Mineralia Slovaca, Web ISSN 1338-3523, ISSN 0369-2086, https://doi.org/10.56623/ms.2022.54.2.3
54, 2 (2022), 163 – 174, © Authors 2022. CC BY 4.0

Comparison of morphology of quartz crystals – "Marmarosh diamonds" – from Paleogene Flysch sequences of Krosno (Silesian) Zone, Dukla Zone in Ukrainian Carpathians, and Intra-Carpathian sequences of Western Carpathians

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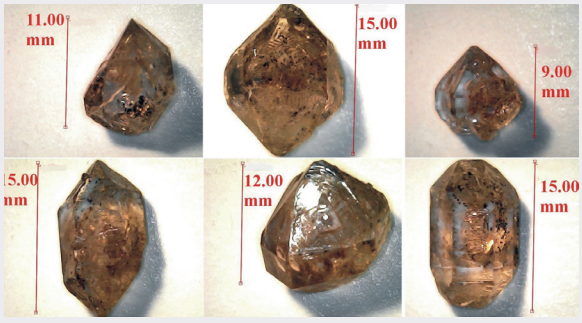
Abstract: Quartz crystals of "Marmarosh diamonds" type were goniometrically studied in Ukrainian Carpathians from the veins in flysch deposits of Krosno (Silesian) unit (137 crystals, locality 1 – New Beskydy Tunnel) and the Oligocene sediments of the Dukla Zone (77 crystals; loc. 2 – Pryslip pass). They were compared with quartz crystals from intra-Carpathian Paleogene sequences of the Western Carpathians in Slovakia (175 crystals; loc. 3 – Šoltysa stream). The analysis of the obtained results allows to state that the "Marmarosh diamonds" from the studied Ukrainian and Slovak localities are generally similar. The main simple forms represent the hexagonal prism m $\{10\bar{1}0\}$ and the rhombohedra r $\{10\bar{1}1\}$ and z $\{01\bar{1}1\}$. The following types of crystal habit have been identified: hexagonal-dipyramidal, pseudocubic, hexagonal-prismatic, trigonal-prismatic. For the polyhedra from the Ukrainian Carpathians, minor forms are less typical, such as the trigonal dipyramid s $\{11\bar{2}1\}$ and the trapezoid x $\{51\bar{6}1\}$. Statistically, the shape of "Marmarosh diamond" crystals from the Ukrainian Carpathians is closer to isometric. For them, elongation along the main crystallographic axis is even less typical than for polyhedra from the Slovak localities. In addition, "Marmarosh diamonds" from the W. Carpathians in Slovakia are more often flattened at $\{10\bar{1}0\}$. In the process of crystal growth with decreasing temperature, the habit changes from hexagonal-dipyramidal to trigonal-prismatic. Quartz from Krosno (Silesian) zone of Ukrainian Carpathians was found in the association with calcite. There are numerous hydrocarbon inclusions in both minerals. The mineralogical crystallographic and geochemical investigations (especially of the migrating hydrocarbon fluids), are important for oil and gas geology of the Carpathian oil and gas-bearing province.

Key words: quartz crystal morphology, hydrocarbon inclusions, "Marmarosh diamonds", Carpathians

Graphical abstract



Highlights

- Quartz crystals of "Marmarosh diamonds" type from Paleogene sequences of W. and E. Carpathians in Slovak and Ukrainian territories were studied goniometrically. Obtained results indicate their general similarity.
- Numerous hydrocarbon inclusions in these crystals indicate the importance of crystallographic and geochemical investigations for oil and gas geology of the Carpathians.

Introduction

Quartz crystals of "Marmarosh diamonds" type can be found in many regions of the world (Alps, Carpathians, Crimea, Donbas, Caucasus, etc.). They were first discovered within the Marmarosh massif of the Eastern Carpathians. The perfection of the morphology of the "Marmarosh diamonds", for which they got their name, has attracted the attention of researchers since the first mention of their findings (Fichtel, 1791; Zipser, 1817; Tokarski, 1905; etc.). The first crystal morphological description of this quartz was made by Leidolt in 1885. Later it was supplemented by research by Arkhipova (1951, 1961), Lazarenko et al. (1963) and Vozniak et al. (1974).

"Marmarosh diamonds" are widespread in carbonate-quartz veins in flysch deposits of the Carpathian

thrust-fault structure of the ages from the Cretaceous to Paleogene and Neogene (Kolodii, 2004). In Slovakia "Marmaros diamonds" occur in the vicinity of Uličˇ, Veľký Lipník, and Starina localities. The best known occurrences in the Ukrainian Carpathians are found in the surroundings of Kobylets'ka Polyana, Pidpolozzya, Nyzhni Vorota, Mizhgirya, Volovets' and Byckiv (Udubasa et al., 2002). These are transparent colorless quartz crystals with a typical glass luster. The size of the crystals along the main crystallographic axis is usually from the first millimeters to 1.0 cm, occasionally up to 3.0 cm. Quartz fills fractured zones in sedimentary rocks, being in paragenesis with calcite and close association with bitumen of different composition. Goniometric studies have shown that the main habitual forms of such quartz are the hexagonal prism $\{10\bar{1}0\}$, rhombohedra $\{10\bar{1}1\}$, $\{01\bar{1}1\}$, less often usually poorly developed trigonal dipyramid $\{11\bar{2}1\}$.

The first complete crystal morphological description of "Marmarosh diamonds" from the Ukrainian Carpathians was done by Matkovskiy (1961). As a result of goniometric studies of many crystals, the scientist identified two main types of habitus:

- columnar-prismatic with predominant development of prism faces (characteristic of "Marmarosh diamonds" from Eocene deposits of the Pidpolozzia village area);
- dipyramidal with predominant development of rhombohedral faces (characteristic of "Marmarosh diamonds" from flysch deposits of the Chivchyn Mountains area).

Vozniak et al. (1974) in the Ukrainian Carpathians identified three types of habitus of "Marmarosh diamonds" (Fig. 1):

- prismatic with the predominant development of the faces of the prism;
- rhombohedral with predominant development of rhombohedral faces;
- pseudocubic with a sharp predominance of positive rhombohedron faces and without or with weak prism face development.

