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A. V. Emetz, V. M. Zagnitko, V. L. Prykhod'ko

Mineral compositions and genesis of the ore bodies of the Zhyrychi Cu deposit (North-Western Ukraine)

The paper presents scientific information about mineral composition of the ore bodies of the Zhyrychi Cu deposit found in the North-Western Ukraine at the end of the last century. The deposit is located in the Vendian basaltic flows and intraflow pyroclastics in central part of the Volhyn trappean province, originated during the Tornquist rifting. The majority of copper is concentrated in native form and occurs as disseminated grains, veinlets and nuggets. Locally native silver, Cu-sulphides (chalcosite, digenite, bornite and covellite) and cuprite replace native copper. The ore bodies are controlled by faulting and occur as strata-bound, but are locally enriched in nuggets in tuffs and fissured zones in basalts. Ag, Pd, Rh and Au can also be important at an economy of the Zhyrychi deposit. The major Cu ores were deposited together with prehnite-pumpellyite paragenesis, originated in the succession: pumpellyite — prehnite (± native copper) — laumontite (or wairakite) (± native copper). The ore bodies were formed during cooling of the mineral-forming hydrothermal system at the end of the Vendian volcanic activity. The syngenetic intergrowths of native copper with prehnite precipitated after pumpellyite and homogenization temperature of fluid inclusions in later wairakite (210–335 °C) [2, 3] indicate that the major precipitation of native copper took place at 200–400 °C. The following propylitization, smectitization and analcimization of the country rocks probably occurred during attenuation of the hydrothermal activity after magmatism ceased. All these processes were accompanied by dissolution of Cu ore and its redistribution with local enrichment in copper nuggets.

E-mail: emetz_a@igmr.relc.com

1. Introduction

Native copper occurrences are common in many basalt provinces, but the high-grade economic native copper ores are rare. Consequently, a unique process, which resulted in the unusual metallic Cu accumulation in one place, is probably of similar nature in many basalt provinces. Numerous native copper deposits of the most famous Michigan Cu district (Keweenaw Peninsula) occur within the Mid Proterozoic basalt flows and intraflow conglomerates, filling the 1.1 Ga North American Midcontinent rift system [13]. Some similar native copper deposits are well known in the volcanic rocks of Canada and USA [15], China [19], Russia (Tunguska Syneclise) [5] etc.

All these deposits contain mineral associations of so-called prehnite-pumpellyite facies of metamorphism, including quartz, albite, prehnite, pumpellyite, epidote and chlorite; which spatially grades into zeolite facies, more often comprising quartz, analcite and laumontite. On the other hand, all these minerals widely originate in modern hydrothermally active regions [11]. However, distinct association of native copper with gangue minerals is still unclear. On the base of mineralogical mapping Stoiber and Davidson [18] displayed that native copper deposits in the Michigan Cu district are mainly located near the boundaries of zones enriched in quartz, but also occur where quartz is not abundant.

Economic copper was prospected in Western Ukraine since 1929 when Małkowski [17] provided the first published information about finding of native copper nuggets in basalts of the village Velykiy Midsk (present-day Rafalovka-Berestovets Cu field) (Fig. 1, 2). The most extensive review of the mineralogical studies about the Volhynian Cu-bearing basalts have been carried out by Lazarenko et al. [7]. The last mineralogical and geochemical studies on hydrothermal alterations in the ore volcanics can be found in the papers [2, 3].

The discovery of the Zhyrychi Cu deposit in the volcanogenic rocks of the Volhyn Province of the North-Western Ukraine [8] is a first success of Ukrainian Geological Survey in the

Fig. 1. Sketch map of the Western Ukraine

ore prospecting and fixes new Volhyn Cu Province. In the present work, we provide new data on the mineralogy of the Zhyrychi deposit. At the end of this paper the authors interpret the ore-forming processes.

2. Methods

The core descriptions and sampling have been performed in the core storage of the Kovel Branch of the Ukrainian Geological Survey, providing active boring in the area studied. Polished and thin sections were prepared both in the laboratories of the Institute of Geochemistry, Mineralogy and Ore Formation (IGMOF) (Kyiv, Ukraine) and AGH University of Science and Technology (UST) (Krakow, Poland).

Atomic absorptive analyses (ASA) and inductively coupled plasma mass spectrometry (ICP-MS) analyses of the samples have been carried out in the laboratories of UST.

The minerals described in the present paper were identified both megascopically and microscopically, and by SEM, microprobe and X-Ray diffraction analyses.

Microprobe analyses were obtained at UST using ARL SEMQ microprobe (voltage 20 kV, probe current 120 mA, sample current 10 nA and counting time 20 s). Kα lines were used to detect Fe, Cr, Ti, Ca, K, Si, Al, Mg, Na, Mn, Cu, Ni, Co, Fe, Cr and S; Lα — Ag and Pd; Mα — Au and Pt.

X-Ray diffraction analyses were performed on approximately 1.5 g of packed powder of the carefully extracted minerals. CuKα radiation, a scan from 2 to 70° 2Θ at a speed 0.25°/min were used for the analyses. The obtained data have been interpreted using X-Rayan software.

3. Tectonic setting

The Zhyrychi Cu deposit is situated in the western part of the Ratne high (Fig. 2), one of the horst-type highs of the Lukow-Ratne swell. The swell strikes 350 km E — W in the East-European Craton from Ukrainian Shield to the Slavatychsky high in Poland [9] (Fig. 2). These tectonic phenomena probably arose at the end of Vendian and were developed as residual blocks during Late Devonian when the region plunged after Hercynian regional uplift [12].

Westward and eastward the Ratne high was cut by the adjoining dips, which were also responsible for its separation from the neighbouring Hoteshov and Hotyslav highs respectively (Fig. 2). Southward the Precambrian beds were shifted down about 650 m along the South-Prypyat faults bounded the Ratne high on the Volhyn depression. Northward the sedimentary beds flatly and down some stepwise low-amplitude faults of the North-Prypyat fault zone deep towards the Podlasie-Brest depression.

Tectonically the Ratne high consists of the most elevated central horst, surrounded by tectonically separated blocks, stepwisely burying along the boundary and radial faults, ranging in amplitude from 10 to 200 m.

4. Brief review of geological structure and petrography

The oldest rocks in the deposit are found in the central horst below the Late Cretaceous beds. They are represented by 1.2 Ga gneisses and granitoids, containing syenite and gabbro intrusions dated at 1–1.1 Ga old [9]. These rocks are bordered by the boundary faults against the eroded Late Riphean or Vendian beds.

