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THE MINERAL-FORMING ENVIRONMENT OF "MARMAROS DIAMONDS"

Abstract. Microscopic, thermo- and barometric studies of fluid inclusions demonstrated a relatively complex nature of the mineral-forming environment of the "Marmaros diamonds". Infrared spectroscopic investigations of the chloroform extract from inclusions revealed that the principal components of mineral-forming fluids were aliphatic hydrocarbons, with other hydrocarbons present in minor amounts. Gas analysis on a mass spectrometer showed that the main gaseous component of the fluid was methane and sometimes hydrogen. The "Marmaros diamonds" crystallized from a polyphase, heterogeneous environment. During crystallization both the pressure and composition of the fluid was subject to pronounced changes. The occurrences of the "Marmaros diamonds" are evidence of migration of liquid and gaseous hydrocarbons in the Carpathian Flysch rocks under dynamic conditions.

INTRODUCTION

The "Marmaros diamonds", also referred to as *dragomites*, are fine, euhedral, generally transparent and colourless quartz crystals reported from many localities in the Flysch Carpathians. Their classical occurrence is known from Marmaros.

In the Polish Carpathians they are fairly abundant, occurring in the area between the Silesian Beskid Mts and the Bieszczady Mts, and in the Flysch of Podhale. They have been mentioned by several Polish authors but have never been the object of extensive studies. A comprehensive morphological study of the "Marmaros diamonds", together with some suggestions concerning their authigenic character, was presented by Tokarski (1905) and Łaskiewicz (1960). They were also discussed to a limited extent by Mastella and Koisar (1975), who associated their origin with bituminization phenomena in the Podhale region. Abundant data on the morphology of crystals, the nature of mineral-forming solutions, and the gas phase composition of inclusions in the "Marmaros diamonds" were provided by Ukrainian investigators (Woźniak *et al.* 1974). Thermometric and cryometric studies (Kozłowski 1982) revealed the presence of liquid methane and probably liquid nitrogen in the inclusions.

This paper is an attempt to explain the genesis of the "Marmaros diamonds" through the determination of variability of conditions and the nature of the mineral-forming fluid.

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EXPERIMENTAL

Inclusions in quartz crystals were subjected to microscopic and fluorescence studies, using a Biolar FL microscope. Thermometric investigations were carried out in a thermal chamber designed by the authors. Pressures in the inclusions at room temperature (19°C) were determined by means of a crushing stage of Roedder's design, and gases were liberated in the medium of castor oil.

After crushing, chloroform extract was made from quartzes containing substantial amounts of organic matter (asphaltite, semi-fluid and liquid hydrocarbons). The concentrated extract was transferred in the form of film onto an NaCl plate, and its infrared spectra were recorded with a Carl Zeiss IR-75 spectrometer between 4000 and 400 cm^{-1} . The instrument settings used were: time constant 30 sec., slit 2, amplification 6, recording time 11 min.

Table 1

Composition of gases contained in the inclusions of "Marmaros diamonds" (vol. — %, H_2O being not taken into account)

Locality	Konina*		Pod Karczmą*		Pasternik Stream			Łapsze Niżne		
	temp. °C	70	150	100	700	100	200	500	150	600
comp.										
CH_4	100	100	83.69	10.96	73.16	85.04	36.21	37.76	21.50	
C_2H_6	—	—	7.66	2.93	5.47	5.46	5.12	2.08	7.52	
C_3H_8	—	—	—	1.27	—	—	2.17	—	1.95	
C_4H_{10}	—	—	5.44	0.88	3.78	6.89	2.47	—	3.91	
C_3H_6	—	—	—	—	—	—	1.95	—	6.11	
CO_2	—	—	3.31	83.95	2.34	2.61	16.77	3.20	32.93	
H_2	—	—	—	—	—	—	32.71	56.96	26.08	
N_2	no	no	no	no	14.34	—	1.70	no	no	
Ar	no	no	no	no	0.91	—	0.90	no	no	

* Samples clearly contain water, no — not determined.

The analysis of gases contained in fluid inclusions was carried out on an MI 1201 mass spectrometer (USSR) with a resolution of $\Delta \frac{m}{m} = 1000$ and a sensitivity with respect to argon of 10^{-4} vol. %. The gases were liberated from inclusions in a vacuum apparatus made of silica glass, using thermal method (temperature ranges in Tab. 1). This apparatus was an integral part of the proportioning system, enabling one to introduce the liberated gases directly into the source of ions of the mass spectrometer. The results were corrected for air.

OCCURRENCE

The "Marmaros diamonds" are generally found in steeply inclined joint fissures in sandstones and siltstones, less commonly in clay shales. They occur in close association with calcite and a black bituminous substance — asphaltite. The samples

studied were collected from the tectonic window of Mszana Dolna, where the Krosno Beds and older beds outcrop from under the Inoceranian Cretaceous of the Magura nappe. Quartzes commonly appear in fissures filled with calcite and asphaltite in the so-called black Cretaceous that makes up the bottom of the Inoceranian Beds. Quartz occurrences are mainly confined to stream and river valleys.

The samples to be investigated were collected along the Konina and Koninka streams (the Mszanka river basin), along the Pasternik stream (a tributary of the river Raba), and on the Raba near the village of Pod Karczmą. In all these localities, the "Marmaros diamonds" were found in the middle parts of open, as a rule, fissures that crosscut the sandstones and are filled with brownish or white calcite and unevenly distributed asphaltite concentrations.

