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Thermal Regime of the Podhale Geothermal System (Poland) in the Light of Organic Matter Maturation and Other Research Methods

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ABSTRACT

It is very difficult, and perhaps impossible, to make a precise reconstruction of the thermal conditions in the Mesozoic complex, and make a comparison between the Paleogene filling complex and the Mesozoic basement complex in the Podhale Trough, based on organic-matter data only. The rate of transformation of the organic matter is strongly influenced by the nature of the host sediments. The maturation of the Paleogene organic matter from Podhale Trough increases gradually with depth and in a lateral south-east direction. This observation concords with the results of the diagenetic study of the clay minerals. Maturation of organic matter in the Mesozoic sedimentary rocks is much more complex and possibly a result of its complicated geological history and/or oxidation of the organic matter during hydrothermal fluid migration.

1. INTRODUCTION

For over fifteen years the Podhale geothermal system in Poland was the subject of studies aimed at the construction of a geothermal regional heating network. This research has been summarized in Kepinska (2003) and Dlugosz (2003). New methods have been adopted along with the more classical ones, such as the definition of the characteristics of thermal organic matter maturation by means of vitrinite reflectance, studies of the distribution of organic compounds, and analyses of the thermal transformation of some clay minerals. The methods used for the Podhale system have proven to be very useful for studying the low-enthalpy geothermal system connected with sedimentary formations of complex tectonic evolution. It is also worth noting that Podhale, like many other geothermal systems in sedimentary environments, contains fluids and bitumens. Their common occurrence and genesis can be revealed by means of the methods mentioned in this paper. These techniques can be successfully implemented in other similar systems, especially where there are no distinct 'classical' indicators of a thermal evolution (for instance, secondary mineralization or fluid inclusions). The paper will describe briefly the thermal history and present conditions of the Podhale system. A group of methods based on the thermal transformation of organic matter dispersed in rock formations (destined to become the geothermal aquifers and caprock formations) was used.

2. GEOLOGICAL SETTINGS

The Western Carpathians structure is divided into two parts, the Central Carpathians and the Outer Carpathians. The junction is marked by the Pieniny Klippen Belt (PKB). The Central Western Carpathians (CWC) comprise several pre-Alpine massifs (crystalline + Mesozoic basements) surrounded by troughs filled with Tertiary sediments. The Tatra Mountains are the northernmost core-massif in the CWC. The Podhale Trough is a structural depression confined to the north by the Pieniny Klippen Belt and to the south by the Tatra Mts. block. The Mesozoic basement of the Podhale Trough has a typical Alpine structure consisting of numerous nappes, overthrusts and folds on every scale. The nappes were transported over the Paleozoic crystalline core of the Tatra Mts. during the late Cretaceous – Paleocene (Birkenmayer, 1974). A Paleogene transgressive carbonate series and a flysch formation were deposited on the basement rocks. Both the Tatra Mts. block and Podhale Trough are cut by NE-SW trending tectonic zones. Some of these developed during Alpine orogenesis, mainly in late Cretaceous times, but some were re-activated and others formed during Neogene vertical movements. As a consequence, the Mesozoic basement exhibits a poly-block structure. Both faults and fractures control fluid and heat circulation.

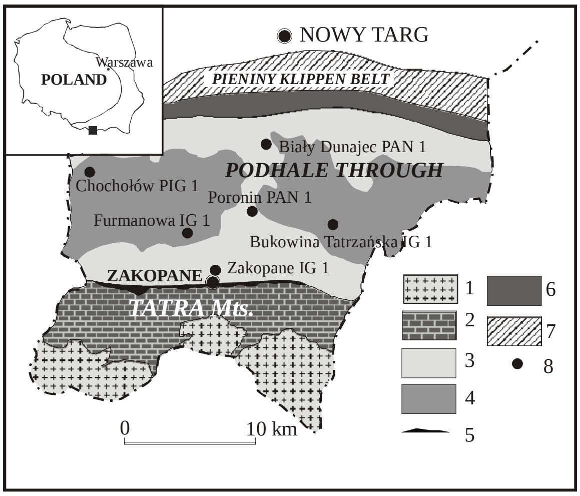

Figure 1: Location of sampling points. 1) crystalline core of the Tatra Mts.; 2) Mesozoic sequences of the northern cover of the Tatra Mts.; 3) to 6) Paleogene, where 3) Zakopane beds; 4) Chocholowskie beds; 5) Eocene; 6) Szaflary beds; 7) Pieniny Klippen Belt; 8) boreholes

3. SAMPLES AND METHODS

For the investigations reported here, the following drill-cores were sampled: Zakopane IG-1 (Paleogene and Mesozoic), Chochołów PIG-1 (Paleogene and Mesozoic), Furmanowa IG-1 (Paleogene), Poronin PAN-1 (Tertiary and Mesozoic) and Biały Dunajec PAN-1 (Tertiary and Mesozoic) (Figure 1).

