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Hydrocarbon inclusions in vein quartz (the "Marmarosh diamonds") from the Krosno and Dukla zones of the Ukrainian Carpathians

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Fluid inclusion studies were conducted in the vein quartz known as the "Marmarosh diamonds" of the Krosno and Dukla zones of the Ukrainian Carpathians, which are potentially oil- and gas-bearing. The "Marmarosh diamonds" contain different types of fluid inclusions which record the evolution of the quartz formation. The inclusions were studied by means of gas chromatography, microthermometry and fluorescence. The following sequence has been observed: methane inclusions displaying characteristic features due to crystallography, light hydrocarbons, complex inclusions with a variety of bitumens, and gas-liquid inclusions with two different hydrocarbon phases. The regions where the light hydrocarbon inclusions occur seem to be the most promising as regards oil and gas prospects.

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Key words: Ukrainian Carpathians, "Marmarosh diamonds", quartz, hydrocarbon inclusions, methane, bitumens, light hydrocarbons.

INTRODUCTION

The Krosno and Dukla zones occur in the central part of the structure of the Carpathians in the territory of Ukraine (Fig. 1). They are built of Cretaceous-Paleogene sedimentary rocks and display a nappe structure. Numerous fracture zones occur, which are important as regards the migration of hydrocarbons and the formation of hydrocarbon accumulations of commercial significance (Kudriavcev, 1963; Kopystianskij, 1978; Dolenko, 1986).

The Krosno and Dukla zones may contain oil and gas. Along strike in Poland, the same structures, known as the Silesia and Dukla zones, contain recognised oil and gas fields (Karnkowski, 1993).

The first description of the "Marmarosh diamonds" in the Ukrainian Carpathians was by Matkovskij (1961). Subsequently, mass spectrometric analyses and cryometric studies identified methane and heavier hydrocarbons (up to pentane), in the inclusions as well as carbon dioxide and nitrogen (Zacycha, 1975; Bratus *et al.*, 1981; Dudok, 1996). Some determinations of the concentrations of the hydrocarbons were made (Kaliuznyj and Lomov, 1990, 1992; Bratus *et al.*, 1991; Vityk *et al.*, 1995). The possibility of using the fluid inclusion data to interpret the tectonic history of the Ukrainian Carpathians was suggested by Vityk *et al.* (1996). Aspects of the phase composition and the problems of classifying the hydrocarbon inclusions were described by Dudok *et al.* (1997), and preliminary fluorescence studies were reported by Dudok and Jarmołowicz-Szulc (1999).

This paper gives the latest data on the hydrocarbon inclusions in the quartz of the "Marmarosh diamonds" and reconstructs fluid evolution in the Ukrainian part of the Carpathians.

GEOLOGICAL AND MINERALOGICAL SETTING

Tectonic fractures within the Krosno and Dukla zones show various orientations. The most pronounced systems have NE (40–60°) and NW (40–60°) trends. These are ore present throughout. Their orientation is parallel to the main regional tectonic trends. There occur also three other fracture directions, as: two near N–S (340–350 and 10–20°) and one approximately transverse to these (255–275°). These fractures are best seen in the Middle and Upper Paleogene deposits.

These fractures are filled with various vein minerals. Calcite and quartz are predominant, together with bitumens such as e.g.

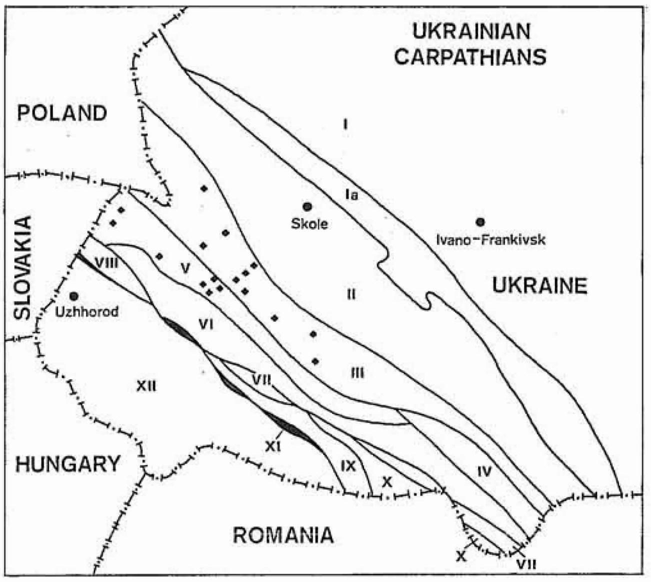

Fig. 1. Schematic tectonic map of the Ukrainian Carpathians (after Kruglova and Cypko eds., 1988)

I — SW margin of the East European Craton, Ia — Boryslav–Pokutsk zone, II — Skiba zone, III — Krosno zone, IV — Tschernogorsk zone, V — Dukla zone, VI — Porkulensk zone, VII — Rakov zone, VIII — Magura zone, IX — Marmarosh Klippen Belt, X — Marmarosh crystalline massif, XI — Pieniny Klippen zone, XII — Carpathian Intradepression; points show sample locations of the "Marmarosh diamonds" in the Krosno and Dukla zones

anthraxolite, elkerite and asphaltite. The thickness of veins ranges from some millimetres to 10–20 cm, averaging some centimetres.