Quartz samples were also collected from the banks of the Łapszanka stream (the Dunajec river basin) near Łapsze Niżne on Spisz, where they usually occur in asphaltite inserts in the bottom parts of sandstones, or as the filling of fissures in spherosiderites.

In fissures with the walls covered with brownish or white calcite, quartz crystals appear in the central parts and are readily separable from calcite druses. When the rock is broken, the quartz crystals often fall out together with asphaltite platelets. In larger asphaltite inserts or concentrations, quartz crystals are embedded in asphaltite, and their extraction requires the breaking of asphaltite substance. The "Marmaros diamonds" are sometimes encountered in the loosened cores of small folds, in which they also occur in association with calcite and asphaltite.

MORPHOLOGY OF CRYSTALS

The "Marmaros diamonds" are usually colourless and transparent. Partly milky crystals are relatively scarce. Occasionally completely or partly blackened grains are found, their colour being due to numerous inclusions of asphaltite. Crystals vary from 0.1 mm to sporadically 1.5 cm in size, averaging 2–3 mm.

The crystals appear in several combinations of forms: hexagonal prism ($10\bar{1}0$), rhombohedra ($10\bar{1}1$) and ($01\bar{1}1$), and exceptionally, poorly developed trigonal pyramids ($11\bar{2}1$) (Fig. 1; Phot. 1.). The crystal habit is fairly diversified, and crystals of different habit have been found to occur side by side. Crystals showing a prismatic habit with poorly developed rhombohedra are prevalent in fissures filled with calcite, while in asphaltite concentrations more common are crystals with predominant rhombohedron faces and poorly defined prism faces. Crystals with a pseudocubic habit are also found, showing well-defined faces of the positive ($10\bar{1}1$) rhombohedron and poorly developed or no faces of the negative rhombohedron and hexagonal prism.

Fairly abundant are various crystal intergrowths, in which small isometric crystals with well-defined rhombohedra faces usually grow on a larger crystal. The most common are parallel intergrowths.

Etching showed the presence of left- and right-handed quartz crystals, as well as Dauphiné twinnings (Matkowski 1961, *vide* Woźniak *et al.* 1974).

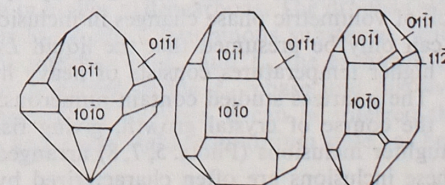


Fig. 1. The most common habits of the „Marmaros diamonds”

A typical feature of many crystals is subtle striation of the prism faces whereas the faces of rhombohedra are smooth. On very rare occasions, single flat, triangular vicinal accessories can be observed on their surface.

FLUID INCLUSIONS

Inclusions are unevenly distributed in the quartzes studied. There are quartzes containing numerous inclusions and ones altogether devoid of them. The size of inclusions varies over a wide range from μm to 0.1 mm, the maximum size being 1 mm. Primary inclusions are generally large and irregular in shape. Their occurrence is connected with the growth pyramids of rhombohedra (Phots 1—3), and they often show flattening concordant with the crystal faces. Smaller inclusions are usually shaped like negative crystals (Phot. 9; Phot. 13), and their presence is often associated with the planes of rhombohedra (Phot. 4).

The fillings of primary inclusions are varied and difficult to identify unequivocally. Common are two-phase inclusions which at room temperature contain two immiscible liquid phases (L_1+L_2 , $L_1=1-10\%$) (Phot. 6; Phots 11, 12, 13), or very similar liquid-gaseous ($G+L_1$) or gaseous-liquid (L_1+G) phases (Phots. 2,3; Phot. 10). In the (L_1+L_2) — type inclusions, the liquid phase L_1 is a hydrocarbon displaying light-blue fluorescence. Cryometric studies (Woźniak *et al.* 1974, Kozłowski 1982) have revealed that it is liquid methane, sometimes with an admixture of heavy hydrocarbons. According to Kozłowski (1982), the other liquid, L_2 , could be liquid nitrogen. During the heating of the (L_1+L_2) inclusions, the difference between the refractive indices of L_1 and L_2 decreases markedly. The rise in temperature causes the meniscus of the liquid L_2 to shift towards L_1 (Phot. 12 *a,b*), and in the case being discussed, homogenization into liquid phase (Phot. 12 *c*) takes place at 38.2°C. The inference that it actually is a liquid phase is borne out by the fluorescence of the content of the whole inclusion in the homogeneous state. During cooling, small globules of the liquid L_2 are initially separated, subsequently merging with one another to form a clearly distinct phase (Phot. 12 *d*). The homogenization temperatures of the (L_1+L_2) inclusions vary over a fairly wide range from room temperature (20°C) to about 75°C (Phot. 6), averaging 30—40°C. Some higher homogenization temperatures of inclusions of this type can be accounted for by the admixture of heavy hydrocarbons in the L_1 phase. Monophase inclusions, liquid at room temperature, from which the L_2 phase separates at 10—15°C, have also been assigned to the (L_1+L_2) type. These inclusions are readily discernible in ultraviolet light as they display dark-blue fluorescence of the same kind as the (L_1+L_2) inclusions in the homogeneous state.