Zatsikha et al. (1984) in the Ukrainian Carpathians identified dipyramidal and dipyramidal-prismatic types of habitus of "Marmarosh diamonds".

Kvasnytsia (2016) described rare form – rhombohedron $\{01\bar{1}2\}$, being established for the first time not only for the "Marmarosh diamonds" but also for quartz crystals from various hydrothermal mineralizations of Ukraine.

Typical representatives of "Marmarosh diamonds" are crystals of rhombohedral and pseudocubic habit. Information on the shape, habit and morphology of all these species are summarized in Matkovskyi (2011).

In addition to the habit of crystals, an important typomorphic feature of "Marmarosh diamonds" is the presence of different hydrocarbon inclusions. They are indicators of the sequence of growth of individuals, changes in the chemical composition of the mineral-forming fluid (from high-density hydrocarbon-water in the initial stages to oil-water, and sometimes with significant impurities of carbon dioxide in the final). Accordingly, this testifies to the important role of "Marmarosh diamonds" in the reproduction of hydrocarbon migration processes during the formation of industrial accumulations of oil and gas condensates in oil and gas provinces. Therefore, "Marmarosh diamonds", as a new genetic type of quartz – skeletal crystals with hydrocarbon inclusions (Vozniak et al., 1978), are of fundamental importance as fixers of chemical composition and PT parameters of migration processes of hydrocarbon compounds and direct connection with oil and gas, as well as the evidence of a detailed PT history of the Folded Carpathians (Vityk et al., 1996).

The hydrocarbon inclusions in the crystals "Marmarosh diamonds" from the Western Carpathians on Slovak territory (in further text Slovak Carpathians) are described by Hurai et al. (1995). The morphology of "Marmarosh diamonds" polyhedra from the Veľký Lipník locality is described by Fulín (1997).

In current paper we present morphology of "Mararosh diamonds" in three localities. Two of them (Krosno zone and Veľký Lipník area) were already described (Dudok et

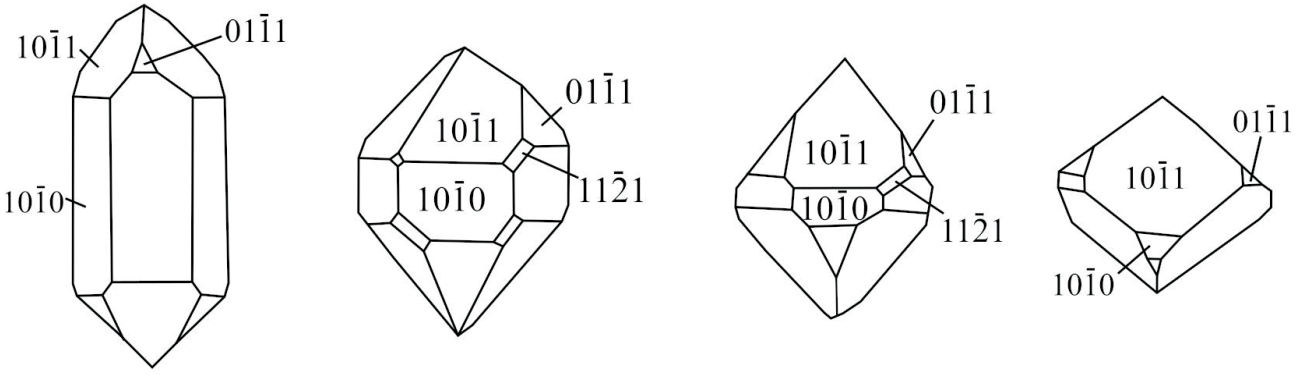


Fig. 1. Types of habit of "Marmarosh diamonds" (Vozniak et al., 1974).

al., 2002; Vovk et al., 2018; a.o.), but the New Beskydy Tunnel was only recently built, and all presented research results from there are new and less known to the scientific community. Obviously, the comparison of new results with data obtained earlier allows to present wide spectra of "Marmarosh diamonds" morphology and their genesis from different localities. Therefore, the main focus is on the new studied locality of the Krosno (Silesian) structural-facial unit of the Ukrainian Carpathians in the area of the New Beskydy Tunnel. We will consider only the peculiarities of the crystal morphology and genesis of "Marmarosh diamonds" from the Ukrainian Carpathians and compare them with individuals from the Slovak Carpathians, which are described mainly in (Dudok et al., 2002).

Methodology

As it was mentioned above, the investigated crystals were selected in three localities. The first of them is located in the Krosno (Silesian) zone of the Ukrainian Carpathians, in the area of the New Beskydy Tunnel. Field geological studies were carried out during the construction of the tunnel, if possible, directly with the geological service of the tunnel. They included the selection and description of stuffs, macroscopic analysis of structural and textural features of the veinlet-impregnated mineralization and host rocks.

Altogether 137 crystals of "Marmarosh diamonds" were selected for goniometric research from the veinlet-impregnated mineralization in the flysch deposits of the Krosno (Silesian) structural-facial unit of the Ukrainian Carpathians in the area of the New Beskydy Tunnel (Figs. 2 and 3). Samples were taken from observation points along the tunnel recorded at a distance of 1 247.6 m, 1 435 m, 1 445 m, 1 464 m, 1 505 m, 1 508 m, 1 522 m, 1 544 m and 1 612 m.

General mineralogical approaches were used to provide mineralogical studies. Determination of the composition of volatiles, relative gas saturation as well as water saturation of fluid inclusions was performed by the mass spectrometry on the MX-3A mass spectrometer (IGGC of the National Academy of Sciences of Ukraine, analyst B. Sakhno). A mineral (rock) sample weighing 200 mg of the +1–2 fraction was crushed in a specially designed mortar; before analysis, the inlet system of the mass spectrometer was vacuumed to values of the order of 1.10^{-3} Pa. Relative gas saturation ΔP, Pa – pressure increase in the inlet system of the mass spectrometer (relative to the residual pressure of the order of 1.10^{-3} Pa in it), which is created as a result of the release of volatile components (without taking into account the water vapor sorbed on P_2O_5, placed in the inlet system) from inclusions and closed pores when grinding the sample. It can represent a comparative value for the same weights. The chemical composition of minerals of the veinlet-impregnated mineralization was determined using

Fig. 2. The map with position of sampling localities: 1 – veins in the flysch deposits of the Krosno (Silesian) structural-facial unit of the Ukrainian Carpathians in the area of the New Beskydy Tunnel; 2 – Oligocene deposits of the Dukla zone (observation point 1 502, Pryslip pass); 3 – the Inner-Carpathian Paleogene (observation point 1 527, Veľký Lipník area, Šoltysa stream).

scanning electron microscopy and X-ray microanalysis based on the PEMMA-102-02 raster electron microscope – microanalyser (analyst R. Serkis).

