CHARACTERISTIC FEATURES OF THE VEIN FORMATIONS IN SE PART OF THE POLISH CARPATHIANS

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Abstract : Quartz, calcite and bitumens are the main vein minerals in SE part of the Polish Carpathians. Quartz has the character of the Marmarosh diamonds and contains various fluid inclusions, both hydrocarbon and aqueous ones. Isotopic and homogenization studies point to the slightly positive delta $^{18}$O composition of the aqueous paleofluids. They were migrating together with hydrocarbon fluids of the methane and light oil compositions.

Key words: vein minerals, calcite, quartz, Marmarosh diamonds, Carpathians

Introduction

Since several tens of years hydrocarbon fluid inclusions have been studied as the indicators of hydrocarbon accumulation and migration in the faulted Carpathians (e.g. Rypin, 1970; Wozniak et al., 1973).

In the present paper - quartz in form of the Marmarosh diamonds, calcite and bitumens were studied in the veins in SE part of the Polish Carpathians aiming at the characteristics of the fluid inclusions there and determination of the character of the migrating paleofluids (Jarmolowicz-Szulc, 2000).

The Marmarosh diamonds are euhedral, transparent quartz crystals which display an ideal crystal habit and contain hydrocarbon inclusions. They were analysed together with the other vein fillings in two tectonic units from the Polish Carpathians in the area spreading from Komancza in the west through Ustrzyki Gorne to the Polish-Ukrainian boundary. Samples were studied by means of different methods, as: isotopic analyses of quartz and calcite; microscopic research on fluid inclusions in quartz; geochemical analyses of the organic matter (Jarmolowicz-Szulc, 2001). The results represent a part of a larger study comprising both sides of the Polish-Ukrainian boundary (Jarmolowicz-Szulc, Dudok, 2000).
Methodology

Studies were conducted in two stages. They comprised research on the vein minerals (calcite, quartz, anthraxolite) and on fluid inclusions in quartz and calcite.

The methodology has been generally based on the standard procedures both in case of the fluid inclusion studies (e.g., Jarmolowicz-Szulec, 2000) and in cases of chemical analyses of minerals (gas chromatography, spectrometry) as well as oxygen and carbon stable isotopes determinations. Some data were obtained for quartz by SIMS method (principles – Hervig et al., 1992).

Sampling was done in the Bieszczady and Bieszczady Foreland in the area spreading from the north-west to the south-east according to the elongation of the main tectonic units – the Silesian and Dukla ones - from Komancza to the Polish-Ukrainian boundary.

Two techniques of the quartz section preparation were used (Jarmolowicz-Szulec, 2001), namely: sample preparation with crystals glued onto the glass slide; sinking of the crystals in the balm and polishing to reach the crystal interior. Calcite was analysed in double-sided polished sections.

The microscopic studies were conducted both in the transparent and reflected lights (UV). Crystals were studied in two size intervals – below 1 mm and between 3-4 mm.

Fluid inclusion studies

Fluid inclusions were observed in fluorescence (uV) and in the transparent polarized lights. It has been generally known due to bibliography (e.g. Walderhaug, 1990) that brines do not fluoresce in contrary to the oils.

In the studied samples several types of fluid inclusions have been stated, in that those of the aqueous solutions and different hydrocarbon fillings. The observed hydrocarbon inclusions display fluorescence in white, white-blue or yellow colours in the ultraviolet. Different quartz samples show differentiated luminescence. Calcite contains small, primary, non-fluorescing aqueous inclusions and secondary, hydrocarbon ones showing blue-white colour of the extinction in uV.

Fluid inclusions were also studied thermometrically, both in heating and freezing modes of the Fluid Inc. System.

The following results may be in short presented basing on the FI studies.

Hydrocarbons are mostly present in the Marmarosh diamonds, in calcite – the aqueous inclusions or (less frequently) gas-liquid hydrocarbon inclusions. The primary inclusions with hydrocarbons may be divided into three phase groups of state. There occur homogeneous and heterogeneous inclusions. The homogeneous inclusions in the solid state comprise different
bitumens. The liquid inclusions, mostly connected with the external crystal growth zones are filled with one or two non-mixing fluids. Gas inclusions contain methane with some admixtures of heavier hydrocarbons. The heterogenic inclusions contain the following fillings: gas and liquid hydrocarbon and aqueous solution; gas and heavy hydrocarbon and aqueous solution and solid bitumens; liquid hydrocarbons and solid bitumens.

**Vein minerals characteristics**

*Quartz* occurs in steep fissures in sandstones and claystones, less frequently in clay schists (Karwowski, Dorda, 1986; Dudok et al., 1997). It forms associations with calcite and black organic matter. In the studied area the Marmarosh diamonds are present in the central parts of the fissures, generally open, which are also filled with brown or white calcite and bitumen concentrations, heterogenetically dispersed. They occur in the asphaltite inclusions, too, being there observable due to the XRD data. Some relation between crystallographic forms of the "diamonds" and the occurrence site may be observed. The prismatic quartz grains with weakly developed rhombohedrons prevail in the calcite fissures, while the domination of the rhombohedron development over the prism seems to be characteristic for the quartz crystals from the asphaltitic fillings.

The isotopic composition of the quartz corresponds in average to delta $^{18}$O$_{SMOW}$ value of about $+22.3$‰ which points to the slightly positive ($+5$‰ to $+10$‰) isotopic composition of the aqueous paleofluid co-occurring with this quartz, if we adopt an average homogenisation temperature of the aqueous inclusions as the trapping estimate (Jarmolowicz-Szulc, 2000).

*Calcite* occurs as the primary mineral in the veins, filling them either totally or partly. It displays a whole fan of colours and a variated crystal habit. Chemically the composition of this mineral is generally homogeneous in both units sampled, but the strontium and zircon contents. These are lower in the Dukla unit.

The isotopic data of delta $^{13}$C$_{PDB}$ and delta $^{18}$O$_{PDB}$ lie for the calcite in the intervals of: from $–3.05$ to $–0.35$‰ and from $–7.56$ to $–9.38$‰, respectively. Oxygen data calculated to SMOW are in their values close to the isotopic data for quartz.

*The organic matter* fills a free space between the calcite grains, forms some inclusions and covers loose crystals. Due to the geochemical studies of the organic matter performed by Kotarba et al. (2000) high values of the hydrogen index have been stated and low values of the delta $^{13}$C (kerogen). The R$_0$ data (results obtained by Kotarba et al., op cit; Swadowska, personal communication) suggest that the primary organic matter had an algal, petroleum-producing character.
Conclusions

The veins in the tectonic units in SE part of the Polish Carpathians (Bieszczady, the
Bieszczady Foreland) are filled with calcite, quartz in type of the Marmarosh diamonds and the
organic matter.

The Marmarosh diamonds there contain differentiated hydrocarbon and aqueous inclusions.

Veins have been formed during the process of migration of complex aqueous-hydrocarbon
fluids. These paleofluids were rich in water, light hydrocarbons (methane) and heavy hydrocarbons
(petroleum), as well as, in some localities, also in the carbon dioxide. Distinct amounts of the
carbon dioxide point to the regions of the ore mineralization.

References

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