Ukrainian Geological Association (UAG) in the person of Expert Advice of the Union of Geologists of Ukraine, “EA UAG” (http://eauag.hol.es/) (in which it is 100% Founder) in accordance with the INTRAW project objectives during 2015 – May, 2016 the Ukrainian side is satisfied:

1. MANAGEMENT AND REPLACEMENT OF CRITICAL RAW MATERIALS. CONDUCTING RESEARCH IN THE MINERALOGICAL STUDY OF PLATINUM GROUP ELEMENTS AND RHENIUM, DIAGNOSED IN ULTRAMAFIC ROCKS OF THE UKRAINIAN AND LYON-LIBERIAN SHIELDS.

Under this objective we have analyzed all of the results obtained as of today on this issue.

Introduction

Until some time ago rhenium metal resources was not known on Earth planet. The first discovery of rhenium metal phase (extremely rare trace element which clark $7*10^{-8}$ is the lowest one among all platinoid and lanthanides elements) in ultrabasites of Dniester-Bug megablock of Ukrainian Shield (US) was made by our team in 2005-2006. According to preliminary results that we obtained about its geological and structural conditions of localization, its mineralogy, rhenium content in ores, our attempts of rhenium resources assessments there are strong evidences for proving and development of new Ukrainian rhenium deposit of new geological and industrial type, low cost one, but with fundamentally new conditioning parameters.

An increasing number of elements were assessed as “highly critical” such as indium, cobalt, niobium, tantalum, rare earth elements, lithium and the platinum group metals, including rhenium. Its belonging to a certain class of elements in the light of recent data is problematic.

For the first time in the world practice we have identified numerous native rhenium phases and its natural inter-metallic compounds in the Precambrian geological systems of Ukrainian Shield. To date, in geological systems rhenium is known either as isomorphic impurity in molybdenite (chalcopyrite, pyrite [21] and other minerals [13]) or in quite rare natural sulphides (rhenite, dzhezkazganite [13]), or in composite volatile compounds being released through degassing of diverse-temperature (low-temperature – 200-300^{o}C, and high-temperature – 600-800^{o}C [13]) vapour-gas mixtures in volcanoes like Kudryaviy on Kurilian Iturup Island [13, 21]. It is also well-known that increased rhenium content is observed in metal-organic compounds of coal, combustible bituminous shales (according to [13, 21] – up to 4.3 g/t), solid bitumens (up to 5 g/t), and oil (0.05-0.12 g/t).

Phases of metallic rhenium on planet Earth authentically established only in Allende meteorite (Fig. 1). Other reports of the presence of metallic phases rhenium sufficiently large (greater than 1 micron), unfortunately, is problematic, because they do not contain the necessary evidence.

In the world mining practice rhenium is being extracted only as by-product together with the major mineral commodities from molybdenum (molybdenite), copper (chalcopyrite) and lead (galena) concentrates with fairly low recovery (42-43% after [13], and by some confidential data – much less). Thus, nowadays rhenium comprises the practical interest only in cases of proven economic value of the major component. The pure rhenium deposits are not known (except the disputable one in mentioned Kudryaviy volcano).

In the paper are disclosed the new data concerning discovery and first experience in description of native rhenium phases and complex inter-metallic compounds. In addition, rhenium is identified in some rare minerals which composition and structure currently are being studied. Native rhenium is encountered in various ultramafic rocks, calciphyres and calciphyre-like rocks, as well as in various types of chromite ores in Kapitanivskiy Massif, Ukrainian Shield. Occurrences are also found in the rocks of other massifs of the known Pobuzka Group; respective results will be disclosed elsewhere.

Fig. 1. A sample of the Allende meteorite (source: http://dic.academic.ru/dic.nsf/ruwiki/1349879)

Prior to the direct result description with regard to ore-mineralogical study of rhenium-bearing rocks we will present the review of geological setting of ultramafic massif in the frame of mega-block as well as vertical crustal structure in respective Shield segment by geological-geophysical data.

Rhenium is extensively applied for modern technologies. The brightest application is in processing of rigid materials, because rhenium hardness is highest among all known composites (ReB_2) at the planet. Its application to catalysis of high-octane gasoline production makes this process more effective by orders of magnitude. It can be used in chemical, electrical, petrochemical, medical productions, jewellery making, nuclear power production, rocketry construction et al. So, rhenium is the highly liquid strategic metal. Currently, demand for rhenium is unlimited - whatever rhenium quantity anybody produces can be completely sold at the market.

Rhenium – is the metal of the future with a wide range of application, unexpected properties and unlimited demand. It belongs to so-called "critical" metals. Relatively high estimated concentrations of this metal in ultrabasites of some massifs of Kapitanivka group (Ukrainian Shield), the number of such massifs (over 10), their large area (and therefore - resource potential) makes these promising resources of metal are almost unlimited. Experts estimated that demand for rhenium will only increase with time. Considering actually low cost of rhenium production from this ore that contains natural metallic rhenium, Ukrainian society can get highly liquid and almost unlimited source of one of the most strategic metals today.

Expected works have to answer several important questions, without which creation of the mineral resource base, and then, creation of Ukrainian infrastructure for mining of so-called "critical" modern metals (and, first of all, rhenium) is not possible.

Thus, for creation of this scientific and practical background it is highly important to clear up some questions for the development of criteria basis of rhenium forecast, searching and exploration. We need to solve the following key issues:

- the scale of rhenium metal phases manifestation in ultrabasites;
- the composition of massifs? What ores compose them? With which of them release of renium phases can be associated?
- causes or factors control the localization of metal rhenium manifestations in natural complexes?
- rhenium place in ore and geological evolution processes of this specific crust segment?
- age and duration of processes of ore generation and deposition,
- mechanisms and pT parameters of ore genesis.

For this we planing to go through a series of science-based steps to implementation of project goals.

Realization of the goal are possible in number of consistent and interrelated studies, such as:

1) Analytical and mineragraphic verification of rhenium markers, inspection of their stability and high concentrations of metallic rhenium in ultrabasites (the most important pre-condition for this step is standartization of the main rock complexes with ore-bearing masses and outlining of main favorable structural and geological situations of their localization), and after this –

2) Development of complex of independent criteria for recognition of rhenium localization in ores and rocks through the identification of environmental factors that control the mobilization of its sources;

3) Using of science-based approaches for determination of transition forms and causes of metallic rhenium deposition in the composition of natural intermetallic compounds.

This it follows from the need to solve the following more detailed goals:

- to analyze the level of formation sequence and formation composition (on the basis of paragenetical sequence) of lower Precambrian of Ukrainian Shield (US);
- to clarify the internal structure of the main structural-formation and formation complexes and formations that compose them;
- to argue and outline structural-formation conditions that are favorable for rhenium mineralization;
- to divide geological formations (from metallogenic point of view), according of its ore-bearing;
- to conduct metallogenic and ore-formation analysis of geological formations;
- to conduct geological formational and metallogenic analysis in the areas where conditions are favorable for rhenium genesis and in the areas across the boarders of these sites for already known and probable ore manifestations;
- to clarify the physical-chemical conditions of gold concentration processes at different depths using complex thermo- baric and geochemical studies of fluid inclusions in minerals;
- to create a complex of geological-formational, metallogenic, geochemical and thermobarogeochemical (TBGC) criteria and signs for promising inspections of Lower Precambrian (US) rhenium mineralization objects;
- to develop a variety of geological - geochemical and physicochemical criteria of industrial rhenium-bearing, to recognize promising areas of various ore formations that are responsible for rhenium concentration;
- to identify rhenium concentration ranges in ores;
- to make preliminary assessments of the resource potential of conditional of subjunctive rhenium in massifs of the Middle Pobuzhya (Dniester-Bug megablock of Ukrainian Shield) region;
- to evaluate expediency of new investigations in this field.

1.1. METAL RHENIUM IN ULTRABASITIC MASSIFS OF DNIESTER-BUG MEGABLOCK OF UKRAINIAN SHIELD: REASONING FOR WORLD-CLASS DISCOVERY, FORECAST AND RESOURCE ASSESSMENT

Geologic and tectonic setting

Ultramafic massifs, studied in details due to rhenium discovery, are located in the eastern part of Dniester-Bug megablock of Ukrainian Shield (Fig. 2, 3) in so called Golovanivska Suture Zone [33].

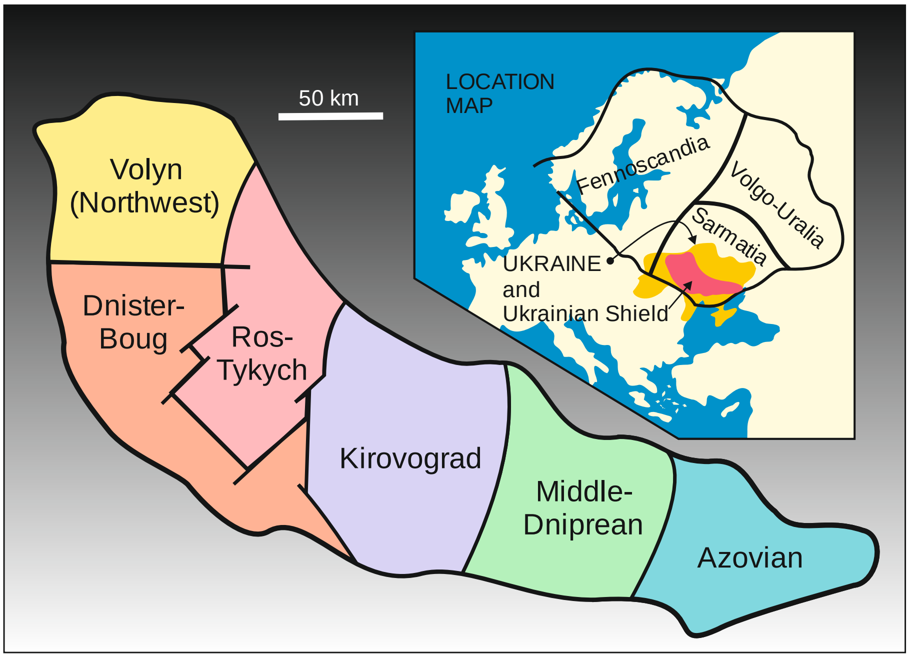


Fig. 2. Major geoblocks of the Ukrainian Shield

Dnistersko-Buzkiy mega-block represents the family of granulite-gneiss terrains and is composed of mainly Archean rocks. In the section of stratified rocks two floors are distinguished: the lower one composed of Paleo-Archean Dnistersko-Buzka Series and the upper floor of Neo-Archean Buzka Series.

According to the correlation chrono-stratigraphic scheme of Early Precambrian in Ukrainian Shield, ***Dnistersko-Buzka Series*** includes high-grade (granulite facies) gneisses and mafic gneisses with interbeds of calciphyres, ferruginous and barren quartzites occurring as remnants within enderbites, charnockites, Berdychivski and Pobuzki granitres and migmatites in the upper and middle course of South Boug river, in the left bank of Dnister river, and in the upper courses of Teterev and Sluch rivers. Five sequences are distinguished in the vertical column (upward): ***Tyvrivska*** (two-pyroxene gneisses and mafic gneisses with calciphyres), ***Gnivanska*** (pyroxene and garnet-biotite gneisses and mafic gneisses with calciphyres), ***Pavlivska*** (pyroxene and garnet-biotite gneisses with magnetite, mafic gneisses, ferruginous quartzites) – these three sequences are being correlated each other by lateral; the section is capped by two same-aged ***Bereznenska*** (garnet-biotite gneisses with minor mafic gneisses and calciphyres) and ***Zelenolevadivska*** (leucocratic garnet- and pyroxene-bearing gneisses often leptite-like).

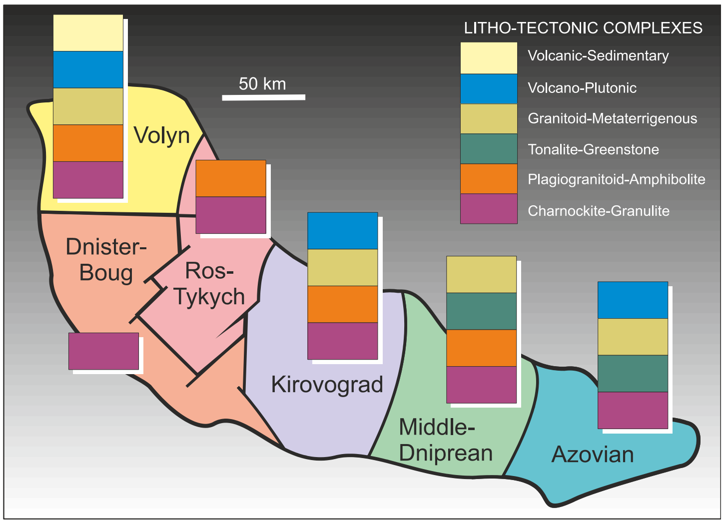


Fig. 3. Distribution of litho-tectonic complexes over geoblocks of Ukrainian Shield.

Buzka Series is relatively locally developed in the mega-block. The rocks are confined to the narrow north-west-trending synclines in Middle and Lower Pobuzhzhya: Kosharo-Oleksandrivska, Khashchuvato-Zavallivska, Moldovska, Tarnovatska, Grushkivksa, Kapitanivska, Chausivska, Derenyukhinska etc. The Series is divided in two Suites: Kosharo-Oleksandrivska (lower) and Khashchuvato-Zavallivska (upper).

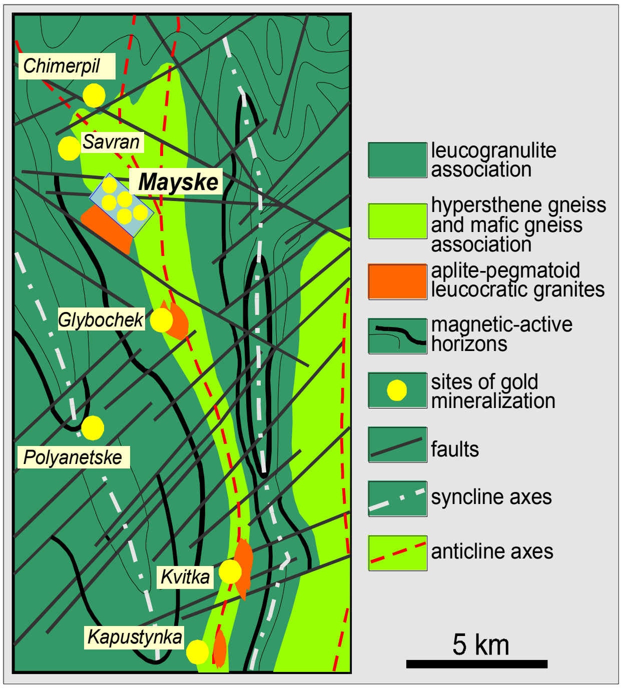


Fig. 4. Sketch geology of Savran ore field, where rocks complex has been studied as fully as possible

General representation of area geology gives Geological setting of Savran ore field (Fig. 4). This area is the most investigated.

In the surface magnetic field the deposit fold structure is reflected in magnetic anomaly 90-425 nTL. Magnetic-active beds almost everywhere are expressed as a single body. In area of flexure turn occurs lateral bifurcation of magnetic-active horizons and splitting of a single anomaly in two ones.

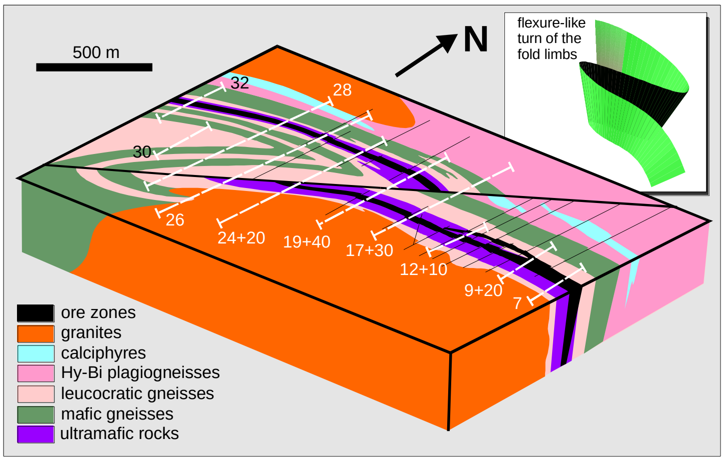


Fig. 5. Local sketch geology of Mayske deposit.

The geological structure of this age level of the rocks is well illustrated by geology Maisky gold deposit. His geological cross-sections studied more fully. Therefore, an overview of the features of the structure of rock complex gives this site.

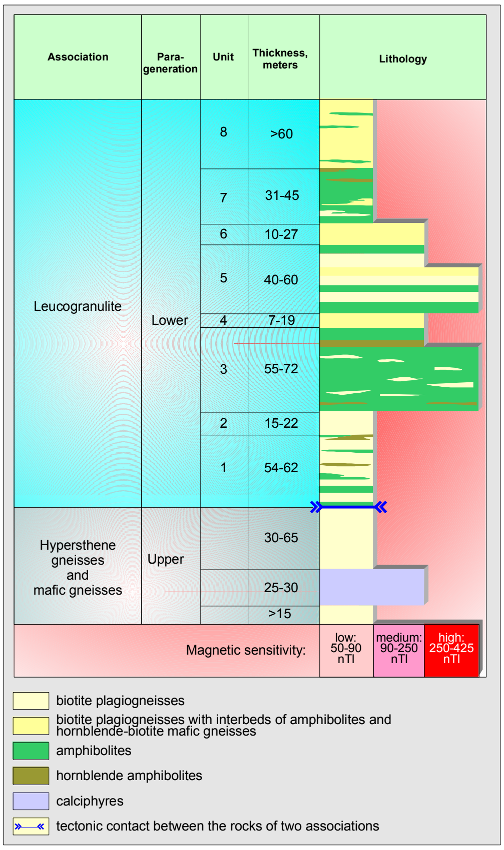


Fig. 6. Generalized lithology column of Mayske deposit area

South-western portion is almost not displaced whereas north-eastern one is clearly displaced eastward over distance about 650 m. Along individual magnetic-active horizons (295-305^{o} strike) occurs a system of cutting faults (30-40^{o}) that bound small blocks and cause dismembering of magnetic-active horizons into short (from 30-60 to 200-300 m long) units.

The main fault that split deposit into northern and southern parts is treated as reverse shear by geological and tectonic features. Flexure hinge is almost vertical in area of its limbs junction. Northern limb of west-north-west strike is steeply (80-85^{o}) overturned to north-east. In the turn area, however the dipping becomes normal to north-east being steep enough (80-85^{o}) still. In the southern limb the rock bedding is overturned in the interval between main fault and profile line N 22+50, getting to be vertical in between profiles NN 22+50 and 17+30, and further to south normal north-east steep dipping occurs (see Fig. 5).

Host rock composition. The rock band that occur in between two synclines in Fig. 4 (Slusarivska is west and Savran in east) comprises transition zone between upper part of hypersthene gneiss-mafic gneiss and lower part of leucogranulite associations (see Fig. 3). Stratified rocks include biotite plagiogneisses, hornblende-biotite mafic gneisses, amphibolites, orthopyroxene and hornblende metaultramafic rocks. Eight individualized units are distinguished in the generalized rock column (Fig. 6).

The generalized lithology column of Mayske deposit area is:

Unit 1. Alternation of biotite plagiogneisses, hornblende-biotite mafic gneisses and amphibolites with ultramafic interbeds (54-62 m).

Unit 2. Biotite plagiogneisess with some interbeds of hornblende-biotite mafic gneisses, amphibolites and metaultramafic rocks (15-22 m).

Unit 3. Alternation of hornblende-biotite mafic gneisses, amphibolites and ultramafic rocks with interbeds of biotite plagiogneisses (55-72 m).

Unit 4. Biotite plagiogneisses with interbeds of hornblende-biotite mafic gneisses and ultramafic rocks (7-19 m).

Unit 5. Alternation of biotite plagiogneisses and amphibolites with interbeds of hornblende-biotite mafic gneisses and ultramafic rocks (40-60 m).

Unit 6. Biotite plagiogneisses with interbeds of hornblende-biotite mafic gneisses and amphibolites (10-27 m).

Unit 7. Alternation of biotite plagiogneisses, hornblende-biotite mafic gneisses and amphibolites (31- 45 m).

Unit 8. Biotite plagiogneisses with thin interbeds of biotite-hornblende mafic gneisses, amphibolites and metaultramafic rocks (more than 60 m).

The total thickness of this pile exceeds 370 m. Each unit consists of two- or three-fold rhythms defined by regular alternation of amphibolites, hornblende-biotite mafic gneisses and biotite plagiogneisses in variable proportions.

The rocks units NN 1-3 and partly 4 occur in north-western and south-eastern flexure limbs whereas units NN 5-8 are mainly restricted to the core section. In the south of area the latter rocks are substituted with Southern massif of leucocratic aplite-pegmatoid granites.

Thickness of all units increases from north-west to south-east, and in the same direction in those units composed of contrasted rocks amount and thickness of amphibolite and metaultramafic rock interbeds also increase while amphibolite and hornblende-biotite mafic gneisses appear in essentially plagiogneiss units.

Fig. 7. Olivine-dolomite calciphyre.

In thin section serpentine-phlogopite pseudomorphs occur after olivine. DH 6521, depth 263,3 m. Plane-polarized light, enlargement 20.

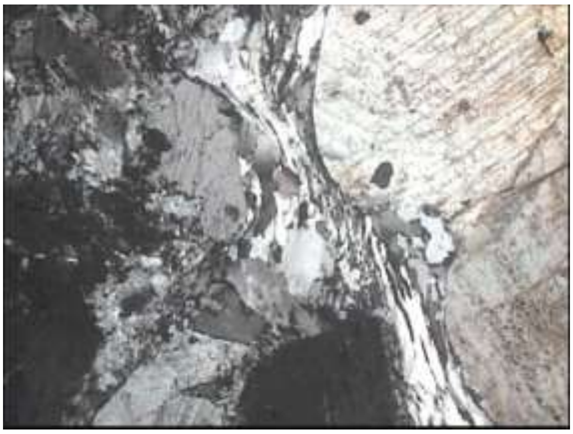


Fig. 8. Leucocratic granite vein in milonite zone with pseudo-fluidal quartz.
DH 6764, depth 197,1 m. Cross-polarized light, enlargement 20.

Fig. 9. Spinel-phlogopite metasomatites. DH 6764, depth 135,9 m. Plane-polarized light, enlargement 20.

Lower leucogranulite association rocks are observed in the north of deposit. They include blastic gneisses, calciphyres (Fig. 7), and orthopyroxenites. Gneisses are granitized, tectonitized, cataclased and often silicified (Fig. 8). Diverse metasomatites are developed after carbonate and pyroxene rocks (Fig. 9).

In major-element composition biotite plagiogneisses correspond to dacite, rhyolite and plagiorhyodacite, amphibolites – to leucobasalts, basalts, and olivine basalts. Least altered hornblende amphibolites and amphibolitized orthopyroxenites resemble pyroxenite-hornblendites.

It is supposed that stratified rocks modification had occurred synchronously with deposit structure formation. Retrograde metamorphism and anatexis under amphibolite-facies conditions accompanied by silica-alkaline metasomatism with subsequent acid leaching had caused wide range of rocks that are grouped in the single plutono-metamorphic association. Formally, all these rocks are migmatites formed in metamorphic differentiation, plagio-migmatization, and blastesis with following biotitization, feldspatization and silicification. There are distinguished *differentiated biotite gneisses*, *plagiomigmatites after amphibole-biotite mafic gneisses*, *plagiomigmatites after amphibolites, and two-feldspar migmatites*. If primary rock is clearly defined, adverb *plagiomigmatized* is being added to the rock name, and if exact nature of primary rock is obscured - the adverb *shadowed*. In the plutono-metamorphic association a large group of metasomatic rocks is also distinguished: *augen metablastic gneisses, metasomatically altered plagiomigmatites after amphibolites, biotite-quartz-oligoclase metasomatites, sillimanite-cordierite-garnet-biotite-quartz metasomatites*.

Fig. 10. Differentiated and silicified plagiogneiss. DH 6539, depth 148,7 m.

In the deposit *differentiated plagiogneisses* are widespread. These are grey, banded, dirty-banded fine-medium-grained rocks (Fig. 10) with segregations of melanocratic (biotite 20-55%) and leucocratic (biotite 0-10%) bands 0,1-5 cm thick. Leucocratic bands consist of fine-medium-grained aplite-like often K-feldspatized biotite-quartz-plagioclase aggregates. Somewhere rocks occur in fine isocline folds. Least altered varieties of plagiogneisses have the following mineral composition (%): plagioclase (andesine-oligoclase) 40-65; quartz 15-40; biotite 10-20; apatite < 1-2; zircon <1; hornblende <1; epidote <1; sphene <1; opaques <1-5. In places of oligoclase blastesis fibrolite, muscovite and film potassium feldspar occur.

According to U-Pb isochrone dating of plagiogneisses in DH 6546 (depth 203,0-349,0 m) the zircon age is estimated as 2918±7 Ma and monazite age as 1979±1,7 Ma (unpublished data of L.M.Stepanyuk, A.B.Bobrov et al., 2002).

Hornblende-biotite mafic gneisses (Fig. 11) are intermediate in composition between plagiogneisses and amphibolites. By texture and mineralogy the leucocratic varieties are close to plagiogneisses and melanocratic – to amphibolites. These are greenish-grey fine- to medium-grained rocks, often biotitized and silicified. The rocks contain (in %): plagioclase (andesine) 30-65; quartz 10-30; biotite 25-50; hornblende <1-20; apatite <1-5; zircon <1; epidote <1-2; opaques <1-2. In altered varieties also found fibrolite and garnet.

Fig. 11. Granitized biotite-hornblende mafic gneiss. DH 6532, depth. 90,6 m. Plane-polarized light, enlargement 20.

Amphibolites comprise grey-green to greenish-black medium-grained sheared and sometimes massive rocks. They have nematogranoblastic and parallel texture (Fig. 12-13). Unaltered amphibolites contain (%) green hornblende 40-60 and plagioclase (bitovnite-andesine) 40-60. Somewhere occurs clinopyroxene (up to 15%), quartz (<1-5%), and apatite (0,1-5%). Magnetite (1-10%) represents opaque minerals. Almost throughout amphibolites are biotitized and silicified (Fig. 12). In close relation to amphibolites occur *metaorthopyroxenites* (Fig. 13).

Fig. 12. Amphibolite.
DH 6738, depth 37,0 m. Plane-polarized light, enlargement 20.