The crystals were measured on a two-circle goniometer GD-1 (analyst O. Vovk). Gnomostereographic projections were built on the basis of research materials, based on which the axonometric projections of polyhedra were drawn. All axonometric projections of quartz crystals constructed using the Shape program (demo version) are made at the position of the projection pole φ = 71.5° and ρ = 80°.

The second locality represents the Oligocene deposits of the Dukla zone (observation point 1 502, Pryslip pass; Figs. 2 and 3). Altogether 77 quartz crystals of the "Marmarosh diamond" type were selected from cracking zones in the relevant rocks, represented by sandstones and siltstones. At the observation point 1 502 the azimuth of the dip of the host rocks is 140°, the angle of dip is 70–80° (140/70–80°); concerning cracks – the dip azimuth is 190–200°, angle of dip 70–80° (190–200/70–80°). At observation point 1 527 in the host rocks it is 150/30°; 125/80–90° and 185/80–90°. The thickness of the cracks varies from the first millimeters to 3.0 cm.

The third locality occurs in the Inner Carpathian Paleogene in Slovakia (observation point 1 527, Veľký Lipník area, Šoltysa stream; Figs. 2 and 3). Altogether 175 quartz crystals of the "Marmarosh diamond" type were goniometrically studied. According to Fulín (1997) "Marmarosh diamonds": are found in the grey-blue sandstones, in weathered samples having yellowish brown colour. Sandstones are characterized by the presence of NW-SE trending cracks with a dip of 70–90° to SE. The "Marmarosh diamonds" from the W. Carpathians are typical with all types of hydrocarbon inclusions described for similar quartz from the Ukrainian and Polish Carpathians (Dudok, 2000; Kalyuzhnyi et al., 1998).

Fig. 3. Tectonic map (Birkenmajer & Gedl, 2017) with position of sampling points: 1 – veins in the flysch deposits of the Krosno (Silesian) structural-facial unit of the Ukrainian Carpathians in the area of the New Beskydy Tunnel; 2 – Oligocene deposits of the Dukla zone (observation point 1 502, Pryslip pass); 3 – the Inner-Carpathian Paleogene (observation point 1 527, Veľký Lipník area, Šoltysa stream).

Results and discussion

Crystal morphology and habits

Polyhedra of "Marmarosh diamonds" from both – the Ukrainian and Slovak parts of Carpathians are two-headed, their size is up to 1 cm, rarely up to 3 cm along the main crystallographic axis L_3. The faces of the hexagonal prism m $\{10\bar{1}0\}$ and the rhombohedra r $\{10\bar{1}1\}$ and z $\{01\bar{1}1\}$ are present on all crystals. The development of these faces determines the crystals habit. In addition, a trigonal dipyramid s $\{11\bar{2}1\}$ was found on about a third of individuals from the Dukla zone and on 13 % of crystals from the Inner Carpathian Paleogene. This form was not detected on the studied polyhedra from the Ukrainian Carpathians. Acute rhombohedra are rare. All these forms are described in the special literature, in particular in Goldschmidt (1922).

The habitus of the crystals is isometric or short-column, rarely columnar. There are several types of individuals by habit (see Tab. 1).

Hexagonal-dipyramidal habit with approximately equal development of the faces of rhombohedra r $\{10\bar{1}1\}$ and z $\{01\bar{1}1\}$ and underdeveloped faces or without faces of the prism m $\{10\bar{1}0\}$ (Fig. 11.1). Crystals of this habit are quite common in the Slovak part of Carpathians, almost half of them have dipyramids. In the Ukrainian Carpathians, in particular in the flysch deposits of the Krosno (Silesian) structural-facial zone, this type is also manifested (Vovk et al., 2018, 2019), but less frequently.

Pseudocubic (Fig. 11.2) crystals are characterized by well-developed faces of one of the rhombohedra (positive or negative) and small faces of the prism and the other rhombohedron. Such individuals are rare in both the Ukrainian and Slovak Carpathians. Crystals of transitional habit between hexagonal-dipyramidal and pseudocubic are more typical for the Slovak Carpathians (Fig. 11.3). Dipyramide was found in only 5 % of the total number of crystals.

Hexagonal-prismatic. This type is divided into two subtypes:

I. – Short-prismatic. Crystals of this subtype are characterized by uniform development of three main forms: hexagonal prism, positive and negative rhombohedrons (Fig. 11.4). Such individuals in the Slovak Carpathians make up 18 % of the total number of crystals. Dipyramide was found in a third of them (Fig. 11.5). Such polyhedra are even more typical of the Krosno (Silesian) structural-facial zone. Their frequency is 30 %.

II. – Actually prismatic (Fig. 11.6). The main form is a prism, rhombohedra are evenly developed, but are of secondary importance. Such individuals are very rare for both the Ukrainian and Slovak Carpathians, no dipyramid has been found in them.

