn^{3+}, V^{3+}. The content of Mg, Fe and Al can vary significantly [1, 5, 26]. Depending on the element in the X-position, the following mineral species are distinguished (approved as independent mineral species) [12]:

• pumpellyite-(Al) — $Ca_2Al_3(Si_2O_7)(SiO_4)(OH, O)_2 \cdot H_2O$ — Al-species in the pumpellyite

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series (International Mineralogical Association (IMA) 2005-016*)*;

- pumpellyite-(Fe^{2+}) — $Ca_2Fe^{2+}Al_2(Si_2O_7)(SiO_4)(OH,O)_2 \cdot H_2O$ — Fe^{2+}-species in the pumpellyite series (renamed (Rn) 1973 special procedure (s.p.)); the species has been known since 1965;
- pumpellyite-(Fe^{3+}) — $Ca_2Fe^{3+}Al_2(Si_2O_7)(SiO_4)(OH,O)_2 \cdot H_2O$ — Fe^{3+}-species in the pumpellyite series (Rn 1973 s.p.);
- pumpellyite-(Mg) — $Ca_2MgAl_2(Si_2O_7)(SiO_4)(OH)_2 \cdot H_2O$ — Mg-species in the pumpellyite series (Rn 1973 s.p.); known from 1925, renamed in 1973;
- pumpellyite-(Mn^{2+}) — $Ca_2Mn^{2+}Al_2(Si_2O_7)(SiO_4)(OH)_2 \cdot H_2O$ — Mn^{2+}-species in the pumpellyite series (Rn 1980-006).

The first mention of pumpellyite dates back to 1925: the mineral was discovered at the Kewinavan copper deposit (Michigan, USA) and named after the American geologist R. Pumpelli [25]. However, V.S. Sobolev in his work [24] noted that pumpellyite was found much earlier — in 1900 — in the valley of the Lotru River in the Southern Carpathians on the territory of Romania. The researcher G.M. Murgoci, who studied this mineral, named it *lotrite* after the place of discovery (Murgoci, 1900). According to the "Mineralogical Dictionary" [13], lotrite is a synonym of pumpellyite. The dictionary [12] does not have the term *lotrite*, as the name is considered outdated.

Pumpellyite has been described in Austria (Styria), Great Britain (Cornwall, Scotland), Germany (Hesse), Italy (South Tyrol), Norway (Iveland), USA (the states of California and Michigan), Czech Republic (Královéhradecký kraj), Japan (Honshu Island), etc.

The **purpose** of our research is to find out the possible crystallization conditions of the pumpellyite from metabasalts of the Rakhivsko-Chyvchynskyi and Uholskyi magmatic complexes of the Ukrainian Carpathians based on the analysis of the published results and the new data we received.

Research methods. The complex of performed works included geological observations in natural rock outcrops and laboratory petrographic, mineralogical and petrogeochemical studies of metabasalts of the Rakhivsko-Chyvchynskyi and Uholskyi magmatic complexes. We studied the mineral composition and structural and textural features of the rocks in thin sections using Olympus polarizing microscopes.

Microanalytical studies of pumpellyite were performed in the laboratory of the Faculty of Physics of the Ivan Franko National University of Lviv using a REMMA-102-02 scanning electron microscope (Sumy, Ukraine), equipped with an EDAR energy-dispersive analyzer, analyst R. Serkiz. Polished sections were studied. The parameters of the analysis are as follows: accelerating voltage — 20 kV, sample current — 10 nA, beam diameter — 1—5 μm. Mineralogy set standards НЭРМА.ГЕО1.25.10.74ГТ (Firm — "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 received data.

X-ray structural analysis was performed on 6 metabasalts in the X-ray laboratory of the Faculty of Geology of Lviv University on a DRON-3 diffractometer, analyst A. Dvorianskyi. Analysis parameters: $Cu_{K\alpha}$-radiation, voltage — 40 kV, current — 25 mA, rotation speed — 1 deg/min, in the range 2θ: 4°—70°. Minerals were identified using the Internet resources MINCRYST, Mindat and using the program Match (version 9).

Analysis of previous studies. In Ukraine, pumpellyite is known in the Ukrainian Carpathians, Donbas and Crimea [23]. It was first discovered by V. Sobolev [24] in thin sections of altered diabases, diabase porphyrites and their tuffs from the region of the Pip Ivan and Petros mountains in Transcarpathia, apparently of Upper Jurassic or Lower Cretaceous age. Here, the mineral is present in amygdules and veinlets together with quartz, chlorite and albite, and it, together with carbonates and prehnite, replaced plagioclase. Amygdules filled with pumpellyite reach 2—3 mm.

Almost similar forms of the manifestation of pumpellyite, described under the name lotrite, were recorded in the basic effusive rocks of the Marmarosh massif [21].

Pumpellyite was found in altered gabbro-diabases and spilites of the Uholka River. The mineral was thoroughly investigated and characterized by V. Kaliuzhnyi in the work [10]. In altered gabbro-diabases, pumpellyite is represented by two varieties. The first variety is small needles with a length of 0.07—0.10 mm and a thickness of 0.02 mm, which often form radiate-fibrous growths and spherulites in small cavities. Sometimes such randomly oriented needles grow on the walls of the cavities in the form of microdruses. The refractive indexes of the mineral are as follows: $n_g = 1.716 \pm 0.002$, $n_p = 1.696 \pm 0.001$, $n_g - n_p = 0.020$—0.022. The second variety is represented by fine grains replacing plagioclase or in the form of tablets <0.05 mm in size filling the cavities together with quartz and calcite in weakly crystalline spilites. Based on the results of the chemical wet analysis, the following crystal chemical formula of the mineral was determined:

$$Ca_{4.05}(Al, Fe^{3+})_{4.03}(Fe^{2+}, Mg, Mn)_{1.41}(OH)_5 [Si_{5.94}Al_{0.05}O_{20.95}(OH)_{0.05}].$$

In the mentioned article, V. Kaliuzhnyi analysed the post-magmatic alterations of the studied volcanics, among which he singled out albitization processes of spilites and gabbro-diabases and peri-fissure metasomatosis, which belongs to the lowest-temperature stages of metamorphism and associated with the formation of pumpellyite.

Pumpellyite was also found among the altered volcanics of the basic composition, which were discovered by wells within the Zhabievska (Verkhovynska) depression among the Eocene flysch rocks of the Skybovi Carpathians [8]. Here it occurs in highly fractured twinned pyroxene phenocrysts, as well as in microamygdules together with zeolites and possibly chlorite.

Pumpellyite is found in the Upper Jurassic diabases of the stream Kamianyi Potik, in the Lower Cretaceous diabases of the Kvasnyi stream and gabbro-diabases of the Uholka River [18]. In the streams of Kvasnyi and Kamianyi, it is easy to diagnose the mineral due to its green, bluish-green or yellow-green colour; index of refraction n_m is 1.700. Pumpellyite replaces plagioclase (sometimes together with epidote) and fills amygdales — together with chlorite, albite, associated by quartz and calcite.