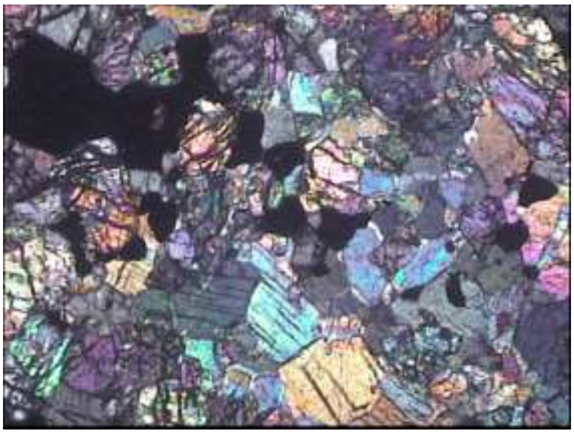


Fig. 13. Amphibolitized and phlogopitized orthopyroxenites.
DH 6521, depth 247,0 m. Cross-polarized light, enlargement 20.

Fig. 14. Lens-augen blastic milonites.

The augens consists of oligoclase blasts in between which occur lenses of plate quartz and re-crystallized biotite. DH 6708, depth 201,8 m. Cross-polarized light, enlargement 20.

Meta-ultramafic rocks under granitization transform into hornblende amphibololites, amphibolitized orthopyroxenites, cummingtonite amphibololites and biotitites. In turn, granitization of apo-amphibolite biotitites leads to formation of quartz-oligoclase-biotite metasomatites with garnet, sillimanite and cordierite. Behaviour of leucocratic hornblende-biotite mafic gneisses in the mentioned range of modification resembles one of plagiogneises whereas melanocratic rocks are close to amphibolites.

Just in the time and after crystallization of major rock-forming minerals occurred extensive ductile deformations. Transition from the latter to milonitization took place in close relation to the deformation along sub-conformable zones. Milonite and blastic milonite formation is found after all rocks types (Fig. 14).

Plagiomigmatites after amphibolites and hornblende-biotite mafic gneisses. Most of the rocks in section are represented by banded, dirty-banded and spotty biotitized and silicified plagiomigmatites. Mafic part 0,1-15 cm thick is enriched in hornblende and biotite in various proportions, sometimes with clinopyroxene. Leucocratic part 0,1-10 cm thick consists of aplite-like plagiogranite (Fig. 15). In case of extensive plagiomigmatization formed *shadowed plagiomigmatites* with aplite-like and quartz-plagioclase material amount up to 80-90%.

Two-feldspar migmatites are widespread in outer contact zones of granite massifs. They change to leucocratic granites through shadowed varieties, and to differentiated plagiogneisses and plagiomigmatites in other places. Often two-feldspar migmatites occur outside the igneous bodies. In formation of two-feldspar migmatites primary rock textures normally are preserved. These are grey-pink and red fine-banded and spotty rocks. Their leucocratic part consists of extensively K-feldspatized plagiogranites, aplite-like leucocratic granites, pegmatoid rocks 0,1-100 cm thick. Paleo-mafic bands are enriched in biotite, sillimanite, cordierite, and garnet.

Fig. 15. Silicified plagiomigmatite after amphibolite with pyrite-magnetite dissemination restricted to mafic bands. DH 6539, depth 168,5 m.

Augen metablastic gneisses comprise leucocratic light-banded, spotty, irregular-grained rocks formed by metasomatic modification of differentiated plagiogneisses. Structure is parallel, lens-banded, and sometimes massive. The rocks are composed of alternating melanocratic (quartz-biotite-oligoclase and biotite-oligoclase) and leucocratic (oligoclase-quartz and quartz-oligoclase) bands 1-5 mm thick. Re-crystallization of aplite-like quartz-plagioclase portion leads to formation of the bands and single spots composed of medium-coarse-grained to giant-grained biotite-quartz-oligoclase K-feldspatized metasomatites 1-20 cm thick (rarely 2-3 m) or lens- and vein-shaped plagioclase-quartz fractions 1-50 cm thick (Fig. 16). Metasomatites comprise 10-50% of the rock volume.

Fig. 16. Conformable oligoclase-quartz vein in differentiated plagiogneisses.
Fine pyrite-pyrrhotite dissemination occurs in gneisses. DH 6539, depth 181,2 m.

Mineral composition is as follows (%): plagioclase (oligoclase # 16-20) 40-65; quartz 20-40; F-feldspar <1-8; biotite 5-25; sillimanite <1-5; muscovite <1-5; apatite <1-3; zircon <1; opaques (magnetite, ilmenite and sulphides) <1-5. Sometimes occur garnet <1-3, gahnite <1, tourmaline <1, and epidote <1.

Metasomatically altered plagiomigmatites after amphibolites and hornblende-biotite mafic gneisses form the bodies up to 20 m thick in flexure limb in close proximity to the granite massifs. Although plagiomigmatite texture features are preserved there are widespread re-crystallization, biotitization and silicification in metasomatites. These are greenish-grey to light-grey banded, light-banded (shadowed), spotty irregular-grained rocks that are normally silicified, weakly K-feldspatized and contain abundant conformable layers of biotite-quartz-oligoclase and biotite-oligoclase-quartz metasomatites 1-20 cm thick. The following mineral composition is characteristic (%): plagioclase (from bitovnite to andesine) 40-45; hornblende 5-40; quartz 5-55; biotite 5-37; apatite <1-5; epidote <1-7, opaques <1-5; carbonate <1-5. Somewhere pyroxene relicts are preserved. Mafic bands (up to 70% of mafic minerals) are composed of (%) hornblende 40; biotite 30-35; plagioclase 20; quartz 5-10. Leucocratic bands has aplite-like plagiogranite composition with mafic minerals <10% (hornblende 5-7; biotite 3-5; plagioclase 55-65; quartz 20-35).

Metaultramafic rocks – amphibolitized orthopyroxenites and hornblende amphibololites. Amphibolites consist of green hornblende or magnesium cummingtonite. Apparently hornblende amphibolites formed after clinopyroxenite and websterite.

Biotitites (biotitized and silicified metaultramafic rocks) comprise black schistose lens-banded fine- to coarse-flaky rocks of the following mineral composition (%): biotite 70-96; quartz 2-25; apatite <1-4; opaques <1-3; zircon <1. The boundaries between biotitites and metaultramafic rocks are normally sharp.

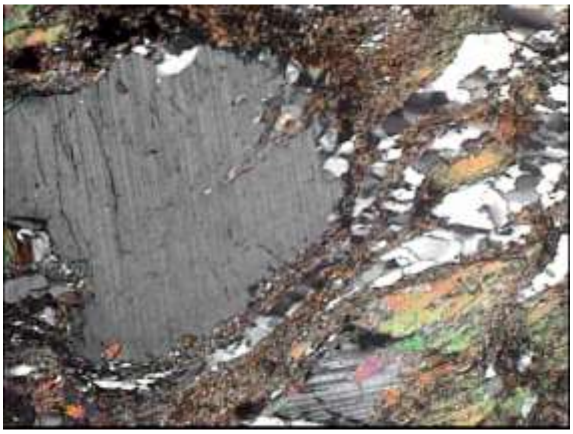


Fig. 17. Quartz-oligoclase-biotite metasomatite.
Quartz is pressed, platy. DH 6738, depth 46,1 m. Cross-polarized light, enlargement 20.

Biotite-quartz-oligoclase metasomatites include group of rock varieties formed by high-temperature silica-alkaline metasomatism. From augen gneisses they differ in larger grains of oligoclase (45-50%), greater amount of quartz (40-55%), and lesser biotite content (<1-10%, rarely up to 25%). Potassium feldspar content is <1-3%. Few muscovite and sometimes tourmaline occur. Opaque ore minerals occur in amount of 1-20%. Ratio of rock-forming minerals in metasomatites depends on the source rock composition after what they were formed. Biotite-quartz-oligoclase varieties predominate with less amount of oligoclase-quartz-biotite (Fig.17), quartz-andesine-biotite, biotite-oligoclase-quartz, oligoclase-biotite-quartz, and oligoclase-quartz metasomatites. Three latter varieties often contain garnet and gahnite.

Metasomatites look as light- and greenish-grey, pinkish medium-coarse-grained to giant-grained, irregular-grained, banded, spotty, and massive rocks. Plagioclase-quartz aggregates form bands and lenses. Abundant are single porphyry-blasts of plagioclase, lens-shaped quartz, aggregates or bands of coarse-flaky biotite (Fig. 18). In the central parts of metasomatite zones semi-transparent violet-grey quartz forms the veinlets, segregations, vein-like units with oligoclase, biotite, apatite, garnet, tourmaline, and muscovite. Selvages of these quartz units are enriched in ore minerals. Relicts of primary rock source are preserved somewhere in metasomatites such as lenses and bands of differentiated plagiogneisses or plagiomigmatites after amphibolites, sometimes – sillimanite-cordierite-garnet-quartz-biotite residuals. Extensive K-feldspatization influences pegmatoid biotite-quartz-microcline rocks with apatite and plagioclase relicts.

Biotite-quartz-oligoclase metasomatites occur in sub-conformable bodies and are rather fixed in the section with respect to their position. Most favourable for these rocks formation appear to had been the units of alternating rocks located along the contacts of granite massifs. In the central parts of these units occur thick (first tens of meters) zones that include biotite-quartz-oligoclase metasomatites and re-crystallized plagiomigmatites. External portions of the metasomatic zones are composed of augen metablastic gneisses. Metasomatites occupy from 10-30 to 50% of these zones by volume.

Fig. 18. Coarse-grained biotite-quartz-oligoclase metasomatite.
DH 6539, depth 284,7 m

Post-pegmatite metasomatism.

In the K-feldspatized gneisses, migmatites and metasomatites there occur aggregates of crest-shaped oligoclase-albite and intergranular albite around microcline grains. Felsic plagioclase replacement of potassium feldspar marks the transition from alkaline to acid metasomatism and precedes acid leaching stage. Sillimanite is widespread and mostly formed together with the rocks. In K-feldspatized gneisses, migmatites and K-feldspatized plagiogranites occur abundant sillimanite-quartz lenses and veinlets up to 10 mm thick. These rocks formed in quartz-sillimanite facies of acid leaching. Sometimes sillimanite-quartz assemblage is substituted by mono-quartz or quartz-muscovite. In quartz aggregate occur relicts of feldspar and biotite. Somewhere appears tourmaline in intergrowth with quartz. Muscovite formed after fibrolite, biotite and also found in intergrowth with K-feldspar and quartz as well as substitutes sillimanite. In the contacts of Southern granite massif are widespread the bodies of *sillimanite-garnet-cordierite-biotite-quartz metasomatites* with muscovite, plagioclase, microcline, magnetite, and sulphides. These rocks are supposed to be the final products of amphibolites and metaultramafic rocks transformation on the stage of silica-alkaline metasomatism and related acid leaching.

Thus, in pre-ore stage the rocks underwent essential metasomatic modifications through processes of silica-alkaline metasomatism and accompanied leaching. Earlier rocks and marginal portions in the metasomatic zones are composed of the rocks mainly formed by leaching and silica metasomatism (augen metablastic gneisses and biotite-quartz-oligoclase metasomatites). Spatially these rock varieties are substituted with products of silica-potassium metasomatism (K-feldspatized rocks and pegmatoids). In post-pegmatoid stage the rocks underwent acid leaching.

In general, chemical composition of the rocks changes toward increasing of K, Na, and Si and removal of Ca and Mg. Stratified rocks of mafic composition are modified to the biotitites, quartz-biotite and biotite-quartz rocks, quartz-oligoclase-biotite, quartz-biotite-oligoclase, sillimanite-cordierite-garnet-quartz-biotite and biotite-garnet-oligoclase-quartz metasomatites. Continuing K-feldspatization leads to formation of K-feldspatized metasomatites. Metablastic gneisses and biotite-quartz-oligoclase, biotite-garnet-oligoclase-quartz metasomatites are formed after plagiogneisses. The final products of silica-alkaline metasomatism and acid leaching are presented by pegmatoids, essentially quartz mobilizates, and leucocratic aplite-pegmatoid granites.

Plutonic rocks. In the deposit important contribution is addressed to the zoned Southern massif of two-feldspar alaskite-like granites about ~6 km^2 in size that assimilate southern limb of ore-control flexure. This body is composed of fine-medium-grained leucocratic aplite-pegmatoid granites with characteristic inclusions of sillimanite in oligoclase and microcline. Other features include K-feldspar mirmecitization, biotite muscovitization, and development of chlorite, carbonate and sulphides. In the external and inner contacts the veins of pegmatoid granites accompany granites (Fig. 19). Outward the contact amount of the veined material gradually decreases while pegmatoid composition changes to feldspar-quartz and quartz.

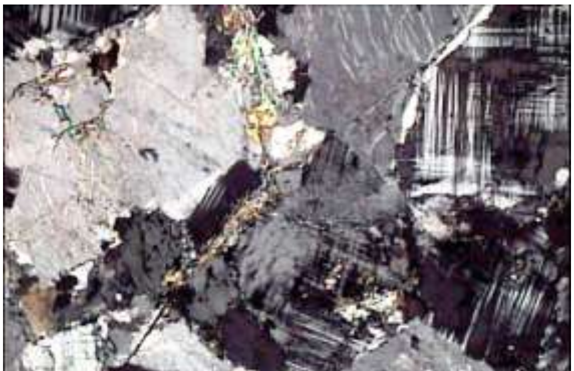


Fig. 19. Leucocratic pegmatoid granite. Southern massif. DH 6496, depth 255,5 m. Cross-polarized light, enlargement 20.

Fig. 20. Tourmaline-bearing silicified granite. Northern massif. DH 6521, depth 158,7 m. Cross-polarized light, enlargement 20.

The age of granite formation induced from isotope dating is within the range 1,9-2,4 Ga [29]. In chemical composition the granites correspond to leucogranites of variable alkalinity, from normal to alkaline. Primary-magmatic origin of aplite-pegmatoid granites is inferred from a number of evidences including contact alteration patterns and petrography of the rocks (relic euhedral textures, pegmatite graphic elements, relic melted inclusions in quartz of aplite varieties).

In the northern part of deposit occurs a fragment of small (~2 km^2) Northern granite massif composed of pegmatoid tourmaline granites (Fig. A4-3.19). The rock composition is as follows (%): plagioclase 25-37 (albite # 10-18); microcline 20-3-; quartz 38-45; garnet <1-1; tourmaline 4-5; muscovitized fibrolite ~2; sillimanite <1; muscovite <1-4; sphene 0-<1; apatite <1; zircon <1; opaques <1. Northern granites are similar to pegmatite rocks in Chimerpol gold prospect and Yanyshevskiy massif granites [2, 3, 29]. Their age determined by direct thermo-emission method on zircon ^{207}Pb/^{206}Pb ratio is about 1960 Ma. By chemical composition these rocks are close to sub-alkaline leucogranites whereas granites from injections have comendite composition, and Yanyshevskiy massif rocks are defined as sub-alkaline granites.

Kosharo-Oleksandrivska Suite (up to 800 m thick) is composed of quartzites, high-alumina gneisses and mafic gneisses (often with graphite). ***Khashchuvato-Zavallivska Suite*** (2.1 km thick) includes carbonate rocks (marbles and calciphyres) in association with graphite-biotite, garnet-biotite (in places with sillimanite), biotite and pyroxene gneisses, as well as ferruginous quartzites alternating with pyroxene-bearing gneisses and mafic gneisses.

The oldest igneous rocks in the mega-block are Subarivskiy Complex mafites and ultramafites occurring as xenoliths in Gayvoronskiy Complex enderbites. The latter are banded due to thin rock alternation from diorite to trondhjemite. Enderbites display high Sr content, very low Rb-Sr ratio (0.03-0.04), low content of heavy oxygen isotope (□^{18}O – 6.2-7.5‰), relatively low primary strontium isotope ratio (0.703-0.706), low content of slightly-fractionated REE with prominent europium maximum.

In Neo-Archean are known the mafic and ultramafic rocks of dunite-harzburgite-peridotite-gabbronorite ***Kapitansko-Derenyukhinskiy Complex*** that cut the Buzka Series. This Complex is specialized for nickel and platinoids and also contains chromite mineralization (in dunite-harzburgite association).

Table 1. Vertical succession and relationships of various-type rock associations in charnockite-granulite litho-tectonic complexes

Rock associations		
Stratified	Plutono-metamorphic	Plutonic
		Meta-dunite-harzburgite (hyperbasite)
Eulisite		
Condalite		
Marble-calciphyre		

High-alumina-quartzite		
Leucogranulite	Gneiss-alaskite	Alaskite-like granites
Hypersthene plagiogneiss-mafic gneiss	Gneiss-enderbite	Enderbite-charnockite
Kinzigite	Kinzigite-granite and hypersthene-garnet blastites (vinnitsite*)	

* it is developed in the zone of post-genetic re-working of kinzigite and hypersthene plagiogneiss-mafic gneiss associations

Litynskiy Complex charnockitoids are mainly developed in Upper Pobuzhzhya where they constitute minor (residual) bodies within granites and migmatites of Berdychivskiy Complex. In Middle Pobuzhzhya these charnockitoids replace enderbites of Gayvoronskiy Complex. By chemical composition charnockitoids do correspond to quartz diorites, granodiorites, plagiogranites, normal and sub-alkaline granites.

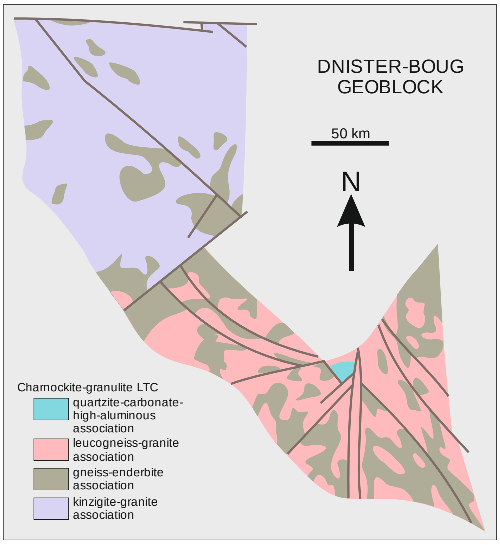


Fig. 21. Dnister-Boug megablok

Paleo-Proterozoic rocks include leucocratic, aplite-pegmatoid, often pyroxene-bearing granites of ***Pobuzkiy Complex***. And granitoid magmatism in the area is completed by formation of ***Berdychivskiy Complex*** which includes re-mobilized high-alumina granites that form giant batholite-like massif about 15,000 km^2 in size in the north-western part of mega-block. Complex includes garnet-biotite and cordierite-garnet-biotite granites (in places with hypersthene), granite-gneisses and migmatites with minor leucocratic biotite and alaskite granites, aplite-pegmatoid granites and pegmatites with monazite. Internal structure of the massif is complicated due to numerous residual bodies and xenoliths of Dnistersko-Buzka Series, enderbites and charnockites; intercalation of granites with biotite gneisses and migmatites often occur.Two-feldspar granites of ***Khmelnitskiy Complex*** are thought to be a bit younger of Berdychivskiy Complex granitoids.

The magmatism in mega-block is finished with formation of alkaline and sub-alkaline rocks of ***Proskurivskiy Complex*** and dyke rocks of various age (Paleo- and Meso-Proterozoic). Proskurivskiy Complex includes syenites and granosyenites (aplitoid fenites), ijolite-melteigites and nepheline syenites wuth minor pyroxenites and apatite pyroxenites. These rocks constitute the massif about 12 km^2 in size located in the south-western part of mega-block.

It is revealed from geochronology studies that the rocks of Dnistersko-Buzkiy mega-block were formed over more than 1.5 Ga time interval [28].

The oldest U-Pb isotopic date – 3.65 Ga received by ion-ionic microprobe method [1, 2] for the first zircon generation from enderbite-gneisses developed to the west of Zavallya, in our opinion, reflects the time of granitization process in the rocks of Dnistersko-Buzka Series. This conclusion does not contradict to the results of these rocks dating by Sm-Nd method suggesting for the rock deposition might occur as early as 3.9-3.7 Ga [11].

Granulites facies metamorphism of Dnistersko-Buzka Series occurred about 3.2-3.1 Ga [22]. The second phase of metamorphic re-working the rocks locally underwent at the end of Archean (2.8-2.6 Ga). Zircons with determined age about 2.8 Ga are encountered in charnockitoids of Lupolivskiy Dome [19] and in Gaivoronskiy Block [18]. Previously we have studied zircons in plagiogneisses of Mayske gold deposit with superimposed monazite mineralization (DH 6546, interval 203-349 m). By U-Pb isotopic dating the zircon age is 2917±7 Ma, monazite – 1979.4±1.7 Ma [6].

As a result of the local metasomatism (mainly silica-potassium) the rocks of lower tectonic floor underwent the metamorphic and metasomatic modifications reflected in various re-crystallized leucocratic gneisses (granulites) and migmatites after them. By zircon U-Pb isotopic dating the granulite formation had occurred 2.78 Ga [19].

Approximately that time (2.72 Ga) the secondary (apparently metamorphogenic) brown zircon was crystallizing in the rocks of mafic and ultramafic composition. Lacking of earlier zircons in the bodies of mafic and ultramafic granulites allows conclusion that mafic-ultramafic magmatism in Zavallivskiy Block had occurred prior to 2.72 Ga [24].

Formation time of Buzka Series rocks is not determined confidently. The lower time limit can be taken as 2820±20 Ma received by U-Pb method for clastogenic zircon from quartzites of Kosharo-Oleksandrivska Suite [30], and the upper one – 2576±152 Ma of zircons from biotite-two-pyroxene plagiogneiss of Khashchuvato-Zavallivska Suite [27].

New data (Shrimp II) for the study of the uranium-lead isotope systems of different generations of zircon from the hypersthene-plagioclase enderbitic gneiss) of Dnistersko-Buzkiy mega-block (Cossack Yar quarry) give numerical values verified (concordant) ages at 3.65 Ga.

The second phase of intrusive mafic-ultramafic magmatism in Middle Pobuzhzhya is related to the development of structures filled with the rocks of Buzka Series. The mafic and ultramafic granulites were formed in association with enderbite-gneisses and contain two generations of zircon. The age of ultramafic rocks in Kapitanivsko-Derenyukhinskiy Complex is the same (valid Correlation Scheme). Emplacement of these rocks is limited by two time boundaries: lower one, 2.72 Ga – crystallization time of the oldest zircon generation in mafic and ultramafic granulites of the first dyke complex, and upper one, 2.31 Ga – crystallization time of the early zircon generation directly in the rocks involved [24].

At the end of Early Proterozoic one more phase of intrusive magmatism occurred in Dnistersko-Buzkiy mega-block (the third one in Middle Pobuzhzhya) resulted in formation of numerous mafic dykes. And at the end of Early- beginning of Middle Proterozoic (2.01-1.94) the mafic rocks were metamorphosed into mafic gneisses [19, 25, 26].

Mafic gneisses of the third group contain zircons of only one generation, mainly so called “precious” zircon, although other crystal types are also known in the rocks of Upper Pobuzhzhya. The zircon age is 1.93-1.96 Ga in mafic gneisses of Middle Pobuzhzhya [19, 26] and 2.02-2.00 Ga in Upper Pobuzhzhya [25]. The zircon is of metamorphogenic origin as it contains inclusions of amphibole, quartz and oligoclase, the minerals of undoubtedly metamorphic genesis.

In the time interval of 2.1-1.96 Ga the mega-block was involved in orogenesis accompanied by extensive and fairly long-term granite formation process. In turn, granite formation was supplemented by potassium metasomatism resulted in formation of autochthonous and allochthonous granitoids and pegmatites, charnockitoids etc. [8, 24, 27, 29].

Mentioned combination of various age-different stratified, plutono-metamorphic and plutonic rocks constitute the columns of the oldest charnockite-granulite litho-tectonic complexes (LTC) developed in the lower tectonic floor of the layered crustal structure in Ukrainian Shield and known actually in all its mega-blocks. It is notable that being developed over large crustal segments in the Shield, these rocks are known only in Dnistersko-Buzkiy, Middle-Dniprean and Azovian mega-blocks.

Depending on preservation degree of rock associations on the vertical column of mentioned mega-blocks, variations in PT-conditions and scale of subsequent modifications (metamorphism, ultra-metamorphism, retrograde metamorphism) three types of LTC are distinguished [14, 33]: Pobuzkiy, Slavgorodskiy and Pryazovskiy. Their relations are briefly summarized in Table 1 and are described in details elsewhere [14, 33].

In Dnistersko-Buzkiy mega-block (Fig. 2) Pubuzkiy type of charnockite-granulite LTC is developed and its complete section is observed in the area of Zavallivska structure only. This LTC type includes numerous ultramafic massifs of Kapitanivsko-Drenyukhinskiy intrusive complex concentrated mainly in the eastern part of mega-block at the contact with Ingulskiy mega-block. This contact zone coincides in space with so called Pushkivskiy gravity maximum (as counterpart of Golovanivskiy or Pervomaysko-Golovanivskiy block; Golovanivska suture zone) and diagonally-oriented Kapitanivska zone of deep-seated fault marked by the system of tightly-deformed bodies of mantle ultramafites. On the ground of geological-geophysical data analysis [15] this zone is interpreted as the frontal part of Emylivsko-Pervomayska thrust zone where minor ultramafic bodies of Kapitanivsko-Drenyukhinskiy complex are treated to be the macro-boudines (tectonic detachments).

Geology of Pobuzka group of ultramafic massifs

In Dnistersko-Buzkiy mega-block of Ukrainian Shield the ultramafic massifs are located (Fig. 22) in three ore camps of Golovanivskiy Block. The latter is bounded by sub-longitudinal fault zones: Pervomayska in the east and Talnivska in the west. With various precision degree, 62 bodies are mapped in the Block. The bodies are composed of two rock associations: dunite-peridotite-gabbro-norite and dunite-harzburgite. The first one is mainly comprised of variously serpentinized dunites, lherzolites and harzburgites, as well as pyroxenites, amphibolized gabbro-norites and norites with discrete sulphide copper-nickel mineralization. The second association is mainly composed of dunites and harzburgites (also highly serpentinized) with strongly subordinate pyroxenites and mafic rocks; chromite mineralization is related to this association, in places in economic deposits like Kapitanivske.

Fig. 22. The location of ultrabasite massifs of Captain-Derenyuhinsk complex in Golovanevsk part of the Dniester-Bug megablock

Most authors suppose that the rocks of dunite-peridotite-gabbro-norite association occur in sheet-like bodies conformable to the host rocks of Buzka Series, often in syncline structures like Kosharo-Oleksandrivska, Khashchuvato-Zavallivska, Moldovska, Tarnuvatska, Grushkivska, Kapitanska, Chausivska, Drenyukhinska, etc. Their nature as plicative structure forms of certain type, unfortunately, has never been argued. However, previously, based on structure-geometric analysis of the rock contact planes, behavior of the rock bedding and sub-conform schistosity poles, structure-geologic restoration of the spatial position of fold limbs, hinges and centricline closures [31] we have established the complex mode of formation in one of such structures at least – Sekretarska (Tarnuvatska) as the fold with conic type of deformation formed through the complex folding mechanism with elements of rotation motions in combination with subsequent compression. As a result, the fold had got the form of tight narrow syncline structure with the rotation axis oriented in the plane of limb strike under steep angle to the surface; the general north-western extension of the fold coincides with the orientation of the deep-seated fault zone.