The inclusions discussed above show high susceptibility to decrepitation, so that in many cases the homogeneous state cannot be reached.

Inclusions of the (L_1+G , $G+L_1$) type (Phots 2, 3; Phot. 10) contain a gaseous phase besides the liquid hydrocarbon phase L_1 . Not a single value of homogenization temperature was obtained for these inclusions as they decrepitated during heating and did not, as a rule, show any tendency to change the volume of the gas bubble. Decrepitation usually occurs at 40—60°C, exceptionally at about 200°C. The lack of volumetric phase changes in inclusions of these types is hard to explain, and it can only be presumed that the liquid L_1 present in the inclusions decrepitating at higher temperatures consists of heavy hydrocarbons.

The quartzes studied contain numerous, now liquid inclusions that decrepitated in the course of crystal growth, giving rise to a large number of submicroscopic daughter inclusions (Phots. 5, 7, 8) arranged in planes favoured by quartz cleavage. These inclusions are often characterized by the presence of unidentified, probably

organic, phases in the form of translucent yellowish or pale brown-grey globules (Phot. 7) and birefringent hairlike crystals (Phots 7, 8). The rise in temperature does not cause the globules to dissolve, and only the hairlike crystals dissolve in organic liquid. As the temperature increases, many of these inclusions decrepitate, this process being promoted by the existence of small daughter inclusions on cicatrised fissures in the closest surroundings.

Hydrocarbons present in the inclusions display light-blue fluorescence before heating. After heating the inclusions to a temperature of 100—150°C and their cooling, the liquid phase displays the same fluorescence while the translucent yellowish globules show pink-purple fluorescence. This testifies to irreversible changes in chemical bonds in response to heating.

The described type of inclusions also comprises liquid inclusions probably filled with aqueous solution, which fail to display any fluorescence but contain dark-brown globules. These inclusions were also subject to decrepitation during crystal growth.

A different type is represented by scarce inclusions characterized by the presence of aqueous solution (L_3) and a gas bubble (G) surrounded by liquid organic substance (L_1) (Phot. 14; Phots 15—19). These inclusions also contain fine opaque phases considered to be asphaltite, and hairlike crystals sometimes appearing in the liquid organic phase. The volume fraction of the latter is insignificant. The behaviour of inclusions of this type during heating is most characteristic and diversified.

At room temperature, the inclusion presented on Phots 15—17 contained the L_1 , L_3 and G phases, as well as numerous birefringent hairlike (presumably organic) crystals within the L_1 phase, and fine opaque phases of the asphaltite type. When the inclusion was heated to 50—75°C, the hairlike crystals dissolved and did not reappear even after cooling to 0°C. A further increase in temperature caused the gas bubble to shrink until it became homogenized in the bituminous phase at 122°C. After partial homogenization, the inclusion was slowly cooled. During cooling, numerous tiny globules appeared in the L_3 phase (Phot. 17), resembling a solution on the boil. The globules partly moved towards the walls of the vacuole, forming flat round drops on its surface (Phot. 16). At the interface of L_1 and L_2 the intense exchange of components took place, involving the movement of globules from L_1 and L_2 towards the interface. On reaching the interface, the globules disappeared and new ones formed, moving in the opposite direction. At 112°C a few small gas bubbles appeared in the L_1 phase and rapidly merged into a single, larger one. At about 70°C an additional gas bubble formed from the globules moving from the interface appeared in the L_1 phase. No further changes were observed after room temperature was reached (Phot. 16). The vacuole walls were covered with drops of a liquid immiscible with aqueous solution, and the additional gas bubble was still present in the L_1 phase. Several-times repeated heating of the inclusion to the temperature of homogenization of the gaseous phase only caused the disappearance of the additional gas bubble. Neither the separation of droplets from aqueous solution nor the exchange at the interface was observed. The liquid drops deposited on the vacuole walls remained there irrespective of temperature changes up to 195°C, when the inclusion decrepitated.

The interpretation of the above phenomena presents considerable difficulties. It seems that the L_1 phase is a liquid rich in higher hydrocarbons. The droplets separating from the aqueous solution are undoubtedly a bituminous substance, which is indicated by their fluorescence. At the interface of L_1 and L_2 the exchange can have taken place between water vapour dissolved in the L_1 phase and dissolved liquid hydrocarbons. Since these phenomena fail to recur, it can be inferred that some irreversible changes have occurred, and a new stable equilibrium state has been reached.

Slightly different behaviour was shown by the inclusion with similar phase relations to the one described above (Phots 18, 19). The inclusion in question contained a substantial concentration of opaque asphaltite substance (*A*). Up to 62°C the gas bubble diminished at the minimal increase of the L_1 phase. At this temperature the bituminous envelope L_1 of the *G* phase concentrated at one side of the gas bubble, the contacting surface being very small. As the temperature was raised, the bubble began to shrink until it disappeared at 126°C, while the L_1 phase decreased in volume by about 10%. At 110°C a new liquid phase, immiscible with aqueous solution, appeared in the vicinity of asphaltite. At 131°C a gas bubble, slightly increasing in volume, appeared in the new-formed liquid phase. It seems that the inclusion was depressurized. As the temperature continued to rise, the gaseous phase ceased to expand and began to shrink again to about 200°C. The cooling of the inclusion to room temperature only caused an increase in the volume of gaseous phase (Phot. 19). Although the inclusion was heated several times up to 200°C, the only changes observed were those in the volume of gaseous phase.