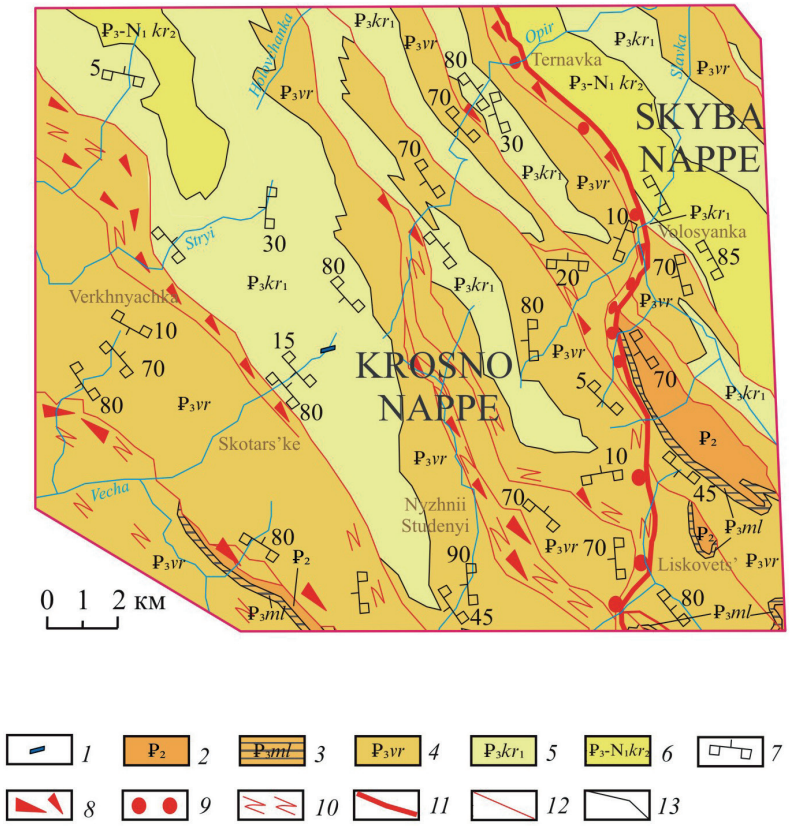


Fig. 4. Geological map of the eastern part of the Krosno Nappe and the adjacent segment of the Skyba Nappe in the basins of the upper reaches of the Stryi, Opir, Vecha, Rika rivers: 1 – Research area; 2 – Eocene flysch; 3 – Menilite Fm.; 4 – Verets (Transitional) Fm.; 5 – Lower Krosno Fm. (sandstones); 6 – Middle Krosno Fm. (bedded flysh); 7 – strike, dip angle and position of the bed bottom; 8 – tectonic breccia; 9 – tectonic mélange; 10 – intensively folded deposits; 11 – tectonic boundary between the Krosno and Skyba nappes; 12 – secondary faults; 13 – geological boundaries.

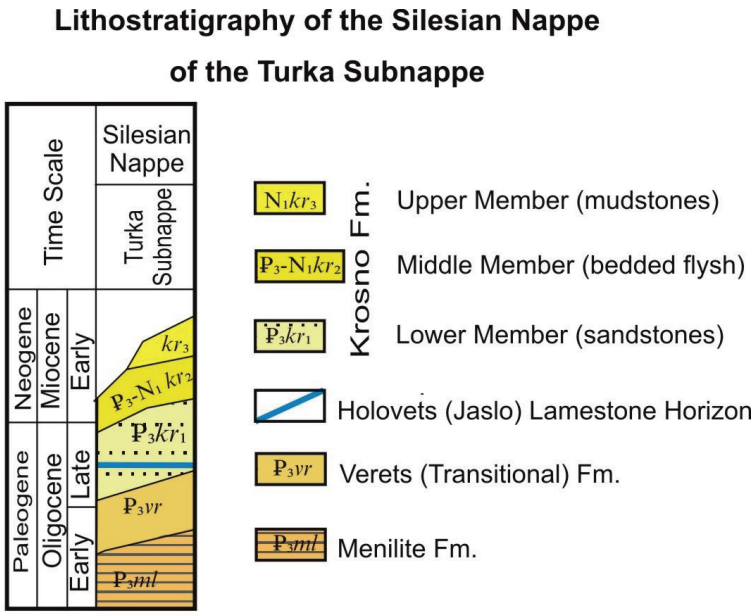


Fig. 5. Lithostratigraphic column of the flysch zone with depicted Krosno (Silesian) zone (Hnylko et al., 2021). The samples of quartz crystals were taken from Lower Member P_3kr_1.

Fig. 6. The New Beskydy Tunnel.

Fig. 7. The outcrop with crystals of "Marmarosh diamonds" in the area of the New Beskydy Tunnel.

Trigonal-prismatic is also divided into two subtypes:

I. – Short-prismatic. The prism and one of the rhombohedra are well developed, the other rhombohedron is of secondary importance (Fig. 11.7). Such crystals are rare in Slovak Carpathians, dipyramid was found in one of them. Such polyhedra are very typical for the Krosno (Silesian) structural-facial zone of the Ukrainian Carpathians, their frequency is 54 %;

II. – Actually prismatic. The hexagonal prism dominates the rhombohedra of different sizes (Fig. 11.8). Individuals of this type represent 2 % (Inner Carpathian Paleogene) and 9 % (Dukla zone) of the total number of crystals. Dipyramid was found on two of them. In the Krosno (Silesian) zone of the Ukrainian Carpathians, the frequency of such polyhedra is slightly higher – 9 %.

According to the analysis of statistical data it can be concluded that in the process of growth (i.e. with decreasing temperature), the habit of crystals changes from hexagonal-dipyramidal to trigonal-prismatic. The presence of dipyramid is typical for individuals of hexagonal-dipyramidal and hexagonal-prismatic (short-prismatic) habit from the Slovak Carpathians.

In addition to the crystals described above, which are close to ideal, the distorted individuals are quite common. The macroscopic symmetry of real crystals may differ from the true one both in the direction of decrease and in the direction of increase. The greatest symmetry is in individuals of hexagonal-dipyramidal and hexagonal-prismatic habit. The appearance of the sixth-order pseudoaxis is due to the equal development of positive and negative rhombohedra, and the pseudoplanes arose in the absence of the faces of the dipyramid s $\{11\bar{2}1\}$ and the trapezoid x $\{51\bar{6}1\}$. Such highly symmetric crystals are formed under conditions of chaotic rotation of the crystal in a medium with maximum symmetry ∞L∞∞PC (symmetry of a sphere) or L∞∞PPS (symmetry of a stationary cylinder), provided that the axis of infinite order of the medium coincides with the axis of third order quartz. The flow of matter to all faces of the crystal is uniform. In nature, under such conditions, crystals grow that rotate continuously in the melt or in solution. Therefore, dipyramidal crystals are charac-

teristic with paramorphoses of trigonal quartz on hexagonal quartz in quartz porphyries and for late hydrothemal quartz of ore and quartz-carbonate veins. Crystals of prismatic habit grew under conditions of more intense influx of matter to the faces of the prism. Such conditions can occur if the crystal is attached to the head of the rock. Individuals grow under the condition of a homogeneous liquid slick with the symmetry of a circle, in the case of identical sides of the slick - with the symmetry of the cylinder. The second head of such crystals is often regenerated due to the fact that the crystal broke off from the attachment.

