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### PECULIARITIES OF THE DISTRIBUTION OF THICKNESS AND PALEO-SURFASE RELIEF OF BASALTS OF LUCHYCHI STRATA (WESTERN VOLYN)

Purpose. The main purpose of this paper is to investigate the peculiarities of the spatial distribution of thickness and paleorelief of continental flood basalts of Luchychi stratum of Ratne suite of the Ediacaran of the Ratne-Kamin-Kashyrskyi Area in Western Volyn using maps of the thickness and relief of the paleosurface. The study also focuses on correlation between the specified parameters of the stratum and the spatial change of concentrations of native mineralization and its localization relative to the roof (sole) of the stratum. Method. The research applies a number of methods, including field geological surveys; petrography of basalts, structural features (degree of crystallization of mesostasis, structural position of minerals and, in particular, copper, ratio of globular formations and minerals that surround them, relationship between globules), macro- and microtextural features of rocks; geochemical research: determination of the content of the main chemical components of the rocks by the method of gross chemical analysis and copper content; geological and morphostructural studies: construction of a map of paleorelief and thickness of continental flood basalt of the Luchichiv stratum (according to the section of wells). Results. The constructed maps of the thickness and paleo surface of the Luchychi stratum show the spatial variability of the basalt thickness and the reflection of the effective tectonic situation on its paleo surface, which can be "read" by relief elements. It is established that high copper content in basalts is spatially confined to areas of maximum thickness and shifted vertically to the near-roof and, partially, plantar parts of the basalt thickness, and the degree of their crystallization increases in the direction of the inner parts of bodies. This situation with the spatial arrangement of native mineralization indicates the existence within these areas of local isolated thermostated systems. They evolved in their internal parts in conditions close to the intrusive ones (relatively slow decrease in melt temperature, crystallization of rock differences almost devoid of volcanic glass - dolerite-basalts with the transition to dolerites in the central part). Such physicochemical conditions caused long-term migration of gaseous, gaseous-liquid and liquid fluids, providing concomitant extraction, concentration, transfer and deposition not only of native copper, but also a number of petrogenic oxides (alkalis, iron, partially calcium, silicium). The latter subsequently formed a number of low-temperature minerals, the most common of which are zeolites, calcite, and iron compounds. In areas with small and minimum thickness of basalts, the above facts are observed in a reduced form, and in some places are virtually absent. The research has established the complete absence of signs of hydrothermal copper ore mineralization. The latter indicates the lack of evidence about the formation of native mineralization of the hydrothermal type. We provide the geological and petrogeochemical facts that give grounds to consider the scenario of the process of formation of native copper mineralization in relation to the fluidliquidation hypothesis, earlier developed and proposed by the authors. Scientific novelty. For the first time, the study made it possible to construct maps of the thickness and relief of the paleo surface of the basalts of the Luchychi strata of the Ratne-Kamin-Kashyrskyi area of Western Volyn. Based on the actual material it is shown that the vertical distribution and localization of native mineralization within basaltic bodies are naturally related to their thickness. The value of native copper is directly related to body thickness, reaching a maximum in areas with maximum thickness and background values at the minimum thickness. Practical significance. For the first time, geological, petrographic, geological and morphostructural data were compared with the copper content in basalts of the Luchichi stratum. The proposed approach can be used by geological production organizations in conducting exploration work to prepare promising areas for exploration of the North-Hirnyky and Rafalivka ore fields (ore nodes) within the Ratne Horst anticline. The obtained original material can be distributed as a new method of native mineralization search in other areas of the continental flood basalts distribution.

Key words: continental flood basalts, Ediacaran, thickness, paleorelief, Luchychi stratum, Ratne-Kamin-Kashyrskyi area, Western Volyn.

#### Introduction

The constant growth of Ukraine's needs in copper has increased the interest in the recent decades to the continental flood basalts of the Western Volyn as a promising source of copper raw materials [Prikhodko et al., 1993, Prykhodko, 2005; Melnychuk, 2010]. Native-copper mineralization is associated with sedimentary-volcanic Volyn series of Ediacaran of the platform cover of the Volyn-Podillya plate of the Eastern

European platform. As part of the series, the Gorbash sedimentary volcanic-sedimentary and Zabolottya, Babyne, and Ratne volcanic suite have been identified (starting from the oldest sediments) [Volconyk, 1975]. Volcanogenic deposits are of the greatest interest and possible prospects for the detection of industrially significant native mineralization. We studied them during 2006–2012 within the Ratne–Kamin-Kashyrskyi area, which is a territorial part of the Volyn Copper

Ore Province. The latter is located in the joint zone of the Volyn Paleozoic uplift and the Volyn-Podillya monocline (Fig. 1) Melnychuk, 2014]. Already known North-Hirnyky and Rafalivka ore fields (ore nodes) are located along with this area on the wings of Ratne Horst-Anticline. [Melnychuk, 2018]. We believe that our research and the results obtained can be disseminated primarily for the successful conduct of exploration work and the approbation of the proposed method.

#### Purpose

A significant amount of geological materials was collected during study of the basalt rocks of trapps. The data were obtained from the study of the internal structure of the suite and strata (establishment and nature of boundaries between suites, strata and individual flows within the latter, the thickness and internal zonation of individual flows, the degree of crystallization), thicknesses of individual stratigraphic units and flows. Particular attention was paid to the spatial distribution of copper mineralization within stratigraphic units and individual flows. At the same time, the study analyzed the materials on the copper concentration distribution in wells that completely or partially crossed one or another stratigraphic unit, morphology of copper formations, their structural position, and petrographic features of basaltic differences [Fedoryshyn et al., 2010].

Empirically, high and maximum concentration of copper was linked to the flows of medium and maximum thickness for particular wells that crossed a certain strata or suite., And copper mineralization in these wells tended to the roof, partially plantar parts of the flows.

Analysis of those results led toreasonable questions Firstly, what is the relationship between the thickness of the flow and the value of native copper? Secondly, under what conditions is the completion (completeness) of the extraction process, further concentration and movement to the final localization achieved?

Therefore, the purpose of our study is to find out whether the empirically obtained results for individual wells will be valid for the entire Ratne–Kamin-Kashirskyi area. The research takes into account the long tectonic events in the area (including the Hercynian stage of tectonic activity), stratigraphic gaps in the process of successive formation of continental flood basalts and their overlying sedimentary stratum by the Phanerozoic.