The majority of Meso-Cenozoic diabases, spilites and keratophyres are characterized by a greenschist facies alteration [14]. Two types of changes have been distinguished: (1) mafic minerals and possibly glass replaced by chlorite, carbonate, quartz, epidote, hematite. Occasionally, secondary pumpellyite and prehnite develop as pseudomorphs after mafic minerals, epidote very rarely, while plagioclase is albitized; (2) pyroxenes remain unaltered or only weakly replaced, while plagioclase is almost completely replaced by carbonate, quartz, and rarely pumpellyite and prehnite. The same minerals form veins and fill the amygdales.

According to "Minerals of the Ukrainian Carpathians. Silicates" [17] pumpellyite from Mesozoic igneous rocks is easily diagnosed by its green or blue-green colour, sometimes very bright, less often it has a yellow-green colour and pleochroism. Colourless crystals occur among needle-like varieties of pumpellyite. Mineral from diabases of the Rakhiv massif has $n_m = 1.690$, $n_p = 1.672$, birefringence — 0.020; 2V = 55—57°. In the diabase porphyrites, the spherulite crystals have straight extinction, and the cryptocrystalline and fine-grained aggregates are almost isotropic and coloured in a uniform deep blue colour or spotted, which is caused by different grain orientations. Pumpellyite from diabases of the Kvasnyi stream and gabbro-diabases of the Uholka River are characterized by slightly higher refractive indices ($n_g = 1.716$, $n_p = 1.696$), strong dispersion $r < v$, birefringence is 0.020—0.022, 2V = 65°. In altered Upper Eocene volcanics, pumpellyite can also be easily diagnosed by its bright green coloration and pleochroism from colourless to pale blue. The mineral has strong dispersion of optical axes, the maximum refractive index is 1.690, the minimum is 1.670 [17].

Pumpellyite is classified as a post-volcanic (hydrothermal-metasomatic) formation. It closely associates with chlorite, albite, calcite, potassium feldspar, quartz, prehnite. It was formed as a result of the replacement of plagioclase with the formation of pseudomorphoses on it, rarely replaced pyroxene. Its "needles" intergrow quartz, potassium feldspar and carbonate, and no direct contacts with prehnite were found.

Geological position of the object of research. We studied pumpellyite and pumpelly-

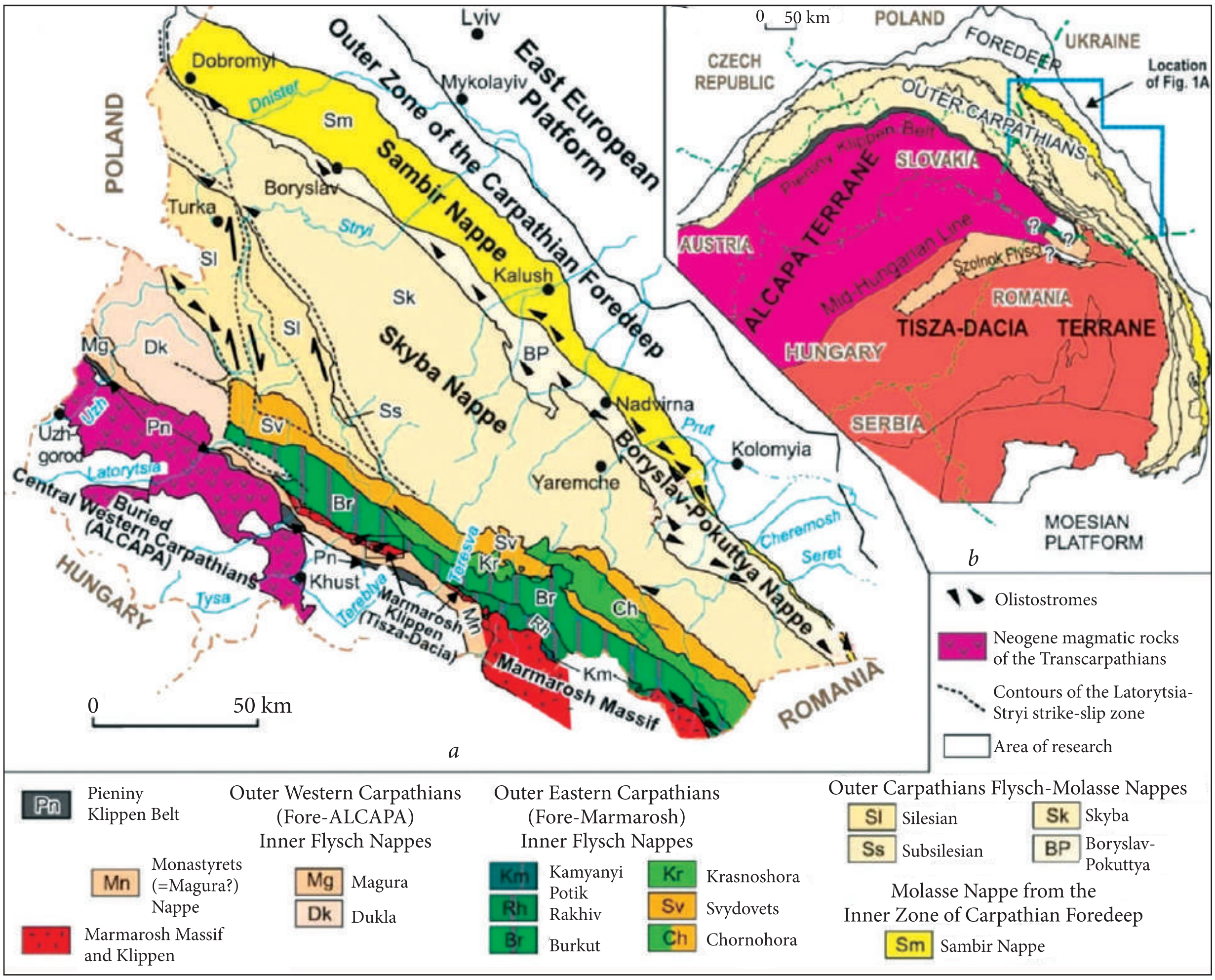


Fig. 1. Main tectonic units (*a*) and tectonic position of the Ukrainian Carpathians (*b*) according to O. Hnylko [9]

Fig. 2. Outcrops of Mesozoic volcanics in the Kamianyi Potik basin

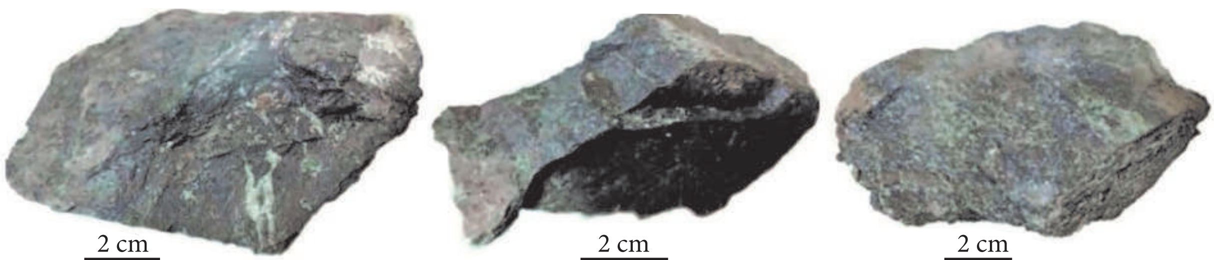


Fig. 3. Metabasalts of the Rakhivsko-Chyvchynskyi complex (Kamianyi Potik)