Colourless quartz is the most informative mineral in this association. Quartz crystals display two pyramids and have a prismatic, rhombohedral as well as pseudocubic habit (Fig. 2). Such characteristic crystals were first found in the Marmarosh Massif in the Carpathians and were called "Marmarosh diamonds". Quartz of this type has been described from many regions of the Alpine province, and characteristically contains hydrocarbon inclusions (Vozniak *et al.*, 1973).

The "Marmarosh diamonds" from the Krosno and Dukla zones range in size from millimetres to 3–3.5 cm. Generally they are 2–8 mm.

FLUID INCLUSIONS: EVOLUTION OF MORPHOLOGY, COMPOSITION AND P-T PARAMETERS

Fluid inclusions of various size were studied in quartz crystals from regions where "Marmarosh diamonds" commonly occur in the Ukrainian part of the Krosno and Dukla zones (Fig. 1).

In the Krosno zone, such quartz occurs in the Czernaja Tisa river basin (close to Jasinia), along the Rika and Ripinka rivers and their tributaries (around Miezgorije, Sojma, Ripinnoje, Riechka, Majdan, Goliatin and Bielasownica) and along the Latorica river (the region of Volovec, Nizni Vorota, Oporec, Lazy, Abramka and Jabliunica).

In the Dukla zone — the "Marmarosh diamonds" occur in the basin of the Uz river (near Stavne) and Pinia (near Ploskoje).

The nomenclature of Dudok *et al.* (1997) is used in this paper: G — gas phase containing mainly methane; L — liquid, water-like phase with a low concentration of salts; L_1 — liquid, hydrocarbon-like phase; L_2 (G_2) — condensed methane-butane mixture, gaseous in normal conditions; B — solid phase represented by bitumens of different composition.

The hydrocarbon inclusions correspond to four groups: methane, oil-methane, methane-oil, and oil.

Representative images of the inclusions are shown in Figures 3–5. Sample numbers correspond to the site (e.g. 723) and the individual crystal studied (e.g. 723/2).

Methane inclusions L_2 (G_2) are those earliest ones in the "Marmarosh diamonds" from the Ukrainian part of the Carpathians. They either display a negative crystal form (Fig. 3a, b) or are characteristically elongated (Fig. 3c, d). Methane is at the supercritical stage and contains a little water (3–5%). Its homogenisation temperatures fall into the interval of –145 to –90°C (into the liquid phase) and –110 to –85°C (into the liquid phase) in the Krosno and Dukla zones, respectively. The inclusions display a white-blue to blue fluorescence in the ultraviolet light.

The walls of the vacuoles of some inclusions are covered with a yellow-brown film of hard paraffin. This film formed in