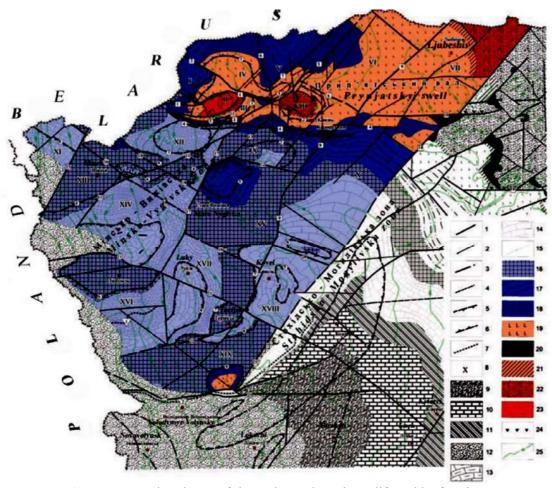
To achieve this purpose, for the first time, maps of thicknesses and relief of paleo-surfaces for all stratigraphic units were built. However, in this article we confined the materials to those that relate to the Luchychi strata of the Ratne suite. It is explained by the manifestation of the ore-volcanic activity processes within it, which in our opinion, demonstrates maximum completeness, and, therefore, the collected material is the most comprehensive.

#### Actual material

The promising Ratne–Kamin-Kashyrskyi area spatially covers the joint zone of the Volyn Paleozoic uplift and the Volyn-Podillya monocline. Sediments of the continental flood basalts of the Ediacaran are usually recorded here at depths of 150-400 m. More than 200 wells were drilled within the district. We processed the core material that comprised 117 wells for the Luchychi stratum. This made it possible to construct a map of thicknesses and paleorelief with the maximum possible reliability. Data on these wells included absolute marks of the surface and sole, and the results of determining the copper content. The completeness of the information from the well logs allowed us to determine the number of flows for each of them and to make a deep link between sampling for copper content. Actually, the obtained material became the basis for the construction of maps of thicknesses and paleorelief, in this case, for the Luchichi strata. In parallel, we studied the petrographic features of basalts of the hardening zone, soles, roofs, internal zones of flows of different thickness, structural position of different morphological differences of copper and magnetite formations, their structural position, vertical distribution of copper content relative to individual flows, and features of globular texture.

#### Methodology

- 1) field geological research: description of lump of rocks and core, collection of samples for analytical studies;
- 2) petrographic studies of the composition, texture (degree of de-crystallization of mesostasis), macroand microstructural features of rocks;
- 3) geochemical research: determination of the content of the main chemical components in rocks by the method of gross chemical analysis (at the chemical laboratory of the department of geochemistry of sedimentary strata of oil and gas provinces of IGGCM of the NAS of Ukraine, analysts L. K. Bilyk, V. L. Kryzhevych):
- 4) geological and morphostructural research: construction of maps of thicknesses (based on the available thickness marks in all wells in the studied area, isolines of thickness are constructed and digitized by means of the computer software MapInfo) and paleo-surface relief maps (based on the absolute marks of height, isolines of a surface are constructed and digitized), their correlation with each other and comparison with copper content.



**Fig. 1.** A tectonic scheme of the Volyn Paleozoic Uplift and its framing, according to [Melnychuk, 2014]:

1-4 - faults: 1 - main valid; 2 - main probable; 3 - end Secondary valid; 4 - end Secondary probable (the numbers in the squares): 1 – Lagozhansk; 2 – Kortelsk; 3 – Ratne; 4 – West-Ratne; 5 – Schitinsk; 6 – Sirchansk, 7 – Katushsk; 8 – Bronnitsk; 9 – Kamin-Kashirsk; 10 – Politsk; 11 – Krimnivsk; 12 – Datinsk; 13 – Zamshansk; 14 - Novochervyschansk; 15 - Pulminetsk; 16 - Zabolottja; 17 - Teklinsk; 18 - Gransk; 19 - Smidinsk; 20 – Steblensk; 21 – Lyubomlsk; 22 – Kratsk; 23 – Tulichivsk; 24 – Volodymyr-Volinskiy; 25 – Krasnostav; 26 – Kuhotskovolsk; 27 – Bilsk); 5–7 – plicated structure: 5 – brachyanticlines (numbers in circles): 1 – Ratne; 2 – Hoteshiv; 3 – Katushsk; 4 – Shack; 5 – Teklinsk; 6 – Lyubomlsk; 7 – Turiysk; 8 – Ovadniv; 9 – Krychevets; 10 - Volodumiriv; 11 - Lokachiv); 6 - brachysinclines (figures in circles): 1 - Zalisnynsk; 2 - Doshnivsk; 3 – Holovnyansk; 4 – Ladin-Smidensk; 5 – Bilashivsk; 6 – Solovytsk; 7 – Podgorodna; 8 – Krylyvetsk; 9 - Bubno-Holobska); 7 - flexures (the numbers in the triangle: 1 - Mosyrsk; 2 - Ustylug-Holobska); 8 - tectonic blocks that bounded by major faults: I - Divynsk; II - Girnitsk; III - Postupelsk; IV - Richytsko-Brodiv; V - Schedrohirsk; VI - Katusk; VII - Lyubeshov; VIII - Hoteshiv; IX - Veryhyn; X - Polytsk; XI – Tomaszewsk; XII – Zalisyn; XIII – Nikolsk; XIV – Holovnyansk; XV – Chevelsk; XVI – Lyuboml; XVII – Lukiv; XVIII – Kovel; XIX – Ovadniv; 9 – formation of clay-sandstonecoal-bearing (C<sub>1</sub> ol, vl us, pr, iv, ls, bz, mr) structural storey of early Carboniferous; 10-15 - formation of structural storey of upper-middle Devonian: 10 – carbonate-siliciclastic, in places molasa (C<sub>1</sub> ol, hr, kl; D<sub>3</sub> vv, zpb, lt); 11 – carbonate (D<sub>3</sub> rt, mt, zl, rm); 12 - terrigenous-sulfate-carbonate (D<sub>3</sub> pb, D<sub>2</sub> bt, kr, pd, vm, pl, lp); 13-15 - formation of structural storey of Ordovician-lower Devonian: 13-14 - clay-carbonate (13 - under formation of grey graptolit-limestoneargillites (D<sub>1</sub> sl, S<sub>2</sub>-D<sub>1</sub> tm, S<sub>2</sub> gč, ml, nv, ol, zb, tr, gr, S<sub>1</sub> kl); 14 - under formation of limestones (S<sub>2</sub> ks, rd, vt, lg, gr, tr, sb,  $S_1$  kr, sg); 15 – conglomerate-sandstones-limestone ( $O_2$  gr,  $O_1$  sm1), limestones ( $O_2$  pč,  $O_1$ sm2); 1–18 – formation of structural storey of upper Vendian–Cambrian: 16 – transgressive clay-sandstone ( $\mathfrak{C}_3$  vr,  $\mathfrak{C}_2$  gt, lc,  $\epsilon_2$  or, dm, lb, sv), clay-sandstone with glauconite ( $\epsilon_1$  rv, st), 17 – siltstone-sandstone, variegated ( $\epsilon_2$  zt, rk), 18 – volcanoclastic clay-conglomeratesandstone (V2 kl, rz, bz); 19-22 - formation of structural storey of lower Vendian-Riphean: 19 – traps effusive  $(V_1 zb, bb, l\check{c}, zr, jk)$ ; 20 – intrusive traps  $(vV_1 ht)$ ; 21 – clastogenic-clay-sandstone  $(V_1 zb, bb, l\check{c}, zr, jk)$ ; 20 – intrusive traps  $(vV_1 ht)$ ; 21 – clastogenic-clay-sandstone  $(V_1 zb, bb, l\check{c}, zr, jk)$ ; 20 – intrusive traps  $(vV_1 ht)$ ; 21 – clastogenic-clay-sandstone  $(V_1 zb, bb, l\check{c}, zr, jk)$ ; 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24 – melange of sophisticated origin (breccia manifestations); 25 – isolines of the premesozoic to the surface. Volyn Paleozoic Uplift displayed colors.

