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Fluid circulation and formation of minerals and bitumens in the sedimentary rocks of the Outer Carpathians – Based on studies on the quartz–calcite–organic matter association

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ABSTRACT

Different methods have been used to examine minerals and/or solid bitumens in three adjacent Carpathian regions of Poland, Ukraine and Slovakia. The minerals fill smaller and larger veins and cavities, where they occur either together or separately. They usually co-occur with the solid bitumens. All $\delta^{13}C_{PDB}$ values measured for calcite lie in a relatively wide interval between −6.25‰ and +1.54‰, while most values fall into the narrower interval from below 0 to about −3‰. The general range of calcite $\delta^{18}O$ results for the whole studied region is between +17.13‰ and +25.23‰ VSMOW or from about −11 to −5‰ VPDB, while the majority of these values are between +20.0 and 23.5‰ VSMOW (−10.53 and −8.00‰ PDB, respectively). $\delta^{18}O_{VSMOW}$ results for quartz vary between +23.2 and 27.6. The carbonate percentage determined in some samples falls between from <2% $CaCO_3$ to >90% $CaCO_3$, while the TOC values changes from 0.09% to over 70%.

The aliphatic fraction predominates in all studied samples, mainly in bitumens and oils. The composition of the aliphatic fraction is relatively homogeneous and points to a strong aliphatic, oil-like paraffin character of the bitumens. Such a composition is characteristic of the Carpathian oils and different from the rocks studied that contain the higher percentage of a polar fraction. The content of the aliphatic fraction in bitumens is only slightly higher than that in two oils used for comparison. The distribution of *n*-alkanes is variable in rocks, solid bitumens as well as inclusions in quartz and calcite. Two groups of bitumens may be distinguished. Those with a predominance of long-chain *n*-alkanes in the C_{25}–C_{27} interval (in some cases from C_{23}–C_{25} and without or with a very low concentration of short-chain *n*-alkanes in the interval of C_{14}–C_{21}) show also a high content of isoprenoids i.e. of pristane (Pr) and phytane (Ph). In all but one bitumen samples, Pr predominates over Ph. The second group comprises oils and rock samples with a characteristic predominance of short-chain *n*-alkanes in the interval from C_{13}–C_{19} and a low percentage of the long-chain *n*-alkanes from the *n*-C_{27}–*n*-C_{33} interval. Pristane and phytane exhibit a concentration comparable to that of C_{17} and C_{18} *n*-alkanes with a Pr predominance over Ph. Due to high maturity, only small amounts of the most stable compounds from the hopane group have been observed in the samples, also oleanane in one case. Among the aromatic hydrocarbons, phenanthrene and its methyl- and dimethyl-derivatives are dominant in bitumens, source rocks and inclusions in calcite and quartz. Occurrence of cyclohexylbenzene and its alkyl-derivatives as well as cyclohexylfluorenes in solid bitumens suggest that they formed from oil accumulations under the influence of relatively high temperatures in oxidizing conditions.

Homogenization temperatures for aqueous/brine inclusions in quartz within the Dukla and Silesian units (Polish and Ukrainian segments) are between 125 and 183.9 °C, while salinities are low in the interval of 0.2–5.5 wt% NaCl eq. The inclusions in calcite homogenize at higher temperatures of almost 200 °C and the brine displays higher salinity than the fluid in the quartz. Two quartz generations may be distinguished by inclusion and isotope characteristics and the macroscopic diversity. Oil inclusions homogenize at 95 °C. One phase inclusions in quartz contain methane, CO_2 and nitrogen in variable proportions.

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1. Introduction

Many previous studies on minerals and organic matter filling veins in the Carpathians have been conducted mostly concerning quartz–calcite and bitumen associations. Tokarski (1905) and Łaszkiewicz (1960) studied the morphology of the vein quartz called the Marmarosh diamonds. Mastella and Kojsar (1975) considered this mineral variety to be the result of the bituminization process of the Podhale area (Central Carpathians). Thermometric and cryometric studies (Kozłowski, 1982) showed the presence of methane and most probably nitrogen in inclusions. Karwowski and Dorda (1986) characterized the environment of formation of the Marmarosh diamonds in the Mszana Dolna tectonic window, while Kozłowski et al. (1996) conducted studies in the central part of the Polish Carpathians. In Ukraine the hydrocarbon inclusions in the Marmarosh diamonds have been interpreted as indicators of hydrocarbon migration and accumulation in the folded Carpathians (e.g. Ripun, 1970; Vozniak et al., 1973). Over the years the problem of hydrocarbon migration has been also discussed in connection with fluid inclusion studies (e.g. Matkovskyi, 1961; Karwowski and Dorda, 1986; Hurai et al., 1989; Vityk et al., 1996).

The clayey and siliceous Oligocene Menilite Formation is believed to be the primary petroleum source rock of the Carpathian flysch with a total organic carbon (TOC) exceeding 20 wt% (Kotlarczyk and Leśniak, 1990; Bessereau et al., 1996; Koltun et al., 1998), and studies on the source rock–oil correlation for the Polish and Ukrainian Flysch Carpathians were performed (Kotarba et al., 2007). The interpretation was based on the comparison of rocks extracts with bulk properties, oil fraction, stable carbon isotopes and biomarker compositions of produced oils (ten Haven et al., 1993) and oils generated during hydrous pyrolysis experiments (Curtis et al., 2004), as well as on the comprehensive biomarker, isotope, oil and gas studies (Kotarba et al., 2007).