The methods used are as follows:

3.1 Petrography

Petrographic observations of polished rock fragments and vitrinite reflectance (R_o) measurements were carried out at the Faculty of Earth Sciences, University of Silesia.

3.2 Rock Eval

Rock-Eval analyses were performed using a Delsi Model II Rock Eval instrument equipped with an organic carbon module as described by Peters (1986).

3.3 Extraction and fractionation

The analysed source rocks were Soxhlet-extracted in pre-extracted thimbles with dichloromethane. Extracts were further separated using pre-washed TLC plates coated with silica gel (Merck, 20 x 20 x 0.25 cm). The TLC plates were activated at 120°C for 1 hour beforehand. The plates were loaded with the *n*-hexane soluble fraction and developed with *n*-hexane. Bands comprising aliphatic (R_f 0.4-1.0), aromatic (R_f 0.05-0.4) and polar (R_f 0.0-0.05) fractions were collected.

3.4 Gas Chromatography – Mass Spectrometry (GC-MS)

GC-MS analyses were carried out using a HP6890 II gas chromatograph equipped with a fused silica capillary column (60 m x 0.25 mm i.d.) coated with a 95% methyl/5% phenylsilicone phase (DB-5MS, 0.25 μm film thickness) and a 50% methyl/50% phenylsilicone phase (DB-17MS, 0.25 μm film thickness). Helium was used as carrier gas. The GC oven was programmed from 35°C to 300°C at a rate of 3°C min^{-1}. The gas chromatograph was coupled with a HP 5971A mass selective detector (MSD). The MSD was operated with an ion source temperature of 200°C, an ionisation energy of 70 eV, and a cycle time of 1 sec in the mass range 40-600 Daltons. Individual compounds were identified on the basis of mass spectra retention indices (Lee et al., 1979) and, for the phenyl-derivatives of polycyclic aromatic compounds (Ph-PAC), by co-injection with internal standards (Marynowski et al., 2001; 2002).

3.5 Isotope analysis

Isotope analyses of separated aliphatic and aromatic fractions were performed as follows: about 3 mg of hydrocarbon material from each sample was combusted with CuO wire in a sealed quartz tube, under vacuum at 900°C. The CO_2 gas was cryogenically purified and then introduced into a mass spectrometer (Finnigan Mat CH7 with a modified inlet and detection system). The carbon stable isotope ratio ($\delta^{13}C$) was measured with precision of 0.05‰. Values are quoted relative to PDB international standard.

4. VITRINITE REFLECTANCE

4.1 Mesozoic basement of the Podhale Trough

The Mesozoic rocks of the Podhale Trough basement are predominantly carbonate-rich (limestones, dolomitic limestones) and organic-poor complexes. In the case of the carbonate lithologies, R_o data are scanty since the vitrinite clasts are rare or absent. Vitrinite reflectance values spread over a relatively wide range. Measured values range from 1.02% (Chochołów IG1) and 1.0% (mean value - Biały Dunajec PAN 1 borehole) to 1.11 - 1.43% (Poronin PAN 1 borehole) and 2.30% (Zakopane IG 1 borehole).

4.2 Paleogene rocks of the Podhale Trough

The Paleogene rocks are lithologically variegated dark gray and black shales (intercalated mudstones and siltstones) and tectonic breccias. The organic matter is irregularly dispersed with laminar concentrations in mudstone lithologies. In the Tertiary rocks the mean vitrinite reflectance values generally increase with depth, from 0.83 - 1.02% (Chochochołów PIG-1) to 1.08 - 1.14 % (Bukowina Tatrzańska PIG-1) and up to 0.85 - 1.22% (Bańska IG-1). Extremely high values characterize mineralized tectonic zones: 2.37 - 2.42% (Zakopane IG-1). R_o values show a gradation from low values in the west to higher R_o values in the southeast. As large numbers of allochthonous, reworked vitrinite clasts are present, the results should be treated with some caution. Measured mean R_o values are usually higher than the values calculated from the methyphenanthrene index - Rc (Figure 1) as a result of the presence of redeposited vitrinite in the Paleogene rocks.