### Brief information about the geological structure of Ratne-Kamin-Kashyrskyi area

Continental flood basalts on the territory of the Eastern European platform are quite widespread. Volcanic-sedimentary formations, which are a part of the Volyn series, form a strip up to 150 km wide along the Teiseire—Thornquist line (in the direction from Lublin to Chisinau). Volyn volcanites are located in the northern part of the region [Volovnik, 1975; Velikanov et al., 1983; Volovnik, 1990].

The platform cover consists of a strata that vary in terms of facies affiliation, composition and age. The Riphean red terrigenous formation – a thick (up to 600 m) section of sandstones of the Polissya series (R<sub>2-3</sub>pl), overlapped by the formations of the Volyn series, lies with a sharp angular and stratigraphic unconformity on the Early Proterozoic crystalline basement (Fig. 2).

The sedimentary-volcanic stratum of the Volyn series of the Lower Ediacaran unites four suites (from bottom to top). Gorbashi is basal coarse-fragmentary-terrigenous suite(up to 50 m); Zabolottya, Babyne and Ratne are exclusively volcanogenic with a total thickness of more than 450 m [Prikhodko et al., 1993; Melnychuk, 2010].

The Luchychi strata is stratigraphically part of the Ratne suite and lies directly on the Babyne suite. Up to 4 flows of toleite basalts can be distinguished according to geological features in the wells that open the most complete section of the Luchychi strata. The volcanic-terrigenous stellar stratum is above the section in the Ratne suite. The section of the Ratne suite is completed by the Yakushi volcanic stratum, which contains up to 7 flows, lavoclastic breccias, and various tuffs. Volcanogenic formations are grouped together under the name of trapps, which are used for platforms. Rocks of intrusive facies such as dolerites, gabbro-dolerites, and dolerito-basalts can be found in the continental flood basalts (and this is typical for Volyn continental flood basalts). All these basaltoid rock deviations are considered to be derivatives of poorly differentiated basalt magma [Volovnik, 1975; Prykhodko, 2005].

#### Results and discussion

Below are the results of research on the Luchychi strata, obtained on the basis of the above-mentioned factual material. Partially obtained results have been published in Ukraine and abroad [Batsevych et al., 2018; Batsevych et al., 2019; Naumko et al., 2020].

#### Ratne suite V<sub>1</sub>rt

Ratne suite conformally occurs over Babyne suite. Basalt flows, lava-tuff-breccias, tuffs alternate in its section. The works of recent years on Ratne-KaminKashyrskyi Area allowed us to divide the Ratne suite into three strata (from the sole to the roof): Luchychi, Zoryane and Yakushiv. In this article, we focused on the detailed study of the Luchychi stratum.

**Luchychi stratum** –  $V_1$ lč. Deposits of the Luchychi stratum of the Ratne suite of the Volyn Ediacaran series within Ratne–Kamin-Kashyrskyi Area are composed of several (up to four) flows of toleite basalts, separated by packs of lavoclastic breccias, sometimes with layers of different fragments of pyroclastic rocks of basaltic composition. Basalts are dark gray, with a greenish tinge, fine crystalline, amygdaloide or aphanitic, occasionally with cracks. The upper parts of the basalt flows are often weathered.