This behaviour has been accounted for in the following way. As the temperature rises, the gas dissolves initially in the L_1 phase and then in the L_1 and L_3 phases. During heating, lighter hydrocarbons separate from asphaltite substance, forming a new liquid L_1 phase that displays light-blue fluorescence. The further increase in temperature causes the primary L_1 phase to be impoverished in volatile matter. The reappearance of gaseous phase may be due to the merging of the inclusion with a smaller one, rich in readily volatile matter, or else it may be assumed that the gaseous phase has evolved from asphaltite. At this point the system attains a new equilibrium state.

Gas-liquid inclusions containing aqueous solution of low salt concentration (Woźniak *et al.* 1974) and a gas bubble also occur sporadically in the "Marmaros diamonds".

To gain a better understanding of the nature of the mineral-forming environment, the voluminal ratios of gases evolved from inclusions were determined (Tab. 1). Although the data presented are the averaged values for the whole populations of inclusions decrepitating at temperatures given in Table 1, they show that the composition and voluminal ratios of gases contained in inclusions differ depending on the place of occurrence of quartz. The most common gas in the inclusions is methane, which is sometimes the only gaseous component. Ethane, propane and butane are of minor importance. A feature deserving note is the high content (nearly 57%) of hydrogen in the inclusions from Łąpsze Niżne. CO₂ contents are similar in the majority of samples studied. Nitrogen was detected in one sample only, and its presence could substantiate Kozłowski's hypothesis (1982) concerning the occurrence of liquid nitrogen phase in inclusions.

The presented voluminal ratios of gases in the inclusions studied differ somewhat from the results obtained by Ukrainian investigators for two single inclusions (Woźniak *et al.* 1974): CH₄ (67.9%; 94.9%), CO₂ (2.0%; 1.6%), N₂ (23.0%; 3.5%), H₂O (7.1%; 0.0%) and no H₂, CO or Ar.

Table 1 also gives the analyses of gases evolved in the temperature range 500—700°C. Experiments were carried out in the same apparatus on a mixture of gases of a composition similar to that of gases evolving from inclusions at 70—200°C. It appears that from 500°C the components enter into reactions with each other, making the analytical data unreliable. The results obtained for higher temperatures may only be useful for a quantitative determination of hydrocarbons of higher molecular weight.

Infrared absorption spectra recorded for chloroform extracts (Fig. 2, Tab. 2) from quartz (Pasternik stream) have revealed that both gaseous and heavy hydro-

Table 2
Interpretation of absorption bands in the IR spectrum of chloroform extract from the „Marmaros diamonds”

Wave number cm ⁻¹	Identification
3650—3100	ν O—H of carboxylic acids or alcohols, phenols, ν N—H
3050	ν C—H _{ar} , ν C—H of alkenes
2900	ν _{as} CH ₂
2850	ν _s CH ₂
2330	CO ₂ from air
1700	ν C=O of carboxylic acids or ketones
1650	ν C=O, ν C=C of alkenes, δ N—H
1600	ν C=C _{ar}
1440	δ _s CH ₂ , δ _{as} CH ₃
1360	δ _s CH ₃
1260—1000	ν C—O of alcohols or acids, ethers, esters, ν C—N
1125	ν _s C—O—C of ethers
920	δ O—H in dimers of carboxylic acids
690—750	δ _s CH ₂
720	ρ _s CH ₂

ν — stretching vibrations, δ — bending vibrations, ρ — rocking vibrations, ar — aromatic compounds, as — asymmetric vibrations, s — symmetric vibrations.

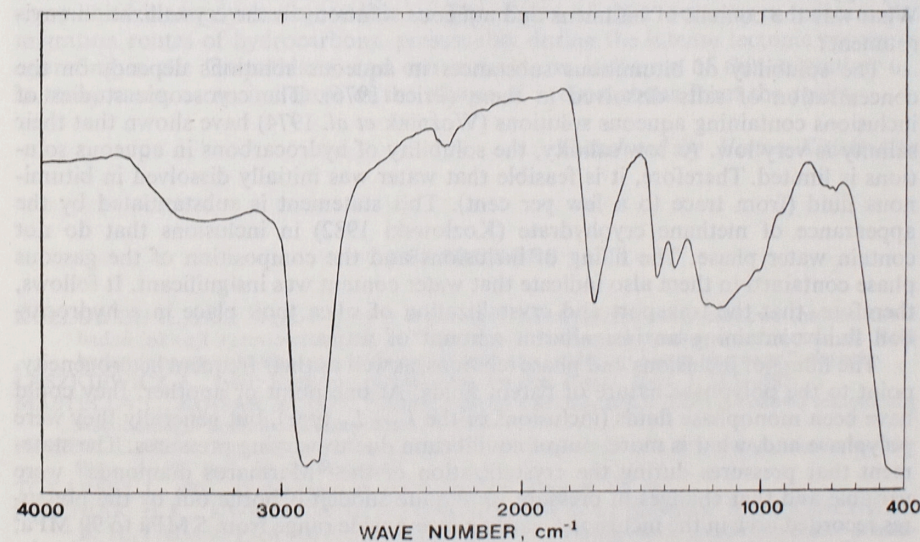


Fig. 2. Infrared absorption spectrum of bituminous substance extracted from inclusions in the "Marmaros diamonds" (Pasternik stream), recorded between 400 and 4000 cm⁻¹

carbons entered into the composition of the mineral-forming fluid. The results show that the bulk of bituminous substance consists of aliphatic hydrocarbons with minor amounts of aromatic compounds and presumably alkenes, carboxylic acids, ethers and esters. It should be noted, however, that not all organic matter was extracted, and a substantial amount of black crumbly asphaltite substance was left in quartz.