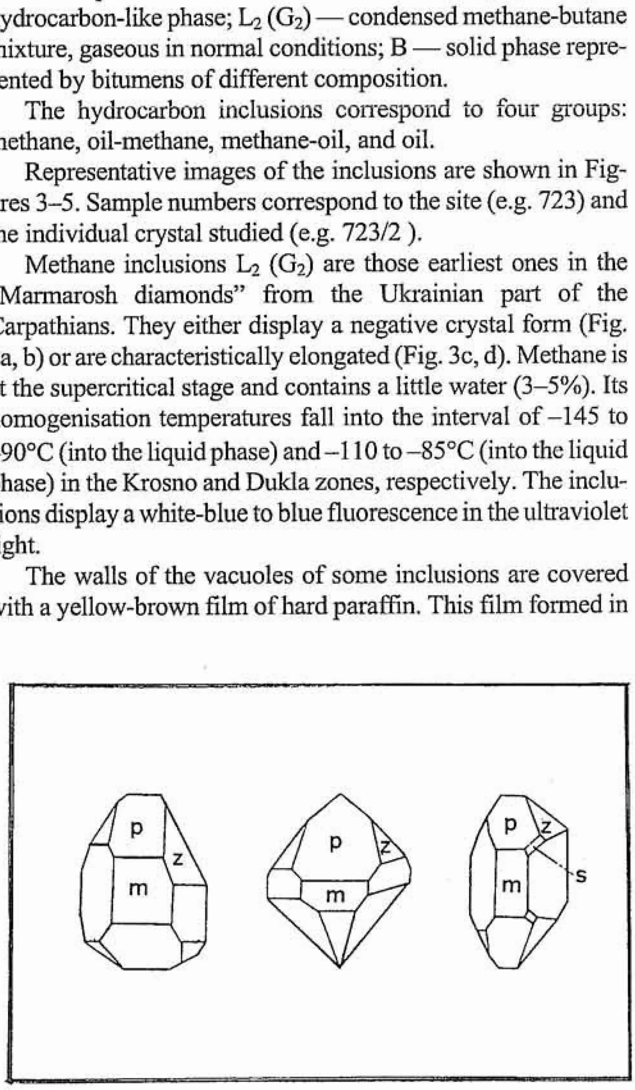

Fig. 2. Morphology of the crystals of the "Marmarosh diamonds"

m — prism; p, z — rhombohedrons (right, left); s — trigonal bipyramid

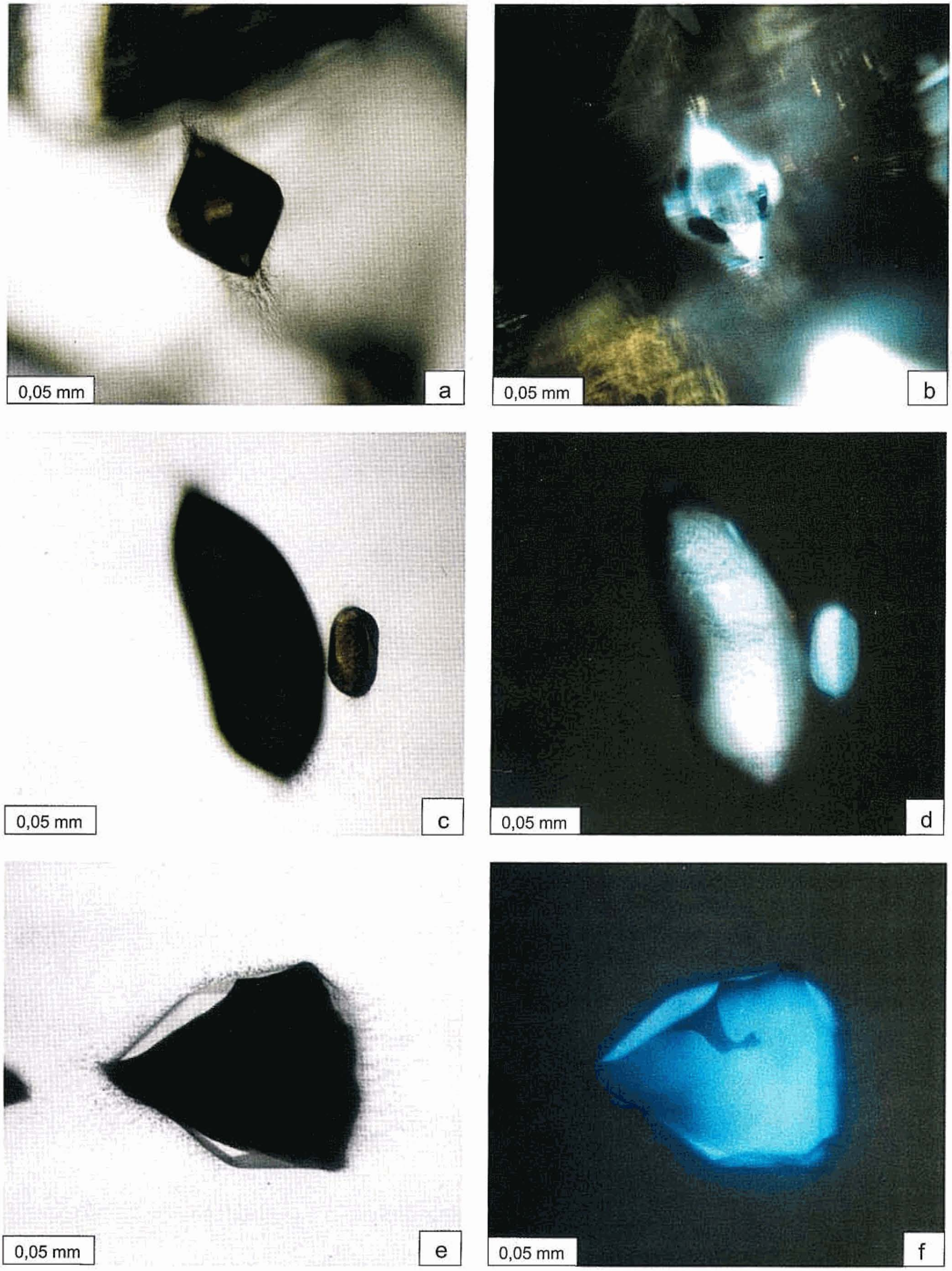

Fig. 3. Primary methane inclusions of L_2 (G_2) type with re-equilibration textures

