МІНЕРАЛОГІЯ, ГЕОХІМІЯ ТА ПЕТРОГРАФІЯ

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CALCLITHITES OF THE KROSNO ZONE IN THE EAST CARPATHIANS (UKRAINE)

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Results of carbonates distribution in the flysch rocks of the Krosno Zone (Ukrainian Carpathians), which are composed mainly by interstratification of sandstones, argillites and aleurolites, and sporadically limestones, dolostones and marls as well as estimations of contents are analysed in this article. Carbonates are widely distributed in variable amounts in the rocks outcropped into the new Beskyd tunnel at the Carpathians watershed and surrounding area. Most high values of carbonates (up to 77,11 wt. %) as well as its lowest contents (a few per cent) were found in different sectors. According to X-ray powder diffraction observations on whole-rock samples carbonates are represented by calcite and dolomite. Dolomite is dominant phase and its total amount is about three times more than calcite.

Two main different age morphological and mineralogical generations of carbonates are distinguished within the flysch rocks after petrographic studies and microbeam analyses. Early generation of the carbonates is represented by coarse grained detrital dolomite and finer calcite as cement. Late generation of big in size crystals of carbonates is main component of the carbonate, carbonate-quartz, and carbonate-sulphide druses and veins, which are distributed locally. Studied carbonate-bearing rocks are regarded as calclithites after the Folk's classification due to significant amounts of terrigenous carbonates. Carbonates from the initial flysch rocks have $\delta^{13}C$ and $\delta^{18}O$ values similar to those of the typical marine limestone carbonates and are limited in a relatively narrow field. It is additional evidence of local sources for the flysch formations rich in carbonates.

Keywords: calclithites, flysch, Krosno zone, sandstones, carbonates, C and O isotopes.

Introduction. Carbonates are widespread in variable amounts in the flysch rocks of the Ukrainian Carpathians, which are composed mainly by interstratification of sandstones, argillites and aleurolites, and sporadically limestones, dolostones and marls. The above-mentioned rocks in different proportions are typical for all regional units of the studied territory [1, 4, 6, 7] and surrounding parts of the Carpathians [11, 14].

Most of these rocks are represented by terrigenous components – quartz, plagioclase, carbonates, mica, chlorite, zircon, titanite, tourmaline, rutile, etc. Two main different age, morphological and mineralogical generations of carbonates were distinguished within the flysch rocks. Earlier generations of the carbonates are represented by coarse grained detrital fragments and finer carbonate as cement [5]. Total contents of carbonates in the sandstones and shales are fluctuating from parts of tenth percent up to dozens percents [1, 6, 7], and commonly regarded as cement of terrigenous rock varieties.

In commonly used classifications of clastic rocks by mineral composition, scientists consider three components: quartz, feldspar and other terrigenous material [20]. Special group of terrigenous rocks that mainly consists of eroded limestones and other carbonate rocks fragments was for the first time systematically described by R. L. Folk in 1959 [12] and defined as calclithite. He studied composition of the sedimentary rocks and identified species with a predominance of silt-sand-gravel carbonate fraction more than 50 per cent in the composition of terrigenous material. The grain size of these rocks could range from siltstones (rare) to sandstones (fairly common) and to conglomerate (most common). The rocks often are product of intense orogeny early phases and, particularly in its early phases before the sedimentary cover has been stripped off the source area. Their formation is possible in case of intensive erosion and short detritus transport distance [12, 13]. Absence of uniform classification of terrigenous rocks complicates analysis of rocks with a high content of carbonates and leads to disparate treatment of geological terms. That's why, calclithite should be considered as distinct terrigenous rocks and form a terrigenous rocks group equivalent to the orthoquartzite, arkose, or greywacke. Thus the triangle composition for sandstones should be expanded to a tetrahedron and include terrigenous carbonate rocks [9, 12, 13].

Calclithites were discovered and described in different age formations and numerous regions (the Miocene Oakville Formation of the Central Texas [15], the Permian Phosphoria Formation in the Idaho [19], the Palaeogene Formation of the Tajo Basin, Spain [10], rocks of the Laramide basement uplifts of the Rocky Mountain foreland (Late Cretaceous-Late Eocene) [17], Upper Miocene arenites of the central Apennines, Italy [18]. These are evidence of permanent presence of calclithites among other terrigenous rocks.

