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I.S. Konchakivskyi,
S.I. Tsikhon, Cand. Sci. (Geol.-Min.), Assoc. Prof.,
V.B. Stepanov, Cand. Sci. (Geol.-Min.), Assoc. Prof.,
R.Ya. Serkiz

Ivan Franko National University of Lviv, Lviv, Ukraine, e-mail: BF@U.LVIV.UA.EU.NET

SPECIAL FEATURES OF CHLORITES OF THE VYSHKOVO ORE FIELD METASOMATIC ROCKS (TRANSCARPATHIA, UKRAINE)

І.С. Кончаківський,
С.І. Ціхонь, канд. геол. наук, доц.,
В.Б. Степанов, канд. геол.-мін. наук, доц.,
Р.Я. Серкіз

Львівський національний університет імені Івана Франка, м. Львів, Україна, e-mail: BF@U.LVIV.UA.EU.NET

ОСОБЛИВОСТІ ХЛОРИТІВ МЕТАСОМАТИЧНИХ ПОРІД ВИШКІВСЬКОГО РУДНОГО ПОЛЯ (ЗАКАРПАТТЯ)

Objective. To investigate the features of morphology, chemical composition, structure and formation conditions of metasomatic rocks chlorite of the Vyshkovo ore field metasomatic rocks. To determine changes of the mineral in the gold-plumb-zinc mineralization area.

Methodology. The microscopic, electron probe and X-ray crystal methods were applied to investigate the chlorite.

Findings. It has been found out that the chlorites of Bania and Shute ore occurrences belong mainly to the picnochlorite-brunsvigite group, partially to the diabantite and repidolite. In direction to the mineralization area, the chemical composition change of the chlorite has been detected, i.e. decreasing of *Fe* content and increasing of *Si, Al, Mg, Mn* content. The defined chlorites formation temperature is 180–280°C.

Originality. It is the first research of the composition and some features of the metasomatic rocks chlorites on gold mineralization within the Vyshkovo ore field; in direction to the mineralization area, the chemical composition change and the formation temperature have been defined.

Practical value. The chlorites composition is an important prospecting indicator that can be used for the hidden gold-plumb-zinc mineralization prospecting. The thermal regime of the creation of beresites formation chloritization area has been determined. The obtained results can be used for comparison with other regions where the gold-plumb-zinc mineralization is spread or possible.

Keywords: *chlorite, chloritization, metasomatic rocks, formation temperature, the Vyshkovo ore field, Transcarpathia*

Problem statement. The chlorites are a group of minerals characterized by a stratified structure and they are quite common in metamorphic, metasomatic, igneous and sedimentary rocks. They form within a wide temperature range, namely 150–450°C, in case of pyroxene, amphibole and biotite. Within the limits of the Vyshkovo ore field (VOF) chlorites occur in metasomatic rocks that mainly are presented by beresites and argillizites, and sporadical propylites [1].

The majority of researchers interpret every phase of metasomatosis as the component of a single process. It is known [2] that propylitic alteration is associated with the build-up of hypabyssal intrusions; gold-plumb-zinc mineralization is attributed to beresitization while mercurial one is attributed to argillization. Metasomatic column within the VOF has a specific mineral composition. For beresites it is as follows: unaltered granodiorite-porphyrites – chloritization zone – sericitization zone – quartz reef, in dirty rocks: unaltered quartz diorites – a chlorite zone – kaolinite zone – quartz zone. The chlorite content in the like zone amounts up to 30–35%. The chemical composition of the VOF chlorites has not been researched yet.

Object of research – chloritization zones in the metasomatic column of beresites of the Bania and Shute ore occurrences within the VOF located in the southeastern part of Transcarpathia and associated with the upthrown blocks of the pre-Neogene basement of Transcarpathian depression. Here deposits of mercury and gold ore occurrences are located. The ore field rocks are intruded by numerous ore field hypabyssal intrusive bodies composed of granodiorite-porphyrites, quartz diorite porphyrites, less frequently of gabro-porphyries, gabro-diabases. Beresites being formed per granodiorite-porphyrites and quartz diorite porphyries within the Vyshkovo hypabyssal intrusive complex are described by us. Within the complex, Bania and Shute gold-galena-sphalerite ore occurrences are concentrated, their localization being controlled by basement faults [2].