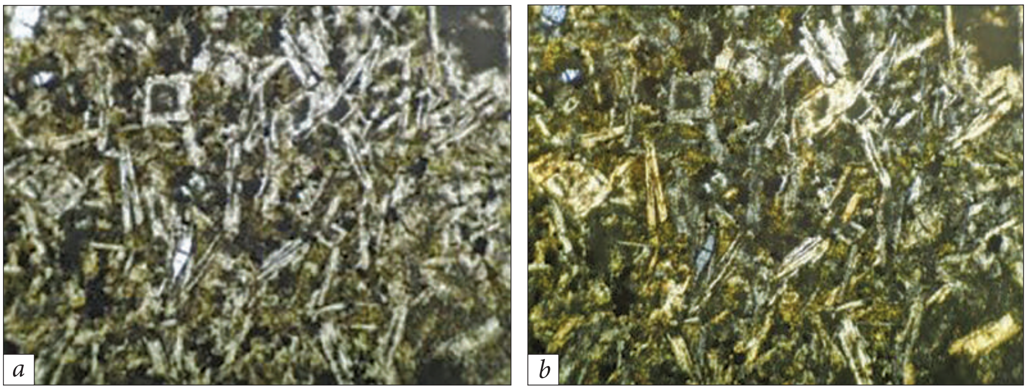


Fig. 4. Spilitic texture of metabasalts, field of view — 2 mm: *a* — plane-polarised light (PPL); *b* — cross-polarised light (XPL)

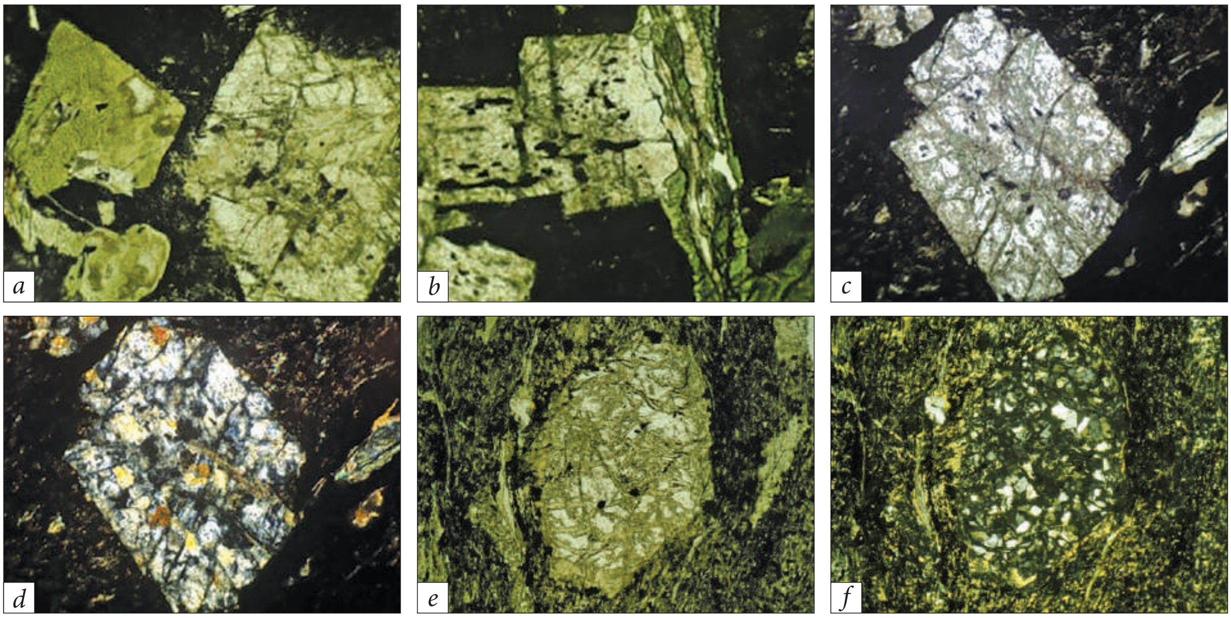


Fig. 5. Phenocrysts of altered plagioclase from metabasalts, field of view — 2 mm: *a*, *b*, *c*, *e* — PPL; *d*, *f* — XPL. Secondary minerals: *a*, *b* — chlorite, pumpellyite; *c*, *d* — pumpellyite, quarz; *e*, *f* — chlorite, pumpellyite, quartz

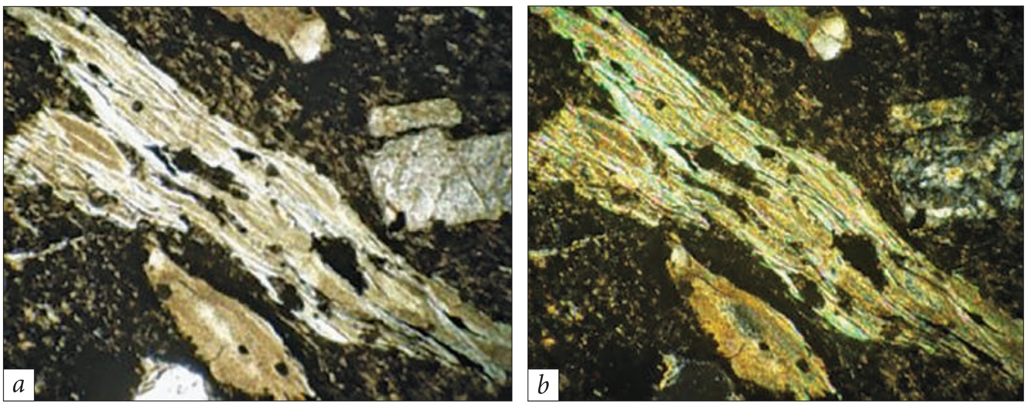


Fig. 6. A lens of secondary minerals (muscovite, carbonates, etc.) in metabasalts, field of view — 2 mm: *a* — PPL; *b* — XPL

ite-bearing mineral assemblages in Mesozoic magmatic formations (Fig. 1). Five magmatic complexes have been identified among them — Rakhivsko-Chyvchynskyi, Trostianetskyi, Uholskyi, Zakarpatskyi, and Vulkhovchytskyi [15, 19, 22].

Rocks of the Rakhivsko-Chyvchynskyi complex incline towards the thrust zone of the Marmarosh massif on the flysch rocks of the Rakhivska zone. Usually these are amygdaloidal basalts and diabases. In the basins of the Sarata and Mala Shopurka rivers (Rynovatyi and Tevshak streams) outcrops of ultramafic rocks are known, which are almost identical to the metabasites of the Uholskyi complex. Occasionally, gabbro-diabase and gabbro-dolerite bodies occur.