The spatial coexistence of various ultramafic rocks in these structures allows some authors supposing certain part of these rocks to be volcanic (meta-komatiite) combined with the cutting bodies of plutonic ultramafic rocks of dunite-harzburgite association which deep parts in places contain schlieren, lenses and sheet-like bodies of chromite ores.

The typical bodies of dunite-peridotite-gabbro-norite association in Middle Pobuzhzhya include Tarnuvatskiy, Kumarivskiy, Kamenovatskiy, Grushkovskiy, Skhidnolyushnevatskiy, Demovyarskiy, Derenyukhinskiy, Chausovskiy, Zavallivskiy, Krymkivskiy, Kamyanobalkivskiy, Kosharo-Oleksandrivskiy, Bogdanivskiy, Danylkivskiy, Lozovatskiy, Raznoshenskiy, Polokhivskiy and other moderately elongated (1:2.5 – 1:5.5) massifs. According to the published data, the mafic rocks are locally developed, mainly in the upper parts of intrusive bodies, and also occur in their periphery where they are associated with pyroxenites. All massifs are irregularly-shaped but roughly are conformable to the fold structure of host rocks. Normally these are minor syncline folds with limb range of first kilometers, with contiguous ultramafic massifs, jointly (afterward) deformed and arranged with the host stratified rocks of Buzka Series.

Dunite-harzburgite association in Middle Pobuzhzhya includes Kapitanivskiy, Zavodskiy, Lypnyazkiy, Pervomayskiy, Burtyanskiy, Lypovenkivskiy and other massifs (Fig. 3). The massifs are either sheet-like and lens-like with width to length ratio from 1:7 to 1:60 or isometric (Lypnyazkiy, Pervomayskiy massifs). The width varies from 50 to 350 m and their length attains 2.5 km. The massifs are composed of serpentinized dunites and harzburgites with minor mafic rocks which normally from cutting vein bodies.

In dunite-peridotite-gabbro-norite association peridotites include harzburgites and lherzolites with rare verhlites. The latter are completely lacking in dunite-harzburgite association while lherzolites are locally developed. Average orthopyroxene iron content in the rocks of the first association is higher (17% in comparison to 13% in dunite-harzburgite association).

Ultramafic rocks of both associations throughout contain chromespinelides but in dunite-peridotite-gabbro-norite association their content does not exceed first percents whereas in the rocks of dunite-harzburgite association it may attain 6% and more. The rock affinity to one or another association, in view of many authors, is clearly indicated by composition of their chromespinelides: magnesium (24.8 and 38.9% respectively), chromium (45.9 and 53.0%) and alumina (9.7 and 33.4%) content.

From the results of prospecting and exploration works in Middle Pobuzhzhya it was thought that different metallogenic specialization of the above associations is established. Specifically, dunite-harzburgite association is chromite-bearing. Occurrences of silicate nickel are known in weathering crust after the massifs of both associations while discovery of sulphide copper-nickel ores is thought problematic. Chromite ores as well as the rocks of dunite-peridotite-gabbro-norite association are considered to be potentially platinum-bearing being weakly-studied.

Geology of Kapitanivskiy massif

Kapitanivskiy massif is extended in the north-western direction over the distance of about 2.5 km at the width of ultramafic rocks at the crystalline basement surface 40-220 m. The massif is widest in the northern and central parts. To the south its width decreases and in general the massif looks like baseball bat (Fig. 23). The contacts with country rocks dip to the north-east at the angle 75-80^{o}.

The massif is composed of serpentinized dunites, peridotites, pyroxenites, calciphyres (calciphyre-like rocks) and chromite ore bodies (Fig. 24).

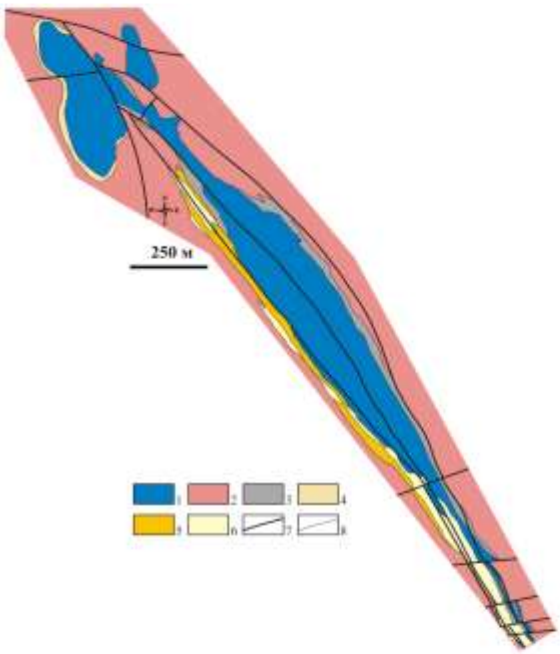


Fig. 23. The scheme of the geological structure of Captain ultrabasite array

Legend:
1 – serpentinite
2 – leucocratic biotiteplacing granite-gneiss
3 – calciphyre (aposerpentinite ophicalcite)
4 – biotite, garnet-biotite plagiogneiss
5 – garnet-sillimanite-biotite cordieriteplacing plagiogneiss
6 – apogneiss secondary quartzites
7 – major faults
8 – geological boundaries

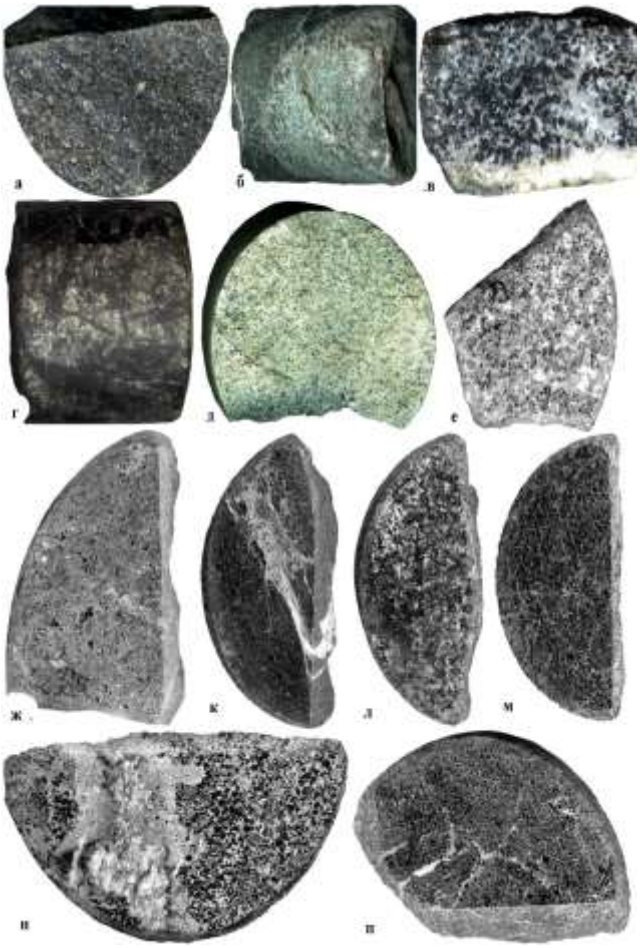


Fig. 24. Rock and ore types of Captain ultrabasite array:

а – dolerite dike, well H01 depth 95,2 m;
б – carbonized hydromica apoperidotite serpentinite, well H01 depth 170,7 m;
в – calciphyre, well H01 depth 181,3 m;
г – spinifex structural metakomatiite, well H01 depth 218 m;
д – apodunite serpentinites with scattered chromite inclusions, well H01 depth 237,5 m;
е – scattered chromite inclusions in calciphyre, well H02 depth 109,6 m;
ж – veinlet-impregnation segregation of ore minerals in apodunite serpentinites, well H01 depth 123,6 m;
к – continuous chromite ore with crushing areas that are filled with carbonate material, well H01 depth 177,8 m;
л – medium embedded chromite ore in calciphyre, well H01 depth 179,5 m;
м – densely embedded chromite ore , well H01 depth 228,8 m;
н – chromite inclusions and schliere excretion in apodunite serpentinites, well H01 depth 242,1 m;
п – densely embedded magnetite-chromite ore among calciphyres, well H01 depth 249,6 m.

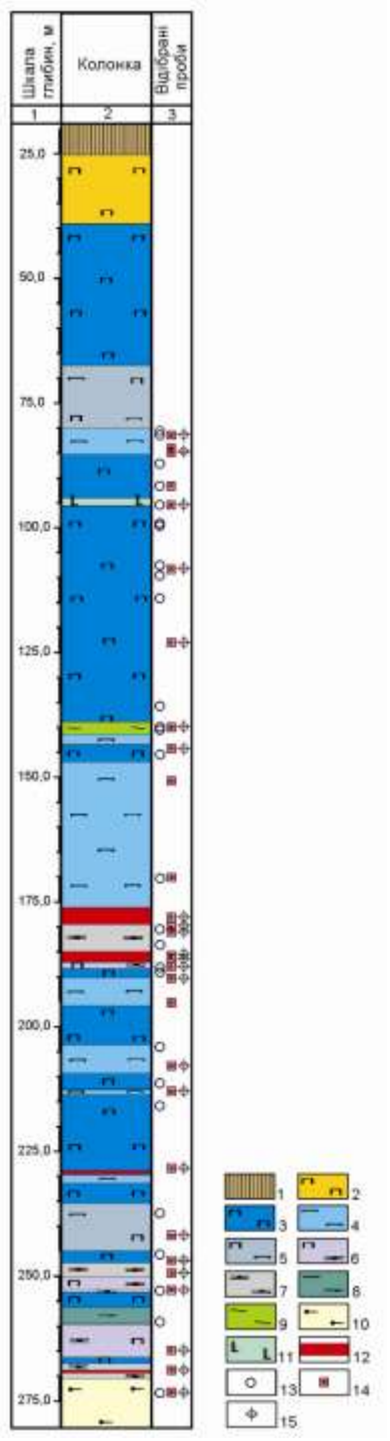


Fig. 25. Column for exploration borehole №H01 Captain ultrabasite array

Legend:
1 – weathering crust
2 – weathered apoperidotite serpentinites
3 – apoperidotite serpentinites
4 – apodunite serpentinites
5 – alternation intervals of apoperidotite and apodunite serpentinites
6 – carbonized apoperidotite serpentinites (rocks of intermediate composition between apoperidotite serpentinites and calciphyres)
7 – calciphyres
8 – amphibolites
9 – biotite-amphibolite crystalcherts
10 – cordierite-biotite-sillimanite-garnet plagiogneisses
11 – dolerite
12 – solid and densely disseminated bodies of chromite ore
13 – samples for petrographic research
14 – samples for mineragraphic research
15 – samples for microprobe X-ray spectral research

Meta-dunites (Fig. 24) are most developed; these are rock of massive structure and medium-fine-grained panidiomorphic (euhedral) texture. Besides this, looped, fibrous, parallel-fibrous textures occur. Mineral composition: olivine (up to 70%), orthopyroxene (up to 5%), chromite (up to 8%), and secondary minerals (serpentine, actinolite, carbonate).

Meta-peridotites (Fig. 24) are locally developed in thin lenses. Harzburgites predominate with more rare websterites. Serpentinization and amphibolization are observed. These are full-crystalline massive medium-fine-grained rocks with hypidiomorphic (subhedral) and panidiomorphic (euhedral) texture. Mineral composition: olivine (up to 50%), ortho- and clinopyroxenes (up to 60%), spinel (up to 5%), and serpentine.

Calciphyres (Fig. 24) include diverse-grained (fine-, medium- and coarse-grained) varieties of massive, spotty and banded structure. In the section they are observed both in contiguous up to 7-8 m thick separate bodies having clear contacts with ultramafic rocks (Fig. 6g), and in some spotty aggregates and vein-like bodies in ultramafites.

Relicts (?) of meta-basites comprise massive fine-medium-grained ***amphibolites*** and fine-medium-grained banded and schistose ***quartz-amphibole-biotite-plagioclase mafic gneisses***.

The ***meta-dolerites dykes*** with clear cutting contacts with all host rocks are also observed in the massifs (Fig. 6a).

Many authors also suppose that besides plutonic ultramafic rocks the massifs also contain their extrusive analogs – diverse meta-komatiites with distinct textures resembling "coarse spinifex". However, no one of the authors in relevant publications available do present required reciprocal petrographic (micro-textures), geological (flow layering) and petrochemical data confirming their conclusions which are necessary for their correctness. Instead, detailed studies of the drill-hole core sections, comprising ultramafic rock varieties with textures visually very similar to those from spinifex-textured zones, have shown that these are full-crystalline igneous rocks of no affinity to meta-komatiite lavas (Fig. 24). Under microscope, in the rock, between dark thin pseudo-skeletal spinifex-like grains the full-crystalline aggregate of serpentinized and chloritized olivine and pyroxene idiomorphic grains is observed, but not uncrystallized volcanic glass replaced by secondary minerals (this must occur in case of classic spinifex-textured flow zone). The vertical layering in the fragments of meta-komatiite lava flows or respective trends in structure-texture patterns of these rocks comprise perhaps the major evidences for meta-komatiite rock type while just the petrochemical data are insufficient. However, occurrence of meta-komatiites in the sections of ultramafic massifs in Pobuzhzhya cannot be completely refused. The issue requires further detailed studies. Nevertheless, the far-reaching conclusions being made on this ground concerning both the massifs and their host rocks affinity to greenstone belts, are incorrect. The theoretic probability (again, not properly confirmed so far with necessary set of evidences) of meta-komatiite occurrence in respective volcano-plutonic associations, assumed to be developed in the ultramafic massifs, at any rate does not provide the automatic indication for their "greenstone" nature. Generalized column of ultramafic maffis in Pobuzhzhya principally differs from one of greenstone belts (theoretically to be correlated with) in classic granite-greenstone terrains. Instead, all data available on the rock associations and generalized column in the massifs and their envelope suggest for their affiliation with the charnockite-granulite LTC described in details in many publications.

Extensive development of thin variously-oriented fractures filled with carbonates also comprises characteristic feature of Kapitanivskiy massif.

Ore mineralogy, electronic microscopy, microprobe analysis (main results in brief)

All rock varieties of Kapitanivskiy massif contain chromite or chromite-magnetite dissemination. Magnetite occurrence is clearly indicated by “peak” values in drill-hole magnetic logging curves while chromite enrichment, conversely, is expressed in negative values of magnetic susceptibility. In places (mainly in sites of fracturing) bunch-like aggregates and thin veinlets of millerite are observed in the rocks.

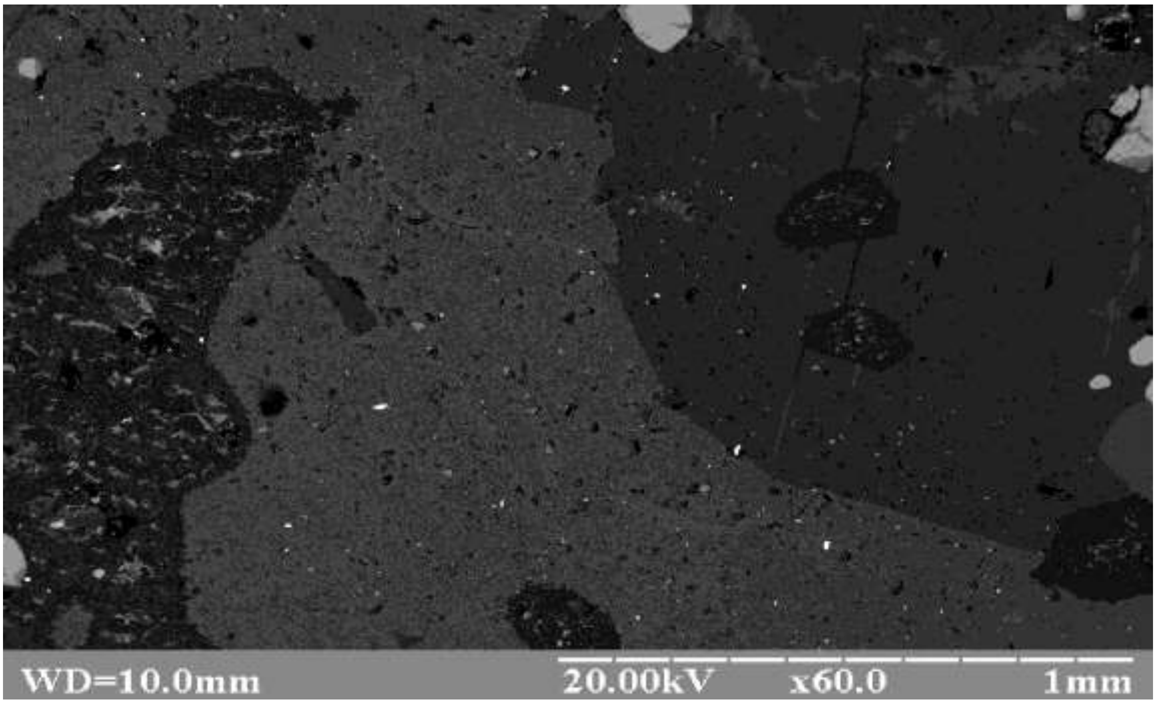
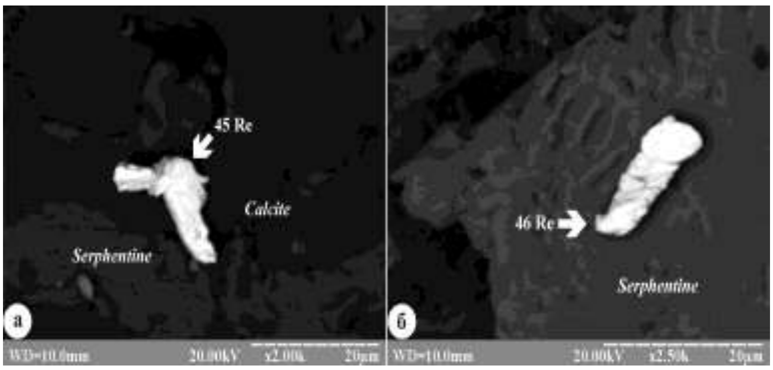


Fig. 26. Numerous starlike phase separation of native rhenium in serpentine-carbonate matrix



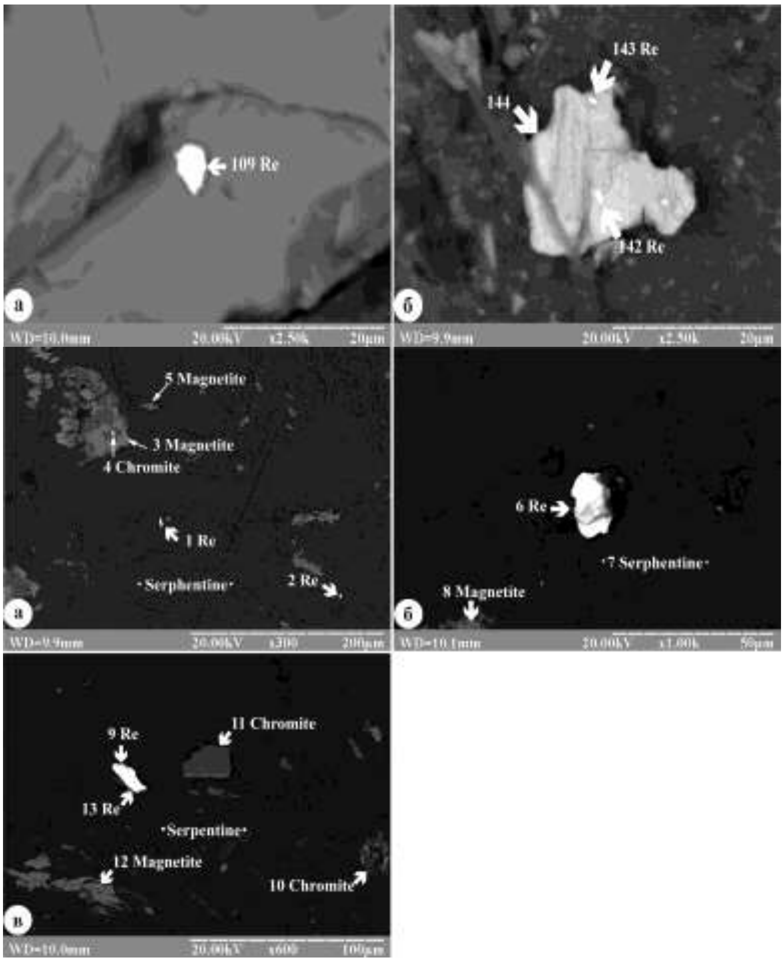


Fig. 27. Forms of native rhenium phase separation
in serpentine-carbonate matrix

Mineragraphic and microprobe studies allowed definition of about 50 ore minerals in Kapitanivskiy massif that form the evolution-time range of some mineral assemblages from early-magmatic stage to the latest one comprising the stage of low-temperature supergene alteration. In comparison to our previous publication [9], detailed studies of ore-mineral assemblages allow some corrections to be made.

In the order of temperature descend the mineral assemblages are set as follows:

I. Chromite (magmatic stage). In Kapitanivskiy massif the minerals of this assemblage comprise chrompicotite. General formula of the mineral is (Mg, Fe)(Cr, Al)$_2$O$_4$.

II. Chromespinel-magnetite (as a result of primary-magmatic chromite chrompicotite break-up).

III. Native-metal assemblage includes native iron and rhenium as well as graphite and inter-metallides of variable composition (natural composites of iron, chrome, nickel, cobalt).

IV. Arsenopyrite-gersdorffite with iridium, osmium and ruthenium sulpho-arsenides of variable composition. Obtained data suggest for occurrence of irarsite

$(RuOsIr(AsS_2))$, osarsite $(OsRu(AsS))$ and laurite (RuS_2) in the assemblage. Loellingite, niccolite, maucherite(?), as well as native silver, lead, zinc, and copper are also included in this assemblage. Similar set of native elements in sulpho-arsenide assemblages is described in [10] devoted to the behavior of nickel and cobalt minerals in post-magmatic processes.

V. Ilmenite-pyrrhotite-pentlandite-chalcopyrite with sphalerite and molybdenite. Rare enough scheelite and wolframite are also included in this assemblage.

VI. Pyrite-millerite (apparently with godlevskite, heazlewoodite, davsonite (?) $(Pb_{11}Sb_{12}S_{29})$, calcite, barite, rutile and second-generation magnetite) assemblage also contains galena, electrum and native gold. Some of these minerals appears through low-temperature hydrothermal alteration of the previous one whereas other minerals are newly-formed due to new components input or redistribution (specifically, Sb, Pb, Ag, Au).

VII. Violarite-marcasite mineral assemblage is least-temperature and is formed at the stage of transition from hydrothermal ore formation to the processes of supergene alteration. It also includes chlorite, calcite, goethite, hematite, valeriite $(4(Fe,Cu)S\ 3(Mg,Al)(OH)_2)$, and mackinavite (Fe_9S_8).

Electronic-microscope studies of native phases and ore minerals as well as their microprobe studies by wavy analyzer REM-106 are conducted in the laboratory of precise studies of UkrSGRI (analysts – O.Voloshyn, A.Bilous).

Established features of ore mineralization are observed over entire Kapitanivskiy massif in the zoned mode in relation to chromite ore bodies.

Composition of unaltered chrompicotite from the sites of chrome ore development is widely variable: Cr_2O_3 – from 42.15 to 63.82 wt. %, $FeO+Fe_2O_3$ – from 16.87 to 36.15 wt. %, MgO – from 6.21 to 13.26 wt. %, and Al_2O_3 – from 5.71 to 19.91wt. %. Traces of SiO_2 are frequently observed – up to 1.66 wt. %, and in some places MnO, TiO_2 and CaO occur. The chromium-enriched varieties (Cr_2O_3 > 60 wt. %) are observed at the chrompicotite grain junctions in separate unclearly-bounded enclaves and in observations under electronic microscope they differ in higher brightness. In the high-chromium varieties the sum of $MgO+Al_2O_3$ is decreased and does not exceed 20 wt. %.

Chemical composition of primary chrompicotite break-up products now being studied in detail. Their definition is grounded on the observations over mineral phase relations under the ore microscope and subsequent microprobe analyses. In view of the compositional variability and gradual transitions, these minerals are conventionally enough divided into three groups: chrompicotite-II, chromemagnetite and magnetite. In the optical and electronic-microscope investigations just the magnetite identification is unequivocal. It is confidently identified by grain morphology and optical properties (including reflected electrons). Normally magnetite is observed in the rims and delicate aggregates around chrompicotite or inside its grains. Chrompicotite-II and chromemagnetite are being developed by the solid solution break-up scheme. Emulsion dissemination of mentioned minerals is observed in the core or peripheral parts of the early chrompicotite grains continuously developing over entire chrompicotite volume. Often the process causes formation of the complete pseudomorphs. It is especially characteristic in the sites of disseminated chromite mineralization development.

As it is evidenced from the Table 4, in comparison to the primary phase chrompicotite-II is depleted in Cr_2O_3 (from 18.38 to 37.49 wt. %) and enriched in $FeO+Fe_2O_3$ (from 34.15 to 58.59 wt. %). In addition, Al_2O_3 content is increased (4.37 wt. % in average) and MgO content is decreased (1.24 wt. % in average). In some cases MnO, TiO_2 and CaO are identified.

Chromemagnetite in Kapitanivskiy massif is defined on the ground of the sharp drop in MgO (0-3.08 wt. %), Cr_2O_3 (11.29-21.30 wt. %) contents and considerable jump in $FeO+Fe_2O_3$ content (up to 69.86-88.71 wt. %).

Magnetite composition is characterized by high $FeO+Fe_2O_3$ (93.53-98.65 wt. %), minor Cr_2O_3 (0.24-2.75 wt. %) contents and negligible amounts of MgO and Al_2O_3.

In the chrompicotite break-up products silica is determined in amount from 0.86 to 3.72 wt. %.

Considerable results of electronic-microscope studies include definition of the native-metal assemblage containing metallic rhenium.

The rhenium “mineralization” is encountered both in various types of chromite ores (massive, disseminated, more or less chromite-enriched host rocks etc.) and outside the ores. Metallic rhenium particles are observed in fine dissemination and in star-like cloudy accumulations with single phase size up to 20 microns and in amount of 60-70 particles per 2-3 mm^2 of sample space (Fig. 10, 11, 13, 14). Average size of rhenium phases is first microns. Colour of the mineral is bright-white.

