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INTRODUCTION

The main reservoirs of thermal waters in Poland occur within the sedimentary basins of Polish Lowlands and crystalline massifs of the Sudetes Mts. The Polish part of the Carpathian Mts. constitutes the so-called Carpathian Geothermal Province which consists of two geologically distinct parts: (i) the Inner Carpathians – the southern part, composed of crystalline rocks and Mesozoic sediments, folded during the Late Cretaceous; (ii) the Outer Carpathians (Flysch Carpathians) – the northern part, composed of Cretaceous and Paleogene sedimentary formations, folded during the Neogene (Fig. 1).

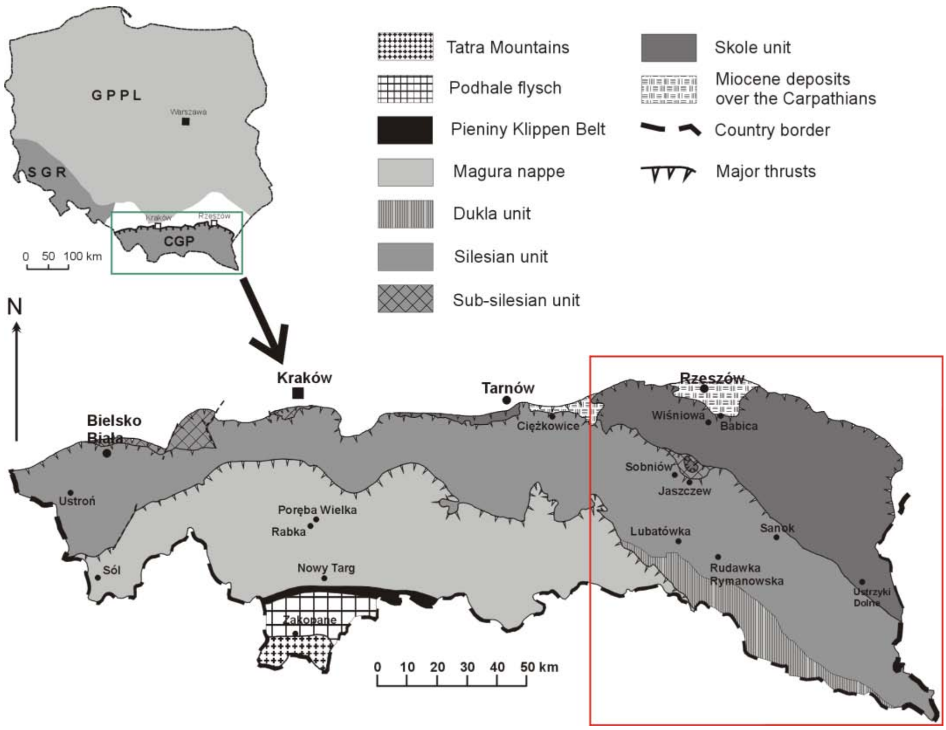

Figure 1. Generalized structural sketch of the Carpathian Geothermal Province (CGP). The red square shows the study area. GPPL – Geothermal Province of Polish Lowlands, SGR – Sudetic Geothermal Region.

Especially the Outer Carpathian Geothermal Region is the area where thermal water potential is still under investigation. Due to complex geological and tectonic structure and hydrogeological settings this region is poorly recognized with respect to thermal water occurrence, resources and possibilities of their utilization. This paper is focused on the eastern part of the Outer Carpathian Geothermal Region, especially on the Silesian Unit. To evaluate the potential occurrence of hydrogeothermal systems in this region in the light of their prospectiveness to further exploration of thermal waters, we took an attempt to apply the selected isotopic and chemical geothermometers to assess the maximum possible temperatures which may be encountered at depth. The results of the geothermometric studies have been compared with actual geothermal gradient, origin of waters and thermal conditions of main geochemical processes responsible for the formation of mineralized and thermal waters encountered in this region.

HYDROGEOLOGICAL SETTINGS IN THE AREA OF STUDY

The Outer Carpathians are composed entirely of flysch-type sedimentary rocks deposited in a deep sea (Książkiewicz 1972, 1975; Kuśmierek, 1995). Dominant are detritic rocks as claystones, mudstones, sandstones, conglomerates, and shales. The sedimentary sequence shows a continuity of marine sedimentation from Late Jurasic (western part) and Early Cretaceous (eastern part) to Oligocene. The characteristic feature of the Outer Carpathians is complex, folded and thrusted structure. They are composed of several nappes that were thrusted over one another approximately from the south (Fig. 1). The nappes differ in tectonic style and litho-stratigraphic inventory as a consequence of regional differentiation of sedimentary systems and the distance from the alimentation zones. One of the largest and best developed is the Silesian Nappe. The easternmost part of the Silesian Nappe constitutes a large tectonic structure called the Central Carpathian Synclinorium built of the thickest sequence of flysch, dominated by coarse-grained sediments of the Upper Cretaceous to Oligocene. Within the Central Carpathian Synclinorium from seven to eight thrusted anticlines (folds) are distinguished (Ślączka 1977). Almost all of these folded structures in their ridge parts contain hydrocarbon deposits and associated mineralized waters.