From the fact that a minimal rise in temperature already causes the decrepitation of inclusions it can be inferred that high pressures prevailed inside the inclusions. After being extracted from rocks, some "Marmaros diamonds" decrepitated under the influence of heat radiated by the sun. The same phenomenon was observed when the crystals were picked under the microscope. The rise in temperature caused by the luminous flux of the illuminator resulted in the decrepitation of some inclusions. The studies of crystals also point to earlier decrepitation, when the inclusions were still in the rock. These phenomena indicate that pressures inside the inclusions were of the order of 80 MPa.

Pressures determined for inclusions at room temperature by means of a crushing stage vary over a wide range from very low, less than 5 MPa, up to 99 MPa. The highest pressure values were obtained for inclusions from Łapsze Niżne (80—99 MPa).

The calcites accompanying the "Marmaros diamonds" in fissures do not practically contain any whole inclusions. The structure of calcite and the resulting perfect cleavage are responsible for the escape of volatile matter from the inclusions, so that only heavy hydrocarbons remain. Infrared absorption studies have revealed a close similarity in the composition of hydrocarbons between quartz and calcite.

DISCUSSION

From the above studies of fluid inclusions in the "Marmaros diamonds" it appears that their mineral-forming environment was complex.

Several questions arise at this point: Were the mineral-forming solutions mono- or polyphase in nature? In the latter case, were they or were they not at equilibrium? What was the content of bitumens and aqueous solutions in the crystallization environment?

The solubility of bituminous substances in aqueous solutions depends on the concentration of salts dissolved in them (Price 1976). The cryoscopic studies of inclusions containing aqueous solutions (Woźniak *et al.* 1974) have shown that their salinity is very low. At low salinity, the solubility of hydrocarbons in aqueous solutions is limited. Therefore, it is feasible that water was initially dissolved in bituminous fluid (from trace to a few per cent). This statement is substantiated by the appearance of methane cryohydrate (Kozłowski 1982) in inclusions that do not contain water phase. The filling of inclusions and the composition of the gaseous phase contained in them also indicate that water content was insignificant. It follows, therefore, that the transport and crystallization of silica took place in a hydrocarbon fluid containing an insignificant amount of water.

The filling of inclusions and phase relations, as well as their frequent heterogeneity, point to the polyphase nature of parent fluids. At one point or another, they could have been monophasic fluids (inclusions of the $L_1 + L_2$ type), but generally they were polyphase and, what is more, out of equilibrium due to varying pressures. The statement that pressures during the crystallization of the "Marmaros diamonds" were variable and that changes in pressure were quite sudden is borne out by the pressures recorded now in the inclusions, varying over a wide range from 5 MPa to 99 MPa, as well as by the decrepitated and clefted inclusions occurring commonly in the crystals.

Variations of pressure were also responsible for phase changes, reflected in varying phase relations in the inclusions. At elevated pressures, volatile matter (CH_4 — C_4H_{10} , N_2) was enclosed in the vacuoles in the liquid state, while at lower pressures it could have entered into the composition of gaseous phase or into the solution in heavy hydrocarbons. The mineral-forming fluids were most evidently polyphase in the final stage of crystallization. This can be inferred from the substantial amounts of asphaltite in the inclusions, occurring in the outermost parts of crystals and often accompanied by liquid hydrocarbons and aqueous solutions. These inclusions are usually contaminated by calcite dust. Since asphaltite is a residue after petroleum (aged), its presence in the inclusions suggests the crystallization and the inflow of fluid proceeded by stages.

The qualitative and quantitative, sometimes very pronounced, variation in the ratio of gas components in the inclusions (Tab. 1) points to the local differences in the composition of fluids.

Thermometric studies failed to yield precise data on the temperature conditions prevailing during crystallization. Some evidence, indirect as it is, is provided by the irreversible changes occurring in the filling of inclusions with the rise in temperature (the change in the nature of bonds in bituminous substance, new stable phase equilibria, the separation of light hydrocarbons from asphaltite). Basing on these phenomena, the upper temperature limit of mineral-forming processes can be determined, with a good deal of probability at about 100°C. In the authors' opinion, the optimum temperature range for the crystallization of the "Marmaros diamonds" is between 30° and 60°C. It is conceivable, however, that at times the temperatures were much lower because if the expansion of gas components due to sudden drops in pressure.

Both the composition of gases and less volatile organic phases in the inclusions and the close association of the "Marmaros diamonds" with asphaltites indicate that they crystallized from fluids of the petroleum type, rich in light (gaseous) fractions.

