# PRELIMINARY MINERALOGICAL AND PETROGRAPHICAL STUDIES OF VEINS WITHIN THE COUNTRY ROCKS OF THE NEOGENE VOLCANITES OF THE PIENINY KLIPPEN BELT AS INDICATORS OF POTENTIAL GEOTHERMAL PROCESSES

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**Abstract:** Field and as mineralogical and petrographical examinations of sedimentary rocks present in the area surrounding the Pieniny Klippen Belt were performed. The aim of these investigations was to identify the symptoms of hydrothermal processes within the studied rocks. Moreover, the areas prospective for the occurrences of geothermal waters, alternative source of thermal energy instead of traditional power production using fossil fuels, were indicated. Analytical investigations were focused mainly on mineralogical composition of rocks as well as on the frequency of occurrences of various veins (mainly built of carbonate minerals) intersecting the rocks from the neighbourhood of Neogene andesitic rocks from the Pieniny Klippen Belt. The highest quantity and thickness of the veins was observed in the rocks from the area of Piekiełko stream near Krościenko. The clastic rocks (sandstones) from this area contain many fractures which are crucial for potential geothermal water circulation.

Key words: diagenesis, hydrothermal activity, geothermal energy, Pieniny Klippen Belt.

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# INTRODUCTION

The economic and civilization development of many countries is responsible for growing demand for various mineral resources. Growing global demand for energy causes increasing need of alternative energy sources. Large scale use of geothermal energy (direct use and local heating systems, electricity generations, geothermal heat pumps etc.) is globally important as a perspective renewable energy source. In Poland, geothermal heat stations at Mszczonów, Pyrzyce, Słomniki, Uniejów and Stargard Szczeciński have been completed yet. However, the interest in geothermal energy is still growing (*e.g.* Sokołowski, 1995; Kępińska *et al.*, 2000; Kępińska, 2001, 2006; Kępińska & Łowczowska, 2002; Chowaniec, 1989; Chowaniec *et al.*, 1999; Pawlikowski & Mazurek, 2000).

The Pieniny Klippen Belt is a northern barrier for the Podhale geothermal system (Kępińska, 2001, 2006). The zero electromagnetic induction anomaly is ascribed to it, what suggests the occurrence of geothermal waters at great depths (Jankowski *et al.*, 1982). In the tectonic contact zone between the Podhale Basin and the Pieniny Klippen Belt, a surface thermal positive anomaly was recorded at 0.5–1°C above the average background values (Pomianowski, 1988). It is probably caused by the increased heat (water?) transport from the lower crust and upper mantle towards the Earth surface in the peri-Pieniny strike-slip fault.

The Pieniny Klippen Belt is geologically completely different from the Podhale Basin system, which is an important reservoir of thermal waters (Kępińska, 2006). In this re-



Fig. 1. Location of sampling sites

gion, numerous outcrops of magmatic rocks can be found (Małkowski, 1948, 1958; Wojciechowski, 1955; Birkenmajer, 1958, 1962, 1965, 1979; Pawlikowski & Wiewiórka, 1979; Parachoniak & Pawlikowski, 1980). Tectonic engagement of both clastic and carbonate rocks was also observed. Carbonate rocks showing high permeability and numerous fractures are preferred sediments for karst processes. These conditions are favourable for geothermal water occurrence. The above mentioned premises call an argue for the existence of geothermal waters in some parts of the Pieniny Klippen Belt. The towns as Szczawnica and Krościenko, situated in the Pieniny Mts., are still waiting for ecological heating systems using geothermal energy. The question if these renewable energy sources can be acquired just from the Pieniny Klippen Belt resources is still open.

The bibliography on geology as well as on mineralogy and petrography of rocks present in the examined area is very rich (Małkowski, 1948, 1958; Birkenmajer, 1958, 1962, 1965, 1979, 1986; Birkenmajer & Pécskay, 2000; Golonka *et al.*, 2005, and others). However, in this region the geothermal investigations have not yet been carried out in detail. Consequently, adequate studies of geothermal energy potential in the Pieniny Klippen Belt should be initiated as soon as possible. The interest in possible geothermal waters occurrence there is still increasing. Potential investors are encouraged by the fact that in the adjacent Podhale region (Bańska, Zakopane), thermal waters have been exploited for heating and recreation purposes for a dozen of years (Sokołowski, 1984, 1995; Kępińska & Łowczowska, 2002). In Bukowina Tatrzańska, Białka Tatrzańska and Zakopane, different geothermal investments are still in progress. On the other hand, in Slovakia, geothermal waters are used for balneotherapy and recreation in much broader scope than in Poland (Fendek *et al.*, 1995; Fendek & Franko, 2000). Thermal spas, water recreation centers in Poprad, Vranov and Bešenova and many others offer allyear-round wide choice of various services and attractions.