In this article we described calclithites from the Krosno zone, which are developed in the new Beskyd tunnel and surrounding areas, and tried to give information on their origin.

Geological settings. Due to construction of the new Beskyd tunnel at the Carpathians watershed there was a direct access to the artificial outcrops and geological study with sampling of materials from flysch formation rocks of the Krosno Zone which changed minimally. Beside the tunnel, similar clastic rocks with a high content of carbonates were found in different sectors of the Krosno Zone near Skotarske, Guklyvuy, Volovets villages, etc.

Krosno (or Silesian) Zone is located in the central part of the Outer Carpathians [11, 14]. General structure of this zone is similar to other Outer Carpathians nappes. Its internal subzones were thrusted onto the outer ones in north-east direction, as well as other main Ukrainian Carpathians units. Geological boundaries and structural features of this zone differ on various tectonic schemes of the Ukrainian Carpathians [3, 14].

The flysch series is composed of interstratification of light gray massive sandstones (up to 90 % of the cross section), and dark to black argillites and aleurolites, sporadically limestones, dolostones and marls. They are regarded [1–3, 11] as a part of the Oligocene Lower Krosno Formation. General dipping of the Krosno Formation stratum in limits of the tunnel is south-western, under varying angles from 30° up to 60°. In some places there are flexures and orthogonal or (rarely) perpendicular fractures in the rocks which are often filled with late veins and druses (thickness up to 50 centimeters) of the newly formed minerals.

Calcite druses and veins dominate; they contain small crystals of quartz, which has all the features of the Maramures "diamonds" [5]. Hydrocarbons seeps (yellow-green in color) on surfaces of the late druse in flysch rocks were found in the new Beskyd tunnel. In these places quartz contains a large number of liquid and solid hydrocarbons inclusions.

Sampling and analytical techniques. Beside routine geological investigation and sampling petrographic studying of thin sections were carried out to determine of crystallization ordering for minerals of carbonate-bearing rocks, which are typical for the Krosno Zone, as well as to check shapes and heterogeneity of individual minerals of these rocks.

To estimate total amount of carbonates in the rocks we used its solution by hydrochloric acid of different concentrations (5 % and 10 %) and temperature (with heating or without it). Weight method was involved for resulting calculation. Carbonate compositions were determined on whole-rock samples using a DRON powder diffractometer.

Taking into consideration the results from thin sections observations, microbeam analyses of mineral grains were carried out using a REMMA-10202 scanning electron microscope equipped with an energy-dispersivedetector "EDAR" (Lab of the Faculty of Physics, National University of Lviv, named after Ivan Franko) on the previously cleaning and prepared samples by carbon fine film decoration. Set of the carbonate grains were used to determine its shape and size, inner heterogeneity and coexisting phases. Analyses included general investigations of chemical composition of separate phases.

The oxygen and carbon isotopic compositions in the whole-rock carbonates were analyzed in the Institute of the Geochemistry and Ore Formation, Kyiv. Carbon dioxide was released from carbonates using the $PbCl_2$ under 500 °C. The relative difference in oxygen and carbon isotope ratios in CO_2(gas) was measured on a MI-1201MV mass spectrometer. The laboratory CO_2 was used as standard GIN-1 during isotopic measurement, which is connected to the International PDB and SMOW standards respectively. The accuracy of $\delta^{13}C$ and $\delta^{18}O$ measurement in whole-rock samples was ±0,1 ‰ and ±0,2 ‰ respectively. The Craig correction was taken into consideration for the determination of $\delta^{13}C_{samp}$ (PDB) and $\delta^{18}O_{samp}$ (SMOW). The oxygen correction was taken into account for $\delta^{13}C_{samp}$ (PDB).

Results and discussion. Medium- and coarse-grained and sometimes up to gravelitic (Fig. 1, 2) sandstones (up to 90 % of the total volume), and dark to black fine-grained argillites and aleurolites are main rocks of the three components flysch in the studied area. Beds of dark-gray to black limestones, dolostones and marls are sporadically found along the geological sections.