Uholskyi complex contains igneous rocks of the Velyka and Mala Uholka-river basins in the Marmarosh zone of rocks. The main types of rocks are serpentinized spinel lherzolites and diabases, which usually up to 300 m in size.

Results of studies of pumpellyite and associated minerals from metabasalts of the Rakhivsko-Chyvchynskyi complex. In the Kamianyi Potik basin (the right tributary of the Tisza River), outcrops of effusive rocks extend for more than 500 m. These are massive and amygdaloidal metabasalts and metadiabases with isolated rounded fragments and thin (30—50 cm) layers of marbleized limestones Most likely, the limestones were captured by the ba-

Table 1. **Chemical composition (wt. %) and crystal-chemical formulae of feldspars from metabasalts of the Rakhivsko-Chyvchynskyi complex**

Component	Analysis number *											
	3	4	7	8	13	14	17	19	20	21	22	30
SiO_2	67.64	49.08	67.88	53.85	58.77	53.59	54.49	59.21	54.5	53.69	54.53	57.45
TiO_2	0.02	0.74	0.06	0.17	b. d. l.	b. d. l.	0.39	b. d. l.	0.3	0.12	b. d. l.	b. d. l.
Al_2O_3	19.5	31.66	19.7	27.88	25.97	28.48	27.64	24.76	27.69	28.43	27.38	25.54
FeO	0.38	3.32	0.51	1.01	0.71	0.99	1.07	0.66	1.08	1.17	1.19	0.63
MnO	0.13	0.29	0.25	b. d. l.	b. d. l.	0.02	0.09	b. d. l.	b. d. l.	0.34	0.12	0.11
MgO	0.53	1.1	0.27	0.47	0.23	0.56	0.52	0.53	0.62	0.19	0.57	0.38
CaO	b. d. l.	0.21	0.14	11.58	6.74	11.26	11.08	6.34	10.52	11.76	10.59	7.85
Na_2O	11.7	0.51	10.66	4.73	6.05	4.94	4.45	7.32	5.09	4.33	5.42	6.56
K_2O	0.1	12.29	0.53	0.31	1.52	0.16	0.27	1.18	0.2	0.16	0.18	0.45
Total	100	99.2	100	100	100	100	100	100	100	100.19	100	98.99
Si	2.97	2.33	2.98	2.45	2.63	2.43	2.47	2.66	2.47	2.44	2.48	2.61
Al	1.01	1.77	1.02	1.49	1.37	1.52	1.48	1.31	1.48	1.52	1.47	1.37
Ti	0	0	0	0.01	0	0	0.01	0	0.01	0	0	0
Total	3.98	4.1	3.99	3.95	4.01	3.96	3.96	3.97	3.96	3.96	3.94	3.97
Ca	0	0.01	0.01	0.56	0.32	0.55	0.54	0.3	0.51	0.57	0.52	0.38
Na	0.99	0.05	0.91	0.42	0.53	0.43	0.39	0.64	0.45	0.38	0.48	0.58
K	0.01	0.74	0.03	0.02	0.09	0.01	0.02	0.07	0.01	0.01	0.01	0.03
Mg	0.03	0.08	0.02	0.03	0.02	0.04	0.04	0.04	0.04	0.01	0.04	0.03
Fe	0.01	0.13	0.02	0.04	0.03	0.04	0.04	0.02	0.04	0.04	0.05	0.02
Mn	0	0.01	0.01	0	0	0	0	0	0	0.01	0	0
Total	1.05	1.02	0.99	1.07	0.98	1.07	1.02	1.07	1.05	1.03	1.09	1.04
Ab	0.99	0.06	0.96	0.42	0.56	0.44	0.41	0.63	0.46	0.4	0.48	0.59
An	0	0.01	0.01	0.56	0.35	0.55	0.57	0.3	0.53	0.59	0.51	0.39
Kfs	0.01	0.93	0.03	0.02	0.09	0.01	0.02	0.07	0.01	0.01	0.01	0.03

N o t e. 19 — oligoclase; 3, 7 — albite; 4 — alkali feldspar; 8, 14, 17, 20—22 — labradorite; 13, 30 — andesine. FeO = = $FeO+Fe_2O_3$; b. d. l. — bellow detection limit. * The analysis numbers in all tables correspond to polished sections from 12 samples from the Rakhivsko-Chyvchynskyi complex, and 9 from Uholskyi.

salt flow at the time of their extrusion and marbled as a result of the temperature effect of the lava. Metabasalts predominate among the exposed volcanics — greenish-grey, greenish-purple massive or breccia-like rocks with an amygdaloidal structure and globular jointing (Figs. 2, 3).

The porphyritic texture of the rock, as well as the hyalopilitic and spilitic textures of the groundmass, can be seen in the thin sections (Fig. 4). Rocks are composed of microliths or laths of plagioclase, sometimes completely replaced by secondary minerals (Fig. 5), and glassy or afanitic matrix, partly replaced by chlorite and carbonates. Phenocrysts are represented exclusively by plagioclase — these are tabular (0.2—2.8 mm) and irregularly shaped (up to 1.3 mm) grains.

The rocks contain rounded and oval amygdales 0.2—1.0 mm in size, filled with secondary minerals — chlorite, a mixture of chlorite and carbonate, or chlorite and montmorillonite. Chlorite in thin sections is from almost colourless to dark green. In addition to amygdales, it also replaces the rock matrix forming of fine-scale aggregates. Carbonate in the form of block masses often fills numerous cracks from 0.05 to 1 mm thick; muscovite is often associated with it.

There are many ore minerals in metabasalts — titanomagnetite, magnetite, hematite. Characteristic skeletal forms indicate rapid solidification of the magmatic melt. Rocks often retain traces of tectonic influence (boudins, fissures, fragments of crystals, the presence of fragmented areas); orientation of boudins, cracks, plagioclase laths in the matrix is subparallel. Available lenses composed of secondary minerals — chlorite, muscovite, carbonates, etc. (Fig. 6), sometimes there are inclusions of irregular shape up to 3 mm in size, filled with albite-carbonate-chlorite aggregate.

The composition of Na-Ca plagioclase ranges from albite to labradorite (Table 1). Two generations of plagioclase were identified: the mineral of the first generation has a more basic composition, and the later segregations of plagioclase, which develop along the grains of the first generation, are more acidic (Fig. 7).

Rocks are intensively altered due to the processes of chloritization and carbonatization.

