

## GEOLOGY, MINERALOGY AND ORIGIN OF THE ZHYRYCHI NATIVE COPPER DEPOSIT (NORTH-WESTERN UKRAINE)

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**Abstract:** The paper presents geological settings, resources and mineral composition of the ore bodies of the Zhyrychi copper 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 trapean province, originated in the Late Vendian during Tornquist rifting. The majority of copper is concentrated in native form and occurs as disseminated grains, veinlets and nuggets. Locally native silver, copper-sulphides (chalcocite, digenite, bornite and covellite) and cuprite replace native copper. The ore bodies are controlled by faulting and occur as stratabound, but are locally enriched in nuggets in tuffs and fissured zones in basalts. Ag, Pd, Rh and Au can also be economically important. The major copper 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) indicate that the major deposition 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 copper ore and its redistribution with local enrichment in copper nuggets.

**Key words:** native copper, deposit, Ukraine, basalt, tuff, prehnite-pumpellyite paragenesis, ore genesis.

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### INTRODUCTION

Native copper occurrences are common in many basalt provinces, but the high-quality economic native copper ores are rare. An 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 Copper district (Keweenaw Peninsula) occur within the Mid Proterozoic basalt flows and intraflow conglomerates, filling the 1.1 Ga old North American Midcontinent rift system (Sims, 1976; Grant *et al.*, 1988). Some similar native copper deposits are well known in volcanic rocks of Canada and USA (Wilton, Sinclair, 1988; Kirkham, 1996), Chile (Ruiz *et al.*, 1971), China (Zhu & Zhang, 2003), Russia (Tunguska Syncline; D'ujkov *et al.*, 1977) etc.

All these deposits contain mineral associations of the so-called prehnite-pumpellyite facies of metamorphism (Phillipotts, 1976), 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 (Bird *et al.*, 1984). However, distinct association of native copper with gangue minerals is still unclear. Based on mineralogical mapping, Stoiber and Davidson (1959 a, b) displayed that native copper deposits in the Michigan volcanics are often located near the boundaries of the zones enriched in quartz, but also occur in the places where quartz is not abundant.

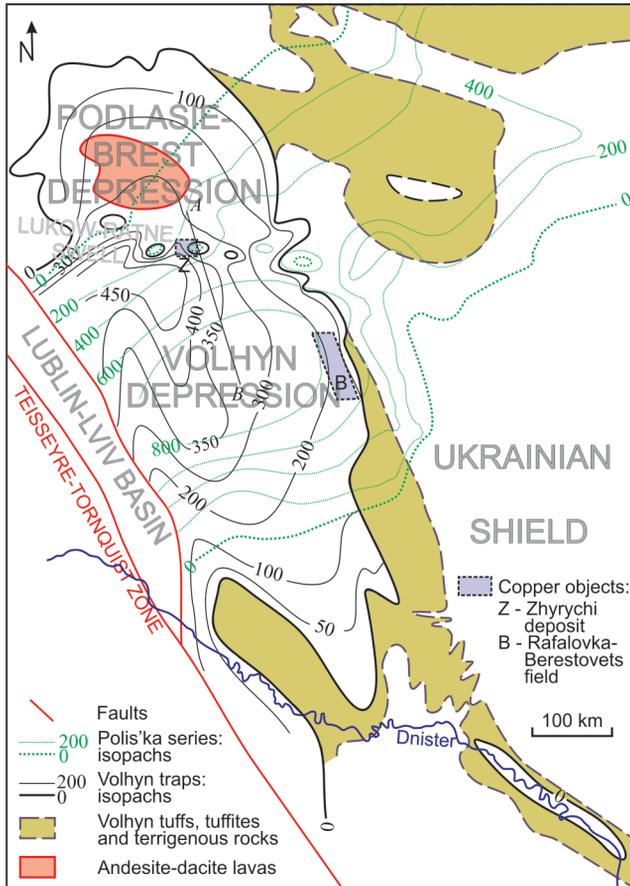


Fig. 1. Sketch map of the Western Ukraine (after Emetz *et al.*, 2004)

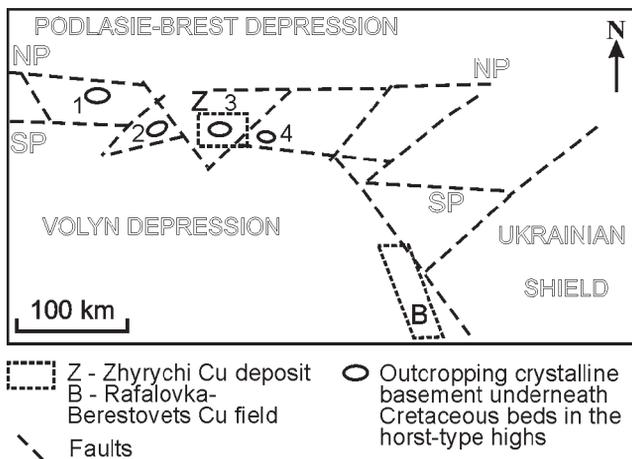


Fig. 2. Sketch of the tectonic positions of the Zhyrychi Cu deposit (Z) and Rafalovka-Berestovets Cu field (B). Fault zones: SP-SP – South-Prypyat; NP-NP – North-Prypyat. Horst-type highs of the Łuków-Ratne swell: 1 – Wishnice; 2 – Hoteshov, 3 – Ratne, 4 – Hotyslav

Economic copper was prospected in Western Ukraine since 1929 when Małkowski (1929) 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), but the first written information about Volhynian basalts was provided in 1862

and 1867 by Tyszecki and Blumel respectively (Wojciechowski 1971). The mineralogical studies of the Volhynian Cu-bearing basalts were carried out by Kamiński (1929), Małkowski (1931, 1933, 1939), Bohdanowicz (1932), Krajewski (1935). The mineralogical study on hydrothermal alterations in basalts was carried out by Szaszkina (1958). In this publication laumontite, natrolite, thomsonite, heulandite and ptylolite were described, but the first record about ptylolite was given by Małkowski (1933). The most extensive review of the mineralogical studies about the Volhynian Cu-bearing basalts was carried out by Lazarenko *et al.* (1960). The last mineralogical and geochemical studies on hydrothermal alterations in the ore volcanics can be found in the papers of Derevska *et al.* (2001, 2002), Emetz and Lugova (2006).

The discovery of the Zhyrychi copper deposit in the volcanogenic rocks of the Volhyn Province of the North-Western Ukraine (Pryhodko *et al.*, 1993) is the first success of the Ukrainian Geological Survey in ore prospecting and fixes new Volhyn Copper Province. In the present work, we provide new data on geological setting, resources and mineralogy of the Zhyrychi deposit and the interpretation of the ore-forming processes.

## METHODS

The core descriptions and sampling have been performed in the core storage of the Kovel Branch of the Ukrainian Geological Survey, providing prospecting works 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 the AGH University of Science and Technology (Krakow, Poland). Geological map and cross section of the deposit were compiled based on bore holes, seismic survey, gravimetric and magnetometry data.

Atomic absorption analyses (AAS) and inductively coupled plasma mass spectrometry (ICP-MS) analyses of the samples have been carried out in the laboratories of AGH.

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 AGH using ARL SEMQ microprobe (voltage 20 kV, probe current 120 mA, sample current 10 nA and counting time 20 s).  $K\alpha$  lines were used to detect Fe, Cr, Ti, Ca, K, Si, Al, Mg, Na, Mn, Cu, Ni, Co, Fe, Cr and S;  $L\alpha$  – Ag and Pd;  $M\alpha$  – Au and Pt.

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

## TECTONIC SETTING

The Zhyrychi copper deposit is situated in the western part of the Ratne High (Figs 2, 3), one of the horst-type

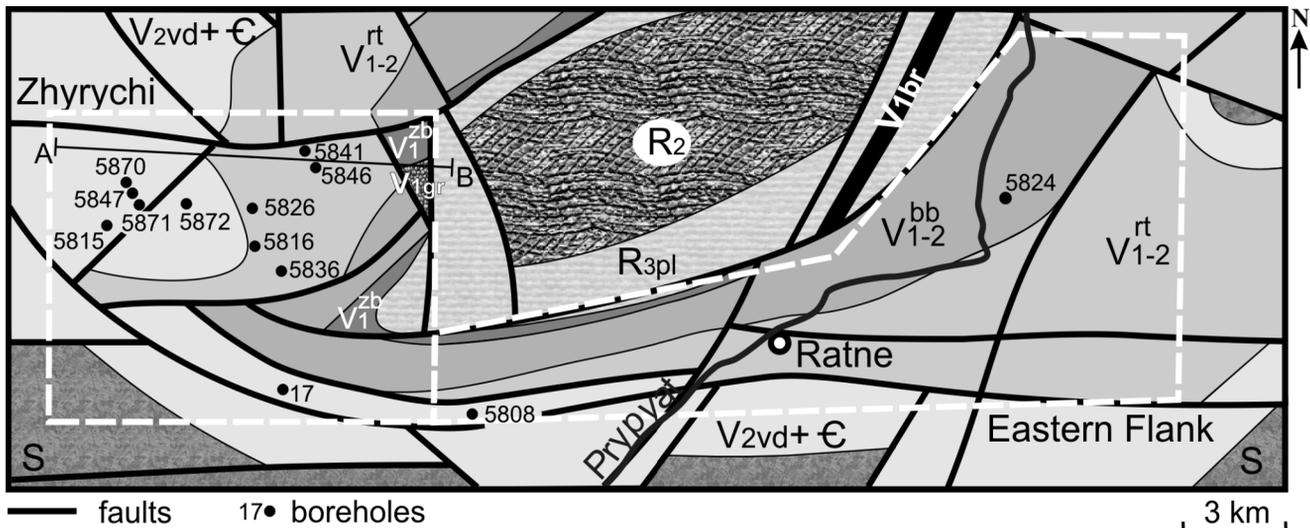


Fig. 3. Sketch geological map of the Zhyrychi deposit without Cainozoic cover (see Fig. 5 for symbol explanation)

highs of the Łuków-Ratne swell. The swell strikes 350 km E – W in the East-European Craton from the Ukrainian Shield to the Slavatytsky High in Poland (Semenenko (ed.), 1968) (Fig. 2). These tectonic phenomena probably took place at the end of Vendian and were developed as residual blocks during the Late Devonian when the region plunged after Hercynian regional uplift (Emetz *et al.*, 2004).

