Acta Geologica Polonica, Vol. 68 (2018), No. 2, pp. 181–206
DOI: 10.1515/agp-2018-0001

The genesis of the carbon dioxide in the Polish Outer Carpathians – Szczawa tectonic window case study – new insight

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ABSTRACT:

Oszczypko, N., Wójcik-Tabol, P. and Oszczypko-Clowes, M. 2018. The genesis of the carbon dioxide in the Polish Outer Carpathians – Szczawa tectonic window case study – new insight. *Acta Geologica Polonica*, **68** (2), 181–206. Warszawa.

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 occur mainly in the Krynica Subunit of the Magura Nappe, between the Dunajec and Poprad rivers, close to the Pieniny Klippen Belt (PKB). The origin of these waters is still not clear, this applies to both "volcanic" and "metamorphic" hypotheses. Bearing in mind the case found in the Szczawa tectonic window and our geological and geochemical studies we suggest that the origin of the carbon dioxide may be linked with the thermal/pressure alteration of organic matter of the Oligocene deposits from the Grybów Unit. These deposits, exposed in several tectonic windows of the Magura Nappe, are characterized by the presence of highly matured organic matter – the origin of the hydrocarbon accumulations. This is supported by the present-day state of organic geochemistry studies of the Carpathian oil and gas bed rocks. In our opinion origin of the carbon-dioxide was related to the southern, deep buried periphery of the Carpathian Oil and Gas Province. The present day distribution of the carbonated mineral water springs has been related to the post-orogenic uplift and erosion of the Outer (flysch) Carpathians.

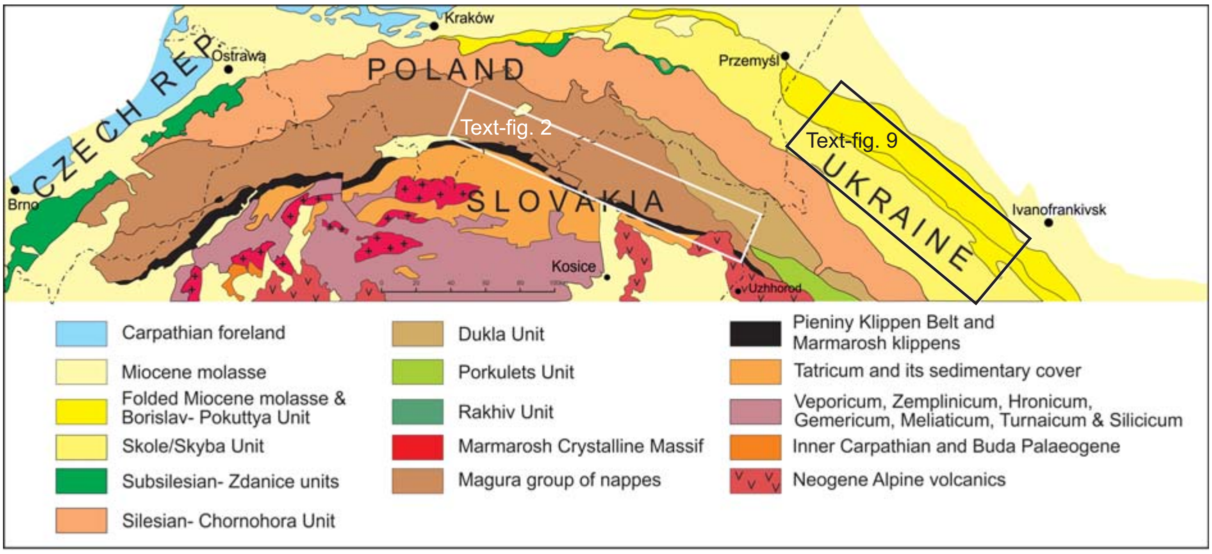
Key words: Outer Carpathians; Grybów Unit; Szczawa tectonic window; Mineralogy; Geochemistry; Organic matter; Carbonate mineral waters; Carbon dioxide.

INTRODUCTION

In the Outer Western Carpathians (OWC) both salted (chloride) and acidic (carbonate) mineral waters have long been known. The chloride waters are usually associated with oil and gas fields, while it has been suggested that the carbonate waters with carbon dioxide are connected with volcanic activity.

In the Krynica Sub-unit of the Magura occur the carbonate mineral waters, saturated with carbon dioxide, commonly known as the "shchava". These waters occur mainly between the Dunajec and Poprad rivers, close to the PKB. An exception are the carbonate mineral springs, placed west of the Dunajec River, in the small tectonic window of the Grybów Unit at Szczawa village (Text-figs 1, 2). The carbonate waters are characterized by low mineralization of dissolved solids and by the content of free carbon dioxide being at least 1 g/dm^3. The mineralization of these waters was formed by infiltration and circulation of atmospheric waters into flysch deposits (eg. Borysławski *et al.* 1980; Chowaniec 2009; Rajchel 2012). 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 the carbon dioxide of the OWC car-



Text-fig. 1. Tectonic sketch-map of the Western Carpathians and adjacent Ukrainian Carpathians (based on Oszczypko *et al.* 2005b)

bonate waters is still under discussion. The most popular is opinion, from the beginning of the last century, proposed the volcanic origin of the CO_2 (Keilhack 1917). An alternative point of view was presented by Nowak (1938), who regarded the carbon dioxide as the final product of complete oxidation of hydrocarbons into CO_2 and H_2O, along the southern periphery of the Carpathian oil and gas province. This point of view was criticized by Świdziński (1965, 1972), who supported the concept of the volcanic origin of the CO_2. These views were partially questioned by isotopic analyses of carbon dioxides from the Krynica sub-Unit (Dowgiałło 1978; Leśniak and Węcławik 1984; Zuber and Grabczak 1985; Leśniak 1998; Oszczypko and Zuber 2002 and references therein) which suggested rather the diagenetic or "metamorphic" origin of CO_2 in this area. Unfortunately these studies did not clarify how geological processes can be responsible for the generation of the carbon dioxide. Recently Rajchel (2012) in a comprehensive monograph "Carbonate waters and water containing carbon dioxide of the Polish Carpathians" associated the origin of the CO_2 with the Miocene andesite intrusions along the PKB.

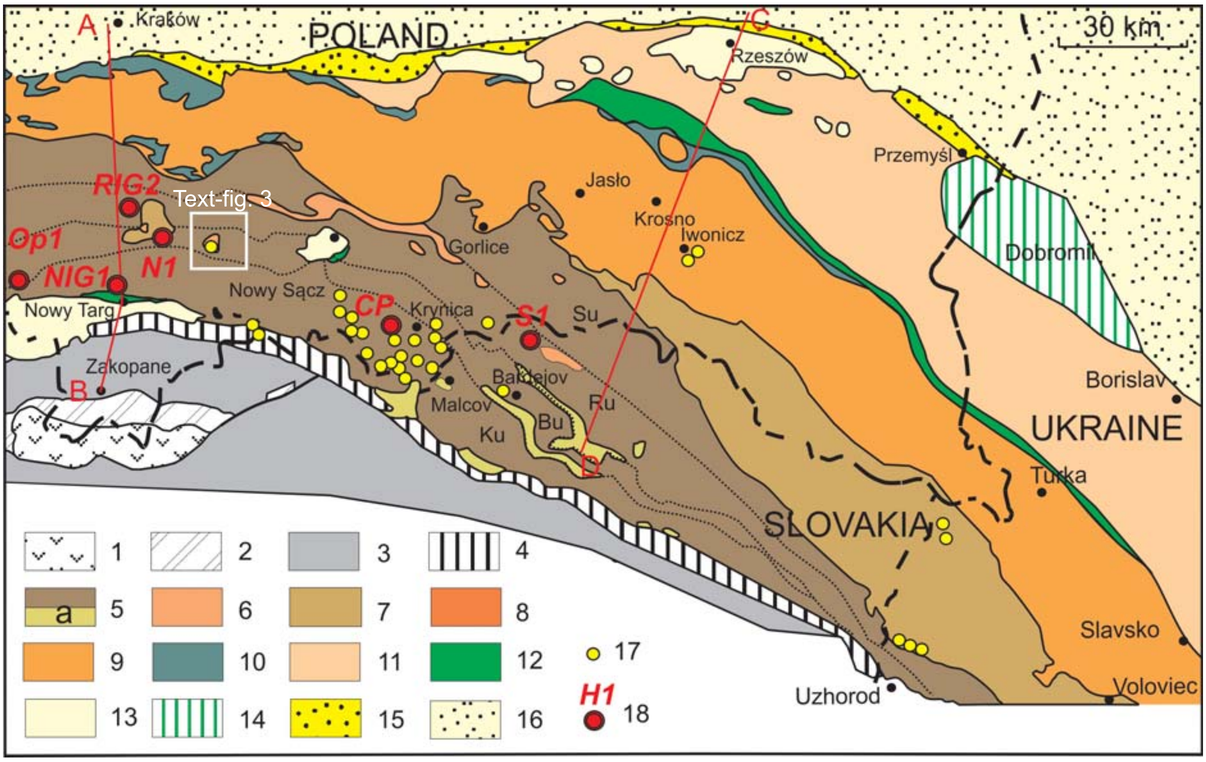
Our interest in the origin of carbon dioxide in the Polish sector of the Magura Nappe has been focused on the case of the Szczawa Tectonic Window (STW) of the Grybów Unit, where the Oligocene bedrock of the hydrocarbons (CH_4) and the carbon dioxide of the carbonate mineral waters coincide. The aim of this paper is attempt to clarify the relationship between the origin of the hydrocarbons, and the genesis of the CO_2 in the OWC.

PREVIOUS WORK

The first detailed distribution and description of the natural carbon-dioxide exhalations in the Polish and Slovak Carpathians has been given by Świdziński (1965). According to this author, the springs of carbonate waters in the OWC are cold and hot (thermal) in the Central Carpathians (CWC). The main area of distribution of carbonate springs is located between the Dunajec and Poprad rivers (Świdziński 1975; Ciężkowski (2002); Chowaniec and Zuber 2008; Miśkiewicz *et al.* 2011; Rajchel 2012). In the Slovakian sector of the OWC carbonate springs are located near Bardejov and Stropkov (Text-fig. 1) .

In Poland Świdziński (1975) described large area of exhalations at Złockie near Muszyna (Text-fig. 1) as well as documenting the close relation between exhalations of carbon-dioxide with springs of carbonate mineral water. This work also included information about the explosion of dry CO_2 with an admixture of CH_4 (5.35–5.70%) in borehole "Zuber"II (Krynica (1933). Taking to account the geological structure of the studied area, Świdziński (1965) came to the conclusion that the CO_2 in these areas is of deep-seated and probably volcanic origin. This paper also reported the case of the carbon dioxide explosion in the Zuber II borehole at Krynica, which took place in 1933. The chemical analysis of dry gas extracted from this drilling showed dominantly carbon dioxide with only a few percents of nitrogen and methane.

The origin of the carbon dioxide in the bicarbonate mineral waters has been discussed by the



Text-fig. 2. Tectonic map of the Northern Carpathians (compiled by Oszczypko-Clowes 2001). 1 – crystalline core of the Tatra Mts., 2 – High Tatra and sub-Tatra units, 3 – Podhale flysch, 4 – Pieniny Klippen Belt, 5 – Magura nappe, 5a – Malcov Formation, 6 –Grybów Unit, 7 – Dukla Unit, 8 – Fore-Magura Unit, 9 – Silesian Unit, 10 – Sub-Silesian Unit, 11 – Skole Unit, 12 – Lower Miocene, 13 – Miocene deposits upon the Carpathian, 14 – Stebnik (Sambir) Unit, 15 – Zgłobice Unit, 16 – Miocene of the Carpathian Foredeep, 17 – mineral springs, 18 – deep boreholes: OP1 – Oravska Polhora 1, RIG-2 – Rabka IG2, N1 – Niedżwiedż 1, CP – Czarny Potok 1, S1 – Smilno 1, NIG1 – Nowy Targ IG1

following authors: Dowgiałło (1978), Leśniak and Węcławik (1984), Leśniak and Dowgiałło (1986), Leśniak(1988), Oszczypko and Zuber (2002) and Kotarba and Nagao (2008) These studies essentially exclude the volcanic origin of the carbon dioxide in the carbonate waters of the OWC.

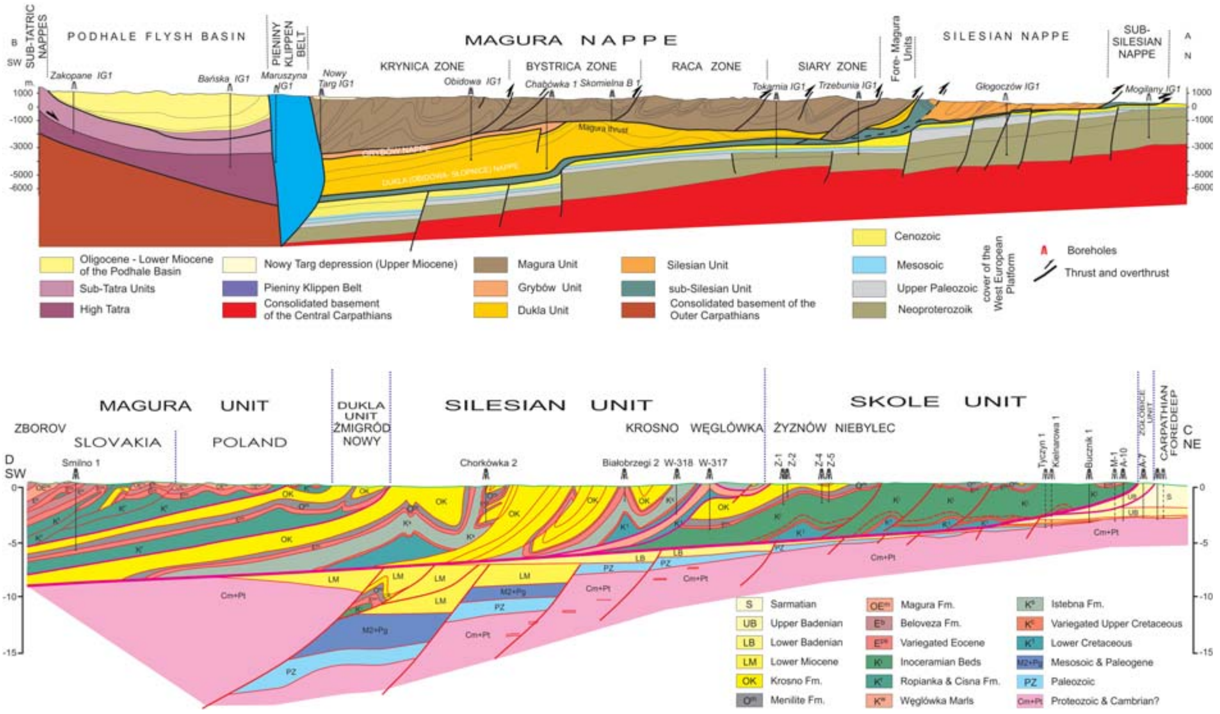
GEOLOGICAL SETTING

In the Magura Nappe of the Polish Carpathians there have been recognized eleven tectonic windows of the Grybów Unit (Książkiewicz 1972, 1977). The majority of them are exposed to the east of the Dunajec River. To the west of Dunajec are located only that at Sopotnia, near Żywiec, and the Mszana Dolna and Szczawa tectonic windows (Text-fig. 2 see also Oszczypko-Clowes and Oszczypko 2004). Further to the West, the Grybów Unit was also drilled, at a depth of 1298–2417 m, in the Oravska Polhora well in Slovakia (Žakovič *et al.* 1989).