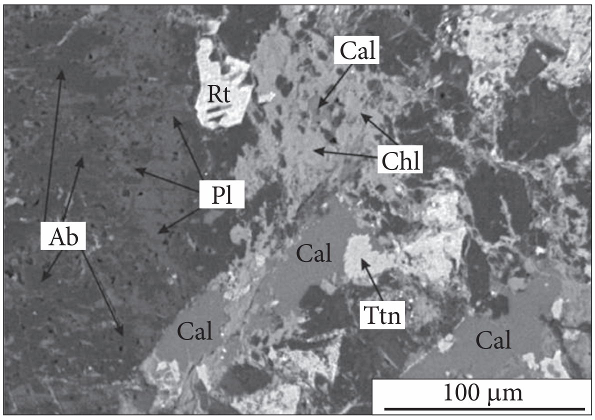


Fig. 7. Development of albite (Ab) along labradorite (Pl); other minerals: Cal — calcite, Ttn — titanite, Rt — rutile, Chl — chlorite; BSE image

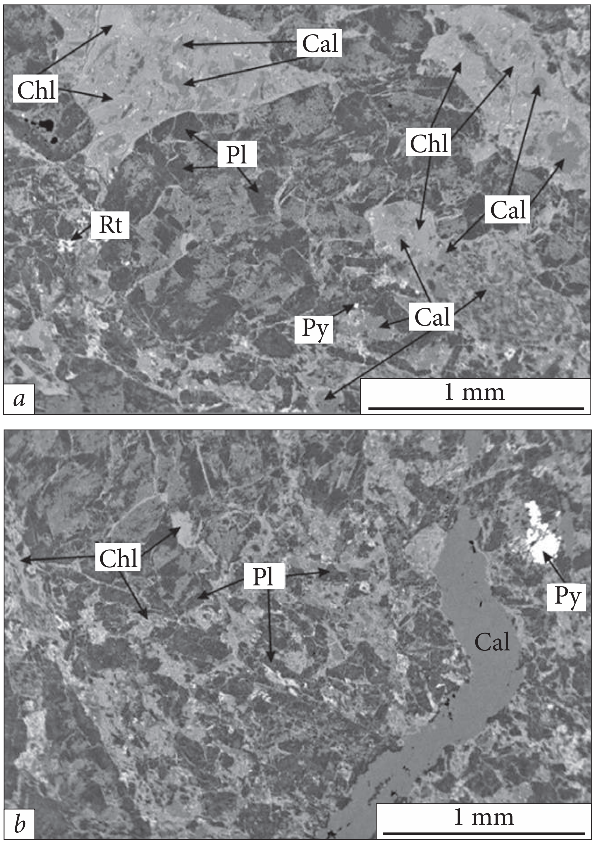


Fig. 8. Development of chlorite in metabasalts, BSE image. Minerals: Pl — plagioclase, Py — pyrite (see Fig. 7 for the rest)

Chlorite forms margins around the grains of plagioclase and calcite (Fig. 8) and develops along the microcracks of the cleavage of these minerals, and also forms elongated needle-like segregations along the cracks and in the interstices of minerals up to 0.5 mm in size. The results of the electron microprobe analyses of

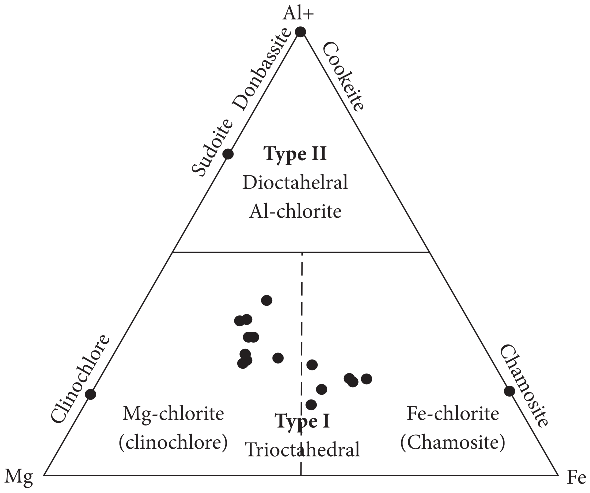


Fig. 9. Classification diagram of the compositional fields of rock-forming chlorites according to [28]

chlorites are given in the Table 2. According to the classification of A. Zane and Z. Weiss [28], the studied chlorite belongs to type I (i.e., $X_{Mg} + X_{Fe} \geq X_{Al} + X_{vacancy}$) trioctahedral chlorites and is chemically transitional between magnesium chlorite (clinochlore) and ferrichlorites (chamosite) (Fig. 9).

Pumpellyite is represented by grains ranging in size from 0.01 to 0.60 mm. The smallest grains were formed as a result of the replacement of plagioclase with the formation of pseudomorphs on it (together with chlorite, muscovite, albite, carbonate) (Fig. 10, *a, b*). Larger pumpellyite crystals (0.40—0.60 mm) are found in amygdales and veins together with quartz, chlorite, and albite (See Fig. 10, *c*).

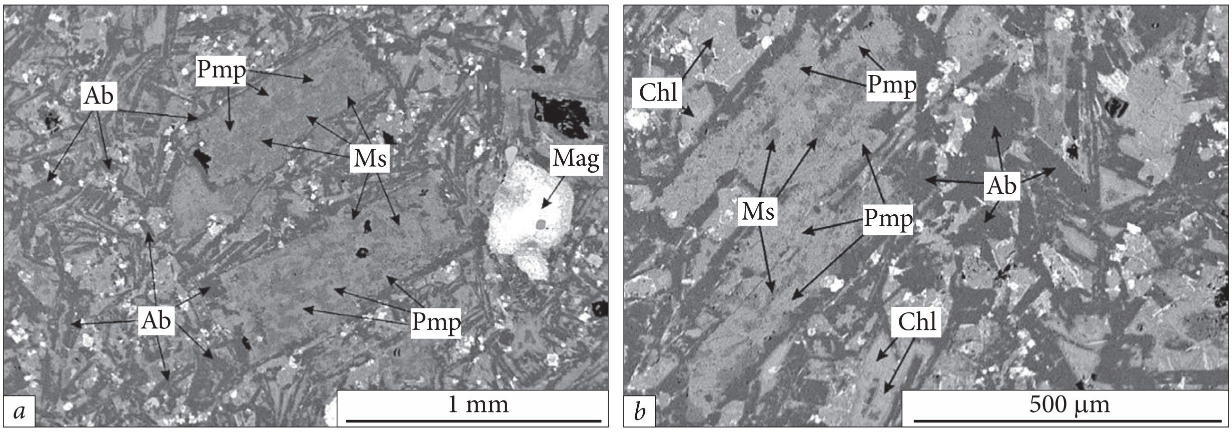
According to the results of microprobe analysis (Table 3) and based on the data [12], the mineral can be called as pumpellyite-(Fe).