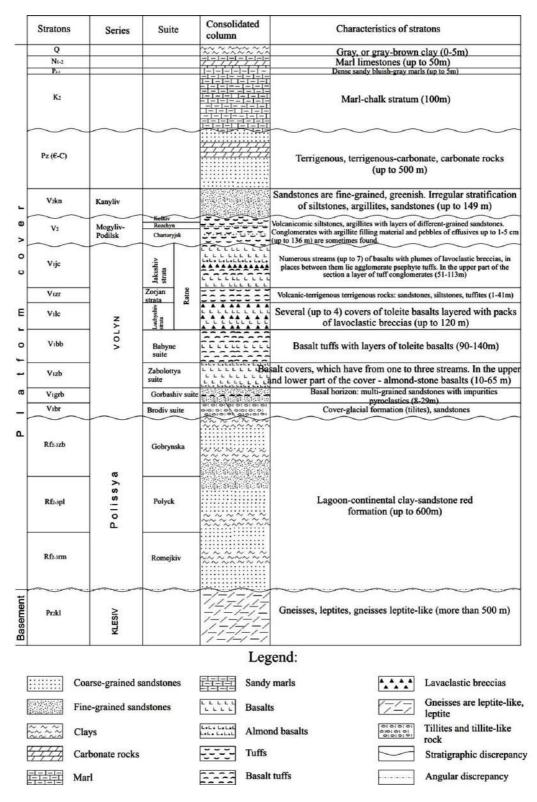
We studied the peculiarities of their internal structure on the example of the most powerful flows, as L. Chetverikov once did on the natural outcrops of Siberian trapps on the banks of the Vilyuy River [Chetverikov, 1959], with the purpose of establishing an actual number of poured on the surface flows. According to the study, it was established [Fedoryshyn et al., 2012] that the central zone of the flow is represented by rocks of dolerite-diabase composition with typical structures. At the same time, liquation-type structures (globular, nest-globular, lenticular-globular) are widely developed in this zone. These structures indicate the maximum possible manifestation of the liquation for the flow. And the crystallization conditions in this zone were similar to those for a "closed system". In the following zones of flow (zone of Mandelstein, transition and hardening) the degree of crystallinity of rocks naturally changes, the size of globular formations decreases, a larger volume of volcanic glass appears, and the degree of decrystallization inside the globules changes. The presence of at least two phases of preserved volcanic glass can be considered indisputable and reliable evidence of liquation within the flow. This condition is fulfilled in the studied rocks. According to one of the most authoritative works of recent decades [Drever, 1960], a number of petrographic proofs of the liquation were established at the microscopic level. However, it should be noted that they appear with different completeness in the flow section.

In this context, it should be noted that there is the highest copper content in the basalts of the Luchychi strata, in which the liquation processes were most clearly manifested at the maximum thickness. It reaches 1200 g/t in the roof (in the intervals from 16–18 to 20 m distance from the roof) (well No. 8262). In addition, there is a general trend of increasing the intensity of copper mineralization up the section (Fig. 3) [Naumko, Batsevych, 2016].

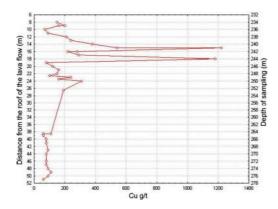
Analysis of the surface of the paleorelief (Fig. 4) and the spatial distribution of the thickness of the deposits of the Luchichi strata (Fig. 5) showed a vivid reflection of the elements of block tectonics in the relief of this area. This demonstrates the following.

The central latitudinal band of the studied area, its southern and northern slopes are characterized by maximum absolute marks. We are able to observe a noticeable decrease in relief to the north and south of this strip. The established relief pattern enables fairly accurate reproduction of the specified area block structure, as well as the spatial location of the

main tectonic faults and their satellites. The latitudinal direction of the main faults caused a handful of latitudinally oriented uplift, and the diagonal faults, which are traced by linear depressions, and are satellites of the main faults.



**Fig. 2.** A schematic consolidated section of the continental flood basalts of Volyn-Podillya (according to [Melnychuk, 2010]). Scale 1:10 000.



**Fig. 3.** Variations of copper concentrations in the section of the Luchychi stratum of the maximum thickness (well No. 8262).

The variations in thickness of the basalts (Fig. 5) demonstrates that the largest accumulations of lava formations are characteristic of the lower parts of the relief. They gradually decrease as the absolute marks increase. The range of thickness changes varies from 3.3 m to 95.2 m (Fig. 5). All this corresponds to the formation conditions of continental flood basalt rocks of all provinces of this type without exception, taking into account that trapps are formed by the active manifestation of fractured volcanism.

In the method mentioned above, we established a spatial combination of high concentrations of native copper and volcanic eruptions [Batsevych et al., 2016]. Theompiled maps allow us to spatially track the boundaries and configuration (scale) of potential industrially significant native mineralization. The real possibility of its formation due to liquation processes was highlighted in earlier publications as a hypothesis of fluid-liquation formation of native mineralization [Naumko et al., 2016, 2017].

It should be noted that there are different views among Ukrainian researchers on the nature of the native mineralization in trapps. They are substantiated differently and are based on different volumes of the studied material.

The point of view of hydrothermal formation of native mineralization is the most common and discussed among geologists. Let us consider the main features that are inherent in ore hydrothermal systems. The most common forms of hydrothermal bodies are veins, stockworks, layered and irregularly shaped deposits. They reach a length of several kilometers with a width of several centimeters to tens of meters. Hydrothermal bodies are surrounded by a scattering halo of the elements that form them (primary scattering halos), and the adjacent rocks are hydrothermally transformed. Among the processes of hydrothermal changes in rocks, the most common are quartzification, alkaline type transformations, which are caused by the introduction of potassium and the subsequent formation of muscovite, sericite and clay minerals, and the introduction of sodium – the formation of albite. According to the composition of the majority of minerals, the following main types of hydrothermal

ores are distinguished: 1) sulfide, which form deposits of copper, lead, zinc, molybdenum, bismuth, nickel, cobalt, antimony and mercury; 2) oxide, typical for deposits of iron, tungsten, tantalum, niobium, tin, uranium; 3) carbonate, characteristic of some deposits of iron and manganese; 4) native, known for gold, silver; 5) silicate, which form deposits of non-metallic minerals (asbestos, mica) and some deposits of rare metals (beryllium, lithium, thorium, rare earth elements). Hydrothermal and other views on the origin of copper in the trapps studied by us are systematized and set forth in [Kvasnytsia et al., 2009].

Obviously, it is necessary to have conditions close to intrusive to form and develop the ore-generating system as part of the fluid molten physicochemical system, i.e. to ensure the possibility of separating ore-forming chalcophilic solutions from silicate magmatic melt [Ovchinikov et al., 1982]. Such conditions are achieved only at significant thicknesses of flows, when a promising rock-ore complex is slowly cooled by a natural drop in temperature. It has time to undergo processes of liquation, extraction, transfer and concentration of copper [Nesterovych, 2014].