The investigations of geothermal systems are very advanced in Europe (e.g. Fournier & Truesdell, 1973, 1974; Kristmannsdottir & Tomasson, 1978; Browne, 1978, 1993; Arnorsson, 1983; Kępińska, 2001, 2006). Consequently, the recognition of hydrothermal activity symptoms within the country rocks of Pieniny Klippen Belt was the main aim of this paper. These hydrothermal processes have resulted from the circulation of mineralized solutions within the country rocks during and after andesites crystallization (Szeliga *et al.*, 2005). The presented results include macroand microscopic studies and cathodoluminescence (CL) observations of 26 rocks samples hosting numerous mineralized veins.



**Fig. 2.** Geological sketch-map of Szczawnica-Krościenko area. 1 – Palaeogene flysch (Magura Nappe); 2 – Pieniny Klippen Belt (Grajcarek Unit, Klippen nappes, Klippen cover: Jurassic–Cretaceous); 3 – amphibole-andesite intrusions (1st phase), exposed at the surface; 4 – subsurface andesite intrusions as traced by magnetometric survey; 5 – northern boundary strike-slip fault (Early Miocene) of the Pieniny Klippen Belt; 6 – transversal and oblique strike-slip faults (Middle Miocene) (after Birkenmajer & Pécskay, 2000)

## **METHODS**

Field works included the sampling of selected rock series cut by many veins filled with minerals (Figs 1, 2). The presence of contact zones of various geological units (e.g. between the Pieniny Klippen Belt rocks and Magura Palaeogene series, Podhale Palaeogene flysch), the zones of faulting as well as the proximity of andesite outcrops were additional criteria for sampling (Fig. 2). The samples of rocks containing mineralization veins were mostly collected along the streams. The frequency of veins occurrence (amount per m<sup>2</sup>) within the rocks was determined in the scale of 1–5 (were 1 is the smallest and 5 is the highest). Their thickness was measured during field works too (Table 1).

The macro- and microscopic investigations of the rocks were carried out at the laboratories of Department of Mineralogy, Petrography and Geochemistry, Faculty of Geology, Geophysics and Environmental Protection, AGH-UST (University of Science and Technology) in Kraków, and in the Polish Geological Institute in Warsaw (cathodoluminescence analysis).

Standard optical analyses were carried out on polished thin sections with the use of a polarizing microscope (Olympus BX 51 with DP 12 camera).

Cathodoluminescence analyses (CL) were carried out on polished thin sections using the Cambridge Image Technology CCL 8200 MK3 device (cold cathode) linked to a Nikon Optiphot 2 polarising microscope. CL photos were taken using a Microflex UFX–DX camera.

The microscopic and cathodoluminescence analyses were applied to describe mineralogical and petrographical character of the studied rocks as well as the vein mineralization.

#### RESULTS

The results of **macroscopic characterization** of the rocks (sandstones and limestones) are shown in Table 1. Various forms of veins intersecting these rocks are presented on figures 3A and 3B. The most numerous and thickest vein mineralization (on the base of about 50 measurments) appears within rocks sampled from the vicinity of the Piekiełko stream situated west of Krościenko (sample nos 5, 6, 7) and from the region between Szczawnica and the Homole ravine reserve (samples nos 25, 26) (Figs 5, 6).

Medium frequency of veins in the studied rocks is most often observed (Fig. 5). It is noted at following outcrops 1-5 and 8-22, while the maximum frequency was observed at points of sampling nos 6, 7 and 23-27. The thickest veins were observed at the same places were they are most frequent (Fig. 6).

The **microscopic observations** have shown that the majority of veins intersecting the rocks are composed mainly of carbonate minerals (calcite) and subordinately of