Chemical composition of native rhenium by microprobe analysis is consistent enough. The metal content varies from 84.74 to 100 wt. %. Impurities frequently include iron and chromium (0.77-7.82 and 0.23-4.86 wt. % respectively). Nickel (1.36-2.65 wt. %), cobalt (0.99-7.08 wt. %), copper (1.27-1.69 wt. %) and magnesium (3.02-8.24 wt. %) are determined in some points and a single case of molybdenum content. Obviously, amount of impurities notably decreases with increasing the size of mineral grains (to 10-20 microns). Apparently it is resulted from the native rhenium refining in the course of its growing and re-crystallization. High contents of iron, chromium, nickel and cobalt in some points are caused by the contamination of mineral occurring in the fine inclusions in Co-Ni-Fe inter-metallide or in chrompicotite.

Native iron comprises abundant counterpart of the native-metal assemblage occurring in the grains with sculptured surface, single wire-like particles, rarely dendrites, or in the meandering veinlets filling fractures in chromepicotite.

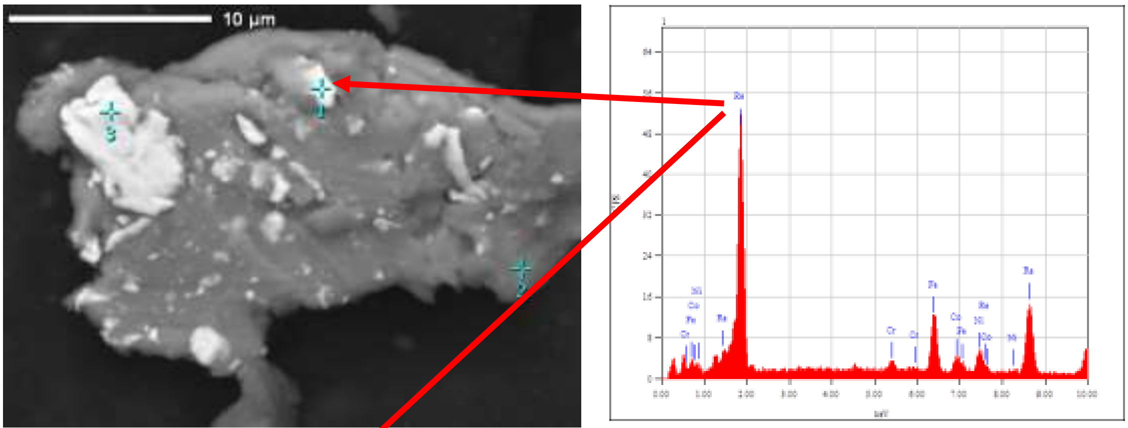
The mineral contains iron – 84.81-99.20 wt. %, and chromium – 0.29-15.57 wt. %. In three of six points silica in determined in amount 0.92-1.83 wt. %.

The inter-metallides of variable composition are closely associated with native rhenium; their principal elements include (in descending order of content) Co, Cr, Ni and Fe. The element contents in minerals are fairly variable: Fe – 2.85-73.12 wt. % (47.37 wt. % in average), Ni – 8.84-72.94 wt. % (31.96 wt. % in average), Cr – 0-23.51 wt. % (12.06 wt. % in average), Co – 0-17.04 (6.87 wt. % in average). Apparently these compounds comprise continuous isomorphic ranges having native iron and nickel as the marginal members. It should be noted that native nickel is not found in the massif so far.

Arsenopyrite-gersdorffite mineral assemblage in the rocks of Kapitanivskiy massif is encouraging in term of platinum-group elements. The phases identified in this assemblage include iridium, osmium and ruthenium sulpho-arsenides of variable composition. These compounds are classified as irarsite, osarsite, laurite or their mixtures. It should be noted that diagnostics of PGE sulpho-arsenides (as it is reveled from published sources) is normally equivocal due to the continuous gradual isomorphic substitutions and frequent fine inclusions providing composition irregularity of mentioned minerals even in the micron scale.

Concerning the distinct feature of the PGE distribution, platinum is not found in the own minerals while it is sporadically observed in sulpho-arsenide impurities in amount up to 6.77 wt. %. In single cases rhodium and molybdenum are also identified. The latter is apparently related to the occurrence of molybdenite micro-inclusions.

It should be noted that complete description of mineral assemblages is not possible in this paper and the detailed results of mineralogical studies in Kapitanivskiy massif will be given in the subsequent papers.



Element	(keV)	mass%	Error%	At%	Compound	mass%	Cation	K
Cr K	5,411	1,2	0,1	3,35				1,1544
Fe K	6,398	11,35	0,11	29,6				12,179
Co K	6,924	3,12	0,13	7,7				3,4438
Ni K	7,471	4,81	0,15	11,93				5,5663
Re M	1,842	60,63	0,32	47,43				47,6676
Total		81,09		100				

Fig. 28. Rhenium in the intermetallic compound and its chemical composition was:

Expected ore types (fantasies)

The peaks of rhenium concentrations, by preliminary observations, are observed both in chromite-enriched portions of the massif and in the associated rocks (for example, in calciphyres) with minor chromite content (first percents) or without chromite at all. Thus, two ore types at least are distinguished: chromite-bearing and actually chromite-less.

The ***first, chromite-bearing ore type*** comprises spatially joined age-different ore-mineral assemblages located in chromite ores with variable chromite grade (depending on the ore types). Selective extraction[1] of defined platinoids and rhenium using common technological processing schemes will include various complex extraction and beneficiation technologies with elements of metallurgy.

The ***second, actually chromite-less ore type*** comprises carbonate-silicate matrix of calciphyres and calciphyre-like rocks re-crystallized in various extents, as well as plutonic-facies ultramafites (including probable cumulative zones of meta-komatiite flows if this is proven unequivocally) carbonatized in various extents. This ore type seems to be most suitable for the further economic development.

Conclusions

In the course of research works on ultramafic massifs in Middle Pobuzhzhya, for the first time in the world geological practice and using high-precision analytical equipment, we have identified previously unknown types of potentially economic ore objects with significant concentrations of native rhenium and (besides platinum and palladium traditionally known in Kapitanivskiy massif) a range of rare platinoids (osmium, iridium, ruthenium, rhodium). From our preliminary results, in some ultramafic massifs of Kapitanivske ore field discovery and spatial parametrization of at least two ore types is expected of which one is easily beneficiated (gravity separation, flotation) and high-grade in term of the valuable component.

The following reasons define the value of this discovery:

- for the first time in the world practice we have identified in the natural geological systems the native (metallic) rhenium – quite rare trace element with the least Clark value ($7*10^{-8}$) among the platinoids and lanthanoids. So far rhenium was known either in isomorphic impurities or in rare own minerals (rhenite, dzhezkazganite) of no economic value and was extracted from other minerals (molybdenite first of all);
- if the further works confirm appraisals of rhenium content in newly-defined ore types and its total resource potential one can talk about the discovery of previously unknown geological-economic rhenium ore type (coupled with aforementioned platinoids is their contents are also economic).

[1] The issue of ore beneficiation schemes will be considered elsewhere in special paper.

Preliminary evaluated economic parameters of ore zones and bodies allow expectation for the discovery of large and unique by reserves, as well as unknown in the world to date the independent and complex deposits of platinum group metals, chromium, nickel, cobalt and other metals of described type.

Thus, obtained results indicate that in ultramafic rocks of Pobuzhzhya geologo-genetic types of mineralization are encountered previously unknown in the world geological practice, and a range of the fundamental ore-mineralogical discoveries is made which can be the ground for immediate initiating the prospecting works over the area of closely-spaced minor (first km^2) ultramafic massifs similar in composition and geological setting.

The work is conducted and financed in compliance with the Law of Ukraine "On the Whole-State Program for Development of Raw Mineral Commodity Base of Ukraine for the Period to the year 2010" under the State budget of Ukraine costs in the course of research project of Ukrainian State Geological Research Institute No. 673 "Appraisal of potentially platinum-bearing structures of Ukraine aiming definition the local perspective sites for the platinum group metals".

The primary materials include core section of boreholes drilled in 50-60th by Pravoberezhna Geological Exploration Expedition of the State Regional Geological Enterprise "Pivnichgeologiya" in the course of prospecting and exploration works for chromite and nickel ores within the contour of reserves approved by the State Commission on Mineral Reserves of Ukraine for Kapitanivske chromite deposit, as well as new boreholes drilled by this Enterprise over last years in the course of exploration and reserve estimation in the southern flank of mentioned deposit. Essential contribution to the results is also obtained in our studies of the five boreholes drilled by the "Ferrexpo" Company in the central part of this deposit in 2005-2006.

Key objective of work in this area for 2016 and 2017 - developing a set of criteria for the localization of rhenium in similar rock complexes of ancient shields of the world. We are planning to carry out such work in Ukrainian (Ukraine), Baltic (Finland, Russia), Aldan (Russia) and Lyon-Liberian (Sierra Leone, Liberia) shields.

1.2. FIELD WORKS IN SIERRA LEONE. Main Resoult.

We carried out geological-geophysical investigation of few prospective areas in the north of Sierra Leone (Western Africa) by order of MIR company during 26 NOV- 13 DEC 2015. Main results are presented in A.Bobrov, A Pivtorak CONTRACT REPORT «The result of the geological-geophysical investigation of Yana Area» carried out in November-December, 2015. West Africa. The Republic of SIERRA LEONE.

Main focus of our studies next areas:

License area of Revolution Minerals Ltd

Main site of interest was Flower Valley, Doleritic and Forrestry (that belongs to Revolution Minerals Ltd)

License area of Style Research (SL) Ltd № EL11/2014 (Kabala)

Having regard to the similarity of geological situation another site of our interest was licensed area of EL 11/2014 (Kabala), which area was 248.6 km^2. Its owner is the company Style Research (SL) Ltd. Author carried out reconnaissance investigations for verification of the test results of May 2013.

One can suppose from obtained data (including direct analytical data of minerals of potentially productive rocks) that, with high probability, new kimberlite fields can be identified and parameterized there.

In addition, our unique finding in these samples should be mentioned. It was large enough (6 microns) phase of the metal rhenium (possibly it was rhenium sulphide, such as ReS_2). Until now, similar discovery was made by author (Bobrov et al., 2007) during his study of ultrabasites in Kapitanovskii group in the Ukrainian Shield.

In the samples from these sites variety of nickel minerals, natural intermetallides with platinoids were found in ultrabasites. This is evidence of high metallogenic potential of this territory and its diversity. Successful study of these sites requires complex operational geological and geophysical studies.

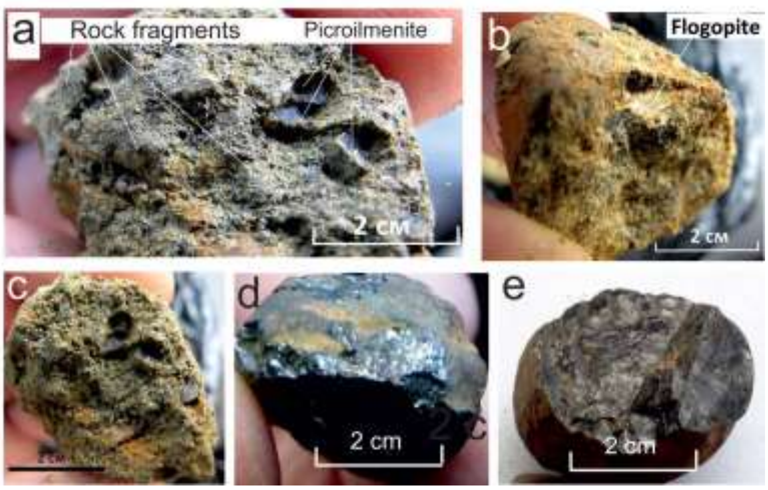


Fig. 29. Comparison between phenocrysts in kimberlite (a, b, c) and samples of picroilmenites of talus SL-5 (d)

a, b, c - fragmental kimberlite with phenocrysts of olivine, phlogopite and picroilmenite; d-picroilmenite as a fused phenocrysts from kimberlite rocks SL-5 (in the southern part of the license area EL13/2013)

At the license area of «STYLE RESEARCH (SL) LIMITED» company, which area is 250 km^2, complex decoding and geomorphological (neotectonic) data analysis were used. As result, we marked areas that contained promising mineralization of different geological and industrial types with bedrock localization and areas with favorable characteristics for the formation of industrial placer deposits of gold, diamonds and rare earth metals. Some of them contain direct indications that these types of mineralization are present. They need address additional study by complex of geophysical methods, by parametric drilling (or by sinking of pits) and adequate verification tests. This series is characterized by gold and rare metals resources that belong to P_2 and P_3categories

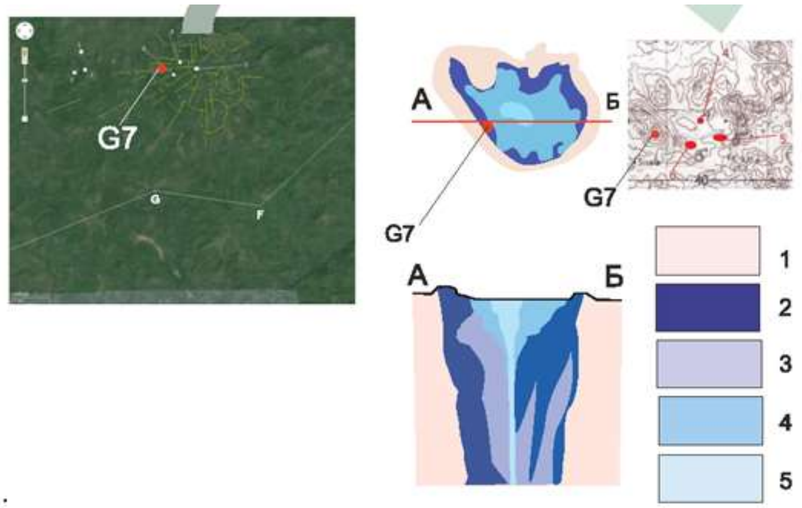


Fig. 30. Caldera complex with true signs of talus kimberlite presence

1- granitoids of basement; 2- kimberlites of tuff-lava facies; 3- massive kimberlites; 4- caldera complex (supposed lava-breccia); 5-inlet pipe channel

License area EL 2013 is located close to the traditional diamond Sierra Leone provinces - Koidu and Tonga, where high-quality diamonds are mined. Showings of kimberlite pipes presence and their caldera complexes were found (Fig. 9.3). Directional geological, geophysical and analytical studies are needed can help to discover diamondiferous rocks and geological structures If estimates of resources/diamond reserves will be successful (exploration → report→ sale of object/objects), financial prospects of this part of the project can go beyond the bounds of normal project giving him the status of high liquid one.

As capitalization of geological information is possible, financial forecast for the prospects of this project is very optimistic, in whole.

License area of Magnum Link (SL) Limited № EL04/2013

Another license area was Exploration Licence № EL 04/2013, which area was 124 sq.km at the territory of Kassunko Chiefdom in the Koinadugu District, Northnern Province. It belongs to Magnum Link (SL) Limited. The presence of the caldera Mabore was determined after remote sensing studies. We found several areas with potential clusters by swarms of kimberlite pipes in this territory. It was described in details in a special report.

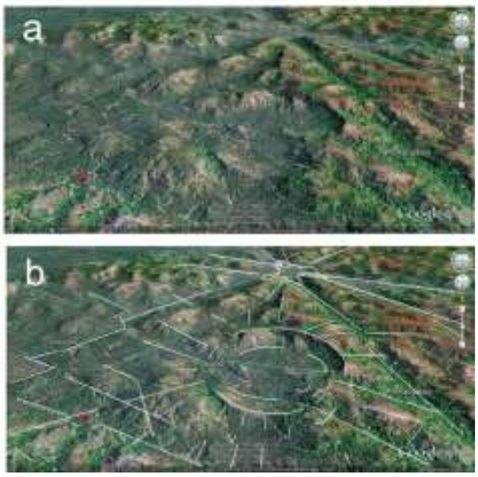


Fig. 31. Mabore Caldera on satellite photo (a) and the results of decoding (b) of circular and radial fractures

In all these areas, and geostructures in the ultrabasic rocks revealed the presence of metallic rhenium phases.

Very good example - is the rhenium phase from the kimberlite dyke (Fig. 32-34).

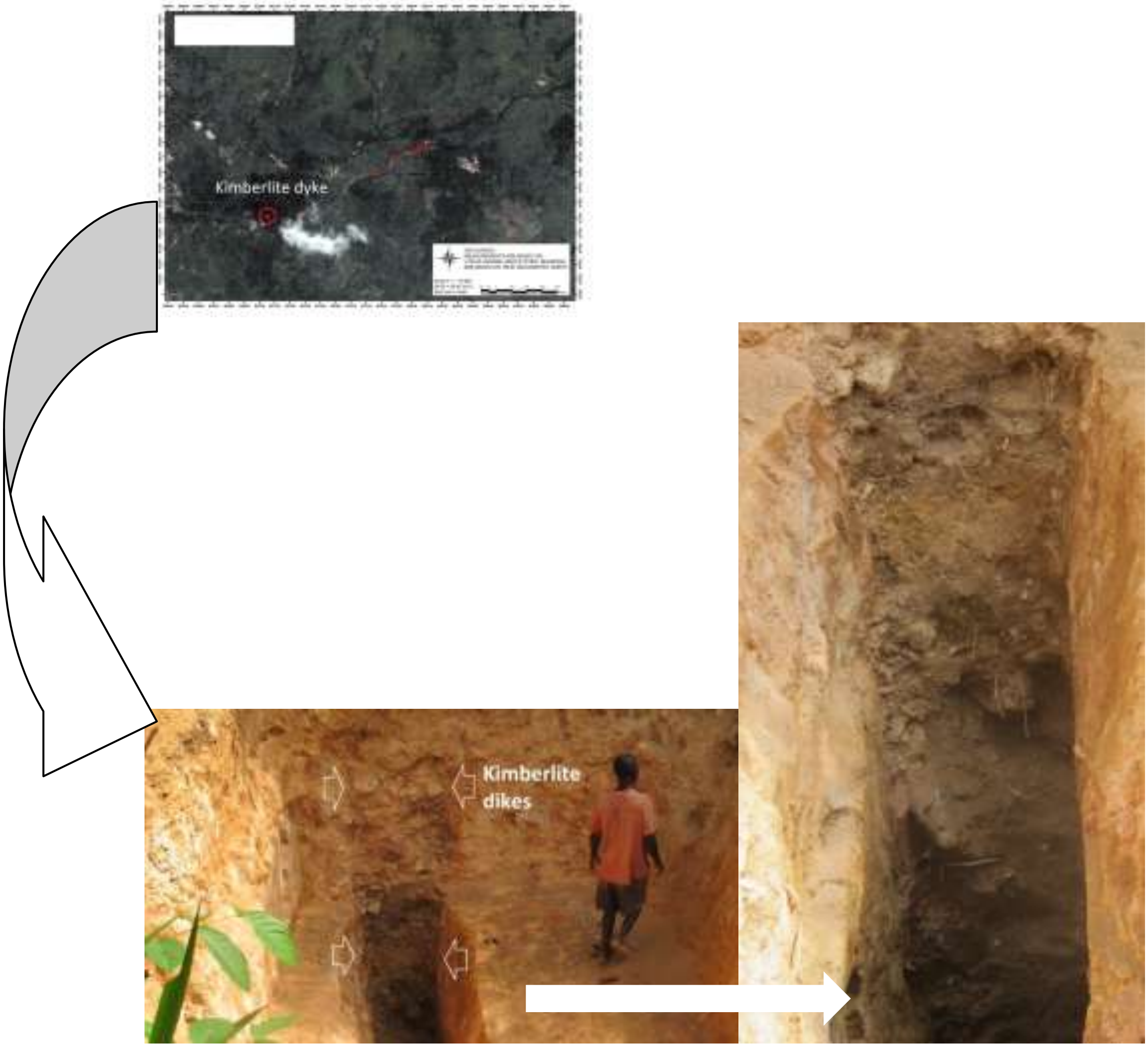


Fig. 32. Kimberlite dyke (Koidu region, Sierra Leone)

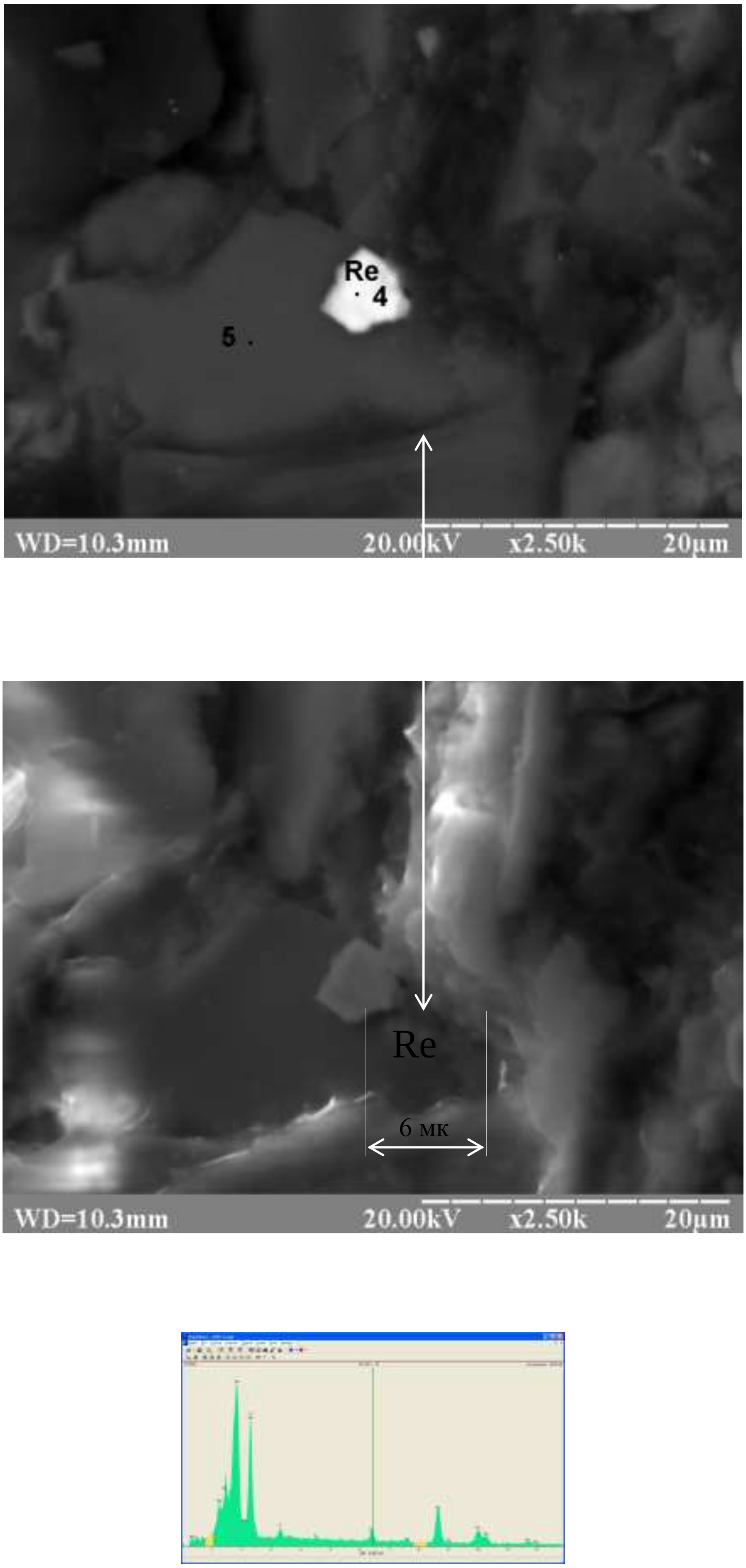


Fig. 33. Rhenium phase and range (down) from the kimberlite dyke

For the reporting period (2015-May, 2016) we have completed work on an additional study for the first time open greenstone structures of the eastern part of the Ukrainian Shield. Below provides a summary of the main results of their study.

2. GREENSTONE STRUCTURES OF THE OREKHOVO-PAVLOGRAD ZONE: FIRST EXPERIENCE OF THE GEOLOGICAL DESCRIPTION

2.1.NOVOGORIVSKA GREENSTONE STRUCTURE

During 2015 we are finished work on preparation of materials of the results of the study greenstone structures Orekhovo-Pavlograd tectonic zone, where traditionally allocated basement rocks of greenstone belts Ukrainian shield.

We have been gave a historical analysis of the identification and description of greenstone structures within the Orekhovo-Pavlograd deep fault zones. For the first time described the structural and tectonic position, ordering the internal structure and composition the rocks of the Novogorivska structure that was discovered among the real and genetically different types of rock associations – the basement of greenstone formations.

We had assesses the radiological age of the rocks, involved in its structure. Based on the characteristics of the mineral composition of the rocks and their position we are described three distinct parts (KT-1, KT-2 and KT-3) of the metakomatiitic-tholeiitic-formation and their stratigraphic analogues (surska, olzinska suits and kosivtsivska stratum).