It is well known that Polish Part of the Carpathians Mts. abounds with mineralized waters utilized in many spas for balneological treatment.

Many aspects of the occurrence of such waters, chemical and isotopic composition, resources and origin have been investigated and discussed in wide literature, for example: Dowgiałło 1976, 1980; Dowgiałło and Sławiński 1979; Dowgiałło and Leśniak 1980; Leśniak 1980; Zuber and Grabczak 1985, 1986, 1987; Chowaniec 1989, 2009; Chowaniec et al. 2001; Porowski 2001a, 2001b, 2001c, 2004, 2006. However, the waters of temperature at least 20°C at the outflow were not studied here sufficiently. They have been encountered only in several exploratory drillings (in majority connected with oil and gas exploration and were liquidated if missed) for example: in the vicinity of Ciężkowice, Lubatówka, Rudawka Rymanowska, Wetlina and Polańczyk; in Skole Unit - in the vicinity of Wiśniowa and Babica (Fig. 1), (Chowaniec et al. 2001). The maximum outflow temperature of 84°C was found in water extracted from Wiśniowa-1 exploratory borehole, where water bearing horizons occurred in Lower Cretaceous sandstones at depth intervals 3696 – 3698 and 3790 – 3793; surprisingly the water had a quite low value of TDS in the range of 7 g/dm^3. Generally the vast majority of thermal waters in the eastern part of the Outer Carpathians is brackish and saline, in various degrees associated with oil and gas deposits encountered in folds, local thrust or flexure structures. Thus they represent both, the typical oil-field brines (because they are extracted together with oil as a byproduct, for example waters from wells Jaszczew 32a and Sobniów 29) or the so-called edge oil-field waters (i.e. these which are not in direct contact with oil deposits, like for example water from the well Lubatówka 12 belonging to Iwonicz Zdrój spa and extracted for production of mineral bathing salts). Both types of waters are additionally enriched in various degrees in specific compounds as bromine, iodine, boron, barium, strontium, lithium; in the gas phase CH_4 is dominant.

Usually, the perspective horizons with thermal waters occur in depth of about 1000 m and more. Their TDS values vary from below 10 g/dm^3 up to about 60 g/dm^3; outflow temperatures usually do not exceed 45–50°C, but exceptionally may reach 84°C (for example vicinity of Wiśniowa). The geochemical types of thermal waters are variable from HCO_3-Cl-Na through Cl-

HCO_3-Na to Cl-Na. Nevertheless, the distinction of individual hydogeothermal systems in the area of Outer Carpathians is hardly possible. Moreover, there is no significant differences in chemical and isotopic composition of thermal and mineralized waters in this area. The recharge areas for thermal as well as mineralized waters are still not known, their origin is poligenetic and their resources might be limited.

DISCUSSION

Mineralized and thermal waters in the area of study are always linked to flysch sediments. The isotopic composition of 54 waters from working mineral and thermal water wells and oil wells from the area of Silesian and Magura nappes show their complex and diverse origin (Fig. 2). Majority of them are at least two component mixtures of meteoric waters (these of modern and/or palaeoinfiltration) and connate seawater-like end-member of diagenetic or methamorphic origin (Dowgiałło and Leśniak 1980, Leśniak 1980, Zuber and Grabczak 1985, Oszczypko and Zuber 2002, Porowski 2004a, 2004b, 2006). Previous studies have shown that the most probable geochemical process which is responsible for the formation of such isotopically enriched end-members is dehydration of clay minerals (Leśniak 1980; Oszczypko and Zuber 2002; Porowski 2004a, 2004b, 2006).