This logically follows from our proposed new fluid-liquation hypothesis of the native mineralization origin [Naumko et al., 2016, 2017]. According to it, the process begins with the actual liquation phenomena at the magmatic stage and continues at the postmagmatic stage. It is recorded by the transition from early high-temperature inclusions melts [Bakumenko, Fedoryshyn, 2005] to the late, highly concentrated water-salt inclusions in cooling cracks at the hydrothermal stage of mineralogenesis [Nesterovych, 2014]. Thus, the liquation process is multi-stage and is observed at different stages of the evolution of the ore-rock system.

The revealed facts of fluid-liquation interaction at different stages of formation of native copper deposits indicate [Naumko et al., 2013] that copper in the form of small droplets already existed in the melt at the time of formation of continental flood basalts (raising magmatic melt and spreading it on the day surface). This is evidenced by small impregnations of native copper in the first porphyry-like crystals of plagioclase. Thus, copper droplets were actually formed before the appearance of the first crystalline phases. This point can be attributed to the first stage of liquidation of the ore phase. It is fair to say that in the same way the phase of native iron appeared, which was discovered by many researchers. In the process of liquation, the copper droplets separated from the silicate melt, then were redistributed and transferred to the upper horizons of lava flow. According to our data, the transfer of copper droplets to the near-surface part of lava flows began with gas bubbles (the presence of tuffs and pysolites indicates a significant gas saturation of the melt [Nesterovich et al., 2014]). The processes of copper migration to the effluent surface could also be intensified due to the presence in the melt of highly thermobaric streams of liquid carbon dioxide [Kvasnytsya et al., 2009]).

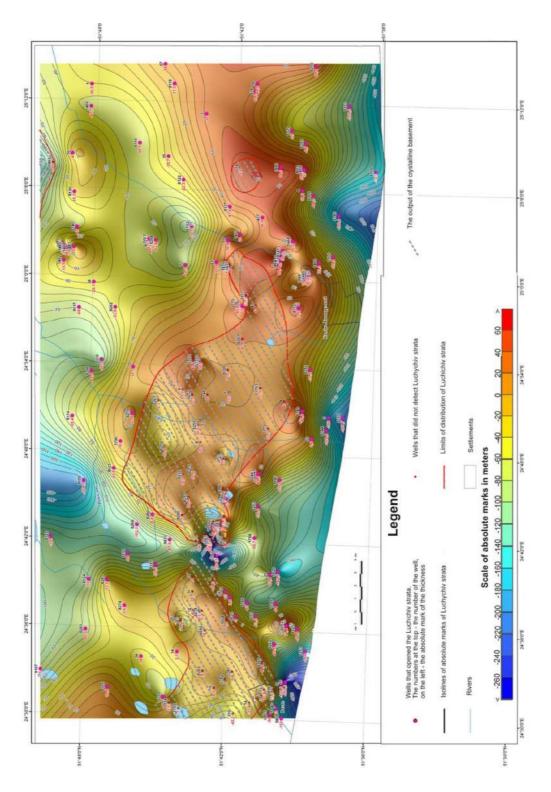


Fig. 4. The paleo-surface relief map of of basalts of the Luchychi stratum within the Ratne–Kamin-Kashyrskyi Area. Scale 1:100 000 (Yu. S. Myshchyshyn with the direct participation of N. V. Nesterovych (Batsevych).

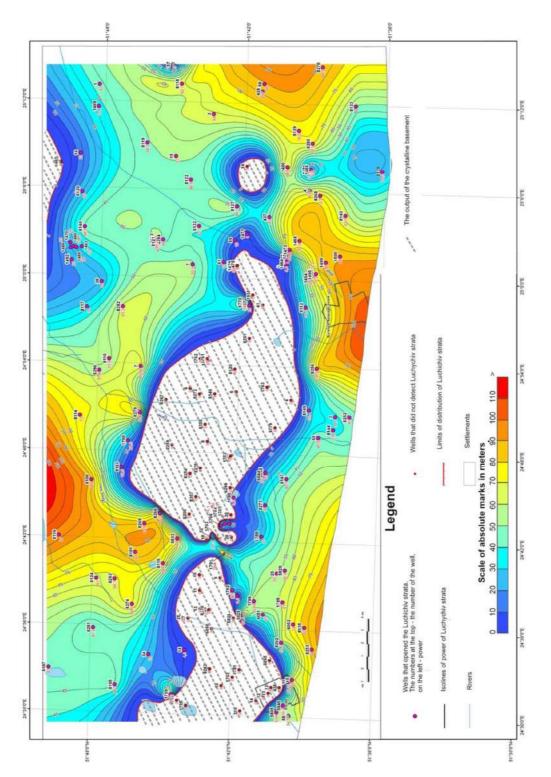


Fig. 5. The thickness map of basalts of the Luchychi stratum within the Ratne–Kamin-Kashyrskyi Area. Scale 1: 100 000 (Yu. S. Myshchyshyn with the direct participation of N. V. Nesterovych (Batsevych).

Then, copper was transferred by chloride complexes, in particular, during its transportation in the direction of the quenching zone of the flow. This explains the positive correlation of chlorine and copper contents and the "dumping" of the latter on the corresponding geochemical barriers in the process of lowering the temperature and supersaturation of copper solutions. This is confirmed by the significant contents of chlorine ion (CI) in water extracts from basalt rocks of the study area, which reach 266.3–568.0 mg/kg [Nesterovych, 2014].

The high ability of Cl to extract metals from aluminosilicate melts has long been well known [Malinin, Hitarov, 1984]. Experimental studies [Barsukov, Ryabchikov, 1980] showed a virtually universal role of Cl in metal transfer along with the constant participation of chlorides in deep magmatic systems. It involves considering the behavior of ore elements in inseparable connection with the behavior of chlorine. [Weihua, McPhail, 2005] provide the latest data on the migration of copper in a fluid-saturated medium in chloride complexes, such as CuCl<sub>(aqueous)</sub>, CuCl<sub>2</sub>-, CuCl<sub>3</sub><sup>2</sup>- and CuCl<sub>4</sub><sup>3</sup>. In fact, such a course of the process of formation of native mineralization is facilitated by the considerable thickness of individual flows of basalts and volcanic formations in general.