The Grybów tectonic windows are dominated by younger deposits (Eocene and Oligocene), such as the Sub-Grybów Marls and the Grybów Shales, equivalents of the Menilite Beds in the more outer units (Skole/Skyba. Silesian and Dukla). These deposits are regarded as the main bed-rocks of the hydrocarbons in the Western and Eastern Outer Carpathians. According to Książkiewicz (1977) the rocks of the Grybów Unit are more intensely altered diagenetically than is the case in the outer tectonic units, because they were covered by the Magura Nappe.

Szczawa Tectonic Window

The Szczawa Tectonic Window (STW) is located 15 km SE of Mszana Dolna, within the Bystrica Subunit of the Magura Nappe. In this area, the oldest deposits of the Bystrica Subunit belong to the Malinowa Shale Formation (Malata and Oszczypko 1990) composed of red, non-calcareous shales. Higher up occur graded calcareous marls (Hałuszowa Formation, op. cit.), thick-bedded, Szczawina Sandstones (Maastrichtian–Palaeocene), Ropianka Beds (Palaeocene) as well as



Text-fig. 3. Geological cross-section Zakopane-Kraków (after Sikora *et al.* 1980; Oszczypko 2006, modified)

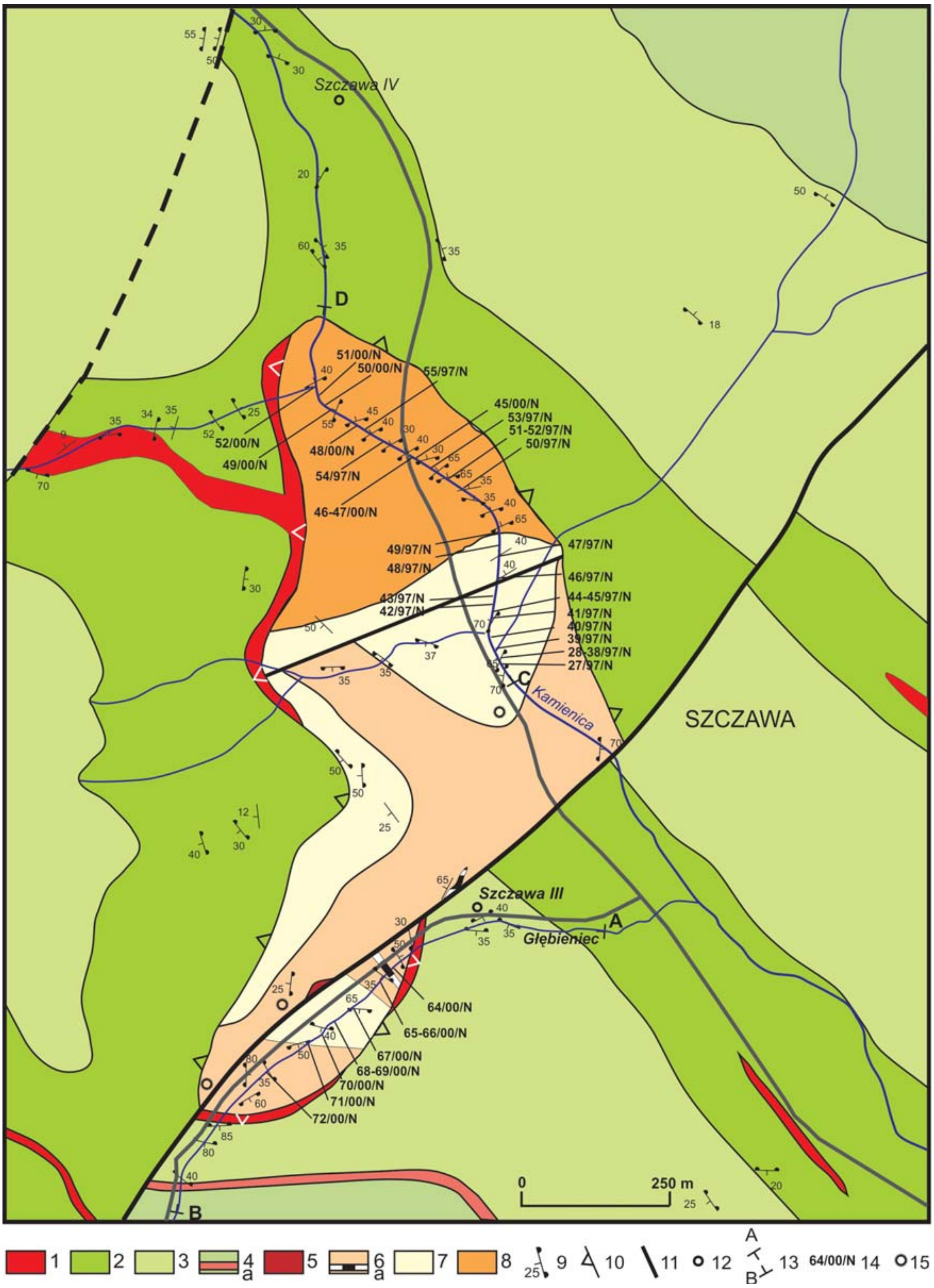
the younger Eocene deposits of the Bystrica Subunit (Łabowa, Beloveza, Bystrica, Maszkowice and Magura formations).

The STW is composed of strongly tectonized Oligocene deposits of the Grybów Unit (Chrząstowski 1971, 1992; Paul 1980; Cieszkowski *et al.* 1987, 1989; Oszczypko *et al.* 1991; Oszczypko-Clowes and Oszczypko 2004) overthrust by the Upper Cretaceous/ Palaeocene deposits of the Bystrica Sub-Unit of the Magura Nappe (Text-fig. 2). The STW is triangular-shaped (ca. 1.1 sq km). Its eastern boundary with the Magura Nappe runs along the NE/SW oriented Głębieniec Fault (Text-fig. 3), while the western boundary is erosive and the Oligocene deposits of the STW dip gently beneath the Magura Nappe (Text-figs 4, 5). On the western periphery of the STW, in the Kamienica valley, the borehole Szczawa IV pierced the Grybów Unit at a depth of 97 m (Text-figs 4, 6).

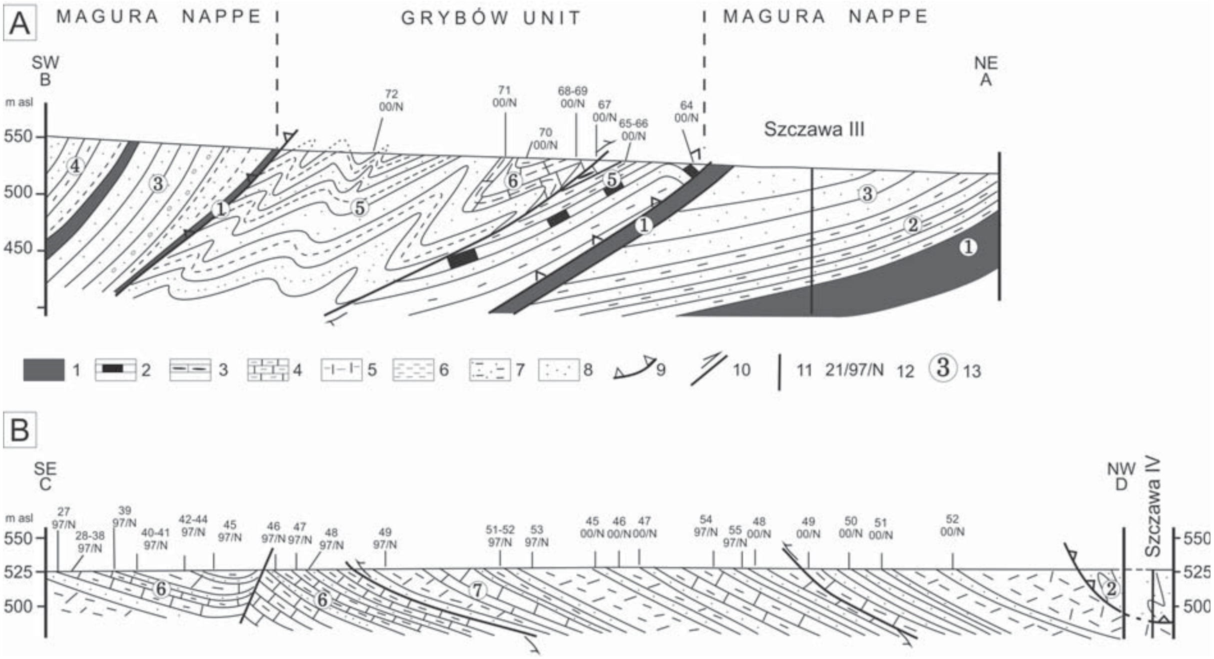
The Oligocene deposits (Grybów and Cergowa beds) belonging to the Grybów Unit (Text-fig. 7A–D) occur beneath the Magura Nappe in the STW. The Grybów Beds are subdivided into two members (Oszczypko-Clowes and Oszczypko 2004). The basal portion of the Grybów Beds, exposed in the lower flow of Głębieniec stream (Text-fig. 7B), is represented by black-brown, massive, non-calcareous shales, with a few intercalations of black hornstones. These shales, up to 60 m thick, have sporadic thin-bedded fine grained glauconitic sandstone intercalations. The upper part of the Grybów Beds, up to 50 m thick, is well exposed in the Kamienica river, is developed as dark grey marly mudstones with intercalations of thin-bedded turbidite sandstones (Text-fig. 7D). These turbidites pass upwards into brown and dark, massive or fine-laminated marls with black marly shales. The total stratigraphic thickness of the Grybów Beds is at least 110 m. The Cergowa beds, up to 200 m thick are composed of thick-bedded conglomeratic sandstones, overlain by laminated marls with thin-bedded sandstones followed by dark-grey massive marls with sporadic intercalations of Cergowa type thick-bedded sandstones. On the basis of their calcareous nannoplankton content the Grybów and Cergowa beds have been included to the Oligocene (Oszczypko-Clowes and Oszczypko 2004).

Borehole Szczawa IV

This borehole, 161 m deep, was drilled in 1980–1981 by the “Hydropol” Company from Kraków. The lithological profile of the borehole was as follows



Text-fig. 4. Geological map of the Szczawa tectonic window. 1-4 – Magura Nappe, 1 – Malinowa Shale Formation (Turonian–Santonian), 2 – Kanina Beds (Campanian), 3 – Szczawina Sandstones (Maastrichtian), 4 – Ropianka Beds (Maastrictian–Palaeocene), a – varigated shales; 5-8 – Grybów Unit, 5 – Eocene variegated shales; Upper Eocene–Oligocene, 6 – Grybów Beds-black non calacareous shales, a – hornstones, 7 – black and grey marly shales and marls, 8 – Cergowa Beds – grey marls and thick-bedded sandstones, 9 – deep and strike, 10 – overthrust, 11 – faults, 12 – borehole, 13 – cross-section, 14 – samples localities, 15 – mineral springs



Text-fig. 5. Geological cross-sections in Szczawa, A – along the Głębieniec stream; B – along the Kamienica stream. 1 – variegated shales, 2 – hornstones, 3 – spherosiderites, 4 – black and grey laminated marls, 5 – grey thick-bedded marls, 6 – black non calcareous sheles, 7 – thin to medium-bedded turbidites, 8 – thick-bedded sandstones, 9 – Magura overthrust, 10 – fault, 11 – sample, 12 – borehole, 13 – lithostratigraphic units: 1 – Malinowa Shale Formation and Hałuszowa Formation, 2 – Kanina Beds, 3 – Szczawina Sandstones, 4 – Ropianka Beds, 5 – Grybów Beds-black non calcareous shales, 6 – black marly shales and marls, 7 – Cergowa Beds

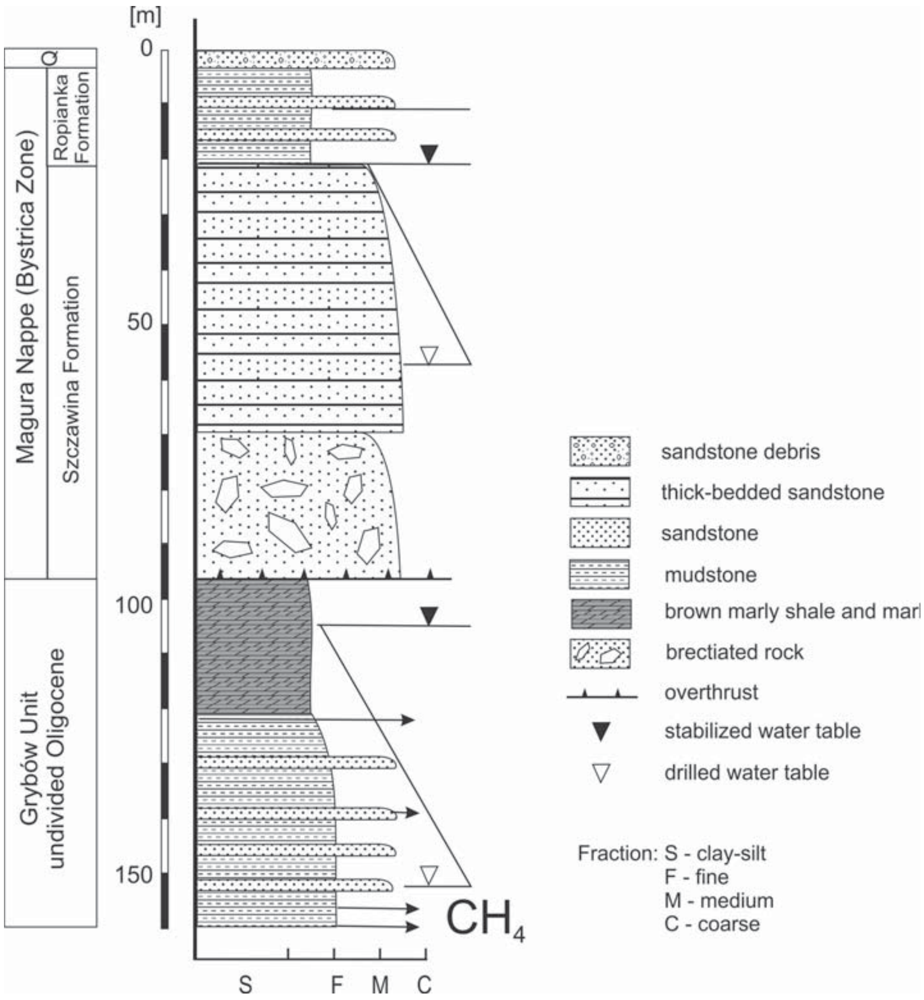
(Text-fig. 6) (m): 0–2 m, weathered clayey sandstone debris (Holocene), 2–11 m, thin-bedded, fine-grained muscovitic calcareous sandstones and grey claystones; 11–70 m, fine to medium-grained, medium to thick-bedded, muscovitic sandstones with calcite veins, 70–97 m, sandstones as above, but strongly fractured, 97–100 m, thin-bedded sandstones and dark grey claystones, 100–122 m, dark-grey and black claystones with intercalations of thin-bedded sandstones, 122–161 m, thin-bedded muscovitic sandstones with intercalations of dark-grey to black claystones. During the drilling, at depths of 122, 140, 155 and 161 m there took place violent outflows of gas (methane). The average measured from the borehole outflow was 2 m^3/h. Following the failure of the well it was abandoned in the interval 101.5–161 m. In the borehole two sub-artesian aquifers were recognized: at a depth of 56 m, stabilized at 12 m, and a depth of 152 m, stabilized at a depth of 106 m. The higher horizon contained fresh water, the lower carbonate mineral water. Given the fact that Szczawa IV was drilled by the impact method, its lithological profile must be restored in an indirect way: to a depth of 97 m probably occurred deposits belonging to the Szczawina Formation (Maastrichtian/Paleocene) of the Magura Nappe, while below 97 m probably occurred the Grybów Formation (Oligocene) of the Grybów Unit.