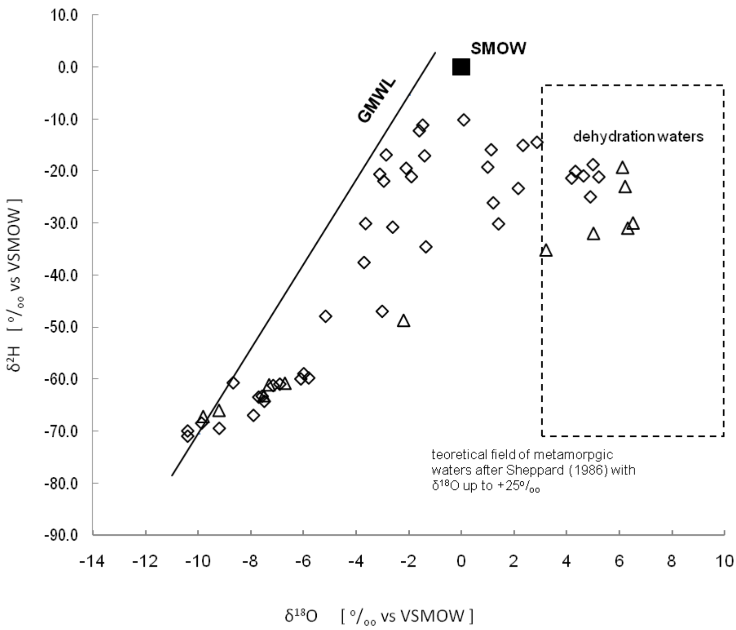

Figure 2. Isotopic composition of Carpathians mineralized and thermal waters. Rhombs represent waters form Central Carpathian Synclinorium, Silesian nappe; triangles – represent selected waters form Magura nappe: Rabka, Wysowa, Szczawa and Szczawnica (data after Oszczypko and Zuber, 2002; and Leśniak, 1980) . SMOW refers to Standard Mean Ocean Water, GMWL – Global Meteoric Water Line (after Różański et al. 1993). For further explanations see the text.

The most significant modifications are observed in illite/smectite dominated shale systems, where the increased temperature and pressure induce the dehydration of clay minerals (Powers 1967, Burst 1969, Perry and Hower 1972, Yeh and Savin 1977, Yeh 1980, Morad *et al.* 2000).

The process of dehydration itself is a mineralogical reaction in which smectite is transformed into illite, i.e. hydrated smectites lose water and form illites within illite/smectite mixed-layers:

- smectite + Al^{3+} + K^{+} → illite + Si^{4+} (Hower et al., 1976), or
- smectite + K^{+} → illite + Si^{4+} + cations (Ca^{2+}, Mg^{2+}, Na^{+}, Fe^{2+}) (Boles & Franks 1979).

During this process, the dissolution of smectite and subsequent crystallization of illite occurs, resulting in the increase of the amount of illite in the illite/smectite mixed-layers. The crystallization of a new mineral occurs in isotopic equilibrium with surrounding interstitial water. According to Perry & Hower (1972), dehydration should occur in each sedimentary basin where shale sediments are subjected to increased temperatures during diagenesis. These authors stated that geothermal gradient of about 2.4°C/100 m would be enough to initiate dehydration at the depth of about 3000 m. Taking into account the geological settings of the Outer Carpathians it seems very probable that this process could occur here. First of all, the flysch sediments include numerous thick shale intervals, where clay minerals constitute about 70% of rock. The dominant is mixed-layer illite/smectite (J. Środoń, personal information). The geothermal gradient in the CCS is in the range 2.3 – 2.6°C/100 m (Plewa, 1994). The observed petrographical effects of diagenetic processes suggest that temperatures during the periods of maximum burial were higher than those ones observed nowadays (Porowski 2004b). Moreover, in typical sedimentary basins the generation of oil occurs in temperatures ranging from 50 to 175°C, with maximum intensity in temperatures of about 90°C (Hunt, 1979). The isotopic composition of the crystalline structure of clay minerals always reveals considerable enrichment in ^{18}O and also considerable depletion in D relative to VSMOW, which is in agreement with systematic of isotopic composition of dehydration waters in the studied area (see fig. 2). An attempt of model the isotopic composition of water in equilibrium with mixed-layer smectite/illite undergoing dehydration in particular temperatures and particular water-to-rock ratios was presented by Porowski (2006). Despite of the specific assumptions needed to be taken to calculations, the results showed, that calculated final isotopic composition of seawater in equilibrium with mixed-layer clay minerals in the temperature range 103–173°C and rock/water ratio 5%, is in the range of $\delta^{18}O$ from +5.5 to +10.3‰, and $\delta^{2}H$ from -14.4 to -18.1‰, respectively. Such promising results of calculations strongly suggest that dehydration waters encountered in the flysch Carpathians may be considered as indicators of thermal conditions in the geological system at least at depth of their origin and time of dehydration.