Psammitic textures and massive structures are typical for sandstones, which are composed mainly by quartz-carbonate lithocrystalloclastic varieties. Separate fragments (0,1–0,5 mm in size) are represented by quartz (up to 50 % of volume), carbonates (more than 50 % of volume), and microquartzites, plagioclase, microcline, mica (first per cents) and rare biotite and glauconite. Some foraminifera and ore minerals relicts are also found. Clay-carbonate cement of the sandstones (about 5 % of the volume) is mainly film-like.

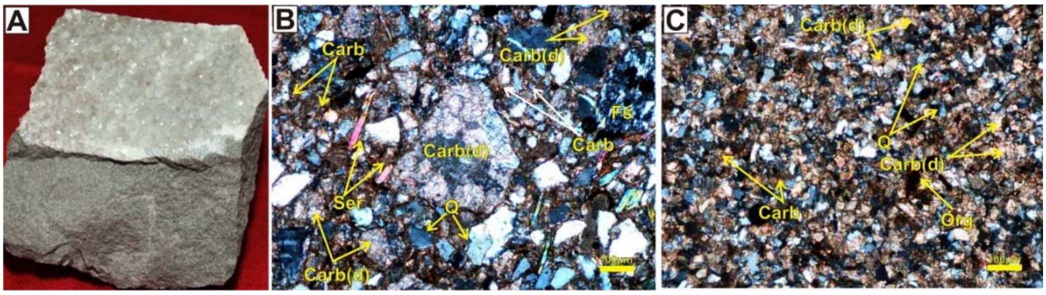

Fig. 1. Sandstone with late calcite druse (A) and typical thin sections of the carbonate rocks from the Krosno Formation: B – poorly sorted, fine-grained clastic sandstone (Skotarske village, left bank of the Vicha river); C – sericitic, well sorted, fine-grained clastic sandstone (Skotarske and Guklyviy villages); Symbols used:
Carb (d) – detrital carbonate, Q – quarts, Carb – carbonate cement, Fs – feldspar, Ser – sericite, C – calcite veins

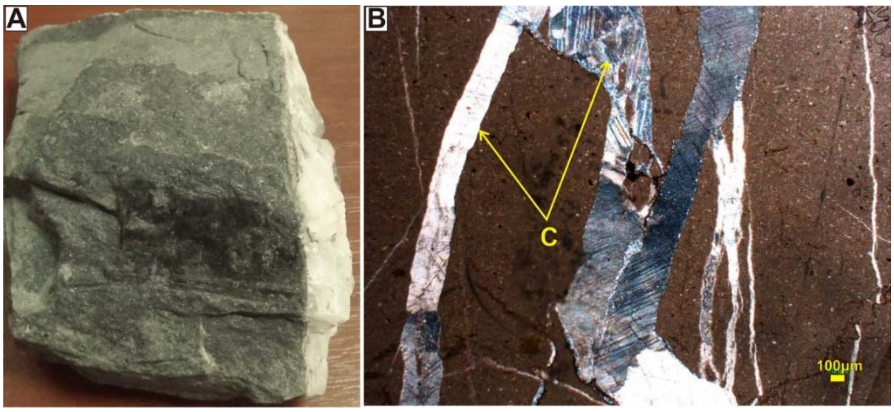

Fig. 2. Siltstone (A) and typical thin section of the carbonate rocks from the Krosno Formation – siltstone with late calcite veins, new Beskyd tunnel (B). Symbols used: C – calcite veins

Mineral composition of the argillites, aleurolites and sandstones is similar, but with lower amounts of quartz (less than 5 %), sericite (less than 50 %), and carbonates (more than 50 %).

Pelithomorphic (rich in clay) limestone includes point-like quartz grains and separate plagioclase grains, and is characterized by pelitic texture and massive structure. The rocks contain coal-clay, sometimes ore minerals, and fragments (0,01–0,08 mm in size). Cement of the rocks is clay-carbonate, sometimes clay-ferrous-carbonate. Texture of rocks is aleuropelitic, structure – massive, sometimes massive-banded due to intercalations of intervals with different proportions of clay and carbonate amounts.

Separate sandstone beds have most significant thickness (up to 10 m) in comparison to subordinated thickness of argillites and aleurolites (up to few meters). Thickness of limestones, dolostones and marls layers are not more than a few centimeters.