Mineral waters of the Szczawa tectonic window

Currently in Szczawa there are exploited four sources (springs and boreholes) of mineral water, including 3 located in the Głębieniec valley and one source in the Kamienica valley (Rajchel 2012). The mineral waters are exploited by 5 boreholes with a depth of 8 to 100 m (op. cit). The general mineralization of the water ranges from 5.13–12.69 g/l in shallow boreholes to 16.11–22.36 g/l in deep boreholes with a depth of 82 to 100 m (cited above). The mineral waters contain between three and four ions: HCO_3-Na-Ca + CO_2 and HCO_3-Cl-Cl + Na-CO_2 (Rajchel 2012). In Szczawa IV borehole waters containing Cl-HCO_3-Na-CO_2 were recognized.

Heat flow and geothermal field

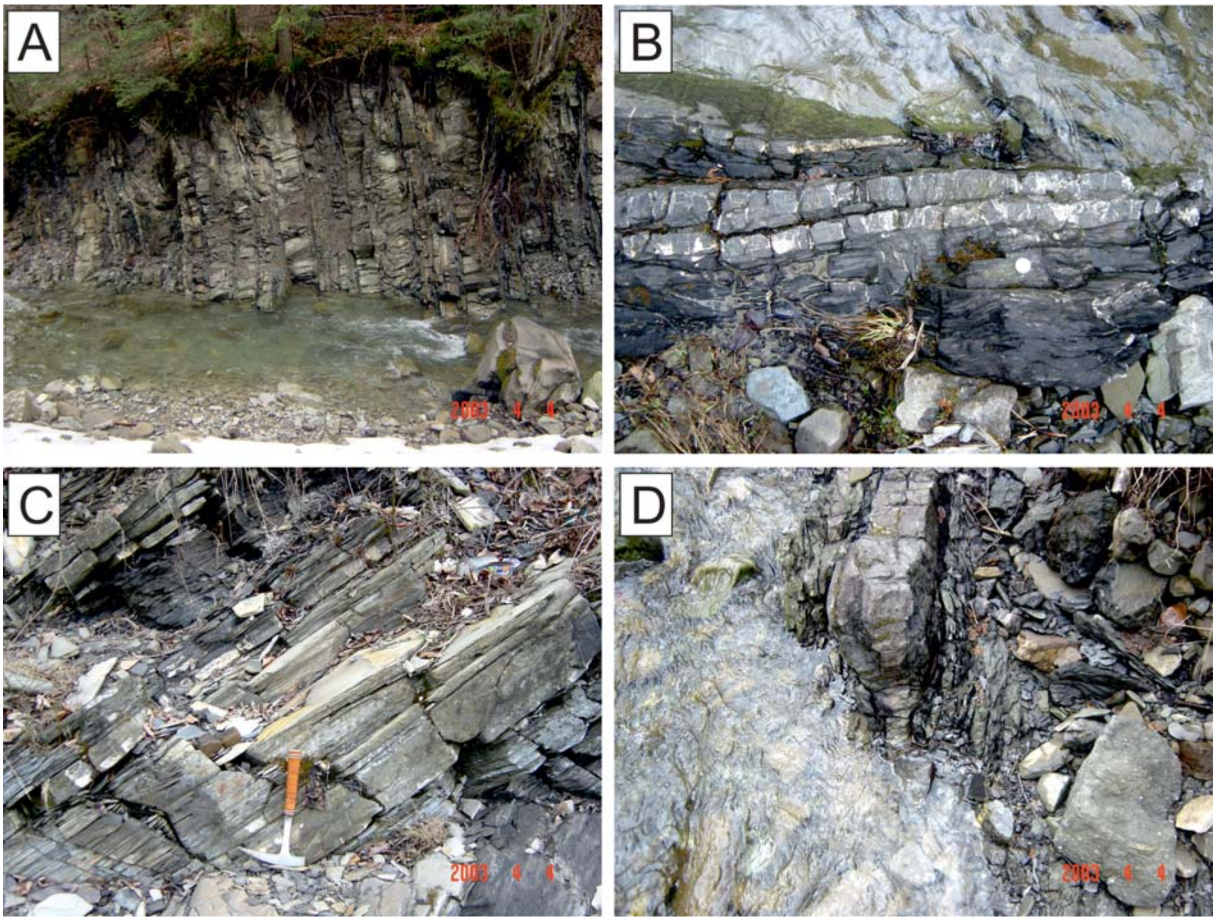
On the basis of the existing data it can be concluded that the area of POC geothermal field displays a generally low surface heat flux. The map of the heat



Text-fig. 6. Szczawa IV borehole

flow of the Carpathian foredeep basin is characterized by values in the range of 50–60 mWm^{-2}. Slightly higher values (60 mWm^{-2}) were recorded in the POC and Podhale region (CWC). In the area of Krynica, these values increase to 70 mWm^{-2}. SE of Krynica at the contact zone between the Magura Nappe and the PKB, heat flux reaches 80–90 mWm^{-2}. In the vicinity of Krynica and Muszyna, reliable geothermal measurements were made in several wells. In Banska IG-1 borehole near Nowy Targ geothermal profiling showed an increase in temperature from 16 °C on the surface to 127 °C at a depth of 4750 m. This makes the geothermal gradient 23.37 °C/km with an average degree geothermal of 42.793 m/°C. Similar geothermal gradients were recorded in bore-holes Maruszyna IG-1 (19.4 °C/km), Obidowa IG-1 (21.0 °C/km) and Poręba Wielka IG-1 (22.7 °C/km). In Eastern Slovakia, 60 km SE of Krynica, at the contact zone of the PKB of the Magura Nappe, Hanušovce 1 borehole was drilled, with a depth of 6003 m. In the interval 10 to 5440 m the average geothermal degree was determined as 34.27 m/°C, i.e. a gradient of 29.18 °C/km (Leško *et al.* 1985). These measurements showed a gradient of 37.96 m/°C (26.34 °C/km) for the depth interval 00–2700 m and 31.74 m/°C (31.51 °C/km) for the interval 2700–5874 m. Another drilling in Eastern Slovakia (Smilno 1 with a depth of 5700 m) was situated within the Magura Nappe (30 km E of Krynica). The geothermal degree here was from 31.25 to 38.25 m/°C (26.14–32.0 °C/km) (Leško *et al.* 1987). Based on extrapolation of the measurements to a depth of 20 km, isotherms for the Bochnia-Krynica section can be constructed. At a that depth the temperature ranges from 400 °C in the Bochnia area to 500 °C in the Krynica area.

After Oszczypko and Hajto (2010), in the area of

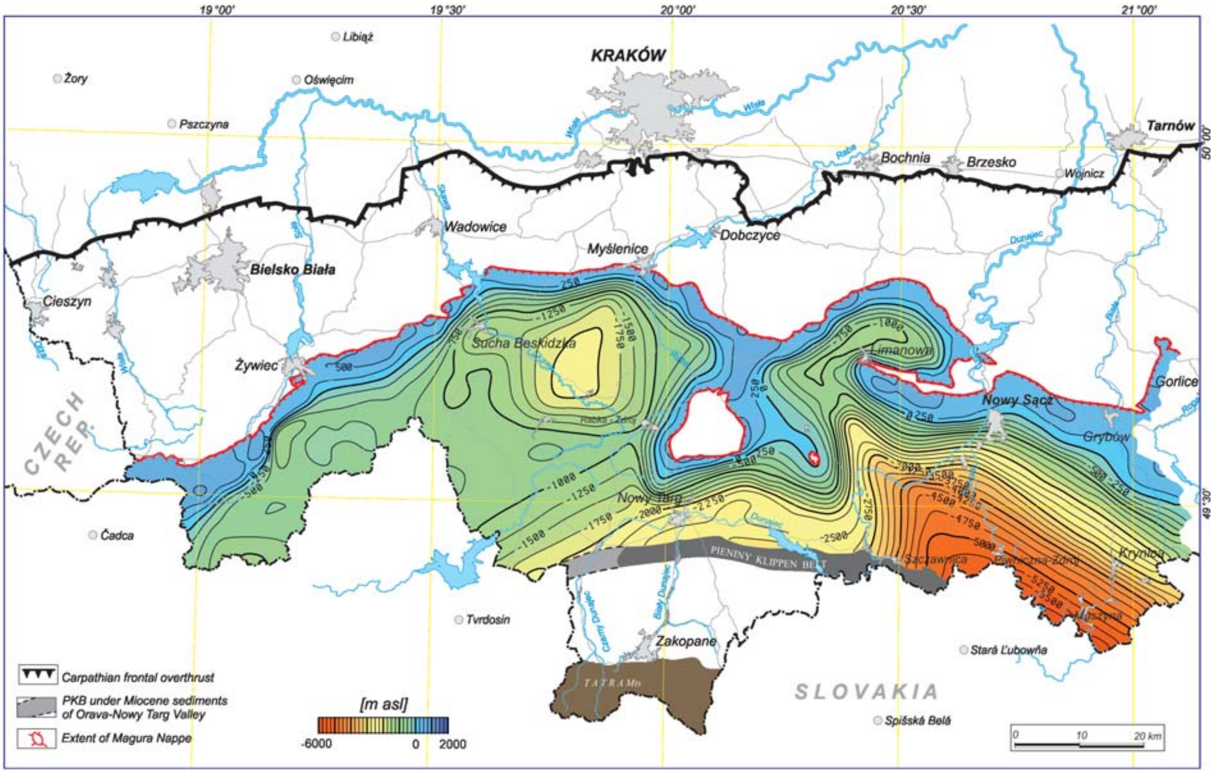


Text-fig. 7. The rocks of the Grybów Unit; A – Right bank of the Głębieniec stream in the Szczawa. The basal part of the Magura Nappe composed of medium to thick-bedded turbidites of the Szczawina Sandstones (Maastrichtian–Campanian); B – Rock Beds of the Głębieniec stream in the Szczawa. The lower part of the Grybów Beds (Oligocene)-black non calcareous shales, with thin-bedded quartzitic sandstones; C – The basal portion of the upper part of the Grybów Beds in the Kamienica stream in Szczawa. Thick-bedded sandstones passing upwards into a thick layer of dark calcareous mudstones. D – The uppermost part of the Grybów Beds (Oligocene) in the Kamienica stream section at the Szczawa. Dark-grey laminated marls with intercalation of thin-bedded sandstone

occurrence of carbonate waters, between Kroscienko on the Dunajec and Piwniczna on the Poprad rivers, the temperature at base of the Magura Nappe ranges from ca. 170–180 °C (Text-fig. 9). At the same time the temperature at the base of the Carpathian Orogeny (ca. 11000 m bsl, Papiernik and Oszczypko 2011) in this area oscillates from 250–350 °C.

The origin of hydrocarbons in the Polish and Ukrainian sectors of the Outer Carpathians

The Carpathian Oil and Gas Province (COGP) is situated along the marginal part of Outer Carpathians in Poland, Ukraine and Romania (Karnkowski 1996; Kolodiy *et al.* 2004, and reference therein). In this area the origin of the hydrocarbons is connected with the Early Cretaceous and Oligocene potential source rocks (Kotarba and Koltun 2006; Kotarba *et al.* 2007; Sachsenhofer and Koltun 2012; Koltun 2013 and references therein). In Poland the hydrocarbon potential of the Early Cretaceous deposits is low or moderate/ while the maturity is low or immature. The most important beds are the Oligocene Menilite Shales widespread in all tectonic units except for the Magura Nappe in Poland and Rakhiv and Marmarosh units in Ukraine. The Total Organic Carbon(TOC) of these shales ranges between 2 and 20%, and similarly the Hydrogene Index (HI) fluctuates between 300 and 600 mg HC/g (Lafargue *et al.* 1994; Ślączka and Kaminski 1998; Kotarba and Koltun 2006). In the Polish sector OWC the hydrocarbon potential has been recognized in several small oil fields of the

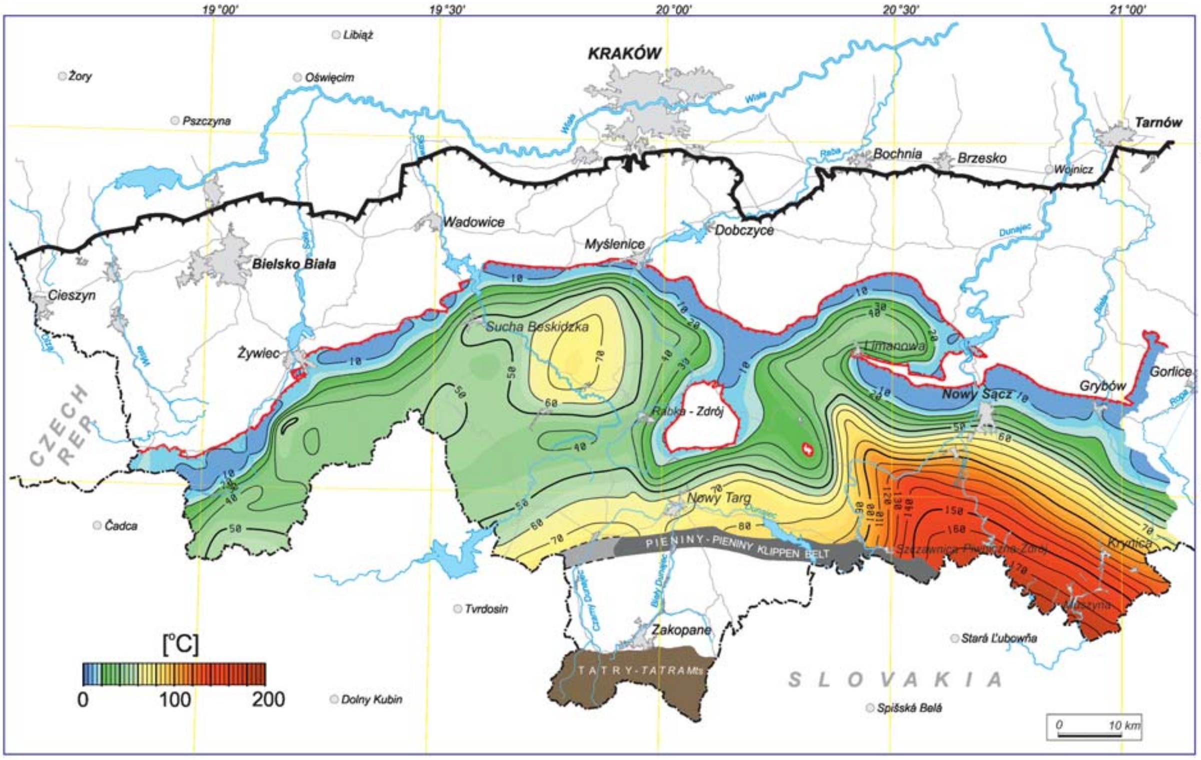


Text-fig. 8. Map of the depth to the base of the Carpathian flysch overthrust in the Magura Nappe (after Oszczypko and Papiernik 2010)

Skole, sub-Silesian, Silesian, Dukla and Fore-Magura/Grybów) units. The most prosperous oil and gas fields have been recognized in the Central Carpathian Depression (Silesian Nappe), between the Biała River on the West and the Polish/Ukrainian boundary on the East (Karnkowski 1996; Kaminski and Ślączka 1998) In the Ukrainian sector the oil and gas are present there in the Boryslav-Pokuttya, Skyba, Krosno/Charnoha and Dukla/Porkulets units. According to Kotarba and Koltun (op. cit.) the Menilite shales display mainly the II and III type of kerogene, and high petroleum potential. The maturation process of organic matter proceeded in two stages, initially with the basin subsidence caused by deposition of the overlying sediments and then during the Miocene by the loading of the overthrusting nappes. The present day position of matured hydrocarbon source rocks at different levels is a result of Early/Middle Miocene nappe thrusting and post Sarmatian or syntectonic erosion (op. cit). In the Polish sector of the WOC, the depth of the thermal maturity of the Menilite shales decreases from north to south: 5000 m (Skole Unit), 1200 m (Silesian Unit) and the present day surface in case of the Dukla and Grybów units (see Kotarba and Koltun 2006). This means that the present day position of the thermal matured/overmaturated Menilite shales of the Dukla and Grybów units is the result of uplift and erosion of the overthrust Magura Nappe (op. cit).