There are several degrees of elongation of the crystals in the ratio of sizes along the L_3 axis to the L_2 axis: short-prismatic (elongation 2.5); long-prismatic (~ 4); needle (> 6); very shortened (< 1.5). The studied crystals from the Slovak Carpathians are strongly shortened or short-prismatic. Long-prismatic individuals are extremely rare, and no needles are present. Polyhedra from the Ukrainian Carpathians are strongly shortened (over 90 %), or short prismatic (up to 10 %), long prismatic and needle-shaped among the studied individuals are not detected (Fig. 9).

Crystals with reduced visible symmetry were also found: flattened prisms and rhombohedra (with visible L_2 symmetry), wedge-shaped and pseudotriclinic.

Crystal morphological studies of quartz also determined the flattening size of crystals n, i.e. the ratio of

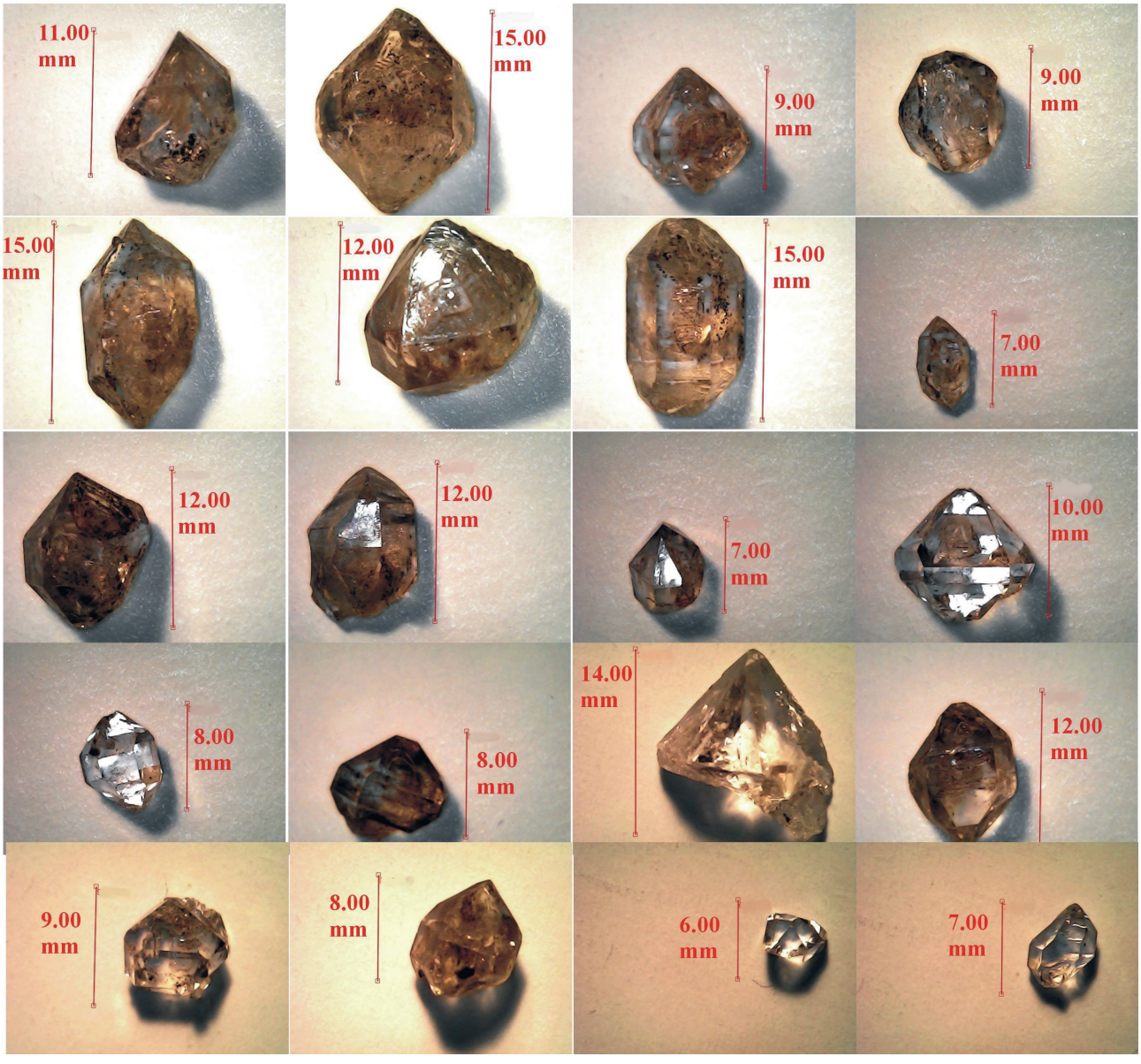


Fig. 8. The crystals of "Marmarosh diamonds" from the Krosno (Silesian) structural unit of Ukrainian Carpathians (the area of the New Beskydy Tunnel).

crystal sizes in L_3 to the distance between opposite faces $\{10\bar{1}0\}$ perpendicular to the flattening direction. In our case, the value of n ranges from 1 : 1 to 1 : 3 for individuals from the Slovak Carpathians and up to 1 : 2 for polyhedra from the Ukrainian Carpathians. Individuals are flattened on the faces $\{10\bar{1}0\}$ or $\{01\bar{1}0\}$. The macrosymmetry of such crystals is pseudorhombic, individuals were attached to the prism face to the rock wall, which caused a more intense influx of matter to the two opposite faces of the prism. Crystals flattened on a rhombohedron grew in the conditions of a bilateral slick with symmetry of the cylinder. The axis of infinite order of the medium coincided with L_2 in the crystal, so the symmetry of individuals is monoclinic. Wedge-shaped crystals with symmetry P grew under conditions close to those in which pseudorhombic individuals flattened by $\{10\bar{1}0\}$ grew. They were also attached to the face $\{10\bar{1}0\}$ to the rock wall, but the symmetry of the medium was less. Mineral-forming fluids moved along the crystal in the direction from the more developed crystal top to the less developed one. Due to the unilateral direction of flows on individuals of all elements of symmetry, only the pseudoplane is preserved. Wedge-shaped crystals are very valuable genetically, because they contain information about the directions of migration of mineral-forming fluids.