Carbonate contents and its composition. Total amounts of carbonates in the studied flysch rocks of the Krosno Formation are variable (Table 1). Besides samples with late carbonates we determined significant contents of carbonates almost all over the investigated area. Most high values of carbonates (up to 73,38–77,11 wt.%) as well as its lowest contents (first per cents) were found among the different sectors. There is no important distinction in carbonate contents within the flysch rocks different in composition and structures.

According to X-ray powder diffraction observations on whole-rock samples, carbonates are represented by calcite (dn/3,029; 2,088; 1,912; 1,869) and dolomite (dn/2,89; 2,65; 2,18; 1,78). Due to higher intensity of basal reflects dolomite is dominant phase in the observed samples and its total amount is about three times more than calcite.

Microbeam analyses were carried out on the previously prepared and polished samples of the carbonate-bearing flysch rocks. Quartz, dolomite, calcite, muscovite, illite, albite in different proportions are main minerals of the rocks (Fig. 3). Detrital coarse fragments of quartz and dolomite have irregular shapes and are cemented by fine-grained calcite, muscovite, illite, and rare grains of plagioclase.

Table 1. **Carbonate contents in flysch rocksfrom the Krosno Formation**

№ of samples	Sectors of location	Total amount of carbonates, wt. %
1A	Beskyd	21,04
6A	Beskyd	67,52
7A	Beskyd	24,65
13A	Beskyd	27,21
15A	Beskyd	25,10
33	Skotarske	23,60
36	Skotarske	33,65
37	Skotarske	29,12
38	Skotarske	73,38
39	Skotarske	63,76
49	Huklyvyy	36,02
53	Huklyvyy	77,11
54	Huklyvyy	36,77
55	Huklyvyy	35,75
64	Volovets	10,50
66	Volovets	14,32

Separate dolomite clasts (see Fig. 3) have different size (from 100 up to 200 mk) and almost pure chemical compositions. Crystallochemical formula of the dolomite – $Ca_{1,01–1,04}(Mg_{0,90-0,93}Fe^{2+}_{0,00–0,01})_{0,91–0,93}[CO_3]_2$ reflects very low concentrations of the iron admixture and is similar for dolomite cores and rims in different observed sectors.

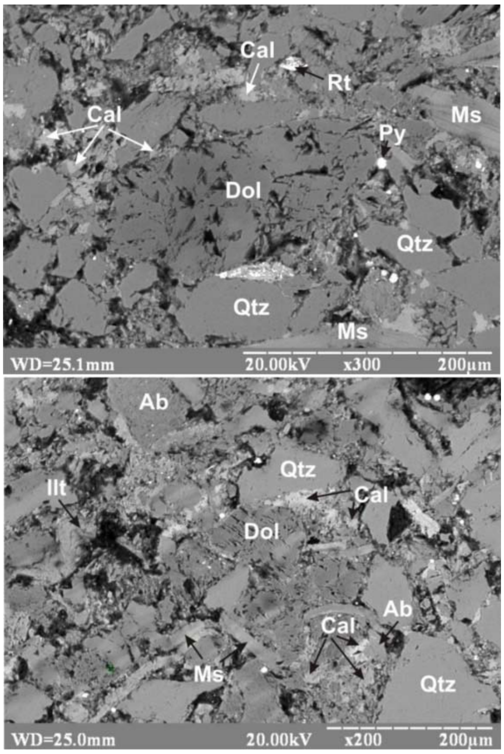

Fig. 3. Back-scattered image of the sandstones: detrital dolomite (Dol) and calcites (Cal) cement, Ms – muscovite, Py – pyrite, Rt – rutyl, Qtz – quartz, Ab – albite, Ilt – ilmenite

Calcite, muscovite, illite, plagioclase are common minerals of the cement. Isometric grains of pyrite (up to 10 mk) and short columns up to needle shape rutile crystals (up to 20 mk) are found sporadically, too. Fine grained and commonly isometric calcite (up to 20 mk) is typical cement of dolomite and quartz irregular clasts (see Fig. 3).

According to calculated crystallochemical formula – $Ca_{0,90–0,95}(Mg_{0,02}Fe^{2+}_{0,00–0,02})_{0,95–0,98}[CO_3]_2$ calcite has also pure chemical composition. no significant admixtures are found in different grains of calcite.

C and O isotope composition. Carbonates from the initial flysch rocks have $\delta^{13}C$ and $\delta^{18}O$ values similar to those of the typical marine limestone carbonates and are limited in a relatively narrow field (Fig. 4).