In the Ukrainian sector of the EOC, the Menilite Shales (Borislav-Pokuttya and Skiba units) reach thermal maturity (oil window) at a depth 4.5–6 km (Koltun 2013), and this increases towards the south (Krosno Unit) to surface level (op. cit.) to 5.8–6 km. Below the depth of the "oil window", increase of temperature generated gases, initially dry methane and then carbon-dioxide (Senkovsky *et al.* 2004).

Mineral waters. The Polish Outer Carpathians are dominated by the bicarbonate-sodium type (HCO_3-Na) of mineral water (Text-fig. 10; Boryslawski *et al.* 1980). In the southern part of the Magura Nappe, between the Dunajec and Poprad rivers, these waters are enriched in carbon dioxide (see also Rajchel 2012). Chloride-calcium (Cl-Ca) or chloride-sodium (Cl-Na) and mixed bicarbonate-sodium and chloride calcium (HCO_3-Na/Cl-Na) waters are subordinate (e.g. HCO_3-Cl-Na+CO_2+(H_2S) mineral waters from Rabe with total mineralization up to 5 g/l). In the eastern sector of the Polish Outer Carpathians, mineral waters, associated with oil and gas fields (Boryslawski *et al.* 1980; Porowski 2007), are distributed. According



Text-fig. 9. Map of the distribution of temperatures of the Carpathian flysch overthrust in the Magura Nappe (after Oszczypko and Hajto 2010)

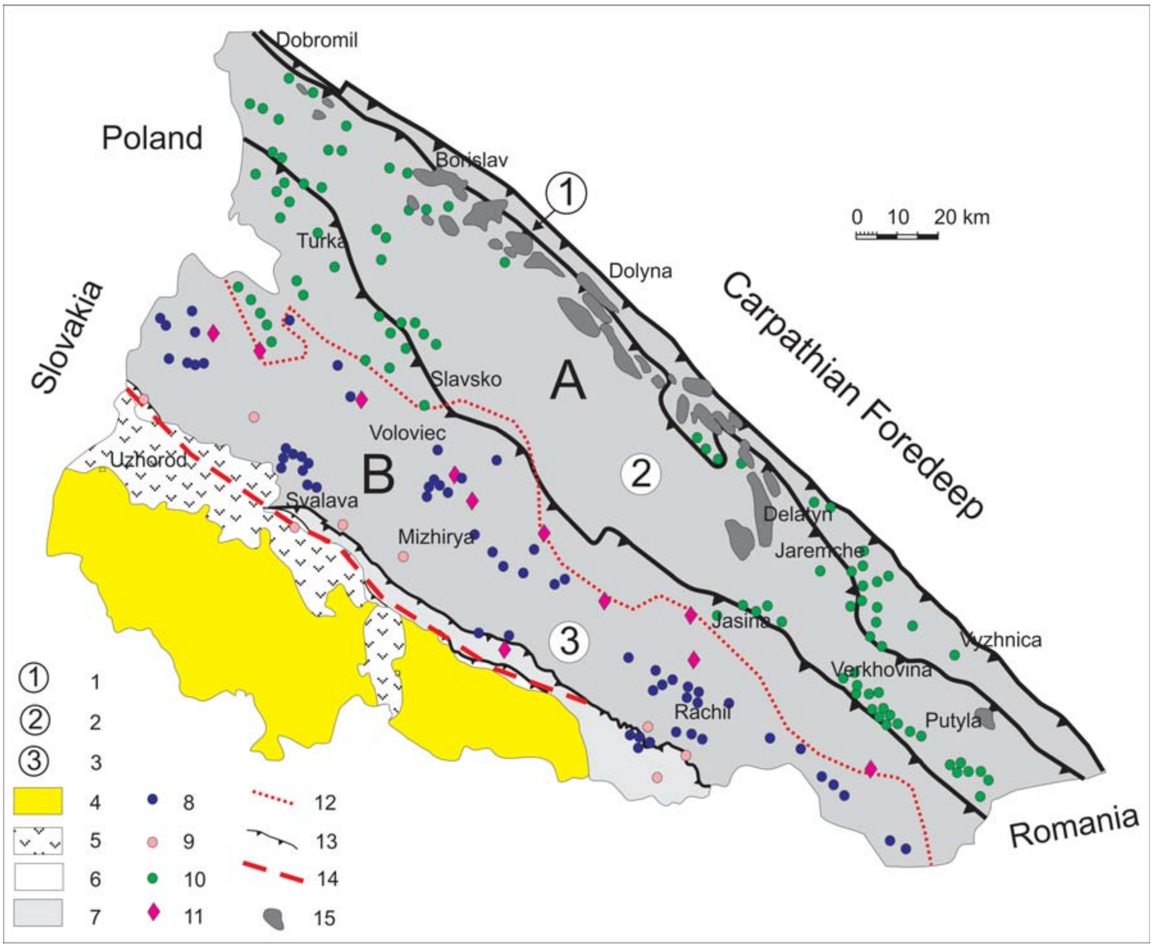
to Boryslawski *et al.* (1980), the mean total content of dissolved solids (in g/dm^3) of these waters, are as follows: Skole Unit (53.2 g/dm^3), Marginal folds of the Sub-Silesian and Silesian units (20.3 g/dm^3), Central Carpathian Synclinorium (13.3 g/dm^3) and Dukla/Grybów units (12.1 g/dm^3). On the plots of mineralization with depth these waters display maximum mineralization, connected with oil and gas traps at depth 400–700 m and below 2200 m (op. cit).

In Ukrainian Outer Carpathians (see Kolodiy *et al.* 2004) mineral waters are known from Skyba (e.g. Hrebeniv, Maidan, Skole); Krosno, Dukla and Magura units (e.g. Rozluch, Kelechyn, Sil, Ust-Chorna, Chornoholova, Soymy and Kostryno). Carbonate waters dominate with carbon dioxide, and with methane in the chloride waters (op. cit). Carbonate waters highly saturated with carbon dioxide (1600–3000 mg/dm^3) are known from the Cretaceous and the Paleogene sediments of the Krosno/Charnohora; Rakhiv and Dukla units, while the methane rich waters occur only at great depths, below the zone of hypergenesis, together with the nitrogen rich waters of the oil and gas fields.

In the Ukrainian Carpathians the zonal distribution of hydrocarbon and hydrothermal fields has been documented (Krupski *et al.* 2014; Shlapinski 2015). The hydrocarbon field is manifested by the occurrence oil fields and manifestations of crude oil (Borislav-Pokuttya, Skyba (Skole) and partly Krosno (Silesian) nappes). The width of this zone oscillates between ca. 30 km at the Ukrainian-Romanian border, and up to 60 km at the Polish-Ukrainian border (Text-fig. 10). The oil fields are limited from the south by the hydrothermal field with mineral waters of the “shchava” type and exhalation of gases (CH_4, CO_2). The northern boundary of the hydrothermal field coincides with the overthrust of the Burkut Nappe. The hydrothermal field from the SE contacts with the Marmarosh Massif to SE and the Vihorlat-Hutin volcanic massif to the NW. This boundary is manifested by carbon dioxide/methane exhalations and the occurrence of the Marmarosh diamonds. Kolodiy *et al.* (2004) recognized in the “Marmarosh diamonds”, in several localities, the inclusion both of hydrocarbons and carbon dioxide (Table 1).

In the Magura Nappe of Eastern Slovakia symptoms characteristic of hydrothermal fields (CH_4 and CO_2) were found, inter alia, in the deep boreholes Hanušovce 1 (6003 m, Leško *et al.* 1985) and Smilno 1 (5700 m, Leško *et al.* 1987).

The position of southern boundary of the Carpa-



Text-fig. 10. Zonal occurrence of hydrocarbons, mineral waters and dry gas exhalations in the Ukrainian sector of the Easter Outer Carpathians (Krupski *et al*. 2014, modified by Shlapinski 2015). 1 – Boryslav-Pokuttya Nappe, 2 – Skyba (Skole) Nappe, 3 – Krosno (Silesian) Nappe, 4 – per-Carpathian Foredeep, 5 – Vihorlat-Gutin volcanic area, 6 – Pieniny Klippen Belt, 7 – Marmarosh units, 8 – mineral water spring and CO2 eruption, 9 – methane exhalation, 10 – oil expulsion, 11 – Marmarosh diamond, 12 – extend of hydrothermal field, 13 – overthrust, 14 – Transcarpathian fault, 15 – hydrocarbon fields, A – hydrocarbon field, B – hydrothermal field

thian Oil Province (COP), in the Polish Outer Carpathians is not so clear. This boundary, with some approximation, can be routed (Text-fig. 10) along the northern boundary of the carbonate mineral waters in the following places: Rabe at the front of Dukla Unit (Bieszczady) and Iwonicz-Rymanów area (Silesian Unit). Further to the west that boundary runs inside of the Magura Nappe (Wysowa, Tylicz, Krynica Muszyna), and along the PKB (Leluchów, Krościenko and Szczawnica).

		CH_4 [wt.%]	N_2 [wt.%]	HHC [wt.%]	H_2 [wt.%]	CO_2 [wt.%]
Lower Cretaceous (Rakhiv Unit)	Kosivka	88.9	11.1			
	Perkalab	91.4		8.1		
Upper Cretaceous (Dukla Unit)	Stavne	89.7	8.1		2.2	
	Luta	97.5	2.5			
Eocene (Silesian (Krosno) Unit)	Sojmy	4.7	7			88.3
Oligocene (Silesian (Krosno) Unit)	Riczka	82.9	7.4		2.4	7.3
	Volovec	97.7	2.3			
	Nyzhni Vorota	62.2	5.4			1

Table 1. Composition of inclusions from the “Marmarosh diamonds” (after Kolodiy *et al.* 2004). HHC – heavy hydrocarbons (bitumens)

West of the Dunajec River this boundary marks the STW, with carbon dioxide rich mineral waters and exhalations of methane (this paper). Exhalations of CO_2 and CH_4 were traced also beneath the Magura Nappe in several boreholes: e.g. Rabka IG-2 and Poręba Wielka IG1 (Paul *et al.* 1996).

The southern border of the COP is defined also by the distribution of the so-called "Marmarosh diamonds", known both from the Ukrainian Carpathians, and the Western Outer Carpathians in Poland and Slovakia (Rabe near Baligród, Velky Lipnik, Koninki and Poreba Wielka in Poland (Burtan and Łydka, 1978) and Oravska Polhora 1 borehole (W Slovakia, Żakovič *et al.* 1989)

THE MINERALOGY AND GEOCHEMISTRY OF THE OLIGOCENE DEPOSITS OF THE GRYBÓW UNIT

The lithology of the Oligocene Grybów Succession in the Szczawa TW differs from that in the Ropa and Grybów TWs. The sediments of the Szczawa TW are more enriched in allochtonous material and they contain less amounts of organic matter. Their counterparts from the Ropa and Grybów TW represent more pelagic, marly sedimentation enriched in organic matter. It might be expected that the macroscopical differences seen would be indicators of variations in the mineralogy and geochemistry. In this work, we compare samples of the Grybów Unit collected from three tectonic windows in terms of their mineral composition, organic petrology, content of organic carbon, type and maturity of kerogen, stable C and O isotopes, and distribution of major and selected trace elements. We take into consideration that the Ropa and Grybów TWs are located in the more marginal, southern part of the Magura Nappe relative to the Szczawa TW. Additionally, the Szczawa TW is the most southern place where the "shchava" waters occur in the Polish Carpathians, whereas in the Ropa and Grybów TWs occur oil and gas instead of mineral waters. We attempt to find proofs that (1) CO_2 was released during kerogen destruction and (2) brines influenced the Grybów Unit more intensely in the Szczawa TW. The results of our mineralogical and geochemical studies are compared with previous works concerning the depth of burial of the Grybów Unit as indicated by the thermal alteration of smectite and vitrinite, its affinity to the hydrothermal and hydrocarbon fields in the Polish and Ukrainian Outer Carpathians and the genesis of carbon dioxide.

Samples and methods

Representative samples of marls, turbiditic mudstones and clayey shales differing in colour (black, brownish-black, olive-green and grey) were chosen for mineralogical and geochemical investigations. They represent the complete sequence from the Sub-Grybów Beds (S-GB) through the Grybów Marl Formation (GMF) to the Krosno Beds in the Ropa, Grybów and Szczawa tectonic windows.

The mineral composition of the rocks was determined using X-ray diffraction (XRD). Twenty samples of rock were ground before testing in a ceramic mortar. The mineral composition analyses were performed using a Philips X'Pert diffractometer with a PW1870 generator and a PW3020 vertical goniometer, equipped with a graphite diffracted-beam monochromator. CuKα radiation was used with an applied voltage of 40 kV and 30 mA current. The random mounts were scanned from 2–64° 2Θ at a counting time of 1 second per 0.02° step.

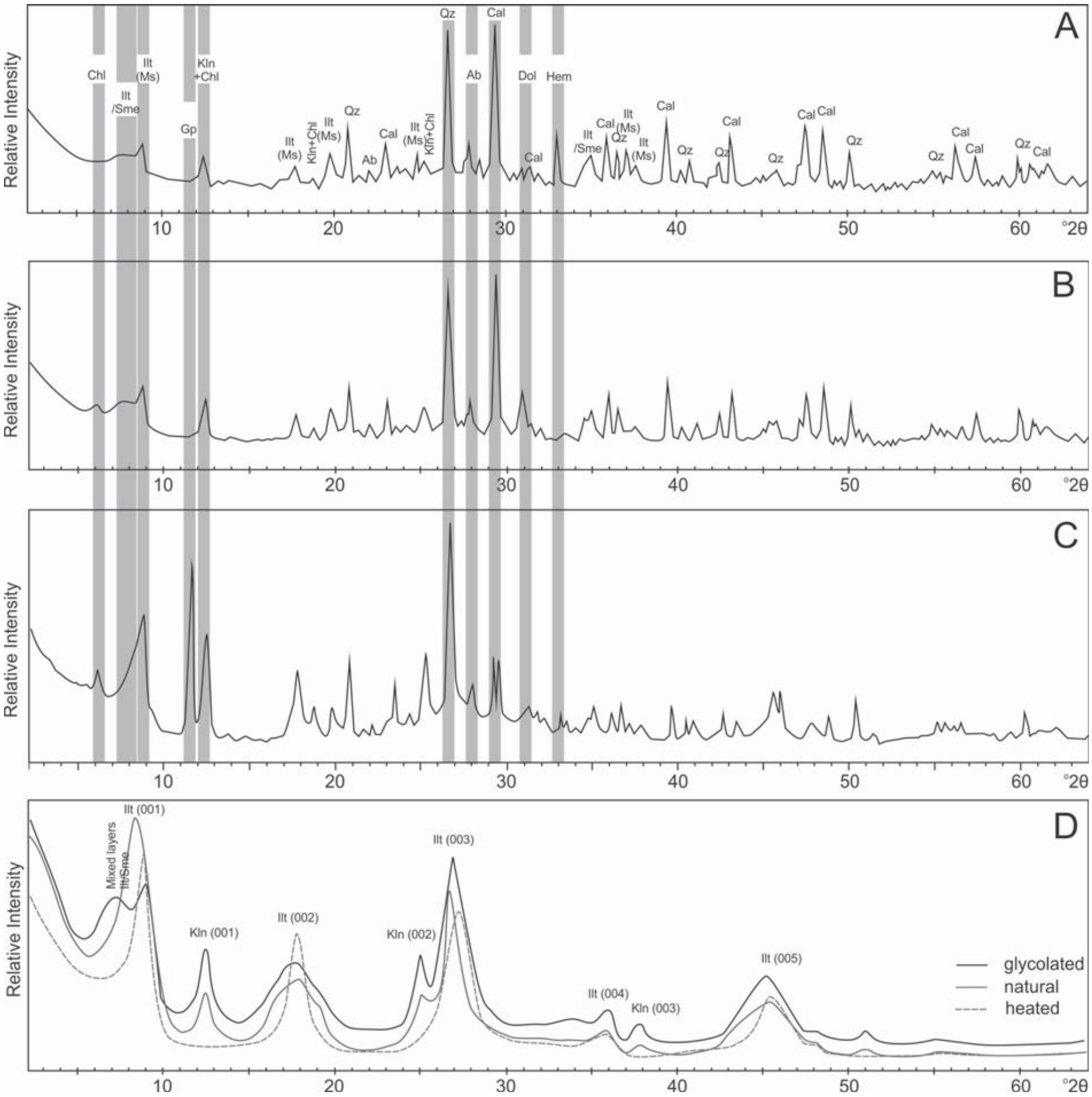
The petrology and microstructures were examined in thin-sections using a Nikon-Eclipse 600 POL polarized (transmitted and reflected) light microscope. Investigations under blue UV light were also performed. The fluorescence microscopy system used is the Nikon-Eclipse 600 microscope which is fitted with a 100 watt mercury lamp equipped with an excitation filter (EX 450–490 nm), dichroic mirror (DM 505 nm) and barrier filter (BA 520 nm) (cf. Wójcik-Tabol 2015, 2017).