From the foregoing discussion it is evident that the "Marmaros diamonds" crystallized under dynamic conditions. The places of their occurrence indicate the migration routes of hydrocarbons, presumably during the intense tectonic processes operating in the Carpathians, and can serve as an indicator of this migration or, in many cases, as an indicator of the escape of hydrocarbons from the rocks.

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ŚRODOWISKO MINERALOTWÓRCZE "DIAMENTÓW MARMAROSKICH"

Streszczenie

„Diamenty marmaroskie” — to euhedralne, drobne, na ogół przezroczyste kryształy kwarcu znane z terenu Karpat Zewnętrznych. Licznie występują na terenie Karpat polskich. Występują one głównie w pionowych szczelinach tnących skały klastyczne, w ścisłej asocjacji z bitumicznym kalcytem i asfaltytami. Często kwarcy te są „zawieszane” w soczewkach i skupieniach asfaltytowych. Inkluzje fluidalne w nich występujące są wypełnione mieszkankami węglowodorów przy niewielkim udziale wody. Badania faz ciekłych jak i gazowych wskazują, że fluid składa się głównie z węglowodorów alifatycznych i zasobny jest w składniki lotne (CH_4 — C_4H_{10} , N_2 , H_2). W trakcie krystalizacji kwarcu panowały zmienne warunki ciśnieniowe w granicach od 5 do 99 MPa. Krystalizacja następowała etapowo z najczęściej heterogenicznego (polifazowego) fluidu. Autorzy sugerują, że zachodziła ona w stosunkowo niskich temperaturach rzędu 30—60°C.

Krystalizacja „diamentów marmaroskich” następowała w warunkach dynamicznych. Miejsca ich występowania są drogami migracji węglowodorów, prawdopodobnie w trakcie intensywnego zaangażowania tektonicznego górotworu karpackiego i mogą służyć jako wskaźnik tej migracji, a w wielu wypadkach jako wskaźnik ich ucieczki ze skał.

OBJAŚNIENIA FIGUR

- Fig. 1. Najczęściej spotykane pokroje „diamentów marmaroskich”.
Fig. 2. Widmo absorpcyjne w podczerwieni substancji bitumicznej wyekstrahowanej z inkluzji „diamentów marmaroskich” znad potoku Pasternik, w przedziale częstości drgań 400—4000 cm^{-1} .

OBJAŚNIENIA FOTOGRAFII

Plansza I

- Fot. 1. Rozmieszczenie inkluzji fluidalnych w strefach wzrostu „diamentów marmaroskich.” Pow. 50×
Fot. 2. Pierwotne inkluzje gazowo-ciekłe (ciekły węglowódor + gaz) powstałe na styku piramid wzrostu romboedrów. Pow. 50×.
Fot. 3. Powiększony fragment fot. 2. Pow. 200×

Plansza II

- Fot. 4. Ciekłe i gazowo-ciekłe (bitumiczne) inkluzje rozwinięte na płaszczyźnie romboedru. Pow. 160×
Fot. 5. Wielofazowe, płaskie inkluzje ułożone wzdłuż płaszczyzny 0001, schodkowo do płaszczyzny romboedru
A — asfaltyt, B — inkluzje bitumiczne. Temp. dekrepitacji — 59°C. Pow. 200×
Fot. 6. Inkluzja dwufazowa ciekła, równoległa do płaszczyzny słupa
L₁ — ciekła faza bitumiczna, L₂ — niezidentyfikowana faza ciekła, T_h — 75,4°C. Pow. 180×

- Fot. 7. Bitumiczna inkluzja ciekła z okrągłymi skupieniami przeświecającymi szarobrunatno oraz z drobnymi włosowatymi dwójłomnymi kryształami (organicznymi). Inkluzja otoczona drobnymi inkluzjami potomnymi (daughter). Pow. 200×
Fot. 8. Bitumiczna ciekła inkluzja z wydzieleniem włosowatych, dwójłomnych kryształów. Pow. 200×
Fot. 9. Inkluzja ciekła lub gazowa o kształcie negatywnego kryształu z drobnymi, okrągłymi wydzieleniami substancji organicznej. Pow. 240×

Plansza III

- Fot. 10. Bitumiczna inkluzja gazowo-ciekła, ścianki wakuoli pokryte są dwójłomną brunatną substancją. Temp. dekrepitacji — 49°C, Pow. 200×
Fot. 11. Inkluzja dwufazowa — ciekła
L₁ — węglowódor ciekły (metan), L₂ — niezidentyfikowana ciecz. Inkluzja zdekrepiowała przed homogenizacją w temp. 52°C. Pow. 300×
Fot. 12. Dwufazowa inkluzja ciekła w trakcie ogrzewania i chłodzenia
a — temp. 19°C, b — temp. 29°C, c — temp. 38,2°C, d — 35,1—35,9°C. Pow. 160×
Fot. 13. Inkluzja ciekła dwufazowa homogenizująca w temperaturze 31°C
L₁ — ciekły węglowódor, L₂ — niezidentyfikowana faza ciekła. Pow. 180÷
Fot. 14. Pierwotna trójfazowa inkluzja gazowo-ciekła. Temp. dekrepitacji — 164°C przed osiągnięciem stanu homogenicznego
L₁ — ciekły węglowódor, L₃ — roztwór wodny, G — pęcherzyk gazowy. Pow. 200×