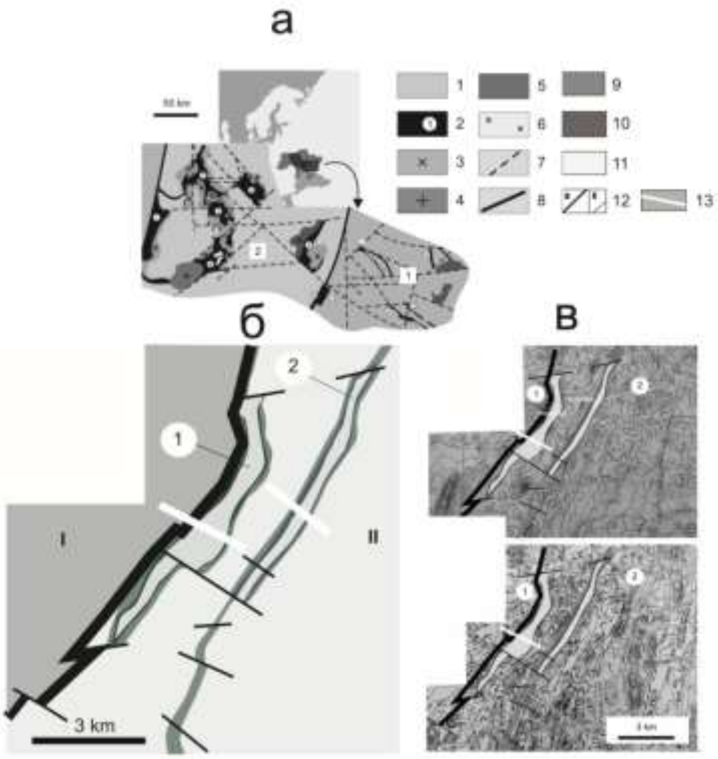


Fig. 2.2.1. Location of the Novohorivka (1) and Chystopillya (2) greenstone structures (GS) in the Azov block of the Ukrainian Shield and character of its manifestation in the physical fields:

a — greenstone structures location within the Middle-Dnieper granite-greenstone terrain (square *2*) and Azov granulite-greenstone terrain (square *1*) areas: *1* — migmatite basement (Auly series, Dnipropetrovsk complex); *2* — greenstone structures (the numbers in circles): *1* — Kryvyi Rih, *2* — Verhivtseve, *3* — Sofiivka, *4* — Chortomlyk, *5* — Sura, *6* — Konka, *7* — Haichur (Kosyvtseve), *8* — Sorokyne, *9* —Pav livka, *10* — Novohorivka, *11* — Chystopillya, *12* — Berestivka); *3* — tonalite-plagiogranite formation (Sura complex); *4* — granite formation (Tokiv and Mokra Moskivka complexes); *5* — migmatite basement of the Azov granulite-greenstone terrain (Zakhidne-Azov series, Saltychiya complex); *6* — subvolcanic rhyodasites (Sura complex); *7* — regional faults; *8*— abyssal fracture; *b* — schematic geological map of the Novohorivka and Chystopillya GS: metakomatiitic-tholeiitic formation (Sura suite): *9* — parageneration KT-1; *10* — parageneration KT-2; *11* — parageneration KT-3; *12* — abyssal fracture (*a*) and faults (*b*); *13* — drilling profiles: *I* — Middle-Dnieper block; *II* — Azov block; *c* — structures localization in gravitational (Bouguer reduction, top) and magnetic (Δ*T*, below) fields

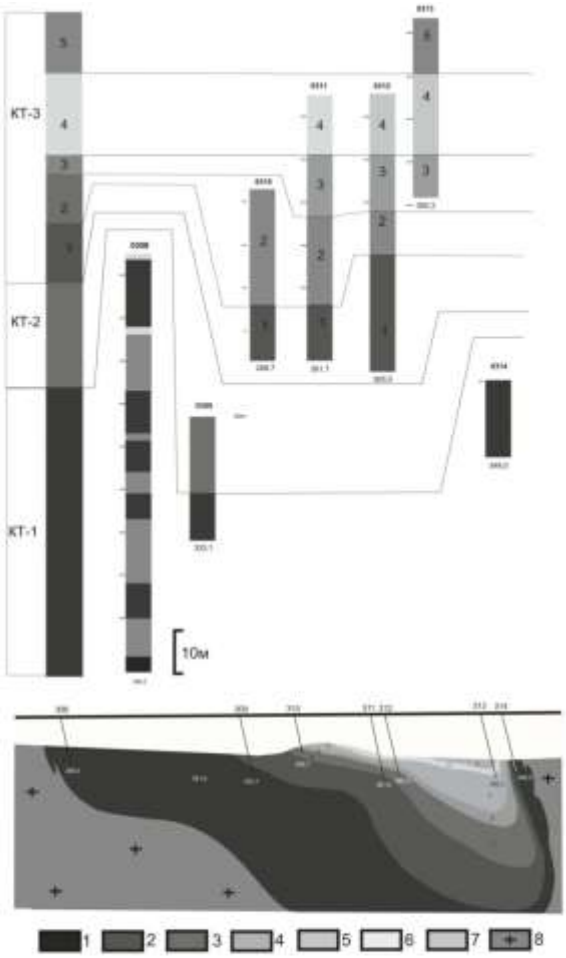


Fig. 2.1.2. Schematic generalized geological cross-section and correlation column in core drilling wells in the profiles of boreholes No 308-314 through Novohorivka GS:

metakomatiitic-tholeiitic formation (analogues: Sura/Olginske suites, Kosyvtseve stratum): *1* — lower metabasite parageneration; KT-1; *2* — lower metaultrabasite parageneration KT-2; overhead metaandesite-basite parageneration KT-3; *3* — horizon KT-31; *4* — horizon KT-32; *5* — horizon KT-33; *6* — horizon KT-34; *7* — horizon KT-35; *8* —granitoids of bordering

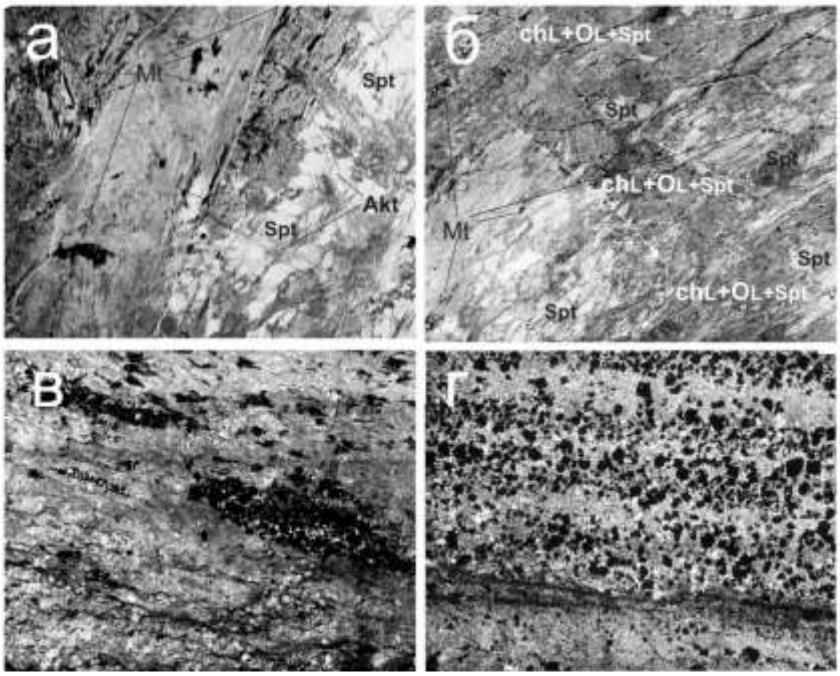


Fig. 2.1.3. Petrotypes of the lower metaultrabazalt association KT-2 of the Novohorivka GS:

a — ultrabasites with structure of "coarse" spinifeks (bore hole No 309, depth 289.1 m); *b* — the same (borehole No 311, depth 360.1 m); *c* — ±magnetite-cummingtonite-chlorite schists with the blastopsammitic textures relicts (borehole No 309, depth 288.0 m); *d* — ±garnet-magnetite-chlorite schists with the relicts of blastopsammitic textures (borehole No 311, depth 359.5 m); Akt — actinolite, Chl — chlorite, Mt — magnetite, Ol — relict olivine, Spt — serpentine

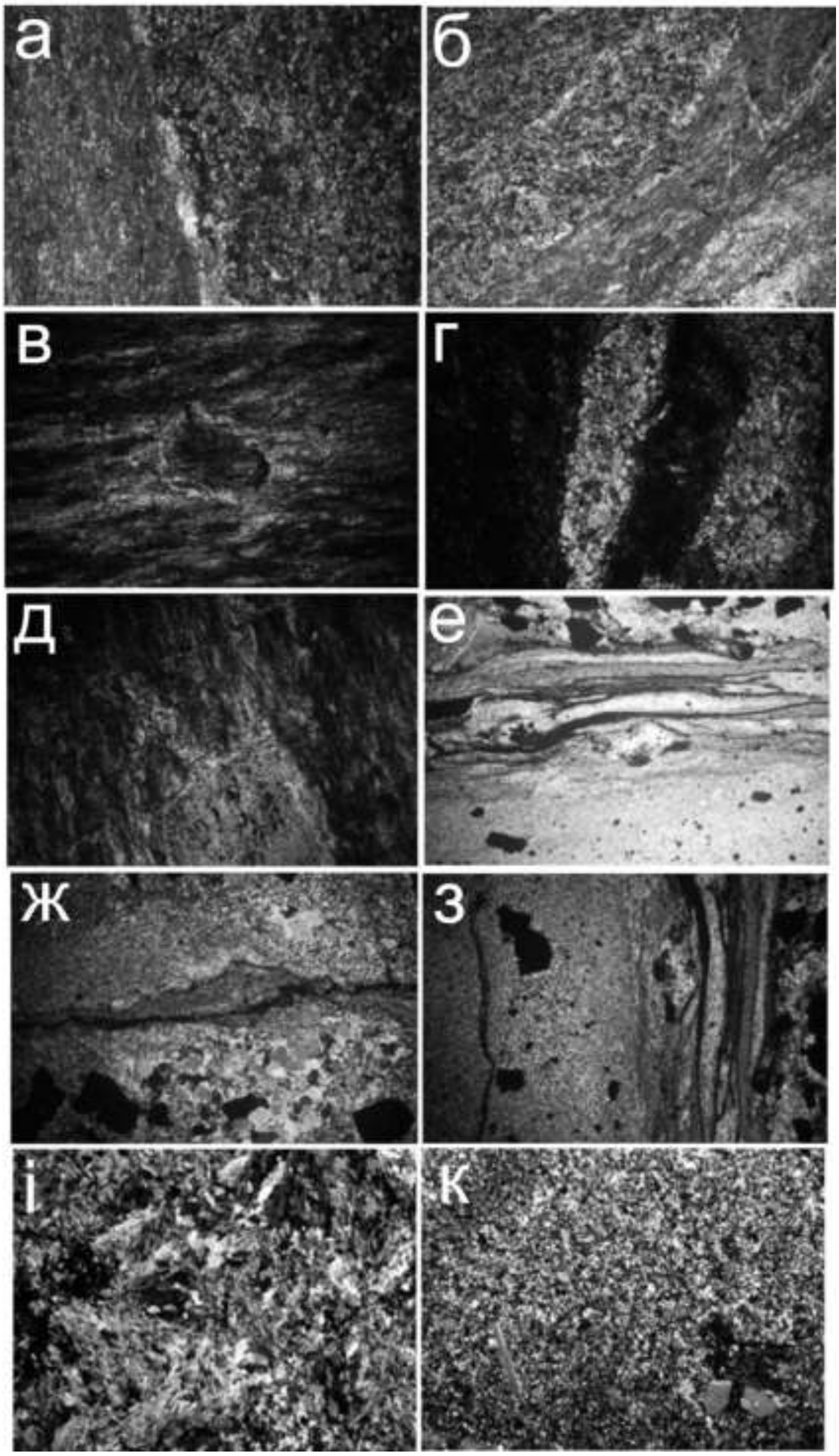


Fig. 2.1.4. Petrotypes of the lower metaultrabazalts paragenerationKT-3 of the Novohorivka GS:

a — *e* — crystal-clastic welded tuff basic composition (*a* — borehole No 0310, depth 243.2 m; *b* — borehole No 0311, depth 280.8 m; *c* — borehole No 0312, depth 270.1 m; *d* — borehole No 0313, depth 300.6 m; *e* — borehole No 0313, depth 284.6 m); *f* —*h* — litho-crystal-clastic welded tuff andesitic composition (*f* — borehole No 0313, depth 320.8 m; *g* — borehole No 0311, depth 260.4 m; *h* — borehole No 0310, depth 311.5 m); *i* — metaandesites (borehole No 0312, depth 284.7 m); *j* — metarhyodacites (borehole No 0311, depth 358.6 m)

2.2. CHISTOPOLSKA GREENSTONE STRUCTURE

We are made the first described structural and tectonic position, the ordering of the internal structure and rocks composition of the Chystopilska structure.

This is one of the two greenstone structures, which are first described by us in 1989-1990. The Structure is discovered within the area of the Orihovo-Pavlograds'ky deep fault zone among of totally different types of the strongly metamorphosed basement rocks associations. Cross-section of the drill- holes profile (№ 0300-0301) across structure (according to the obtained data) has a three-part internal structure. The lower part is represented significantly lower metabazalts association (KT-1) of the metakomat-tholeitic formation (a complete structural, composition and age analogous of the rocks of Surska suite, mesoarchean konkska series). The middle part of the section presented by significantly lower ultrabasitic paragеneration KT-2, and the top part – by andesite-bazaltic paragеneration KT-3, which are characterized the increased role of the tuff-lava facies. Cross-section correlation of the Novohorivska, Chystopilska and other typical structures of Near Azovian megablock (Kosyvtsivska and Sorokynska) whose status is undisputed showed complete resemblance of cross-section rocks filling, structural and textural features of the rocks, the ordering of the same type of internal structure, his relative stratigraphic position.

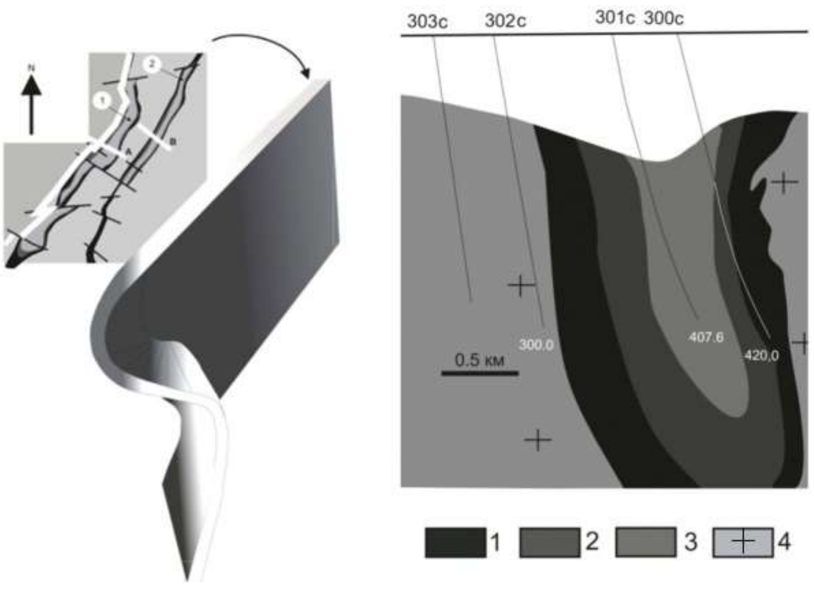


Fig. 2.2.1. Cross-section along profile of boreholes No 301—300 of the Chystopillya GS and its volumetric model: metakomatiitic-tholeiitic formation (Sura/Olzhinske suites, Kosyvtseve stratum): *1* — lower metabasite paragеneration KT-1; *2* — lower metaultrabasite paragеneration KT-2; *3* — overhead metaandesite-basite paragеneration KT-3; *4* — bordering granitoids

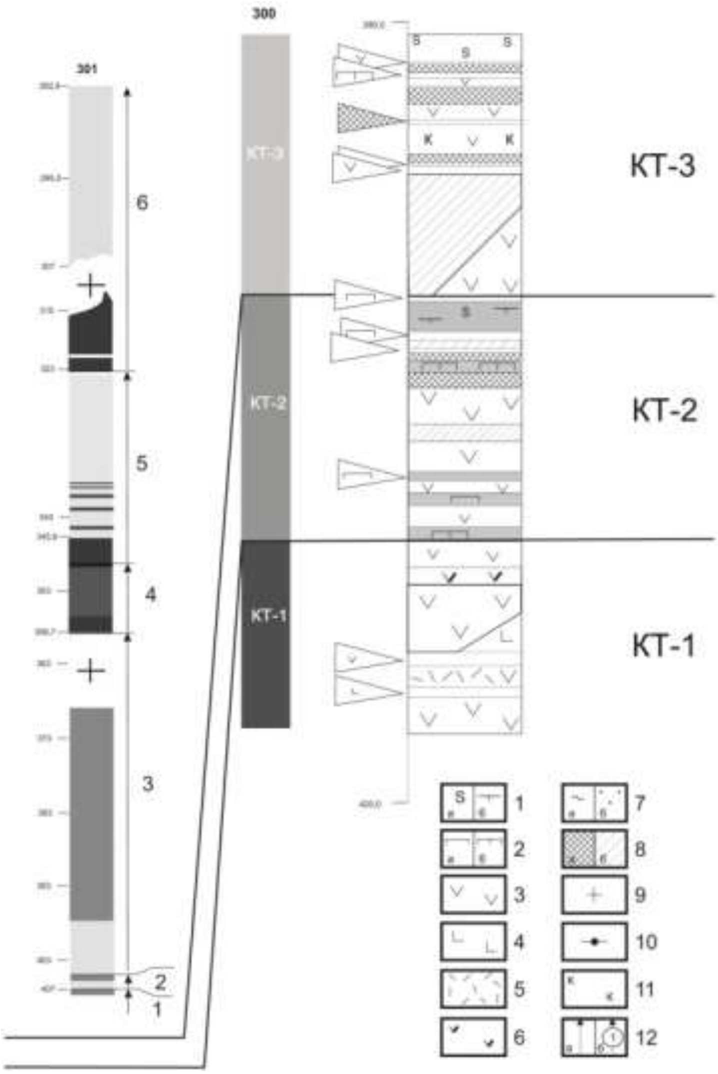


Fig. 2.2.2. Lithofacies column boreholes No 301, 300 and their lithologic-formational correlation:

1 — peridotitic metakomatiites: *a* — serpentinites with tremolite/chlorite; *b* — talc schists with tremolite/carbonate/chlorite; *2* — pyroxenite metakomatiites and its pyroclastic analogues: *a* — actinolitites, *b* — tremolitites; *3* — metabazalts (±quartz-plagioclase-amphibole schist with carbonate, chlorite); *4* — metaandesite (±biotite±quartz-plagioclase-amphibole schists); *5* — metarhyodacites (±muscovite-biotite-quartz-plagioclase schists); *6* — litho-crystalloclastic tuffs and tuff-lava; *7* — metatuffs: *a* — aleuritic; *b* — psammitic; *8* — metabasite facial characteristics: *a* — lavas; *b* — clastolavas; *9* — granites; *10* — blastotectonitic rocks; *11* — metasomatites on the metabasites; *12* — directed change and their numbers

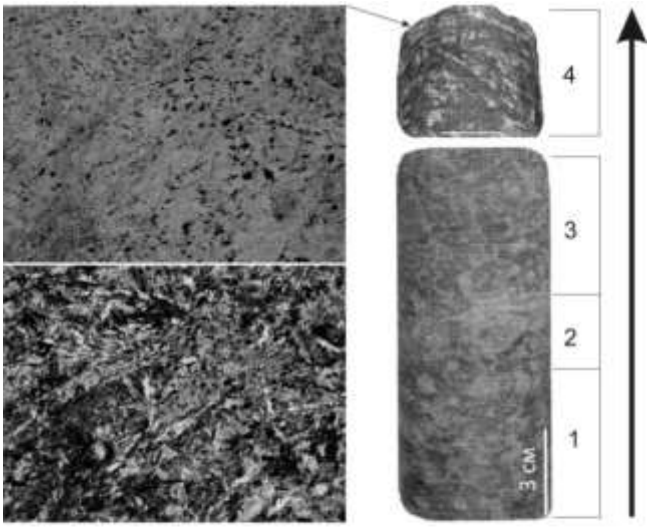


Fig.2.2.3. Metakomatiites (borehole No 300, depth 323.5—324.1 m)

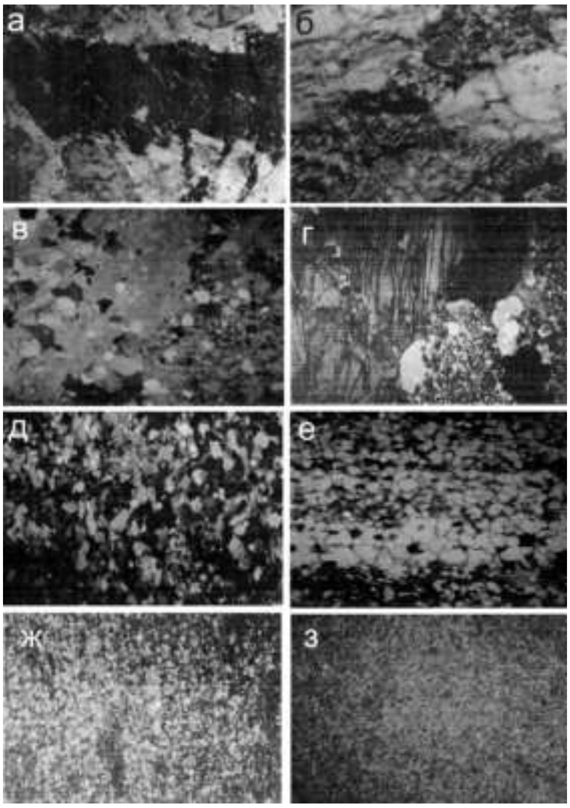


Fig. 2.2.4. Main type of the rocks in Chystopillya GS:

a, *b* — "coarse spinifeks" texture — transition zone to the cumulate (lower) part of the komatiitic flow; *c*, *d* — crystal-clastic welded tuff-lava (bazaltic composition); *e* — tuff-sandstone; *f* —cummingtonite-magnetite layered quartzite; *g* — lithoclastic tuffs of the andesite-bazaltic composition; *h* — rhyodacite

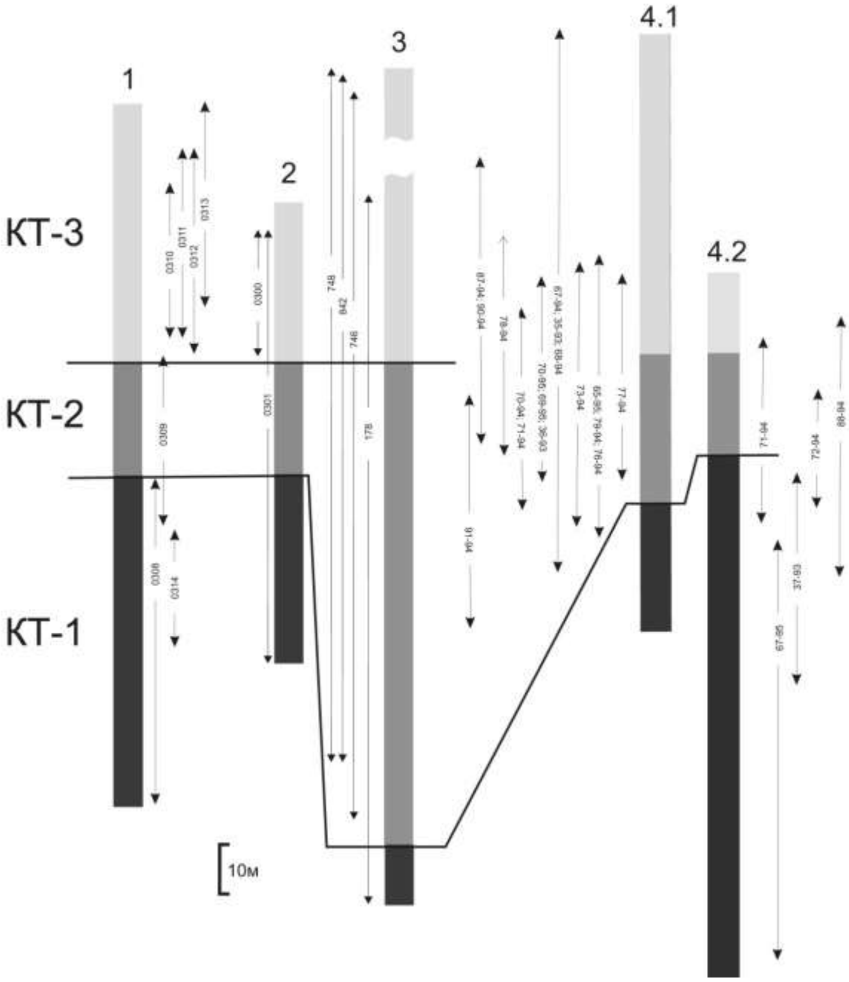


Fig. 2.2.5. Generalized correlation columns along the typical cross-sections of the greenstone structures of the Azov megablock of the Ukrainian Shield:

1 — Novohorivka GS; *2* — Chystopillya GS; *3* — Kosyvtseve GS; sides of the Sorokyne GS (Hutir Soroky area): *4.1* — South-West side; *4.2* — North-East side

3. GEOLOGICAL SETTING, COMPOSITION AND AGE OF THE PECHANOVSKIY LITHIUM-ORE GRANITOIDS MASSIF

In the context of the objectives of the INTRAW project we carried out research on the new site of the Ukrainian Shield where there are prospects of finding a new type of lithium deposits associated with pegmatites. Up to this time of the lithium-ore pegmatites here it was not known. Under the scientific supervision of prof. Alexander Bobrov in November, 2015 completed last PhD dissertation work by Mr. Mikhaylo Geichenko, who is an experienced geologist – practitioner (Specialized Expert Council № Д 26.162.02 for defense of theses. Institute of Geological Sciences of the National Academy of Sciences, Ukraine).

Title of PhD dissertation work is:

Geychenko M.V. Geological setting, composition and age of the Pechanovsky massif's granitoids (The Dniester-Boug and Volyn megablocks junction zone, Ukrainian Shield). – Manuscript. PhD dissertation work for a candidate degree in geology science by specialty 04.00.01- general and regional geology.- Ivan Franko Lviv National University., Lviv, 2015.

In this manuscript author described Pechanovsky massif on the base work on geological mapping 1:50 000 scale. Continued study of the massif gave a new factual material on the structural features of the geological position magmatic rocks and host granitoids, the composition of rocks, their petrographic and geochemical characteristics and accessories to a particular complex.

Author gave a new factual material on the study of all available outcrops, focused drilling in the contact portion and within the massif, first conducted systematic studies aimed at establishing the entire spectrum of basic petrotypes massif and the host granitoids.

From a geological point of view Pechanovsky massif is a part of a homogenized ultrametamorphic modified basement represented different supercrustal rocks (Vasilievka suite, Teterivska series). The findings suggest that certain areas of most homogenized plutonic features acquire homogeneous character and creates the possibility of intrusion servings anatektoidic melt. This gives paraautochthonous signs to the granitoids.