The last decade has brought studies on the material filling in the calcite–quartz veins as well as of bitumens and fluid inclusions in the eastern part of the Polish Carpathians and in the western part of Ukraine (Dudok and Jarmołowicz-Szulc, 2000; Jarmołowicz-Szulc and Dudok, 2005). In the Slovak territory in the Western Carpathians, Hurai et al. (2002) studied the origin of methane in quartz.

In the present paper, we report our research conducted in the Dukla and Silesian tectonic zones (Jankowski et al., 2004, 2007; Ślączka et al., 2006) and a part of the mélange zone (Jankowski, 2008). It is a continuation of publications by Dudok and Jarmołowicz-Szulc (2000) and Jarmołowicz-Szulc and Dudok (2005), combining results from three countries – Poland, Slovakia and Ukraine. Earlier papers dealing with fluid inclusions in minerals in the Carpathians (Karwowski and Dorda, 1986; Vityk et al., 1996; Świerczewska et al., 2000; Dudok and Jarmołowicz-Szulc, 2000; Hurai et al., 2002) were mostly limited to sampling in one country and/or within a single locality in the tectonic unit (Fig. 1A and B).

The aim of the present paper is to define the character of mineralization in three adjacent areas in the eastern part of the Western Carpathians and western part of the Eastern Carpathians, and to approximate mineralogical and geochemical conditions of mineral and bitumen formation in the Polish-Ukrainian-Slovak Carpathians (Fig. 1). Studies of both mineral and organic materials filling the fractures in rocks of the Flysch Carpathians were aimed at defining fluid inclusion and TOC contents, the type of the organic matter, thermal maturity and petroleum potential examined in rocks, solid bitumens and minerals.

The results have an interdisciplinary character, and are an example of a combination of field work, mineralogical analysis and organic geochemical analyses.

2. Geological and mineralogical setting

The Outer Flysch Carpathians are an Alpine fold-and-thrust belt, thrusted northeastwards over the European Platform. It comprises several structural units and sub-units composed of nappes and thrust sheets. The arc of the Outer Carpathians (Fig. 1A) is mostly built of folded Cretaceous–Neogene sediments, including stacked thrust sheets: Magura Unit, Dukla Unit, Silesian Unit (called the Krosno Unit in the Ukrainian territory) and the Skole (Skyba) Unit (e.g. Oszczypko et al., 1989, 2006; Ślączka et al., 2006; Janočko et al., 2006). Recently, the Boryslav–Pokuttya Unit has been also defined as a main unit (Jankowski et al., 2004). Folded and thrusted foredeep deposits of Miocene age occur in front of the Skole and Boryslav–Pokuttya Unit. The Silesian Unit (nappe) can be divided into two parts – the Central Carpathian Depression (sub-unit) and the Foredukla sub-unit in Poland (Oszczypko et al., 1989; Rubinkiewicz, 2000; Ślączka et al., 2006). The latter has not been distinguished in Ukraine.

The study area lies in the Western and Eastern Carpathians, along the Polish–Ukrainian and Polish–Slovak frontiers (Figs. 1B and 2). It extends from north-west to south-east from Komańcza through Wołosate in Poland, and from the Stavne to Miezhgorie (Soymy) villages in the Ukraine. In the south it reaches the Dara–Prislop settlements in the Slovak segment. Additionally, two tectonic windows in Poland and Slovakia were included in the study (the Mszana Dolna and the Smilno–Cigla windows, respectively).

According to modern structural concepts, the Polish-Ukrainian-Slovak borderland of the Carpathians includes two main tectonic units: the Silesian–Krosno and Dukla units. The flysch succession of the Polish, Ukrainian and Slovak Carpathians covers a stratigraphic range from Early Cretaceous to Early Miocene. The oldest rocks in the study area are of Early Cretaceous age. The Upper Cretaceous, Paleocene and Eocene successions comprise the flysch sequence with Oligocene-Early Miocene strata at the top. The Menilite Formation, being the principal source rock formation in the Polish, Ukrainian and Slovak Carpathians, shows significant changes in facies and thickness increasing from the Dukla to Silesian units and further toward NE.

Several fracture systems can be distinguished in the Carpathians (Rubinkiewicz, 2000; Tokarski et al., 1999). The fractures which display an orientation of 190–210° and 70–90° are filled with vein minerals such as calcite and quartz, as well as with the organic matter (Ripun, 1970; Dudok et al., 1997). The thickness of these veins varies from microns to cm. The veins occur in the rocks in the Silesian and Dukla units (cf. Dudok and Jarmołowicz-Szulc, 1999). In the adjacent Magura Nappe, the quartz–calcite associations occur in joints and small-scale faults (Świerczewska et al., 1999; Tokarski et al., 1999). Calcite usually is primary. It is white or milky-white, sometimes honey-yellow in color. The individual crystals are twinned and occur in the form of rhombohedrons. In the Krosno unit, the calcite is covered with a thin film of hard bitumens. Quartz occurs in many localities of the Western Carpathians in Poland, Slovakia and Ukraine and is known as the "Marmarosh diamonds". Apart from the hitherto mentioned minerals, dolomite, anhydrite and pyrite are present in the quartz–calcite and quartz–calcite–bitumen veinlets (Jarmołowicz-Szulc and Jankowski, 2010).

3. Methodology

3.1. Sampling

Samples of calcite, quartz, solid bitumens and rocks from different localities in the Outer Carpathians from the Dukla and Silesian units were taken for mineralogical and geochemical analyses. Surface sampling was conducted to provide the best geographic coverage from the parts of these units in the studied area (Fig. 2). Additionally – samples of the solid bitumens, carbonates and quartz