In the process of fieldwork over 100 samples of metasomatic rocks within the Vyshkovo ore field were yield.

Research methods and peculiarities of results interpretation. Since the volume of chlorite segregations is low, we used the following methods to study them: the chemical composition was determined by energy-dispersive analysis using electron microscope-microanalyzer REMMA-102-02 in the laboratory of scientific-technical and training centre of Low Temperature Studies at Lviv Ivan Franko National University; structural features were studied using X-ray analysis on the basis of interdepartmental laboratory of X-ray diffraction analysis located in the Department of Geology at the

University; morphological features of chlorite segregations were studied in thin sections under a microscope. To reflect changes in chemical and mineral composition of chlorites corresponding charts were plotted.

For further calculations and referencing, the crystallochemical formulae of chlorites were computed. During computation, the content of *Na, K, Ca* and *Ti* was neglected as these are impurities. The formulae were calculated per 28 oxygen atoms. It should be noted that during microprobe analysis all ferrum is defined as divalent without dividing into Fe^{2+} and Fe^{3+}, but, as it is specified in [1], the content of Fe^{3+} in chlorite does not exceed 5% out from the total ferrum, thus we recognize all ferrum as Fe^{2+}.

To present and interpret the results of chemical analysis we used the classification of chlorites proposed in 1954 by M.H. Hey. This classification allows to assess the alternation of main components content (*Fe, Mg, Si*) of a mineral and attach each sample under investigation to a specified chlorites group. The temperature of chlorites formation was defined per the content of formula *A1* in tetrahedral position (method of A.R. Kotelnikov et al. [3]): T,°C = 39,73+180,64*$(Al^{IV})^x$ (±15 °C).

Analysis of recent research. The chlorites group was studied by many researchers both in Ukraine and abroad. Among Ukrainian scientists chlorite was studied by E.K. Lazarenko et al. (1960, 1963), E.O. Lazarenko et al. (1963, 1973, 1981), O.I. Matkovskyi (1971), Yu.R. Danylovych (1988), O.M. Platonov, G.L. Kravchenko (2010) and others. The morphology, properties and composition of chlorites sampled from various rocks of the Ukrainian Shield, the Dnieper-Donets depression, Carpathian region, Volyno-Podilla, Kerch Peninsula etc. [4] was described. In foreign literature among works on chlorite the following ones are of our interest: M.H. Hey (1954), M. Cathelineau, D. Neiva (1984), A.R. Kotelnikov (2012) and others. They, in detail, characterize the areas of chloritic rocks incidence, thermodynamic conditions of their formation, variation of mineral chemical composition, as well as propose the classification of chlorites.

Chlorites of the Vyshkovo ore field are documented in the monograph by I.P. Sherban et al. 1988 and by O.I. Matkovskyi et al. [5].

Article objective statement. Chlorites of polymetallic and plumb-zinc deposits are represented by magnesium and ferruginous varieties: pennine, ripidolite, minerals like a thuringite type. In beresites metasomatite column the chamosite and magnesian types are usually found. Within the limits of the VOF beresites are spread in the gold-plumb-zinc ore occurrences of Bania, Shute, Malorakoskiy, Chyrse and Za-gadkoviy, so it is interesting to prospect them to determine the possible mineralization. Up until now, no detailed studies of the VOF chlorites chemical composition have been perfor-med. As it is known, chlorite is of great importance in detecting plumb-zinc deposits, especially its magnesian-chamosite types that are common both in ores and wall-rocks. The sig-nificant variations of *Mg, Fe, Al,* SiO_2 and H_2O content are re-corded in chlorites. Thus, the chemical composition features of the VOF chlorites can be used as a prospecting indicator in respect of gold-plumb-zinc mineralization. These data can also be used to correlate or compare chlorite with a mineral from other regions, where chloritic rocks are widespread.