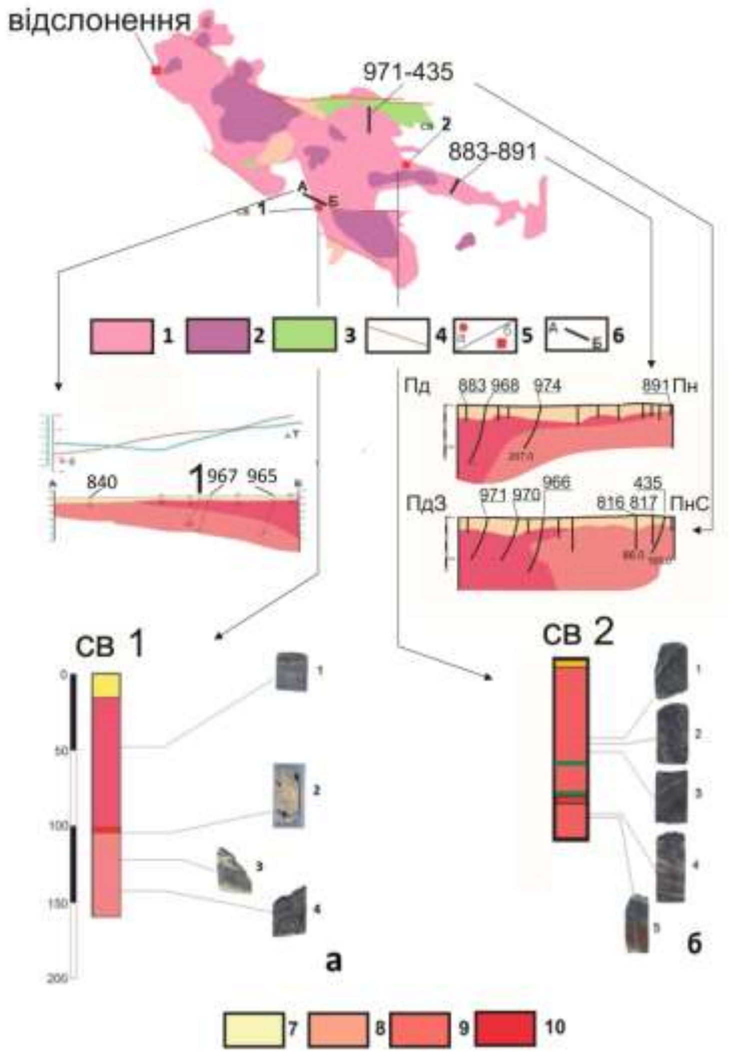


Fig. 1.1. The geological map and cross-sections of Pechanovsky massif

Legend:

1 - tonalite, plagiogranites 2 - quartz diorites, diorites; 3 - gneisses, amphibolites (Vasylivska suite); 4 - faults; 5 – a - parametric wells №1, № 2; b – exfoliation; 6 – профілі свердловин Profiles of wells; 7 – deposits of sedimentary mantle at cross-sections; 8 – migmatites of Berdichev complex 9 – plagiogranites, tonalites, quartz diorites of Pechanivsk massif (Sheremetiv complex); 10 - pegmatites. The blue curve above cross-section A-B - the intensity of the magnetic field (ΔT); red curve - the intensity of the gravitational field Δg in along the profile. The dotted line of the well № 1 - its projection onto the plane of the profile. The numbers on the figures – petrotypes of obtained cross-section: Well № 1: quartz diorite (Sheremetiv complex); 2 – rare metal pegmatite; 3 – amphibolite xenoliths (out of scale; 4 – paleosomic migmatites (Berdichevsky complex). Well № 2: 1 –hornblende plagiogranite; 2, 3 – amphibole-biotite tonalite; 4, 5 – tonalites, injected by subcross veins of corresponding gneiss and quartz-feldspar veins. Yellow - sedimentary mantle formation; green - relicts of substrate (Vasylivska suite); red - pegmatites.

As a result of researches we are established (isochronous uranium-lead method) in the tonalites radiological zircon’s age (2076.7 ± 6.2 Ma), clarified composition, volume and semantic content of the Sheremetyevo granitoids complex.

Radiological age of the ultrametamorfic biotite plagiogneisses of the Vasilevska suite that were largely homogeneous source of the Pechanivsky massif granitoids - 2104.7 ± 6 Ma (zircon) and age of the postmagmatic transformation products the ultrametamorfic anatektoidic melt mobilization - 2045.1 ± 5 Ma (monazite).

Refined metallogenic specialization of granitoid massif in zones of abnormal heat/fluid streams in the areas among contact of the blocks. Granitoids characterized by pronounced rare-metallogenic specialization and spatial control the perspective molybdenum, lithium, and germanium targets. We are - the first discoverers the diopside-spodumene pegmatites, which are the primary exploration targets in the region.

4. JOINT EDUCATIONAL AND SKILLS PROGRAMMES (PREPARATION OF INFORMATION PACKAGES AND OFFERING TO EUROPEAN UNIVERSITIES UNIQUE SPECIALIZED POLYGONS FOR DIFFERENT DIRECTIONS STUDENT PRACTICE)

Also, according to main issues outlined in Agreement between EFG and the Expert Council of the Union of geologists Ukraine we are prepared several sites for students practice of geological specialties (see below).

4.1. TARGET A1. KRYVYJ RIG BELT

The uniqueness of this cross-section are in the fact that here are uncovered (and therefore available for direct study) rock complexes of different ages from Archaean to Proterozoic.

Introduction to geology and metallogeny. General information

Kryvyj Rig (Krivoy Rog from Russian pronouncing) belt is one of the most interesting and famous geological objects in the Ukrainian shield. The belt contains uniquely large iron ore deposits altogether forming so called Kryvbas - Kryvyj Rig Iron-Ore Basin (KRIOB). The distinct structure of Kryvyj Rig belt (KRB) resulted from the complex geological history of the region, which reflects all major stages of the entire Ukrainian shield development. In tectonic respect the KRB is confined to the boundary between two age-different geoblocks. To the west this is Kirovograd Block composed of Lower Proterozoic metamorphic volcanic-sedimentary and gratinoid rocks, and to the east this is Middle Dniprean Block that is characterized by association of the Middle Archean plagiogranitoids and Upper Archean greenstone belts.

The KRB includes four sequential rock complexes separated by geological interruptions (from below): metavolcanogenic-sedimentary, metaterrigenous-ferruginous, carbonate-carbonaceous-metaterrigenous and metaterrigenous (Fig. A1-0.1).

Metavolcanogenic-sedimentary complex in the stratigraphic respect corresponds to the Konka Series of Upper Archean. The rocks occur in the section base and are mapped along eastern limb of KRB and also found in the Eastern-Gannivka Band of Northern KRIOB. In the south (excursion area) and along so called Saksagan Strike and in the base of the Eastern-Gannivka section the complex is represented by ***metadacite-andesite-tholeiite rock association (RA)***. It consists of amphibolites, biotite-amphibole, chlorite-biotite-amphibole, biotite-amphibole-plagioclase and biotite-quartz-amphibole schists that are metamorphic equivalents of tholeiites, andesites and dacites. Less abundant are mica quartzites, quartzite-sandstones and schists of quartz-biotite, quartz-feldspar-biotite composition with characteristic balstic-psammite textures (Fig. A1-0.2). Tholeiites predominate in the section (up to 60% by thickness) with subordinate metaandesites (up to 25%) and dacites (up to 15%). The thickness of RA varies from 300-600 m in the southern and central parts of KRB up to 800 m in the north.

In the Eastern-Gannivka Band the rocks of metadacite-andesite-tholeiite RA are conformably overlain by ***metakomatiite-jaspilite-tholeiite RA*** (Table A1-0.1) composed of association of actinolite, tremolite with carbonate and talc schists (metakomatiites), amphibolites, plagioclase-amphibole, amphibole, amphibole-chlorite schists (metatholeiites and metaandesites) and ferruginous quartzites and schists of amphibole-magnetite, carbonate-magnetite-cummingtonite composition (see Fig. 2). Somewhere occurs also muscovite quartzites and micaceous (muscovite- and biotite-sericite, muscovite-biotite) schists. The thickness of this RA is about 300-400 m.

The rocks of this complex are of epidote-amphibolite grade (southern part of KRB and Eastern-Gannivka Band) and greenschist grade (Saksagan area) of regional metamorphism.

Mafic rocks from the Eastern-Gannivka Band yield 2825-2615 Ma age [1, 7].

Metaterrigenous-ferruginous complex overlies the previous one with stratigraphic and angular unconformity. This complex is built up with four RA (from below): metaconglomerate-schist, metaconglomerate-sandstone-schist and jaspilite banded iron formation (see Table A1-0.1).

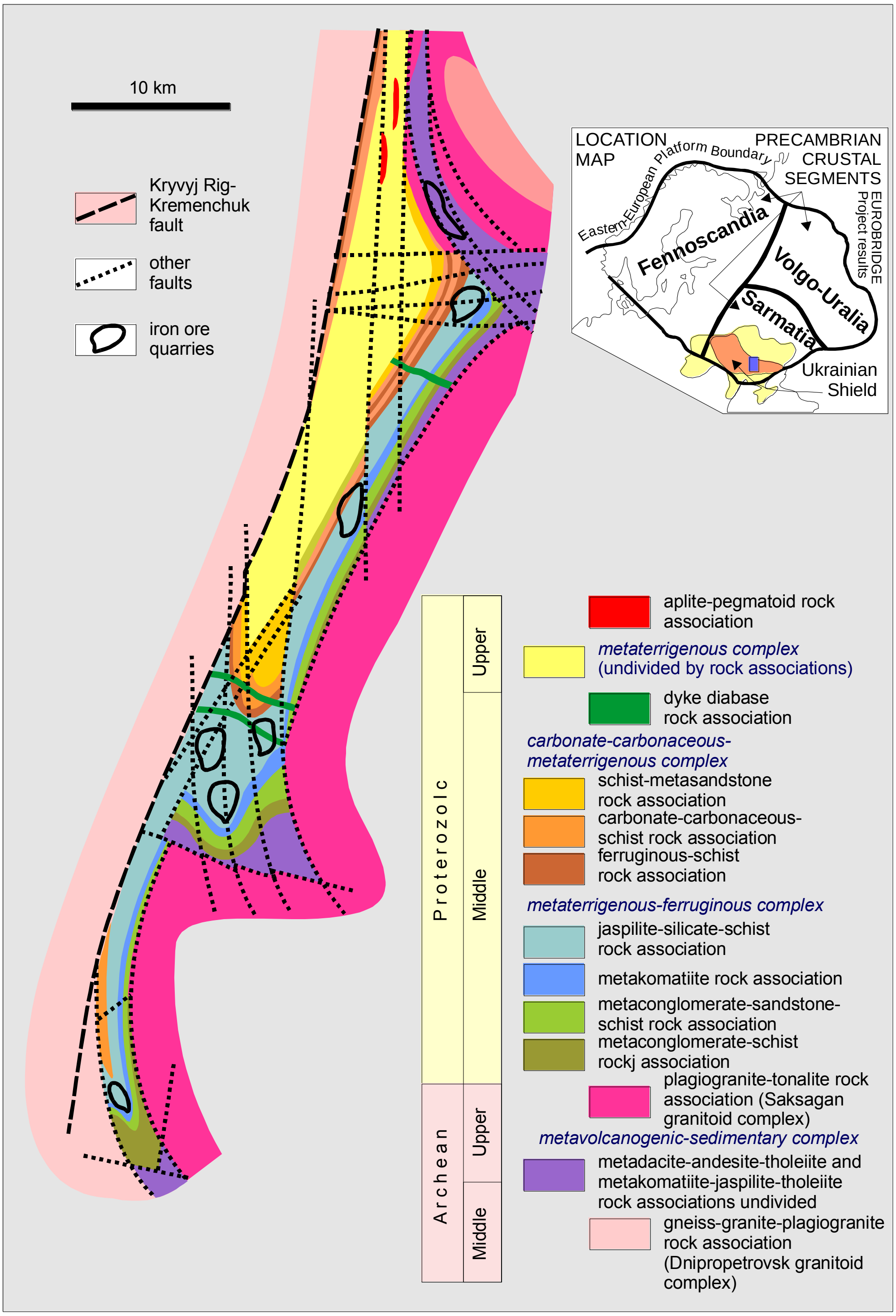


Fig. A1-0.1. Sketch geological map of the Kryvyj Rig belt

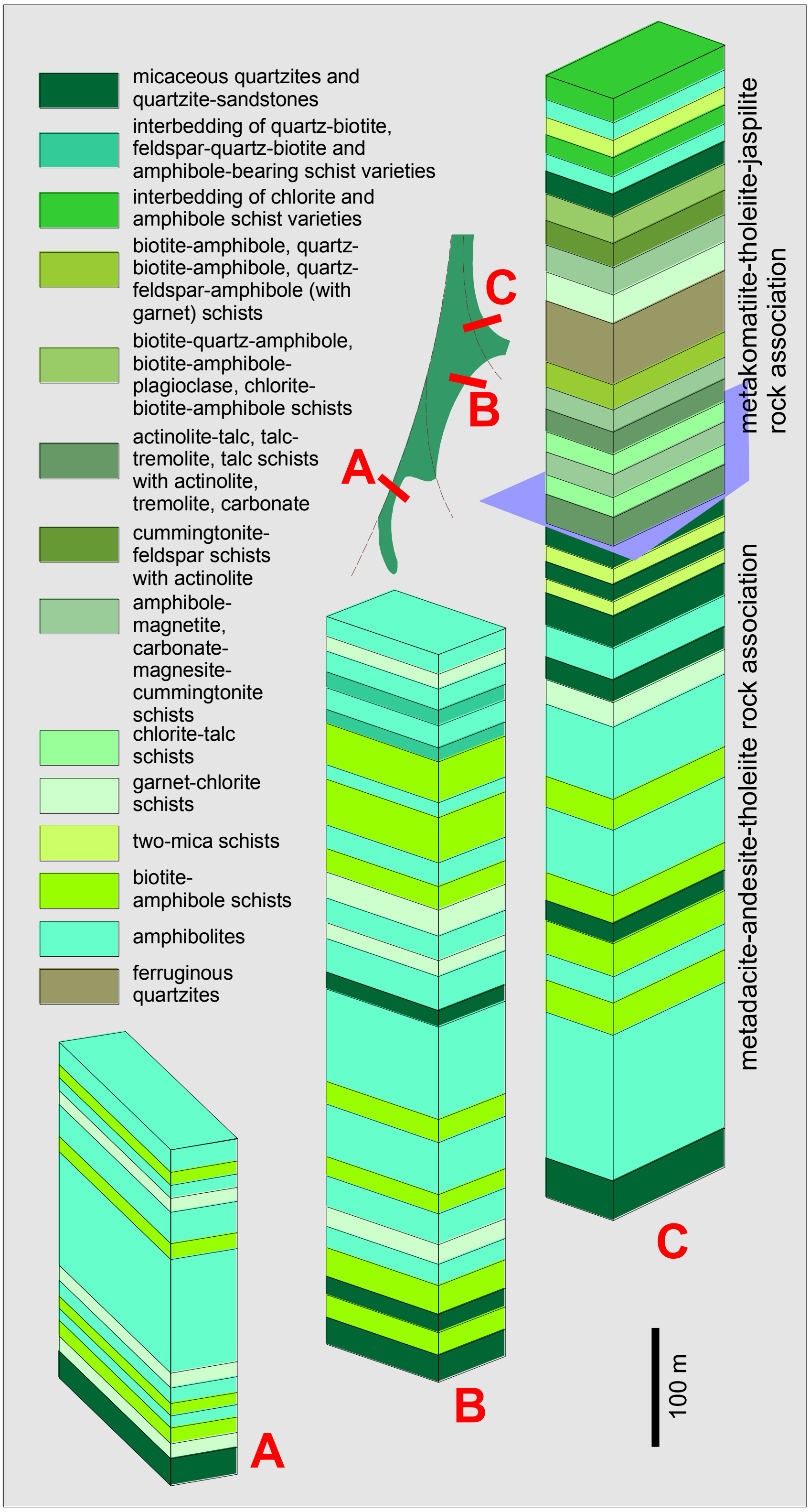


Fig. A1-0.2. **Structure of the section of metavolcanogenic-sedimentary complex of KRB.**

A - southern part;
B - Saksagan Strike
C - South-Gannivka Band

Table A1-0.1 Stratigraphic sketch of the Kryvyj Rig belt

Age	Rock complexes, associations		Thickness
R_3	**Metaterrigenous complex**		About 2500 m
	Metaconglomerate rock association Polymictic metaconglomerates, quartz-feldspar metasandstones, biotite-quartz, quartz-biotite schists	***Metasandstone-schist rock association*** Feldspar-quartz metasandstones, quartz-biotite, feldspar-quartz-biotite schists with garnet and amphibole	
	Interruption of sedimentation		
R_2	**Carbonate-carbonaceous-metaterrigenous complex** ***Schist-metasandstone rock association*** Interbedding of quartz-biotite, amphibole-quartz-biotite schists and metasandstones		Up to 400 m
	Carbonate-carbonaceous-schist rock association Graphite-bearing micaceous schists and carbonate rocks		100–400 m
	Ferruginous-schist rock association Magnetite-quartz-chlorite, quartz-sericite-chlorite schists, barren quartzites, metasandstones; rarely - ferruginous quartzites, carbonate rocks, rich iron ores		Up to 300 m
	Interruption of sedimentation		
R_1	**Metaterrigenous-ferruginous complex** ***Jaspilite-silicate-schist rock association*** Interbedding of schist and ferruginous para-generations; schist ones composed of silicate schists and barren quartzites, ferruginous ones represented by association of magnetite, silicate-magnetite, carbonate-silicate-magnetite quartzites, silicate schists and barren quartzites		Attains 1300 m
	Metakomatiite rock association Talc, carbonate-, chlorite-, actinolite-, tremolite-talc schists, metasandstones, phillites		From 10–20 to 220 m
	Metaconglomerate-sandstone-schist rock association Metamorphosed quartz conglomerates, sandstones, gravelites, quartz-biotite, sericite-quartz-biotite (sometimes with graphite) schists (phillites)		From 20–30 to 320 m
	Metaconglomerate-schist rock association Quartz-sericite-chlorite, quartz-amphibole-biotite schists, polymictic metasandstones, schistose metaconglomerates		From 20–30 to 300 m
	Interruption of sedimentation		
R_3	**Metavolcanogenic-sedimentary complex** ***Metakomatiite-jaspilite-tholeiite rock association*** Amphibolites, amphibole, plagioclase- and chlorite-amphibole schists (metatholeiites, metaandesites); amphibole-magnetite, carbonate-magnetite-cummingtonite quartzites and schists; tremolite, actinolite schists with carbonate and talc (metakomatiites)		From 300 to 450 m
	Metadacite-andesite-tholeiite rock association Amphibolites, amphibole-biotite, amphibole-plagioclase, biotite-amphibole-plagioclase schists (metatholeiites, metaandesites, metadacites); micaceous quartzites, quartzite-sandstones, quartz-biotite, quartz-biotite-plagioclase schists (metaterrigenous rocks)		From 300 to 600 m

Metaconglomerate-schist RA is characterized by the sharp facial changes along strike with schist rock substitution by coarse-grained varieties. In the section predominates association of quartz-biotite-chlorite and quartz-hornblende-biotite schists with minor interbeds of polymictic metasandstones with chlorite cement and garnet-chlorite-biotite schists. The sections in the eastern limb pinch (area of Northern Plant) and in the deposit “Shaft V.I.Lenin” provide the exceptions where mainly conglomerates abundant (Fig. A1-0.3). The schists were formed under metamorphism of the marine-redeposited weathered rocks of metavolcanogenic-sedimentary complex. Characteristic for the conglomerates are coarse- and middle-rounded clasts composed of quartz-biotite-chlorite, quartz-hornblende-biotite schists fairly resembling those described above. Sometimes occur the pebbles of veined quartz as well as metamorphosed mafic volcanics and amphibole schists. The polymictic sandstones form the conglomerate cement with variable composition including clasts of quartz, feldspar, garnet and carbonate in the chlorite-sericite and quartz-chlorite-sericite groundmass. It is assumed that metaconglomerates formed in underwater canyon-like troughs due to bedrock breakdown by sea streams and schist rocks mudslides.

In the local stratigraphy this RA is being considered as Novokryvorizka Suite. The thickness varies along the KRB from 20-30 m to 150-300 m with the maximum known in the occurrences of schist metaconglomerates.

Metaconglomerate-sandstone-schist RA conformably overlies the rocks of metaconglomerate-schist RA. In this RA predominate quartz, feldspar-quartz metagravelites, metasandstones, oligomictic metaconglomerates and the schists of biotite, quartz, sericite and sericite-quartz-biotite composition that are known as “phillites”.

Depending on the ratio of petrography varieties and internal structure this RA can be divided in two sub-formations that reflect sea regression and transgression respectively.

Regressive part from first meters up to 160 m thick is composed in the base of alternate quartz metasandstones and oligomictic metagravelites. Upward in the section the amount and thickness of metasandstones decrease and oligomictic metaconglomerates substitute their position, that is, association metasandstone+metagravelite gradually changes into metagravelite+metaconglomerate one.

Lower portion of the regressive section about 50-80 m thick is composed of alternate feldspar-quartz metasandstones, sometimes occur thin beds and lenses of the fine-pebble metaconglomerates. The upper portion of the regressive section consists of association of feldspar-quartz metasandstones and phillite-like schists (see Fig. A1-0.3).

Given RA displays poly-facial features: its conglomerate-gravelite-sandstone (regressive) part corresponds to the alluvial-proluvial fan deposits redistributed in the tidal zone of the sedimentary basin while its upper (transgressive) part consists of marine deposits.

In the local stratigraphy this RA corresponds to the lower and middle (quartzite-arcose and flisch) sub-suites of the Skelevatska Suite of the Kryvorizka Series.

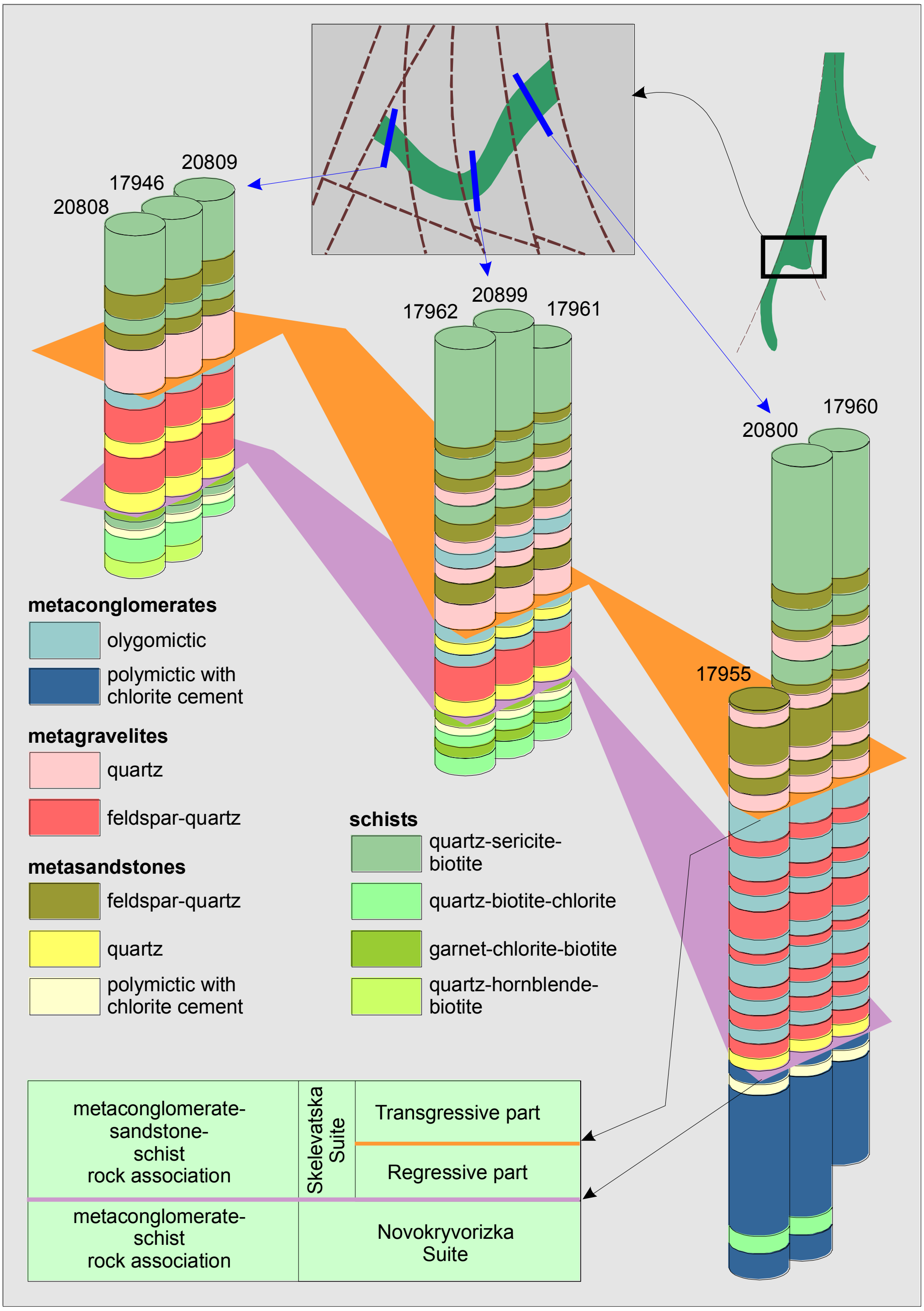


Fig. A1-0.3. Composition of the metaconglomerate-schist and metaconglomerate-sandstone-schist RAs in the area of the Main KRB pinch.

Metakomatiite RA conformably overlies the rocks of metaconglomerate-sandstone-schist RA and is composed of chlorite-talc, carbonate-chlorite-talc-actinolite, actinolite-chlorite-talc, carbonate-actinolite-tremolite-talc schists, actinolitites, tremolitites, and talc-carbonate rocks (metamorphic equivalents of peridotite, pyroxenite komatiites and komatiite basalts). Less abundant are metasandstones, metagravelites, quartz-biotite, biotite-quartz-chlorite schists and barren quartzites - primary-terrigenous rocks that are characteristic for the marginal sections of this RA. In the section (Fig. B1-0.4) peridotite komatiites predominate forming up to 60-80% by thickness. Pyroxenite komatiite and komatiite basalt contribution does not exceed 10-25%.

The total thickness of RA changes from first tens up to 250 m ("Shaft M.V.Frunze") being 120-160 m in average.

In the local stratigraphy this RA corresponds to the upper (carbonate-talc) sub-suite of the Skelevatska Suite of the Kryvorizka Series.

Jaspilite BIF caps the vertical section of the metaterrigerous-ferruginous complex. This RA is characterized by the regular alteration of the schist and iron-ore association (commonly used term are "schist-" and "iron horizons" respectively). In the general section up to 1300 m thick about seven distinct rhythms can be distinguished (Fig. A1-0.5) where each starts with the schist and finish with iron-ore batches or para-generations (PG).

The schist PGs are composed of amphibole-chlorite-biotite, biotite-chlorite-amphibole, graphite-chlorite-biotite, sericite-chlorite, sericite-biotite-chlorite, biotite-chlorite with graphite, chlorite-biotite, cummingtonite-chlorite schists and barren (non-iron) quartzites. Formerly these were fine-grained sediments - clays with minor silt and sand matter.

Iron-ore PGs include magnetite, silicate-magnetite, magnetite-silicate, silicate-carbonate-magnetite, iron-mica-magnetite, amphibole-chlorite-magnetite, riebeckite-magnetite quartzites formed under metamorphism of jasper-like iron-silicate or mixed carbonate-clay-iron-silicate chemogenic sediments. The ration of carbonate-clay and iron-silicate counterparts defines the mineralogical zonation in the sections. The central portions with primary "fresh" iron-silicate composition are composed mainly of magnetite quartzites whereas marginal zones are richer in carbonate-clay material and represented by carbonate-silicate-magnetite and magnetite-silicate varieties. In the areas of extensive metasomatism (central part of KRB) occur the richest iron ores of magnetite-martite, martite, and martite-hematite composition.