It should be noted that there is some inhomogeneity in the distribution of native mineralization. It is due, on the one hand, to the uneven distribution of gas-fluid flows (the paths of these flows are reflected in the uneven distribution of low-temperature mineral phases). On the other hand, cracks, primarily of the contraction type, played not the last role in the inhomogeneous distribution of copper ore. Cracks for residual melt are a kind of "shock" medium. There is an instantaneous change in physicochemical conditions, which can sometimes lead to explosive phenomena and instantaneous liquation and crystallization of the residual melt. We observed similar phenomena, in particular, in the formation of products of granitoid composition or liquation veins with a clear division into native and ferruginous phases. Zones with such formations are most often confined to the roof parts of the flow, less often closer to the sole.

Actually such and similar fluid-conducting zones, according to our data [Naumko, 2006; Naumko et al., 2013a, 2013b], could migrate fluids of magmatogenic origin. The presence of these fluids is an important prerequisite for new genetic and practical conclusions, which, in the end, will help identify the migration processes of the ore phase and detail the criteria for predicting copper mineralization in the trapps of Volyn [Melnychuk, 2018].

The study presented above, allows us to conclude that the main part of copper was formed by fluid-liquation interaction. D roplet-like release of copper, which is characteristic of liquation processes. A nd besides, the typical signs of hydrothermal ore formation are not observed.

#### Scientific novelty

For the first time, maps of the paleo-surface thickness and relief of the Luchychi strata basalts were constructed. Luchychi strata is an integral part of the continental flood basalts of Ratne–Kamin-Kashyrskyi area in Western Volyn, The study revealed the role of the tectonic factor in the formation of the block morphostructure of the surface of the Luchychi stratum of Ratne–Kamin-Kashyrskyi area. It also defined the ways of lava spreading and the area of its maximum accumulation .

Based on the regular correlation between the copper content and the basalts thickness of the Luchychi stratum, it became possible to spatially delineate potentially promising ore areas, where the ore-producing process was most pronounced. Therefore, the volume of exploration work can be significantly reduced. The obtained original material can be offered for testing not only within Western Volyn, but also in other areas where continental flood basalt is widespread.

#### Practical significance

The analysis of the original materials obtained by us, will help to identify the temporal and spatial relationships between the components of the Volyn series and the lower- and upper-located sedimentary strata. It will facilitate identification of fluid-conducting zones confined to the intervals of de-densification (fracturing) or to angular and stratigraphic unconformity between the deposits – the main migration routes of mineral-forming fluids, which were the source for the formation of paragenesis with native copper. In this context, it is planned to use them in search and evaluation works in order to prepare promising ore occurences (deposits) for exploration, in particular, of the North-Hirnyky and Rafalivka ore fields (ore nodes) within the Ratne Horst Anticline.

#### **Conclusions**

- 1. For the first time, the research resulted in building maps of the thickness and paleorelief of basaltic flows of the Luchychi strata of Ratne–Kamin-Kashyrskyi area in Western Volyn. The study was based on the data of the materials of wells drilled for many years for mapping and exploration purposes.
- 2. According to the data on determining the copper content in basalts and the vertical distribution of copper concentrations, it was established that the values of copper concentrations are spatially correlated with the thickness of individual flows and the total thickness of basaltic rocks of Luchychi stratum. At the same time, it was found that there is a direct relationship between the total copper content and the thickness of the flows in specific wells, and the maximum concentrations of copper mineralization are spatially confined to the roof (rarely to the bottom) parts of the flows. Instead, in the flows with a minimum

- thickness, we usually observe copper content at the level of Clark.
- 3. Tectonic rearrangements, which appeared after the formation of continental flood basalts, somewhat complicated the spatial picture of the spatial location and integrity of the initially integral ore fields and, possibly, individual ore bodies. This is eloquently evidenced by the morphostructural map of the paleosurface, serving as a reliable reflection of paleotectonic movements.
- 4. The basic principles of functioning of inextricably linked physicochemical, magmatic and oregenerating systems are established. Spatial features of copper mineralization distribution, numerous petrographic features (discovered for the first time) and spatial-structural location of native copper in basalts give grounds to claim that the basaltic magmatic system and its ore-generating part correspond to the principles set forth by us in the form of the fluid-liquidation hypothesis of continental flood basalts and native mineralization.
- 5. In the case of taking our research as a basis, the data obtained can be used as a fundamentally new method of exploration work for copper, as most of the necessary and most costly work was carried out by manufacturing companies in previous years.

#### References

- Bakumenko, I. T., Fedoryshyn, Yu. I. (2005). Melt inclusions in plagioclases of Volynian basalts. *Mineralogical Museums*. Saint-Peterburg: Department of Mineralogy, SPbSU, 215.
- Barsukov, V. L., Rjabchikov, I. D. (1980) On the source of ore material. *Geochemistry*, 10, 1439–1449 (in Russian).
- Batsevych, N. V., Myshhyshyn, Yu. S., Naumko, I. M. (2018). Relief of paleo-surfase and thickness of basalts of Luchychi Strata of the trappean formation within the limits of the Ratno–Kamin-Kashyrsk Area (Western Volyn). Modern Problems of Lithology of Sedimentary Basins of Ukraine and Adjantent Territories: Proceedings of the International Scientific Conference (Kyiv, Ukraine, September 24–26, 2018). Kyiv, 2018, 16.
- Batsevych, N. V., Naumko, I. M., Bilyk, L. K. (2016). Petrochemical features of volcanites of the trap formation of the joint zone of the Volyn Paleozoic uplift and the Volyn-Podillya monocline. *Geodynamics*, 1 (20), 75–93 (in Ukrainian). DOI: 10.23939/jgd2016.01.075.
- Batsevych, N., Naumko, I., Fedoryshyn, Yu. (2016). Peculiarities of copper behavior in mineral-forming fluids during the formation of native mineralization in the volcanites of trap formation of the Western Volhynia. *Tenth scientific readings named after Academician Yevhen Lazarenko: materials (Lviv-Chinadiyeve, September 9–11, 2016)*. Lviv: LNU imeni Ivana Franka, 13–15 (in Ukrainian).
- Batsevych, N. V., Naumko, I. M., Repyn, I. V. (2019). Some features of the relief of the paleo-surface

