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National Museum of Natural History, National Academy of Sciences of Ukraine
15 Bogdan Khmelnitsky Street, Kiev 01601, Ukraine

KSENIIA RUDENKO, KATERYNA DEREVSKA

# New Data about Ore-Bearing of the Neoproterozoic Flood Basalts (the Ratno Beds, Volhyn, Ukraine)

Nowe dane dotyczące rudonośnych pokryw lawowych z neoproterozoiku
(skały osadowe, pokłady, struktury sedymentacyjne w Ratnie, Wołyń, Ukraina)

**Keywords**: Neoproterozoic flood basalts, the Ratno Beds, native metals, alterations, mineralization

**Słowa kluczowe**: neoproterozoiczne pokrywy lawowe, pokłady, struktury sedymentacyjne, skały osadowe w Ratnie, metale naturalne, zmiany, mineralizacja

## INTRODUCTION

Volcanic formations were always an object of geologist's interest due to their metallogenic features. Neoproterozoic flood basalts are not an exception. Neoproterozoic flood basalts spread in the eastern part of Poland, the south-western Belarus, northern Moldova, and western Ukraine (Bakun-Czubarow ed. 2001, 2002, Machnacz ed. 2001, Bialowolska, 2002, Justkowiakowa, 1989). It occupies a vast territory (up to 200,000 km$^2$) in the South-Western part of East European Craton. This part of the East European Craton is a passive continental margin, which includes the Volhyn-Polisia depression and Lukov-Ratno horst zone. Their geological structures are explored in detail by Znamenskaja T.A. Czebanenko, I.I. (Znamenskaja ed. 1979, 1985, Znamenskaja, 1992). The main tectonic structures of Volhyn-Polisia depression are Chartoryisk fault zone trending north-west and Manevychi circular structure (Znamenskaja ed. 1979, 1985, Znamenskaja, 1992, Maksimczuk 1999).

Volhyn-Polisia depression is filled by Riphean (the Polisia Series) and Vendian (the Volhynian and the Valdai Series) rocks. The Polisia Series lies with angular unconformity on crystalline basement and has uniform lithological composition: sandstones with interbedded of siltstone and mudstone (Czebanenko, 1990, Bakun-Czubarow ed. 2001, 2002).

The Volhynian Series ($V_1$vl) consists of five beds (from bottom to top): the Brody Beds (breccias, conglomerates and mudstone, up to 40 m), which are developed sporadically; the Gorbashi Beds (~ 50 m) of gravelites and sandstones; the Zabolottya Beds (to 85 m) of mainly basalts; the Babino Beds (100-200 m) - basaltic tuffs and lava breccias; the Ratno Beds - interbedded basalts, their tuffs and lava breccias, tuff conglomerates (up to 200 m). The general thickness of the Volhynian Series exceeds 450 m. It should be noted that the Zabolottya Beds, the Babino Beds and the Ratno Beds put together the Neoproterozoic flood basalts (Szumłjanskij W.A. ed. 2006). The Valdai Series covers the Volhynian Series and is represented with coarse-grained sandstones with kaolin cement (Czebanenko 1990).

The Paleozoic, Mesozoic and Cenozoic deposits are less thick. The section of the Paleozoic deposits in the western part of Volhyn-Polisia depression basin ends with Carbon. The deposits of the Mesozoic (Jurassic, Cretaceous) overlay Paleozoic deposits with stratigraphic unconformity (Czebanenko 1990).

The active prospecting work for native copper in Neoproterozoic flood basalts was held within the Volhyn-Podolsk plate for last decades. There are 4 native copper districts: Ratno, Kuhol'skovolsky, Rafalivka, Shepetivka (Szumłjanskij W.A. ed. 2006). This research focuses on Rafalivka ore district.

Rafalivka ore district is located on the western slope of the Ukrainian Shield, in his submeridional band, featured with shallow crystalline basement gradually descending towards the west (Fig. 1). North-western part of this territory is crossed with Chartoryisk fault zone strike northwest. The south-eastern boundary of Rafalivka district is Gorynska fault zone (Maksimczuk ed. 1999). Crystalline basement is descended to a depth of 900 m and covered by sedimentary and volcanic rocks represented with the Neoproterozoic, Cretaceous, Paleogene, Neogene and Quaternary formations.

The Volhyn series in Rafalivka ore district (tuffs of the Babyno Beds, interbedding of basalt, tuffs and lava breccias of the Ratno Beds) is overlaid with sediments of the Chartoryisk beds. The thickness of the Ratno Beds is not exceeding 100 m here. Meso-Cenozoic sediments thickness is up to 40 m.