Pseudotriclinic crystals indicate that the symmetry of the medium was not maximal, and the elements of symmetry of the crystal did not coincide with the elements of symmetry of the medium. That is, individuals grew obliquely in relation to the directions of migration of mineral-forming fluids.

As a result, the analysis of literature data (Vozniak et al., 1974; Lazarenko et al., 1963; Matkovskiy, 1961) and own goniometric studies of crystal morphology of "Marmarosh diamonds" from the deposits of the Ukrainian (Krosno, now Silesian and Dukla zones) and Slovak Carpathians (Dukla zone and Intra-Carpathian Paleogene zone) allowed to state that in general that the "Marmarosh diamonds" from the Slovak and Ukrainian Carpathians are similar. However, in (Dudok et al., 2002) it is said that the described individuals from the Slovak Carpathians are less characterized by polyhedra of prismatic habit. Our studies of "Marmarosh diamonds" and the Krosno (Silesian) zone of the Ukrainian Carpathians show that prismatic individuals are even rarer than in the Slovak Carpathians.

Anyway, there is the conclusion about the evolution of habit from hexagonal-dipyramidal to trigonal-prismatic by decreasing of the temperature during growth (Vovk et al., 2019).

Inclusions in quartz in "Marmarosh diamonds" from the Krosno zone

The polyhedra of rhombohedral and pseudocubic habit with a strong lustre of the "Marmarosh diamond" type were formed in a hydrocarbon-saturated (oil-saturated) fluid medium in a calm tectonic situation, when the tectonic overprint had already ended, creating a system of fractured

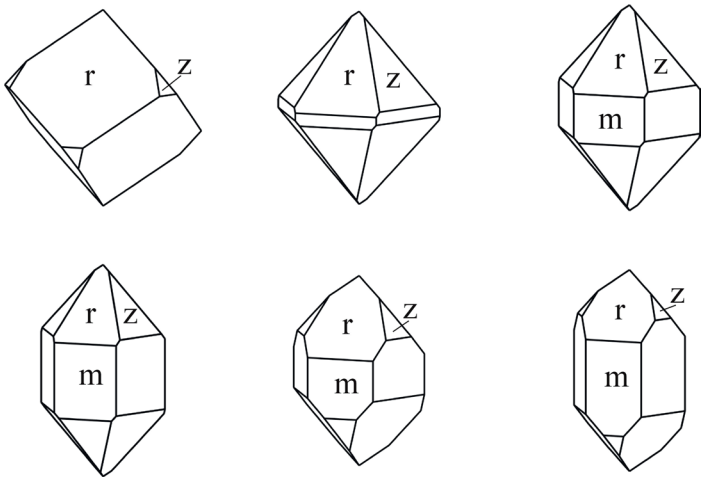


Fig. 9. Crystal types of "Marmarosh diamonds" from the Krosno (Silesian) structural unit of Ukrainian Carpathians (Vovk et al., 2018). Simple forms m $\{10\bar{1}0\}$, r $\{10\bar{1}1\}$ and z $\{01\bar{1}1\}$.

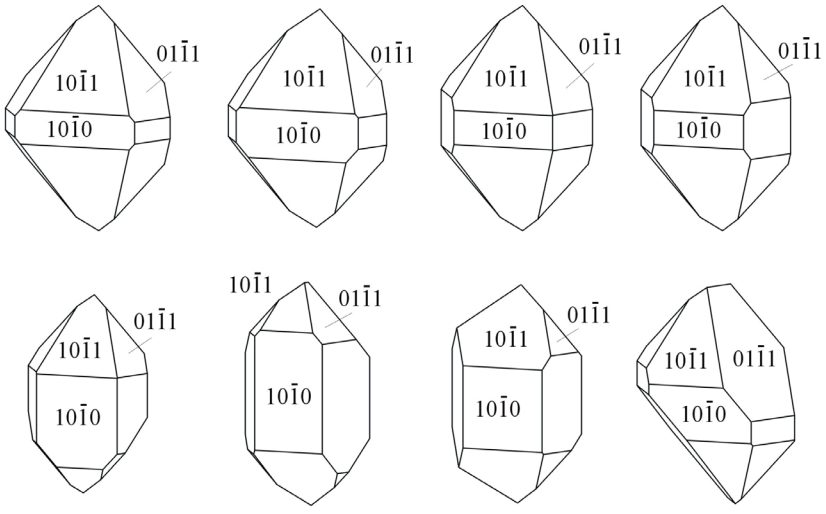


Fig. 10. Crystal habit of "Marmarosh diamonds" from the Krosno (Silesian) structural unit of Ukrainian Carpathians (the area of the New Beskydy Tunnel).

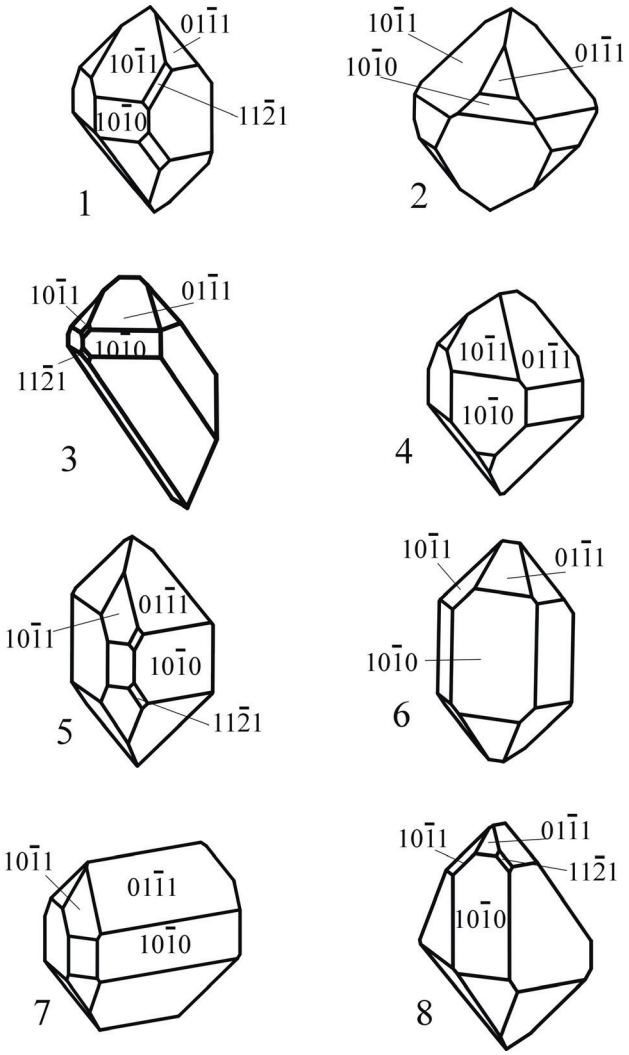


Fig. 11. Crystal habit of "Marmarosh diamonds" from Slovak Carpathians (Dudok et al., 2002).