a, b — sample 723/2 (Veca river, the Krosno zone), Th = –118°C (into liquid): a — in polarised light, b — in ultraviolet; **c, d** — sample 713/14 (settlement Ploskoje, the Dukla zone), Th = –102°C (into liquid): c — in polarised light, d — in ultraviolet; **e, f** — multicomponent inclusion in the Krosno zone, sample 723/7 (Veca river) — primary colourless methane inclusion with re-equilibration zones formed on the thin anthraxolite plate: e — in polarised light, f — in ultraviolet

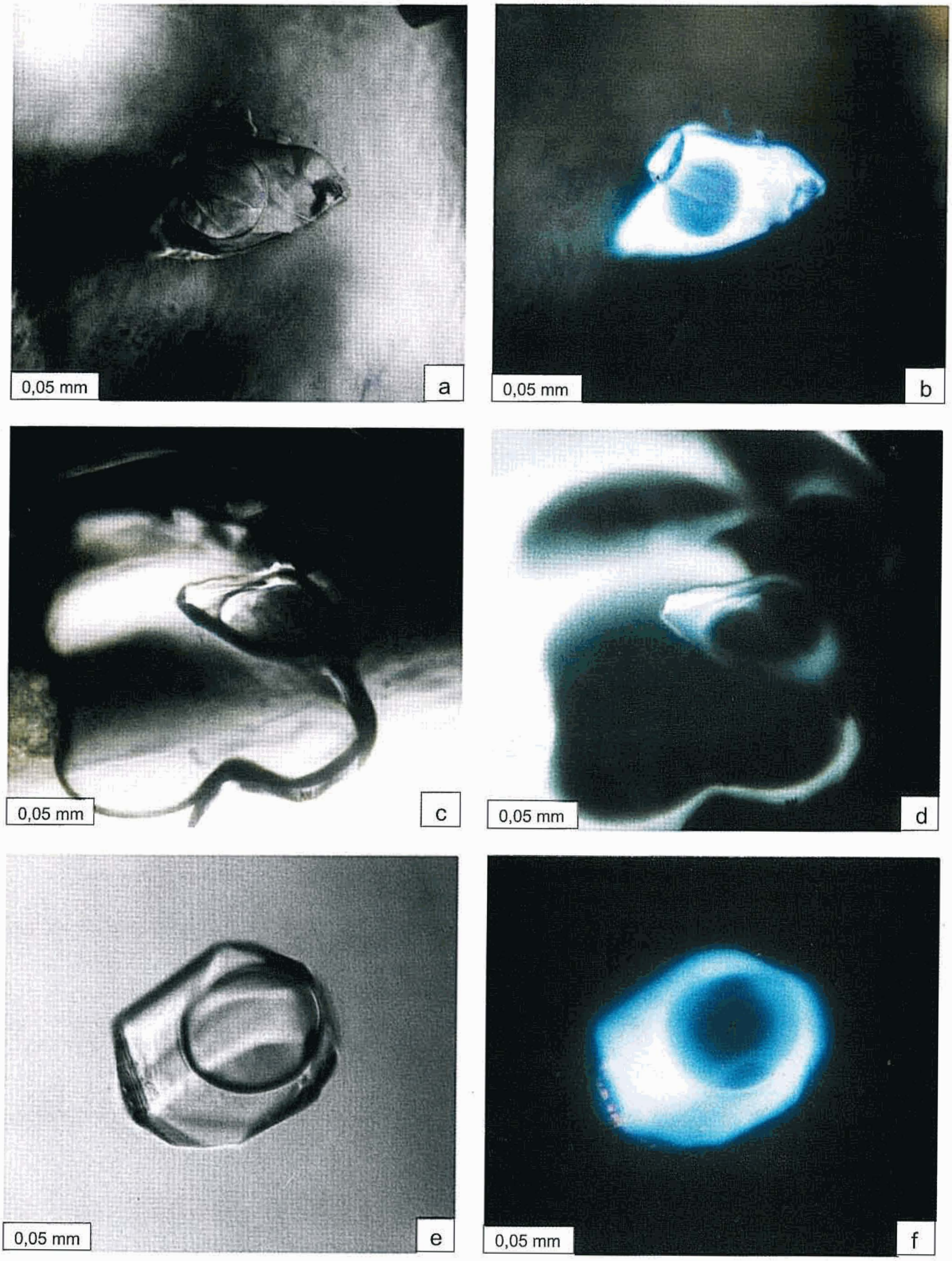

Fig. 4. Different multicomponent inclusions

a, b — multicomponent inclusion in the Krosno zone, sample 709/1 (settlement Ripinnoje) — methane inclusion with hard phase of of type $L_2 + B$ (L_2 — methane in critical state, B — black anthraxolite): a — in the polarised light, b — in ultraviolet; **c, d** — different multicomponent inclusion in the Dukla zone, sample 762/41 (settlement Stavne) — hydrocarbon inclusion with organic mineral in hard phase, Th = 