Previous mineralogical and geochemical studies of volcanic rocks of Neoproterozoic flood basalts show irregularity of alterations and increase of native metals mineralization concentration throughout the section. The nature of secondary (mineralogical and tectonic) changes of volcanic rocks were described by many authors (Bernadska 1958, Derewska ed. 2003, 2008, Mełniczuk, 2004,

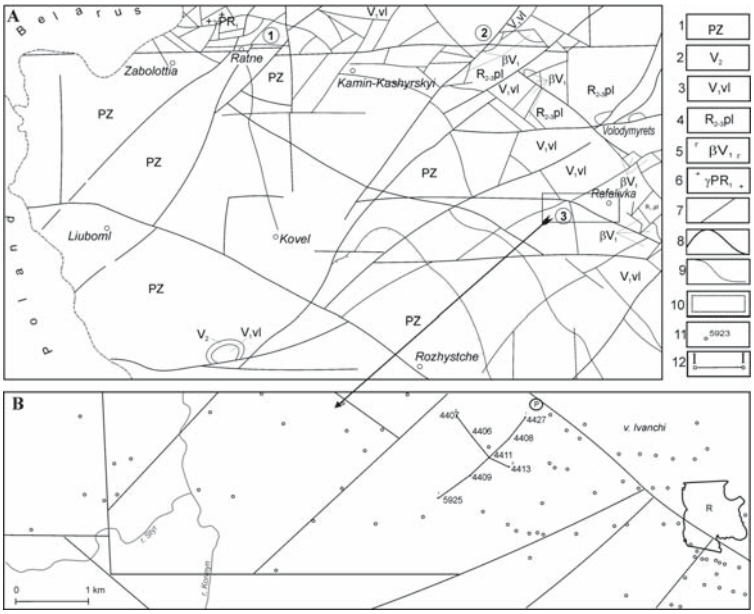


Figure 1. Geological map of the area of investigation (within Rafalivka ore district) (modified (Szumljanskij W.A. ed. 2006, Derewska ed. 2006)) 1 – Paleozoic (Cambrian-Carbon) sediments; 2 – the Mogilev-Podilia Series; 3 – the Volhynian Series (basalts, tuffs, lavobreccias); 4 – the Polisie Series of middle-upper Riphean (sandstones, siltstones); 5 – intrusive complex of the lower Vendian; 6 – granite of the Osnitsa complex; 7 – faults; 8 – boundaries of depressions; 9 – geological boundaries; 10 – investigation area: 11 – drillhole and its number; 12 – investigation cross-sections. Ore districts (numbers in circles): 1 – Ratno, 2-Kuhol'skovolsky, 3 – Rafalivka. Quarries: P – Polytsi; R – Rafalivskyi

Szumljanskij Ł.W., 2006, Skakun ed. 2006). Despite this, the issues related to the regularity of native metals mineralization distribution in Neoproterozoic flood basalts remain unsolved.

## METHODS OF EXAMINATION

The samples of effusive rocks from Rafalivka, Polytsi quarries and drillholes were collected during field works. Detailed study was provided for two sections: I–I – drillholes 5925 – 4427; II–II – drillholes 4407–4413. Thin sections were examined with the microscope both in transmitted and reflected light. The chemical composition of rocks was defined with ICP in Laboratories of DGRP "Pivnichgeology" and National Academy of Sciences. Mineral composition was defined with scanning microscope *JSM-6490LV and РЭМ-106 with* X-ray spectroscopy probe. Analyses of drillholes data was provided with ranking methods and Gis software package at Geological faculty of Lviv National University.

## RESULTS

The Ratno Beds within the territory of investigation consist of one to four basalt flows with interbedded tuffs and lava breccias. Mineralogical, geochemical and petrographic study of various years (Bernadska 1958, Bakun-Czubarow ed. 2001, 2002, Derewska ed. 2003, 2008, Ciłmak 2006 etc.) found that the most mineralized and altered rocks are the lowest volcanic flow of *the Ratno Beds*. Thus, we selected this flow to determine the mineralogical and geochemical control of secondary mineralization.

The Ratno Beds consist of three basaltic flows and tuffs between them within the investigation area (Fig. 2). Basaltic flows differ from each other in rock-forming minerals quantities, alteration degree, structural and textured features, and also presence of amygdales, veins and vesicles.

The lower basaltic flow has a complex composition. There are three types of basalts: aphyric, porphyritic and amygdaloidal. They all display fine-grained, holocrystalline, tholeiitic texture. Volcanic glass was completely substituted with palagonite. The amygdales in amygdaloidal basalts are filled with chlorite, chalcedony and zeolite. The porphiric impregnation is represented with magnetite and plagioclase.

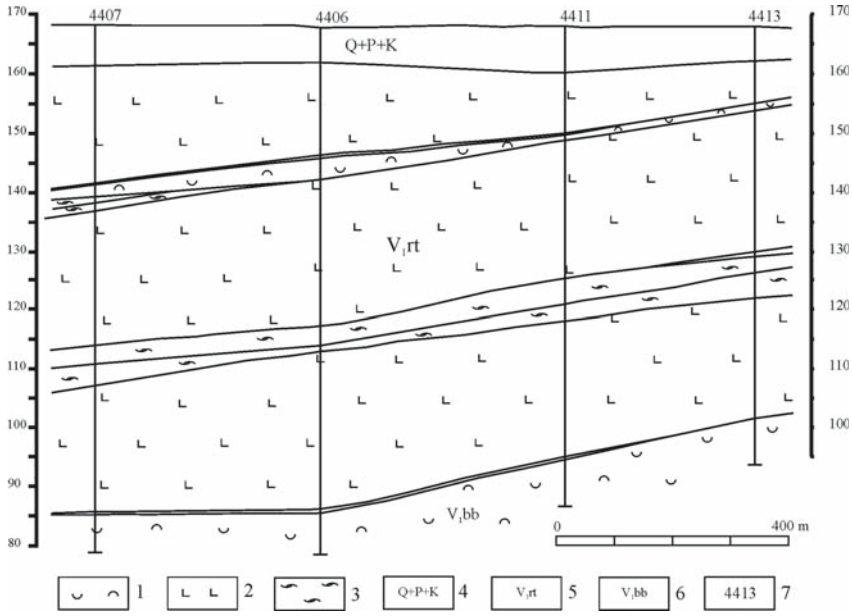


Figure 2. Geological cross section along the line II–II (drillhalls 4407–4413) within the Rafalivka ore district: 1 – tuffs, 2 – basalts, 3 – lavobreccia, 4 – rocks of Createaceous, Paleogene, Quarternary age; 5 – the Ratrno Beds; 6 – the Babyno Beds; 7 – drillhore's numbers