On the other hand, an attempt of application of selected chemical geothermometers was made in order to estimate the possible "signal" of maximum temperatures which could be carried out by dehydration waters. The geothermometers have been applied for all the waters considered as dehydration ($\delta^{18}O \geq \sim 3$‰) and for a few thermal waters from eastern part of the Outer Carpathians. As can be seen from Table 1, the maximum reservoir temperatures estimated by chemical geothermometers are diverse and variable. The chalcedony geothermometer indicate the lowest range of reservoir temperatures and estimate quite well the outflow temperatures of some waters. It strongly suggest, that this geothermometer is sensitive on re-equilibration and indicate the last phase of groundwater flow and cooling down. The Na-K geothermometer presented here is derived for the Na and K exchange equilibria with some clay minerals (Arnórsson 1998).

Table 1. The results of application of selected chemical geothermometers to the assessment of possible thermal conditions in the outer flysh Carpathians. D – total depth, TDS – total dissolved solids, to – temperature measured at the outflow, tG – bottom hole temperature calculated from geothermal gradient, tCh - temperature estimated by chalcedony geothermometer (Arnórsson et al. 1983), tNa-K - temperature estimated by Na-K geothermometer (Arnórsson 1998), tMg-Li - temperature estimated by Mg-Li geothermometer (Kharaka and Mariner 1987). For explanation see the text.

Name of well	D [m]	Chemical type	TDS [mg/dm^3]	$\delta^{18}O$	δ^2H	t_o	t_G	t_{Ch}	t_{Na-K}	t_{Mg-Li}
Lubatowka 12	958.0	Na-Cl-HCO_3	19215.8	1.2	-26.2	21.2	31.9	19.8	51.9	105.2
Sobniów 29	2240.0	Na-Cl	21148.75	5.2	-21.2	25.2	63.4	54.6	94.9	125.7
Jaszczew 32a	2530.0	Na-Cl-HCO_3	15400.9	4.9	-25.0	22.1	70.5	50.0	70.7	116.4
Rudawka 11a	407.1	Na-Cl	29650.7	4.3	-20.1	14.8	18.5	13.5	67.1	143.2
Moderówka 7	1800.0	Na-Cl	20087.7	4.6	-21.0	16.6	52.6	28.6	38.9	121.1
Iskierska 18	345.6	Na-Cl	27825.0	4.2	-21.4	13.0	16.9	12.5	32.0	88.2
Łodyna 76	546.1	Na-Cl	48967.2	2.3	-15.1	12.0	21.9	9.9		87.7
Jajko	1000.0	Na-Cl	12516.0	2.9	-14.5	10.5	33.0	4.1	23.1	61.1
Wysowa, well Aleksandra[1,2]	100.0	Na-HCO_3-Cl + CO_2	24980.0	6.5	-30.0	12.5	11.0	14.8	92.9	151.8
Wysowa, well 14[2]	50.0	Na-HCO_3-Cl+ CO_2	20388.0	3.2	-35.2	9.9	-	8.9	97.1	133.6
Szczawnica, Magdalena spring[1,2]	spring	Na-HCO_3-Cl + CO_2	26304.0	5.0	-32.0	10.8	-	44.2	91.0	108.9
Szczawno: well Szczawa II[1]	100.0	Na-HCO_3-Cl + CO_2	27848.0	6.3	-31.0		11.0	19.3	31.1	126.9
Rabka: well-18[1]	120.0	Na-Cl	25727.9	6.2	-23.0		11.5	3.3	50.2	159.9
Rabka: well Krakus[1]	20.0	Na-Cl	21167.0	6.1	-19.3		-	22.9	75.4	148.4

[1] – data after Dowgiałło (1976); [2] – data after Lesniak (1980, 1998);

Although, for some waters it indicate the reservoir temperatures more than 60°C (the temperature of 60°C is considered to be the border from which the dehydration process may start in favorable geological conditions) the influence of clays-water ion-exchange reactions in low temperature conditions surely affect the final concentration of Na and K in water. The Mg-Li geothermometer is the most interesting here. It is specially recommended for estimation of reservoir temperatures in the areas of oil fields (Kharaka and Mariner 1987). The maximum temperatures estimated by this geothermometer are between 61–159°C. That range of temperatures in geological system of flysh Carpathians, although quite wide (probably connected with isotopic composition of water) agrees with probable range of temperatures of dehydration of clay minerals and generation of dehydration waters encountered in this area. Moreover, such range of temperatures is in good agreement with thermal conditions of Carpathian oil generation. It is difficult to answer the question, whether these temperatures are possible nowadays for deep groundwater horizons in this part of the Carpathians? This problem needs of course further investigation taking into account the complex origin of waters in this area.

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