FLUID INCLUSIONS IN "MARMAROSH DIAMOND-LIKE", QUARTZ CRYSTALS FROM CRNGROB, SLOVENIA

BOROJEVIC-SOSTARIC, S.[1], PALINKAS, L. A.[1], STRMIC-PALINKAS, S.[1], HERLEC, U.[2]
[1] Department of Mineralogy and Petrology, Faculty of Science, Horvatovac bb, 10000 Zagreb, Croatia.
[2] Department of Geology, Faculty of Natural Sciences and Engineering, Askerceva 12, Ljubljana, Slovenia.
E-mail: sborojev@iskon.hr

Geological and Mineralogical data

Crngrob, quartz mineralization, hosted in Upper Triassic organic-rich limestones is situated on the eastern slopes of Križna gora Mt., 20 km NW of Ljubljana. This is a vein-type mineralization, containing abundant euhedral quartz crystals with some dolomite and scares adularia. Quartz crystals contain primary, eye visible, liquid-vapor, aqueous and aqueous-hydrocarbon inclusions, that resemble to "Marmarosh Diamonds" (euhedral, oil-bearing quartz crystals from Ukrainian Carpathians, developed within soft Cretaceous-Paleogene sediments). Patches of black organic matter are common constituents of the crystals as well. Mineralization occurs in faults, joints, and fissures and as cavity fills. Quartz crystals are imbedded in clays, placed in-between silificified limestone. Organic-rich limestones with widespread chert nodules, appeared to be of Carnian age, as confirmed by conodonts (Ramovs, 2000).

Fluid Inclusion Characteristics

Fluid inclusion microtermometry, micro Raman analyses and UV microscopy provide data on fluid chemistry. Three major inclusion types were distinguished;

Type (I) Aqueous inclusions with hydrocarbons (L+V); multiphase inclusions with liquid H_2O-phase and hydrocarbon-rich bubble, heavier then CH_4, recognized by yellow fluorescence in ultraviolet light. Clathrate dissociation temperatures were not higher then 13.1°C. Vast majority of Type I inclusions homogenize by vapor disappearance at temperature range between 189° and 308°C, and only two inclusions display homogenization by liquid disappearance at temperature of 380 and 382°C.

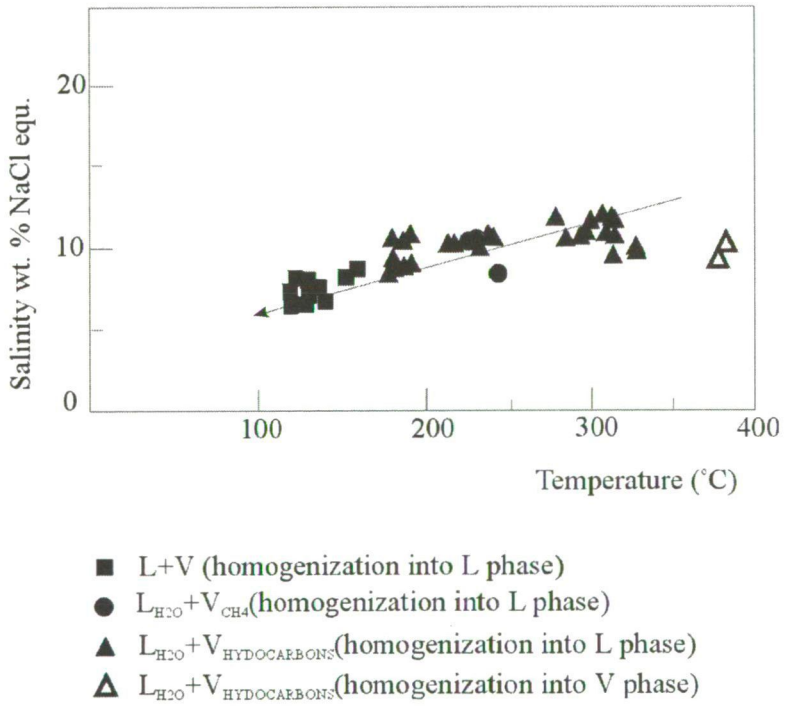

Fig. 1 Temperature of homogenization-salinity relationships in all inclusion typs from Crngrob mineralization.

Type (II) Aqueous inclusions with methane, ($L+V\pm S_{dolomite}$); multiphase inclusions with H_2O liquid phase and bubble rich in CH_4 and dolomite daughter minerals. These complex inclusions show several phase transitions in temperature range from –136° to +242°C, and they all homogenize by vapor disappearance. High positive dissociation temperature of clathrates, from +10.1° up to +13.8 °C indicates presence of CH_4-clathrates. The presence of CO_2 was not observed by micro-Raman spectrometry. Appearance of liquid phase in the crinkled vapor bubble during process of freezing, at temperatures from -87° to –92.5°C indicate presence of methane. Total homogenization by vapor disappearance proceeds at temperature range from 217° to 242°C.