Western and eastern borders of the Ratne High were formed by the adjoining faults, which were also responsible for its separation from the neighbouring Hoteshev and Hotyslav highs respectively (Fig. 2). In the south, the Precambrian beds were shifted down about 650 m along the South-Prypyat faults bounding the Ratne High on the Volhyn depression. In the north, the sedimentary beds were segmented by some stepwise low-amplitude faults of the North-Prypyat fault zone and dipping 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, attaining in amplitude about 200 m (Figs 3, 4).

## STRATIGRAPHY

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 (Semenenko (ed.), 1968; Velikanov & Korenchuk, 1997). These rocks are bordered by the boundary faults against the eroded Late Riphean or Vendian beds.

The 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 (Fig. 5). These deposits were eroded from the Middle Devonian to Early Cretaceous, down up to the Early Proterozoic metamorphic rocks. The Late Cretaceous chalk and marly beds, 120 m to

180 m thick, cover the eroded surface. The Quaternary clayey and sandy sediments, varying in thickness from 20 m to 80 m, unconformably cover this unit.

Late Riphean strata (Polis'ka suite), 400–500 m thick, unconformably cover the metamorphic complex as red continental sandstones and siltstones with clayey interbeds. The strata comprise four successive sedimentary cycles (Garetsky (ed.), 1981), which filled the Mid-Baltica rifting system during the Late Riphean (Emetz *et al.*, 2004). These strata contain the Vendian dolerite dikes and sills, which sinter the country rocks in the contact zones and in some places are intensively hydrothermally altered.

The Volhyn Series includes Gorbashi and Berestovets suites.

The Gorbashi suite consists of brown arkose gravel and sandstone beds which conformably overlap 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 suite is composed of the trappean formations originated within Vendian rifting, which opened the Tornquist Ocean between Baltica and probably Amazonia ancient continents at the end of Vendian (Bingen *et al.*, 1998). These beds strike concordantly with the present-day Teisseyre-Tornquist margin (Emetz *et al.*, 2004).

The Berestovets suite has been subdivided into Zabolotta or lower basalt beds, Babino or predominantly tuff beds, and Ratne or upper mainly basalt beds (Biryulev, 1967). These subdivisions are recently in use for mapping in the Ukrainian Geological Survey. However, they do not display the correct structure of the trappean province or development of the volcanic province and can not be quite simply used to correlate the strata-bound ore bodies.

Emetz *et al.* (2004) have documented that the Vendian volcanic province developed during four successive volcanic cycles, which produced regional lava ejections in this region. As follows from that paper, the trappean province comprises seven subdivisions: flood basalts A, B, C and D, and lower, middle and upper tuffs. All have been found by boreholes in the Zhyrychi deposit (Figs 4, 5).

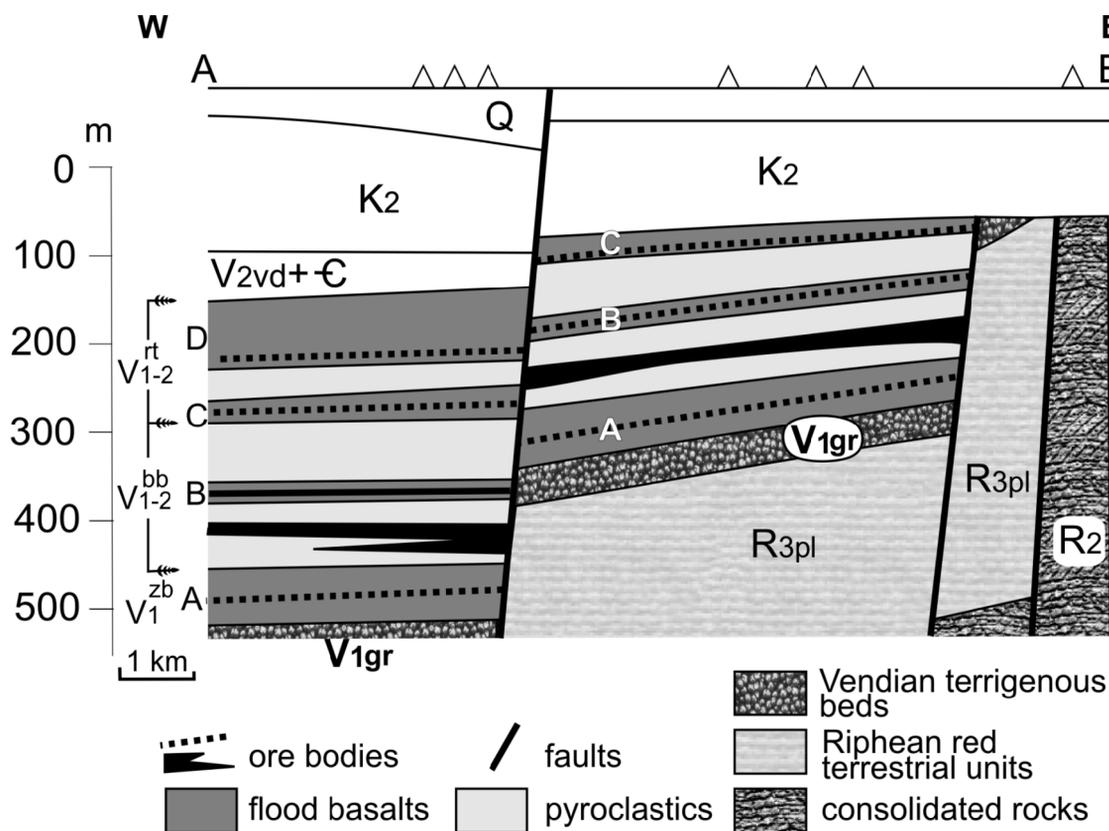


Fig. 4. Geological section of the Zhyrychi deposit. A, B, C, D – lava floods (see Fig. 5 for symbol explanation)

The flood A, 60–70 m thick, is represented by green-grey flows of massive and amygdaloidal basalts and dolerite-basalts. In different places of the deposit, the flood A comprises from 1 to 3 tuff intercalations, up to 3 m thick. The tuffs are red or brown-red in colour, fine- to coarse-grained.

The lower tuffs, overlaying the flood A, consist of a 50–80 m thick unit of thin-bedded red and brown-red tuffites and tuffs. Two or three interbeds of green tuffites, varying in thickness from 0.4 m to 3 m, have been found within the strata. The pyroclastics are thin-bedded and differently grained from psammitic to psephitic. Fine-rounded pebbles, consisting of both the basalts and tuffs, often occur within the coarse-grained tuffites.

The flood B is represented by flows of black, green-grey and dark-grey massive basalts. The flood contains interlayers of hydrothermally altered pink-grey and greenish basalts. The thickness of the flood B varies from 25 m to 30 m (Fig. 4). Locally, a tuff layer, up to 0.4 m thick, divides the flood. The intraflow tuffs are fine-grained and brown coloured.

The middle tuffs overlain flood B as a 55–65 m thick package of interbedded dark-brown and red-brown tuffs and tuffites. Commonly, these tuffs have greenish tint because of dispersed powder-like smectite.

The flood C, 35–40 m thick, contains flows of black massive basalts, grading upwards into amygdaloidal varieties. Both in the bottom and in the top the flood includes lava-breccia flows, consisting of lava clasts cemented with hydrothermally altered glass (Fig. 14a). The top lava-

breccia flow ranges from 4 m to 10 m in thickness, but laterally grades into massive fissured basalts which contain rare chlorite, smectite and zeolite amygdaloids. The maximum thickness of the bottom lava-breccias is only 1 m. It often pinches out.

The upper tuffs, 24–45 m thick, are represented by thin-bedded, dark-grey and brown tuffites and tuffs. The pyroclastics are differently grained and often include layers enriched in fine-rounded pebbles of both basalts and tuffs. The thickness of the upper tuffs increases from 24 m in the northern flank of the Zhyrychi deposit to 45 m in its southern part.