# Table 1

## Characteristics of veins from country rocks of the Pieniny Klippen Belt

Sample No	Localization	Characterization of rocks containing the secondary mineralization	Max. thickness of veins (cm)	Frequency of veins occurrence (scale 1-5)
1	Ochotnica - the Gorcowy stream	Brown-gray fine-grained sandstone	0.4	1
2	Ochotnica - the Jurgowski stream	Brown-gray fine-grained sandstone with the admixture of silt matrix	0.5	2
3	Ochotnica exit	Brown-gray fine-grained sandstone	0.8	1
4	E bank of the Dunajec river	Brown-gray fine-grained sandstone with the admixture of carbonate cement	0.05	2
5	The Piekiełko stream	Brown- gray micrite limestone	3.5	5
6	N bank of the Krośnieński stream	Brown-gray fine-grained sandstone	3.0	4
7	Kluszkowce	Yellowish fine-grained sandstone	3.5	2
8	The drift on the way to Sromowce	Gray-brownish fine-grained sandstone	1.5	1
9	Niedzica, the castle neighbourhood	Gray micrite limestone	2.0	2
10	Červeny Klaštor	Gray-brown sandstone with the admixture of carbonate cement	2.0	3
11	The stream, E from Červeny Klaštor	Gray-brown medium-grained sandstone	1.5	1
12	The stream, E from Červeny Klaštor	Brown-gray fine-grained sandstone	1.5	2
13	W bank of the stream in Łapsze	Brown-gray sandstone with the admixture of silt matrix	1.0	1
14	W bank of the stream in Łapsze	Brown-gray fine-grained sandstone	0.9	2
15	W bank of the stream in Łapsze	Brown-gray fine-grained sandstone	2.2	2
16	W bank of the stream in Spišska Stará Ves	Brown-gray coarse-grained sandstone	0.9	2
17	W bank of the stream in Spišska Stará Ves	Brown-gray fine-grained sandstone	2.7	2
18	W bank of the stream in Spišska Stará Ves	Brown-gray coarse-grained sandstone	1.6	2
19	W bank of the stream in Spišska Stará Ves	Brown-gray fine-grained sandstone	1.0	1
20	The Wielka Leśna stream, W bank	Brown-gray fine-grained sandstone with the admixture of carbonate minerals	0.8	1
21	The Wielka Leśna stream, W bank	Brown-gray fine-grained sandstone with the admixture of silt matrix	0.6	1
22	The stream between Spišska Stará Ves and Červeny Klaštor	Brown-gray fine-grained sandstone	2.2	3
23	The stream between Spišska Stará Ves and Červeny Klaštor	Brown-gray fine-grained sandstone	4.2	4
24	N bank of the Dunajec River, over Sromowce Wyżne	Gray micrite-sparite limestone	4.5	4
25	The Grajcarek stream near Szczawnica	Brown-gray coarse-grained sandstone	1.5	4
26	The Grajcarek stream near Szczawnica	Brown-gray fine-grained sandstone	1.5	4

**Fig. 3. A**, **B** – macrophotographs of sandstones with carbonate veins (sample no 15 and 6), **C** – concentration of pyrite crystals in central part of a calcite vein (sample no 6; partly crossed polarizers), **D** – three generations of calcite in veins: fine crystalline (the oldest generation), medium crystalline (younger generation), coarse crystalline (the youngest generation), sample no 10, partly crossed polarizers; **E** – idiomorphic quartz crystal (Q) at the contact with coarse crystalline calcite (C), sample no 16, partly crossed polarizers; **F** – idiomorphic quartz crystal concentrated along the contact of vein with sandstone (sample no 20, crossed polarizers); **G** – accumulation of organic matter between calcite crystals of two generations occurring in veins (sample no 23, partly crossed polarizers); **H** – deformed structure of calcite crystals (present in vein) in a fissure subject to tectonic movements (sample no 16, partly crossed polarizers)





quartz. Fe sulphides and organic substance occur in traces. The sizes of calcite crystals range from very small (5  $\mu$ m) xenomorphic – to large (1.5 cm) idiomorphic individuals showing perfect rhombohedral cleavage. Fe sulphides (mainly pyrite, subordinately marcasite) are observed in veins cutting rocks occurring near Krościenko (Fig. 1, sample nos 5, 6). They form microcrystalline concretions or idiomorphic crystals occurring both in the centre of veins and in the contact zone of the veins with the rock (Fig. 3C).

Several calcite generations were observed in carbonate veins intersecting sedimentary rocks (sandstones, limestones) both in Poland and Slovakia (Fig. 3D). Their occurrence indicates that the crystallization of this mineral took place during repeated broadening and contracting of the fissures within the rocks in question.

Quartz occurs only in veins from the Palaeogene sandstones of the Slovak part of the Pieniny Klippen Belt (outcrops nos 23–27). It is located in the centre of carbonate veins (younger generation) or at the contact zone of the vein and the host rock (older generation). The quartz forms idiomorphic crystals up to 4 mm in size (Fig 3E, F) and sometimes is surrounded by ore minerals (iron suphides).

The microscopic observations show that the mineralizing solutions, which penetrated fractured rocks, also contained hydrocarbons. Their accumulation between grains of different calcite generations were observed in veins present at Slovak outcrops of these rocks (Fig. 3G).

The solid inclusions of platy minerals showing low interference colours (kaolinite?) occur in the close vicinity of quartz crystals, in central part of veins (*i.e.* the youngest generation of veins).

The cyclical nature of post-magmatic and tectonic activity of the Pieniny Klippen Belt is manifested by the presence of several calcite generations within the veins as well as by diversified renovation of fractures. It is observed both in central parts of veins (symmetrical fissures along the vein axis) and at the contact with the host rock. Petrographic character (mostly orientated structure of rocks) seems to indicate the place mode of renewing process of the fissures. In compact sandstones with carbonate cement, calcite crystals filling veins are firmly connected with the host rocks and the fissures appear only within the veins itself. On the other side, in sandstones with less compact cementing material composed of *e.g.* clay minerals, the fissures can be found at the contact between the vein and host rock.