The middle basaltic flow is zonal and representing: amygdaloidal – aphyric – amygdaloidal basalts. All of them display fine-grained, evengrained, allotriomorphic, tholeiitic texture. Volcanic glass was almost completely replaced with palagonite and chlorite. The amygdales are filled with chlorite, zeolite, analcite, quartz.

The upper basaltic flow represented with the least altered aphyric basalts. The texture is fine-grained, evengrained, intersertal, aphyric, allotriomorphic, tholeiitic. There is a volcanic glass in basalts, so that initial mineral composition of basalts is preserved. There wasn't influence of basin fluid solution.

The crystal-vitric tuffs of the investigating area, which are lying between basalt flows, are highly altered and contain veins, threads and interstices filled with analcite, chlorite, and quartz.

*Volcanic rock alterations*

The rocks of the Ratno Beds of Neoproterozoic flood basalts underwent extensive secondary alterations. These alterations determined the formation of chlorites, palagonite, zeolites, quartz, calcite, epidote.

There are a lot of amygdules of different shapes and sizes, filled with palagonite, chlorite, zeolites, interspersed with copper, sometimes carbonates in the upper and lower parts of the flows. Lava breccias and tuffs form thin lenticular bodies composed of basalt and tuff fragments in different proportions, which are cemented mainly by secondary mineral formations that are analcite, chalcedony, quartz, chlorite, sericite.

On the basis of summarizing the data of geological, mineralogical and geochemical studies, we have built a schematic map of newly formed minerals distribution in the lowest flow of the Ratno Beds (Fig. 3). This allows to identify a zone of intense secondary alterations within Chartoryisk fault zone: 1) regional alterations are presented with palagonite, chlorite, zeolite, analcite, chalcedony, iron hydroxides; 2) local zone of quartz-carbonate-sulphide mineralization. Sulfides are presented with pyrite mainly, pyrrhotine, chalcopyrite and chalcocite.

*Native metals mineralization*

Ore mineralization in the Ratno Beds rocks is represented with ilmenite, titanomagnetite, magnetite, native metals (copper, silver, gold, iron, nickel, chromium), tenorite, pyrite, chalcopyrite, chalcocite, cuprite, malachite, azurite. In addition, the geochemical anomalies of lead, vanadium, zinc, barium, and mercury were reported in volcanic-sedimentary rocks of the Volhyn series on the western slope of Ukrainian shield (Szumljanskij W.A. ed. 2006).

Native copper in Volhyn was first found and described by S. Malkovsky in basalt outcrops near the village Velykyi Midsk in 1927 (Łazarenko ed. 1960). Na-

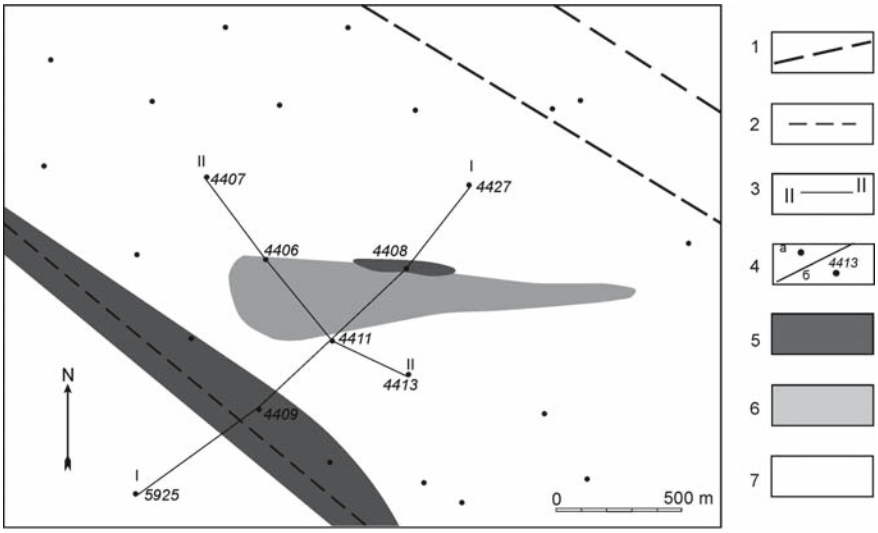


Figure 3. Scheme of secondary mineralization distribution in the middle of the lowest basalt flow (the Ratno Beds): 1 – main faults of Chartoryisk fault zone; 2 – other faults of Chartoryisk fault zone; 3 – investigation cross-sections; 4 – drillholes (a) and its number (b); 5 – zone of sulphides; 6 – quartz-calcite zone; 7 – chlorites-zeolites-palagonite-chalcedony zone