57°C (into gas): c — in polarised light, d — in ultraviolet; **e, f** — sample 713/2 (settlement Ploskoje) — light brown paraffin showing orange fluorescence in the hard inclusion phase, Th = 48°C (into liquid): e — in polarised light, f — in ultraviolet

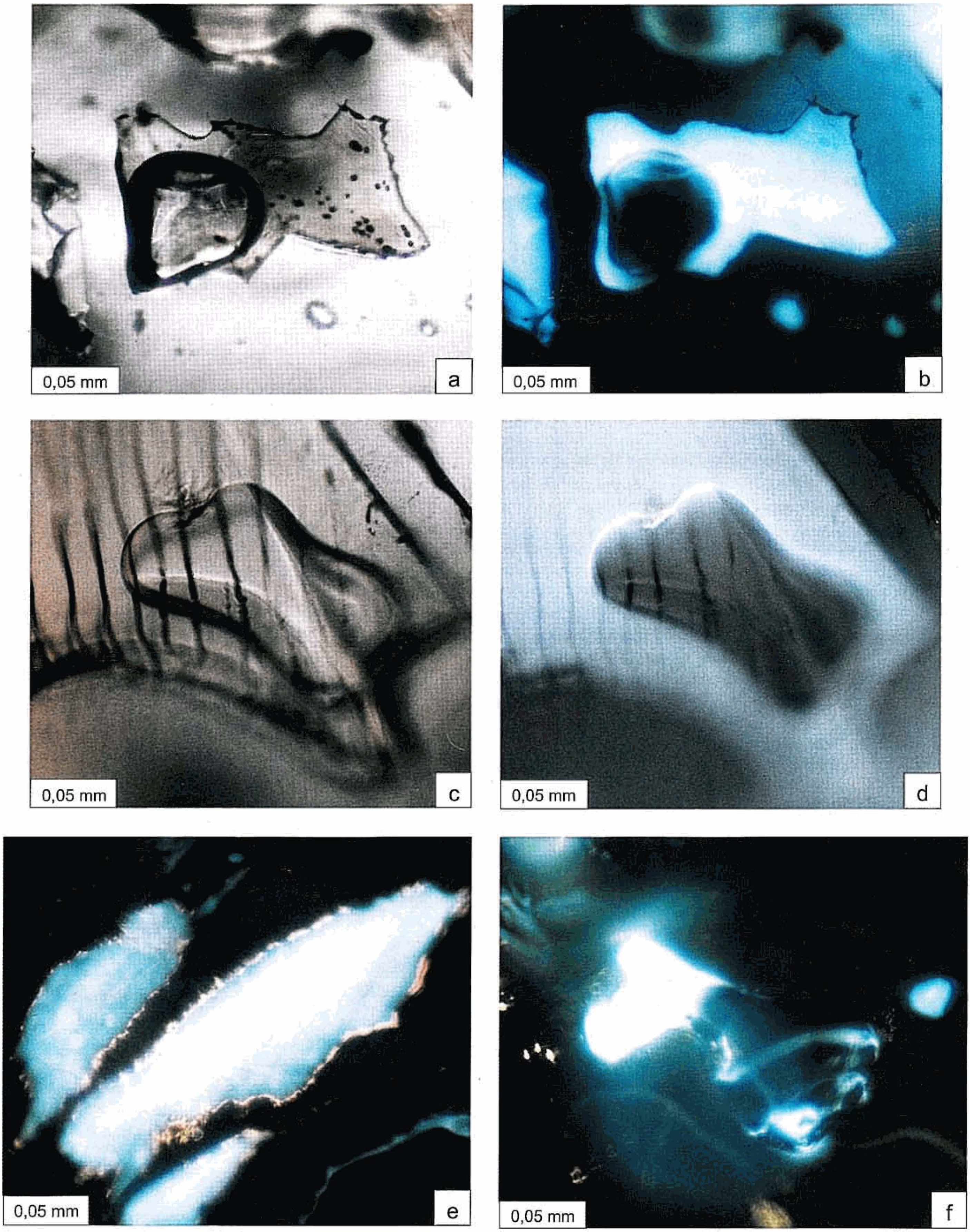

Fig. 5. Primary hydrocarbon inclusions with oil droplets of brown colour

a, b — sample 799/10 (Krosno zone): a — in polarised light, b — in ultraviolet; **c, d** — sample 700/7 (Krosno zone): c — in polarised light, d — in ultraviolet; **e, f** — two different hydrocarbon phases in the inclusions, large primary methane inclusion with crystalline organic matter in the walls of the vacuole: e — in ultraviolet; f — secondary gas-liquid inclusions with hydrocarbons of "light oil" type, in ultraviolet the inclusion vacuole after a decrease in p-T conditions. The film looks to have a complex crystalline structure, indicating "structuralisation" of the organic matter into characteristic shapes.