The effects of tectonic processes within the sandstones studied can be manifested by the deformation and dislocation of components of veins. Numerous elongated and deformed calcite crystals are observed (Fig. 3H). After the renovation and extension of veins, as a result of mechanical activity, a new generation of crystals was formed. The cathodoluminescence observations confirm that the vein mineralization in the studied rocks proceeded in several stages. Carbonate veins show light and dark orange CL colour, attributed to several calcite generations. Complex structure of these veins, intersecting the forms of different genesis, as well as multiple opening and healing of fissures can be easily found during CL analysis (Fig 4. A, B). Some thin veins running inside larger ones, which are invisible under microscopic observations, are well observed on CL photos. Some carbonate veins exhibit zonal structure. It is observed that the crystallization process started on fissure walls and proceeded toward the centre (Fig. 4C, D).

Calcite occurs also in intergranular spaces of sandstones and sometimes forms pseudomorphs after quartz (?). Three generations of calcite, showing various CL colours, can be distinguished within one concentration of the carbonate cement, but the determination of their sequence of generations is difficult.

Ankerite was identified in one carbonate vein (sample no 13). It does not show luminescence in CL due to the significant amount of iron in its structure (Fig. 4E, F).

Kaolinite is another mineral which appears in carbonate veins in dispersed form within calcite crystals. Sometimes it fills voids within the veins and occurs along the stylolite seams. On the CL photos, kaolinite shows dark blue luminescence colour (Fig. 4G, H).

Quartz was found in two crystalline forms: *i.e.* idiomorphic crystals (found near the veins' walls) and irregular individuals (filling the fractures within calcite veins). It does not show CL colour what indicates its low-temperature origin.

#### CONCLUSIONS

Literature data concerning mineralogical and petrographical investigations of reservoir rocks hosting geothermal aquifer from the Podhale region indicate that the vein mineralization consists mainly of calcite, dolomite and subordinately of siderite, quartz, clay minerals, while Fe-sulphides and hydrocarbons appear only in traces (Chowaniec *et al.*, 1999; Kępińska, 2001, 2006; Cebulak *et al.*, 2004). Similar mineral phases were recognized by the present authors within veins intersecting country rocks of the Neogene andesites from the Pieniny Klippen Belt. Microscopic observations have shown that calcite was the main component of these veins. In the rocks from the Polish part of the Pieniny Mts. Fe-sulphides were found, whereas in the sandstones from Slovakia quartz, kaolinite and organic substance (hydrocarbons?) were identified.

**Fig. 4.** A – several generations of calcite in veins formed in fine grained sandstone (sample no 8, crossed polarizers); **B** – CL image of calcium carbonate veins (*vide* Fig. 4a); **C** – fragment of a vein built of coarse-crystalline calcite (sample no 16, crossed polarizers); **D** – CL image of a calcite vein (*vide* Fig. 4c) with kaolinite (?) concentration (violet CL colour); **E** – fragment of a vein built of coarse-crystalline calcite (sample no 13, crossed polarizers); **F** – CL image of a vein (*vide* Fig. 4E). Accumulation of ankerite (black CL colour) in the centre of a calcite vein (orange CL colour); **G** – concentration of kaolinite in a calcite vein (sample no 16, crossed polarizers); **H** – CL image of a vein (*vide* Fig. 4G). Concentration of kaolinite (violet CL colour)



Fig. 5. Occurrence frequency of calcite veins within cover rocks of the Pieniny Klippen Belt

The frequency of occurrences and thickness of the veins in the studied rock samples is presented in figures 5 and 6. The crystallization of minerals within these carbonate veins took place in stages. This is the result of several repeated tectonic episodes affecting sandstones from the Pieniny Klippen Belt and of the cyclic nature of solutions that gave rise to crystallization of minerals within the fractures. The largest quantity and thickness of veins was observed in the rocks from:

- the surroundings of the Piekiełko stream (3 km west of Krościenko);

- the region between Szczawnica and the Homole ravine.

The thickness and frequency of occurrence of veins from the Haligovce and Spišská Stara Ves region (Slovakia) is similar to the same features observed in Piekiełko region in Poland.

Basing only on vein mineralization and the effects of tectonic activity observed within the studied rocks, the above mentioned regions seem to be prospective for the occurrences of geothermal waters. However, the presented studies should be treated as preliminary. More advanced geological and drilling investigations should be applied in the near future to solve the problem in question. The recognition of deep-seated geological structures and geothermal gradient are the factors which could confirm the selected areas as geothermally prospective.

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**Fig. 6.** Maximal thickness of calcite veins (cm) within country rocks of the Pieniny Klippen Belt

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