Sedimentary cover in the Ratne high comprises Late Riphean red beds, Vendian basalt flows and intraflow pyroclastics, Late Vendian — Cambrian rhythmic sedimentary sequence and Silurian limestones. These deposits were eroded from Middle Devonian to Early Cretaceous down the Early Proterozoic metamorphic rocks. The Late Cretaceous chalk and marly beds, ranging from 120 to 180 m thick, cover the eroded surface. The Quaternary clayey and

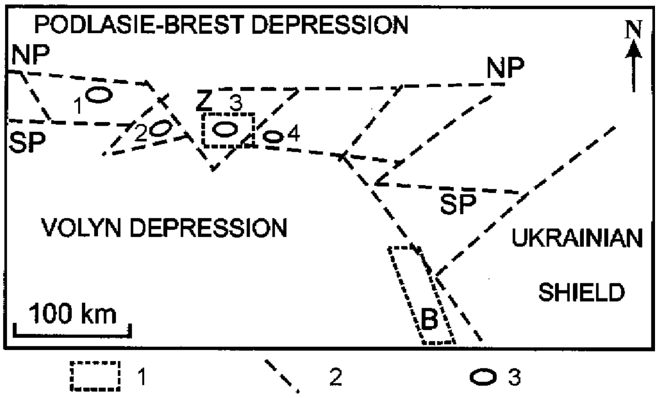


Fig. 2. Sketch of the tectonic positions of the Zhyrychi Cu deposit (Z) and Rafalovka-Berestovets Cu field (B). *Fault zones*: *SP-SP* — South-Prypyat; *NP-NP* — North-Prypyat. Horst-type highs of the Lukow-Ratne swell: *1* — Wishnice; *2* — Hoteshov, *3* — Ratne, *4* — Hotyslav. *Legend: 1* — Zhyrychi Cu deposit, *B* — Rafalovka-Berestovets Cu field; *2* — faults; *3* — outcropping crystalline basement underneath Cretaceous beds in the horst-type highs

sandy sediments, varying in thickness from 20 to 80 m, unconformably cover this unit.

Late Riphean strata (Polis'ka suit), 400–500 m thick, unconformably cover the metamorphic complex as red terrestrial sandstones and siltstones with clayey interbeds. The strata comprise four successive sedimentary cycles, which filled the Mid-Baltica rifting system during Late Riphean [12]. These strata contain the Vendian dolerite dikes and sills, which sinter the country rocks in the contact zones and in some places were intensively hydrothermally altered.

The Volhyn suite includes Gorbashi and Berestovets series.

The Gorbashi series consists of brown arkose gravel and sandstone beds, which conformably overlaps the Riphean red beds. Its thickness ranges from 40 to 80 m. The clastic material contains quartz, feldspar, plagioclase, granitoids, pyroclastics and red sandstones.

The Berestovets series is composed of the trappean formations originated within Vendian rifting, which opened Tornquist Ocean between Baltica and probably Amazonia ancient continents at the end of Vendian. The range of these beds is concordant with the present-day Teisseyre-Tornquist margin [12].

The Berestovets series has been subdivided into Zabolottya or lower basalt beds, Babino or predominantly tuff beds and Ratne or upper predominantly basalt beds [1]. These subdivisions are recently in use for mapping in the Ukrainian Geological Survey. A. V. Emetz et al. [12] have displayed that the Vendian volcanic plateau developed during four successive volcanic cycles produced regional lava ejections in the region. As follows from this paper, the trappean plateau comprises seven subdivisions: flood basalts *A*, *B*, *C* and *D*, and lower, mid and upper tuffs; which have been found by boreholes in the Zhyrychi deposit. The floods comprise some successive lava flows divided by thin layers of pyroclastics. The thickness of the floods varies from 25 to 70 m, whereas of the intraflow pyroclastic beds — from 24 to 80 m.

The major rock minerals, which compose basalts are represented by plagioclase (50–60 %), monoclinic pyroxene (predominantly augite) (30–40 %) and magnetite (or titanomagnetite) (5–10 %). Many specimens from the lowermost and mid parts of the basalt flows contain nearly no glass and are similar to fine-grained dolerites, testifying slow cooling of the basaltic melt within the flows. Towards the top almost each basalt flow ranges from megascopically massive rocks into poikilitic and amygdaloidal, but dolerite-basalts grade into fine-crystalline and glassy basalts. Usually, the content of glass in these basalts does not exceed 10 %.

Tuffites often dominate among the intraflow tuff series. They consist of fine-rounded clasts of basalts and tuffs (Fig. 3, *b*). Both red and green tuffites comprise sequences of the cross-bedded layers, formed in intermediate and littoral facies. Clasts of andesites are rarely observed among pyroclastics. Tuffs consist predominantly of different ratio of scoria, glass and basalts.

Both tuffs and tuffites, and often basalts are heavily altered by later hydrothermal processes. Consequently, in many places it is impossible to recognize the primary composition of pyroclastic rocks because of polygenic secondary alterations. Propylitization, hematitization and albitization are the most widespread among the alteration processes. Ca metasomatism is widely spread, however it was structurally controlled by fault zones and therefore developed locally.