The inclusions of L_2 (G_2) type which are parallel to the "c" axis are surrounded by aureoles of daughter gas-liquid inclusions (Fig. 3a, b). They display a light yellow colour and their chemical composition corresponds to that of primary ones L_2 (G_2). When heated to 110°C, their gas bubbles diminish nearly by half, exploding at about 115°C.

The palaeotemperature decrease to 170–180°C resulted in formation of the following types of the inclusions in the "Marmarosh diamonds": light hydrocarbon inclusions (L_1), different bitumens and complex inclusions as — L_2 (G_2) + B, L + L_1 + G, L_1 + G, L_1 + G +B, L_1 + B (Figs. 3e, f and 4a, b). The solid phase developed as block anthraxolite is most characteristic of the methane inclusions (Fig. 3e). Locally, the anthraxolite forms the base for the L_2 (G_2) inclusion (Fig. 3e, f). The solid phase can be also represented by asphaltite (Fig. 4a, b) and occasionally — by organic matter (Fig. 4c, d). No changes have been observed on heating to 250°C. The solid phase has no fluorescence.

Inclusions with liquid hydrocarbons are characteristic of the quartz sampled in the basins of the Uz and Pinia rivers (the Dukla zone) and Latorica (the Krosno zone). Hydrocarbons display bluish-white fluorescence (Fig. 4e, f). When heated to 45–50°C they change their phase relations, generally homogenising either into a liquid or gas phase. The transition temperature of the hydrocarbon fluid into the critical state lies in a wide interval of –43 to 80.8°C (Dudok *et al.*, 1997). In the inclusion of L_1 + G type the separated oil phase is often observed in the form of individual drops (Fig. 5a, b) which may even arrange themselves into some bigger forms perpendicular to the "c" axis of the inclusion (Fig. 5c, d).

The gas-liquid inclusions with two different hydrocarbon phases are the latest ones in the quartz from the Dukla zone. The majority of the vacuole's volume (60–70%) is filled with the lighter hydrocarbon phase (blue fluorescence in UV) being surrounded by heavier hydrocarbons of yellow fluorescence; the gas phase (20%) corresponds to the lighter hydrocarbon phase. Such heavier hydrocarbons fill the gas or gas-fluid inclusions which correspond to the healed fissures in the quartz crystals (Fig. 5e, f). In ultraviolet light these inclusions display yellow or yellow-orange fluorescence.

In the central zones of the crystals, xenogenic inclusions of calcite and small idiomorphic quartz crystals together with anthraxolite may be observed. Their formation took place at a temperature of about 50°C and at pressures of some tens of bars.

Anthraxolite fragments also form zones parallel to the crystal margin, occurring at the crystal surface or filling the central part of the veins.

According to the p-T data for the gas-fluid aqueous inclusions (type L + G), crystallisation of quartz occurred in the temperature interval of 190–230°C and pressures of 2.7 kbar in the Krosno zone and 1.9 kbar in the Dukla zone (Fig. 6).

Table 1

Gas composition in inclusions in the "Marmarosh diamonds" — Ukrainian Carpathians

Sample	Gas amount (10^{-6}g)			Gas percentage (%)		
	CH_4	CO_2	N_2	CH_4	CO_2	N_2
Krosno zone						
704	1.43	0.13	–	91.7	8.3	–
708/1	2.15	0.29	–	88.1	11.9	–
708/2	0.13	0.26	–	33.3	66.7	–
722	0.91	0.09	0.08	84.3	8.3	7.4
723	0.10	0.13	0.03	38.5	50.0	11.5
724	1.57	0.08	–	95.2	4.8	–
725	1.43	0.13	–	86.3	13.7	–
796	0.09	0.12	–	42.9	57.1	–
799	4.92	1.44	0.07	76.4	22.4	1.2
Dukla zone						
711	0.46	–	–	100.0	–	–
712	1.30	0.29	–	81.8	18.2	–
713	0.34	0.29	–	54.0	46.0	–
741/1	0.87	0.25	0.03	75.5	21.7	–
741/2	2.38	0.17	–	93.3	6.7	–
762	3.12	0.17	–	94.8	5.2	–
763	2.02	0.13	0.02	92.7	6.0	–

Sampling localisation and the age: 704 — Sojma, 708 — Miczgorije, 722–724 — Veca, 725 — Lazy, 796 — Ripinnoje, 799 — Beskid depression, 711, 712, 741, 742 (in Tab. 2) — Svalava-Volovec, 713 — Ploskoje, 762, 763 — Stavne

GAS COMPOSITION OF THE INCLUSIONS IN THE "MARMAROSH DIAMONDS"

Analytical studies on the gas composition in the inclusions were performed using the chromatograph "Chrom 5". It was possible to detect N, CO_2 and hydrocarbons until octane. This is the first application of this method to the vein minerals of the Carpathian oil-bearing province.