The spatial and composition relationship between carbonates of the first generation and druse mineralization indicates their commonness. Late carbonates were formed during faults development in lithified rocks: they have the characteristics of the open cavities. Carbon and oxygen data of the late carbonates commonly close to $\delta^{13}C$ and $\delta^{18}O$ values determine for primary carbonates. It can be a good evidence for their inheritance, and formation of the late carbonates from solutions that actively interact with the host rocks. But some calcites enriched in heavy ^{13}C isotope ($\delta^{13}C$ up to +7,2 ‰) were formed from mixing fluids. Late aragonite enriched in heavy carbon isotope ^{13}C ($\delta^{13}C$ up to +9,5 ‰) confirms possible connection between aragonite and neighboring ore mineralization [7].

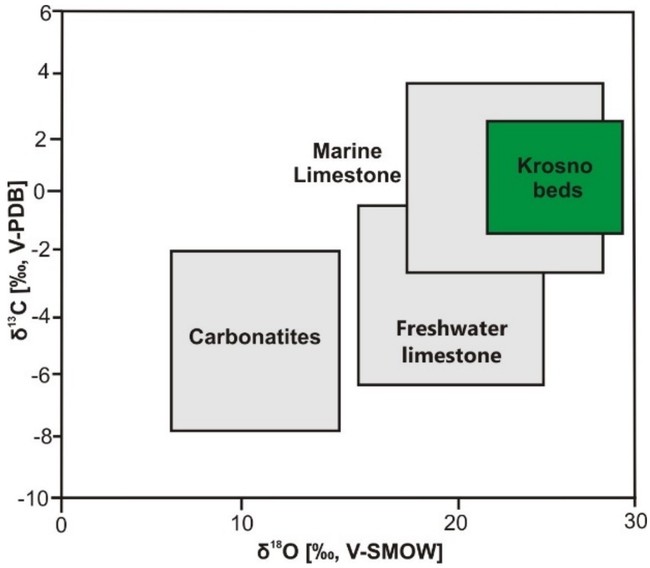

Fig. 4. $\delta^{13}C$ vs. $\delta^{18}O$ diagram shoving field of the stable isotopes values in the measured primary carbonates (green) concerning of the main nature carbon and oxygen reservoirs (after [16])

Conclusions. Sandstones, argillites and aleurolites are main components of the flysch formation of the Krosno Zone within the new Beskyd tunnel at the Carpathians watershed and surrounding sectors near Skotarske, Guklyvuy, Volovets villages, etc. Limestones, dolostones and marls are developed sporadically all over this area.

Carbonates are widely distributed in variable amounts in the flysch rocks. Most high values of carbonates (up to 77,11 wt.%) as well as its lowest contents (a few per cent) were found among the different sectors. Dolomite is dominant phase and its total amount is about three times more than calcite. Two main different age morphological and mineralogical generations of carbonates are distinguished within the rocks of the Krosno Zone. Early generation of the carbonates is represented by coarse grained detrital dolomite and finer calcite as cement. Late generation of big in size crystals of carbonates is main component of the carbonate, carbonate-quartz, and carbonate-sulphide druses and veins, which are developed locally.

Studied carbonate-bearing rocks are regarded as calclithites after the Folk's classification due to significant amounts of terrigenous carbonates. According to calculated petrochemical data (F = 0,11, A = 26, K = –21) investigated flysch rocks of the Krosno Formation are represented by clay greywacke [8] and greywacke – litharenity (K_2O/Na_2O – 0,77 and SiO_2/Al_2O_3 – 4,5) after [20]. Taking into consideration terrigenous carbonates occurring everywhere in the Krosno Zone we should conclude about importance of the third detritus component at the Folk's diagram [12, 13] besides quartz and feldspars. At the same time wide variations of carbonate contents (from 10,50 up to 77,11 wt.%) indicate presence of facial heterogeneity within the Krosno Zone. Paragenetic relationships and similarity of the flysch rocks and significant variations of the detrital carbonates among them point to not only quantitative but also genetic differences between components at the Folk's diagram.

Terrigenous carbonates from the initial flysch rocks have $\delta^{13}C$ and $\delta^{18}O$ values similar to those of the typical marine limestone carbonates and are limited in a relatively narrow field. It is additional evidence of local sources for the flysch formations rich in carbonates.