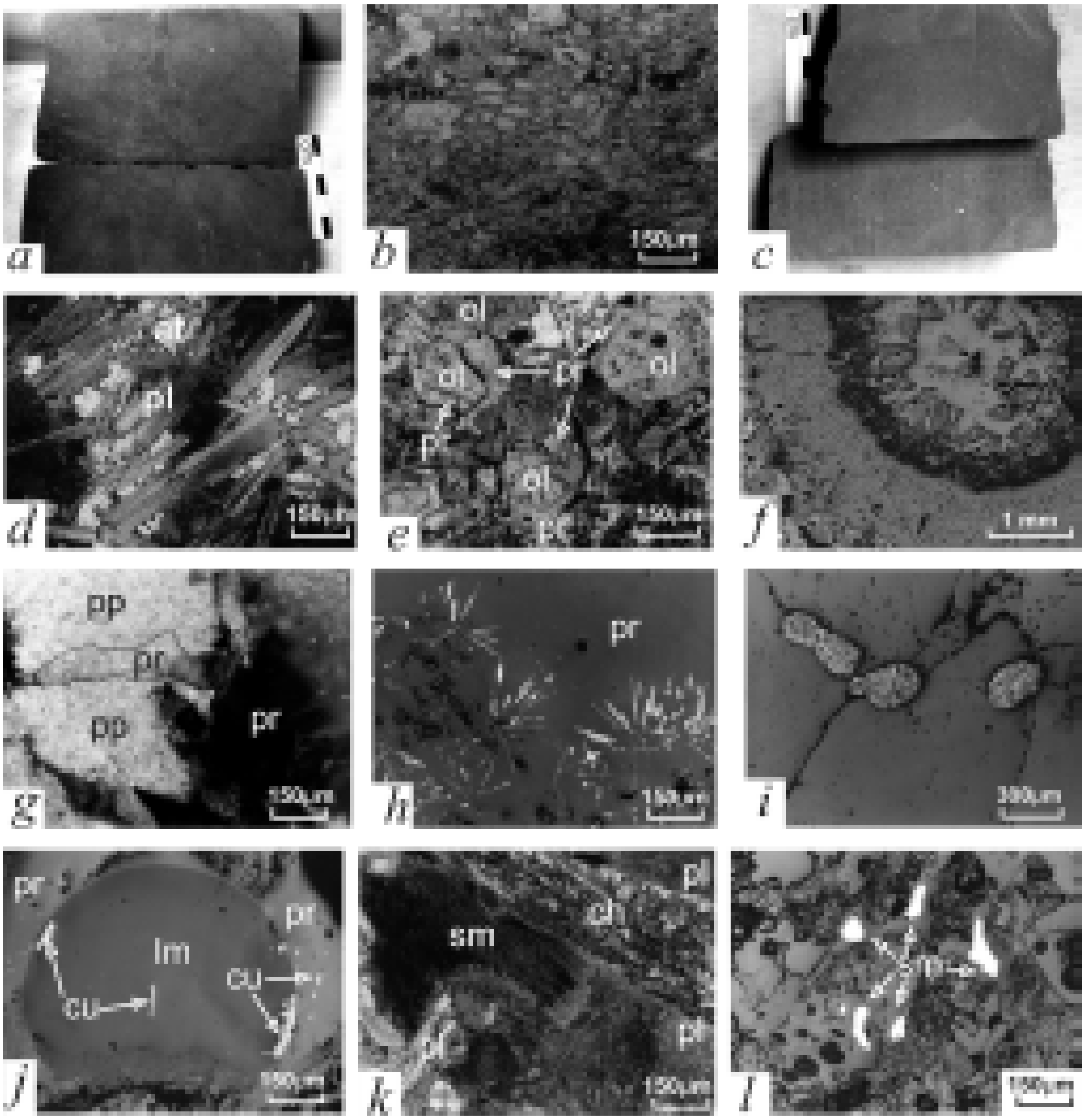
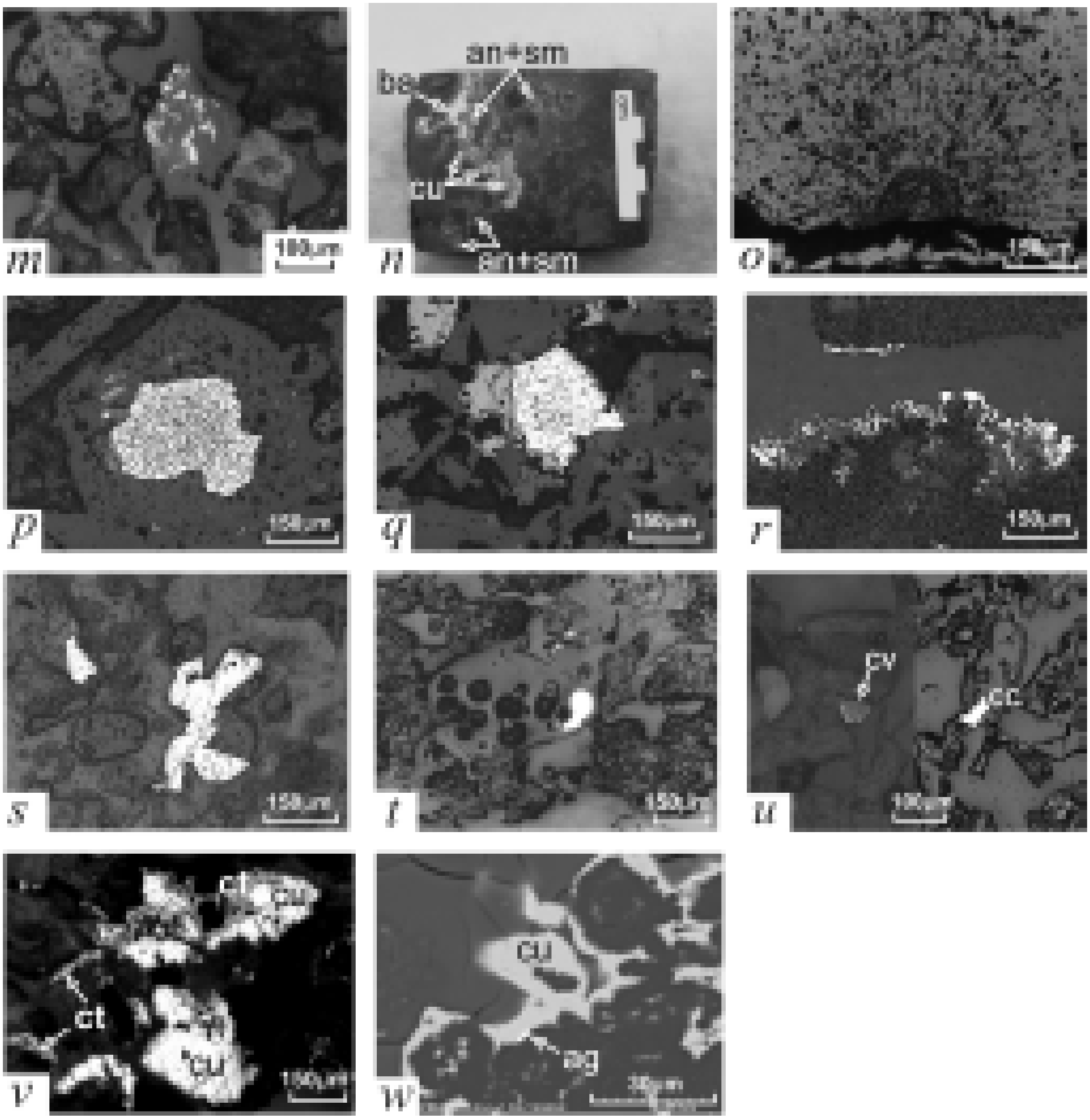


Fig. 3. Rocks and minerals in the ore bodies of the Zhyrychi deposit: *a* — lava-breccias with native copper (white spots), *b* — smectitized green tuffite, *c* — ore-bearing tuff with native copper (white spots), *d* — dolerite-basalts, intersertal texture, *e* — prehnite replaces dolerite-basalt and forms pseudomorphoses after olivine (?), *f* — clinochlore spheroid, *g* — prehnite overgrows and cuts pumpellyite, *h* — syngenetic ingrowths of native copper within plumose prehnite, *i* — native copper crystals in the central part of prehnite veinlet, *j* — laumontite hemisphere with native copper within prehnite, *k* — developing smectite and chlorite in the ore basalts, *l* — smectite overgrows native copper inclusions in the lower tuffs, *m* — native copper inclusions within smectite, *n* — barite-analcime-native copper-smectite veinlets and amygdales in fissured basalt, *o* —

Among magmatic rocks the most altered are coarse-crystalline dolerite-basalts. In many places pyroxene and magnetite were replaced by younger minerals. These minerals impregnated plagioclase skeleton and deposited in amygdales, filling gas bubbles or replacing phenocrysts of pyroxene and plagioclase during hydrothermal alterations. In glassy basalts the secondary minerals are mostly located in amygdales, which in different amount and size are everywhere observed in basalt matrix. The ore-bearing amygdaloidal basalts of the Zhyrychi deposit are predominantly represented by hydrothermally altered tubulated basalts, in which the primary nodules were connected because of intensive leaching. The alteration rate varies laterally and depends on the structure of basalts and fissuring. Intensively altered clayey basalts of the flood A are often soft and brittle.



analcime spherical pseudomorphoses after laumontite hemisphere, *p* — native copper within smectite, developed after olivine(?), *q* — native copper replaces magnetite, *r* — dendrites of native Cu in quartz-chlorite-smectite veinlet, *s* — native copper replaces pyroclast, *t* — native copper fills open spaces in scoria, *u* — covellite and chalcosite in the analcimized tuff, *v* — cuprite replaces native copper, *w* — native silver microparticle on native copper; ag — native silver, an — analcime, at — augite, ba — barite, cc — chalcosite, ch — chlorite, ct — cuprite, cu — native copper, cv — covellite, Kf — K-feldspar, lm — laumontite, ol — olivine, pl — plagioclase, pp — pumpellyite, pr — prehnite, sm — smectite

5. Ore bodies position

The major ores in the Zhyrychi deposit have been found in flood basalts *A*, *B*, *C* and *D* in the lower tuffs. In some places, the ores form five strata-bound bodies, which are enriched in nuggets and veinlets in fissured zones.