The flood D is composed of 2 to 3 major basalt flows. Each flow ranges in thickness from 10 to 25 m. They are separated by intercalations of lava-breccias, tuffs, tuffites, conglomerates and thin basalt flows. Their thickness does not exceed 5 m. The uppermost part of the flood is intensively altered by erosion processes. The total thickness of this flood ranges from 80 to 130 m, but along the border faults it is stepwisely decreased towards the central horst, around which this flood and upper tuffs were completely eroded (Figs 3, 4).

## OUTLINE OF BASALT PETROLOGY

In compliance with Białowolska *et al.* (2002), Korenchuk (1997), the lavas of volcanic phases A and B grade from alkaline to subalkaline basalts. The basalts of the

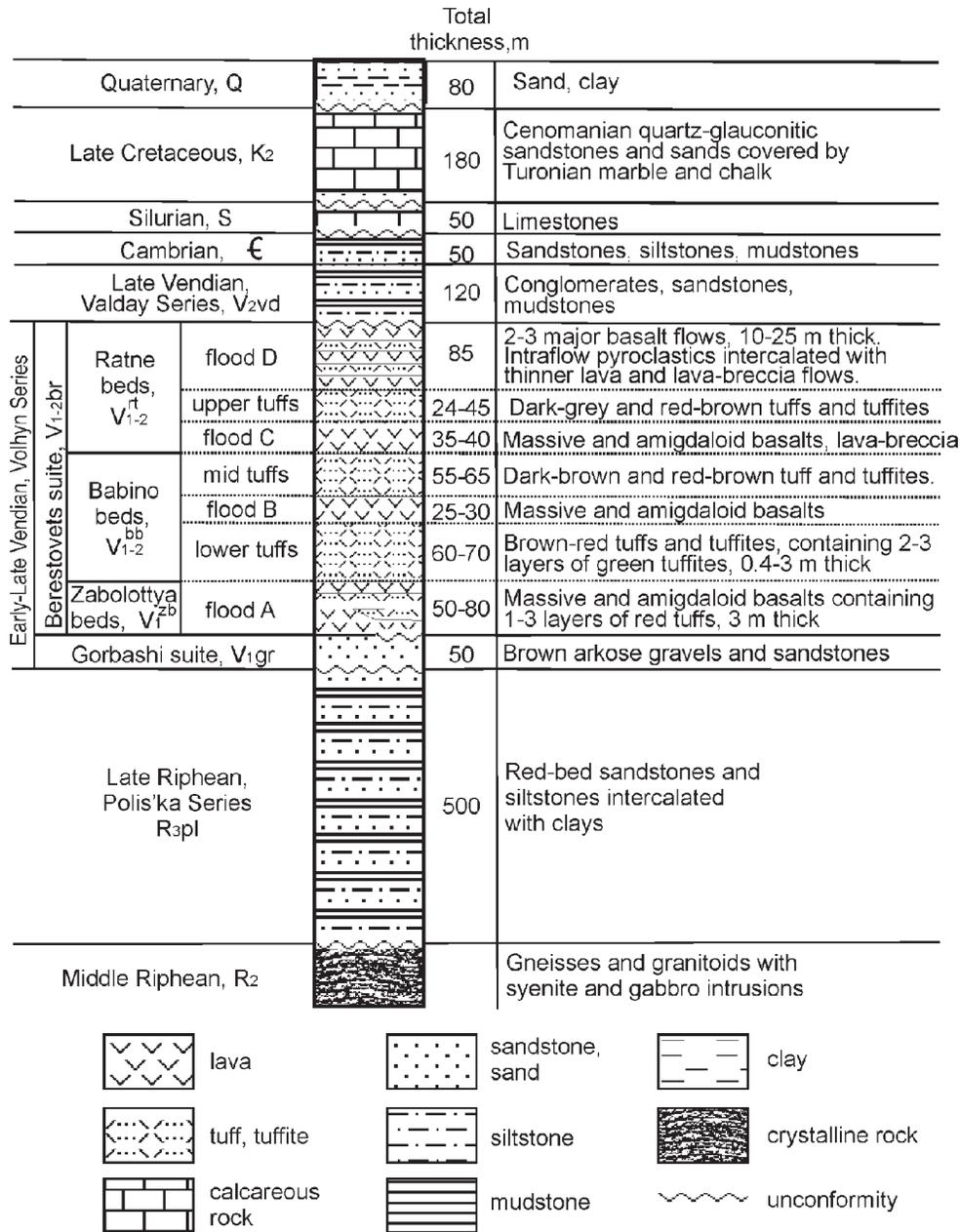


Fig. 5. Stratigraphic column of the Zhyrychi deposit

phases C and D are subalkaline and contain flows of tholeiite basalts, andesite-basalts, trachy-andesites, andesites and andesite-dacites (Korenchuk, 1997).

According to the trend of figurative points of basalts in the diagram Zr/TiO<sub>2</sub> – SiO<sub>2</sub> (Bakun-Czubarow *et al.*, 2002), the volcanism in the studied zone of the trappean province graded from basaltic alkaline through subalkaline (phases A and B) to subalkaline closely to andesitic (phases C and D) (Fig. 6). This trend probably reflects the influence of crust melting which occurred at the last stage of the Vendian volcanic activity (Emetz *et al.*, 2004).

The major minerals of these basalts are plagioclase (50–60%), monoclinic pyroxene (predominantly augite) (30–40%) and magnetite (or titanomagnetite) (5–10%). Many specimens from the lowermost and middle 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 beds. They consist of well-rounded clasts of basalts and tuffs (Fig. 14b). Both red and green tuffites comprise sequences of cross-bedded layers, formed in intermediate and littoral facies. Clasts of andesites are rarely observed among pyroclastics. Tuffs consist predominantly of different proportions 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 com-

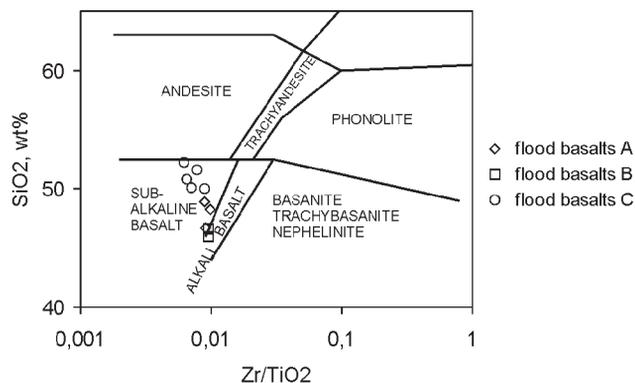


Fig. 6. Basalts of the Volhyn series of the Zhyrychi deposit and Rafalovka-Berestovets field on the  $\text{SiO}_2 - \text{Zr/TiO}_2$  diagram (Winchester, Floyd, 1977)

position of pyroclastic rocks because of polygenic secondary alterations. Propylitization, hematization and albitization are the most widespread among the alteration processes. Ca metasomatism is common, however it was structurally controlled by fault zones and therefore developed locally.

Among magmatic rocks, the most altered are coarse-crystalline dolerite-basalts. In many places pyroxene, olivine and magnetite were replaced by secondary minerals. The latter minerals are impregnating 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 various 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 relatively soft and brittle.

## ORE BODIES AND COPPER RESOURCES

The major ores in the Zhyrychi deposit and in the new area locating in the eastern part of the Ratne Horst (so-called Eastern flank) have been found in the flood basalts A, B, C and D, and in the lower tuffs (Fig. 4). The ores form five strata-bound bodies, which are enriched in nuggets and veinlets in fissured zones.

The data of AAS 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 copper field (Fig. 1) characterize the ores without nuggets. The nuggets were analysed separately because they cause an increase of true contents of Cu and probably of Ag and Rh, which are directly correlated with Cu (Fig. 7):  $C_{\text{Ag}} = 0,0047C_{\text{Cu}} - 5,0716$ ,  $R^2 = 0,8377$ ;  $C_{\text{Rh}} = 3 \cdot 10^{-5}C_{\text{Cu}} - 0,019$ ,  $R^2 = 0,9746$  (where C is the content of metal in ppm, and  $R^2$  – the Pearson coefficient).

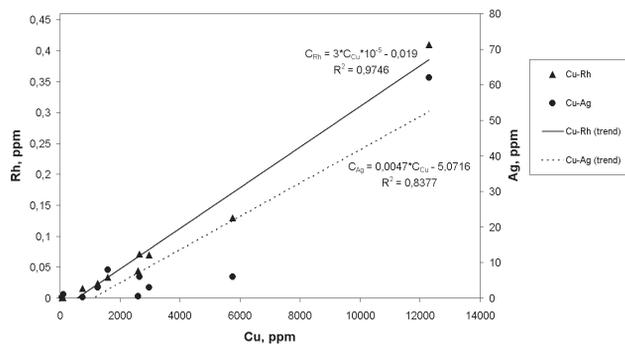


Fig. 7. Cu versus Ag and Rh in the ores of the Zhyrychi deposit

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).

The thickness of the ore bodies in basalts varies from 0.3 cm to 2.5 m, and Cu content from 0.3 to 12 wt% at an average values 1.5 m and 1.6 wt%, respectively. Copper minerals occur as disseminations, veinlets and filling of amygdales. Cu nuggets occur locally along some fissured zones. The most important ore bodies occur in altered dolerite-basalts, amygdaloidal basalts and lava-breccias (Fig. 14a).