5. BULK GEOCHEMICAL DATA

Measured total organic carbon contents (TOC) for the Paleogene rocks (0.1-3.2%) are higher than the values for the Mesozoic sediments (0.1-1.30%). Hydrogen indices obtained from Rock Eval analyses are low for both the Mesozoic and Tertiary sediments (HI = 40-120). These values suggest the presence of type III kerogen in the Mesozoic and Paleogene basins. Because of the high thermal maturation (T_{max} = 460°C) of the Mesozoic sediments, their measured HI values should in fact be treated as false values. HI values between 60-100 measured for the relative immature Paleogene rocks from Chochołów PIG-1 are undoubtedly characteristic of type III kerogene (sensu: Tissot and Welte 1984). Organic fraction contents vary in the analysed samples and do not reveal any definable regional patterns. Both the Paleogene Flysch and the Mesozoic rocks (which contain geothermal aquifers and series that are poorly impermeable) of the Podhale system show a similar range of $\delta^{13}C$ values, typical of marine, algal or mixed-source (marine and terrestrial) material, with a dominant planctonic type of organic matter.

6. SATURATED AND AROMATIC HYDRO-CARBONS

In most of the samples analysed, the major organic compounds from the aliphatic fraction are *n*-alkanes and isoprenoids (pristane and phytane). Biomarkers such as

Table 1. Geochemical characteristics of the samples from Podhale Trough and Western Tatra Mts. TOC : total organic carbon; MPI1 : methylphenanthrene index 1; $MPI_1 = 1.5([2\text{-}MP] + [3\text{-}MP])/([P] + [1\text{-}MP] + [9\text{-}MP])$ (Radke and Welte 1983); $Rc[\%] = 0.40 + 0.60(MPI_1)$; $R_o[\%]$ = vitrinite reflectance; nf = not found.

Locality	Depth (m)	Age	TOC (%)	MPI_1	R_c (%)	R_o (%)
Zakopane IG1	111	Paleogene	-	0.60	0.76	nf
	570	Paleogene	-	0.89	0.93	nf
	1299	Mesozoic	0.60	1.53	1.32	2.42
Furmanowa IG1	1284	Paleogene	-	0.74	0.84	nf
	1953	Paleogene	2.50	1.00	1.00	1.01
	1980	Paleogene	2.70	1.02	1.01	nf
Bukowina Tatrzańska IG1	102	Paleogene	-	0.60	0.76	1.09
	902	Paleogene	1.00	1.31	1.19.	1.25
	1904	Paleogene	-	1.62	1.37	1.41
Chochołów PIG1	193	Paleogene	-	0.28	0.57	nf
	280	Paleogene	-	0.35	0.61	nf
	513	Paleogene	-	0.32	0.59	0.78
	593	Paleogene	0.10	0.31	0.59	nf
	820	Paleogene	-	0.42	0.65	nf
	1283	Paleogene	-	0.47	0.68	nf
	1671	Paleogene	-	0.48	0.69	nf
	2011	Paleogene	2.50	0.50	0.70	nf
	2075	Paleogene	-	0.55	0.73	nf
	2410	Paleogene	-	0.58	0.75	0.95
	2511	Paleogene	-	0.62	0.77	nf
	2900	Paleogene	-	0.81	0.89	1.02
	3154	Mesozoic	0.70	0.47	0.68	1.10
Poronin PAN 1	1390	Paleogene	3.20	0.97	0.97	1.02
	1706	Paleogene	2.20	1.17	1.19	1.00
	1843	Mesozoic	0.50	0.95	0.97	nf
	1866	Mesozoic	1.30	1.03	1.02	nf
	1912	Mesozoic	0.40	0.91	0.95	1.21
	2225	Mesozoic	-	1.68	1.41	1.05
	2356	Mesozoic	-	0.42	0.65	nf
	2956	Mesozoic	0.50	0.51	0.71	nf
Biały Dunajec PAN 1	0	Paleogene	2.50	0.44	0.66	nf
	974	Paleogene	2.20	0.78	0.87	nf
	1500	Paleogene	1.50	0.91	0.95	nf
	1835	Paleogene	1.30	1.02	1.01	1.20
	2076	Mesozoic	0.15	0.79	0.87	nf
	2177	Mesozoic	0.70	0.86	0.92	1.03
	2216	Mesozoic	0.50	0.89	0.93	1.10