The data of ASA and ICP-MS analyses of core samples selected in different places of the Volhyn province are presented in Table 1. The analysed samples from the Zhyrychi deposit and Rafalovka-Berestovets Cu field (Fig. 1) characterize the ores without nuggets. The nuggets were analysed separately because they increase true contents of Cu and probably Ag and Rh, which directly correlate with Cu (Fig. 4): $C_{Ag} = 0.0047C_{Cu}$ — 5.0716, $R^2 = 0.8377$; $C_{Rh} = 3\cdot10^{-5}\,C_{Cu}$ — 0.019, $R^2 = 0.9746$ (where C is a content of metal in ppm, and R^2 is a Pearson coefficient). The ores are also uniformly enriched in Pd (average content — 1.3 ppm) and locally contain Au up to 2.9 ppm (Table 1), however the mineral position of these metals is still not determined.

Disseminated native copper occurs everywhere in basalts, dolerites and intraflow pyroclastics. However, Cu contents in the rocks outside the deposits do not exceed 100 ppm (sample C-60 in Table 1).

The thickness of the ore bodies in basalts varies from 0.3 cm to 2.5 m at Cu content ranging from 0.3 to 12 % and at an average values 1.5 m and 1.6 % respectively. Cu minerals occur as disseminated, veinlets and filling amygdales. Copper nuggets occur locally along some fissured zones. The most important ore bodies occur in altered dolerite-basalts, amygdaloidal basalts and lava-breccias (Fig. 3, *a*).

In the lower tuffs the plentiful disseminated native copper mostly occurs in green interlayers, but in some places has been found around in the red tuffs (Fig. 3, *c*). The thickness of the ore bodies and intensity of mineralization are probably controlled by the stepwise faults, bordering the lower tuffs against the Late Riphean red beds. Abundant mineralization of native copper in the strata-bound bodies grades into scarce at the distance from 1 to 15 m of Cu content from 0.2 to 5 %.

6. Mineralogy of the ore bodies

The mineral composition of the ore bodies is variably depending on the ratio between primary and secondary minerals, occurring in the rocks.

6.1. ***Rock forming minerals.*** Among primary minerals of basalts plagioclase, clinopyroxene, magnetite, Fe or Fe-Ti oxides and volcanic glass are the most common.

P l a g i o c l a s e occurs as idiomorphic crystals, which compose "skeleton" of the intersertal (Fig. 3, *d*) or aphiric basalts, or as scarce phenocrystals in glomeroporphyric basalts. The crystals are often zoned. In fresh basalts plagioclase grades from anorthite to andesine, but in the altered albitized rocks albite is the most common. Thin inclusions of glass and ore minerals locally occur in peripheral sectors of the plagioclase crystals.

C l i n o p y r o x e n e forms prismatic and roundish crystals, filling interspaces of the plagioclase "skeleton" (Fig. 3, *d*). Augite dominates, but in some places pigeonite also occurs. In compliance with the papers [10] the flood basalts of Zabolottya beds and dolerite bodies contain pyroxenes represented predominantly by magnesium augite, but ferroaugite occurs rarely, whereas pigeonite and ferroaugite are often associated with magnesium variety of augite in flood basalts of Babino and Ratne beds.

During present study thin augite crystals were microscopically observed among pyroclastic material in the ore-bearing tuffs. Microprobe analyses show it to represent ferroaugite (Table 2). It argues that the pyroclastics of the lower tuffs (Babino series) ejected after the lavas of phase A (Zabolottya series) were more ferriferous, but the increasing ratio Fe/Mg in pyroxene suggests about cooling of the magma chambers.

Fe a n d Fe-Ti o x i d e s are chiefly represented by magnetite and titanomagnetite. Ilmenite occurs locally. Mostly they fill interspaces between rock minerals and form thin inclusions in peripheral zones of pyroxene and plagioclase crystals. In some parts of the basalt flows and dolerites they occur as skeleton crystals, reaching 0.3 mm in size. The voids of skeletons are filled with later plagioclases and glass. These minerals usually reveal structures of disintegration and replacement.

V o l c a n i c g l a s s is the last solidified phase in basalts. It forms allotriomorphic blebs and fills interspaces between crystals of the magmatic minerals. In tuffs it occurs commonly as numerous lapilli and scoria, which are often replaced by smectite and other clay minerals. In general, volcanic glass in the Zhyrychi deposit is enriched in alumina and displays more acidic composition than basaltic melt. The amount and composition of volcanic glass depend both on temperature of melt crystallization and on velocity of cooling, which led to depletion of secondary melt in mafic components during crystallization of the above-described refractory minerals.

6.2. ***Secondary minerals.*** Both, the composition and ratio of the secondary parageneses differ laterally. The secondary minerals can be conventionally classified as pre-, syn- and post-ore in relation to the origin of the major copper ores. The succession of hydrothermally formed minerals is shown in Table 3. The below-noted homogenization temperatures of fluid inclu-

Table 1. **Contents (ppm) of elements in the ore bodies of the Zhyrychi deposit (Z), Rafalowka-Berestovets field (*RB*) and in the dolerites outside the ore fields (C) (ICP-MS and *ASA* analyses). The probes characterise disseminated ores and veinlets without nuggets**

sions have been measured in the transparent minerals from Rafalovka-Berestovets Cu field [2, 3] and are therefore only approximately related to the mineral-forming temperature of the Zhyrychi deposit.

6.2.1. *Pre-ore minerals.* C l i n o c h l o r e is widespread in basalts of the series *C* and *D*. Its green aggregates fill numerous amygdales and cracks often in association with later smectite. In amygdales it shows spherical microstructure (Fig. 3, *f*).

H e m a t i t e occurs as large nodules or rose-like aggregates in the uppermost parts of the basalt flows, or as numerous pseudomorphs after magnetite. Hematitization occurred along cracks and fissured zones, which are filled with large nodules of this mineral. Intensively hematitized basalts also occur among pyroclastic material in tuffs and as fine-rounded clasts in tuffites. Because of Fe-rich environment hematite was locally stable or metastable along with many later syn- and post-ore parageneses.

A l b i t e is commonly observed as a secondary mineral developed after magmatic plagioclase. It forms pseudomorphs and overgrows plagioclase crystals in basalts and tuffs. Albitization is accompanied by hematitization and dissolution of pyroxenes. Clasts of the albitized basalts with plentiful hematite inclusions are often observed in tuffs and tuffites. It is therefore considered that albitization and hematitization indicates the processes occurred during hydrothermal activity, supporting the volcanic ejections.

P u m p e l l y i t e fills rare amygdales as fine-crystalline light-green aggregates in the lowermost parts of the flows and close to the fissured zones in basalts, which were often albitized and hematitized during earlier hydrothermal processes. In this work pumpellyite was detected by X-Ray diffraction analyses (Fig. 5) at the first time both in the Zhyrychi deposit and in the whole Volhyn volcanic province.

6.2.2. *Syn-ore minerals.* P r e h n i t e was observed in fissured zones and amygdales as radial, grading into fibrous aggregates. Along fissures prehnite is commonly impregnating basalts and contains numerous relics of the both magmatic and pre-ore minerals. Its polycrystalline aggregates form pseudomorphs after plagioclase, pyroxene and olivine (?) (Fig. 3, *e;* 6). Prehnite overgrows and cuts the earlier amygdales of pumpellyite (Fig. 3, *g*). In tuffs prehnite locally fills interspaces.

Native copper occurs commonly as thin inclusions radially oriented along prehnite fibres (Fig. 3, *h*), suggesting about synchronous growth of these minerals. It also occurs as crystals in central parts of prehnite veinlets (Fig. 3, *i*).