Plansza IV

- Fot. 15. Fragment inkluzji wielofazowej
G — pęcherzyk gazowy, L₁ — ciekły węglowódor, L₃ — roztwór wodny. W ciekłej fazie węglowodoru drobne nieprzezroczyste ziarna (asfaltyt), T_h fazy gazowej w fazie cieczy organicznej — 122°C. Pow. 160×
Fot. 16. Inne ujęcie inkluzji (fot. 15) po ostudzeniu do temp. 19°C. W ciekłej fazie organicznej pojawił się dodatkowy pęcherzyk gazu. Z fazy roztworu wodnego wydzieliły się drobne krople fazy węglowodorowej. Pow. 160×
Fot. 17. Inkluzja z fot. 15 i 16 w trakcie studzenia. W fazie roztworu wodnego wydzielają się drobne kuleczki ciekłej fazy, a w fazie L₁ pojawia się drobny pęcherzyk gazu. Pow. 160×
Fot. 18. Wielofazowa inkluzja gazowo-ciekła
L₁ — ciecz organiczna, G — pęcherzyk gazowy, L₃ — roztwór wodny, A — czarna substancja typu asfaltytu, T_h pęcherzyka w roztworze wodnym 126°C. Pow. 160×
Fot. 19. Po ochłodzeniu inkluzja z fot. 18

Лукаш КАРВОВСКИ, Ежи ДОРДА

МИНЕРАЛООБРАЗУЮЩАЯ СРЕДА "МАРМАРОШСКИХ АЛМАЗОВ"

Резюме

„Мармарошские алмазы” это эвгдральные, мелкие, обычно прозрачные кристаллы кварца, известные на территории Внешних Карпат. Они многочисленны на территории польских Карпат. Встречаются главным образом в вертикальных трещинах секущих обломочные породы, в тесной ассоциации с битуминозным кальцитом и асфальтитами. Часто эти кварцы „завешены” в асфальтитовых линзах и скоплениях. Встречающиеся в них флюидальные включения выполнены смесью углеводородов при небольшом участии воды. Исследования как жидких, так и газовых фаз указывают, что флюид состоял преимущественно из алифатических углеводородов и богат был летучими компонентами (CH_4 — C_4H_{10} , N_2 , H_2). В ходе кристаллизации кварца господствовали пере-

менные условия с давлением в пределах от 5 до 99 МПа. Кристаллизация проходила по этапам, чаще всего из гетерогенного (полифазного) флюида. Авторы полагают, что она происходила в сравнительно низких температурах порядка 30—60°C.

Кристаллизация "мармарошских алмазов" происходила в динамических условиях. Места их нахождения являются путями миграции углеводородов, по-видимому, в пределах интенсивного тектонического вовлечения карпатского горного сооружения, и могут служить в качестве индикатора этой миграции, а во многих случаях в качестве показателя их утечки из пород.

ОБЪЯСНЕНИЯ К ФИГУРАМ

- Фиг. 1. Наиболее часто встречаемые габитусы "мармарошских алмазов"
 Фиг. 2. ИК-спектр поглощения битумного вещества, экстрагированного из включений в "мармарошских алмазах", встречающихся над потоком Пастерник, в интервале частот колебаний 400—4000 см⁻¹

ОБЪЯСНЕНИЯ К ФОТОГРАФИЯМ

Таблица I

- Фото 1. Размещение флюидальных включений в зонах роста "мармарошских алмазов" Увел. 50 ×
 Фото 2. Первичные газопо-жидкие включения (жидкий углеводород + газ), образованные на контакте пирамид роста ромбоэдров. Увел. 50 ×
 Фото 3. Увеличение детали фотографии 2. Увел. 200 ×

Таблица II

- Фото 4. Жидкие и газопо-жидкие (битумные) включения, развитые в плоскости ромбоэдра Увел. 160 ×
 Фото 5. Многофазные плоские включения, расположенные вдоль плоскости 0001, ступенчато к плоскости ромбоэдра
A — асфальтит, *B* — битумные включения. Температура декрепитации 59°C. Увел. 200 ×
 Фото 6. Двухфазное жидкое включение, параллельное к плоскости призмы.
*L*₁ — жидкая битумная фаза, *L*₂ — неопределенная жидкая фаза, *T*_x — 75,4°C. Увел. 180 ×
 Фото 7. Битумное жидкое включение с просвечивающими серо-бурыми округлыми скоплениями, а также с мелкими волосоватыми двупреломляющими (органическими) кристаллами. Включение обрамлено тонкими дочерними включениями. Увел. 200 ×
 Фото 8. Битумное жидкое включение с выделением волосоватых двупреломляющих кристаллов. Увел. 200 ×
 Фото 9. Жидкое (или газовое) включение в форме негативного кристалла с тонкими круглыми выделениями органического вещества. Увел. 240 ×

Таблица III

- Фото 10. Битумное газопо-жидкое включение, стенки вакуоли покрыты бурым двупреломляющим веществом. Температура декрепитации — 49°C. Увел. 200 ×
 Фото 11. Двухфазное жидкое включение
*L*₁ — жидкий углеводород (метан), *L*₂ — неопределенного состава жидкость. Включение декрепитировало до гомогенизации в температуре 52°C. Увел. 300 ×
 Фото 12. Двухфазное жидкое включение в процессе подогревания и охлаждения
a — температура 19°C, *b* — 29°C, *c* — 38,2°C, *d* — 35,1—35,9°C. Увел. 160 ×