Type (III) Aqueous inclusions, ($L+V\pm S_{dolomite}$); inclusions comprise H_2O liquid phase, bubble without hydrocarbons, and dolomite daughter minerals (determined by Raman spectrometry). Inclusions (L+V) have uniform phase ratio (F = 0.95), and they homogenize by vapour disappearance at a temperature range from 120° to 163°C. Composition, based on the first melting temp, around -50°C, is attributed to H_2O-NaCl-$CaCl_2$ system. Calculated salinity from the final ice melting temperature range from 4.96 – 11.11 wt% NaCl eq.. and ratio NaCl/NaCl+$CaCl_2$ ranges from 0.65 to 0.9. In three-phase inclusions ($L+V+S_{dolomite}$), vapour phase homogenizes into the liquid at temperature range from 152° to 179°C while total homogenization by dissolution of solid phase was interrupted due to decrepitation. Ratio NaCl/NaCl+$CaCl_2$ ranges from 0.75 to 1 (Fig. 1).

Conclusions

Similar quartz crystals, bearing hydrocarbon inclusions have been found in fissures and joints in the Carpatian flysh zone ("Marmarosh diamonds", Vitky et al, 1995) and in low-temperature metamorphic and sedimentary rocks from many orogenic belts around the world; "Herkimer diamonds" in the Apalachian Mauntins (Roedder, 1984), euhedral quartz crystals in alpine fissures in the Alps (Mullins et.al., 1993), Krym Mountains, Ukraine (Gigashvili et al., 1975) and Caucusus, Georgia (Akhvlediany and Gigashvili, 1975). Hydrocarbon inclusions in euhedral quartz crystals from Crngrob, Slovenia, are probably generated during neo-alpine uplift episode, at the late stage of continental collision. The morphology of quartz suggests growth in soft sediments, clay in the veins, of undetermined origin. The fluid inclusion data imply simple evolution of the hydrothermal system. The hot, moderately saline water, from the deeper source, affected organic-rich Triassic dolomites and distilled out higher hydrocarbons, gradually lowering the temperature, and ability to expel higher hydrocarbons except methane. Finally, hydrothermal water became avoided of organics but enriched in Ca-ion due to metasomatic replacement of limestones.

References

AKHVLEDIANY, R. A., GIGASHVILI, G. M. (1975): Inclusions of hydrocarbons in quartz from hydrothermal veins of the Teletskiy Chain. In: KALYUZHNYI, V. A. (1975): Carbon and its Compounds in Endogenic Processes of Mineral Formation (Data on Studies of the Fluid Inclusions). Abstr. Reg. Meet., Lvov, 57-59. (In Russian; translated into English in Fluid Inc. Res. Proc. COFFI, 1975, 8:2).

GIGASHVILI G. I., STUPKA, O. S., PLOTNIKOV, A. M., (1975): Conditions of migrations and evolution of hydrothermal fluids from liquid hydrocarbon inclusions in hydrothermal minerals of the Mountain Krym. In: KALYUZHNYI, V. A. (1975): Carbon and its Compounds in Endogenic Processes of Mineral Formation (Data on Studies of the Fluid Inclusions), Abstr. Reg. Meet., Lvov, 57-59. (In Russian; translated into English in Fluid Inc. Res. Proc. COFFI, 1975, 8:62).

LAMB, W. L., MCSHANE, C. J., POPP, R. K. (2001): Phase relations in the CH_4-H_2O-NaCl system: Comparison of experiments and equations of state. Eleventh Annual V.M. Goldsmith Conference. MULLIS, J., DUBESSY, J., POTY, B., O"NEIL, J. (1993): Fluid regimes during late stage of a continental collision; Physical, chemical, and stable isotope measurements of the fluid inclusions in fissure quartz from geotraverse through the Central Alps, Switzerland. Geochimica et Cosmochimica Acta, Vol. **58**, No. 10, 2239-2267.

RAMOVS, A. (2000): Crngrob, najbogatejše najdišče fosilov in kremenov kristalov v Sloveniji. PROTEUS, **62**, 128-130, in Slovenian.

VITKY, M. O., BODNAR, R. J., DUDOK, I. V. (1995): Fluid inclusions in "Marmarosh Diamonds": evidence for tectonic history of the Folded Carpatian Mountins. Ukraine. Tectonophysics, **255**, 163-174.