L a u m o n t i t e occurs as hemispheres, which in the intensively leached tubulated amygdaloidal basalts were overgrown with prehnite (Fig. 3, *j*). Probably the hemi-

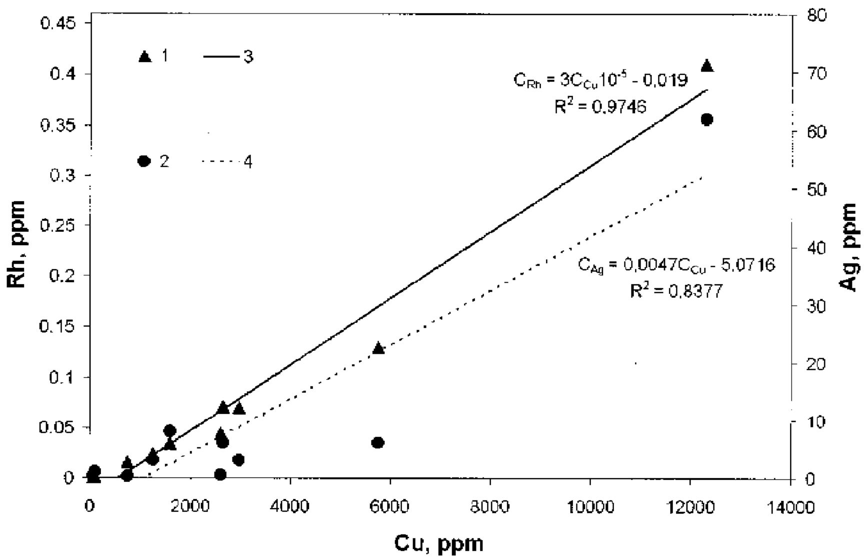


Fig. 4. Cu versus Ag and Rh in the ores of the Zhyrychi deposit: *1* — Cu-Rh; *2* — Cu-Ag; *3* — Cu-Rh (trend); *4* — Cu-Ag (trend)

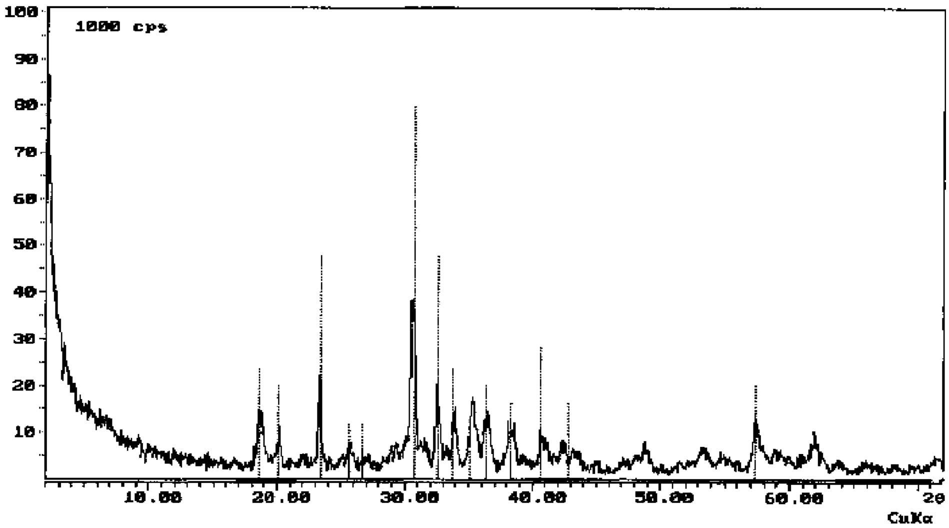


Fig. 5. X-Ray diffraction diagram of pumpellyite from the Zhyrychi deposit

spheres grew in isolated amygdales, but prehnite was developed during progressive leaching or fissuring of amygdaloidal basalts. Laumontite contains blebs of native copper, partially composing peripheral parts of hemispheres (Fig. 3, *j*) or occurring within hemispheres as concentric sectors, indicating the former hemisphere surfaces. Such position testifies to multiple redeposition of Cu in front of the growing laumontite.

W a i r a k i t e has been detected by X-Ray diffraction analyses in the Zhyrychi deposit by K. I. Derevska et al. (2002). It occurs as thin crystals and polycrystalline aggregates in tuffs and fissured basalts. Wairakite often closely associates with native Cu crystals and quartz

Table 2. **Microprobe analyses of augite (Ca, Na)(Mg, Fe, Al, Ti)(Si, Al)$_2$O$_6$ from tuffs of the Zhyrychi deposit (recalculated per 4 cations)**

Probe number	Fe	Cr	Ti	Ca	K	Si	Al	Mg	Na	Mn	Formulae
1–4	0.51	0.00	0.05	0.92	0.01	1.36	0.51	0.44	0.20	0.00	$Ca_{0.92}Na_{0.2}Mg_{0.44}Fe_{0.51}Ti_{0.05}Si_{1.36}Al_{0.51}O_{5.62}$
3–3	0.97	0.00	0.17	0.98	0.01	1.59	0.33	0.20	0.02	0.02	$Ca_{0.98}Na_{0.02}Mg_{0.2}Fe_{0.97}Ti_{0.17}Si_{1.59}Al_{0.33}O_{6.25}$

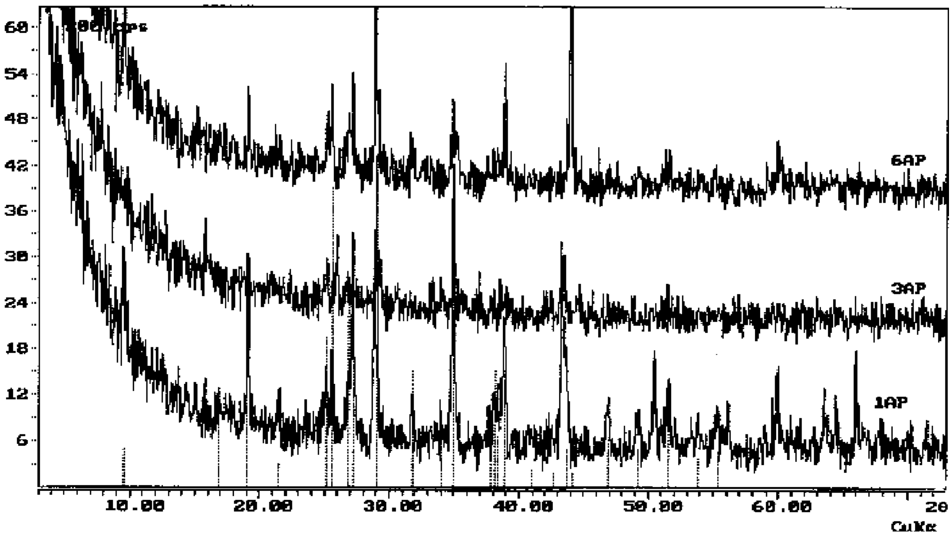


Fig. 6. X-Ray diffraction diagram of prehnite from the Zhyrychi deposit

druses. The fluid inclusions in wairakite have been homogenized at 210–335 °C [2].

6.2.3. *Post-ore minerals.* K-f e l d s p a r occurs in tuffs as thin crystals in the ore and barren zones. It is generally associated with plentiful mineralization of smectite and is apparently partially synchronous with it. In the lower tuffs K-feldspar forms intergrowths with native copper crystals (Fig. 7). The deficit of silica was detected in the both analysed crystals (Table 4).