- and the distribution of basalt thicknesses of the Zabolottya suite of trap formation within Ratno-Kamin-Kashyrsk Square (Western Volyn). Achievements and prospects for the development of geological science in Ukraine: Proceedings of the scientific conference dedicated to the 50th anniversary of the Institute of Geochemistry, Mineralogy and Ore Formation. M. P. Semenenko NAS of Ukraine (Kyiv, May 14–16, 2019), Kyiv: IGMR of the NAS of Ukraine, 2, 13–15 (in Ukrainian).
- Chetverikov, L. (1959). Features of the structure of lava sheets in the river basin Nizym (Central part of the Tunguska basin). *Geology and exploration*, 3, 65–79.
- Drever H. Jf. (1960) Immiscibility in the picritic intrusion at Igdlorssuit, West Greenland // Internat. Geol. Congr. Report (Nord. Copenhagen). S. 21, Part 13, 47–58.
- Fedoryshyn, Yu. I., Tkachuk, A. M, Nesterovych, N. V., Khomyakova, O. G, Repyn, I. V. (2010) Structural and petrographic variability of the internal structure of basaltic outcrops of the Volyn trap formation in connection with liquation processes. *Mineral. Collection*, 60, 1, 47–57 (in Ukrainian).
- Fedoryshyn Yu. I., Naumko I., Nesterovych N., Jakovenko M., Triska N. (2012) The nature of almond-shaped formations in the basalts of Volyn (ontogenic aspect). *Mineral collection*. 62, 1, 63–82 (in Ukrainian).
- Kvasnytsya, I. V., Pavlyshyn, V. I., Kosovskyi, Ya. O. (2009). *Native copper of Ukraine: geological position, mineralogy and crystallogenesis.* Kyiv: Logos (in Ukrainian).
- Lazarenko, E. K., Matkovskyi, O. I., Vynar, O. M., Shashkina, V. P., Hnativ, H. M. (1960). *Mineralogy of igneous complexes of the Western Volyn*, Lviv: Vyd-vo Lviv. Un-tu (in Ukrainian).
- Malinin, S. D., Khitarov, N. I. (1984). Ore and petrogenic elements in the system of magmatic melt-fluid. *Geochemistry*, 2, 183–196 (in Russian).
- Melnychuk, G. V. (2014). Tectonics and the origin of the Volyn Paleozoic uplift. *Geol. Journ*, 3 (348), 28–38 (in Ukrainian).
- Melnychuk, V. G. (2010). Geology and copper-bearing of the ower-vendian trappean complexes of southwestern part of the Easteuropean platform. *Thesis for a doctor's degree in Geology, by speciality 04.00.01. "General and Regional Geology"*, 2010 (in Ukrainian).
- Melnychuk, V. G. (2018). Criteria for forecasting copper mineralization in the trap Volyn. *Mineral. Collection*, 68, 1, 36–39 (in Ukrainian).
- Naumko, I. M. Fluid regime of mineral genesis of the rock-ore complexes of Ukraine (based on inclusions in minerals of typical parageneses): *Thesis for a doctor's degree in Geology by speciality 04.00.02.* "Geochemistry", 2006 (in Ukrainian).
- Naumko, I. M., Batsevich, N. V. (2016). On the role of fluids at different stages of the formation of native-copper concentrations in volcanics of trap formation of the Western Volyn. *Modern problems*

- of theoretical, experimental and applied mineralogy (Yushkin readings–2016): materials of the mineralogical seminar with international participation (Syktyvkar, Komi Republic, Russia, May 17–20, 2016). Syktyvkar, 245–246 (in Russian).
- Naumko, I. M., Batsevych, N. V., Fedoryshyn, Yu. I., Myshhyshyn, Yu. S., Repyn, I. V. (2020). Paleomorphostructural plans and thicknesses distribution of volcanites of the Vend trappean formation within the limits of the Ratno–Kamin-Kashirsk Area (Western Volyn). Precambrian: rock associations and their ore mineralization: Proceedings of the International Scientific Conference (Kyiv, September 22–24, 2020). Kyiv, 86–89. ISBN 978-966-02-9361-8 (electronic edition) (in Ukrainian).
- Naumko, I. M., Fedoryshyn, Yu. I., Batsevych, N. V. (2016). Fluid-liquation hypothesis of the origin of native mineralization in the volcanites of trap formation of the Western Volyn. *Reports of the NAS of Ukraine*, 9, 69–78 (in Ukrainian) DOI: https://dx.doi.org//10.15407/dopovidi2016.09.069.
- Naumko, I. M., Fedoryshyn, Yu. I., Batsevych, N. V. A new fluid-liquation hypothesis of the origin of native cooper mineralization in volcanites of trappean formation of the Western Volyn Area (Ukraine). *East European Scientific Journal*, 4 (20), 1, 41–50 (in Ukrainian).
- Naumko, I. M., Fedoryshyn, Yu. I., Nesterovych, N. V., Telepko, L. F., Sakhno, B. E. (2013a). Conditions for the formation of veinlet-impregnated mineralization in the sediments of the Luchychiv stratum formation of the joint zone of the Volyn Paleozoic uplift and the Volyn-Podillya monocline of the Western Volyn. *Reports of the NAS of Ukraine*, 10, 116–123 (in Ukrainian).
- Naumko, I., Pavlyuk, M., Nesterovych, N., Fedoryshyn, Yu., Triska, N. (2013b). The evolution nature of the processes of fluid transfer and localization of copper in the basic volcanites of trappean formation of the Western Volyn (on the example of the Luchychi stratum). *Geology and geochemistry of combustible minerals*, 1–2 (162–163), 42–59 (in Ukrainian).