In the local stratigraphy the given RA corresponds to the Saksaganska Suite of the Kryvorizka Series.

The reference dating of the rocks is not available yet but some estimations [6] allow supposing its formation in the time span 2300-2000 Ma.

Carbonate-carbonaceous-metaterrigenous complex overlies metaterrigenous-ferruginous one with angular unconformity. The stratigraphic column includes three RA (from below): ferruginous-schist, carbonate-carbonaceous-schist and schist-metasandstone (see Table A1-0.1).

Ferruginous-schist RA is restricted to the Saksagan and southern parts of KRB. This RA is composed of magnetite-chlorite, quartz-magnetite-chlorite, quartz-chlorite, chlorite-carbonate-magnetite schists, metasandstones with ferruginous cement, and quartzite-sandstones. Less abundant are quartz-carbonate rocks, ferruginous and barren quartzites, sediment breccias and conglomerate-breccias.

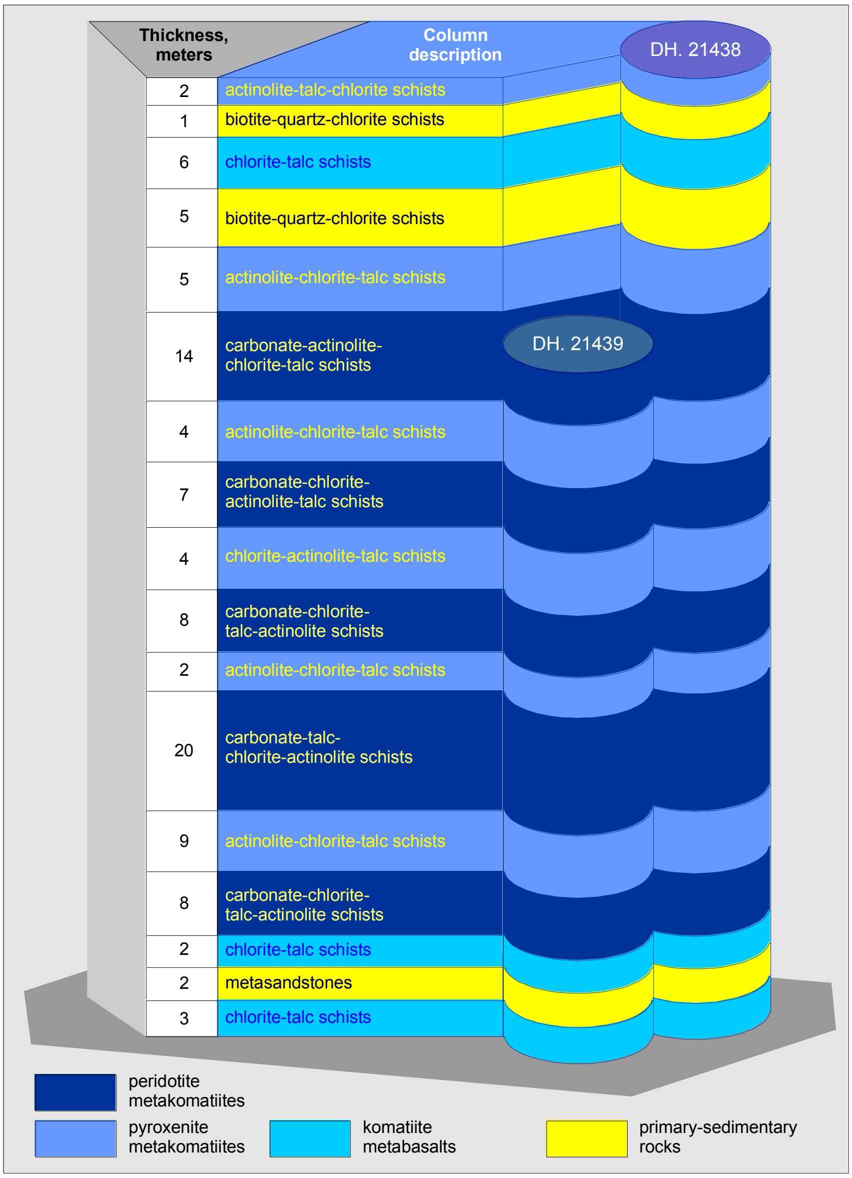
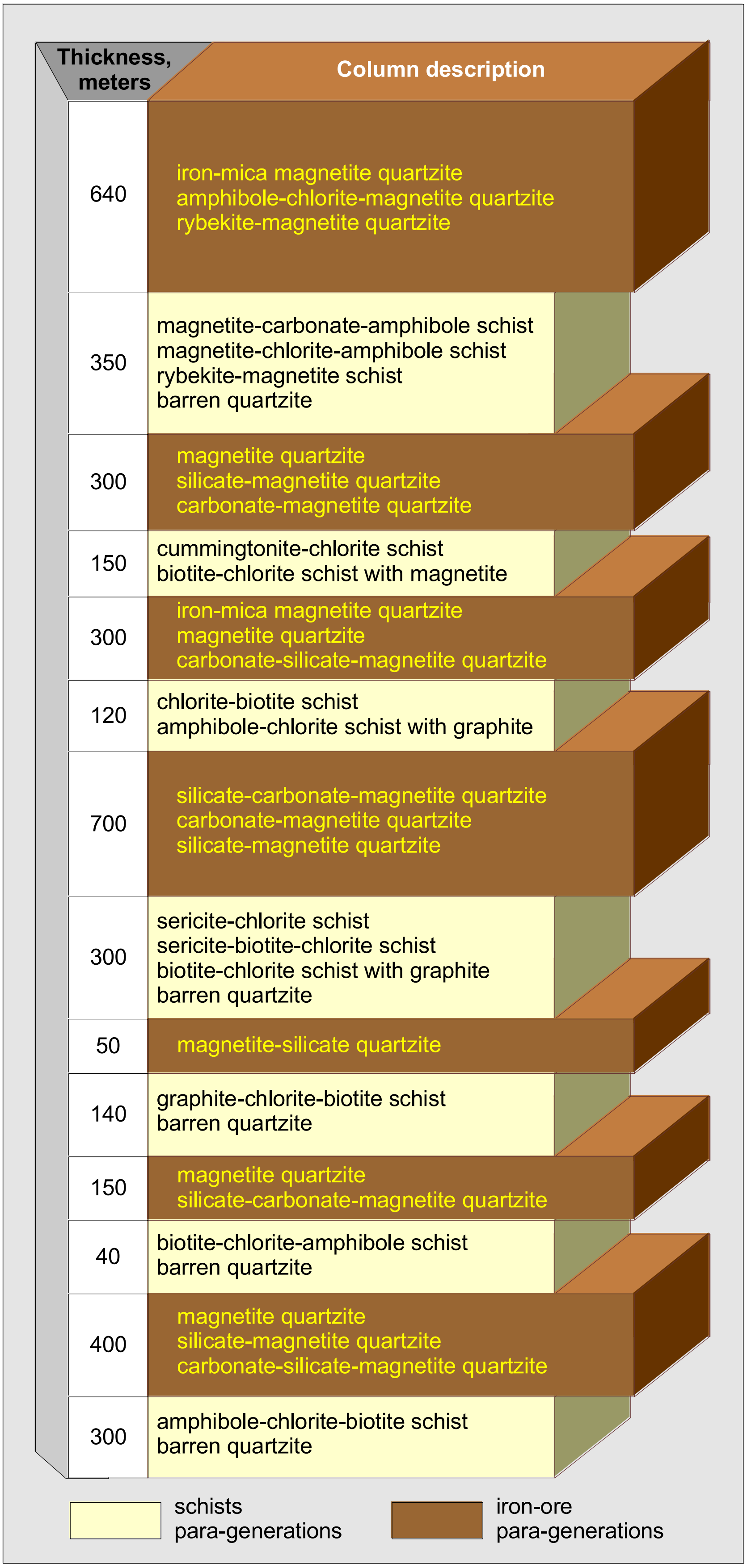


Fig. A1-0.4. Metakomatiite rock association columns in the area of Ingulets ferruginous quartzite deposit (Likhmaniv pinch of KRB).



In the section RA has the rhythmic appearance and three complete rhythms can be distinguished each starts with quartzite-sandstone PG and finish with magnetite-chlorite-schist PG (Fig. B1-0.6). The former is composed of quartzite-sandstone + barren quartzite + metasandstone with ferruginous cement ± quartz-carbonate rocks ± sediment breccias ± iron ores of martite and hematite-martite composition. Magnetite-chlorite-schist PG consists of magnetite-chlorite + quartz-magnetite-chlorite ± quartz-chlorite + sericite-chlorite and quartz-chlorite-sericite schists.

It is characteristic for this RA that the main volume of the rocks (including iron ores) formed from the weathered crust of the ferruginous-metaterrigenous complex (mainly from the rocks of jaspilite-silicate-schist association).

The thickness of the given RA varies along KRB from first tens of meters up to 350 m.

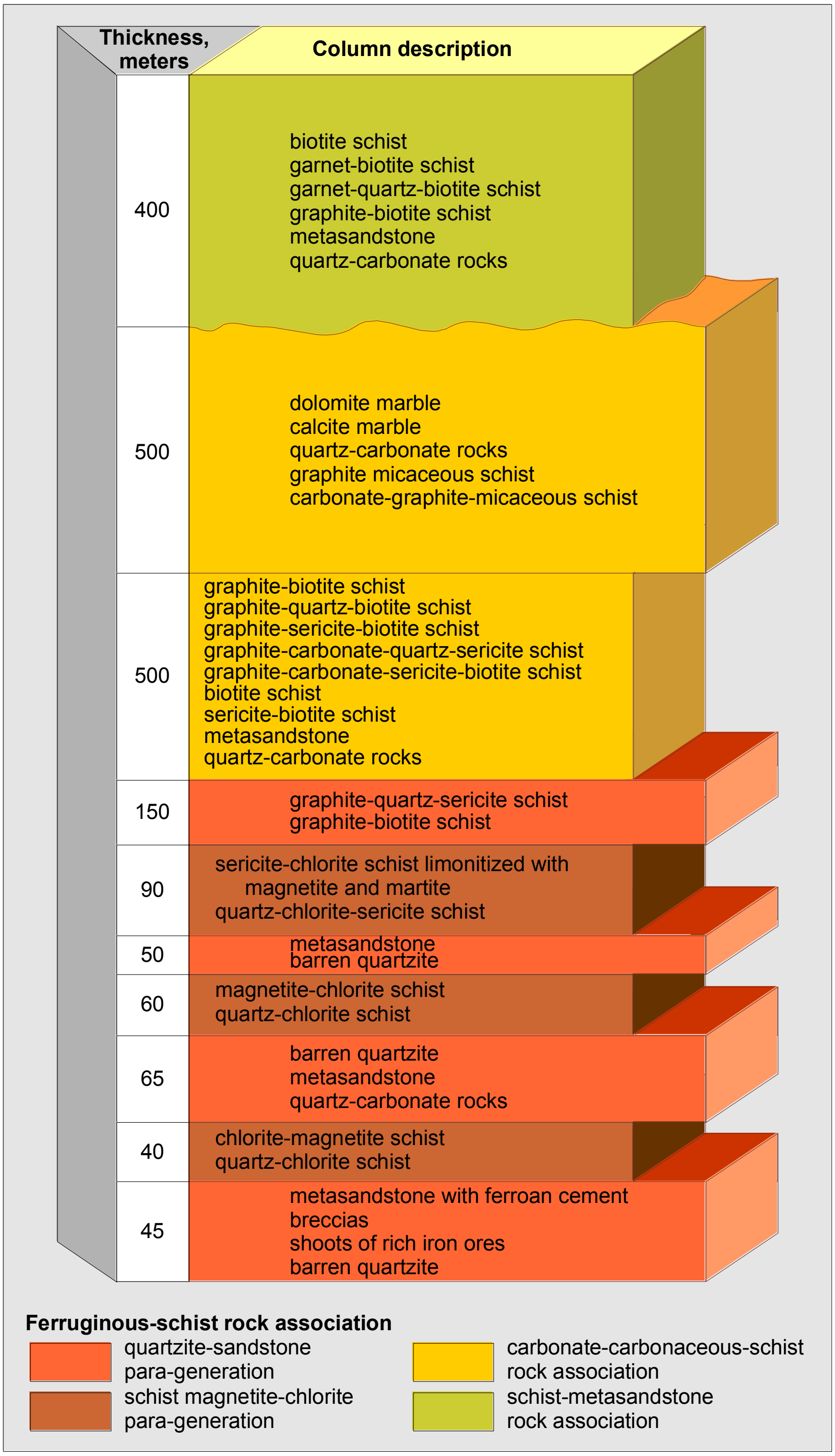


Fig. A1-0.6. Representative column of the carbonate-carbonaceous-metaterrigenous complex

Carbonate-carbonaceous-schist RA conformably overlies the rocks of the previous unit. The constituent rocks include diverse graphite-bearing ("carbonaceous") schists of graphite-quartz-sericite, graphite-micaceous, and graphite-quartz-carbonate-biotite composition with intercalations of quartz-carbonate rocks, dolomite marbles and metasandstones. In subordinate amount occur micaceous schists with garnet, quartz-chlorite-biotite and quartz-chlorite-sericite schists. Graphite-bearing rocks predominate in the lower portion of the column whereas carbonate rocks abundant in the upper one. The thickness of RA attains 450 m. Reconstructions suggest for lagoon-like paleo-environment of the primary sediments deposition.

Schist-metasandstone RA unconformably overlies diverse horizons of the carbonate-carbonaceous-schist RA. This RA consists of quartz-biotite, garnet-quartz-biotite, graphite-quartz-biotite schists and feldfspar-quartz metasandstones with rare thin beds of quartz-carbonate rocks near the bottom portion. The thickness does not exceed 400 m.

Age and stratigraphic positions of the entire carbonate-carbonaceous-metaterrigenous complex are subjected to the discussion so far. Traditionally these rocks are being considered as the Lower Proterozoic Gdantsivska Suite of the Kryvorizka Series. Nevertheless lead isochrone age of the marbles from carbonate-carbonaceous-schist RA measured by O.Iskanderova provides Middle Proterozoic 1810-1760 Ma [8].

Metaterrigenous complex that finalizes the KRB stratigraphic column overlies the carbonate-carbonaceous-metaterrigenous rocks with angular unconformity. This complex includes two rock associations that laterally and somewhere vertically substitute one another: metaconglomerate and metasandstone-schist.

Metaconglomerate RA is composed of polymictic metaconglomerates and feldspar-quartz metasandstones with subordinate quartz-biotite, quartz-feldspar-biotite (sometimes with garnet and amphibole) schist. Association is characterized by rhythmic internal structure. In the lower and central portions mainly two-fold metaconglomerate and metasandstone rhythms predominate whereas in the upper portions schist rocks are being added and the rhythms become three-fold. There found two considerable bodies of this RA in KRB - Saksaganske body located in the central part of KRB and Gannivske occurrence confined to the western limb of the northern KRB. Both occurrences have identical internal patterns and differ just in the source regions of the clastic material. Deposition of the Saksagan body was supplied with clastic material from the east of KRB while the Gannivske body was fed from the northwest. These conditions appear to have been influenced by the vertical block movements in around the Kryvyj Rig paleobasin.

Metasandstone-schist RA is formed with association of feldspar-quartz metasandstone and various schists - quartz-biotite, quartz-amphibole-biotite, garnet-quartz-biotite and quartz-feldspar-amphibole-biotite. The elementary unit (rhythm) of this RA includes metasandstones + schists although three-fold rhythms also known, they include two different types of the schists. The rhyths have transgressive patterns; they start with metasadnstones and finish with the schists.

Lacking of the reference isotope data does not allow the complex development timing properly. According to the adopted schemes the complex represents the Middle Proterozoic Gleevatska Suite. However some paleontological works, for instance, findings of the microfithofossils, oncolites, acrytarchs etc. [2, 4, 5] provide additional arguments for the much younger age of the complex, presumably Upper Proterozoic.

From the **tectonic** point of view KRB has intricate structure and evolution. The rocks of metavolcanogenic-sedimentary and metaterrigenous-ferruginous complexes form the monocline, which is complicated by series of the nappes (Fig. A1-0.7). The rocks of carbonate-carbonaceous-metaterrigenous complex occur in the distinct syncline, which is overlain by longitudinal trough filled with clastic sediments of the metaterrigenous complex.

Complicated structure of the belt is caused by its distinct **geological history**. It is supposed that initial subsidence took place in Late Archean that in adjacent Middle Dniprean region was accompanied by breaking the plagiogranite-amphibolite proto-crust. This had stipulated proto-rift development and formation of greenstone belts. In KRB this period is “imprinted” in the sections of metavolcanogenic-sedimentary complex. Next tectonic cycle also can be considered as rifting since Kryvyj Rig proto-basin was opened and the rock associations of metaterrigenous-ferruginous complex were formed.

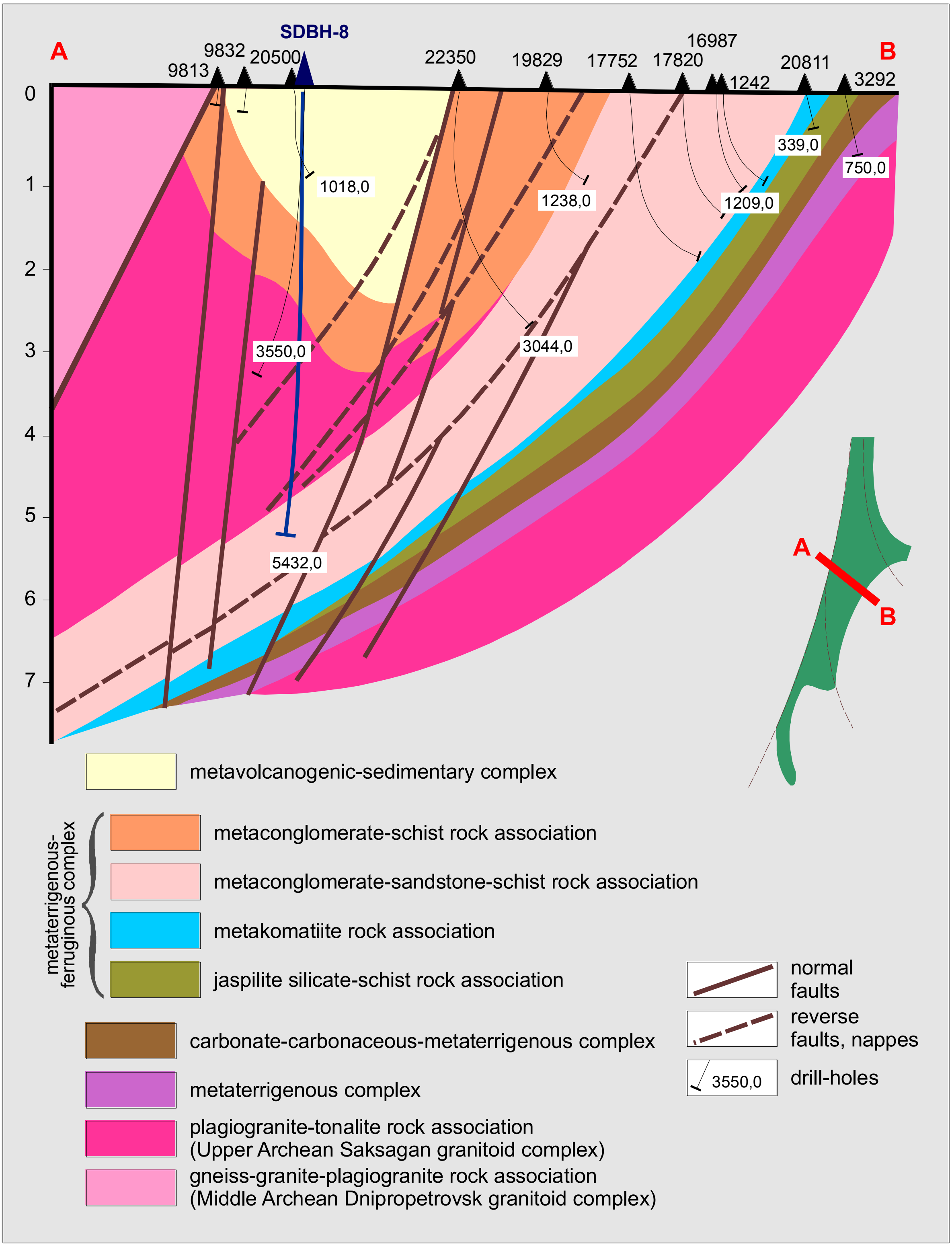


Fig. A1-0.7. Geological sketch section of the central part of KRB.
SDBH-8 - location of the Kryvyj Rig Super-Deep Borehole

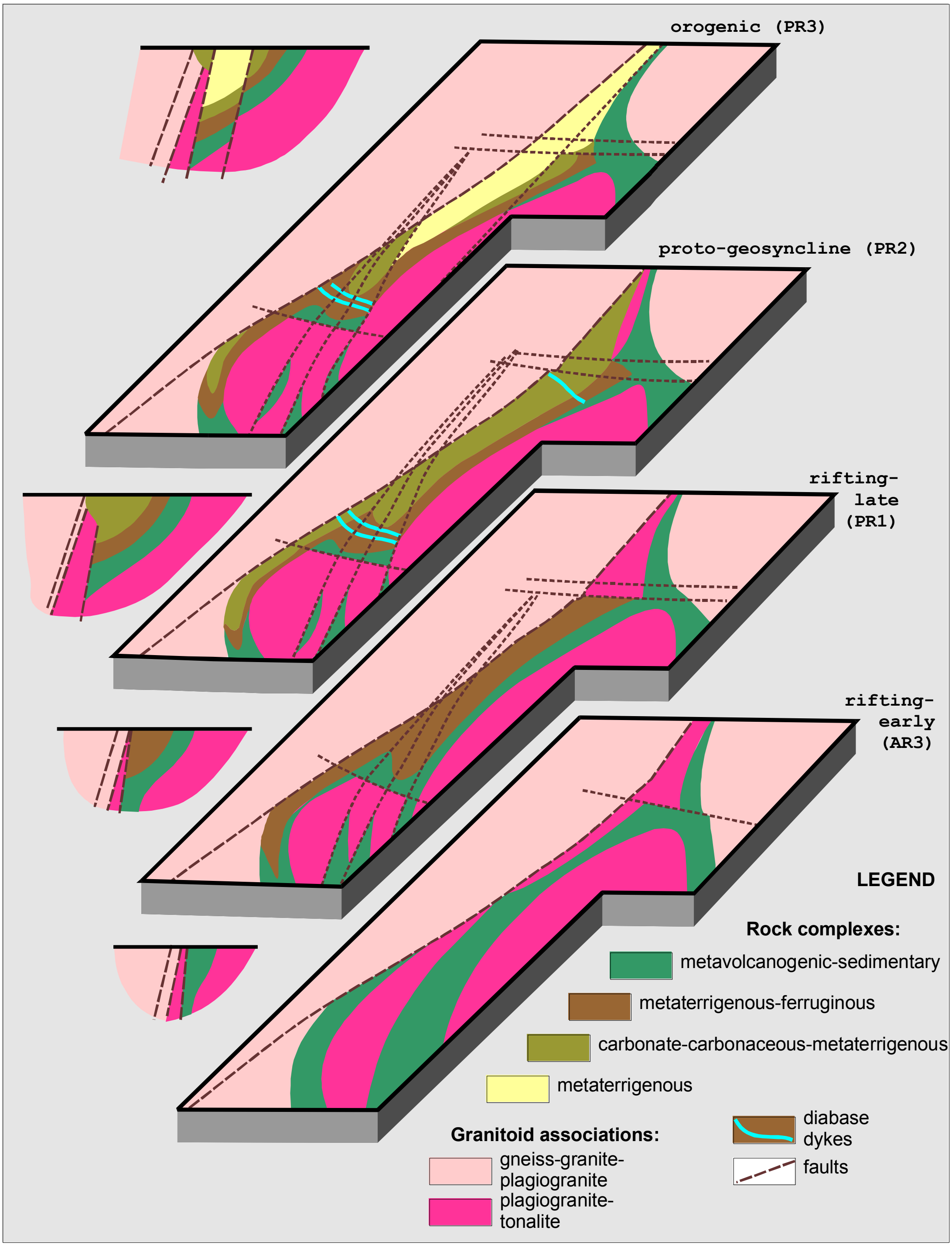


Fig. A1-0.8. Historical sequence of KRB development

The cycle was finished with the folding, formation of nappes, and metamorphism and metasomatism. The latter process is mainly responsible for the formation inside the jaspilite-silicate-schist RA of the series of metasomatic bodies as well as zones of silicification, carbonatization, chloritization, egirinization, sulphidization etc. that essentially bear the metallogeny of KRB. Above processes took place in the time span 2000-1800 Ma, that is, before formation of the carbonate-carbonaceous-metaterrigenous complex.

Deposition of the rock associations of the latter complex occurred in the distinct trough that had inherited tectonic shape of the Kryvyj Rig proto-rift and had resulted from proto-geosyncline tectogenesis.

Completion of tectogenesis in KRB was accompanied by development of sub-longitudinal fault system and vertical orogenic movements that caused subsidence of the central part, formation of the trough-like depression and differential vertical movements of surrounding the blocks. This depression was the depositional site of the metaconglomerate and metasandstone-schist rock associations.