zones. The healing of the formed cracks contributed to the crystallization of perfect crystals of typical rhombohedral and pseudocubic habit, which by their defects-inclusions in the process of growth-synthesis captured and preserved hydrocarbons of various aggregate and phase states (Naumko et al., 2004, 2014, 2017).

Quartz of the "Marmarosh diamond" type in the Krosno (Silesian) zone is associated with calcite. Calcite forms mottled veins (up to 55 mm) of various shapes, the thickness of which varies from microscopic to 2–3 cm and more. Veins with partially or completely leached calcite and traces of sliding are often observed. It is represented by crystalline-granular varieties, mainly fine-grained (0.1 mm) and coarse-grained (over 0.1 mm). Large-crystalline varieties predominate. Large calcite grains reach 4–6 mm. Dense aggregates, druses, and sometimes well-cut crystals are often found (Zankovych, 2016). The chemical composition of calcite of the veinlet-impregnated mineralization of the rock complexes in the area of the New Beskydy Tunnel, is close to the theoretical one. Contains significant impurities of magnesium (0.00–0.37 wt. %), manganese (0.02–0.52 wt. %) and iron (0.06–0.87 wt. %).

Impurities in the chemical composition of quartz were not detected, because their content are near the detection limit. Numerous fluid inclusions of hydrocarbons were found in the investigated crystals of "Marmarosh diamonds" and calcite from the Krosno (Silesian) zone in the area of the New Beskydy tunnel (Naumko et al., 2017). According to mass spectrometry, the composition and ratio of volatiles in them is characterized only by the presence of hydrocarbons, mainly methane and the firsts members of its homologous series (see Tab. 2). In particular, all analysed samples are strongly dominated by methane (87.6–97.3 vol. %). In addition, in quartz crystal (sample NBT-1) there is homologous series of methane to propane (up to 2.9 vol. %), in another quartz crystal (sample NBT-7) – to butane with traces of heavier hydrocarbons, probably of the methane series (12.4 vol. %). It should be emphasized the high weight concentration of hydrocarbon components in the fluid (up to $392.236.10^{-6}$ g per g of the sample), which determines the possibility of its transfer of mineral substances (and hydrocarbons) and crystallization of parageneses with "Marmarosh diamonds" from such a hydrocarbon-containing fluid. The given data indicate the hydrocarbon orientation of upward migrating paleofluids (Naumko et al., 2022).

Conclusions

Common and distinctive features of the morphology of quartz crystals of the "Marmarosh diamonds" type from the Slovak and Ukrainian Carpathians have been revealed.

Common in the "Marmarosh diamonds" from the Slovak and Ukrainian Carpathians are:

1. Presence of basic simple forms of hexagonal prism m $\{10\bar{1}0\}$ and rhombohedra r $\{10\bar{1}1\}$ and z $\{01\bar{1}1\}$.
2. Types of crystal habitus: hexagonal-dipyramidal, pseudocubic, hexagonal-prismatic, trigonal-prismatic.
3. Elongation of the crystals in the ratio of the dimensions along the L_3 axis to the L_2 axis is preferably < 1.5.

The differences in the polyhedra of "Marmarosh diamonds" from the Ukrainian and Slovak Carpathians are as follows:

1. On polyhedra from the Slovak Carpathians, less important simple forms are more common: the trigonal dipyramid s $\{11\bar{2}1\}$ and the trapezoid x $\{51\bar{6}1\}$.
2. In the Krosno (Silesian) zone of the Ukrainian Carpathians, greatly shortened individuals appear even more often.
3. Crystals flattened on $\{10\bar{1}0\}$ are more characteristic of the Slovak Carpathians.

Fluid inclusions of hydrocarbons are present in all

Tab. 1

Habit of "Marmarosh crystals" from Ukrainian Carpathians and Western Carpathians.

Habit	**The area of the New Beskydy tunnel crystals %**	**Dukla zone**	Intra-Carpathian Paleogene
Hexagonal-dipyramidal	7	35	31
Pseudocubic	1	24	23
Hexagonal-prismatic (short-prismatic)	30	18	18
Hexagonal-prismatic (actually prismatic)	1	7	3
Trigonal-prismatic (short-prismatic)	52	7	23
Trigonal-prismatic (actually prismatic)	9	9	2

Tab. 2

The composition of volatiles of fluid inclusions in "Marmarosh diamonds" and calcite of the veinlet-impregnated mineralization and closed pores of host rocks of the Krosno (Silesian) zone in the area of the New Beskydy tunnel) (Naumko et al., 2022).

