New views on the genesis of the carbon dioxide in the Polish Outer Carpathians

NESTOR OSZCZYPKO, PATRYCJA WÓJCIK-TABOL
and MARTA OSZCZYPKO-CLOWES

Institute of Geological Sciences, Jagiellonian University, Oleandry 2a, 30-063 Kraków, Poland

In the Polish sector of the Magura Nappe have long been known and exploited carbonate mineral waters, saturated with carbon dioxide, known as the "shchava (szczawa)".

These waters are characterized by low mineralization and the content of free carbon dioxide by at least 1 g/dm^3. The total mineralization of these waters is formed by infiltration and circulation of atmospheric waters into the Magura flysch deposits (Oszczypko et al., 1981). Another factor which causes the increase in total mineralization of these waters is the dissolution of rocks involving aggressive, endogenous CO_2.

The origin of carbon dioxide in the "shchava" type of waters is still not clear. Traditionally it held the view that the CO_2 is of volcanic origin, associated with intrusions of the Miocene andesites, in the Szczawnica–Krościenko area, at the front of the Pieniny Klippen Belt (PKB) (see Świdziński, 1972; Birkenmajer, 1956; Rajchel, 2012 and references therein). This hypothesis is not confirmed by isotopic studies (e.g., Leśniak, 1998; Zuber and Grabczak, 1985; Oszczypko and Zuber, 2002), which suggested rather diagenetic or "metamorphic" origin of CO_2. An interesting view on the genesis of CO_2 in the Outer Carpathians expressed Nowak (1924, 1938), which tied them with the oxidation of hydrocarbons. Hydrocarbon chains, kerogen and bitumen are thermally degraded during catagenesis at about 50°C to 160°C. This process corresponds to the cracking stage (breaking of C–C bonds), which produces oil and thermogenic gas, also CO_2 (Tissot and Welte, 1978).

These waters occur mainly between the Dunajec and Poprad rivers in the Krynica facies zone of the Magura Nappe. The exception, are the mineral springs occurring in the Szczawa tectonic window, west of the Dunajec valley. This window belongs to the Grybów Unit and is composed predominantly of Late Eocene-Oligocene deposits, linked the Silesian and Magura successions. Characteristic feature of the Grybów Unit is the presence of dark deposits of bituminous shales, analogous to the Menilite Beds of the Silesian Succession. These deposits generally are considered as the source formations for generation of hydrocarbons in the Outer Western Carpathians (Curtis et al., 2004; Kotarba and Koltun, 2006; Wójcik-Tabol, 2015). The total organic carbon content of the Grybów Unit samples is 0.15–6.16 wt.%. The T_{max} values vary between 436 and 454°C. Kerogen is a mixture of type II and III that is prone to oil and oil/gas production.

The Grybów Unit is situated below the Magura Nappe at different depths, from about 250 m a.s.l. on the north to 2000 m– 5000 m b.s.l. along the boundary with PKB. At same time at the base of the Carpathian flysch over thrust south of the Rabka- Nowy Sącz line temperatures are greater than 150°C. Further south on line Szczawnica-Piwniczna-Krynica these values transgress 300°C.

Mineral composition of the Grybów Unit sediments includes quartz, calcite, dolomite, Na-rich plagioclase, muscovite and clay minerals distinctive on the XRD patterns of whole-rock samples. Share of smectite in mixed-layers I/S ranges from 10 to 30%, reflecting palaeotemperatures >165–140°C. The highest illitization was recognized in the Szczawa tectonic window that correspond with the pattern of temperature at the base of the Carpathian flysch over thrust mentioned above. In terms of chemical composition, samples of the Grybów Unit are depleted in major, minor and trace elements, with the exception of CaO. Some samples are enriched in Fe_2O_3 and MgO. In the samples, Nb/Ta and Zr/Hf ratios almost maintain UCC ratios of 13.33 and 36.42, respectively. Ratios of Y/Ho are about the UCC value of 27 and Th/U ratios of samples are mostly <5 typical to UCC. The most scattered values of these ratios describe the Szczawa tectonic window samples. The REE distribution shows light REE (LREE) sloping down to heavy REE (HREE) on UCC normalized plots (Oszczypko-Clowes et al., 2015). Dolomitization, K-addition (associated with illitization) and fractionation of trace elements are mainly explicit in the Szczawa tectonic window and suggest that rocks were infiltrated by brines, possibly being the "shchava" type.