tive copper within Rafalivka ore district concentrated in basalts, lava breccias and tuff of the Ratno Beds (Prichodko ed. 1993, Kwasnicja 2002, 2004, Kwasnicja ed. 2006, Kuzmenkowa ed. 2006, Kwasnicja ed. 2009). Our studies show that it occurs as small grains (impregnation in host rock, in fissure), dendrites, films, veinlets. Native copper can sometimes fill amygdules and cements fragments in lava breccias (Fig. 4). It is associated with chlorites, quartz, chalcedony, analcite, zeolites, native silver, and cuprite. The small isometric native copper grains form inclusions in plagioclase, pyroxene, and volcanic glass or occurs on the boundaries of the grains. The large nuggets of copper (up to 500-1000 g) have been found within Rafalivka quarry recent years. Dendritic copper nuggets (up to 100-200 g) often occur in lava breccias overlaying the Babino Beds tuffs.

Native copper contains Cu 99.97-99.87% with small amounts of Ag, Co, Au and Fe (Table 1). There are impurities of Ni (up to 0.3%), Sb (up to 0.02%), Bi (up to 0.05%), Hg (up to 0.01%), Cr (up to 0.01%), Al and As (Kwasnicja ed. 2009, Rudenko ed. 2011).

Native silver occurs as thin veinlets, in aggregation with native copper, as well as xenomorphic grains, polyhedra and their concretions. It is often associated with native copper, analcite, albite, calcite, quartz. Native silver contains impurities of Cu, Fe, S, traces of Au and Pt (Table 1). Also the presence of Hg in amounts to 2.3%, traces of As and Sb was defined (Kwasnicja ed. 2005, Kwasnicja 2003).

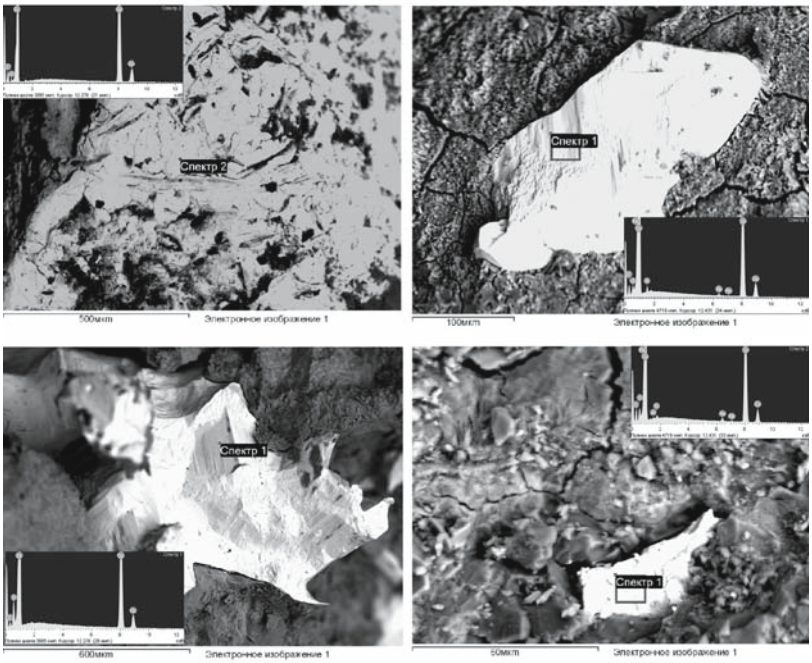


Figure 4. Native copper grains in basalt from Rafalovka quarry (scanning microscope photos)

Increased content of silver and gold was determined during prospecting study, performed DGRP «Pivnichgeologia» in the 1999-2009. The territory of Rafalivka ore district is characterized with enhanced concentration of gold. The gold content in basalts ranges from 2 to 4 ppm in some intervals within Chartoryick fault zone (Mełniczuk ed. 2012). Electrum, rozhkovit, auriferous pyrite and kuproauryt were found in basalts within the study area (Bezugłaja ed. 1999, Kosowskij ed. 2004, Mełniczuk ed. 2012).

The first record of native iron in the Neoproterozoic volcanic rocks of Volhyn was made by O.P. Karpinski in 1873 during the basalt quarries study in Yanova Dolyna and Berestovets (Łazarenko ed. 1960). Native iron was found as small grains (up to 0.22 mm) spread in rock groundmass and in glass (Łazarenko ed. 1960, Kwasnicja ed. 2006). According to our study data, native iron was found in basalts along the dry fissure walls as elongated, rounded or drop-shaped grains and thin films. It is associated sometimes with chlorite and yellow limonite. Typical impurities of native iron are Mn, Cr, Ni, Co and Cu. In some cases, there are also Ti (up to 0.07%), V (to 0.01%) and Mo (to 0.04%) (Tabl. 1).