Q u a r t z is observed chiefly in the upper floods *C* and *D*. It forms coarse-crystalline aggregates or druses in fissured zones, whereas chalcedony nests or nodules are widespread at the subsurface zones of the palaeohydrothermal systems. In general quartz crystals are

Table 3. **Scheme of the mineral succession in the ore bodies of the Zhyrychi deposit**

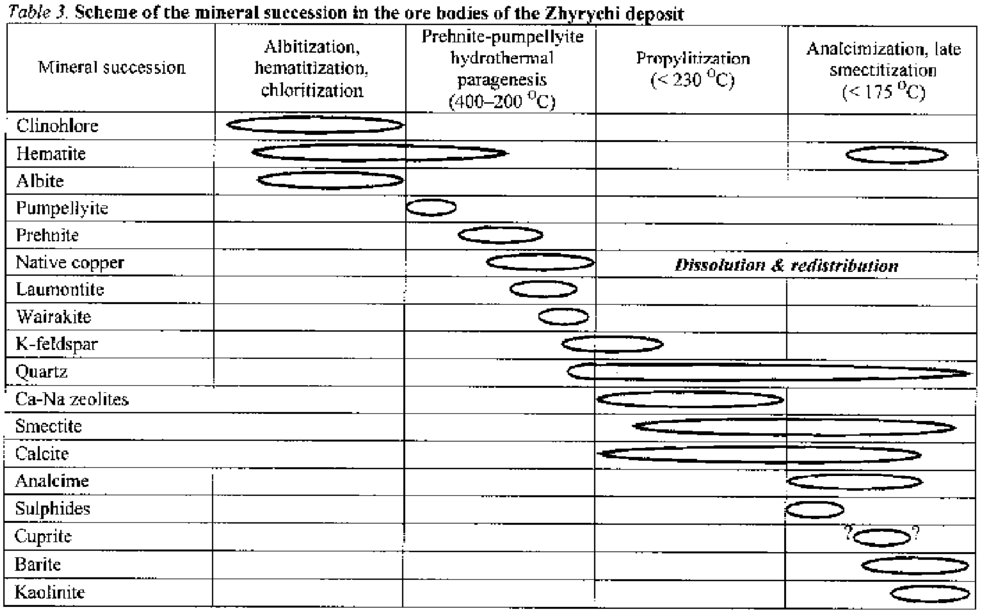


Table 4. **Microprobe analyses of K-feldspar from tuffs of the Zhyrychi deposit (recalculated per 5 cations)**

Probe number	Fe	Cr	Ti	Ca	K	Si	Al	Mg	Na	Formulae
1–3	0.02	0.00	0.00	0.00	0.97	2.81	1.17	0.00	0.03	$K_{0.97}Al_{1.17}Si_{2.81}O_{7.86}$
4–1	0.01	0.00	0.00	0.00	1.06	2.85	1.06	0.00	0.01	$K_{1.06}Al_{1.06}Si_{2.85}O_{7.78}$

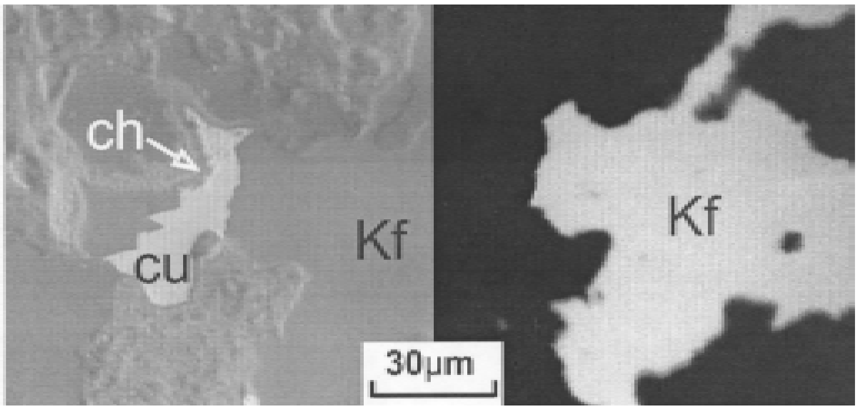


Fig. 7. Scattered electron image of the intergrowing crystals of native copper and K-feldspar (left), and K beam (Kα) image of K-feldspar (right); cu — native copper; Kf — K-feldspar

white or colourless, but locally ametistine quartz druses are also observed. Homogenization temperature of fluid inclusions in quartz varies from 100 to 310 °C [2, 3].

Native Cu is locally observed in quartz veins and nodules. Probably high-temperature quartz, occurring in association with wairakite was crystallized syngenetically with primary native copper.

Stilbite, mordenite, heulandite and thomsonite occur as pink or white hemispheres and fibrous spherical aggregates in amygdaloidal basalts. In general they locally cement tuffs as white and cream-coloured spherolitic and plumose aggregates. Zeolites often contain thin inclusions of native copper. These minerals are widespread in the basalt province, but their mineralization is scarce and probably indicates peripheral parts of the palaeohydrothermal systems.

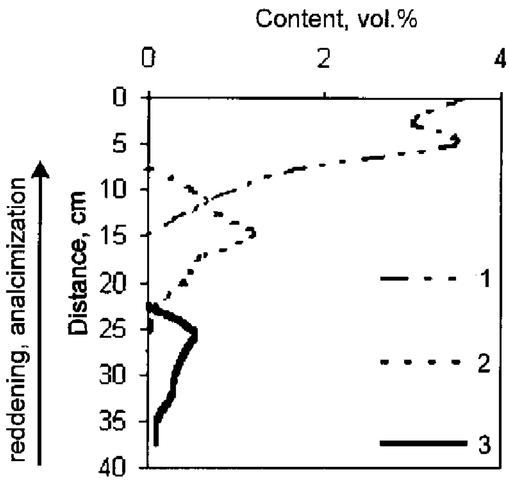
Smectite represents a group of clay minerals, which in different amount impregnate both basalts and pyroclastics. They are observed commonly in the ore basalts (Fig. 3, *k*), but are also abundant in barren zones. Smectite overgrows native copper (Fig. 3, *l*) and locally contains its relics (Fig. 3, *m*), which were preserved in smectite after it replaced pre- or syn-ore minerals. It suggests metastability of native copper during smectitization. X-Ray diffraction analyses mostly show trioctahedral modifications of smectite. Glycolation caused an increase of a basal spacing of smectite layers to approximately 1.7 nm. It is the most common in the ore-bearing lower tuffs. Locally smectite is associated with chlorites, replacing plagioclase (Fig. 3, *k*). According to microprobe analyses it is considered that smectite in the ore bodies represents different minerals, among which saponite, montmorillonite and beidellite dominate.

Calcite occurs in veinlets and amygdales as polycrystalline aggregates. Locally it impregnates tuffs and is associated with sulphide mineralization. Homogenization temperature of fluid inclusions in calcite ranges from 110 to 230 °C [2, 3].

Analcime is observed as polycrystalline aggregates or single crystals in tuffs, or fills numerous amygdales and fissures in basalts. Usually it is pink or white-coloured, but often impurities of smectite or hematite dye it in green or red colour respectively. In green tuffites analcime occurs scarcely, whereas in the red pyroclastics its pink polycrystalline aggregates are often plentiful. The amount of analcime distinctly increases in the red and reddened green tuffs.