Baseline and research results. The microscopical study showed that metasomatic rocks of the majority the VOF gold-plumb-zinc ore occurrences are composed of chlorite, albite, oligoclase, quartz, sercite, biotite, and goethite. The increase in the content of quartz, albite and sercite, the reduction of chlorite and oligoclase in the direction of ore occurrence localization has been detected. In the rock chlorite is contained in a matrix (Fig.1). Its content reaches up to 25–30%. Chlorite forms a pseudomorphous occurrence per the primary mineral. Its colours vary from light yellow to dark green, the interference colours are low. The form of occurrences is table-like and rosette-shaped (Fig. 2), sometimes irregular; it partially or completely replaces biotite (Fig. 1). In the given example it occurs in association with goethite. Sometimes chlorite is developed in plagioclase grains in association with carbonate. Plagioclase is of regional character; oligoclase is located in the central part of grains and it is substituted by sericite partially or in full, the periphery is composed of albite. Among quartz grains the magmatic (formed in intrusive rocks) and metasomamatic occurrences (formed during beresitization) are distinguished. Among accessory minerals the following ones are detected: pyrite, rutile, apatite, etc.

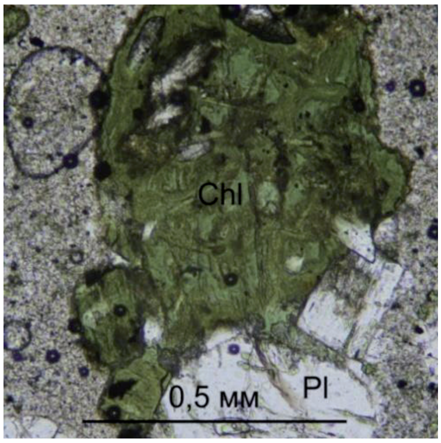

Fig.1. Chlorite that fully substitutes the primary mineral in fine-grained quartz-feldspathic body of rock

In general, to identify the chemical composition more than 100 microprobe analyses of individual chlorite grains taken from metasomatic ores of the Shute and Bania ore occurrences have been performed.

The results of these analyses allowed to calculate crystallochemical formulae per eight samples (Table). The data of microprobe analyses have been re-calculated per the formula concentration of *Si* and *Fe*, and then plotted in accordance with Hey's diagram (1954). It allows to note that chlorites of the Bania and Shute ore occurrences mainly pertain to the pyknochlorite–brunsvigite group, partially – to ripidolite and diabantite (Fig. 3). The mineral chemical composition changes towards the localization of mineralization. Close to the ore zone the reduction of *Fe* and increase of *Si, Al, Mg, Mn* has been observed in chlorite content. Presumably, the reason for this is the process of hydrothermal leaching and removal of iron from the zone of mineralization. Hydrothermal solutions rose up along the faults in already formed hypabyssal rocks.

Magnesium-ferriferous content of chlorites being studied is proved by the results of X-ray diffraction analysis. The obtained X-ray diffraction patterns (Fig. 4) show basal reflection regular for chlorite; less intensive are reflections 001, 003 and 005 if compared with 002 and 004 – this property is characteristic for *Mg-Fe* chlorites.

Taking into account the content of *Al* in tetrahedral position the temperature of chlorites formation has been defined – it ranges from 180 to 280°C (Fig. 5). This temperature values are very close to the previously detected (180–240°C) ones, i.e. those influencing the formation of the Bania ore occurrence beresites.

