On the veinlet-impregnated mineralization in terrigenous strata of the Krosno zone (Ukrainian Carpathians)

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Veinlet-impregnated mineralization is widely distributed in the rock complexes of the Carpathian petroliferous province. It is the consequence of healing fractures formed in the process of formation of great overthrust structures under the influence of the drifting Pannonian plate in the direction of the East European Platform (Vyalov *et al.*, 1981; Matvyenko & Naumko *et al.*, 2004). It is mainly represented by quartz and calcite with admixtures of barite, dolomite, pyrite, halite, gypsum and other minerals (Naumko, 2006). Calcite veins, veinlets and impregnations in the terrigenous deposits of Ukrainian Carpathians are saturated with oil bitumens (in exposures) and oil (in oil fields) noticeably. Regardless of the age of rocks in which they occur (from Cretaceous to Paleogene), the time of the formation of the veinlet-impregnated mineralization is dated as Post-Paleogene (Rypun, 1971).

Significance of its studying within the limits of the Krosno Zone, which is promising for oil and gas (Krupskyi, 2001), is defined by that it can testify to the influence of deep-seated processes in the course of processes of synthesis, genesis and migration of hydrocarbons and their localization in deposits (Naumko, Bekesha, & Svoren, 2008). With that end in view we have studied the veinlet-impregnated mineralization of vein formations in natural exposures of this zone, in particular the Volosyanka, Pre-Duklya, Yavoriv, Lower- and Upper-Turiv and Borynya scales of the Bitlya subcover and the Yabluniv, Ropavske, Limna, Shum'yach-Zavadivka and Gronzyovo scales of the Turka subcover using mineralogical, X-ray powder diffraction and fluid inclusion thermometric methods.

Veins and veinlets fill up ruptures or shear fractures, are deposited on the walls of rock-forming minerals in the form of touchings and hubs. They are mainly subparallel, sometimes of different orientation, often pinched out. The thickness of veins and veinlets is estimated to range from microscopic to over 55 mm.

According to data of mineralogical observations and X-ray analysis it was established that veinlet-impregnated mineralization is mainly represented by calcite with the traces of quartz.

Calcite occurs as granular dense aggregates, druses, sometimes well-facetted crystals (Borynya scale). The size of grains varies from fine-grained (0,1 mm) to coarse-crystalline (4-6 mm).

Crystals are mainly of rhombohedral, prismatic and scalenohedral habit with well-expressed facets of rhombohedron $\{10\bar{1}0\}$ and $\{01\bar{1}2\}$. On the facets one can often observe growth hatching and clevage. Clevage is eminent along the rhombohedron.

The colour of calcite is mainly milky-white, tinted by admixtures of different light colours (grey, yellow), sometimes limpid individuals are also found.

There are two calcite generations. Calcite of the 1st generation is coarser-grained, semi-transparent tinted with yellowish, and calcite of the 2nd generation is opaque, of milky-white colour. X-ray analysis has allowed us to determine insignificant differences in the intensities of calcite of different generations. This can testify to change in the intensity of display of fluid-saturation of migratory mineral-forming fluids.

Inclusions in calcite are located in the healed fractures and along clevage planes (the latter are predominant).

By the phase composition these are one-phase liquid and two-phase – gaseous-liquid. Flat inclusions of irregular form predominate, extended and rectangular ones are present as well. Some vacuoles have a stepped development of the walls that is characteristic of carbonates. In all samples the phenomenon of inclusions unlace is found. Their size is estimated to range from 0.01 to 0.001 mm.

The most widely distributed temperatures of homogenization of fluid inclusions according to data of thermometric analysis are 170-220ºC that correspond to conditions of maximum temperature of preservation of hydrocarbons in the Earth's crust regardless of their origin (Naumko, 2006). The latest inclusions are homogenized at temperatures from 80 to 105ºC. Intermediate value of homogenization temperatures is 135ºC.

Results of our investigations show that veinlet-impregnated mineralization, which is widely distributed in deposits of the Krosno zone of Ukrainian Carpathians, is essentially of calcitic composition, but calcite heals migration fractures in terrigenous strata that cannot be a single source of calcium for the formation of veins, veinlets and impregnations of calcite.

According to data of Svoren & Naumko (2009), the source of Ca+ for the formation of calcite of veinlet-impregnated mineralization is deep-seated high-temperature fluid in the composition of which CaO, CO_2 and CH_4 below 580ºC form a "lime milk". This mixture of CH_4, $Ca(OH)_2$, CO_2, steam – compounds with low coefficients of internal friction migrates at a great distance, in particular in a form of $Ca(OH)_2 \cdot CH_4$, and fills pores, cavities and fractures with the "lime milk".

On decreasing temperatures, they are healed with carbonates that capture relicts of the carbonate-forming medium in the form of inclusions together with methane (and other hydrocarbons).

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