In order to determine the type of kerogen and the quality of the organic matter (TOC) contained, 41 samples of brown and black shales and mudstones (Ropa TW and Grybów TW) were analysed by pyrolysis, using a Rock-Eval Model II instrument, equipped with an organic carbon module (for analytical details see Espitalié *et al.* 1985; Espitalié and Bordenave, 1993) at the Petrogeo Laboratory, Kraków (cf. Wójcik-Tabol 2015, 2017).

Stable carbon isotopes were analyzed in 18 samples which were the richest in TOC (Table 1). The $\delta^{13}C$ values were normalized to NBS-22 and USGS-24 international standards and then reported to the international Pee Dee Belemnite (VPDB) scale (Coplen *et al.* 2006). The analytical precision was ± 0.03‰.

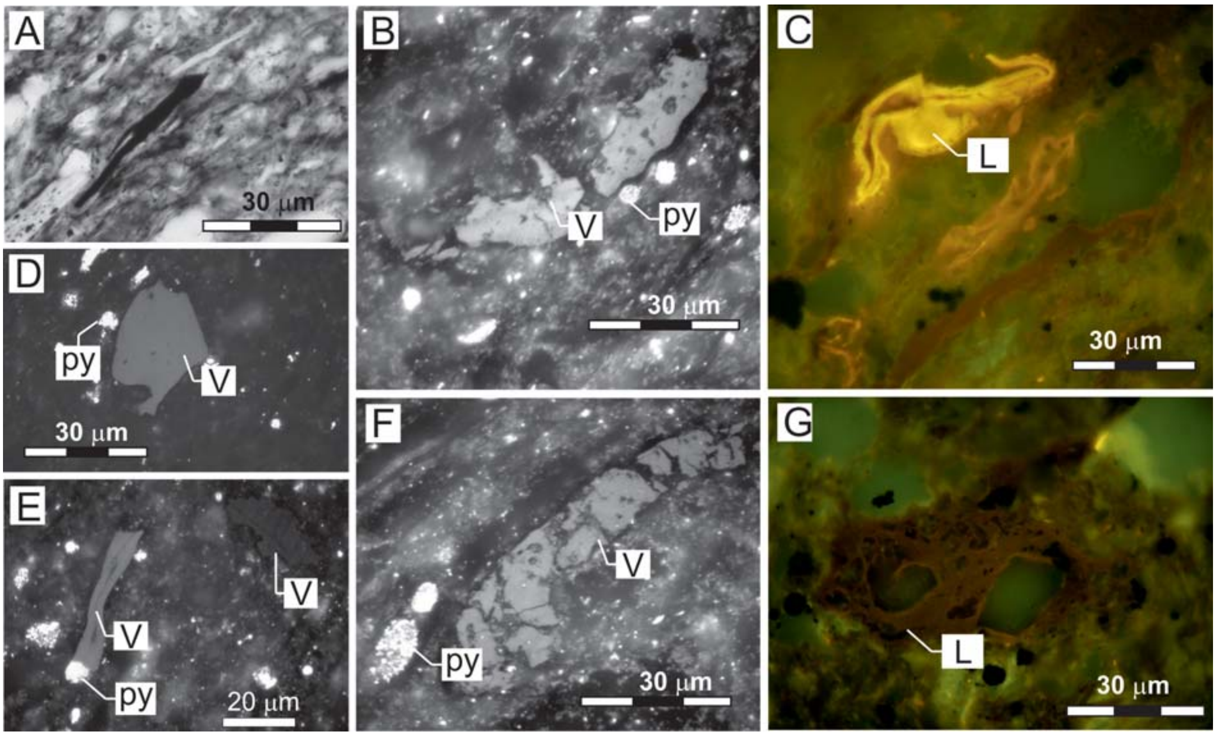
Twenty one calcareous samples from the Ropa TW and Grybów TW were also analyzed for stable isotope $\delta^{13}C_{carb.}$ and $\delta^{18}O$. The isotopic analyses were carried out in the Laboratory of Isotope Geology and Geoecology at Wrocław University.

The XRD and optical analyses were performed at the Institute of Geological Sciences, Jagiellonian



Text-fig. 11. XRD patterns of samples studied, A – Brown marl of GMF, Grybów tectonic window; B – Brown marl of GMF, Ropa tectonic window; C – Grey calcareous mudstone of the GMF, Szczawa tectonic window; D – XRD diffractogram for untreated, heated, and glycolated clay separates from the GMF sample. Abbreviations: Ab – albite, Cal – calcite, Chl – chlorite, Dol – dolomite, Hem – hematite, Ilt/Sme – illite/smectite, Kln – kaolinite, Ms – muscovite, Qz – quartz (abbreviation according to IMA, Whitney and Evans 2010)

University, Kraków, Poland. Sixty rock samples (30 of Ropa TW, 22 of Szczawa TW and 8 of Grybów TW) were crushed and hand-pulverised in an agate mortar and pestle to give a fraction passing 200 mesh. A sample amount typically 0.2 g dry weight was decomposed by lithium borate fusion and dilute acid digestion before a classical whole-rock analysis by ICP emission spectrometry. ICP-OES analyses of the major oxides package includes SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O, K_2O, TiO_2, P_2O_5, MnO, Cr_2O_3 and loss on ignition (LOI), which is measured by weight difference after ignition at 1000 °C.Trace element contents were determined through the ICP-MS technique (ACME Analytical Laboratories, Ltd., 2013). Geochemical analyses were conducted at the ACME Laboratory in Vancouver, Canada.



Text-fig. 12. Polarized light photomicrographs, A, B, D, E, F – Grey mudstones of the GMF from the Szczawa TW (A, B, D, F) and Ropa TW (E) containing vitrinite macerals, transmitted light, parallel nicols (A) and reflected light (B, D, E, F); C, G – Liptinite macerals in the GMF brown marl from Szczawa TW (C) and Ropa TW (G), UV blue illumination. Modified after Wójcik-Tabol (2017). Abbreviations: L – liptinite, V – vitrinite, py – pyrite

The contents of the major, minor and trace elements in the studied material were compared to those in the standard sediments: Post-Archean Australian Shale (PAAS after Taylor and McLennan, 1985), average shales (Wedepohl 1991) and upper continental crust (UCC after Rudnick and Gao 2003; Hu and Gao 2008). The Eu anomaly expressed by the Eu/Eu* ratio was calculated using Eu/Eu* = Eu_N /(Sm_N x $Gd_N)^{0.5}$ ratio. The Ce anomaly was calculated, using the formula Ce/Ce* = $Ce_N/(La_N \times Pr_N)^{0.5}$, where $_N$ means element content normalized to UCC.

Mineralogy and petrographic features

The sediments of the Grybów Unit consist of quartz, calcite, Na-rich plagioclase, muscovite and clay minerals all distinctive on the XRD patterns of whole-rock samples (Text-fig. 11A–C). Some levels of the S-GB and GMF (e.g., samples 19/02/N, 24/02/N, 16/05/N and 33/05/N; G 1/02, 38/97/N, 39/97/N) display clear peaks of dolomite or gypsum. The rocks collected from the Grybów TW are the most calcareous, while the Szczawa TW is enriched in quartz and mica.

The clay mineral assemblages obtained by XRD for the fractions < 0.2 µm involve illite, mixed-layered illite-smectite (I/S), kaolinite and chlorite. In the Grybów Unit, the percentage of smectite in the I/S varies from 20 to 30%. Oligocene rocks in the Grybów TW contain about 10% of S in the I/S (Text-fig. 11D). The I/S is commonly recognized as a palaeotemperature indicator (Pollastro 1993; Środoń 1995). The thermal alteration of the GMF from the Grybów TW and Ropa TW reflects palaeotemperatures of about 140 °C (Wójcik-Tabol 2015), similar to that of the Smilno and Świątkowa tectonic windows , whereas the thermal overprint of GMF registered in the Szczawa TW corresponds to > 165 °C (Świerczewska 2005).

The organic matter revealed during the thin-section examination is represented by translucent macerals of the liptinite groups associated with opaque vitrinite and intertynite (Text-fig. 12). The liptinite macerals are derived from the waxy and resinous parts of plants (spores, cuticles, and resins). Alginite, produced by algae, is a special, possibly marine type of liptynite. The macerals association typical of the

			T_{max}	S1	S2	S3	TOC	HI	OI	Ro	T calc.	δ^{13}C carb.	δ^{18}O
			°C	mg HC/g rock	mg HC/g rock	mg CO_2/g rock	wt.%	mg HC/g TOC	mg CO_2/g TOC		°C	‰	‰
Ropa tectonic window	Sub-Grybów Beds	15/02/N	443	0.39	1.56	0.41	1.25	124	32	0.81	119	n.d.	n.d.
		16/02/N	436	0.2	0.17	0.07	0.19	89	36	0.69	105	n.d.	n.d.
		20/02/N	445	0.4	0.21	0.34	0.18	116	188	0.85	122	n.d.	n.d.
		23/02/N	443	0.53	0.97	0.45	0.66	146	68	0.81	119	n.d.	n.d.
		24/02/N	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-2.53	-6.74
		1/07/N	444	0.19	0.28	0.5	0.45	62	111	0.83	121	-2.49	-6.16
		28/05/N	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	Grybów Marl Formation	25/02/N	438	0.18	0.29	0.09	0.15	193	60	0.72	109	-2.67	-4.64
		27/02/N	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-3.46	-5.56
		28/02/N	440	0.27	1.41	0.26	0.82	171	31	0.76	113	n.d.	n.d.
		31/02/N	442	0.23	0.44	0.35	0.41	107	85	0.80	117	n.d.	n.d.
		36/02/N	449	0.65	1.32	0.39	1.19	110	32	0.92	129	-0.01	-2.40
		37/02/N	454	0.55	1.08	0.52	1.31	82	39	1.01	136	-0.81	-3.07
		16/05/N	447	1.72	9.26	0.81	5.68	163	14	0.87	124	-4.85	-2.19
		15/05/N	446	0.91	3.1	0.47	1.55	200	30	0.89	126	-0.11	-3.57
		18/05/N	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-6.63	-4.94
		19/05/N	449	1.78	9.05	0.31	1.59	569	19	0.92	129	n.d.	n.d.
		20/05/N	445	1.03	6.16	1.42	4.86	126	29	0.85	122	-5.19	-3.71
		30/05/N	444	0.68	3.5	0.35	2.3	152	15	0.83	121	-3.25	-4.69
	Krosno Beds	32/02/N	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-1.18	-4.80
Grybów tectonic window	Sub-Grybów Beds	G1/02	440	0.4	0.67	0.6	0.45	148	133	0.76	113	-1.33	-1.46
		G2/02	441	0.31	1.27	0.34	0.69	184	49	0.78	115	n.d.	n.d.
		G5/02	441	1.05	8.74	0.55	3.64	240	15	0.78	115	-2.25	-2.92
		G6/02	444	0.7	3.68	0.42	0.65	556	64	0.83	121	n.d.	n.d.
	Grybów Marl Formation	G7/02	444	1.55	10.34	1.41	6.16	167	22	0.83	121	-3.40	-3.47
		G8/02	446	0.45	1.2	1.17	1.26	95	92	0.87	124	n.d.	n.d.
		G9/02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-3.09	-3.72
		G10/02	446	0.52	1.85	0.72	0.64	286	112	0.87	124	-1.10	-2.56
		G11/02	444	1.04	7.53	0.57	3.9	193	14	0.83	121	-4.33	-4.76
		G12/02	442	0.61	5.17	0.81	2.89	180	28	0.80	117	-1.26	-2.68
	Krosno Beds	G13/02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-1.68	-4.80
		G17/02	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-1.75	-2.55

Table 2. Rock-Eval pyrolysis data and stable isotopic composition of carbonates (δ^{13}Ccarb. and δ^{18}O) for selected samples of the Grybów Unit sedimentary succession. Modified after Wójcik-Tabol (2015, 2017). n.d. – no data. Ro values were calculated from the formula $Ro = (0.0180 \times T_{max}) - 7.16$ according to Jarvie et al. (2001). Palaeotemperatures Tcalc. were calculated using formula $Tcalc. = (\ln Ro + 1.68)/0.0124$ according to Barker and Pawlewicz (1994)

Grybów TW and Ropa TW is liptinite with trace to minor amounts of vitrinite and inertinite (Wójcik-Tabol 2015, 2017).

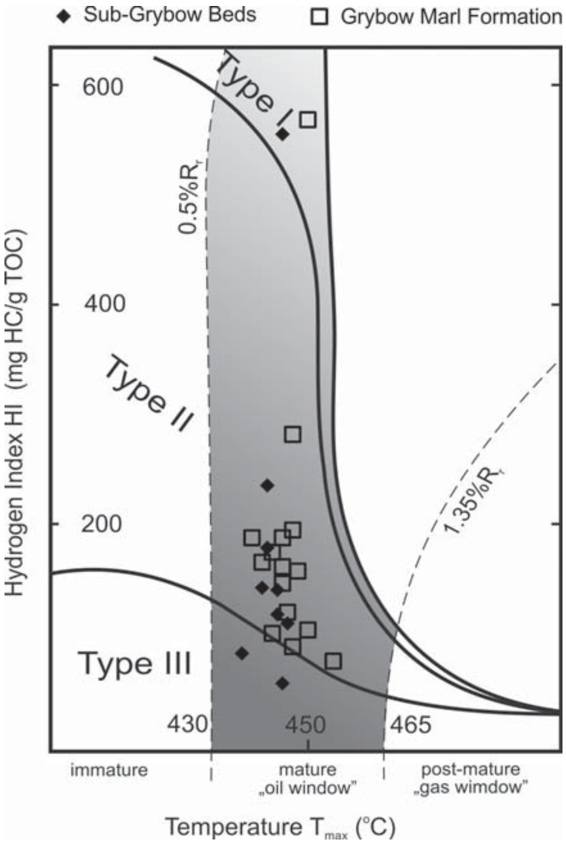
Vitrinite and inertinite macerals derived from woody tissue are prevalent in the Szczawa TW samples. They are structured plant pieces or amorphous and opaque fusainized (high-carbon) material originated from plant material transformed by intense degradation.