X-ray structural analysis revealed the following minerals in the studied metabasalts: plagioclase — 0.376 nm (I = 700), 0.321 (700), 0.318 (1000), 0.403 (800), 0.375 (800), 0.321

Table 2. **Chemical composition (wt. %) and crystal-chemical formulae of chlorites from metabasalts of the Rakhivsko-Chyvchynskyi complex**

Component	Analysis number														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
SiO_2	31.17	29.77	33.85	32.15	28.79	24.85	34.65	23.68	28.27	31.94	30.76	28.55	33.47	32.96	32.43
TiO_2	b. d. l.	0.03	0.01	b. d. l.	b. d. l.	0.27	0.23	0.27	b. d. l.	0.07	b. d. l.	0.12	0.14	0.07	0.31
Al_2O_3	19.96	21.26	22.64	17.36	15.98	18.86	16.43	18.82	19.12	21.44	20.11	22.6	25.27	25.17	22.57
Cr_2O_3	b. d. l.	b. d. l.	b. d. l.	b. d. l.	b. d. l.	b. d. l.	b. d. l.	b. d. l.	b. d. l.	0.12	b. d. l.	0.16	0.15	0.14	0.23
FeO	15.67	18.4	14.8	29.51	28.52	30.9	26.65	32.29	33.89	17.89	18.03	22.23	15.72	14.55	16.54
MnO	0.35	b. d. l.	0.17	0.29	0.6	0.49	0.06	0.04	0.32	0.09	0.03	0.5	0.03	b. d. l.	0.32
MgO	15.13	18.28	12.76	14.93	13.05	10.49	13.27	9.16	11.14	18.7	18.47	15.88	16.83	17.32	17.08
CaO	0.3	0.04	b. d. l.	0.76	0.69	0.22	0	0.12	0.16	0.14	0.24	0.06	0.13	0	0.22
Na_2O	0.38	0.15	0.68	0.57	0.36	b. d. l.	0.17	b. d. l.	b. d. l.	b. d. l.	0.65	b. d. l.	b. d. l.	0.25	0.32
K_2O	1.85	0.57	2.03	0.02	0.21	b. d. l.	b. d. l.	b. d. l.	0.03	0.09	0.03	0.13	0.62	0.64	0.04
Total	84.81	88.5	86.94	95.59	88.2	86.08	91.46	84.38	92.93	90.48	88.32	90.23	92.36	91.1	90.06
Si	3.22	2.97	3.36	3.14	3.08	2.77	3.44	2.72	2.92	3.08	3.06	2.85	3.11	3.09	3.12
Al^{IV}	0.78	1.03	0.65	0.87	0.92	1.23	0.56	1.28	1.08	0.92	0.94	1.15	0.89	0.90	0.88
Total tetrahedral	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Al^{VI}	1.65	1.47	2.00	0.87	1.09	1.27	1.36	1.27	1.24	1.52	1.42	1.51	1.88	1.88	1.68
Ti	0.00	0.03	0.01	0.00	0.00	0.02	0.02	0.02	0.00	0.01	0.00	0.01	0.01	0.00	0.02
Cr^{3+}	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.01	0.01	0.01
Fe^{2+}	1.35	1.53	1.23	2.41	2.55	2.88	2.21	3.10	2.92	1.44	1.50	1.86	1.22	1.14	1.33
Mn	0.03	0.00	0.01	0.02	0.05	0.05	0.01	0.00	0.03	0.01	0.00	0.04	0.00	0.00	0.03
Mg	2.33	2.72	1.89	2.17	2.08	1.74	1.96	1.57	1.71	2.69	2.74	2.37	2.33	2.42	2.45
Total octahedral	5.37	5.75	5.14	5.47	5.78	5.96	5.56	5.97	5.90	5.67	5.67	5.79	5.45	5.45	5.52

N o t e. b. d. l. — bellow detection limit.



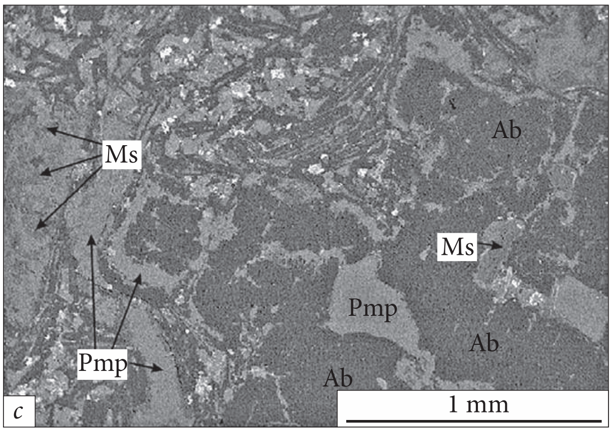


Fig. 10. Forms of pumpellyite (Pmp) segregations in metabasalts. BSE images; Ms — muscovite, Mag — titanomagnetite

Table 3. **Chemical composition (wt. %) and crystal-chemical formulae of pumpellyite from metabasalts of the Rakhivsko-Chyvchynskyi complex (Kamianyi Potik stream)**

Component	2	7	11	13	Component	2	7	11	13
SiO_2	36.21	35.36	36.82	36.88	Ca	2.01	2.00	1.83	1.97
TiO_2	b. d. l.	0.13	b. d. l.	0.13	Al	0.10	0.10	0.14	0.07
Al_2O_3	21.40	21.38	22.03	21.78	Fe^{2+}	0.46	0.62	0.53	0.61
FeO	6.57	8.86	7.71	9.00	Mg	0.30	0.33	0.32	0.28
MnO	0.31	0.14	0.22	0.15	Mn	0.02	0.01	0.02	0.01
MgO	2.39	2.64	2.59	2.36	*Total*	0.88	1.05	1.00	0.98
CaO	22.46	22.46	20.79	22.76	Al	2.00	2.00	2.00	2.00
Na_2O	0.14	b. d. l.	0.16	0.47	Si	3.02	2.94	3.03	2.98
K_2O	0.10	0.05	0.50	0.08	Ti	0	0.01	0	0
Total	89.58	91.02	90.82	93.61	*Total*	3.02	2.95	3.03	2.98

N o t e. b. d. l. — bellow detection limit.

(1000), clinochlore — 0.716 (450), 0.477 (400), 0.358 (100), epidote — 0.290 (400), 0.269 (300), 0.268 (300), muscovite — 0.332 (1000), 0.257 (300), pumpellyite — 0.353 (310), 0.281 (320), 0.197 nm (340).

Results of the study of pumpellyite from metabasalts of the Uholskyi complex. The studied metabasalts, described previously by L. Heneralova et al. [9], are greenish-grey to brownish-green in colour and have a cleavable, often amygdaloidal structure (Fig. 11). The texture of the rock is porphyritic, the texture of the matrix is intersertal (Fig. 12), somewhere pilotaxitic.

The rocks are composed of plagioclase (up to 40 %), chlorite (up to 34%), quartz (up to 20%), carbonates (up to 14%); epidote, monoclinic pyroxene, and iron hydroxides occur. Amygdules 0.5—2.0 mm in size have an isometric-elliptical shape and are filled with quartz-chlorite and quartz-carbonate-chlorite aggregates.

Pumpellyite forms fine-crystalline to needle-like segregations in the rock (Fig. 13). Based on the results of microanalytical studies (Table 4), pumpellyite can be classified as an intermediate member of the Al-pumpellyite-Fe^{2+}-pumpellyite series (http://webmineral.com/).

On the three-component Fe_{tot} — Al — Mg diagram, the pumpellyte compositions of both studied magmatic complexes plot close to the side Fe_{tot} — Al, i.e., they belong to the intermediate members of the pumpellyite-(Fe^{2+}) — pumpellyite-(Al) series (Fig. 14). Regarding the chemical composition of the mineral, pumpellyite from the metabasites of the Rakhivsko-Chyvchynskyi complex contains more MgO compared to the mineral from the rocks of the Uholskyi complex, and there is no significant difference in the Al_2O_3 and FeO contents.