Native nickel was for the first time found and confirmed by X-ray spectroscopy in amygdaloidal basalts (drillhole 5926), tuffs (drillhole 8124) and lava breccias (Rafalivka quarry). It forms small (<0.1 mm) single grains of irregular and

Table 1. Composition of native metals from the Ratno Beds of the Volhynian Series (wt. %)

| Mineral | Native iron | | | Native cromium* | Native silver | Native copper | | | Native nickel | |
|---|---|---|---|---|---|---|---|---|---|---|
| Samples | 5877-1 | 5879-12 | 5881-9 | | 5877-1 | Rafalivka quarry | | | 5926-1 | 8124 |
| Cu | 0.00 | 0.136 | 0.160 | - | 2.11 | 99.931 | 99.970 | 99.876 | - | - |
| Ag | - | - | - | - | 97.21 | 0.068 | 0.020 | 0.062 | - | - |
| Au | - | - | - | - | - | - | 0.011 | - | - | - |
| Fe | 98.21 | 97.06 | 98.380 | 0,28 | 0.565 | - | - | 0.062 | 3,391 | 1.112 |
| Mn | 0.65 | 1.926 | 0.541 | 0,02 | - | - | - | - | - | - |
| Cr | 1.09 | 0.139 | 0.126 | 99,17 | - | - | - | - | - | 0.090 |
| Ni | 0.02 | 0.058 | 0.084 | 0,01 | - | - | - | - | 96,609 | 98.644 |
| Co | 0.11 | 0.128 | 0.114 | - | - | 0.001 | - | 0.001 | - | - |
| Ti | - | - | 0.007 | - | - | - | - | - | - | 0.136 |
| Si | - | - | - | 0.2 | - | - | - | - | - | - |
| Zn | - | - | - | 0,01 | - | - | - | - | - | - |
| Al | - | - | - | 0,09 | - | - | - | - | - | - |
| S | - | - | - | - | 0.117 | - | - | - | - | - |

* Kwasnicja ed. 2005

elongated cubic shape in the rock mass which contains copper mineralization. The chemical composition is characterized by the presence of impurities Fe, Cr and Ti (Table 1).

The presence of positive lead anomalies is marked in Rafalivka area. Previously, thin plate-shaped native lead was found in the tuffs of Volhyn series within Andrushivska fault zone. Native gold, copper, vanadium can be found combined with lead (Szumłjanskij W.A. 2006, Mełniczuk ed. 2012).

Native chromium (Table 1) was observed in the concentrate of the Ratno Beds lava breccia within Rafalivka area (Kwasnicja ed. 2005).

In order to determine the features of the metals spreading in volcanic rocks of the Ratno Beds, schematic maps were built (Fig. 5–7). As shown on the maps, areas of higher concentration of gold and silver coincide as they have close geochemical characteristics and behavior of these elements in the basalt strata. The maximum of their content is observed in drillholes 4408, 4406, 4411, where copper content is very low. Thus, the Ratno Beds show no direct correlation between copper and gold in the Ratno Beds. This data is confirmed statistically.

As shown above, native silver associates with native copper and there are impurities of it in native copper. We can assume there are two generations of silver: the first one is associated with the processes of copper formation, and the second - with sulphides and gold.

Fracturity rocks.

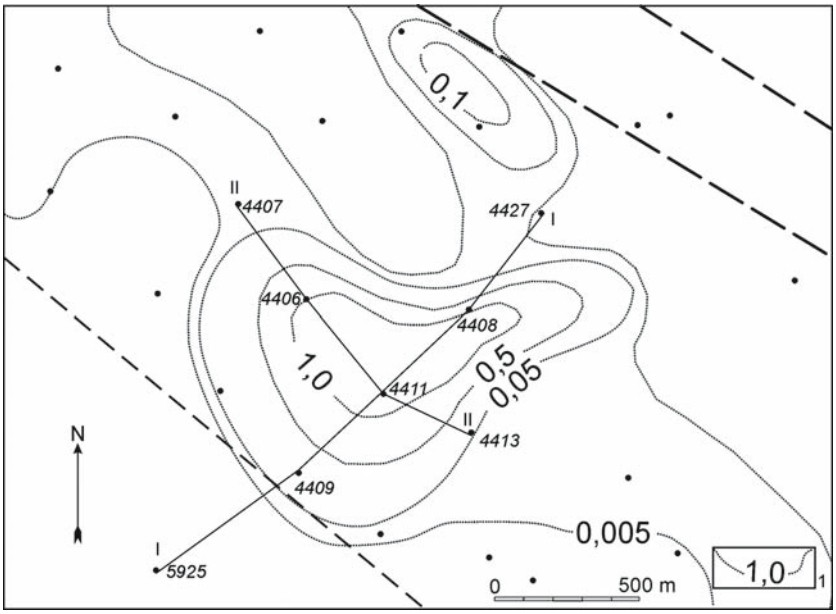


Figure 5. Scheme of gold distribution in the middle of the lowest basalt flow (the Ratno Beds) (in n*$10^{-7}$%)