In the lower tuffs, the plentiful disseminated native copper mostly occurs in green interlayers, but in some places it has been found in the red tuffs (Fig. 14c). The thickness of ore bodies and the intensity of mineralization are probably controlled by stepwise faults, bordering the lower tuffs against the Late Riphean red beds (Fig. 4). Abundant mineralization of native copper in the strata-bound bodies grades into scarce at the distance from 1 to 15 m, where the Cu content varies from 0.2 to 5 wt%.

In total, the Zhyrychi deposit contains 15.6 Mt of copper and is covering the area 120 km<sup>2</sup> whereby the average Cu content is ranging between 0.6 and 2.5 wt%. The resources of the Eastern flank (Fig. 3) have been estimated at 25 Mt on the area 180 km<sup>2</sup>. The major ore body is located in the lower tuffs and contains 8 Mt and 12.2 Mt of metallic Cu in the Zhyrychi deposit and in the Eastern flank respectively.

According to the above-noted equations of the correlations Ag-Cu and Rh-Cu, the total resources of Ag and Rh in the studied area are estimated at approximately 0.19 Mt and 406 t respectively. 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 form of these last two metals are still not determined.

## MINERALOGY OF ORE BODIES

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



Table 2

Microprobe analyses of augite  $(Ca.Na)(Mg.Fe.Al.Ti)(Si.Al)_2O_6$  from tuffs of the Zhyrychi deposit

No	Fe	Cr	Ti	Ca	K	Si	Al	Mg	Na	Mn	O	Sum
wt. %												
1-4	12.62	0.04	1.08	16.33	0.16	16.82	6.06	4.73	2.01	0.00	40.16	100.00
3-3	14.17	0.07	2.65	15.79	0.20	25.52	5.30	3.21	0.31	0.32	32.45	100.00
Formula units per 6 oxygen atoms												
1-4	0.54	0.00	0.05	0.97	0.01	1.43	0.54	0.46	0.21	0.00		
3-3	0.75	0.00	0.14	0.84	0.01	1.35	0.28	0.17	0.02	0.02		

the interspaces between crystals of 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 basalts. The amount and composition of volcanic glass depend both on temperature of melt crystallization and on the velocity of cooling, which led to the depletion of secondary melt in mafic components during the crystallization of the above-described refractory minerals.

### 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 the table 3. The below-noted homogenization temperatures of fluid inclusions have been measured in the transparent minerals from Rafalovka-Berestovets Cu field (Derevska *et al.*, 2001, 2002) and are therefore only approximately related to the mineral-forming solutions of the Zhyrychi deposit.

### Pre-ore minerals

Clinocllore is widespread in basalts of the floods C and D. Its green aggregates fill numerous amygdales and cracks often in association with later smectite. In amygdales it shows spherical microstructure (Fig. 14f).

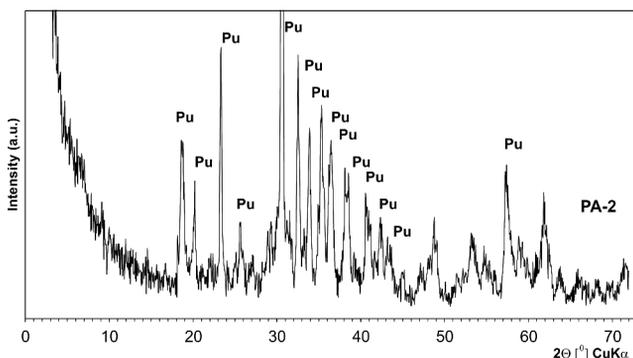


Fig. 8. X-Ray diffraction pattern of pumpellyite from the Zhyrychi deposit

*Hematite* 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.

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

*Pumpellyite* fills rare amygdales as fine-crystalline light-green aggregates in the lowermost parts of flows and close to the fissured zones in basalts which were often albitized and hematitized during earlier hydrothermal processes. Pumpellyite was detected by X-Ray diffraction analyses (Fig. 8) for the first time both in the Zhyrychi deposit and in the whole Volhyn volcanic province.

### Syn-ore minerals

Prehnite 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 (Figs 10, 14e). Prehnite overgrows and cuts the earlier amygdales of pumpellyite (Fig. 14g). In tuffs, prehnite locally fills the interspaces.

Native copper occurs commonly as thin inclusions radially oriented along prehnite fibres (Fig. 14h), suggesting synchronous growth of these minerals. It occurs as crystals or microcrystals in central parts of prehnite veinlets. The latter form (Fig. 14i) argues for copper precipitation under conditions of instability of prehnite.

*Laumontite* occurs as hemispheres which in the intensively leached tubulated amygdaloidal basalts were overgrown with prehnite (Fig. 14j). Probably the hemispheres

Table 3

Scheme of the mineral succession in the ore bodies of the Zhyrychi deposit (temperature ranges are based on the fluid inclusion studies (Derevska et al., 2001, 2002) and experimental data about mineral stability (Liou, 1970, 1971; Phillipotts, 1976))

Mineral succession	Albitization, hematitization, chloritization	Prehnite-pumpellyite hydrothermal paragenesis (400-200°C)	Propylitization (<~230°C)	Analcimization, late smectitization (<~175°C)
Clinocllore	○			
Hematite	○	○		○
Albite	○			
Pumpellyite		○		
Prehnite		○		
Native copper		○	<i>dissolution &amp; redistribution</i>	
Laumontite		○		
Wairakite		○		
K-feldspar		○		
Quartz		○	○	○
Ca-Na zeolites			○	○
Smectite			○	○
Calcite			○	○
Analcime				○
Sulphides				○
Cuprite				○
Barite				○
Kaolinite				○

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. 14j) 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.

*Wairakite* has been detected by X-Ray diffraction analyses in the Zhyrychi deposit by Derevska *et al.* (2002). It occurs as thin crystals and polycrystalline aggregates in tuffs and fissured basalts. Wairakite is often closely associated with native copper crystals and quartz druses. The fluid inclusions in wairakite have been homogenized at 210–335°C (Derevska *et al.*, 2002).

*K-feldspar* occurs in tuffs as thin crystals in the ore horizon 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. 9). The deficiency of silica was detected in both the analysed crystals (Table 4).

**Post-ore minerals**

Quartz occurs predominantly 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 white or colourless, but locally amethyst druses are also observed. Homogenization temperature of fluid inclusions in quartz varies from 100 to 310°C (Derevska *et al.*, 2002).

Native copper is locally observed in quartz veins and nodules. Probably high-temperature quartz, occurring in association with wairakite, has crystallized simultaneously 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 spherulitic and plumose

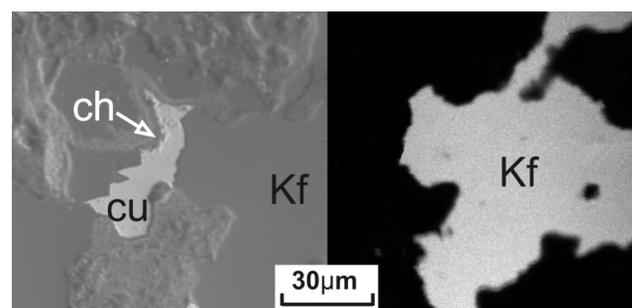


Fig. 9. Back scattered electron image of the intergrowing crystals native copper – K-feldspar (left) and K beam (Kα) image of K-feldspar (right); cu – native copper; Kf – K-feldspar, ch – chlorite

Table 4

## Microprobe analyses of K-feldspar from tuffs of the Zhyrychi deposit

No	Fe	Cr	Ti	Ca	K	Si	Al	Mg	Na	O	Sum
wt. %											
1-3	0.31	0.00	0.00	0.04	13.75	26.80	11.48	0.01	0.23	45.58	100.00
4-1	0.19	0.02	0.00	0.02	14.46	27.98	9.98	0.02	0.10	47.23	100.00
Formula units per 8 oxygen atoms											
1-3	0.02	0.00	0.00	0.00	0.99	2.86	1.19	0.00	0.03		
4-1	0.01	0.00	0.00	0.00	1.00	2.70	1.00	0.00	0.01		

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 palaeohydrothermal systems.

*Smectite* represents a group of clay minerals which in different amount impregnate both basalts and pyroclastics. They are observed commonly in ore-bearing basalts (Fig. 14k), but are also abundant in barren zones. Smectite overgrows native copper (Fig. 14l) and locally contains its relics (Fig. 14m), 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 basal spacing of smectite layers to approximately 17 Å. Locally, smectite is associated with chlorites, replacing plagioclase (Fig. 14k). According to electron microprobe analyses, it is considered that smectite in the ore bodies represents different minerals, whereby vermiculite, montmorillonite and beidellite dominate.

*Calcite* occurs in veinlets and amygdales as polycrystalline aggregates. Locally, it impregnates tuffs and is associated with sulphide mineralization. The homogenization temperature of fluid inclusions in calcite ranges from 110 to 230°C (Derevska *et al.*, 2002).

*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 red and reddened green tuffs.

