

Results of advanced mineralogical and geochemical studies in the Carpathian mélangé zone and selected units (Polish-Ukrainian-Slovak “triangle”)

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The research concerns fracture fillings from the tectonic mélangé zones in the Carpathians and the tectonic units in the area of the borderland of Poland, Ukraine and Slovakia, as e.g. in the south-easternmost part of the Polish Carpathians (within a sort of a Polish-Ukrainian-Slovakian territorial “triangle”). Samples from two localities have been studied in detail. The following research methods were applied: polarizing microscope (cathodoluminescence analysis – CL, fluid inclusion studies - FI), scanning electron microscope (SEM), X-ray diffraction analyses (XRD) and isotopic analysis, as well as the gas chromatography and Rock-Eval studies of the organic matter. The stress has been recently put onto the geochemistry of the bitumens – both in the association with the minerals and in the rocks. The advanced analyses concerned also whole minerals and the inclusions in them. The minerals, as carbonates, quartz, dark bituminous matter as well, have been filling in fractures and “pockets”. The results obtained are light isotope data for calcite that fall into intervals between 20.6 ‰ and 28.6 ‰ and from -1.4 to +0.5 ‰ for oxygen ($\delta^{18}\text{O}_{\text{SMOW}}$) and for carbon ($\delta^{13}\text{C}_{\text{PDB}}$), respectively. They point to at least two calcite generations. The quartz (the Marmarosh diamonds) displays a wide range of $\delta^{18}\text{O}_{\text{SMOW}}$ values from 14.9 to 22.4 ‰ as it results from point data, and from 23.2 to 27.6 ‰, shown by determinations by a classic method. An increase in almost all determination results towards SE may be noticed. Geochemical analyses of bitumens show a great differentiation in three regions almost in all data. XRD studies of black organic aggregates in the form of lenses point to the presence of the following minerals: quartz, dolomite, calcite, clay minerals, gypsum with anhydrite admixture, traces of pyrite and siderite. Feldspars are also present. The pyrolytic Rock-Eval analysis of samples from the Jablonki region showed a variable TOC in the interval from 0.77 to 35.83% TOC, dependant on the sort of material analysed, generally between 0.77 and 4.44 %, with a low HI (from 30 to 116 mg HC/g TOC). Samples display high degree of thermal evolution, which corresponds to the end of generation processes (the end of the oil window). In the composition of the extractable organic matter, the saturated hydrocarbons constitute a majority of 61.3%, that points to adsorption of the generated or migrating oil. Due to the fluid inclusion studies conducted under the microscope in thin sections (calcite) and in glued wafers or loose crystals (quartz), inclusions were characterized in minerals.

Due to the geochemical analyses of the inclusions in the minerals, it can be concluded that the mineral-forming palaeofluids were light mineralized of the chlorine-sulphate-carbonate type. They were the carrier medium for light and gaseous hydrocarbons. In the localities studied, the mélangé zone near Jablonki - Rabe is the most specific area as for its mineralogical – geochemical complexity. As it further results from FI, the formation conditions for the studied members of parageneses and associations in the regions under research were temperatures of about 240-250 °C and diversified pressures. The formation waters must have had composition higher than 10‰ $\delta^{18}\text{O}_{\text{SMOW}}$. The migrating fluids were mineralized waters and hydrocarbons of different composition. On the base of complex studies and fluid inclusion analyses it may be concluded that the mélangé in the Jablonki region is the most specific zone and a hydrocarbon migration path. Hydrocarbons were generated from the terrigenous organic matter which corresponds to the menilite schists, multifold studied within the Silesian unit.