Список використаних джерел

1. Афанасьева И.М. Петрогеохимические особенности флишевой формации южного склона Советских Карпат / И.М. Афанасьева. – К. : Наук. думка, 1979. – 244 с.

2. Габинет М.П. Изотопный состав углерода карбонатов в олигоценовом флише Карпат. / М.П. Габинет, Г.П. Мамчур // Вопросы минералогии осадочных образований. – Львов : Львов. гос. ун-т, 1970. – Кн. 8. – С. 119–125.

3. Гнилко О. Про північно-східну границю Кросненської тектонічної зони в Українських Карпатах / О. Гнилко // Геологія і геохімія горючих копалин. – 2010. – № 2 (151). – С. 44–57.

4. Головченко Д. Мінеральний склад та поширення карбонатних утворень Кросненської світи Українських Карпат / Д. Головченко, Т. Кшановська // Мінерал. зб. – 2004. – № 54, вип. 2. – С. 230–234.

5. Гулій В.М. Пізня сульфідно-кварц-карбонатна мінералізація в породах Кросненської зони в межах траси нового Бескидського тунелю / В.М. Гулій, С.Я. Кріль, І. Ємельянов та ін. // Мінерал. зб. – 2016. – № 66, Вип. 2. – С. 77–87.

6. Даниш В.В. Геологія західної частини південного схилу Українських Карпат / В.В. Даниш. – К. : Наук. думка, 1973. – 116 с.
7. Кріль С. Ізотопний склад жильних карбонатів зони Рахівсько-Тисенського розлому Українських Карпат / С. Кріль // Мінерал. журн. – 2014. – № 3. – С. 30–39.
8. Предовский А.А. Реконструкция условий седиментогенеза и вулканизма раннего докембрия / А.А. Предовский. – Л. : Наука, 1980. – 152 с.
9. Шутов В.Д. Обзор и анализ минералогических классификаций песчаных пород / В.Д. Шутов // Литология и полезные ископаемые. – 1965. – № 1. – С. 95–112.
10. Arribas J. Petrographic evidence of diferent provenance in two alluvial fan system (Palaeogene of the northern Tajo Basin, Spain) / J. Arribas, E. Arribas// Geological Society London Special Publications.– 1991. – № 57(1). – P. 263–271.
11. Bojanowski M. The onset of orogenic activity recorded in the Krosno shales from the Grybyw unit (Polish Outer Carpathians) / M. Bojanowski // Acta Geologica Polonica. – 2007. – № 57(4). – P. 509–522.
12. Folk R.L. Practical petrographic classification of limestones / R.L. Folk // Am. Assoc. Petroleum Geologists Bull. – 1959. – Vol. 43. – P. 1–38.
13. Folk R.L. Petrology of sedimentary rocks / R.L. Folk. – Austin, Texas: Hemphill's Bookstore, 1974. – 182 p.
14. Geology and hydrocarbon resources of the Outer Carpathians, Poland, Slovakia, and Ukraine: general geology / A. Slaczka, S. Kruglov, J. Golonka et al. // The Carpathians and their foreland: Geology and hydrocarbon resources: AAPG Memoir. – Tulsa, Oklahoma, USA., 2006. – № 84. – P. 221–258.
15. Ham W.E. Algal Origin of the 'Birdseye' Limestone in the McLish Formation / W.E. Ham // Proc. Oklahoma Acad. Sci. – 1954. – Vol. 33. – P. 200–203.
16. Hoefs J. Stable Isotope Geochemistry / J. Hoefs. – Verlag-Berlin-Heidelberg: Springer. XII, 2009. – 286p.
17. Ingersoll R. Provenance of impure calclithites in theLaramide foreland ofSouthwesternMontana / R. Ingersoll, W. Cavazza, S. Graham // Journal of Sedimentary Petrology. – 1987. – Vol. 57, № 6. – P. 995–1003.
18. Interpreting siliciclastic-carbonate detrital modes in foreland basin systems: An example from Upper Miocene arenitesof the central Apennines, Italy. / S. Critelli, E.Le Pera, F. Galluzzo et. al. // Geological Society of America Special Paper. – 2007. – № 420. – P. 107–133.
19. Johnson E. Petrographic descriptions of selected rock specimens from the Meade Peak phosphatic shale member, Phosphoria Formation (Permian), Southeastern Idaho. U.S / E. Johnson, R. Grauch, J. Herring. – Geological Survey Scientific Investigations Report, 2007. – № 5223. – 17 p.
20. Pettijohn F.J. Sedimentary rocks / F.J. Pettijohn. – Third Edition. Harper & Row Publishers. N-Y, 1975. – 751 p.