Analcime has grown mostly in fissures (Fig. 14n) or open spaces of both leached 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. 14o) are rarely observed in amygdales in the places of rich laumontite occurrences. Fluid inclusions in analcime were homogenized at 125–175°C (Derevska *et al.*, 2002).

*Barite* is one of the latest minerals of 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. 14n). It often occurs in mixture with younger smectite, kaolinite and (or) quartz.

*Kaolinite* 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 (Dobrovolskaya, Poddubnaya, 1989).

## DISTRIBUTION OF ORE MINERALS

Native copper occurs mainly as disseminated both in basalts and tuffs, although veinlets, nuggets and dendrites are also common. Electron microprobe analyses do not show significant impurities of isomorphic metals.

In ore-bearing basalts numerous native copper inclusions fill abundant pores, where they replace pyroxene and clinocllore. In the bottom part of some Cu crystals, chlorite relics were detected by microprobe analysis (Fig. 9). Native copper has also been found within smectite casing, probably formed by replacing olivine, pyroxene and plagioclase phenocrysts (Fig. 14p). Scarcely, native copper directly replaces magnetite and forms pseudomorphs after this mineral (Fig. 14q). In fissured zones and lava-breccias, it was often precipitated as dendrites (Fig. 14r), wiry forms, 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 vein-

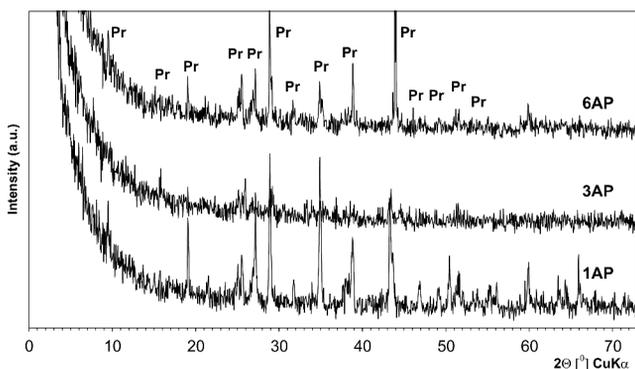


Fig. 10. X-Ray diffraction pattern of prehnite from the Zhyrychi deposit

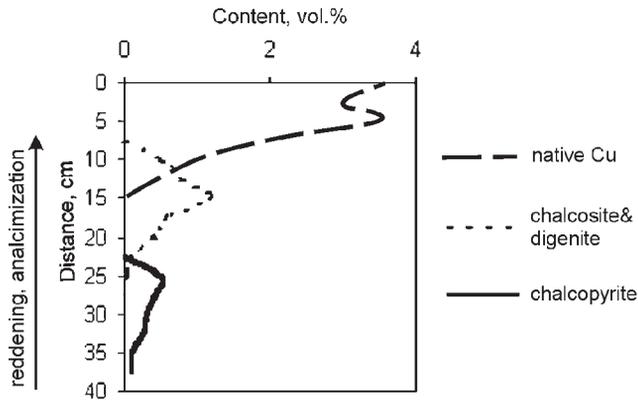


Fig. 11. Vertical profile of Cu mineral distribution in the reddened and analcimized green tuff of the Zhyrychi deposit

lets, containing quartz or analcime, more often associated with smectite.

In the lower tuffs, native copper is dispersed as thin inclusions (Fig. 14c) which differ in position and size when contained in green and red tuffs.

In green tuffs, native copper replaces commonly pyroclasts (Fig. 14s) and fills open spaces (Fig. 14t). Analcimisation and secondary reddening result in disappearing of native copper, converted into Cu sulphides, mostly into chalcocite or digenite. Covellite and bornite occur rarely. Chalcopyrite replaces scarce chalcocite and digenite in peripheral parts of these alteration zones (Fig. 11). Sulphide minerals are locally widespread in tuffs and basalts as veinlets and disseminations, but generally they are scarce (Fig. 14u). The histogram of distribution of size of copper blebs in green tuffites shows the form of a Gauss curve (Fig. 15a). This testifies the single event of nucleation and growth of native copper crystals. 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 (Fig. 15 b). It argues that native copper mineralization in red tuffs was formed during selective recrystallization, i.e. the coarser blebs grew when thinner were dissolved. These large blebs contain numerous micropores and microcrystals of hematite, which were entrapped within growing copper crystals and testify oxidizing hydrothermal environment, 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. 14v) and scarcely occurs in barren zones.

Microscopic particles of native iron have been documented within native copper crystals (Fig. 12) grown in central parts of prehnite veinlets. Single inclusions of native iron were also locally observed both in the ore-bearing and barren tuffs and basalts. Apparently, it was precipitated during magnetite dissolution, saturating the ore-forming environment in Fe.

Native silver mostly occurs within native copper as microparticles in peripheral zones of native copper blebs or within it in pores (Fig. 14w). Such position indicates later origin of native silver mineralization in the ore bodies.

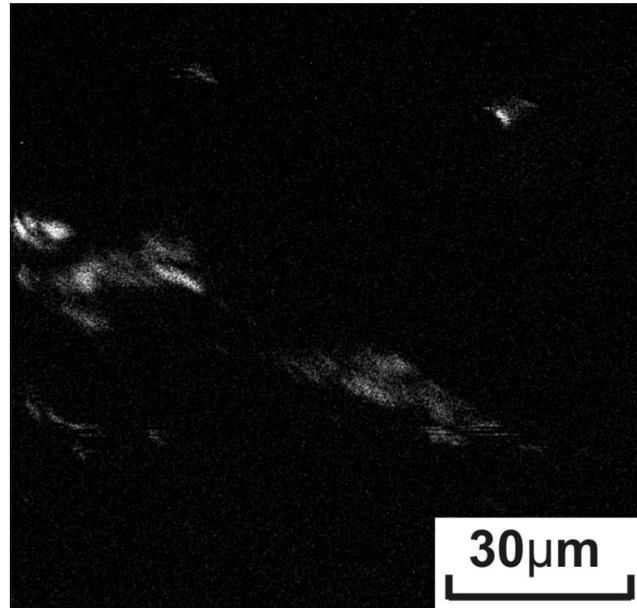


Fig. 12. Backscattered electron image of native iron microparticles (white) within native copper (black)