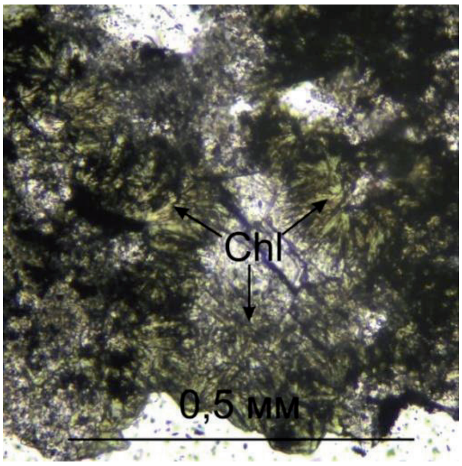

Fig. 2. Rosette-shaped chlorite occurences

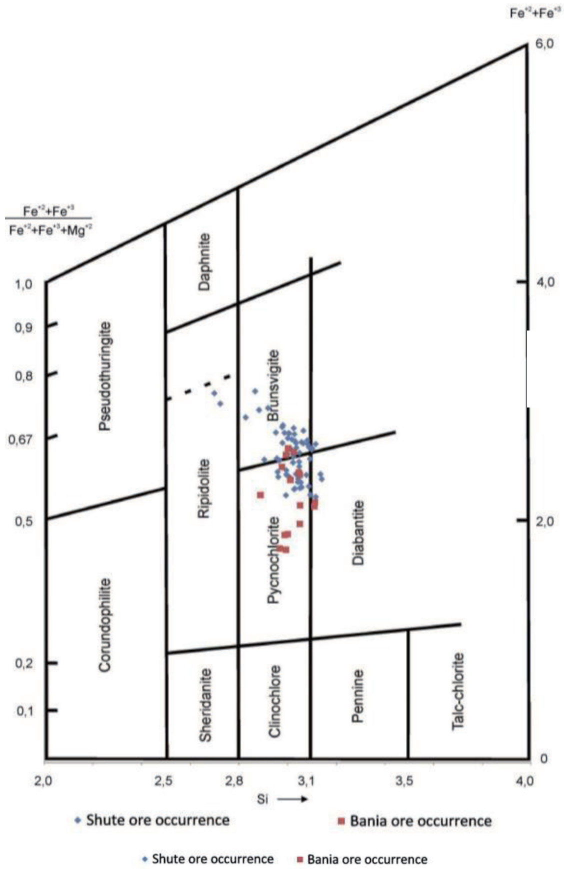

Fig. 3. Chemical composition of chlorites re-calculated per the formula concentration of Si and Fe and plotted on Hey's diagram

Table

Calculated crystallochemical formulae of chlorites taken from the Shute and Bania ore occurrences

Sampling area, Sample Nos.		Crystallochemical formula of chlorite
Shute ore occurrence	6/12 (4)	$(Mg_{2,35}Fe_{2,23}Mn_{0,06})_{4,64}Al_{1,18}[Si_{3,09}Al_{0,91}]O_{10}(OH)_8$
	6/13 (10)	$(Fe_{2,31}Mg_{2,08}Mn_{0,02})_{4,41}Al_{1,33}[Si_{3,09}Al_{0,91}]O_{10}(OH)_8$
	8/12 (4)	$(Fe_{2,99}Mg_{1,53}Mn_{0,05})_{4,57}Al_{1,37}[Si_{2,72}Al_{1,28}]O_{10}(OH)_8$
	8/12a (3)	$(Fe_{2,58}Mg_{1,90}Mn_{0,06})_{4,54}Al_{1,27}[Si_{3,05}Al_{0,95}]O_{10}(OH)_8$
	16/13 (5)	$(Fe_{2,66}Mg_{1,99}Mn_{0,06})_{4,71}Al_{1,16}[Si_{3,04}Al_{0,96}]O_{10}(OH)_8$
	63/13 (5)	$(Fe_{2,34}Mg_{1,92}Mn_{0,06})_{4,32}Al_{1,38}[Si_{3,06}Al_{0,94}]O_{10}(OH)_8$
Bania ore occurrence	76/13 (4)	$(Mg_{2,69}Fe_{1,99}Mn_{0,06})_{4,74}Al_{1,14}[Si_{3,05}Al_{0,95}]O_{10}(OH)_8$
	77/13 (6)	$(Fe_{2,47}Mg_{2,20}Mn_{0,10})_{4,77}Al_{1,15}[Si_{2,98}Al_{1,02}]O_{10}(OH)_8$

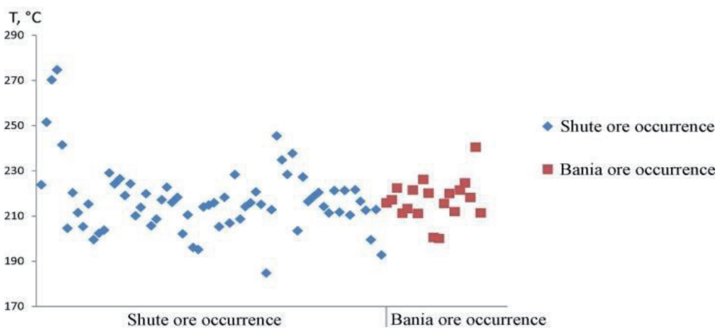

Fig. 5. The results of determining the temperature of chlorite forming, calculated per chlorite geothermometer [3]