References
1. Afanasyeva, I.M. (1979). Petrogeochemical features of the flysch formations at the southern slope of the Soviet Carpathians. K. : Naukova Dumka, 244 p. [In Ukrainian].
2. Gabynet, M.P, Mamchur, G.P. (1970). Carbon isotope composition in carbonate from Oligocene flysch of the Carpathians. Book 8. Voprosyi mineralogii osadochnyih obrazovaniy. Lviv University, 119–125. [In Russian].
3. Gnylko, O. (2010). On the north-eastern boundary of the Krosno tectonic zone in the Ukrainian Carpathians. *Geology and Geochemistry of Combustible Minerals*, 2 (151), 44–57. [In Ukrainian].
4. Holovchenko, D., Kshanovs'ka, T. (2004). Mineral composition and distribution of carbonaceous rocks in the Krosno Suite of the Ukrainian Carpathians. *Mineralogical Collection*, 54 (2), 230–234. [In Ukrainian].
5. Guliy, V., Kril, S., Yemelyanov, I., Kuzemko, Ya., Stepanov, V. (2016). Late sulphide-quartz-carbonate mineralization in the Krosno Zone rocks within the route of new Beskydskyi tunnel.*Mineralogical Review,*66, 2, 77–87. [In Ukrainian].
6. Danysh, V. (1973). Geology of the western part of the southern slope of the Ukrainian Carpathians. K.: Naukova Dumka, 116 p. [In Ukrainian].
7. Kril, S. Ya. (2014).Isotopic composition of the carbonate veins in the Rakhiv-Tysa Fault Zone (Transcarpathians). *Mineral. Journ*., 36, 3, 30–39. [In Ukrainian].
8. Predovskiy, A.A. (1980). Reconstruction of the sedimentation and volcanism conditions in Early Precambrian. Lviv: Nauka, 152 p. [In Russian].
9. Shutov, V.D. (1965). Review and analysis of mineralogical classification of sandy rocks. *Litologiya i poleznyie iskopaemyie, 1, 95–112.* [In Russian].
10. Arribas, J. Arribas, E. (1991). Petrographic evidence of diferent provenance in two alluvial fan system (Palaeogene of the northern Tajo Basin, Spain). *Geological Society London Special Publications,* 57(1), 263–271.
11. Bojanowski, M. (2007). The onset of orogenic activity recorded in the Krosno shales from the Grybyw unit (Polish Outer Carpathians). *Acta Geologica Polonica,* 57 (4), 509–522.
12. Folk, R. L. (1959). Practical petrographic classification of limestones.*Am. Assoc. Petroleum Geologists Bull.*, 43, 1–38.
13. Folk, R. L. (1974). Petrology of sedimentary rocks. Austin, Texas, Hemphill's Bookstore, 182 p.
14. Ślączka, A., Kruglov, S., Golonka, J., Oszczypko, N., Popadyuk, I. (2006). Geology and hydrocarbon resources of the Outer Carpathians, Poland, Slovakia, and Ukraine: general geology. *AAPG Mem*., 84, 221–258.
15. Ham, W. E. (1954). Algal Origin of the 'Birdseye' Limestone in the McLish Formation. *Proc. Oklahoma Acad. Sci.,* 33, 200–203.
16. Hoefs, J. (2009). Stable Isotope Geochemistry. Verlag-Berlin-Heidelberg: Springer. XII, 286 p.
17. Ingersoll, R., Cavazza, W. Graham, S. (1987). Provenance of impure calclithites in the Laramide foreland of Southwestern Montana. *Journal of Sedimentary Petrology,* 57, 6, 995–1003.
18. Critelli, S.,Le Pera, E., Galluzzo, F. et. al. (2007). Interpreting siliciclastic-carbonate detrital modes in foreland basin systems: An example from Upper Miocene arenitesof the central Apennines, Italy. *Geological Society of America Special Paper*, 420, 107–133.
19. Johnson, E., Grauch, R., Herring, J. (2007). Petrographic descriptions of selected rock specimens from the Meade Peak phosphatic shale member, Phosphoria Formation (Permian), Southeastern Idaho. U.S. Geological Survey Scientific Investigations Report, 5223, 17 p.
20. Pettijohn, F.J. (1975). Sedimentary rocks. Third Edition. Harper & Row Publishers. N-Y, 751 p.