Number of the sample	**Interval of selection [m]**	**Mineral (sample mass)**	**Components: volume share, % weight concentrations, n.10^{-6} g/g of the sample[2)]**			**Relative gas saturation Δ P, Pa**	**Total weight concentration, n.10^{-6} g/g of the sample[1)]**
			CO_2	CH_4	C_nH_{2n+2}		
NBT-1	1 247.6	"Marmarosh diamond" crystal (0.16 g)	–	97.3 / 248.430	2.7[3)] / 0.370	36.0	248.800/311.000[2)]
NBT-2	1 435	The same (0.19 g)	–	97.1 / 61.530	2.9[3)] / 0.140	10.8	61.670/64.916[2)]
NBT-3	1 445	The same (0.32 g)	–	97.1 / 113.560	2,9[3)] / 0.250	33.3	113.81/71.130[2)]
NBT-4	–	Calcite crystal (0.43 g)	–	99.0 / 8.420	1.0[3)] / 0.002	3.2	8.422/3.817[2)]
NBT-7	1 464	"Marmarosh diamond" crystal (0.16 g)	–	87.6 / 204.100	12.4[3)] / 11.630	25.3	215.730/392.236[2)]

Notes:

1) – the total weight concentration in samples NBT-1–NBT-4 and NBT-1–NBT-7 was determined relative to the mass of the crystal;
2) – the total weight concentration is reduced to the standard amount of weight – 200 mg;
3) – in samples NBT-1–NBT-4 in the composition $C_nH_{2n+2\,n}$ = 2, 3, in sample NBT-7 – n = 2–4 (up to 6).

calcite and quartz crystals of the "Marmarosh diamonds" type. By the chemical composition data, it is methane with impurities of higher hydrocarbons (up to hexane). The high weight concentration of hydrocarbon components in the fluid determines the possibility of its transfer of mineral substances (and hydrocarbons) and crystallization of parageneses with "Marmarosh diamonds" from such a hydrocarbon-containing fluid.

Detailed studies of the vein mineralization of the rock complexes of the Krosno (Silesian) zone of the Ukrainian Carpathians, exposed by the New Beskydy tunnel, make it possible to obtain important genetic information about the composition and distribution of hydrocarbons in fluid inclusions in non-ore minerals of the veinlet-impregnated mineralization as relics of migrating hydrocarbon fluids within the flysch formation of the region. Therefore, further mineralogical research will contribute not only to obtaining new results from mineralogy, geochemistry and crystallography, but also important data from the oil and gas geology of the Carpathian oil and gas-bearing province.

Acknowledgement:

Authors express their thanks for two anonymous reviewers for valuable comments and suggestions improving the text.

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Porovnanie morfológie kryštálov kremeňa – „marmarošských diamantov" – zo sekvencií paleogénneho flyšu krosnianskej (sliezskej) a duklianskej zóny v Karpatoch na Ukrajine a vnútrokarpatských paleogénnych sekvencií Západných Karpát

Na komparatívny goniometrický výskum kryštálov kremeňa, tzv. marmarošských diamantov, boli použité vzorky z reprezentatívnych výskytov vo Východných Karpatoch na území Ukrajiny – kryštálov v žilách vo flyšových sedimentoch krosnianskej (sliezskej) jednotky (137 kryštálov; lokalita 1 – nový Beskydský tunel; obr. 2 – 7) a tiež v oligocénnych sedimentoch duklianskej zóny (77 kryštálov, lokalita 2 – priesmyk Pryslip; obr. 2 a 3). „Marmarošské diamanty" v Západných Karpatoch na území Slovenska zastupovali výskyty vo vnútrokarpatských paleogénnych sekvenciách na lokalite 3 – Veľký Lipník, vodný tok Šoltysa (175 kryštálov; obr. 2 a 3).

Získané výsledky potvrdzujú, že „marmarošské diamanty" zo študovaných lokalít oboch štátov vykazujú podobné charakteristiky. Dominantne sú zastúpené jednoduché kryštály hexagonálneho prizmatického tvaru *m* $\{10\bar{1}0\}$ a tiež romboédre *r* $\{10\bar{1}1\}$ a *z* $\{01\bar{1}1\}$. Identifikované boli aj nasledujúce polyhedrálne kryštálové tvary: hexagonálno-dipyramidálny, pseudokubický, hexagonálno-prizmatický a trigonálno-prizmatický. Predĺženie kryštálov vyjadruje pomer rozmerov pozdĺž osi L_3 k osi L_2, ktorý vykazuje hlavne hodnoty < 1,5.

V prípade výskytov v Ukrajinských Karpatoch sú trigonálno-dipyramidálny tvar *s* $\{11\bar{2}1\}$ a trapezoidný tvar *x* $\{51\bar{6}1\}$ menej typické. Štatisticky sa kryštálový tvar „marmarošských diamantov" z Ukrajinských Karpát prejavuje ako viac izometrický. Ich predĺženie pozdĺž hlavných kryštalografických osí je menej typické ako v prípade polyhedrálnych tvarov zo slovenských lokalít. Navyše, „marmarošské diamanty" zo slovenského územia Západných Karpát sú častejšie sploštěného tvaru *v* $\{10\bar{1}0\}$. V procese rastu kryštálu sa pri poklesávajúcej teplote tvar mení z hexagonálno-dipyramidálneho na trigonálno-prizmatický.

Kremeň z krosnianskej (sliezskej) zóny Ukrajinských Karpát sa zistil v asociácii s kalcitom. V oboch mineráloch sa vyskytujú početné inklúzie.

Vo všetkých kryštáloch kalcitu a kremeňa „marmarošských diamantov" sú prítomné inklúzie uhľovodíkov. Podľa údajov o chemickom zložení ide o metán s nečistotami vyšších uhľovodíkov (až po hexán). Vysoká hmotnostná koncentrácia uhľovodíkových zložiek vo fluide určuje možnosť prenosu minerálnych látok (a uhľovodíkov) a kryštalizáciu paragenéz s „marmarošskými diamantmi" z tzv. fluíd obsahujúcich uhľovodíky. Podrobné štúdie žilnej mineralizácie horninových komplexov krosnianskej (sliezskej) zóny Ukrajinských Karpát odkrytých novým Beskydským tunelom umožňujú získať dôležité genetické informácie o zložení a distribúcii uhľovodíkov v kvapaline inklúzie v nerudných mineráloch žily, ktorá reprezentuje relikty migrujúcich uhľovodíkových tekutín v rámci flyšovej formácie regiónu. Ďalší mineralogický výskum prispeje nielen k získavaniu nových výsledkov z mineralógie, geochémie a kryštalografie, ale aj dôležité údaje z karpatského ložiska ropy a plynu.

Mineralogicko-kryštalografický a geochemický výskum (so zameraním na migráciu hydrokarbonátových fluíd) poskytuje podstatné informácie pri vyhľadávaní a prieskume výskytov ropy a zemného plynu v karpatskej roponosnej a plynonosnej provincii.

Doručené / Received: 27. 6. 2022
Prijaté na publikovanie / Accepted: 15. 12. 2022