steranes and triterpanes are present only in Paleogene sedimentary rocks from well Chochołów PIG-1 and in near-surface rocks from well Biały Dunajec PAN-1, where thermal maturity is lowest. Due to aromatisation and thermal cracking, organic matter from the other boreholes do not contain biological markers. Analysis of the organic compounds from the aromatic fraction shows large differences between Paleogene organic matter (OM) from the western (low maturity) and south-eastern (high maturity) parts of the Podhale Trough. The values of the methylphenanthrene index (MPI) molecular maturity parameter, calculated to theoretical vitrinite reflectance (Radke and Welte 1983) are presented in Table 1. Maximum temperatures calculated from Rc (Table 1), affecting recent near-surface Paleogene rocks in the western part of the Podhale Trough (Chochołów PIG-1) range between 50-70 °C and increase gradually to temperatures between 100 and 130 °C at a depth of 2000 m, whereas in the south-eastern part (Poronin PAN-1, Zakopane IG-1) temperatures exceed 100-130°C near the surface and increase to 160-200°C at a depth of 2000 m (Figures 2 & 3).

Phenyl derivatives of polycyclic aromatic compounds (Ph-PAC) are present in the Podhale Paleogene Flysch. Their concentrations are low compared to the most common polycyclic aromatic hydrocarbons (PAH) such as methylnaphthalenes, methylphenanthrenes, etc. Mesozoic sedimentary rocks contain higher concentrations of Ph-PAC with respect to most common PAH (e.g. dimethylpyrenes and dimethylfluoranthenes) and the composition of the above-mentioned compounds is more varied. The phenylnaphthalenes, terphenyls and phenylphenanthrenes are present in the Podhale Flysch, while the Mesozoic basement of this sedimentary basin also contains phenylfluorenes, phenyldibenzofurans and phenyldibenzothiophenes. In all the samples analysed, except the shallowest, the phenyl derivatives are dominated by the most thermally stable isomers such as 2-phenylnaphthalene, 3-, 2-phenylphenanthrenes, *m*- and *p*-terphenyls. 1-phenylnaphtalene is present in the 0 to 2000 m depth range in the Chochołów PIG-1 borehole, but this compound disappears below 2000 - 2400 depth. This corresponds to an R_C of about 0.7-0.8 %. Only thermally stable isomers of Ph-PAC and terphenyls are present in all other wells. It is worth mentioning the presence of phenyldibenzothiophenes (PhDBT) in the rocks of the Mesozoic basement only.

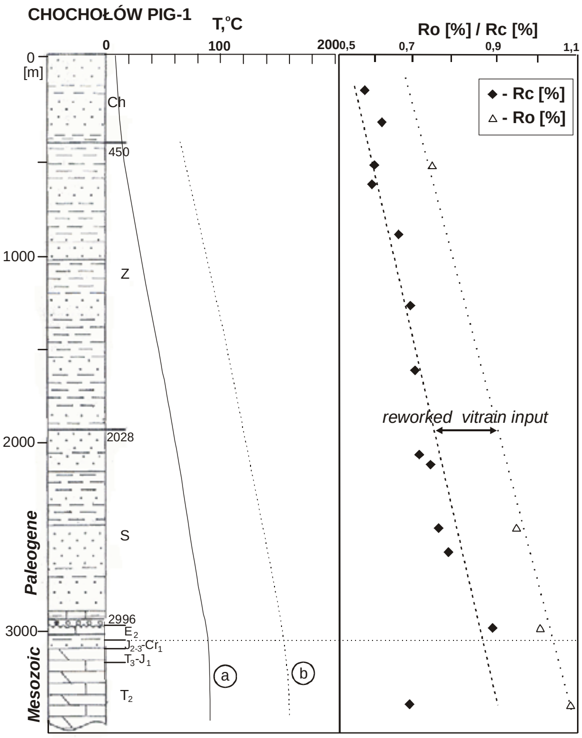

Figure 2. Paleo-temperatures calculated on the basis of illite/smectite crystallinity (Kepinska, unpublished data) compared with measured and calculated (from MPI) vitrinite reflectance in the Chochołów PIG-1 well. a) recent geothermal curve; b) paleothermal curve; Ch) Chocholowskie beds; Z) Zakopane beds; Sz) Szaflary beds; E) Eocene

Perhaps this is a reflection of the advanced diagenesis of more labile organic sulphur compounds originally produced in environments with functioning bacterial sulphate reduction. These compounds are represented by all isomers with domination of most stable 2- and 3-PhDBT. The phenyl derivatives of aromatic compounds are formed by diagenetic, hydrothermal oxidation of organic matter (Marynowski et al. 2002) and their increased concentrations in sedimentary rocks are usually connected with pathways of the hydrothermal fluid migrations. In the case of the Podhale Trough, the oxidized horizons are located in the tectonized Mesozoic carbonates.