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КАЛЬКЛІТІТИ КРОСНЕНСЬКОЇ ЗОНИ СХІДНИХ КАРПАТ (УКРАЇНА)

Наведено результати вивчення розподілу карбонатів і визначення їхньої кількості у флішових породах Кросненської зони (Українські Карпати), які представлені перешаруванням переважно пісковиків, аргілітів і алевролітів, а також вапняками, доломітами і мергелями, які появляються спорадично. Карбонати широко розповсюджені в змінних кількостях у породах, які відкриті при проходженні нового Бескидського тунелю у водороздільній частині Карпат і на оточуючих ділянках. Високий вміст карбонатів (до 77,11 ваг.%), як і їх невеликі кількості (перші відсотки), виявлені на різних ділянках. Рентгенівські дифракційні дослідження проб показали, що в породах присутні кальцит і доломіт. Кількість доломіту приблизно в три рази більша ніж кальциту.

Дві основні різновікові генерації карбонатів встановлено в породах флішу за результатами петрографічних і мікрорентгеноспектральних аналізів. Ранні карбонати представлені грубозернистим уламковим доломітом і тонкозернистим кальцитом, який відіграє роль цементу. Пізні генерації крупних кристалів кальциту є основними в карбонатних, карбонат-кварцових і карбонат-сульфідних друзах і жилах, які розповсюджені локально. Досліджені карбонатоносні породи складені значною кількістю теригенних карбонатів і, згідно з класифікацією Фолка, розглядаються як калькліти. Карбонати вихідних флішових порід мають значення $\delta^{13}C$ і $\delta^{18}O$, які аналогічні значенням виявленим у карбонатах морських вапняків. Їхні фігуративні точки локалізовані у вузькому полі, що є додатковим аргументом на користь місцевих джерел карбонатів у породах флішової формації.

Ключові слова: калькліти, фліш, Кросненська зона, пісковики, карбонати, ізотопи C і O.

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КАЛЬКЛИТИТЫ КРОСНЕНСКОЙ ЗОНЫ ВОСТОЧНЫХ КАРПАТ (УКРАИНА)

Приведены результаты изучения распределения карбонатов и оценки количества их во флишевых породах Кросненской зоны (Украинские Карпаты), которые представлены переслаиванием, главным образом, песчаников, аргиллитов и алевролитов, а также спорадически проявленными известняками, доломитами и мергелями. Карбонаты широко распространены в переменных количествах в породах, вскрытых при прохождении нового Бескидского тоннеля в водораздельной части Карпат и на окружающих участках. Высокие содержания карбонатов (до 77,11 вес.%), как и их низкие содержания (первые проценты), были обнаружены на различных участках. Согласно рентгеновским дифракционным исследованиям образцов пород карбонаты представлены кальцитом и доломитом. Доломит преобладает – его общее содержание примерно в три раза больше, чем кальцита.

Две основные генерации карбонатов, отличающиеся по возрасту, установлены в породах флиша по результатам петрографических и микрорентгеноспектральных анализов. Ранние карбонаты представлены грубозернистым обломочным доломитом и тонкозернистым кальцитом, который играет роль цемента. Поздние генерации крупных кристаллов кальцита являются главной составной частью карбонатных, карбонат-кварцевых и карбонат-сульфидных друз и жил, которые развиты локально. Изученные карбонатсодержащие породы содержат значительное количество терригенных карбонатов и согласно классификации Фолка рассматриваются как кальклититы. Карбонаты исходных флишевых пород имеют $\delta^{13}C$ и $\delta^{18}O$ значения, которые аналогичны карбонатам морских известняков. Их фигуративные точки локализованы в узком поле, что является дополнительным аргументом в пользу местных источников карбонатов в породах флишевой формации.

Ключевые слова: кальклититы, флиш, Кросненская зона, песчаники, карбонаты, изотопы C и O.