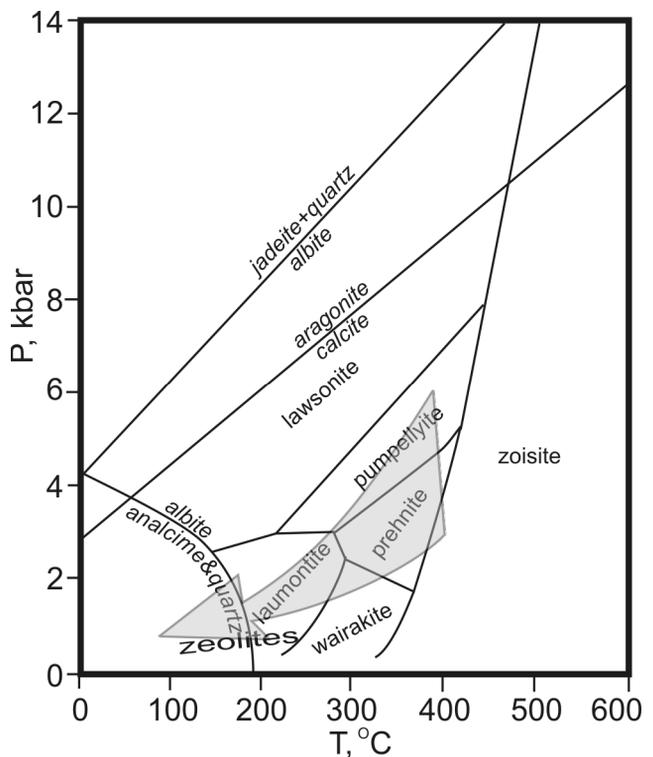
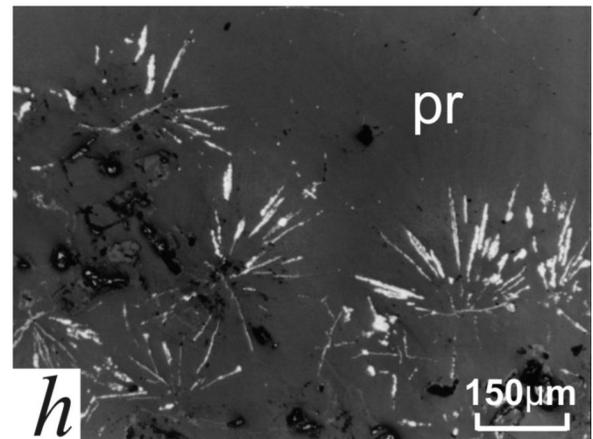
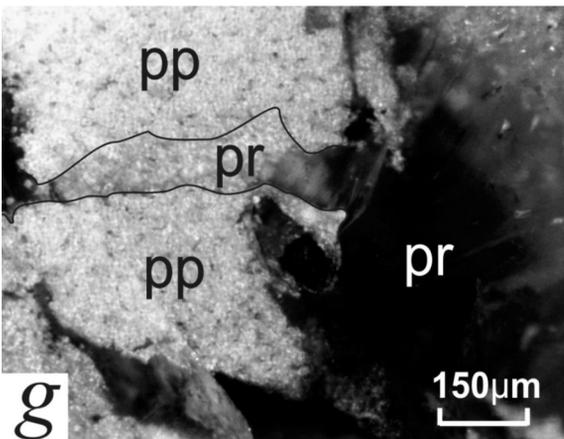
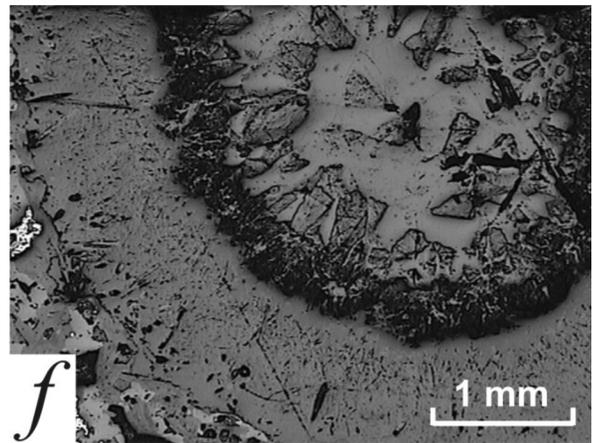
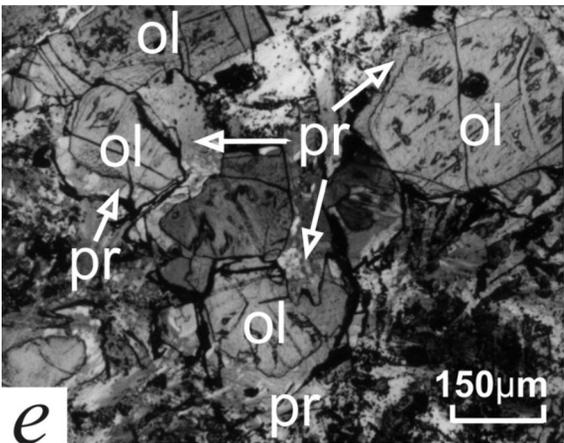
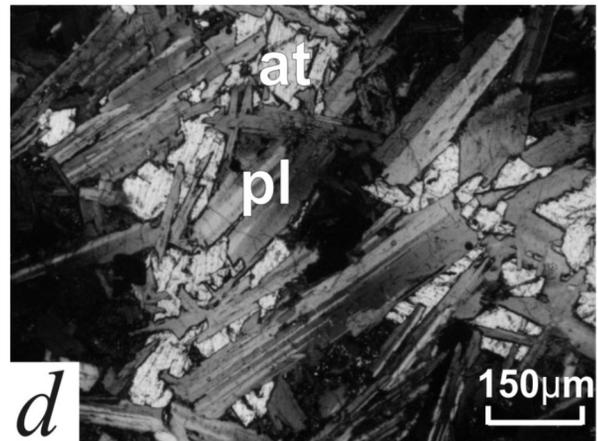
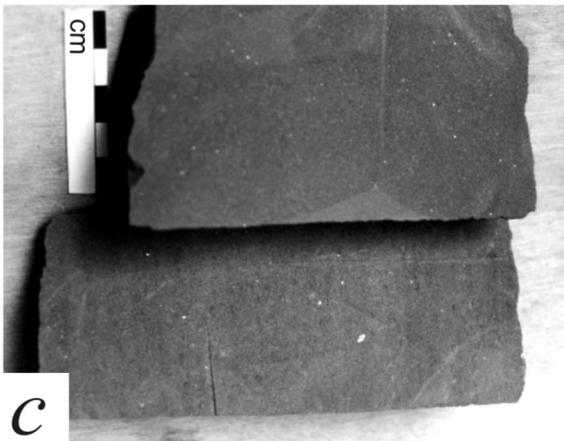
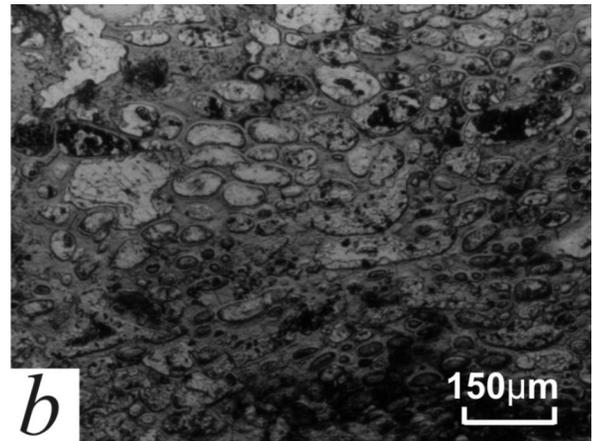
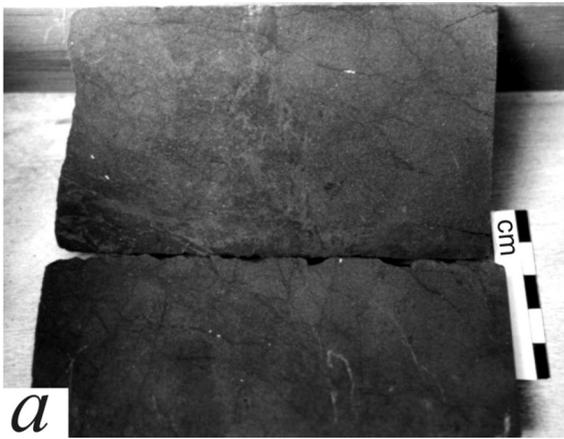


Fig. 13. P-T diagram for numerous critical reactions of the minerals of prehnite-pumpellyite and related metamorphic mineral facies (Liou, 1970, 1971; Phillipotts, 1986). The arrow shows the evolution of the mineral-forming hydrothermal system in the Zhyrychi deposit

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

Alluvial native copper, along with well-rounded grit and pebbles of basalts have been found in the Early Creta-



ceous sandstones, which cover the eroded Vendian volcanics in the Zhyrychi deposit. This ore-bearing horizon is considered to be potentially economic.

## ORIGIN OF COPPER ORES

The results of investigations presented in this study provide a range of key points, explaining both the processes leading to the formation of Cu ores in the Zhyrychi deposit and enabling the prediction of distribution of copper ores in the basalt province studied.

### Time of ore deposition

The major native copper ores occur in the lower tuffs, which along faults are bordered by Late Riphean red beds (Fig. 4), whereas in basalts their presence is often controlled by fissured zones and cracks. They are documented as strata-bound in the lowermost and contrastingly most permeable beds of flood basalts. Such ore localization testifies the activity of upward migrating copper-bearing hydrothermal fluids, which deposited Cu on geochemical barriers in the zones of contrasting permeability and redox potential.

Prehnite veinlets and nodules containing syngenetic native copper 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 is no mineralogical evidence 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.

### Copper-bearing mineral parageneses

The mineralogical evidence indicates that the first-generation native copper 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 modern hydrothermal systems within some recently active volcanic regions (Island, Japan, Kamchatka, New Zealand etc.) (Bird *et al.*; 1984; Brown *et al.*, 1989). In general, this paragenesis is similar to those determined in rocks of prehnite-pumpellyite metamorphic facies (Phillipotts, 1986), but being of hydro-

thermal origin. In the Zhyrychi deposit, the minerals of copper-bearing prehnite-pumpellyite paragenesis were generally precipitated in the sequence: pumpellyite – prehnite ( $\pm$ native copper) – laumontite (or wairakite) ( $\pm$ native copper), although tectonic movements and instability of hydrothermal system promoted periodical intensifications of the palaeohydrothermal activity, leading to the growing of laumontite over prehnite (Fig. 14j).

Redistribution of copper and growth of nuggets are connected with later hydrothermal processes, which provided regional propylitization (K-feldspar-smectite-calcite-zeolite paragenesis), later smectitization with analcimization (analcime-smectite paragenesis) and the formation of quartz bodies. Concordantly with homogenization temperature of fluid inclusions in analcime, quartz and calcite (Derevska *et al.*, 2002), these processes took place at lower temperatures, than those characterising stability of the prehnite-pumpellyite paragenesis.