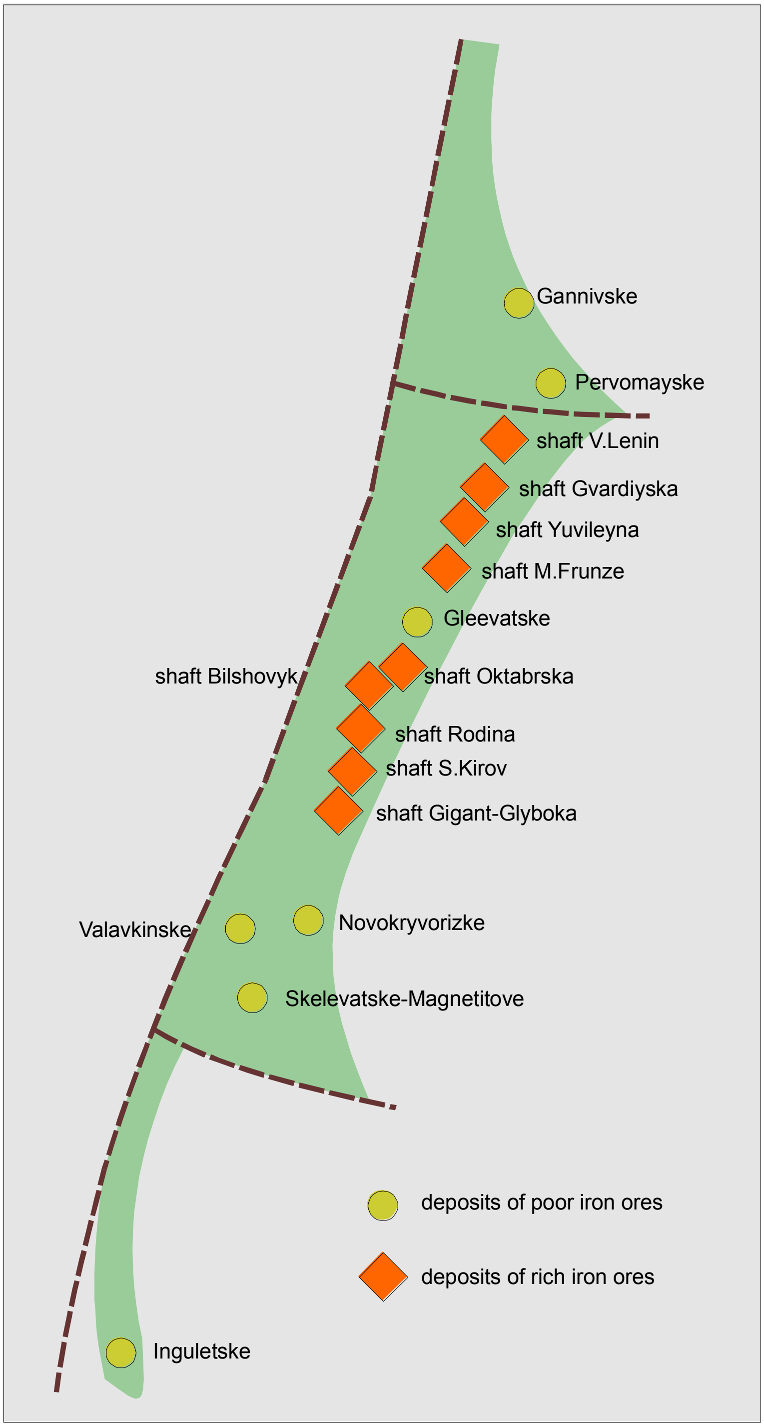


Fig. A1-0.9. Location scheme of the major iron deposits in Kryvyj Rig Iron-Ore Basin.

Intricate geological history of KRB and activity of various endogenous and exogenic processes in the comparatively local crustal segment caused wide diversity of ore mineralization. There are known a lot of occurrences of about 50 kinds of metal and non-metal mineralization that has considerable quality and reserve parameters. All these occurrences form the economic valuable targets inside the iron deposits in operation (Fig. A1-0.10).

The group of ***metal deposits*** includes iron, gold, germanium, scandium, yttrium, lanthanides, zirconium, beryllium, lithium, titanium, chromium, vanadium, nickel, platinum and PGE.

Iron provides the major value of KRB. The iron ores are being exploited over more than 100 years, and the total production for this period is being estimated about 2 mln. tons of the ore. Today in Kryvyj Ryg basin 12 iron ore mines and 5 concentrating mills are in operation. The ores are subdivided in two groups based on the iron content: rich ores (more than 46% of iron) and poor ores or ferruginous quartzites (20-45% of iron) that should be reprocessed in the mills. The rich iron ores commonly form lens-like bodies inside the ferruginous quartzites. Their reserves estimated by the depth 1500 are about 1,6 bln. tons. The ores are being exploited in the shafts. The poor iron ores are being exploited in open pits and reprocessed in the mills to the concentrate. Their reserves also estimated by the depth 1500 m are about 32 bln. tons.

Besides the iron Precambrian rocks in KRB also contain about 15 other types of metal ore mineralization.

Gold is found to be of several genetic types: clastic in metaconglomerates of metaconglomerate-sandstone-schist RA (grade up to 0,4-2,4 g/t); metamorphic syngenetic (grade attains first tenth of g/t); related to post-metamorphic sodium metasomatism of the rocks of jaspilite-silicate-schist RA (average grade 0,34 g/t); in the zones of hydrothermal reworking (grade from 0,2 to 11,3 g/t); in weathered crust of Precambrian rocks.

Germanium: mineralization is confined to the rocks of jaspilite-silicate-schist RA with main minerals that accumulate the metal as magnetite (15-70 g/t), hematite (up to 60 g/t), egirine (up to 80 g/t), riebeckite (up yo 50 g/t), and tetriferribiotite (up to 60 g/t).

Scandium mineralization points found in the rocks of metakomatiite RA where the metal is being contained in ilmenite, titanium-magnetite and magnetite, and also in the zones of sodium metasomatism in the rocks of jaspilite-silicate-schist RA (egirine, riebeckite, tetriferribiotite, cummingtonite and seladonite). Average scandium grade in metaultramafites is about 30-40 g/t, and in metasomatites from 50-60 to 80-200 g/t.

Vanadium: enrichment found in the rocks of metavolcanogenic-sedimentary complex (in magnetite, titanium-magnetite, rarely ilmenite; up to 2000-3000 g/t), in talc schists of metakomatiite RA (in magnetite and titanium-magnetite; 100-

2000 g/t), and in sodium metasomatites in the rocks of jaspilite-silicate-schist RA (egirine, riebeckite, magnesium-riebeckite and tetriferribiotite; 1000-2000 g/t).

Molibdenium: occurrences found in the rocks of metadacite-andesite-tholeiite RA of metavolcanogenic-sedimentary complex in the Eastern-Gannivska Band. At present the value of mineralization is under evaluation while the grade preliminary is estimated from 100 to 1760 g/t.

Yttrium permanently accompanies Sc and V in the sodium metasomatites of the jaspilite-silicate-schist RA with grade attaining 500 g/t.

Lanthanides: increased contents known from the sodium metasomatites where they accompany Sc and V; total grade attains 2000-2500 g/t.

Zirconium in high enough amounts found in the rocks of the jaspilite-silicate-schist RA in the northern part of KRB; Zr grade here attains 2000 g/t, main mineral is zircon with ZrO_2 67,7 % and HfO_2 up to 4,0 %

Beryllium and lithium are confined to the single pegmatite veins found in northern KRB; Be grade up to 1000 g/t, Li - 2000 g/t.

Titanium, chromium, vanadium and nickel form stable association in the rocks of metakomatiite RA. Hosting minerals are: Ti - ilmenite and titanium-magnetite; Cr - chromite, V - magnetite and titanium-magnetite, Ni - magnetite, titanium-magnetite and pyrrhotite.

Platinum and PRE; increased content found in the rocks of metakomatiite RA but hosting minerals not distinguished yet.

Fairly valuable mineral of KRB could be also the ferruginous quartzite tails from the mills and processing plants that progressively are being accumulated in the region.

In case of involvement of new recovery technologies here may be obtained the magnetite concentrate with iron content up to 65-66%, hematite concentrate (up to 66-69% of iron), and also super-concentrate with iron content about 70,0-70,5%.

Kryvyj Rig iron ore basin is also rich [9] in non-metal mineralization from which some types may have economic value: talc, garnet, marble, ochre, red lead, industrial materials (granite, diabase, amphibolite, barren quartzites), and gem and collection minerals (“tiger and falcon eyes”, agate, chalcedony, red banded magnetite quartzites, disperse hematite-quartz-chalcedony and hydro-goethite-quartz-chalcedony jaspers, garnet, crystals and druses of rock crystal, amethyst, citrine, smoky quartz, morion etc.).

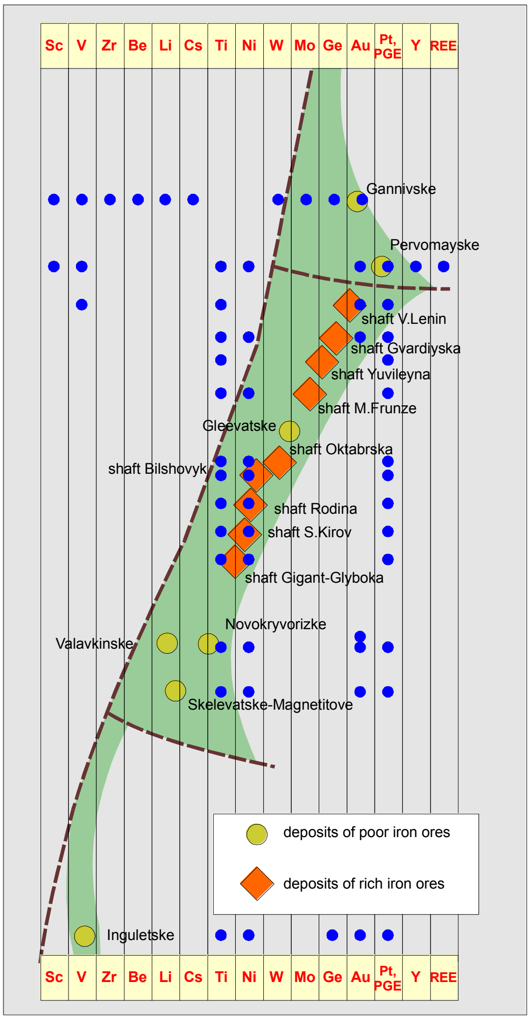


Fig. A1-0.10. Location sketch of the various metal and non-metal mineralization points.

References

1. Artemenko, G.V., 1998. Geochronology of Middle Dniprean, Azovian and Kursk Granite-Greentone Terrains. *Abstracts of Doctor Sci. Dissertation*, Kiev, 32 p. (In Russian).
2. *Ishenko, A.A., Yatsenko, G.M., Paranko, I.S.*, 1988. New findings of organic remnants in Gleevatska Suite of Krivorozhska Series in Ukrainian Shield. *Paleontological Jounral (Ukraine)*, N 23, p.62-70. (In Russian).
3. *Malyuk, B.I., Paranko, I.S.*, 1992. Using of non-standard geological methods in correlation of volcanic-sedimentary units. *Geological Journal (Ukraine)*, No. 3, p.127-137. (In Russian).
4. *Mikhnitskaya, T.P.*, 1991. Metasedimentary strata of platform stage in development of Ukrainian shield and their age by paleophitolitic data *Geological Journal (Ukraine)*, No. 3, p.27-135. (In Russian).
5. *Ryabenko, V.A., Aseeva, E.A., Furtes, V.V., et al.*, 1988. Biostratigraphic and Paleogeographic Reconstruction of the Ukrainian Precambrian. *Kiev: Naukova Dumka Press*, 140 p. (In Russian).
6. *Shcherbak, N.P., Zlobenko, V.G., Zhukov, G.V., et al.*, 1978. Catalogues of Isotopic Data for the Rocks of Ukrainian Shield. *Kiev: Naukova Dumka Press*, 222 p. (In Russian).
7. *Shcherbak, N.P., Artemenko, G.V., Bartnitskaya, E.M., et al.*, 1989. Age of sedimentary-volcanic formations of East-Annovska Band. Repts AS UkSSR, Ser. B, N 2, p. 29.35. (In Russian).
8. *Shcherbak, N.P., Esipchuk, E.K.,. Berzenin, B.Z., et al., 1985*. Precambrian Stratigraphic Columns of the Ukrainian Shield. *Kiev: Naukova Dumka Press*, 168 p. (In Russian).
9. *Evtekhov, V.D., Paranko, I.S., Evtekhov, E.V.*, 1999. Alternative Resource Base of Krivoy Rog Iron-Ore Basin. *Krivoy Rog Technical University Press*, 70 p. (In Russian).

4.2. TARGET B2-1

Greenstone outcrops in Balka Kaynova (lowermost section of Verkhivtsevo greenstone belt, Bazavluk tail)

Verkhivtsevo greenstone belt is located in the northern Middle-Dniprean granite-greenstone terrain (Fig. B2-1.1). Bazavluk tail comprises narrow (1x10 km) south-eastern branch of Verkhivtsevo belt (see Fig. B2-1.1). The tail is composed of the lowermost greenstone rock sequences that are considered to be representatives of the Unit 1 of Sura Suite in the volume of komatiite-tholeiite rock association.

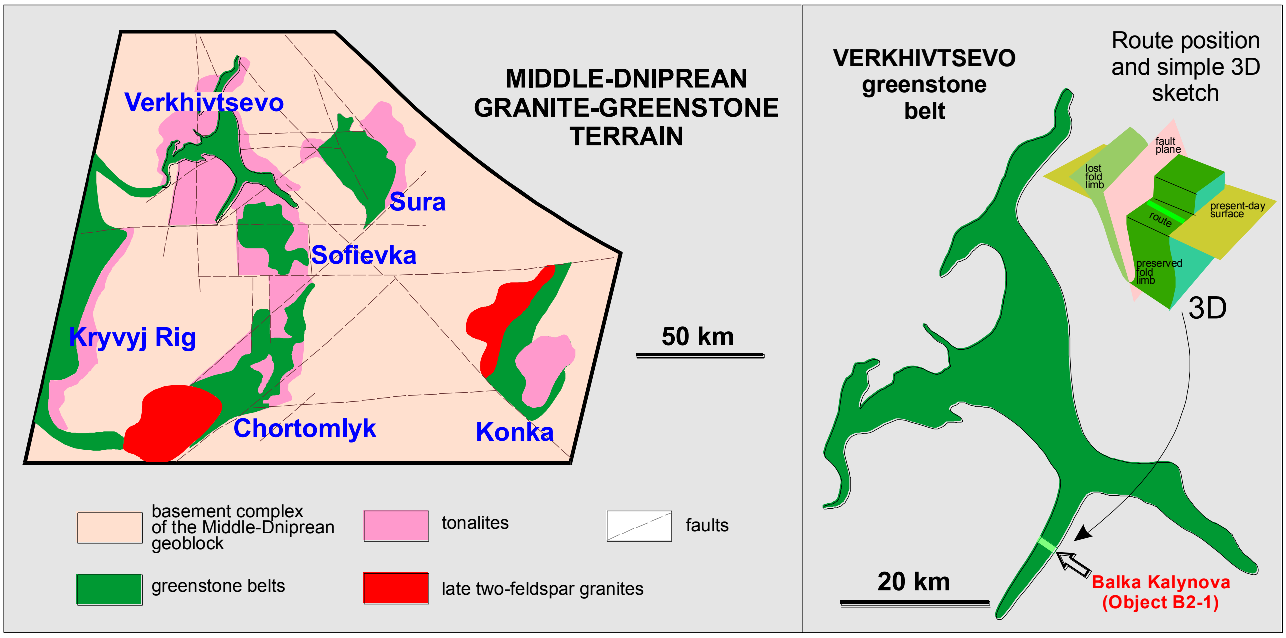


Fig. B2-1.1. Location map of the Object B2-1.

It is Bazalvuk tail only (gullies Kalynova, Ovseeva, Kholodova, Khalabudina) where these lowermost rock associations are known [1] in outcrops. Here Unit 1 is composed mainly of mafic metavolcanics represented by various-textured rocks (diverse-grained amphibolites, metabasalts, green schists after basalts etc.) with minor interlayers of ultramafic metavolcanics like pyroxene komatiites (actinolitites, tremolitites - up to 1-3% by volume), tuffaceous-sedimentary rocks, as well as cutting and sill-like igneous metagabbro, dolerite and diabase bodies that are sub-volcanic to respective volcanic counterparts.

The route starts in the down-swell portion of the gully Kalynova where excursion members can observe classical step-face jointing in metabasalts (Fig. B2-1.2).

Fig. B2-1.2. Step-face jointing in metabasalts (general overview).
Orange lines indicate slopes of the individual metabasalt flow surfaces.

The jointing is expressed in the system of 0.3-0.8 m height steps. Almost each step surface displays distinct synvolcanic textures like grooving, scratching, lineation etc. that are common for exposed mafic lava flows. Step surface orientation is western mainly, dip about 10^{o}. From these evidences one can assume sub-horizontal bedding of the entire metabasalt pile in the same direction. This assumption seems to be not unique however since other records clearly contradict to the flat bedding of the metabasalt sequence. These are as follows:

- Subvetical orientation of the vesicular metabasalt flow contacts (point C-10 etc.) that coincides to the major schistosity plane;

- Subvetical orientation of the tight clenched pillow forms in metabasalt lavas (points V-2, V-15, Fig. B2-1.4);
- Similar orientation of the contacts between principal and minor rock types in the section, for instance, metabasalts and actinolitites.

Fig. B2-1.3 represents conventionalised geological sketch of the excursion object designed after large-scale map and cross-section obtained by two parallel turn-pointed routes (A-B in north-east flank and C-D-E in south-west one) along the gully Kalynova. Limited correlation between the sections in two routes suggests for the cutting fault that occurs along the gully's thalweg and is also observed in aero- and satellite-views. In Fig. 3 the fault displays dextral patterns with marker horizons displacement about 10-15 m.

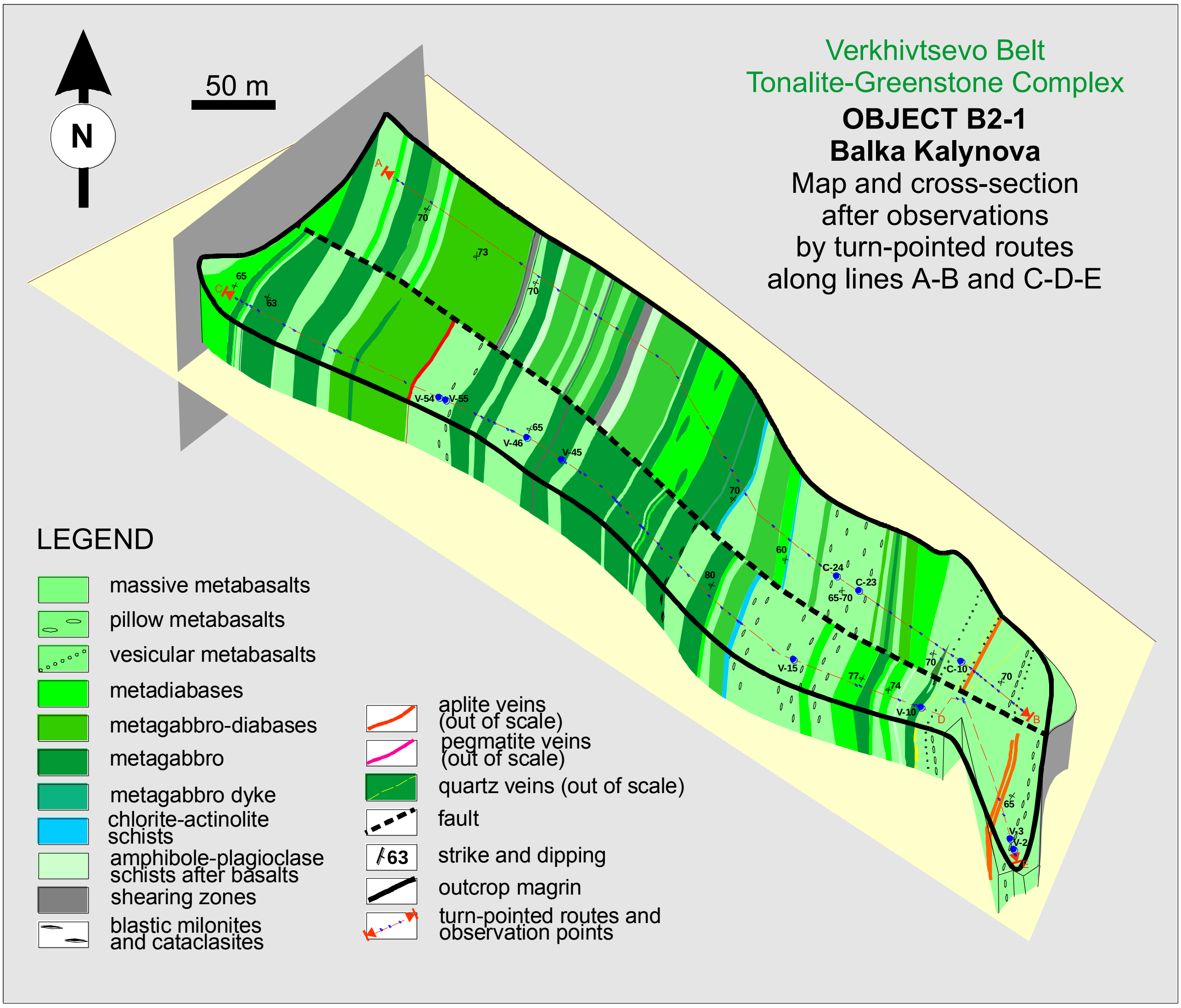


Fig. B2-1.3. Geological sketch of the Object B2-1.

In the down-swell part of the gully Kalynova (point V-2 and interval between the points V-3 - V-10) fine-vesicular (“mandelschtain”) zones occur in metabasalt flows. Vesicles are mainly rounded and irregularly distributed inside the metabasalts, up to 1-2% by volume. Individual bubbles are filled with quartz and calcite, size about 1-3 mm.

In the points V-2, C-23, C-24, V-54, V-55 and others by route (best in the thalweg point V-15, see Fig. B2-1.4) one can observe fine exposed on the flat surface the pillow metabasalts (Fig. B2-1.4). Due to supergene alteration pillow morphology is clearly highlighted just in the south-west well of the small (4x2 m) outcrop.

Fig. B2-1.4. Metabasalt pillow lava (inter-pillow space is impregnated by pegmatite, aplite, vein quartz).

The pillows display extensive flattening (up to 1:5) in schistosity plane (SW270, dip 85). Crosswise individual pillows look like ellipses or lenses from first cm to 30-40 cm wide and from 25-35 cm to 60-90 cm long. Metabasalt pillow shape is clearly highlighted by 0.5-1.5 cm thick marginal chilling zones mainly composed of re-crystallized and enlarged amphibole grains. In the pillow joint areas chilling zones doubling is observed sometimes while inter-pillow space is filled with mineral aggregate of quartz-chlorite-epidote-carbonate, probably of hydrothermal origin (Fig. B2-1.4, 5).

Morphology of the described texture forms and especially their chilling zones are very useful in restoring the patterns of the flow bedding. In case of contrast appearance (see Fig. B2-1.5a) orientation of the individual pillow tails suggests for the dipping of the flow internal portions and, consequently, for the direction of stratigraphy upgrade before extensive tectonic overprinting.

Fig. B2-1.5. Pillow morphology, inter-pillow and interior patterns (hand-writing at outcrops, A.Bobrov)

Depending on degree of the pillow core portion development composed of aggregate of quartz, carbonate, epidote, chlorite and other minerals of hydrothermal origin, the pillows can be subdivided into unzoned (Fig. B2-1.5a, b, d) and zoned (Fig. B2-1.5c); the former varieties predominate whereas the latter are found sometimes only.

In metabasalt piles some metadiabases occur that have characteristic micro-textures and are interpreted as more crystallized uniform portions of the common massive metabasalt flows. These mafic rocks appear to have been crystallized in the most thermostated flow portions (bottom or even cumulative zone). In these associations often occur fine crystallized rocks that resemble metagabbro. In most cases gradual transition can be observed between diverse-grained mafic rocks.

Fig. B2-1.6. Polygonal fragment of the columnar jointing in metabasalts (columns elongation normal to the flow plane).

In the exposed metabasalts also occur the fragments of the polygonal or columnar jointing (Fig. B2-1.6). Individual columns size varies from 10-15 cm to 45-55 cm and more across.

In the almost entire metabasalt section co-magmatic metagabbro bodies are widespread. Their amount increases toward the top of the gully Kalynova. The bodies have sill- or dyke-like appearance.

The contact of metagabbro and metabasalts can be seen in the points V-45 - V-46 (Fig. B2-1.7). Metabasalt flows are represented here by the fragments of ball-pillow, vesicular and massive zones composed of metabasalts, metadiabases (lower portions of restored flows [1]), and various schists developed after above rocks and linked to them through gradual transitions.

Fig. B2-1.7. Patterns of contact between co-magmatic metabasalts (top) and metagabbro (bottom).

By major-element geochemistry mafic metavolcanics of Verkhivtsevo belt including the rocks from Balka Kalynova clearly corresponds to the greenstone belt basalts of tholeiite affinity.

Metabasalts comprise dark-green fine-grained massive rocks composed of amphibole (up to 60-65%), chlorite (up to 25%), often carbonated (up to 10%), silicified (up to 5% of quartz), and epidotized (up to 5%). The rocks are of high-magnetic ($æ_{av.}$ = 1537x10^{-6} units CI) and high-density ($\sigma_{av.}$ = 3,012 g/cm^3) properties. By major-element composition they correspond to the iron-rich tholeiites.

Metadiabases are similar to metabasalts in composition and differ in relic ophite texture. The lava-facies affinity of metadiabases is supported not only by conform bedding but also by their gradual transitions to metabasalts and spatial separation into distinct zones of the common flows. The latter does not allow their consideration as intrusions. At the same time, metadiabases differ from metabasalts by higher density ($\sigma_{av.}$ = 3,073 g/cm^3) and low magnetic properties ($æ_{av.}$ = 701x10^{-6} units CI). In chemical composition the rocks correspond to tholeiite basalts.

Quartz-plagioclase-chlorite-amphibole schists have variable mineral composition and contain quartz (0-15%), plagioclase (20-35%), chlorite (10-40%), and amphibole (30-70%). By physical properties they are dense ($\sigma_{av.}$ = 2,85 g/cm^3) and magnetic ($æ_{av.}$ = 1372x10^{-6} units CI) rocks.

Described rock varieties are represented both in lava and mixed lava-pyroclastic facies with predomination of the latter.

Entire section of the lowermost komatiite-tholeiite rock association is impregnated by single cutting and conform bodies of aplite-like and pegmatoid granites and quartz veins. In the top of gully Kalynova occurs aplite-like granite vein deformed into pseudo-fold (Fig. B2-1.8, 9). Metabasalt schistosity hides into the contact of the fold. Schistosity-induced lineation resembles axis-plane cleavage of this fold. It is characteristic that the texture elements in metabasalts do not follow the “fold” geometry and, therefore cutting vein received its shape after horizontal compression of the metabasalt sequence.

Fig. B2-1.8. Lensed aplite vein in vesicular basalts.

Fig. B2-1.9. Aplite veins deformed into pseudo-fold.

Metavolcanic section (massive and pillow metabasalts) is also intruded by tonalites and plagiogranites of the Sura complex (tonalite-plagiogranite rock association [2]). Granite age according to recent U-Pb zircon measurements [2] is about 2.7 Ga.

Similar geological situation can be observed in 2.5 km to south-west in a series of small outcrops in down-swell part of the gully Ovseeva.

References

1. Bobrov, A.B., Sivoronov, A.A., Berzenin, B.Z., 1981. On pillow metadiabases from Verkhovtsevo and Sura structures (Middle-Dniprean region). *Geological Journal (Ukraine)*, v. 41, N 6, p. 128-133 (In Russian).

2. Bobrov, A.B., 1994. Volcano-Plutonic Association of Greenstone Belts in the Ukrainian Shield (formations, paleovolcanic reconstructions, metallogeny). *Abstracts of Doctor Sci. Dissertation*, Lvov, 40 p. (In Russian).