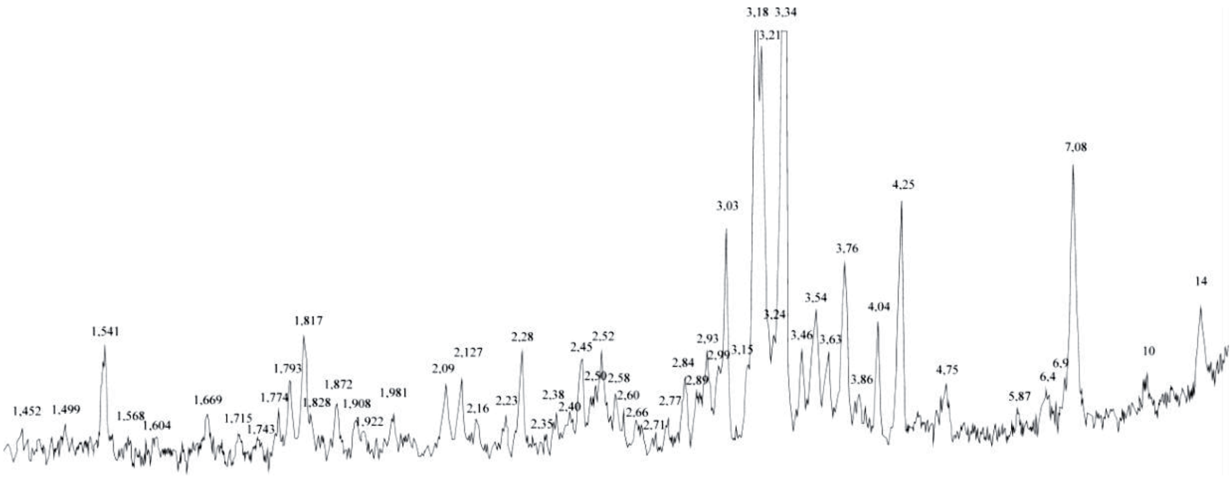

Fig. 4. X-ray diffraction pattern of chlorite and associated minerals taken from the Shute ore occurrence, Å

Conclusions and prospects for further research development. Chlorites are common within the limits of the VOF. They are associated with the metasomatic rocks of beresite and argillizite formation, and they were formed as a result of the replacement of primary *Fe-Mg* minerals − biotite, amphibole, and less frequent pyroxene. Chlorites of the Bania and Shute ore occurrences mainly pertain to the pyknochlorite–brunsvigite group. The change in chlorite chemical composition towards the localisation of mineralisation, i.e. the reduction of *Fe* content and increase of *Si, Al, Mg, Mn* content, has been detected. The temperature of chlorites formation ranges from 180 to 280°C.

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Мета. Дослідити особливості морфології, хімічного складу, структури та умов утворення хлориту метасоматичних порід Вишківського рудного поля. Виявити зміни мінералу в зоні локалізації золото-свинцево-цинкового зруденіння.

Методика. Для дослідження хлориту використано мікроскопічний, електронно-зондовий та рентгеноструктурний методи.

Результати. Визначено, що хлорити рудопроявів Bania та Shute належать, головним чином, до групи пікнохлорит-брунсвігіт, частково – діабантиту й рипідоліту. У напрямі локалізації зруденіння виявлено зміну хімічного складу хлориту – зменшення вмісту *Fe* та збільшення – *Si, Al, Mg, Mn.* Визначена температура формування хлоритів становить 180–280°C.

Наукова новизна. Уперше досліджено склад та деякі властивості хлоритів метасоматичних порід на рудопроявах золота в межах Вишківського рудного поля, визначено зміну їх хімічного складу в напрямі локалізації зруденіння та температуру формування.

Практична значимість. Склад хлориту є важливою розшуковою ознакою, яку можна використовувати під час пошуків прихованого золото-свинцево-цинкового зруденіння. Визначено температурний режим формування зони хлоритизації формації березитів. Отримані результати можна використовувати для порівняння з іншими районами, де поширена або можлива золото-свинцево-цинкова мінералізація.

Ключові слова: *хлорит, хлоритизація, метасоматичні породи, температура формування, Вишківське рудне поле, Закарпаття*

Цель. Исследовать особенности морфологии, химического состава, структуры и условий образования хлорита метасоматических пород Вышковского рудного поля. Выявить изменения минерала в зоне локализации золото-свинцово-цинкового оруденения.