The results of the chromatographic analysis are shown in Table 1. The accuracy of the determinations is as follows: CH_4 — 2 x 10^{-9}g; C_2H_4 — 7 x 10^{-9}g; C_2H_6, C_3H_6 — 5 x 10^{-9}g; C_2H_8 — 4 x 10^{-9}g; C_4H_{10}, *i*-C_4H_{10} — 3 x 10^{-10}g; C_5H_{12} — 4 x 10^{-10}g; C_6H_{12} — 2 x 10^{-10}g; C_6H_{14}, C_7H_{16}, C_8H_{18} — 2 x 10^{-11}g.

Table 2

Hydrocarbon composition (%) of fluid inclusions in the "Marmarosh diamonds" in the Krosno and Dukla zones

Sample	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_{10}	i–C_4H_{10}	C_5H_{12}	C_6H_{12}	C_6H_{14}	C_7H_{14}	C_8H_{18}	Alkanes	
Krosno zone														
704/1	82.05	10.75	5.18	1.71	–	–	0.29	–	–	0.01	–	–	87.54	12.46
704/2	94.41	1.14	–	2.95	1.14	–	0.36	–	–	0.01	–	–	95.91	4.09
708/1	80.93	14.87	2.54	1.03	–	–	0.63	–	–	–	–	–	84.10	15.90
708/2	91.75	7.71	–	–	0.49	–	0.05	–	–	–	–	–	92.29	7.71
722/1	64.75	18.82	3.64	8.09	3.84	–	0.69	0.10	0.02	0.04	–	–	73.07	26.93
722/2	64.68	26.28	0.52	1.87	5.22	–	1.35	–	–	0.07	–	–	71.75	28.15
723/1	77.38	15.39	0.53	3.93	2.28	–	0.42	0.05	–	0.02	–	–	80.68	19.32
723/2	77.90	11.15	5.57	3.97	1.42	–	–	–	–	–	–	–	84.88	15.12
724/1	78.43	1.67	0.90	18.38	0.24	–	0.38	–	–	–	–	–	79.95	20.05
724/2	90.21	5.43	2.06	2.03	–	0.13	0.12	0.01	–	–	–	–	92.54	7.46
725/1	87.22	5.93	2.96	2.75	1.00	–	0.14	–	–	–	–	–	91.32	8.68
725/2	78.42	11.78	3.94	4.92	–	0.50	0.21	0.20	0.03	–	–	–	83.27	16.73
796/1	69.75	14.70	9.75	5.46	0.32	–	0.01	–	–	–	–	–	79.84	20.16
796/2	59.30	18.78	–	16.10	3.76	–	1.34	0.67	–	0.05	–	–	65.12	34.88
799/1	50.90	21.06	2.47	20.56	1.64	0.03	2.32	0.62	0.12	0.21	0.05	0.02	58.26	41.74
799/2	64.24	19.47	–	11.87	2.90	1.05	0.13	0.19	0.04	0.06	0.04	–	68.62	31.38
Dukla zone														
712/1	88.28	6.72	3.18	1.82	–	–	–	–	–	–	–	–	91.46	8.54
712/2	91.11	7.41	–	1.45	–	–	–	–	–	0.03	–	–	91.14	8.86
713/1	80.82	14.76	–	1.81	1.41	0.24	0.52	0.35	–	0.03	0.06	–	83.43	16.57
713/2	83.99	6.57	6.57	1.41	0.66	0.09	0.63	–	0.02	–	0.03	0.01	92.00	8.00
741/1	13.94	0.94	68.49	12.73	3.86	–	0.04	–	–	–	–	–	86.33	13.67
741/2	71.43	4.65	23.92	–	–	–	–	–	–	–	–	–	95.35	4.65
742/1	80.17	10.73	8.10	–	0.99	–	–	–	–	–	–	–	89.27	10.73
762/1	73.45	20.73	0.29	–	2.65	–	2.75	0.10	–	0.02	–	–	79.27	20.73
762/2	74.11	11.44	0.36	12.10	–	1.05	0.78	0.14	0.01	–	0.01	–	76.45	23.55
763/1	83.80	6.89	2.30	3.67	3.18	–	0.12	0.04	–	–	–	–	89.44	10.56
763/2	83.98	9.14	4.48	2.39	–	–	–	–	–	–	–	–	88.47	11.53