- Nesterovych, N. V. (20-14). Geochemistry of fluids of formation medium of copper-bearing parageneses in volcanites of the trappean formation of areas of junction of the Volyn Paleozoic uplift with the Volyn-Podillya monocline: *Thesis for a candidate's degree in Geology (equivalent to Philosophy Doctor) by speciality 04.00.02. "Geochemistry.* (in Ukrainian).
- Nesterovich, N. V., Kosovskij, Ja. A., Naumko, I. M., Fedorishin, Ju. I. (2014). Pyroclastic pisolithes of the trap formation of northwestern Volyn (Lukovsko-Ratnovska horst zone). *Domestic Geology*, 1, 41–47 (in Russian).
- Ovchinnikov, L. N., Banshchikova, I. V., Vasil'ev, E. V. (1982). Inclusions of melts and solutions are direct witnesses of the ore-generating role of magmas. *Thermobarogeochemistry in geology*, Vladivostok: DVNC AN SSSR, 33–37 (in Russian).
- Prykhod'ko, V. L. (2005). Reconstruction of the structural plan and stages of trappean volcanism of Volyn-Podillya in the Late Proterozoic: *Thesis for candidate's degree in Geology by speciality 04.00.01. "General and Regional Geology"*, Kiev (in Ukrainian).
- Prykhodko, V. L., Kosovskij, Ya. O., Ivaniv, I. N. (1993). Prospects of copper-bearing volcanites of Volyn Series Lukowski Ratne horst zone. *Geol. Journ.*, 4, 138–143 (in Ukrainian).
- Velikanov, V. A., Aseeva, E. A., Fedonkin, M. A. (1983). Wend of Ukraine. Kiev: Nauk. dumka (in Russian).
- Volovnik, B. Ja. (1990). Terrigenous-volcanogenic formation. Lower Vend. *Geotektonics of Volyn-Podolia*, Kiev: Nauk. dumka, 76–83 (in Russian).
- Volovnik, B. Ja. (1975). Trap formation of Volyn-Podolia. *Tektonics and stratigraphy*, 8, 28–33 (in Russian).
- Weihua, Liu, McPhail, D. C. (2005). Thermodynamic properties of copper chloride complexes and copper transport in magmatic-hydrothermal solutions. *Chemical Geology*, 221, 1–2, 21–39.

# Ігор НАУМКО, Наталя БАЦЕВИЧ, Юрій ФЕДОРИШИН, Мирослав ПАВЛЮК, Юрій МИЩИШИН, Ігор РЕПИН

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## ОСОБЛИВОСТІ РОЗПОДІЛУ ТОВІЦИНИ І РЕЛЬЄФУ ПАЛЕОПОВЕРХНІ БАЗАЛЬТІВ ЛУЧИЧІВСЬКОЇ ТОВІЦІ (ЗАХІДНА ВОЛИНЬ)

Мета. Дослідити особливості просторового розподілу товщини і палеорельєфу базальтів лучичівської товщі ратнівської світи трапової формації едіакарію Ратне-Камінь-Каширської площі Західної Волині за допомогою карт товщини і рельєфу палеоповерхні для проведення кореляції між вказаними параметрами товщі та просторовою зміною концентрацій самородномідного зруденіння і його локалізацією відносно покрівлі (підошви) товщі. Методика. Включає польові геологічні дослідження; петрографію базальтів, структурні особливості (ступінь розкристалізації мезостазису, структурне положення мінералів та, зокрема, міді, співвідношення глобулярних утворень і мінералів, які їх оточують, взаємовідношення між глобулями), макро- та мікротекстурні особливості порід; геохімічні дослідження: встановлення вмісту

основних хімічних компонентів порід методом валового хімічного аналізу та вмісту міді; геологоморфоструктурні дослідження: побудова карти палеорельєфу і товщини лучичівської товщі трапової формації (за даними розрізу свердловин). Результати. На основі побудованих карт товщини і палеоповерхні лучичівської товщі показано просторову мінливість товщини базальтів та відображення результативної тектонічної ситуації на її палеоповерхні, які можна "читати" за елементами рельєфу. Встановлено, що високі вмісти міді в базальтах просторово приурочені до ділянок максимальних товщин і зміщені за вертикаллю до припокрівельної та, частково, припідошвенної частин товщі базальтів, а ступінь їхньої розкристалізації наростає у напрямку внутрішніх частин тіл. Така ситуація з просторовим розташуванням самородномідного зруденіння вказує на існування в межах вказаних ділянок локальних ізольованих термостатованих систем, які еволюціонували у своїх внутрішніх частинах в умовах, що були наближені до інтрузивних (відносно повільне зниження температури розплаву, кристалізація породних відмін практично позбавлених вулканічного скла – долерито-базальтів з переходом до долеритів у центральній частині). Такі фізико-хімічні умови зумовили тривалу міграцію газових, газово-рідинних та рідинних флюїдів, забезпечуючи супутню екстракцію, концентрацію, перенесення і відкладання не лише самородної міді, але й цілого ряду петрогенних оксидів (луги, залізо, частково кальцій, сіліцій). Останні утворювали згодом низку низькотемпературних мінералів, найбільш поширеними з яких  $\epsilon$  цеоліти, кальцит, сполуки заліза. На ділянках з малою та мінімальною товщиною базальтів вказані вище факти спостерігаються в редукованому вигляді, а подекуди практично відсутні. Встановлено повну відсутність ознак формування гідротермальної міднорудної мінералізації. Останнє підтверджує той факт, що на сьогодні геологічній науці невідомі факти утворення самородномідної мінералізації гідротермального типу. Викладені геологічні та петрогеохімічні факти достовірно нами встановлені і дають підстави розглядати сценарій процесу утворення самородномідної рудної мінералізації стосовно до флюїднолікваційної гіпотези, розробленої і запропонованої свого часу авторами. Наукова новизна. Вперше побудовано карти товщини і рельєфу палеоповерхні базальтів лучичівської товщі трапової формації едіакарію Ратне-Камінь-Каширської площі Західної Волині. Вперше на підставі опрацювання фактичного матеріалу показано, що вертикальний розподіл і локалізація самородномідної мінералізації в межах базальтових тіл закономірно пов'язані з їхньою товщиною, а значення вмісту самородної міді знаходиться у прямій залежності з товщиною тіла, досягаючи максимуму на ділянках з максимальною товщиною і фонових значень при мінімальній товщині. Практична значимість. Вперше геологічні, петрографічні, геолого-морфоструктурні дані зіставлено із вмістом міді у базальтах лучичівської товщі. Запропонований підхід може бути використано виробничими організаціями геологічного профілю при проведенні пошуково-розвідувальних робіт з метою підготовки перспективних площ до розвідки Північногірницького і Рафалівського рудоносних полів (рудних вузлів) у межах Ратнівської горст-антикліналі. Отриманий оригінальний матеріал може бути поширений як нова методика пошуків самородномідного зруденіння на інших площах поширення трапової формації.

*Ключові слова*: трапи, едіакарій, товщина, палеорельєф, лучичівська товща, Ратне–Камінь-Каширська площа. Західна Волинь.

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