The Szczawa TW samples contain a lot of opaque organic debris, whereas the samples of Grybów TW and Ropa TW are enriched in translucent liptynite macerals.

Rock Eval pyrolysis

The total organic carbon content of the samples studied is from 0.15 to 6.16 wt.%. The highest values of TOC are obtained for the brownish-black marly shales of GMF from the Grybów TW. The lowest organic carbon contents (< 0.5 wt.% TOC) characterize grey and green samples (Table 2).

The T_{max} values vary between 436 and 454°C. In the T_{max} *vs.* HI diagram (Text-fig. 13), the samples plot in the field of mature (oil-prone) kerogen type II, admixed with kerogen type III. High values of HI (>200 mg HC/g TOC) suggest that some samples of



Text-fig. 13. Discriminant crossplot of HI *vs.* T_{max} for organic maturity and kerogen type, after Wójcik-Tabol (2015, 2017). Maturity paths of individual kerogen types after Espitalié *et al.* (1985). Abbreviation: Rr – vitrinite reflectance scale

the GMF (G5/02, G 6/02, G10/02, 19/05/N) contain addition of kerogen type I.

Values of T_{max} were re-calculated into vitrinite reflectance values using the equation proposed by Jarvie *et al.* (2001). The Ro values vary between 0.69 and 1.01%, indicating paleotemperatures range 105–136 °C, calculated from the formula according to Barker and Pawlewicz (1994). Values of vitrinite reflectance obtained for the Grybów Unit of the Szczawa TW are from 0.42 to 0.64%, indicating thermal alteration in the 66 to 100 °C range (Zielińska 2017).

Chemical composition

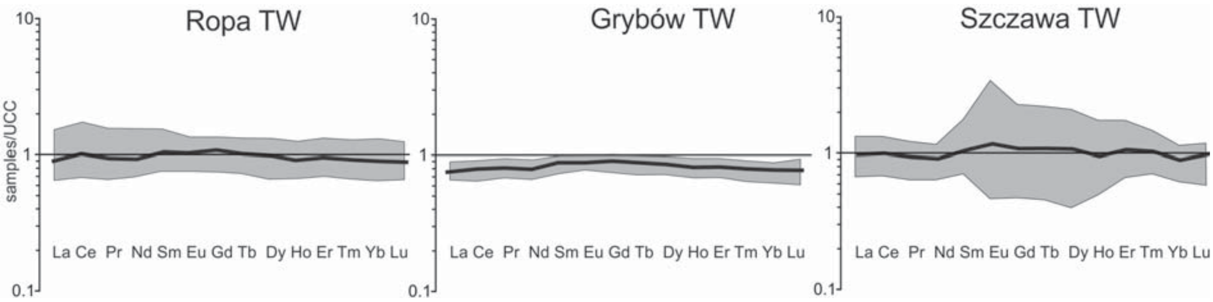
The contents of major oxides, minor elements and trace elements in the Grybów Unit samples are shown in Table 3. The chemical compositions of standards, i.e. Post-Archean Australian Shale (PAAS; Taylor and McLennan 1985) and Upper Continental Crust (UCC; Rudnick and Gao 2003; Hu and Gao 2008) are also listed for comparison. The samples studied are depleted in major, minor and trace elements, with the exception of CaO. The content of CaO is related to calcite, while Al_2O_3 and SiO_2 are recognized as representing allogenic phyllosilicates and quartz, respectively. Some samples of the S-GB (19/02/N, 24/02/N, 24/05/N) and the GMF (16/05/N, G 7/02, G 8/02, 33/97/N, 34/97/N, 35/97/N) are enriched in Fe_2O_3.

The material studied is generally depleted in high field strength trace elements (Zr, Hf, Nb) and Th, U, REE relative to the standards. Th and Nb correlate positively with TiO_2 and Al_2O_3 . TiO_2 correlates positively also with Zr and SiO_2 (Table 4). Therefore, lithogenous derivation of these trace elements is assumed. The Grybów Unit in individual tectonic windows differs in terms of concentrations of carbonate and aluminosilicates. The samples of the Grybów TW and Ropa TW are more calcareous, whereas the samples from the most western Szczawa window are enriched in terrestrial material manifested in their higher contents of Al_2O_3 and SiO_2 as well as of TiO_2, Th, Nb and Zr.

The REE distribution in the material studied is shown relative to UCC. The Ropa and Grybów samples are somewhat depleted in REE in comparison to the Szczawa samples. UCC normalized distribution patterns of REE show some fractionation. If distribution patterns of REE were flat, these patterns would indicate a lithogenous affinity of REE.

Light REE (LREE) sloping down to heavy REE (HREE) is the most common trend on UCC normalized plots (Text-fig. 14). However, some of samples (S-GB 24/02/N and 1/07/N, GMF G7/02, 30/97/N and Krosno Beds: G15/02, G17/02) slope upward from La to Lu. There is often a convex curvature in middle-REE (MREE) with respect to adjacent LREE and HREE (Text-fig. 14). The europium anomaly varies from 0.73 to 1.57 (Table 2). The largest differences between Eu anomalies were obtained for the Szczawa window samples, whereas the samples from the Ropa TW and Grybów TW have a Eu anomaly about one.

The Nb/Ta and Zr/Hf ratios of the samples generally maintain UCC ratios of 13.33 and 36.42, respectively (Rudnick and Gao 2004; Table 3). The Th/U ratios of the samples are mostly < 5, which is typical of UCC (Table 3). Such low ratios are consistent with the addition of U associated with organic matter, especially in the Ropa TW and Grybów TW samples. The measured ratios of Y/Ho are about the UCC value of 27 (Table 3). The most scattered values of these ratios describe the Szczawa TW samples.



Text-fig. 14. Upper Continental Crust (UCC)-normalized REE patterns of the Sub-Grybów Beds, Grybów Marl Formation and Krosno Beds of the Grybów Nappe. UCC data from Rudnick and Gao (2003) and Hu and Gao (2008)

Stable isotope composition of carbonates

The values of both carbon and the oxygen isotopic ratios of carbonates of the Grybów Unit vary across wide ranges (Table 2). Values of $\delta^{13}C_{carb.}$ vary from -0.01 to -6.63‰ VPDB and -1.1 to -4.3‰ VPDB measured in the Ropa TW and Grybów TW, respectively. The oxygen isotopic composition is expressed by $\delta^{18}O$ fluctuating between -1.46 and -6.74‰ VPDB and -1.5 to -4.8‰ VPDB (Ropa TW and Grybów TW, respectively).

$\delta^{18}O$ correlation with $\delta^{13}C$ is flat in the samples of the Chełmski sections (Ropa TW) due to higher concentrations of light C^{12}. The lowest values of $\delta^{13}C$ are measured at the top of GMF (18/05/N, 20/05/N) (cf. Wójcik-Tabol 2017).

The relationship between the Magura Nappe base and the mineralogical features of the Grybów Succession

The samples of the Grybów TW and Ropa TW studied were temperature-affected for a long time, something that is inferred from the positive correlation between both palaeotemperature indicators, vitrinite reflectance (Ro) and the degree of illitization. Waliczek *et al.* (2014) noticed that the illitization process was not strictly dependent on time, whereas the vitrinite reflectance was stabilized in normal burial coalification over a certain period of time. The above conclusions were based on the good correlation between the organic and inorganic palaeotemperature proxies obtained for the mature samples ($Ro \geq 0.7\%$) of the Grybów TW and also of Świątkowa Wielka TW. In contrast, the samples of the Dukla Nappe, containing immature organic matter ($Ro < 0.7\%$) showed inconsistent values of maximum palaeotemperature. The temperature calculated from I/S data was higher than those calculated from Ro (Waliczek *et al.* 2014).

The thermal alteration ranging between 66 and 100 °C reported for the Szczawa TW (see Zielińska 2017) differs from the paleotemperatures deduced from I/S (> 165 °C). This suggests that smectite illitization went more effectively than the maturation of organic matter did, possibly due to rapid burial and subsequent uplift and erosion.

The organic matter from the tectonic windows shows lower maturation than that from the adjacent area. The idea that the thermal alteration had been accomplished before the Magura Nappe was thrust into its current position appears to be justified (cf. Świerczewska 2005).

Uplift and erosion was significantly dependent on the morphology of the Carpathian basement (Poprawa *et al.* 2002; Zuchiewicz *et al.* 2002; Pietsch *et al.*, 2010). The erosion was the greatest above the regional basement slope (RBS), formed during Ottnangian times as a zone of steeply south-verging faults (Ryłko and Tomaś 2001). The minimum thickness of the overlying and eroded rocks was estimated about 6.5 km in the tectonic windows. The Mszana Dolna tectonic window and Szczawa TW are located above the RBS (Świerczewska 2005).

The RBS was a tectonically involved area associated with an anchimetamorphism and hydrothermal alteration supported by special mineralization (Burtan and Łydka 1978; Burtan *et al.* 1992). The Mszana Dolna area is full of quartz crystallized directly on the fissure walls with calcite veinlets (Jarmołowicz-Szulc 2001). The quartz has the character of the “Marmarosh diamonds” that crystallized under unstable pressure from polyphase fluids whose composition changed in time (Karwowski and Dorda 1986; Burtan *et al.* 1992; Hurai *et al.* 2002). The fluids maintained as inclusions inside the “Marmarosh diamonds” include among other things bitumens and hydrocarbons (Jarmołowicz-Szulc *et al.* 2006). Similar compositions of inclusions within the “Marmarosh

			SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	MnO	Cr_2O_3	LOI	Hf	Nb	Th	U	Zr	Y
			%	%	%	%	%	%	%	%	%	%	%	%	ppm	ppm	ppm	ppm	ppm	ppm
		mdl	0.01	0.01	0.04	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.002	-5.1	0.1	0.1	0.2	0.1	0.1	0.1
Ropa tectonic window	Sub-Grybów Beds	1/07/N	62.87	8.10	7.88	1.60	7.67	0.68	1.26	0.66	0.06	0.18	0.013	8.9	9.2	13.1	8.1	4.3	330.9	32.1
		24/05/N	58.21	18.68	6.78	2.82	0.60	0.89	3.76	0.83	0.09	0.03	0.022	7.1	4.2	15.6	14.7	2.8	153.3	24.3
		26/05/N	39.28	13.62	4.49	1.87	18.15	0.73	2.87	0.58	0.06	0.18	0.013	17.9	2.7	10.6	12.2	2.1	93.1	18.6
		28/05/N	40.18	13.45	5.17	2.01	17.33	0.75	2.76	0.59	0.08	0.08	0.014	17.4	3.0	11.2	11.9	2.2	92.9	16.9
		18/02/N	52.36	15.83	6.93	3.27	5.73	0.99	2.92	0.78	0.12	0.25	0.019	10.6	4.3	14.4	13.4	2.9	139.1	24.9
		19/02/N	38.37	10.54	7.61	2.43	19.30	0.45	1.63	0.39	0.08	0.26	0.011	18.7	1.9	7.2	7.4	2.8	64.0	26.6
		20/02/N	57.43	13.18	6.43	2.12	6.46	1.25	2.32	0.73	0.08	0.18	0.027	9.6	5.3	13.7	11.0	3.3	189.5	22.9
		21/02/N	43.85	13.66	6.12	2.94	13.46	0.80	2.80	0.67	0.12	0.17	0.017	15.2	3.4	13.4	11.4	3.1	113.5	23.6
		22/02/N	41.62	13.51	5.81	2.90	15.53	0.80	2.82	0.66	0.11	0.14	0.017	15.9	3.1	12.8	12.3	3.1	110.5	22.1
		23/02/N	36.96	12.83	5.83	2.32	19.62	0.68	2.40	0.58	0.12	0.18	0.018	18.2	3.0	9.8	10.2	3.4	96.8	21.1
		24/02/N	46.92	13.17	6.70	3.03	11.48	1.38	2.25	0.76	0.14	0.11	0.025	13.8	3.8	13.3	10.8	2.8	137.3	20.8
	Grybów Marl Formation	25/02/N	38.71	12.86	5.71	2.36	18.76	0.76	2.58	0.61	0.10	0.10	0.020	17.2	2.8	9.8	11.9	2.9	100.2	21.2
		26/02/N	41.75	13.76	6.08	2.80	14.75	0.79	2.83	0.69	0.14	0.13	0.018	16.1	3.1	13.0	11.5	2.7	105.9	23.4
		27/02/N	39.29	12.07	5.79	2.93	18.14	0.90	2.22	0.60	0.17	0.23	0.018	17.4	3.1	11.0	9.6	2.7	105.8	24.2
		28/02/N	43.65	15.42	5.42	2.12	12.92	0.83	3.01	0.64	0.10	0.09	0.017	15.6	2.7	11.8	12.9	3.1	92.6	22.2
		35/02/N	44.54	14.07	5.94	3.48	11.92	0.90	2.62	0.71	0.15	0.18	0.017	15.3	3.6	13.6	11.8	4.3	112.9	26.0
		36/02/N	36.92	13.12	5.46	2.16	19.45	0.63	2.48	0.57	0.12	0.13	0.021	18.7	2.7	10.1	11.1	7.2	94.2	22.6
		37/02/N	42.77	12.54	5.49	2.21	16.54	0.98	2.46	0.62	0.13	0.09	0.025	15.9	3.6	10.8	10.9	5.8	127.0	24.6
		31/02/N	36.06	13.07	4.68	1.65	20.32	0.53	2.70	0.58	0.06	0.08	0.014	20.0	2.8	10.7	11.7	2.3	88.1	17.7
		30/05/N	41.60	13.19	5.66	1.89	15.09	0.54	2.70	0.58	0.11	0.07	0.017	18.3	3.4	11.1	11.0	5.3	108.0	24.3
		16/05/N	35.76	11.92	7.44	1.45	16.50	0.43	2.12	0.55	0.15	0.30	0.023	23.1	3.2	10.7	9.8	15.5	108.7	23.8
		15/05/N	28.18	9.24	3.67	1.51	27.81	0.44	1.75	0.38	0.13	0.12	0.015	26.5	2.0	7.0	7.6	7.4	69.7	17.5
		18/05/N	39.44	13.16	6.40	2.73	15.51	0.84	2.52	0.63	0.12	0.15	0.025	18.2	3.0	10.3	11.3	7.2	106.2	22.5
		19/05/N	37.33	12.26	4.88	1.55	17.44	0.46	2.17	0.61	0.13	0.34	0.017	22.6	3.5	11.8	10.8	9.9	127.5	25.3
		20/05/N	50.51	12.33	5.60	1.23	8.99	0.53	2.40	0.57	0.19	0.03	0.020	17.4	3.5	11.0	9.7	8.2	115.5	24.0
		31/05/N	38.90	13.76	5.96	2.35	17.02	0.74	2.71	0.60	0.13	0.15	0.021	17.4	2.5	10.5	12.1	2.4	91.2	20.5
		33/05/N	46.19	13.57	5.61	2.97	10.75	0.70	2.79	0.64	0.12	0.20	0.019	16.3	3.4	12.9	11.5	6.1	114.8	22.7
	KB	34/05/N	54.89	21.91	5.47	2.67	0.70	0.97	5.03	0.94	0.09	0.04	0.021	7.1	5.0	17.2	17.9	3.4	148.2	27.5
		21/05/N	45.91	13.06	4.14	2.28	13.58	0.79	2.67	0.67	0.13	0.08	0.023	16.5	4.4	13.2	12.0	4.0	152.6	22.9
		32/02/N	42.13	12.15	4.57	3.94	15.24	0.66	2.49	0.56	0.11	0.08	0.020	17.9	3.2	10.4	9.8	3.5	104.8	20.2
Grybów tectonic window	SG	G 1/02	40.67	12.24	4.92	4.02	14.45	0.60	2.44	0.53	0.11	0.15	0.012	19.7	2.5	10.8	9.2	3.2	89.3	20.8
		G 5/02	34.88	11.49	5.50	1.11	20.38	0.51	1.93	0.50	0.13	0.06	0.016	23.2	2.2	10.3	8.7	19.3	88.3	20.5
	GMF	G 7/02	45.73	12.52	6.62	1.23	10.58	0.67	2.38	0.64	0.24	0.07	0.020	19.1	4.1	12.4	9.8	13.1	148.7	24.2
		G 8/02	40.26	11.96	6.03	1.76	16.64	0.76	2.36	0.55	0.13	0.27	0.014	19.1	2.5	10.5	8.9	5.8	93.6	20.6
		G 10/02	29.41	10.65	3.46	1.15	26.23	0.43	1.66	0.47	0.10	0.11	0.012	26.1	2.3	9.4	7.8	6.4	86.5	17.1
		G 11/02	41.24	11.18	4.69	1.15	16.61	0.55	2.18	0.50	0.19	0.04	0.018	21.4	2.6	9.4	7.8	9.6	94.5	19.4
	KB	G 15/02	40.62	11.27	4.39	2.31	17.79	0.55	2.30	0.52	0.12	0.11	0.013	19.8	2.5	10.8	8.8	2.5	90.3	20.0
		G 17/02	43.37	10.39	4.24	3.00	16.38	0.79	1.97	0.51	0.10	0.10	0.013	18.9	3.5	10.0	7.8	2.3	131.2	20.3
Szczawa tectonic window	Grybów Marl Formation	2/11/N	55.73	22.05	4.79	2.39	0.90	1.10	4.80	0.90	0.10	0.10	0.018	6.9	4.3	17.4	17.3	3.0	147.0	13.1
		3/11/N	54.79	16.07	6.07	2.31	4.69	0.56	3.10	0.79	0.08	0.08	0.018	11.3	5.4	16.3	12.9	3.1	162.0	20.8
		4/11/N	52.50	15.19	5.77	2.15	6.94	0.52	2.95	0.73	0.07	0.09	0.017	12.9	4.3	16.4	11.9	3.4	148.3	24.3
		28/97/N	49.04	19.92	5.29	2.02	4.03	0.62	4.53	1.04	0.09	0.03	0.022	13.1	4.8	21.8	14.8	4.6	168.8	23.7
		30/97/N	56.39	12.33	5.86	1.95	7.19	1.03	2.29	0.69	0.12	0.19	0.017	11.7	7.8	13.8	11.0	3.5	262.9	31.2
		33/97/N	51.14	16.04	9.47	2.73	5.11	0.93	2.28	0.67	1.02	0.03	0.017	10.3	2.5	12.7	11.2	2.6	97.9	48.8
		34/97/N	54.26	18.20	9.79	2.55	0.69	1.05	3.18	0.82	0.15	0.03	0.021	9.0	3.3	14.9	12.2	2.7	117.8	24.9
		35/97/N	56.36	18.46	7.59	2.41	0.73	1.47	3.27	0.87	0.17	0.08	0.028	8.3	4.7	13.8	13.8	3.6	147.6	31.2
		36/97/N	53.03	21.55	5.46	2.15	0.51	0.98	4.48	0.87	0.12	0.15	0.021	10.4	5.8	18.4	16.6	3.7	187.5	23.3
		38/97/N	48.56	18.25	5.36	1.97	5.59	0.75	3.73	0.93	0.06	0.04	0.020	14.5	4.6	18.4	13.7	3.7	154.3	20.2
		39/97/N	38.37	14.38	5.11	3.40	14.08	0.79	3.00	0.69	0.12	0.16	0.017	19.7	3.1	13.6	11.0	3.1	103.8	18.3
		40/97/N	55.37	19.65	7.27	2.27	0.63	1.02	3.83	0.91	0.15	0.14	0.022	8.5	4.6	17.2	14.6	3.4	135.2	24.7
		42/97/N	40.30	15.41	4.74	1.99	13.91	0.68	3.21	0.75	0.05	0.15	0.018	18.6	4.6	14.5	12.8	3.8	137.1	18.9
		43/97/N	39.16	13.94	4.75	2.62	15.85	0.74	2.88	0.59	0.07	0.12	0.016	19.1	2.8	11.7	10.5	3.0	94.2	19.8
		44/97/N	32.34	12.00	4.62	1.58	22.21	0.55	2.35	0.48	0.09	0.13	0.013	23.4	2.1	9.3	9.2	2.2	74.1	18.6
		45/97/N	36.38	11.83	6.80	2.08	18.82	0.49	2.00	0.54	0.04	0.11	0.013	20.6	3.0	10.9	8.5	2.2	93.7	23.2
		47/97/N	50.24	15.92	6.14	2.28	5.73	0.57	3.53	0.76	0.11	0.07	0.020	14.4	4.6	14.9	12.8	4.7	162.3	25.2
	Krosno Beds	50/97/N	25.27	8.68	3.91	1.87	29.08	0.56	1.59	0.38	0.08	0.18	0.010	28.1	1.9	7.3	6.5	2.3	58.7	15.1
		51/97/N	43.42	15.49	5.80	2.95	10.80	0.96	3.19	0.74	0.08	0.18	0.016	16.1	3.6	13.5	11.6	2.3	123.5	15.0
		52/97/N	31.00	10.97	4.70	2.11	23.29	0.61	2.12	0.48	0.06	0.14	0.015	24.3	2.2	7.4	8.2	2.5	73.7	16.7
		53/97/N	39.15	14.89	4.96	1.76	15.81	0.68	2.94	0.72	0.09	0.08	0.015	18.7	3.0	13.3	10.9	2.3	106.8	16.6
		54/97/N	41.56	12.85	5.64	3.47	13.81	0.91	2.60	0.66	0.13	0.13	0.017	18.1	3.4	12.2	9.6	2.8	111.2	21.2
Standards		PAAS	62.8	18.9	6.5	2.2	1.3	1.2	3.7	1	0.16	0.11				19	160	3.1	150	27
		av.sh	58.9	16.7	6.9	2.6	2.2	1.6	3.6	0.78	0.16						140	3.7	130	
		UCC	63.5	15	6.02	3.59	5.25	3.39	2.3	0.69	0.15	0.1				12	82	2.7	97	21