Analcime was grown mostly in fissures (Fig. 3, *n*) or open spaces of leached both basalts and pyroclastic rocks. Consequently, the pseudomorphs of analcime after earlier minerals are relatively rare. For example, roundish radial aggregates of analcime after laumontite hemispheres (Fig. 3, *o*) are rarely observed in amygdales in the places of rich laumontite occurrences. Fluid inclusions in analcime were homogenized at 125–175 °C [2, 3].

Barite is one of the latest minerals in the deposit. Its colour varies from white and transparent to dark-brown. It occurs as lamellar or fine-crystalline aggregates, filling latest cracks, amygdales and central parts of veinlets in the basalt floods (Fig. 3, *n*). It often occurs



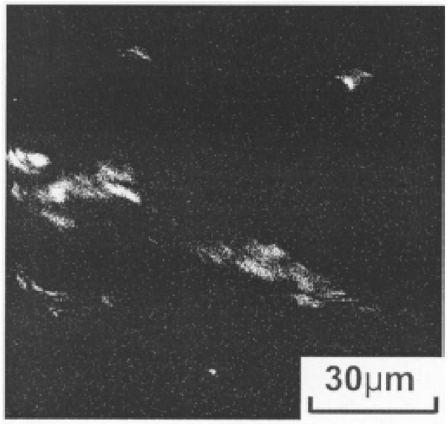


Fig. 8. Vertical profile of Cu mineral distribution in the reddened and analcimized green tuff of the Zhyrychi deposit: *1* — native Cu; *2* — chalcosite + digenite; *3* — chalcopyrite

Fig. 9. Scattered electron image of native iron microparticles (white) within native copper (black)

in mixture with younger smectite, kaolinite and (or) quartz.

K a o l i n i t e has been observed in a mixture with smectite and (or) barite along fissures and amygdales. In tuffs it occurs rarely although often dominates in cement of the underlying Early Vendian, and overlying Late Vendian and Cambrian terrigenous beds [4].

7. Ore mineral distributions

Native copper occurs mainly as disseminated both in basalts and tuffs, although veinlets, nuggets and wires are also common. Microprobe analyses did not show significant impurities of isomorphic metals.

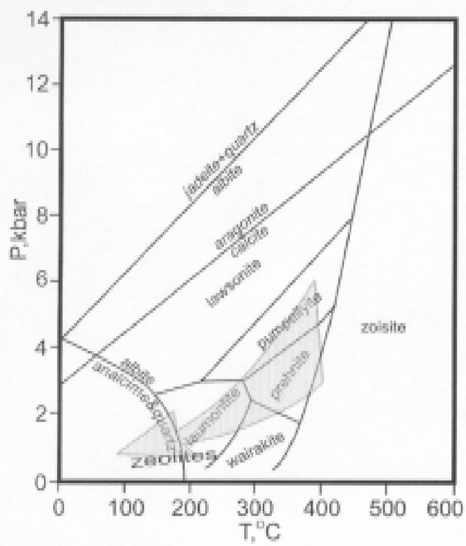
In the ore-bearing basalts numerous native copper inclusions fill abundant pores, where they replace pyroxene and clinochlore. In the bottom part of some Cu crystals chlorite relics were detected by microprobe (Fig. 7). It has also been found within smectite casing, probably formed by replacing olivine (?), pyroxene and plagioclase phenocrystals (Fig. 3, *p*). Scarcely native copper directly replaces magnetite and forms pseudomorphs after this mineral (Fig. 3, *q*). In fissured zones and lava-breccias it was often precipitated as dendrite-like particles (Fig. 3, *r*), wires, large crystals or nuggets. The richest mineralization of native copper in basalts is observed in fissured zones filled with prehnite, although nuggets and dendrites mostly occur in some veinlets, containing quartz or analcime, more often associated with smectite.

In the lower tuffs native copper is dispersed as thin inclusions (Fig. 3, *c*), which differ in position and size when contained in green and red tuffs.

In green tuffs native copper commonly replaces pyroclasts (Fig. 3, *s*) and fills open spaces (Fig. 3, *t*). Analcimization and secondary reddening resulted in disappearing of native copper, often with its converting into Cu sulphides, but mostly into chalcocite or digenite. Covellite and bornite occur rarely. Chalcopyrite replaces scarce chalcocite and digenite in peripheral parts of these alteration zones (Fig. 8). Sulphide minerals are locally widespread in tuffs and basalts as veinlets and disseminated, but generally they are scarce (Fig. 3, *u*).

In different places around green pyroclastic beds red tuffs contain coarse allotriomorphic blebs of native copper and nuggets, whereas fine native copper inclusions are absent. It argues that native copper mineralization in red tuffs was formed during selective recrystallization, i.e. the coarser blebs grew when the smaller were dissolved. These large blebs contain numerous micropores and microcrystals of hematite, which were entrapped within growing copper crystals and testify to oxidizing hydrothermal environ-

Fig. 10. PT diagram for numerous critical reactions of the minerals of prehnite-pumpellyite and related metamorphic mineral facies [16]. The arrow shows the evolution of the mineral-forming hydrothermal system in the Zhyrychi deposit



ment, which led to dissolution and redistribution of the primary copper mineralization.

Both in tuffs and in basalts native copper is locally replaced by cuprite, which typically forms thin rims around Cu blebs (Fig. 3, *v*) and scarcely occurs in barren zones.

Microscopic particles of native iron have been documented within native copper crystals (Fig. 9) grown in central parts of prehnite veinlets. Single inclusions of native iron were also locally observed in the ore-bearing and barren both tuffs and basalts. Apparently it was precipitated during magnetite dissolution, saturating the ore-forming environment in Fe.

Native silver mostly occurs in native copper as microparticles in peripheral zones of native copper blebs or within it in pores (Fig. 3, *w*). V. M. Kvasnytsa et al. [6] described particles of native silver in assemblage with analcime or in association with calcite. The described position of native silver in the ores suggests about its later origin at the end of native copper precipitation or during dissolution of the earlier copper ores. Obviously, native silver precipitation occurred when native copper was dissolved and redistributed in nuggets.

Minerals, concentrating Pd, Rh and Au have not been found. Possibly, Pd and Rh are isomorphically incorporate in native iron.

Alluvial native copper grains among fine-rolled grit and pebbles of basalts have been found in the Early Cretaceous sandstones, which cover the eroded Vendian volcanics in the Zhyrychi deposit. This ore-bearing horizon is considered to be potentially economic.

8. Origin of copper ores

The investigations presented in this study provide the range of key points, explaining both the processes leading to Cu ore formation in the Zhyrychi deposit and rendering possible to predict the distribution of Cu ores in the basalt province.

8.1. Time of ore deposition. Major native copper ores occur in the lower tuffs, which along faults are bordered against Late Riphean red beds, whereas in basalts it is often controlled by fissured zones and cracks, but are also documented as strata-bound in the lowermost and contrastingly most permeable beds of the flood basalts. Such ore localization testifies to upward migrating Cu-bearing hydrothermal fluids, which deposited Cu on geochemical barriers in the zones of permeability and redox contrast.

Prehnite veinlets and nodules containing syngenetic native Cu are distinctly cutting and replacing hematitized and albitized volcanic rocks, but hydrothermally altered rocks are absent in the sedimentary beds, covering the Vendian volcanics. In the ore bodies there are no mineralogical evidences of a polygenic origin of the major ores. These observations suggest that the hydrothermal solutions furnished Cu apparently at the end of the Vendian volcanic activity. Consequently, pumpellyite, syn- and post-ore minerals were probably deposited successively (Table 3) during progressive attenuation of the Late Vendian hydrothermal activity.