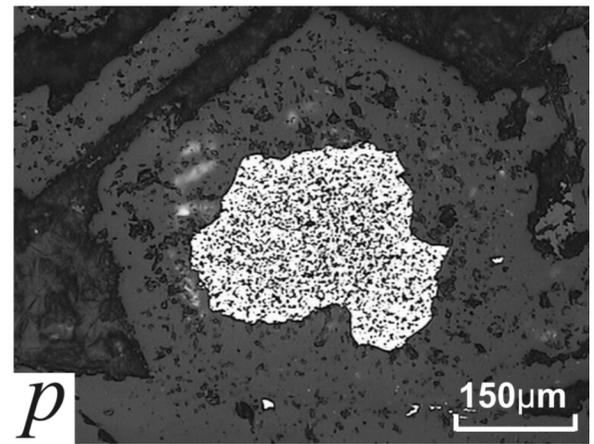
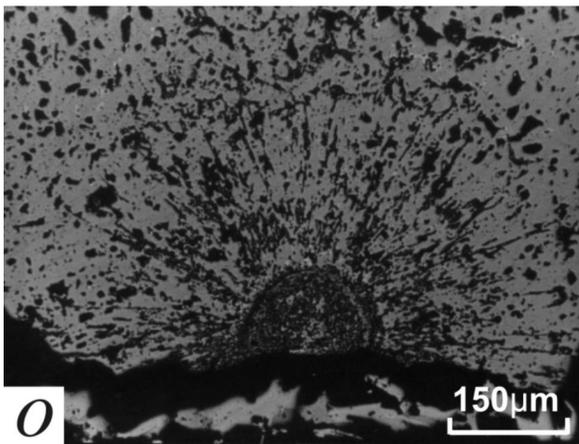
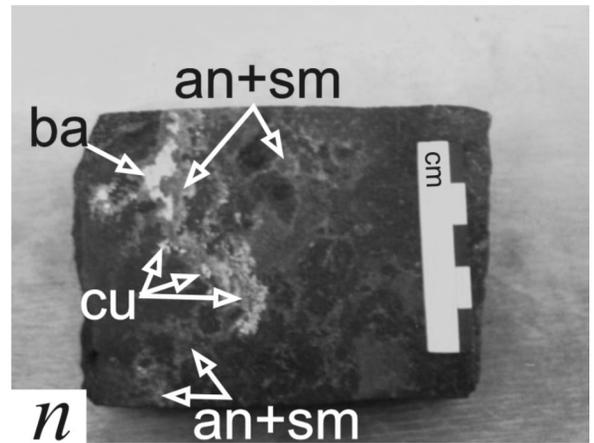
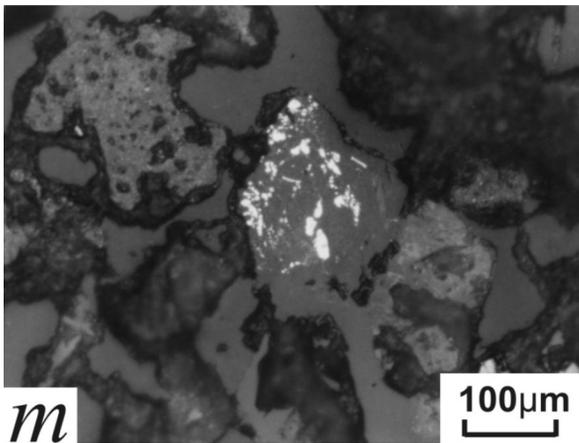
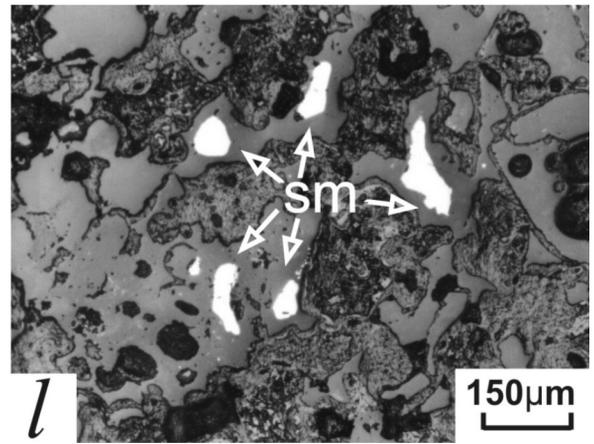
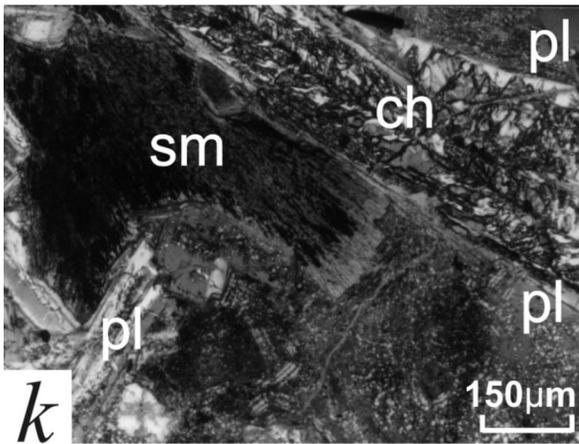
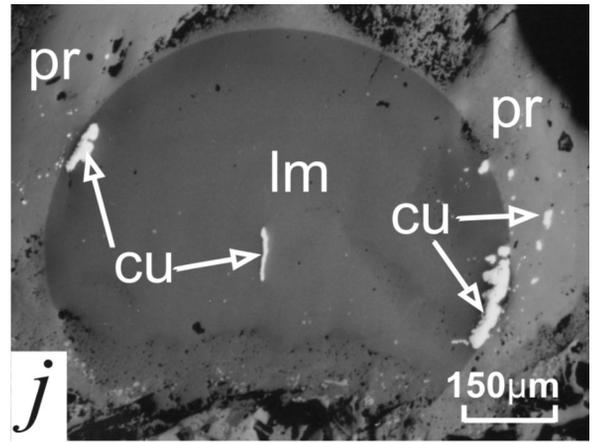
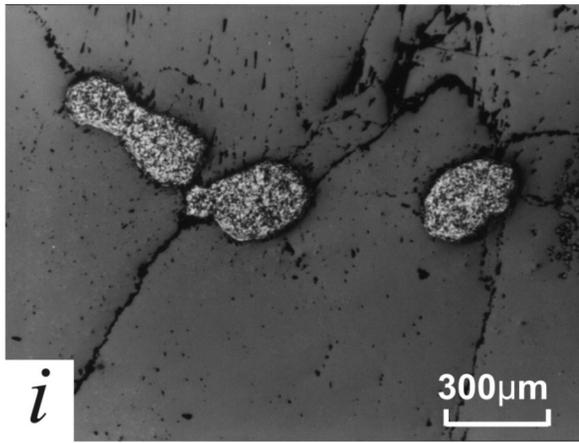
### Ore-forming conditions

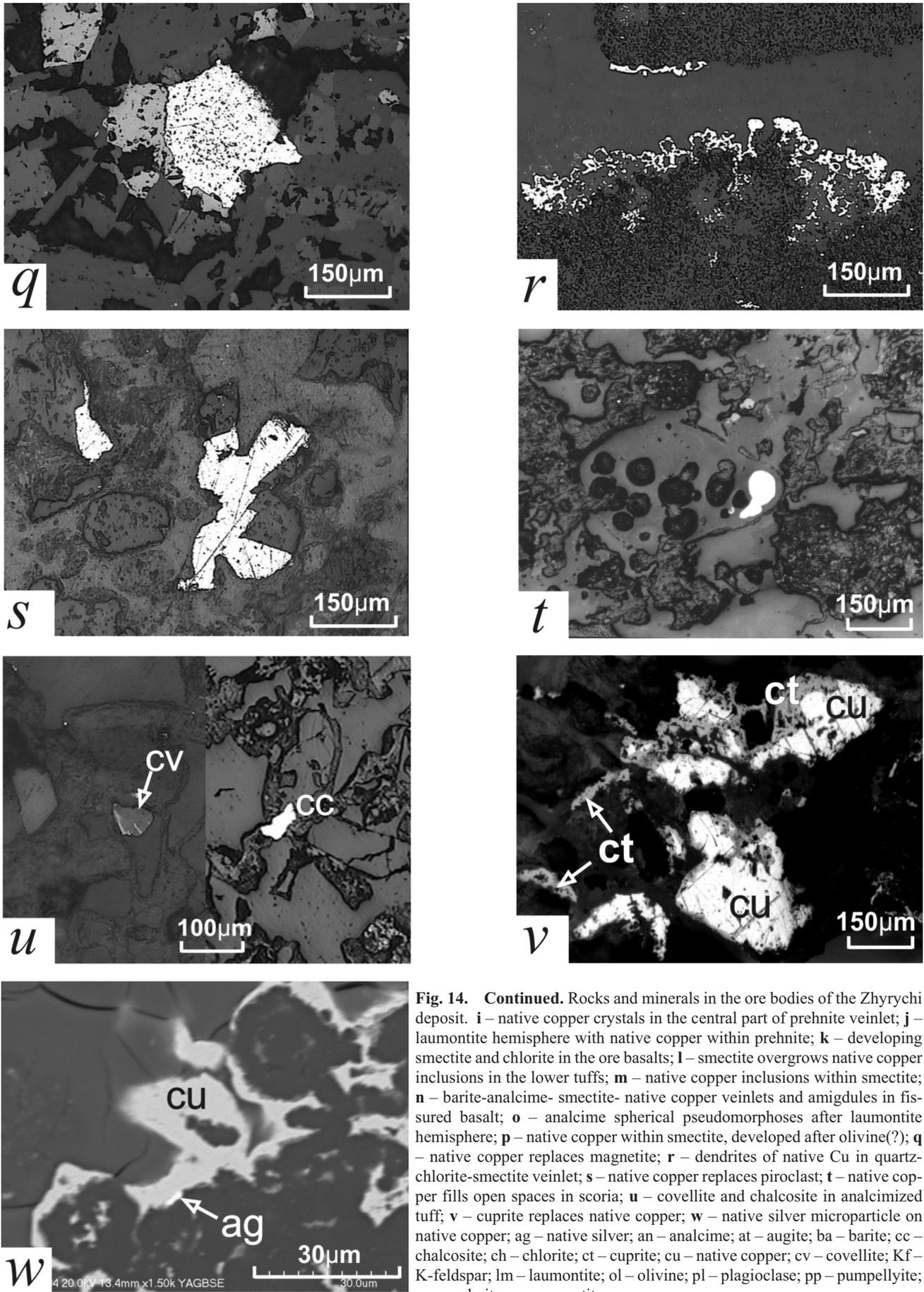
Based on the P-T diagram of stability fields of Ca aluminosilicates (Fig. 13) (Liou, 1970, 1971, Phillipotts, 1976) the succession found in the Zhyrychi deposit: pumpellyite – prehnite – laumontite – wairakite – analcime+quartz, suggests the decrease of both pressure and temperature during mineral precipitation. The stability field of prehnite indicates an approximate temperature and pressure of the first precipitation of native copper in the deposit at 300–400°C and 1.7–4.5 kbar.