Table 3. Chemical composition of the Grybów succession samples. Part of data was shown by Oszczypko-Clowes *et al.* (2015) and Wójcik-Tabol (2015, 2017). KB – Krosno Beds, GMF – Grybów Marl Formation, SG – Sub-Grybów Beds, mdl – detection limit, av.sh. – average shale →

			La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Eu/ Eu*	Ce/ Ce*	Nb/ Th	Zr/ Hf	Th/ U	Y/ Ho
			ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm						
		mdl	0.1	0.1	0.02	0.3	0.05	0.02	0.05	0.01	0.05	0.02	0.03	0.01	0.05	0.01						
Ropa tectonic window	Sub-Grybów Beds	1/07/N	20.9	51.6	5.18	20.0	4.57	1.18	5.12	0.94	5.20	1.04	3.06	0.48	2.88	0.45	1.06	1.17	1.6	36.0	1.9	31
		24/05/N	35.8	92.5	8.65	32.5	6.11	1.21	4.76	0.78	4.35	0.86	2.58	0.40	2.52	0.39	0.97	1.24	1.1	36.5	5.3	28
		26/05/N	26.1	60.3	5.93	22.3	4.10	0.88	3.32	0.57	2.96	0.62	1.77	0.29	1.72	0.27	1.03	1.14	0.9	34.5	5.8	30
		28/05/N	26.0	61.2	6.02	22.5	4.22	0.88	3.41	0.55	2.84	0.60	1.68	0.28	1.70	0.27	1.01	1.15	0.9	31.0	5.4	28
		18/02/N	30.2	74.0	7.36	28.1	5.54	1.14	4.85	0.80	4.45	0.86	2.56	0.39	2.54	0.37	0.95	1.17	1.1	32.3	4.6	29
		19/02/N	23.8	57.9	5.62	22.1	5.05	1.29	5.32	0.87	4.63	0.85	2.12	0.32	1.95	0.28	1.08	1.18	1.0	33.7	2.6	31
		20/02/N	28.2	67.7	6.82	25.6	4.52	0.95	3.87	0.67	3.79	0.74	2.29	0.38	2.36	0.34	0.98	1.15	1.2	35.8	3.3	31
		21/02/N	29.9	68.9	7.19	28.2	5.34	1.12	4.72	0.78	4.26	0.82	2.40	0.37	2.30	0.33	0.97	1.11	1.2	33.4	3.7	29
		22/02/N	29.3	65.2	6.94	26.1	4.83	1.00	4.11	0.70	3.85	0.77	2.32	0.37	2.16	0.34	0.97	1.08	1.0	35.6	4.0	29
		23/02/N	26.5	59.1	6.28	23.3	4.53	0.99	4.09	0.65	3.53	0.70	1.97	0.31	1.96	0.30	1.00	1.08	1.0	32.3	3.0	30
		24/02/N	21.7	50.4	5.46	20.6	4.18	0.89	3.79	0.64	3.52	0.72	2.18	0.33	2.10	0.32	0.97	1.09	1.2	36.1	3.9	29
	Grybów Marl Formation	25/02/N	26.7	59.8	6.38	24.2	4.71	1.01	4.20	0.69	3.74	0.72	2.16	0.33	2.05	0.30	0.98	1.08	0.8	35.8	4.1	29
		26/02/N	27.8	64.1	6.88	27.4	5.51	1.24	5.02	0.79	4.34	0.80	2.30	0.35	2.11	0.32	1.02	1.09	1.1	34.2	4.3	29
		27/02/N	26.3	56.9	6.35	25.6	5.11	1.18	4.81	0.79	4.21	0.83	2.31	0.35	2.05	0.31	1.03	1.04	1.1	34.1	3.6	29
		28/02/N	29.6	68.0	7.03	25.3	5.06	1.08	4.36	0.70	3.83	0.74	2.23	0.34	2.03	0.32	1.00	1.11	0.9	34.3	4.2	30
		35/02/N	30.3	68.9	7.51	29.5	5.77	1.27	5.43	0.86	4.74	0.90	2.50	0.38	2.30	0.35	0.96	1.12	1.2	31.4	2.7	29
		36/02/N	27.8	62.8	6.79	26.1	5.03	1.01	4.37	0.71	3.78	0.77	2.15	0.34	2.09	0.33	0.95	1.05	0.9	34.9	1.5	29
		37/02/N	28.1	62.5	6.80	26.1	5.05	1.04	4.65	0.74	4.04	0.82	2.39	0.38	2.26	0.36	1.00	1.03	1.0	35.3	1.9	30
		31/02/N	25.1	58.3	6.03	22.5	4.43	0.93	3.71	0.60	3.20	0.58	1.82	0.28	1.75	0.26	0.98	1.08	0.9	31.5	5.1	31
		30/05/N	32.0	74.0	7.63	28.0	5.41	1.13	4.77	0.75	4.16	0.82	2.40	0.37	2.36	0.34	0.93	1.08	1.0	31.8	2.1	30
		16/05/N	26.8	57.9	6.35	24.3	4.86	0.99	4.17	0.68	3.89	0.76	2.24	0.34	2.16	0.33	0.93	1.06	1.1	34.0	0.6	31
		15/05/N	20.7	43.6	4.81	19.0	3.61	0.77	3.06	0.52	2.67	0.57	1.65	0.25	1.55	0.24	0.99	1.12	0.9	34.9	1.0	31
		18/05/N	28.1	60.5	6.54	25.8	4.75	0.99	4.28	0.70	3.85	0.73	2.27	0.35	2.17	0.33	0.95	1.05	0.9	35.4	1.6	31
		19/05/N	29.2	61.8	6.74	25.2	4.95	1.03	4.51	0.75	3.89	0.80	2.29	0.36	2.27	0.35	0.95	1.04	1.1	36.4	1.1	32
		20/05/N	28.4	63.1	6.74	26.0	4.79	1.05	4.29	0.69	3.71	0.75	2.19	0.35	2.06	0.31	1.00	1.07	1.1	33.0	1.2	32
		31/05/N	28.4	63.0	6.69	24.8	4.53	1.02	4.12	0.67	3.55	0.70	2.03	0.32	1.98	0.29	1.02	1.08	0.9	36.5	5.0	29
		33/05/N	30.1	63.4	7.07	26.0	4.86	1.03	4.22	0.68	3.78	0.78	2.27	0.34	2.11	0.33	0.99	1.02	1.1	33.8	1.9	29
	KB	34/05/N	47.5	110.1	11.21	42.8	7.32	1.35	5.33	0.87	4.67	0.96	2.98	0.48	3.07	0.45	0.94	1.12	1.0	29.6	5.3	29
		21/05/N	32.2	69.7	7.56	27.5	5.02	1.00	4.19	0.70	3.78	0.76	2.26	0.35	2.16	0.34	0.95	1.05	1.1	34.7	3.0	30
		32/02/N	26.2	54.7	6.10	22.5	4.21	0.87	3.75	0.60	3.33	0.66	1.91	0.31	1.94	0.28	0.95	1.02	1.1	32.8	2.8	31
Grybów tectonic window	SG	G 1/02	26.8	56.3	6.31	23.7	4.49	0.91	3.91	0.65	3.60	0.71	1.96	0.32	1.99	0.29	0.97	1.02	1.2	35.7	2.9	29
		G 5/02	22.2	46.6	5.62	21.2	4.20	0.93	3.79	0.64	3.50	0.71	1.93	0.29	1.84	0.29	1.10	0.98	1.2	40.1	0.5	29
	GMF	G 7/02	27.1	57.8	6.69	24.7	4.66	1.01	4.02	0.70	3.83	0.79	2.19	0.34	2.09	0.34	1.01	1.01	1.3	36.3	0.7	31
		G 8/02	24.1	54.4	5.91	22.5	4.33	0.92	3.82	0.64	3.38	0.68	1.90	0.30	1.82	0.28	1.05	1.07	1.2	37.4	1.5	30
		G 10/02	20.7	41.0	4.91	18.0	3.46	0.79	3.00	0.51	2.85	0.57	1.59	0.24	1.47	0.22	1.43	0.96	1.2	37.6	1.2	30
		G 11/02	22.1	47.7	5.29	19.4	3.89	0.82	3.35	0.55	3.12	0.63	1.77	0.28	1.67	0.26	1.18	1.04	1.2	36.3	0.8	31
	KB	G 15/02	23.8	51.8	5.75	20.7	4.09	0.88	3.65	0.62	3.40	0.67	1.97	0.28	1.85	0.27	1.11	1.04	1.2	36.1	3.5	30
		G 17/02	21.5	47.8	5.29	20.9	3.99	0.83	3.52	0.62	3.38	0.68	1.93	0.31	1.85	0.28	1.11	1.06	1.3	37.5	3.4	30
Szczawa tectonic window	Grybów Marl Formation	2/11/N	40.4	80.1	9.01	31.3	4.15	0.51	2.18	0.35	1.75	0.49	1.68	0.31	2.01	0.33	0.74	0.99	1.0	34.2	5.8	27
		3/11/N	34.9	76.6	8.19	30.5	5.63	1.05	4.33	0.77	3.88	0.79	2.04	0.37	2.43	0.37	0.92	1.07	1.3	30.0	4.2	26
		4/11/N	32.9	72.1	7.79	28.7	5.47	1.19	4.66	0.83	4.50	0.93	2.39	0.37	2.33	0.37	1.02	1.06	1.4	34.5	3.5	26
		28/97/N	42.2	86.3	9.06	33.1	6.54	1.35	5.56	0.89	4.89	0.97	3.36	0.49	2.66	0.44	0.97	1.04	1.5	35.2	3.2	24
		30/97/N	34.4	77.2	8.21	30.6	5.98	1.25	5.75	0.97	5.28	1.13	3.55	0.51	3.00	0.51	0.92	1.08	1.3	33.7	3.1	28
		33/97/N	39.0	89.0	9.50	38.6	9.68	3.66	10.46	1.67	9.01	1.72	4.87	0.59	3.16	0.50	1.58	1.09	1.1	39.2	4.3	28
		34/97/N	36.1	76.2	8.38	29.4	6.12	1.26	5.55	0.92	5.32	1.04	3.27	0.45	2.81	0.45	0.94	1.03	1.2	35.7	4.5	24
		35/97/N	39.6	86.9	8.93	34.0	7.12	1.69	6.66	1.09	6.55	1.22	3.91	0.53	2.97	0.55	1.06	1.09	1.0	31.4	3.8	26
		36/97/N	49.7	105.2	10.57	39.0	5.49	0.88	3.90	0.64	4.10	0.97	3.26	0.47	2.94	0.52	0.82	1.08	1.1	32.3	4.5	24
		38/97/N	39.1	78.7	8.36	30.4	5.23	0.92	3.77	0.63	3.67	0.73	2.66	0.36	2.21	0.42	0.90	1.03	1.3	33.5	3.7	28
		39/97/N	28.6	62.1	6.64	25.3	4.55	0.85	3.94	0.65	3.82	0.74	2.57	0.37	1.99	0.34	0.87	1.06	1.2	33.5	3.5	25
		40/97/N	44.8	94.7	9.86	35.2	6.52	1.28	5.58	0.90	5.10	1.09	3.36	0.46	3.01	0.47	0.92	1.06	1.2	29.4	4.3	23
		42/97/N	35.8	73.5	7.60	28.3	4.94	0.90	3.92	0.64	3.77	0.71	2.53	0.34	2.02	0.35	0.89	1.05	1.1	29.8	3.4	27
		43/97/N	28.4	59.5	6.42	23.1	4.87	0.84	4.05	0.66	3.67	0.76	2.52	0.32	1.88	0.33	0.82	1.04	1.1	33.6	3.5	26
		44/97/N	25.4	53.9	5.62	21.5	3.94	1.01	3.58	0.58	3.30	0.65	2.07	0.29	1.71	0.28	1.17	1.06	1.0	35.3	4.2	29
		45/97/N	26.8	60.1	6.20	23.7	5.03	1.18	4.85	0.76	4.48	0.82	2.68	0.34	1.94	0.34	1.04	1.10	1.3	31.2	3.9	28
		47/97/N	37.6	83.2	8.27	31.7	5.92	1.15	5.23	0.85	4.72	0.87	3.01	0.41	2.83	0.42	0.90	1.11	1.2	35.3	2.7	29
	Krosno Beds	50/97/N	19.1	39.3	4.33	16.5	3.17	1.02	3.06	0.49	2.76	0.52	1.68	0.21	1.41	0.21	1.42	1.02	1.1	30.9	2.8	29
		51/97/N	29.7	66.0	6.37	22.4	3.86	0.72	2.92	0.48	3.03	0.63	2.08	0.29	2.08	0.32	0.93	1.13	1.2	34.3	5.0	24
		52/97/N	22.8	47.6	5.09	20.2	3.87	0.84	3.47	0.55	3.01	0.66	2.11	0.26	1.57	0.28	0.99	1.04	0.9	33.5	3.3	25
		53/97/N	29.3	60.9	6.24	23.3	3.90	0.93	3.54	0.57	3.21	0.66	2.24	0.28	1.89	0.33	1.09	1.06	1.2	35.6	4.7	25
		54/97/N	29.5	60.5	6.33	23.9	4.62	0.95	4.03	0.67	4.15	0.82	2.51	0.37	2.29	0.36	0.95	1.04	1.3	32.7	3.4	26
Standards		PAAS	38	80	8.8	33.9	5.6	1.1	4.66	0.77	4.4	1	2.85	0.41	2.8	0.43			0.1		51.6	27
		av.sh																				
		UCC	31	63	7.1	27	4.7	1	4	0.7	3.9	0.83	2.3	0.37	2.34	0.36			0.1		30.4	25