8.2. *Cu-bearing parageneses.* The mineralogical evidences indicate that first Cu was deposited simultaneously with prehnite and laumontite in basalts and tuffs. These minerals are closely associated with other minerals related with Ca metasomatism (pumpellyite and wairakite). Such a mineral association is widely spread in the modern hydrothermal systems within some recently active volcanic regions (Island, Japan, Kamchatka, New Zealand etc.) [11]. In general, this paragenesis is similar to those determined as prehnite-pumpellyite metamorphic facies [16], but having the hydrothermal origin. In the Zhyrychi deposit the minerals of Cu-bearing prehnite-pumpellyite paragenesis were generally precipitated in the sequence: pumpellyite — prehnite (± native copper) — laumontite (or wairakite) (± native copper), although tectonic movements and instability of hydrothermal system promoted periodical intensifications of the palaeohydrothermal activity, leading to the growing laumontite over prehnite (Fig. 3, *j*).

Cu redistribution and growth of nuggets are connected with the later hydrothermal processes, which provided regional propylitization (K-feldspar-smectite-calcite-zeolite paragenesis), later smectitization with analcimization (analcime-smectite paragenesis) and formation of quartz bodies. Concordantly with homogenization temperature of fluid inclusions in analcime, quartz and calcite [2, 3], these processes took place at lower temperatures, than those characteristed the stability of the prehnite-pumpellyite paragenesis.

8.3. *Ore-forming conditions.* *PT* diagram of stability fields of Ca aluminosilicates (Fig. 10) suggests reducing both pressure and temperature during mineral precipitation in the succession found in the Zhyrychi deposit: pumpellyite — prehnite — laumontite — wairakite — analcime + quartz. The stability field of prehnite indicates approximately the temperature and pressure of the first precipitation of native copper in the deposit at 300–400 °C and 1.7–4.5 kbar respectively.

Wairakite originates at lower pressure than prehnite and at lower temperature and pressure than laumontite (Fig. 10). Consequently, its association with high-temperature quartz druses apparently indicates zones of discharge heads. Analcime displaced Ca minerals with cooling of the system at 100–175 °C (according with the homogenization temperature of fluid inclusions in analcime). Sulphide mineralization is apparently connected with cooling and oxidation of the ascending hydrothermal solutions.

The temperatures of the hydrothermal fluids, precipitating Ca aluminosilicates in the modern hydrothermal systems not exceed 170–400 °C [11]. According with the homogenization temperature of fluid inclusions in wairakite [2], the temperature of the Cu-forming palaeohydrothermal system in the Rafalovka-Berestovets copper field was not less 210–335 °C. These temperatures good confirm the above-described diagram (Fig. 10). In the Zhyrychi deposit wairakite was apparently formed at similar temperatures.

8.4. *Possible* Cu *source.* Following the experimental data by [14], Cu solubility in silicate melts increases with heating from 1300 to 1514 °C and (or) oxidation (acidulation) of the melts.

The volcanic phase *C* in the Volhyn volcanic plateau produced thick flows of lava of more acidic composition, than basalt lavas of the phases *A*, *B* and *D*. This acidulation of the magma was interpreted by [12] as due to crust melting at the end of the Vendian rifting. Thus, the cooling of the acidulated magma chambers could lead to losing of Cu with evolving hot fluids.

9. Conclusions

1. The Zhyrychi deposit is the Michigan-type native copper deposit. Except Cu the ores also contain increased concentrations of Ag, Pd, Rh and Au.

2. The major ores occur within strata-bound bodies in the flood basalts and in the lower tuffs. The ore deposition was probably controlled by faults and zones of permeability and redox contrast. The ore minerals are represented by native copper, occurring in disseminated form, veinlets and nuggets. The major ore horizon is located in the lower tuffs.

3. Cu ores were deposited during ancient hydrothermal activity at the end of Vendian volcanism under P-T conditions of prehnite-pumpellyite paragenesis, consisting of the sequentially formed Ca aluminosilicates: pumpellyite — prehnite — laumontite (wairakite) at temperature 400–200 °C.

4. The post-ore mineralization originated during zeolitization, smectitization and analcimization, leading to Cu ore redistribution, which resulted in local enrichment of all ore

bodies in nuggets, but generally led to Cu ore destruction.

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Inst. of Geochemistry, Mineralogy and Ore Formation
of Nat. Acad. of Sci. of Ukraine, Kyiv
State Reg. Geol. Enterprise (SRGE) "Pivnichgeologiya", Kyiv

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РЕЗЮМЕ. Вивчено мінеральний склад рудних тіл родовища міді Жиричі, відкритого наприкінці XX ст. і розташованого у вендських вулканогенних нашаруваннях центральної частини Волинської трапової провінції. Мідь переважно концентрується в самородній формі у вигляді розсіяної вкрапленості, прожилків та самородків, її локально заміщують самородне срібло, сульфіди міді (халькозин, дігеніт, борніт та ковелін) і куприт. Руди формують стратиформні тіла, подекуди збагачені в зонах тріщинуватості. За результатами атомно-адсорбційного та *ICP-MS* аналізів, економічно важливими при розробці родовища можуть бути також Ag, Pd, Rh та Au. Мідь осаджувалась у складі преніт-пумпелеїтового парагенезису, що розвивався у такій послідовності: пумпелеїт — преніт (± самородна мідь) — ломонтит (чи вайракіт) (± самородна мідь). Рудні тіла формувалися впродовж охолодження гідротермальної системи наприкінці вендської вулканічної діяльності. Сингенетичні зростки самородної міді з пренітом та літературні дані про заміри флюїдних включень у вайракіті (210–335 °С) свідчать, що основна стадія рудоутворення відбулась за температури 200–400 °С. Подальша пропілитизація, смектитизація та анальцимізація вмісних порід, можливо, відбулись впродовж затухання гідротермальної діяльності після завершення вулканізму і супроводжувалися розчиненням та перерозподілом мідних руд з локальним збагаченням рудних тіл.

РЕЗЮМЕ. Изучен минеральный состав рудных тел месторождения меди Жиричи, открытого в конце XX в. и расположенного в вендских вулканогенных наслоениях центральной части Волынской трапповой провинции. Медь преимущественно концентрируется в самородной форме в виде рассеянной вкрапленности, прожилков и самородков, ее локально замещают самородное серебро, сульфиды меди (халькозин, дигенит, борнит, ковеллин) и куприт. Руды формируют стратиформные тела, иногда обогащенные в зонах трещиноватости. По результатам атомно-адсорбционного и *ICP-MS* анализов, при разработке месторождения экономически важными могут быть также Ag, Pd, Rh и Au. Медь осаждалась в составе пренит-пумпеллеитового парагенезиса, который развивался в такой последовательности: пумпеллеит — пренит (± самородная медь) — ломонтит (или вайракит) (± самородная медь). Рудные тела формировались в процессе охлаждения гидротермальной системы в конце вендской вулканической деятельности. Сингенетические сростки самородной меди с пренитом и литературные данные о замере флюидных включений в вайраките (210–335 °С) свидетельствуют, что основная стадия рудообразования состоялась при температуре 200–400 °С. Более поздние пропилитизация, смектитизация и анальцимизация вмещающих пород, возможно, произошли в процессе затухания гидротермальной деятельности после завершения вулканизма и сопровождались растворением и перераспределением медных руд с локальным обогащением рудных тел.