Wairakite originates at lower pressure than prehnite and at lower temperature and pressure than laumontite (Fig. 13). Consequently, its association with high-temperature quartz druses apparently indicates the zones of discharge heads. Analcime has displaced Ca minerals with cooling of the system at 100–175°C (according to the homogenization temperature of fluid inclusions in analcime). The sulphide mineralization is apparently connected with cooling and oxidation of the ascending hydrothermal solutions.

The temperatures of hydrothermal fluids precipitating Ca aluminosilicates in modern hydrothermal systems do not exceed 170–400°C (Bird *et al.*, 1984). According to the homogenization temperature of fluid inclusions in wairakite (Derevska *et al.*, 2002), the temperature of the Cu-forming palaeohydrothermal system in the Rafalovka-Berestovets copper field was not lower than 210–335°C. These temperatures are in good agreement with the above-described diagram (Fig.13). In the Zhyrychi deposit, wairakite was apparently formed at similar temperatures.

**Fig. 14.** Rocks and minerals in the ore bodies of the Zhyrychi deposit. **a** – lava-breccia 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** – clinoclone spheroid; **g** – prehnite overgrows and cuts pumpellyite; **h** – syngenetic ingrowths of native copper within plumose prehnite; **ag** – native silver; **an** – analcime; **at** – augite; **ba** – barite; **cc** – chalcocite; **ch** – chlorite; **ct** – cuprite; **cu** – native copper; **cv** – covellite; **Kf** – K-feldspar; **lm** – laumontite; **ol** – olivine; **pl** – plagioclase; **pp** – pumpellyite; **pr** – prehnite; **sm** – smectite





**Fig. 14. Continued.** Rocks and minerals in the ore bodies of the Zhyrychi deposit. **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- smectite- native copper veinlets and amigdules in fissured basalt; **o** – 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 piroclast; **t** – native copper fills open spaces in scoria; **u** – covellite and chalcocite in analcimized tuff; **v** – cuprite replaces native copper; **w** – native silver microparticle on native copper; **ag** – native silver; **an** – analcime; **at** – augite; **ba** – barite; **cc** – chalcocite; **ch** – chlorite; **ct** – cuprite; **cu** – native copper; **cv** – covellite; **Kf** – K-feldspar; **lm** – laumontite; **ol** – olivine; **pl** – plagioclase; **pp** – pumpellyite; **pr** – prehnite; **sm** – smectite

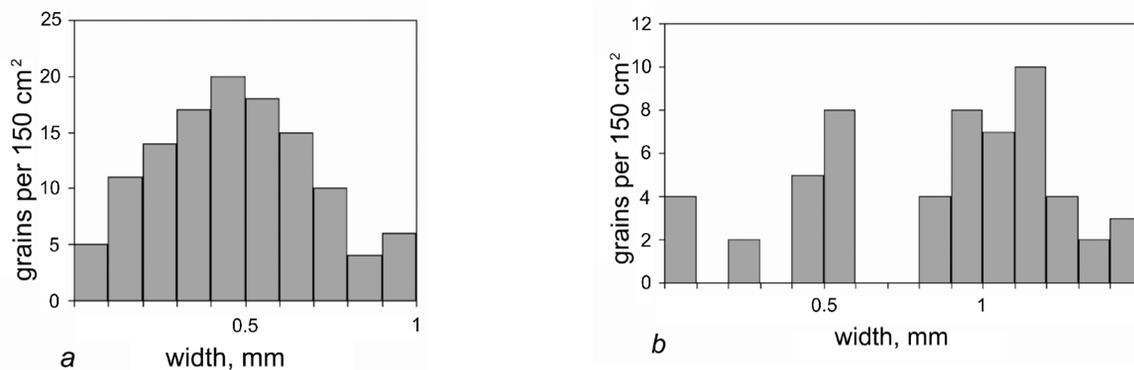


Fig. 15. Size distribution of native copper blebs in green (a) and red (b) tuffites

### Possible copper source

In agreement with Emetz and Lugova (2006) data, the isotopic oxygen ratio in prehnite and analcime of the Zhyrychi deposit testifies magmatic source of ore-forming fluids (recalculated for palaeohydrothermal fluids  $\delta^{18}\text{O}_{\text{H}_2\text{O}(300^\circ\text{C})} = 8.0\text{--}9.4\text{‰}$  and  $\delta^{18}\text{O}_{\text{H}_2\text{O}(145^\circ\text{C})} = 5.5\text{‰}$  respectively).

Following the experimental data by Holzheid and Loders (2001), 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 province 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 Emetz *et al.* (2004) as due to the melting of crust material at the end of the Vendian rifting. Thus, the cooling of the acidulated magma chambers could lead to the loss of Cu by evolving hot fluids.

### CONCLUSIONS

1. The Zhyrychi deposit is the Michigan-type native copper deposit with total resources of 15.6 Mt metallic Cu. The resources of the new territory located eastward of the Zhyrychi deposit, in the eastern flank of the Ratne horst, have been estimated at 25 Mt of metallic copper. The ores also contain significant concentrations of Ag, Pd, Rh and Au.

2. The major ores occur within strata-bound bodies in the flood basalts A, B, C and D and in the lower tuffs. The ore deposition was controlled by faults and zones of contrasting permeability and redox potential. 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. Copper 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 zeoliti-

zation, smectitization and analcimization, leading to the redistribution of copper ore, which resulted in local enrichment of all ore bodies in the form of nuggets, but generally led to Cu ore destruction.

### Acknowledgements

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## Streszczenie

### GEOLOGIA, MINERALOGIA I GENEZA ZŁOŻA MIEDZI RODZIMEJ ZHYRYCHI (NW UKRAINA)

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Praca przynosi nowe informacje na temat złoża miedzi rodzimej Zhyrychi, udokumentowanego w końcu XX wieku na obszarze NW Ukrainy. Złoże miedzi zlokalizowane jest w lawach bazaltowych i dolnych skałach piroklastycznych, rozdzielających cztery cykle wylewów oznaczone jako A, B, C i D (Fig. 4). Wiek skał został ustalony na Vend. Czas powstania trapów bazaltowych wiązany jest z okresem aktywności ryftowej wzdłuż strefy Torn-

quista. Struktura ciał złożowych została określona jako stratabound. W rzeczywistości są to pseudopokłady o miąższości od 0,3 do 2,5 m z zawartością Cu wahającą się w granicach 0,3–12 % wag. Okruszcowanie ma charakter rozproszony. W strefie złożowej występują wzbogacenia spowodowane obecnością rodzimków (nuggetów) i żyłek miedzi rodzimej. Przepuszczalne zasoby miedzi metalicznej w złożu Zhyrichi na obszarze 120 km<sup>2</sup> wynoszą 15,6 Mt, zaś zasoby tzw. wschodniego skrzydła (na E od uskoku Ratne, Fig. 3) szacowane są na 25 Mt (kategoria rozpoznania C2). Główne ciało złożowe zlokalizowane jest w dolnych tufach i zawiera 8 Mt miedzi metalicznej w obszarze Zhyrichi i 12,2 Mt na obszarze wschodniego skrzydła. W strefie złożowej stwierdzono domieszki Ag, Au, Rh i Pd. Zasoby Ag i Rh zostały obliczone na podstawie równania przedstawionego w rozdziale 6 i

wynoszą odpowiednio 0,19 Mt i 406 t. Au i Pd występują lokalnie a ich zawartości sięgają 2,9 ppm i 1,3 ppm.

Miedź rodzima jest głównym minerałem kruszcowym w złożu. Lokalnie spotykane są wzbogacenia w siarczki miedzi: chalkozyn, digenit, bornit i kowelin. Rzadko spotykane jest srebro rodzime oraz kupryt. Minerale kruszcowe występują w asocjacji z pumpellyitem, prehnitem i laumontytem. Wytrącanie minerałów kruszcowych nastąpiło podczas schładzania roztworów hydrotermalnych u schyłku Vendyjskich wylewów trapowych. Asocjacje mineralne wskazują 200–400°C jako przedział temperaturowy krystalizacji miedzi rodzimej. Złoże należy uznać jako hydrotermalne. Dowodem tego są liczne i rozległe strefy zmian hydrotermalnych, takich jak propylityzacja, smektytyzacja i analcymizacja, obserwowane w skałach goszczących.