Table 3 (continued): composition after Wedepohl (1971), PAAS – Post-Archean Australian Shale (after Taylor and McLennan 1985), UCC – upper continental crust (after Rudnick and Gao 2003; Hu and Gao 2008)

	SiO_2	Al_2O_3	CaO	TiO_2	Hf	Nb	Th	U	Zr	Y	TREE
SiO_2	1.00										
Al_2O_3	0.60	1.00									
CaO	-0.94	-0.80	1.00								
TiO2	0.76	0.89	-0.88	1.00							
Hf	0.79	0.32	-0.67	0.61	1.00						
Nb	0.75	0.84	-0.86	0.95	0.63	1.00					
Th	0.61	0.94	-0.76	0.87	0.41	0.81	1.00				
U	-0.19	-0.23	0.16	-0.23	-0.09	-0.17	-0.23	1.00			
Zr	0.78	0.25	-0.63	0.55	0.98	0.59	0.34	-0.04	1.00		
Y	0.50	0.14	-0.45	0.23	0.36	0.21	0.13	0.03	0.38	1.00	
TREE	0.71	0.87	-0.84	0.82	0.49	0.79	0.84	-0.20	0.42	0.55	1.00

Table 4. Pearson's correlation coefficients (r) between selected major and trace elements for Oligocene deposits of the Grybów Unit

diamonds" was obtained from those occurring in the Ukrainian Carpathians (Kolodiy *et al*. 2004).

Silica could be produced during the illitization process and then diffused into the adjacent rocks where it precipitated as quartz overgrowths (Worden and Morad 2009). Whitney (1990) proved experimentally that illitization is significantly inhibited in fluid-deficient systems. Illitization is retarded by low water content in unsaturated sediments or in sediments whose pore spaces are filled up with hydrocarbons. This effect is more pronounced at lower temperatures than at higher temperatures (Whitney 1990). Therefore, the Mszana Dolna-Szczawa region is characterized by advanced illitization, the occurrence of mineral waters and special mineralization. It can be linked to the "hydrothermal field" in the Ukrainian Carpathians (Boychevska *et al*. 2004).In contrast to that, the Grybów-Ropa area belongs to the "hydrocarbon field" distinguished in the northern part of the Ukrainian Carpathians by Shlapinski (2014).

Origin of mineral waters and their impact on the chemistry of the infiltrated rocks

Nowak (1924 1938) connected the origin of CO_2, in the Outer Carpathians, with the oxidation of hydrocarbons. Hydrocarbon chains are thermally degraded during catagenesis. The catagenesis phase is predominant in the deeper subsurface as burial (1,000–6,000 m), heating (60–175°C), and deposition continues. 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). The hydrocarbon generation from kerogen is controlled by the thermocatalytic process where the main factors are temperature and pressure. The thermal maturation of the kerogen has resulted in petroleum release followed by that of gas, CO_2 and H_2O. CO_2 is produced more readily from humic substances, such as those dominant in the Grybów Unit especially in that of the Szczawa TW.

The stable isotope composition of carbonates may be linked to the source of carbon dioxide. CO_2 produced by the oxidation of methane contains relatively light C and heavy O, in contrast to CO_2 from the oxidation of organic matter which is a source of relatively heavy C and light O (Bojanowski 2012; Wójcik-Tabol 2015). The isotopic composition of methane from the Rabka borehole permits the conclusion that the origin of the gas was thermogenic, released during the secondary cracking of petroleum under conditions of high temperature and pressure (Achieved Materials of Rabka IG-2 borehole).

The zonal distribution of hydrocarbons, mineral waters of the "shchava" type and exhalation gases (CH_4 and CO_2) in the Ukrainian Carpathians (Shlapinski 2014) can be extrapolated into the Polish Western Carpathians. The area of the gas fields in the Carpathian Foredeep, and the oil fields of the Outer Carpathian nappes crosses the Polish-Ukrainian border and continues westward (Kotarba and Koltun 2006) to include the Grybów Nappe of the Grybów and Ropa tectonic windows that are the closest the Magura Nappe front. The extent of crude oil is bordered in the south by the Burkut Unit overthrust and the occurrence of the "shchava" type mineral waters and methane exhalations further south. This, called by Shlapinski (2014) a "hydrothermal field", seems to be similar to that in the Mszana Dolna-Szczawa area.

The Szczawa TW sediments were percolated by brines, as inferred from the distinctive mineral precipitation, dolomitization, K-addition (associated with illitization) and fractionation of trace elements.

Zircon is a chemically inert mineral and conserves Zr/Hf ratios during geological evolution. However, the trace-element fractionation in zircons can record different environments of growth (Luo and Ayers 2009; Koreshkova *et al.* 2009; González-Álvarez and Kerrich 2010). The Zr/Hf ratios of samples which have been studied refer to magmatic zircons ranging from -35 to -70 (e.g., Murali *et al.* 1983). The outliers at < 30 in the Szczawa TW may result from differential behavior of Zr and Hf during diagenetic dissolution, overgrowths on detrital zircon, or of both these processes.

The pair of Y and Ho, like Zr-Hf, behaves coherently during most geological processes (Rudnick and Gao 2003; Hu and Gao 2008). The Y/Ho ratios are higher than those of UCC for the Ropa TW and Grybów TW samples and lower for the Szczawa TW samples. Scattered Y/Ho ratios and Zr-Hf fractionations in the Szczawa TW samples might be interpreted as stemming from their mobility due to diagenetic processes. González-Álvarez and Kerrich (2010) showed that oxidized-alkaline brines are responsible for mobility of HREE and HFSE.

DISCUSSION

In our opinion the explanation of the origin of carbon dioxide in the Magura Nappe should be sought in the course of the Miocene orogeny in the Western Outer Carpathians (WOC). Despite many concerns it is the generally accepted idea that the WOC accretionary wedge developed in course of the Middle/Late Miocene collision between the North European continental plate and the Tisza-Dacia micro-plate (Birkenmajer 1986; Oszczypko 1998; Golonka *et al.* 2000; Seghedi *et al.* 2004).

During this collision the Outer Carpathian orogen thrust over the Carpathian Fore-deep basin. In Poland the amplitude of these “telescopic” movements, on the Kraków meridian, was at least 100 km (Oszczypko 1998). This collision was accompanied by calc-alcaline (andesite) volcanism developed along the boundary between the Central Carpathian block and the Carpathian flysch domain.

In the Polish sector of OWC the andesite bodies are located in the Czorsztyn-Szczawnica area, along the contact zone between the PKB and Krynica facies zone of the Magura Nappe (Birkenmajer 2003, see Text-fig. 2). To the east of Szczawnica these intrusions disappear, and appear again 70 km to the east, in the region of Prešov’ (Eastern Slovakia) and they are prolonged further to the East to the Trans Carpathian Ukraine. (see Text-fig. 1). The youngest generation of andesite in the area of Czorsztyn is of Sarmatian/Pliocene age (Birkenmajer 2003; Seghedi *et al.* 2004). Thus, the young age of the andesites near Czorsztyn may suggest that these intrusions have been associated with the post-collision collapse of the Polish Outer Carpathians.

For an explanation of the origin of CO_2 in the Polish sector (WOC) it is necessary to take into account the burial history and temperature/pressure/depth relationships of the Magura Nappe and its allochtonous sedimentary basement composed of the Fore-Magura thrust-sheets. On the basis of the measurements of the geothermal gradient in the boreholes Smilno-1 (5 700 m, Leško *et al.* 1987) and Hanuszovce-1 (6003 m, Leško *et al.*1987), it is possible, with a high probability to calculate the temperature of the deeper parts of the earth’s crust in the Krynica-Muszyna area. Taking to account the average gradient of 29.18° C/km in borehole Hanusovce 1 (Lesko *et al.* 1985) one can demonstrate a constant temperature increase with depth up to 146 °C at 5 km, 292 °C at 10 km and 584 °C at 20 km. In a similar manner, the pressure can be calculated, taking to account Bojdys and Lemberger (1986) data on the density of the upper part of the Earth’s crust in this area as 2.7 t/m^3. The pressures are respectively: 135 MPa at 5 km, 270 MPa at 10 km and 540 MPa at 20 km. These parameters clearly show that in the area of occurence of the carbon dioxide mineral waters, i.e. in the Krynica/Muszyna area, the basal part of the POC and the underlying Mesozoic–Paleozoic platform the sedimentary rocks are in the conditions of pressure and temperature characteristic of shallow and intermediate zones of metamorphism. The processes leading to the release of CO_2 at a pressure of 101.3 kPa may occur in these zones as well as hydration and decarbonatization at temperatures of 185–190 °C. These reactions are accompanied by the formation of new minerals such as talc, tremolite, diopside, forsterite, periclase and wollastonite. In the area of Krynica occurred metamorphism associated with the origin of both CO_2 and mineral waters like “zuberow” (Zuber and Grabczak 1987). In light of the foregoing, it can be assumed that these processes occur at a depth of about 10 km at temperatures in the range 240–305 °C.

CONCLUSIONS

The Carpathian accretionary wedge developed as the result of the Middle/Late Miocene collision between the North European continental plate and the Tisza-Dacia micro-plate and was accompanied by andesite volcanism. HCO_3-Na mineral waters prevail in the Polish Outer Carpathians. Waters enriched in

CO_2 occur in the southern part of the Magura Nappe (between the Dunajec and Poprad rivers) whereas Cl-Na and mixed HCO_3-Na/Cl-Na waters are known from Rabe and Szczawa. These waters are associated with oil and gas fields. The southern boundary of the Carpathian Oil Province can be marked by the extent of the "shchava" springs. This boundary follows the northern borderline of the PKB from Krościenko toward the east. Westward, the boundary of the Carpathian Oil Province manifests itself by "shchava" springs co-occurring with the exhalation of methane in the Szczawa TW and with the occurrence of "Marmarosh diamonds" containing inclusions of bitumens and hydrocarbons collected from Koninki and Poręba Wielka.

The burial history and temperature/pressure / depth relationships of the Magura Nappe and its allochtonous sedimentary basement clearly show that the area where carbon dioxide mineral waters occur, i.e. the Krynica/ Muszyna area, the basal part of the POC and the underlying Mesozoic–Paleozoic platform sedimentary rocks are in the conditions of shallow and intermediate zones of metamorphism, leading to the release of CO_2. It is assumed that these processes occur at a depth of about 10 km at temperatures in the range 240–305 °C.

The thermal maturation of the Oligocene hydrocarbon source rocks (Menilite and Grybów shales) in the Polish sector of WOC had been accomplished before the Early/Middle Miocene Magura Nappe was thrust into its present position. Post Sarmatian or syntectonic erosion has caused the removeal of at least 6.5 to 10 km of the rocks in the tectonic windows areas.

Among the tectonic windows within the Magura Nappe, the Szczawa TW seems to be the most favored for the occurrence of CO_2-rich waters. The regional basement slope accompanied by tectonic faults was a suitable place for the hydrothermal alteration. Thermal alteration of the sediments is proved by the degree of illitization and the vitrinite reflectance. Advanced illitization produced waters that were then CO_2 saturated. The terrestrial organic matter available there was sufficiently matured for the release of CO_2. Thus carbon dioxide was produced during the degradation of kerogen and hydrocarbons. The sediments were percolated by brines something that is inferred from the precipitation of distinctive minerals, dolomitization, K-addition (associated with illitization) and the fractionation of REE and Zr-Hf. The Szczawa region can be linked to the "hydrothermal field", whereas the Grybów-Ropa area belongs to the "hydrocarbon field" of the Ukrainian Carpathians.

Acknowledgements

The field researches have been supported by the Jagiellonian University (DS funds). We are very grateful to Prof. J. Chowaniec (Kraków) and a second unknown reviewer for remarks. The authors express also their gratitude to Rabka Spa for providing geological documentation of the drilling of Szczawa IV.

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Manuscript submitted: 10th April 2017
Revised version accepted: 27th January 2018