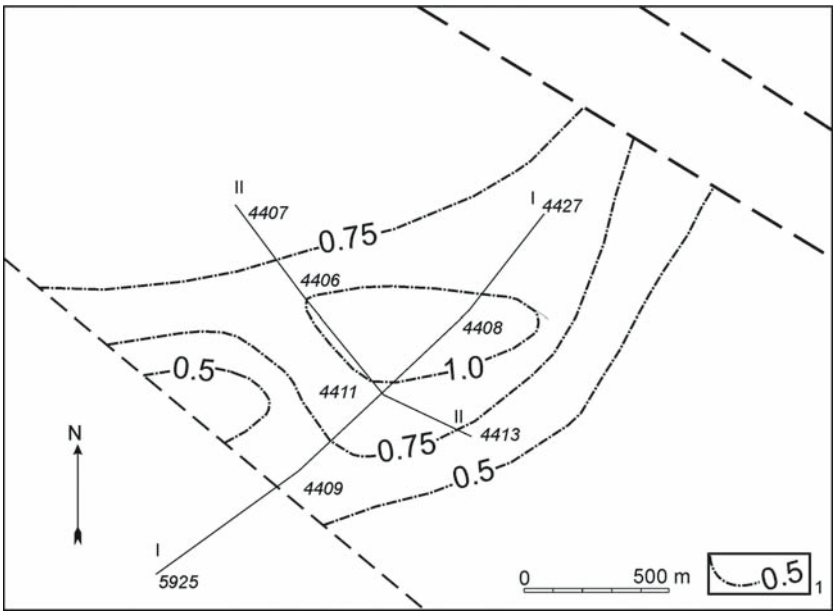


Figure 6. Scheme of silver distribution in the middle of the lowest basalt flow (the Ratno Beds) (in g/t)

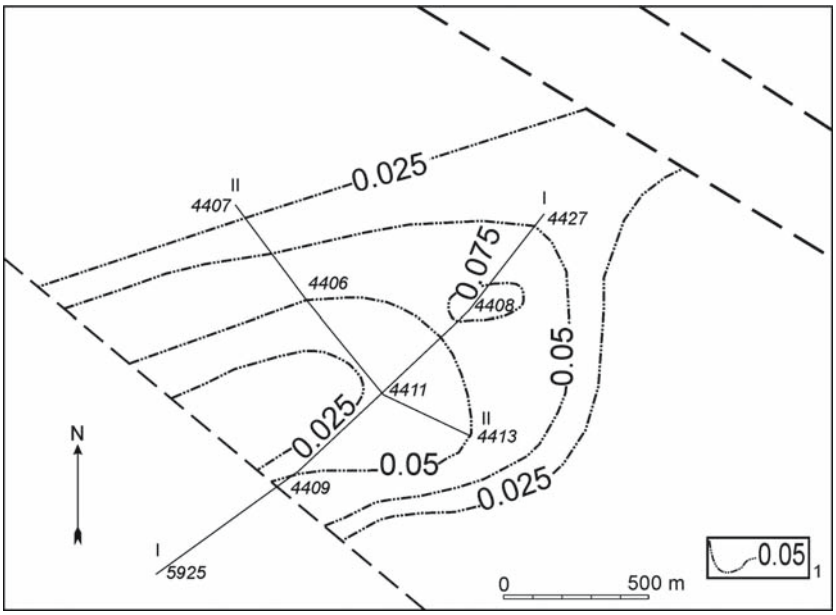


Figure 7. Scheme of copper distribution in the middle of the lowest basalt flow (the Ratno Beds) (in wt%)

The analysis of geological data shows that basalts are intensely altered and fractured, and in some cases crushed to detritus. This fracturing has various origins.

It was defined that lenticular lava breccia bodies, the formation of which can be associated with the movement of the lava flow, occur sporadically on the surface and in the bottom of each flow. The middle part of the lava flow cools much slower and as a result of volume reducing, fissures formed from surface and from the base of the flow. It leads to formation of columnar joint (Koronowskij, Jakuszowa, 1991). Lava breccias on the flow's surface can be formed as a result of basalt weathering during breaks between eruptions. During tectonic activation of region, this rocks and basalts with numerous fissures were the ways for lateral fluids migration. Thus primary layers of interstratal cavities were formed and filled by hydrotherms to form multi stratabound formation of low-sulphide quartz mineralization with a high content of silver and gold.

Defined fractures are of mostly subvertical orientation. The fissures forms due to: 1) cooling flow and the formation of columnar separation; 2) tectonic movements within given area (separation and compression fissures). There are also horizontal and diagonal fractures (cleavage fissures), and ellipse subhorizontal cracks detected in some areas. Fissures from 1 to 8 mm width are filled with secondary minerals in various associations, "dry" cracks are up to 1 mm. They are filled by chlorite, saponite, hizenheryte, chalcedony, zeolites, iron hydroxides, analcite, quartz, calcite, with small native copper grain impregnation.

To define the intensity of rocks fracturing within the selected flow, we had determined the degree of fracturing, characterized by the number of cracks of any origin and direction of one meter of core. We allocated a total of 9 ranks (Table 2). It was found that the most fractured and brecciated basalts are in drillholes 4406 (62.2 m), 4408 (55.3–55.6 m), 5963 (70.6–74.3 m) and 5903 (34.4 m) (Fig. 8). These zones are characterized by sublatitudinal strike. It shows the isometric gradual reduction of fracturity from the central sublatitudinal zone.