- Фото 13. Двухфазное жидкое включение с гомогенизацией в температуре 31°C
*L*₁ — жидкий углеводород, *L*₂ — жидкая фаза неопределенного состава. Увел. 180 ×
 Фото 14. Первичное трехфазное газопо-жидкое включение. Температура декрепитации 164°C до гомогенного состояния
*L*₁ — жидкий углеводород, *L*₃ — водный раствор, *G* — газовый пузырек. Увел. 200 ×

Таблица IV

- Фото 15. Фрагмент многофазного включения
G — газовый пузырек, *L*₁ — жидкий углеводород, *L*₃ — водный раствор. В жидкой фазе углеводорода заключены мелкие непрозрачные зерна (асфальтит), *T*_x газовой фазы в фазе органической жидкости — 122°C. Увел. 160 ×
 Фото 16. Другой вид включения (фото 15) после охлаждения до температуры 19°C. В жидкой органической фазе появился дополнительный пузырек газа. Из фазы водного раствора выделились мелкие капли углеводородной фазы. Увел. 160 ×
 Фото 17. Включение из фотографий 15 и 16 в процессе охлаждения. В фазе водного раствора выделяются мелкие шарики жидкой фазы, а в фазе *L*₁ появляется тонкий газовый пузырек. Увел. 160 ×
 Фото 18. Многофазное газопо-жидкое включение
*L*₁ — органическая жидкость, *G* — газовый пузырек, *L*₃ — водный раствор, *A* — черное вещество типа асфальтита. *T*_x пузырька в водном растворе 126°C. Увел. 160 ×
 Фото 19. Включение из фотографии 18 после охлаждения

EXPLANATIONS OF PLATES

Plate I

- Phot. 1. The distribution of fluid inclusions in the growth zones of "Marmaros diamonds". Magn. 50 ×
 Phot. 2. Primary gas-liquid inclusions (liquid hydrocarbon + gas) formed at the contact of growth pyramids of rhombohedra. Magn. 50 ×
 Phot. 3. An enlarged fragment of phot. 2. Magn. 200 ×

Plate II

- Phot. 4. Liquid and gas-liquid (bituminous) inclusions developed on the rhombohedron plane Magn. 160 ×
 Phot. 5. Polyphase flat inclusions arranged along the 0001 plane, stepwise to the rhombohedron plane
A — asphaltite, *B* — bituminous inclusions. Decrepitation temperature 59°C. Magn. 200 ×
 Phot. 6. Two-phase liquid inclusion, parallel to the prism plane
*L*₁ — liquid bituminous phase, *L*₂ — unidentified liquid phase, *T*_x 75.4°C. Magn. 180 ×
 Phot. 7. Bituminous liquid inclusion with round, translucent grey-brown concentrations and fine, birefringent hairlike (organic) crystals. The inclusion is surrounded by small daughter inclusions. Magn. 200 ×
 Phot. 8. Bituminous liquid inclusion with birefringent hairlike crystals. Magn. 200 ×
 Phot. 9. Liquid or gas inclusion shaped like a negative crystal, with small round concentrations of organic substance. Magn. 240 ×

Plate III

- Phot. 10. Bituminous gas-liquid inclusion. Vacuole walls are covered with birefringent brown substance. Decrepitation temp. 49°C. Magn. 200 ×
 Phot. 11. Two-phase liquid inclusion
*L*₁ — liquid hydrocarbon (methane), *L*₂ — unidentified liquid phase. The inclusion decrepitated at 52°C before homogenization. Magn. 300 ×
 Phot. 12. Two-phase liquid inclusion during heating and cooling
a — 19°C, *b* — 29°C, *c* — 38.2°C, *d* — 35.1—35.9°C. Magn. 160 ×

Phot. 13. Two-phase liquid inclusion homogenizing at 31°C

L_1 — liquid hydrocarbon, L_2 — unidentified liquid phase. Magn. 180 ×

Phot. 14. Primary three-phase gas-liquid inclusion. It decrepitated at 164°C before homogenization

L_1 — liquid hydrocarbon, L_3 — aqueous solution, G — gas bubble. Magn. 200 ×

Plate IV

Phot. 15. A fragment of polyphase inclusion

G — gas bubble, L_1 — liquid hydrocarbon, L_3 — aqueous solution. Fine opaque grains (asphaltite) are visible in the liquid hydrocarbon phase. T_h of gaseous phase in organic liquid phase — 122°C. Magn. 160 ×

Phot. 16. A different view of the inclusion from phot. 15 after colling to 19°C. An additional gas bubble appears in liquid organic phase. Small drops of hydrocarbon phase separate from aqueous solution. Magn. 160 ×

Phot. 17. Inclusion from phot. 15 and 16 during colling. Droplets of liquid phase separate from aqueous solution, and a small gas bubble appears in the L_1 phase. Magn. 160 ×

Phot. 18. Polyphase gas-liquid inclusion

L_1 — organic liquid phase, G — gas bubble, L_3 — aqueous solution, A — black substance of the asphaltite type. T_h of the gas bubble in aqueous solution — 126°C. Magn. 160 ×

Phot. 19. Inclusion from Phot. 18 after cooling