Samples as in Table 1

As it is seen from the table the methane and carbon dioxide contents are between 76–100 and 5–22%, respectively. Only in samples 708/2, 713, 723 and 796 does the CH_4 content decrease to 33–54% together with an increase in CO_2 to 46–67%. This last increase is associated with inclusions of $L_3 + G$ type, where L_3 corresponds to liquid CO_2. These inclusions indicate migration of methane — carbon dioxide fluids, enabling transportation and precipitation of the ore components. In the region of Sojma (sample 796) polymetallic ores occur (Lazarienko *et al.*, 1963). Nitrogen is characteristic only for the samples taken from the boundary between the Dukla zone and the Krosno one, as well as that between the Krosno zone and the Skiba one.

Table 2 gives the hydrocarbon composition of the samples studied, from methane to octane.

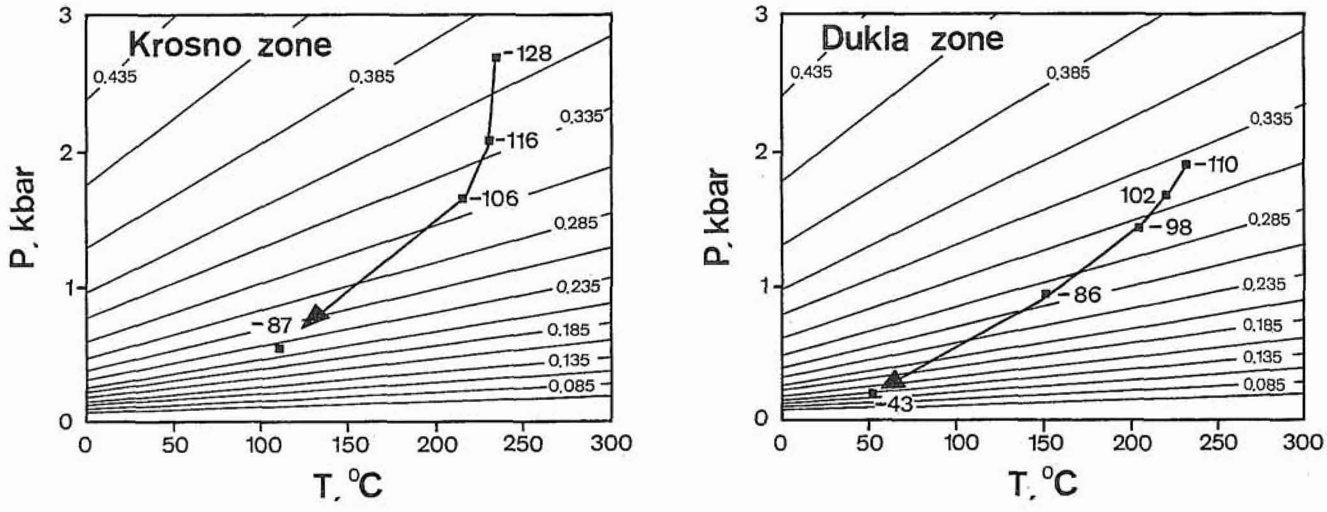

Fig. 6. Results of microthermometric analyses of fluid inclusions in the "Marmarosh diamonds"

Results are shown as a plot of methane isochores (in g/cm^3); the critical isochore of methane lies between 0.135 and 0.185

In general, hydrocarbons from methane to octane occur. Methane predominates with very similar levels in both zones (75.77, 75.01%, respectively). This is a higher percentage of ethylene and propylene in the Krosno zone than in the Dukla one. And, there is a higher percentage of ethane and alkanes in the Dukla zone than in the Krosno zone.

There is a correlation between the composition determined by gas chromatography and the gas composition of the individual fluid inclusions as determined by fluorescence (ultraviolet) and cryometric studies. Liquid hydrocarbons form the inclusions in the Dukla zone (samples: 741 and 762) and in the Krosno zone (samples: 722, 796, 799) displaying a fluorescence in yellow and yellow-orange colours. The hydrocarbon composition of the inclusions is characterised by heavy homologues of methane (from 25.89 to 86.06%).

CONCLUSIONS

The "Marmarosh diamonds" from the Krosno and Dukla zones in the Ukrainian part of the Carpathians display a wide variety of fluid inclusion types.

They include pure methane inclusions, light hydrocarbon inclusions and complex inclusions with bitumens or organic matter. The regions where the light hydrocarbon inclusions occur seem to be the most promising as regards the search for oil and gas.

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