GIS technologies and core documentation data allow us to the maps of the surfaces of the Babino beds and the Ratno Beds flows. As a result, the signs of landslide movement along Chartoryisk fault zone were marked (Fig. 9). At the same time, the surface of the first and next flow of the Ratno Beds do not have such signs. It can be assumed that Chartoryisk fault zone was active after sedimentation of the Babyno Beds and before formation of the first basalt flow of the Ratno Beds. According to Gintov O.B. (2005), the Volhyn basalts field was deformed uniformly in several steps. Original planetary fractures formed first, and later came the regional. Both types of fractures differ only in the orientation of subvertical incidence without faults polishing. However, a significant amount of sliding mirrors with shading that indicates the horizontal shift, localized in

Table 2. The scale of fracturing rocks intensity of the Ratno Beds basalt

| The rank | number of cracks at 1 m |
|---|---|
| 1 | a single crack |
| 2 | 3-5 |
| 3 | 5- 7 |
| 4 | 7-15 |
| 5 | 15-25 |
| 6 | 25-30 |
| 7 | 30-40 |
| 8 | over 40 |
| 9 | brecciated zone |

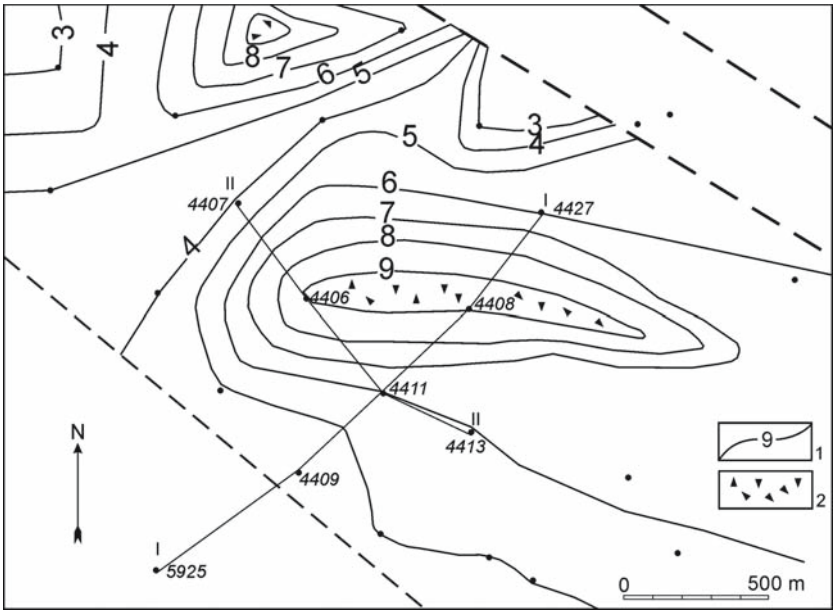


Figure 8. Scheme of the lowest basalt flow tectonic disturbances intensity (the Ratno Beds) within Chartoryisk fault zones. 1 – isolines of fracturing intensity range; 2 - brecciation zone

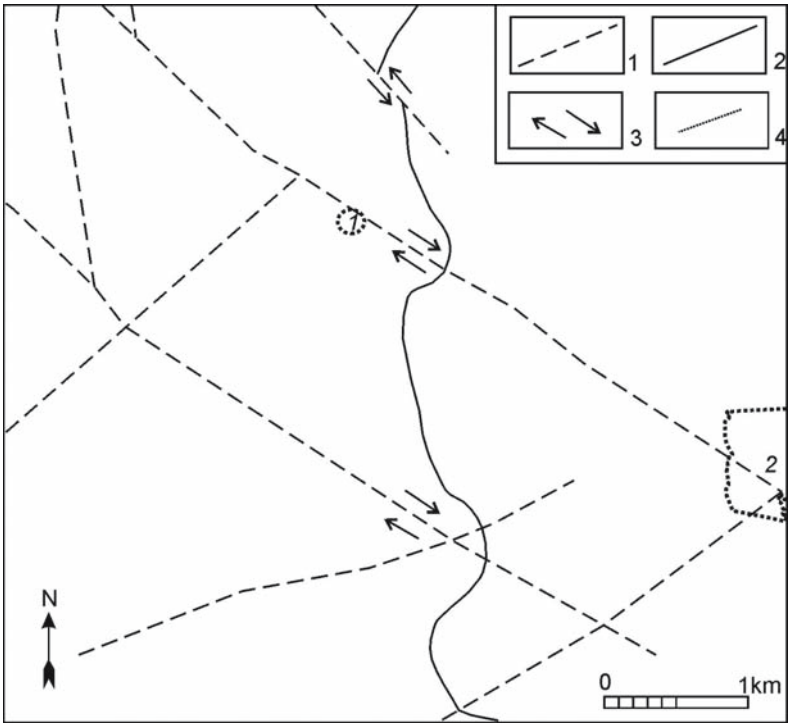


Figure 9. Possible tectonic movements along Chartoryisk fault zone lineaments. 1 – Chartoryisk fault zone lineaments; 2 – isoline of the Babyno Beds (102 m); 3 – direction of movements; 4 – quarries: 1 – Polytsi; 2 – Rafalivskyi

a narrow zone of northwest trending were recorded in the central part of Rafalivka quarry near the dome of Babino Beds sandstones (Gintov, 2005).

After formation of Neoproterozoic flood basalts, re-activation of the territory appeared. Consequently, the faults of northeast, meridional and sublatitudinal direction with brecciation zones were formed. In addition, W.P. Palienko (1992) supposes that sublatitudinal liniaments of Chartoryisk and Gorynsk fault zones havegeomorphological are features of active tectonic structures.

These data indicate that the allocated sublatitudinal brecciated zone in the lower flow is not associated in time with the activation of northwestern liniaments of Chartoryisk fault zone.