Методика. Для исследования хлорита использованы микроскопический, электронно-зондовый и рентгеноструктурный методы.

Результаты. Определено, что хлориты рудопроявлений Bania и Shute принадлежат, главным образом, к группе пикнохлорит-брунсвигит, частично − диабантиту и рипидолиту. В направлении локализации оруденения обнаружено изменение химического состава хлорита − уменьшение содержания *Fe* и увеличение − *Si, Al, Mg, Mn.* Определена температура формирования хлоритов 180− 280°C.

Научная новизна. Впервые исследован состав и некоторые свойства хлоритов метасоматических пород на рудопроявлениях золота в пределах Вышковского рудного поля, установлено изменение их химического состава в направлении локализации оруденения и температуру формирования.

Практическая значимость. Состав хлоритов является поисковым признаком, который можно использовать при поисках скрытого золото-свинцово-цинкового оруденения. Полученные результаты могут быть использованы для сравнения с другими районами, где распространена или возможна золото-свинцово-цинковая минерализация.

Ключевые слова: *хлорит, хлоритизация, метасоматические породы, температура формирования, Вышковское рудное поле, Закарпатье*

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O.V. Haiovskyi

Ivan Franko National University of Lviv, Lviv, Ukraine, e-mail: ogayovskyi@mail.ru

ACTIVATION PERIODS OF KIROVOHRAD PROTOPLATFORM BLOCK (UKRAINIAN SHIELD) AND FORMATION OF DIAMOND-BEARING ROCKS

О.В. Гайовський

Львівський національний університет імені Івана Франка, м. Львів, Україна, e-mail: ogayovskyi@ mail.ru

ЕПОХИ АКТИВІЗАЦІЇ ПРОТОПЛАТФОРМНОГО КІРОВОГРАДСЬКОГО БЛОКА УКРАЇНСЬКОГО ЩИТА ТА ФОРМУВАННЯ АЛМАЗОНОСНИХ ФОРМАЦІЙ

Purpose. Reconstruction of the endogenous diamond-bearing formation stages in the geologic history of the Kirovohrad block (Ukrainian shield) protoplatform structure development for determination of possible diamonds sedimentary reservoirs geological age.

Methodology. Deep geological and geophysical studies of the lithosphere, the structural-tectonic analysis of the Precambrian basement, complex structural-formational division of geological bodies.

Findings. The Kirovohrad block of the Ukrainian shield refers to promising protoplatform diamond blocks due to localization of diamond structures and formations. It has been established that the geological and structural-tectonic preconditions of endogenous diamond-bearing rocks formation were laid in the Early Precambrian at the stage of protoplatform regime. They appeared on the stages of activation, which occurred from Middle Proterozoic till Paleocene in the Kirovohrad block. It is evidenced with lithological, structural and formational features, and age characteristics of rocks which are associated with diamond formations. Alluvial diamond concentration associated with young and modern Phanerozoic sedimentary formations have been caused by the destruction of ancient endogenous sources.

Originality. Geological, structural and epoch conditions of the Kirovohrad block diamond-bearing rocks formation have been considered through the general background of direct evolution development of the Earth crust in the Precambrian and Phanerozoic. Special attention is paid to the Precambrian period, because of favorable geological and structural-tectonic conditions for diamond-bearing rocks formations.

Practical value. Allocation of activation and diamond-bearing rocks formation epochs allows orienting forecast metallogenic studies and applying a number of important control factors during the search and exploration of this type of mineralization: geological-structural, geochronological, stratigraphic, lithological, paleogeographic. Taking into account space-time regular position of diamond-bearing formations while analyzing protoplatform structures it is possible to estimate the probability of diamonds presence on their territory and also to predict the diamond-bearingness of territory.

Keywords: *activation, Kirovohrad block, protoplatform, diamond bearing formation, mantle*

Statement of the problem. The term “activation”, accepted by geologists since the mid-twentieth century, means the processes of epiplatform recovery or intensive strengthening of tectono-magmatic activity in regions that have completed their development. Activation expressed in Germany-type structural-tectonic rearrangement of rigid consolidated structures (development of deep faults regional zones, near-