Metamorphic conditions of the formation of pumpellyite-containing parageneses in metabasites of the Rakhivsko-Chyvchynskyi and Uholskyi complexes. To determine the temperature of mineralization of pumpellyite and associated minerals, we used different geothermometers.

Since the rocks contain plagioclase (from albite to bytownite) and alkali feldspar, it is possible to calculate the temperature of mineral formation using a ternary feldspars geothermometry. According to various authors, it is 260 [6] and 310 °C [7], the average value is 290 °C.

The chlorite geothermometer was first proposed by M. Cathelineau and D. Nieva [2], who discovered a positive correlation between the amount of Al in tetrahedral coordination and the temperature of mineral formation. P. Kranidiotis and W.H. Maclean [11] came to the conclusion that in chlorite the amount of Al in tetrahedral coordination increases with an increase in the value of Fe/(Fe+Mg), and suggested that the amount of Fe and Mg depends on temperature. On this basis, they proposed the following formula:

$$T,\ ^\circ\mathrm{C} = 212\{Al^{IV} + 0.35\,[Fe/(Fe + Mg)]\} + 18.$$

Therefore, the temperature of mineral formation, calculated using a chlorite geothermometry, varies from 170 to 320 °C, the average value is 250 °C.

On the basis of the obtained temperature values, it is possible to determine whether the rocks

Table 4. **Chemical composition (wt. %) and crystal-chemical formulae of pumpellyite from metabasalts of the Uholskyi complex**

Component	1	2	3	4	5	6	7	8	9	10
SiO_2	36.74	36.35	35.88	35.95	36.10	35.38	36.04	36.34	37.06	36.23
TiO_2	0.15	0.04	0.13	b. d. l.	b. d. l.	0.07	b. d. l.	b. d. l.	2.43	0.07
Al_2O_3	25.14	24.44	26.49	25.46	22.09	24.75	24.94	24.32	25.51	24.99
FeO	8.23	9.59	6.65	8.67	13.53	9.96	9.42	9.55	7.55	9.31
MnO	0.05	0.15	0.49	0.24	b. d. l.	b. d. l.	b. d. l.	0.09	b. d. l.	b. d. l.
MgO	0.83	0.37	0.49	0.78	0.78	0.59	0.63	0.82	0.78	0.45
CaO	22.15	22.62	22.82	22.29	21.99	21.18	22.43	21.72	20.89	21.75
Na_2O	0.13	0.23	0.37	0.6	0.62	0.32	0.27	0.37	0.29	0.04
K_2O	b. d. l.	b. d. l.	0.12	0.01	0.01	b. d. l.	b. d. l.	b. d. l.	0.09	0.22
Total	93.43	93.77	93.44	94.00	95.13	92.25	93.74	93.20	94.60	93.05
Ca	1.90	1.95	1.95	1.91	1.91	1.85	1.93	1.88	1.75	1.88
Al	0.37	0.32	0.49	0.40	0.11	0.38	0.36	0.31	0.36	0.38
Fe^{2+}	0.55	0.65	0.44	0.58	0.92	0.68	0.63	0.64	0.49	0.63
Mg	0.10	0.04	0.06	0.09	0.09	0.07	0.08	0.10	0.09	0.05
Mn^{2+}	0.00	0.01	0.03	0.02	0.00	0.00	0.00	0.01	0.00	0.00
Total	1.02	1.02	1.03	1.09	1.12	1.14	1.07	1.06	0.94	1.06
Al	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00	2.00
Si	2.94	2.93	2.86	2.88	2.93	2.89	2.90	2.93	2.91	2.92
Ti	0.01	0.00	0.01	0.00	0.00	0.00	0.00	0.00	0.14	0.00
Total	2.94	2.93	2.87	2.88	2.93	2.90	2.90	2.93	3.05	2.93

N o t e: b. d. l. — bellow detection limit.

Fig. 11. Metabasalts from the Uholskyi complex

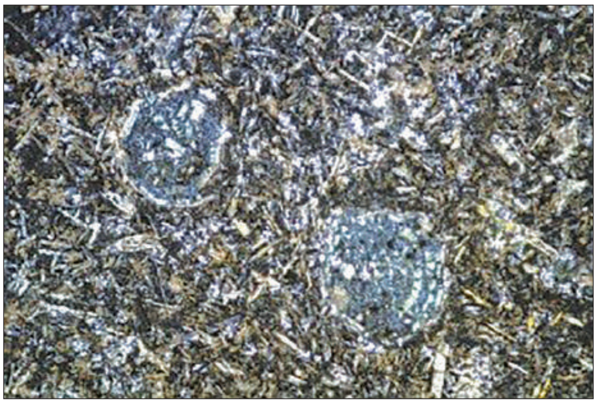


Fig. 12. Chloritized and carbonatized metabasalt of the Uholskyi complex; field of view — 2 mm, XPL

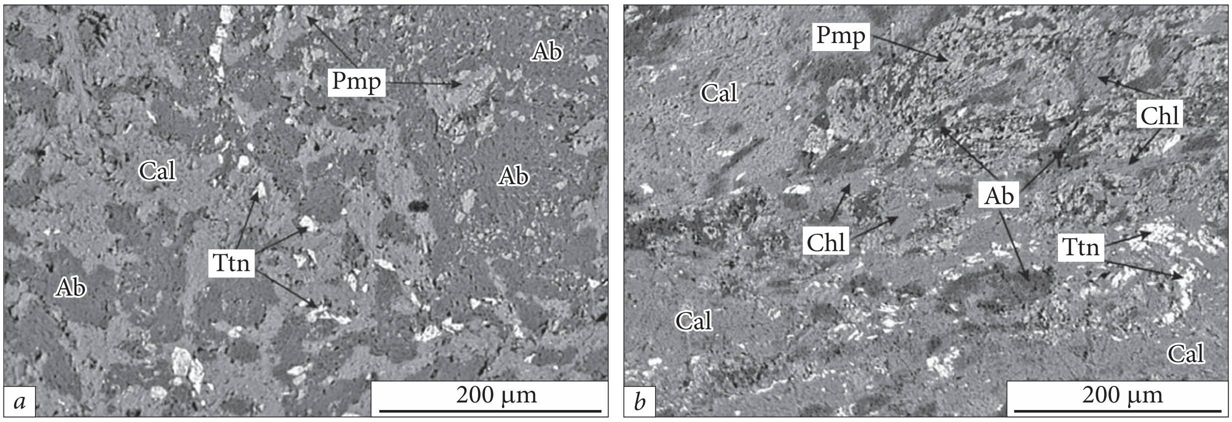
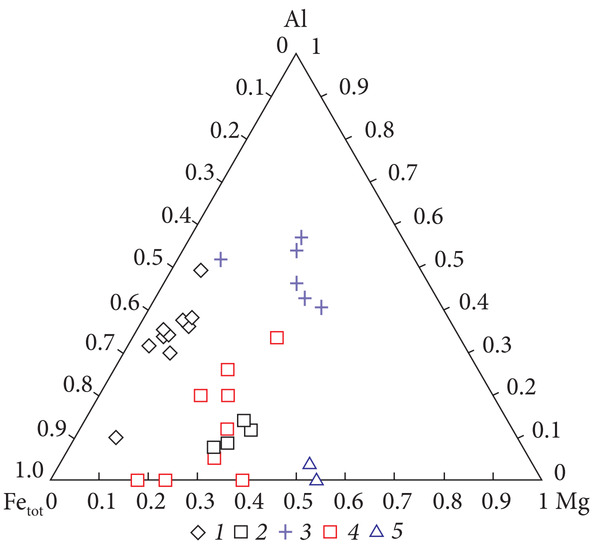