## DISCUSSION OF THE RESULTS

Compilation of generalized schemes of secondary mineralization distribution, and fracture zones with high concentrations of precious metals in volcanic rocks

made it possible to get interesting results (Fig. 10). Evidently, the zone of quartz-carbonate-sulphide mineralization matches with a sublatitudinal zone of intense fracturing and brecciation of basalt. This zone is confined to positive noble metals anomalies. Native copper formation occurs at the initial stages of lava flows cooling. Disseminated mineralization of copper, nickel, iron, silver was deposited with palagonite and chlorite. These native metals came to the surface with basaltic magma in small quantities but due to redistribution during these transformations the ore deposits were formed. It is likely that quartz, sericite, montmorillonite, carbonates, sulfides, barite, and formed higher anomalies of gold, silver, lead and mercury were formed in the later stages of the geological activation.

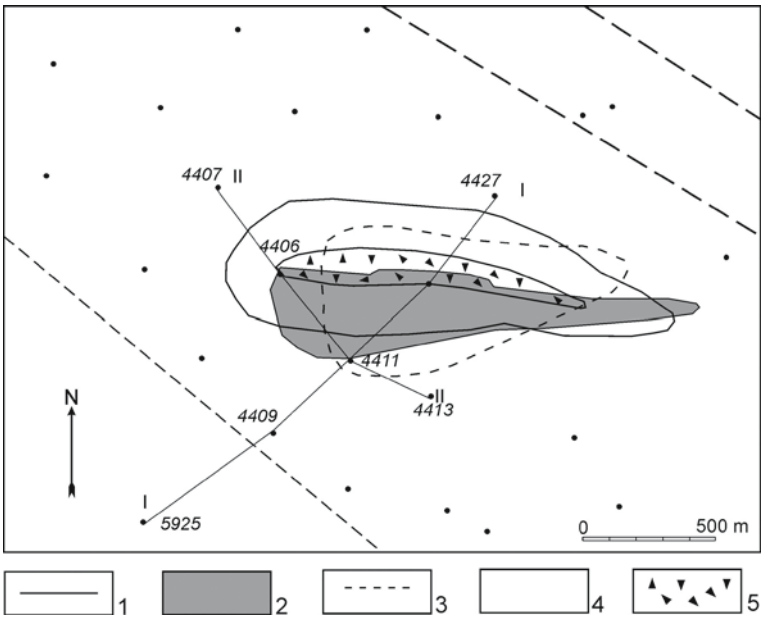


Figure 10. Sketch map of distributions zones of secondary mineralization, fracturing and noble metals in the Ratno Beds (lower flow): 1 – zone of fracturing, 2 – zone of silification and carbonitization; 3 – zone of silver and gold high concentrations, 4 – zone of chlorites-zeolites-palagonite-calcedony; 5 – brecciation's zone

## CONCLUSION

Neoproterozoic flood basalt are enriched with native metals mineralization, which is represented with native copper, iron, silver, nickel, gold, chromium. The correlation of Cu-Ag-Fe and Au-Ag are traced. The Ratno Beds lowest flow within the Chartoryisk fault zone is strongly altered. Regional alterations are chloritization, zeolitization, palagonitization. These changes are associated with native

iron, nickel, copper, silver, lead. Local alterations are silicification, carbonatization, and the sulfides formation, which are confined to the increased fracturing and brecciation zone. Geochemical anomalies of gold and silver are associated with these processes.

Native metals mineralization is associated with the sublatitudinal brecciation zone of the middle of the lowest flow. The last one is not associated with the northwestern lineaments of Chartoryisk fault zone.

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## STRESZCZENIE

Wzory rozprowadzenia drugorzędnej mineralizacji i kwestia tektonicznej kontroli mineralizacji powinny zostać rozpoznane w celu identyfikacji cech formowania się metali naturalnych w pokrywach lawowych z neoproterozoiku (Wołyń, Ukraina). Metoda klasyfikacji zmian pozwoliła na stworzenie mapy pęknięć w strukturach sedymentacyjnych w Ratnie w najniższym potoku w celu określenia intensywności pękania skał w strefie uskoku w Czartorysku. W celu ustalenia cech rozprowadzania mineralizacji metali naturalnych w neoproterozoicznych bazaltach przeprowadzono badania mineralogiczne, petrograficzne i geochemiczne. Analiza chemiczna skał wulkanicznych z miedzią, srebrem i złotem została wykorzystana do stworzenia schematów rozprowadzania metali w najniższym potoku bazaltu w strukturach sedymentacyjnych w Ratnie.

Dzięki temu dowiadujemy się, że skały wulkaniczne w strefie uskoku w Czartorysku przeszły wiele zmian. Neoproterozoiczne pokrywy lawowe przeszły zmiany w sposób nierównomierny i charakteryzują się podwyższoną koncentracją metali szlachetnych.

Regionalne zmiany przybierają formę palagonitu, chlorytu, zeolitów, chalcedonów i analcymów. Wykazano, że kształtowanie nasyconej mineralizacji metali naturalnych (miedź, srebro, nikiel, chrom) jest związane z regionalnymi zmianami w potoku bazaltu w Ratnie. W strefach o podwyższonym pękaniu i brekcji występują kwarc niskotemperaturowy, karbonity i siarczki rozprowadzane miejscowo. Miejsca ostatniej mineralizacji metali (złoto, srebro, ołów) również są miejscowe i związane ze strefami brekcji.