7. THERMAL MATURITY - DISCUSSION

The Paleogene rocks of the Podhale Trough support a model for the basin in which the organic-compound distribution parameters increase progressively with depth (i.e., MPI, Table 1, Figure 2). However, pending a precise reconstruction of thermal conditions in the Mesozoic complex, a comparison between the Paleogene filling complex and the Mesozoic basement complex based on organic-matter data is very difficult and perhaps even impossible.

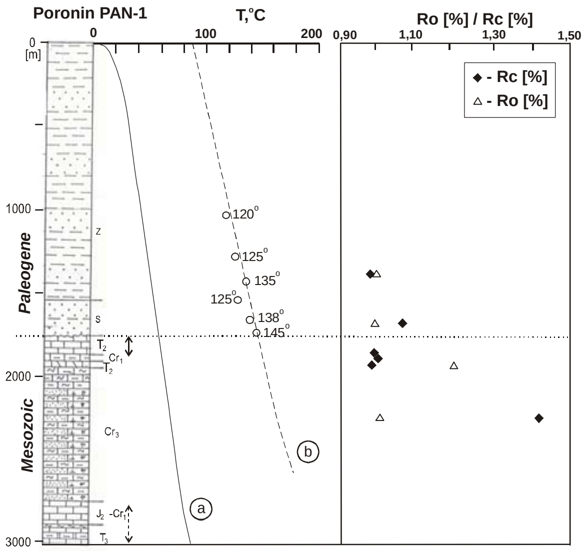

Figure 3. Paleo-temperatures calculated on the basis of illite/smectite crystallinity (Kepinska, unpublished) compared with measured and calculated (from MPI) vitrinite reflectance in the Chochołów PIG-1 well. For explanation of symbols, see Figure 2.

The rate of organic-matter transformation is strongly influenced by the nature of the host sediments. The most important factor is the quantity of clay minerals (and clays/TOC) that act as catalysts for most of the reactions that occur during the transformation (Alexander et al., 1984; van Kaam Peters et al., 1998; Marynowski et al., 2001). Among the other features, MPI values and recalculated R_c values for the Paleogene and Mesozoic rocks bear little comparison. In broad terms, the degree of thermal tranformation of organic matter in the Paleogene rocks from the Podhale Trough increases in a SW direction and is highest in Zakopane IG-1 and Bukowina Tatrzańska IG-1. The lowest degree of thermal transformation was recorded in Chochołów PIG-1. The changes in the thermal maturation level of the Paleogene rocks (type III kerogen) are well evidenced by the MPI1 parameter (and values recalculated to Rc). However, the MPI1 parameter does not work with the marine, mostly carbonate, Mesozoic rocks (Table 1). A crucial factor in any study of the thermal maturity of rocks is the length of the time interval during which the maximum attained temperature affected the Mesozoic rocks such as to cause the present level of maturity. That event might have taken place before or during the overthrusting of the Mesozoic sediments over the Tatra Mts. to their present setting in the Podhale Trough or, alternatively, after the Alpine overthrusting and as a consequence of burial under the Paleogene sediments.

8. CONCLUSIONS

1. Calculated paleotemperatures of Paleogene sedimentary rocks from the Podhale Trough show that the ancient temperatures influencing the geothermal fluids were higher than current values.

2. Maturation of the Paleogene sedimentary organic matter increases south-eastwards, from low-maturity samples of the Chochołów PIG-1 well to the high-maturity samples from Poronin PAN-1 and Zakopane IG-1 wells.

3. Organic matter from the Mesozoic, allochthonous and overthrust rocks is characterized by an overall high degree of maturation, but interpretation and comparison of the Mesozoic complex with the Paleogene is very difficult and perhaps even impossible

4. The Mesozoic sedimentary rocks contain relatively large concentrations of phenyl derivatives of polycyclic aromatic compounds which may formed through scondary, diagenetic oxidation of organic matter during hydrothermal fluid migration.

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