Fig. 13. Fine-crystalline (*a*) and needle-shaped (*b*) segregations of pumpellyite in metabasalt. BSE image



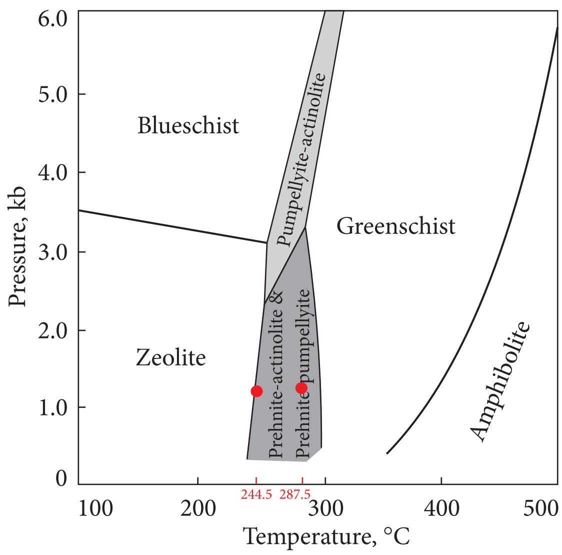


Fig. 14. Variations in the composition of pumpellyite from various rocks in the three-component system Fe_{tot}–Al–Mg (formula coefficients), according to [25] with authors additions: *1* — metabasalts of the Uholskyi complex; *2* — metabasalts of the Rakhivsko-Chyvchynskyi complex; *3* — metadiabases [25]; *4* — volcanic-sedimentary metabasites [18]; *5* — effusive rocks of the basic composition [10]

Fig. 15. The mineral formation temperature data obtained by us (in red) on the *PT*-diagram for metamorphic facies [18], simplified according to [16, 20]

belong to certain facies of metamorphism: on the *PT*-diagram of metamorphic facies [27], the metabasalts of both investigated magmatic complexes fall into the field of the prehnite-pumpellyite subfacies of prehnite-pumpellyite facies (Fig. 15). The absence of clear pumpellyite-actinolite subfacies associations indicates that the pressure in the mineral formation system did not exceed 300 MPa. The predominance of prehnite over pumpellyite proves that the fluids were rich in water. However, usually, according to [16], pumpellyite dominates, and fluids rich in CO_2 lead to the formation of calcite instead of prehnite, as happened in our case.

We associate secondary transformations in the Mesozoic volcanic rocks of the Ukrainian Carpathians with the processes of low-grade metamorphism. The authors of the article [3] associated similar changes in volcanics and greywackes of New Zealand with metamorphism in the conditions of zeolite and prehnite-pumpellyite facies; they noted that such rocks can be studied in the same way as other metamorphic rocks [3, 4]. Two typical mineral associations in prehnite-pumpellyite facies metabasalts could be quartz + albite, prehnite + pumpellyite + + chlorite + quartz + albite. The transition from zeolite to prehnite-pumpellyite facies occurs at a temperature of 250 °C at a depth of 3—13 km. There is enough data in the literature that minerals of low degrees of metamorphism can be formed in different conditions and in different rocks: in subduction zones, on the ocean floor, in island arcs, in gneiss complexes, metadolerites. etc.

Conclusions. Complex studies of pumpellyite and its associated minerals from igneous rocks of the Rakhivsko-Chyvchynskyi and Uholskyi complexes (*MZ*) proved the following. The porphyritic texture and amygdaloidal structure are typical for metabasalts of both complexes. The main minerals are feldspars, quartz, chlorites, carbonates. Amygdules are mainly filled with quartz-chlorite-carbonate aggregate.

In metabasalts of the Rakhivsko-Chyvchynskyi complex, feldspars are represented mainly by plagioclase (albite-bytownite) of several generations. The studied chlorites are trioctahedral and are represented by clinochlore and chamosite. Pumpellyite is represented by two morphological varieties: (1) small grains formed as a result of the replacement of plagioclase with the formation of pseudomorphs in it together with chlorite, muscovite, albite, carbonates; (2) somewhat larger crystals in amygdules together with chlorite and albite. The mineral is classified as pumpellyite-(Fe) according to its chemical composition.

In metabasalts of the Uholskyi complex, pumpellyite forms fine-crystalline to needle-like segregations and associates with chlorite, calcite, and albite. According to its chemical composition, it belongs to an intermediate mineral species between pumpellyite-(Al) and pumpellyite-(Fe^{2+}).

According to two mineralogical geothermometers, the temperature of mineralization during the formation of pumpellyite-containing parageneses was determined: according to the ternary feldspars geothermometry — 265 and 310 °C, according to chlorite geothermometry — from 170 to 320 °C. On the *PT*-diagram for metamorphic facies, the mineral paragenesis of both studied magmatic complexes fall into the field of prehnite-pumpellyite facies.

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ПУМПЕЛІЇТ ІЗ МЕТАБАЗАЛЬТІВ УКРАЇНСЬКИХ КАРПАТ

Загалом у серії пумпеліїтів (водні силікати Ca та Al) розрізняють такі мінеральні види як пумпеліїт-(Al), пумпеліїт-(Fe^{2+}), пумпеліїт-(Fe^{3+}), пумпеліїт-(Mg) та пумпеліїт-(Mn). Ми досліджували пумпеліїт із мезозойських метабазальтів Українських Карпат з метою відтворення температурно-фаціальних умов мінералоутворення. Породи — метабазальти рахівсько-чивчинського й угольського магматичних комплексів, досліджено за допомогою класичних і сучасних мінералогічних, петрографічних і петрогеохімічних методів. У породах рахівсько-чивчинського комплексу виявлено дві морфологічні відміни пумпеліїту-(Al), в угольському комплексі наявний проміжний мінеральний вид між пумпеліїтом-(Al) і пумпеліїтом-(Fe^{2+}). За двома мінералогічними геотермометрами визначено температуру мінералоутворення в процесі формування пумпеліїтовмісних парагенезисів: за плагіоклаз-калієво(лужним)-польовошпатовим геотермометром — 265 і 310 °C, за хлоритовим — від 170 до 320 °C. На *PT*-діаграмі для метаморфічних фацій мінеральні парагенезиси обох вивчених магматичних комплексів потрапляють у поле преніт-пумпеліїтової фації. Відсутність чітких асоціацій пумпеліїт-актинолітової субфації свідчить про те, що тиск у системі мінералоутворення не перевищував 300 МПа.

Ключові слова: пумпеліїт, метабазальт, умови мінералоутворення, мінералогічний геотермометр, мезозой, Українські Карпати.