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Hydrogeochemical anomaly in waters of the pyrite deposit area in Wieściszowice (Western Sudetes Mts., SW Poland)

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ABSTRACT: In the dormant pyrite mine in Wieściszowice (Western Sudetes Mts.) a distinct hydrogeochemical anomaly was discovered, expressed by extremely high concentrations of iron, sulphates and aluminium in surface- and groundwaters. The waters contain also high amounts of such heavy metals, like Cu, Pb, Co, Cr and Zn. Sulphate and iron rich waters that drain the old mine area have great influence on the quality of the surface waters. A strongly acidic reaction pH, frequently below 3, speeds up a process of heavy metals transfer to the solution.

1 INTRODUCTION

Considerable alterations of the chemical composition of groundwater have been observed in many of the deposit areas in the Sudetes in the north-eastern part of the Bohemian Massif (Marszałek & Wąsik, 2000). Long years of drainage of abandoned mines results in changes of the chemical composition of surface waters excluding their use as potable water source (see also Banks et al.,1996). Water seepage from mine dumps could be environmentally dangerous as well.

The iron content (above 670 mgL) and the sulphates concentration (over 4400 mgL) in the waters in the dormant mine in Wieściszowice area belong to the highest in the Sudetes Mts. The intensity of oxidation processes in the deposit zone and the amount of ore minerals make this area unique in Poland (Parafiniuk J.,1996).

The study area is located within the old Paleozoic series of the Rudawy Janowickie Mts. that form the eastern part of the metamorphic cover of the Karkonosze granite. These mountains were one of the areas with the richest metal ore concentration (e.g. Cu, Fe, As, Au ores) in the Sudetes Mts. The exploitation of the pyrite-bearing chlorite-sericite schists lasted from the end of the 18th century until the year 1925, supplying mainly raw material for sulphuric acid production. During that period, about 120 000 tons of ore containing about 13 % of FeS_2 was extracted (Rubinowski, 1990). The pyrite concentration in certain parts of the rock is as high as 80 % (Piestrzyński & Salomon, 1977). The traces of the mining activities have a form of three excavation pits filled in part with water. Mine dumps are present too (Fig. 1).

2 METHODS

In the abandoned excavation area, ground- and surface waters were sampled in 10 points (Fig. 1). In addition, in order to determine the hydrogeochemical background, 3 sampling points were selected outside of the deposit area, and a dozen archival results of chemical analyses of groundwaters from the Rudawy Janowickie Mts. were studied. Basic ionic composition, pH, electrical conductivity, total Fe amount and 9 trace elements were determined in the samples. The ICP emission spectrometer was used for determination of trace elements.

3 GEOLOGICAL AND HYDROGEOLOGICAL SETTING

The pyrite-bearing chlorite-sericite schists form a 200-300 m wide inlier that forms a 4 kilometre long belt within the metamorphic schists (Szałamacha, 1979). These deposit are surrounded by chlorite, chlorite-albite and actinolite schists, as well as by chlorite-calcareous rocks, diabases and gneisses (Fig. 1). The mineral composition of these rocks consists of main minerals such as chlorite, sericite and quartz, and of smaller amounts of e.g. carbonates, ilmenite, magnetite, titanite and iron oxides (Piestrzyński & Salomon,1977). According to Parafiniuk (1996) chlorite was the least stable mineral of the schists. Its decomposition supplied the solutions with considerable amounts of such elements like magnesium, aluminium and iron. The weathering zone of pyrite deposits is rich in sulphate mineral paragenesis that consists of copiapite, pickeringite,

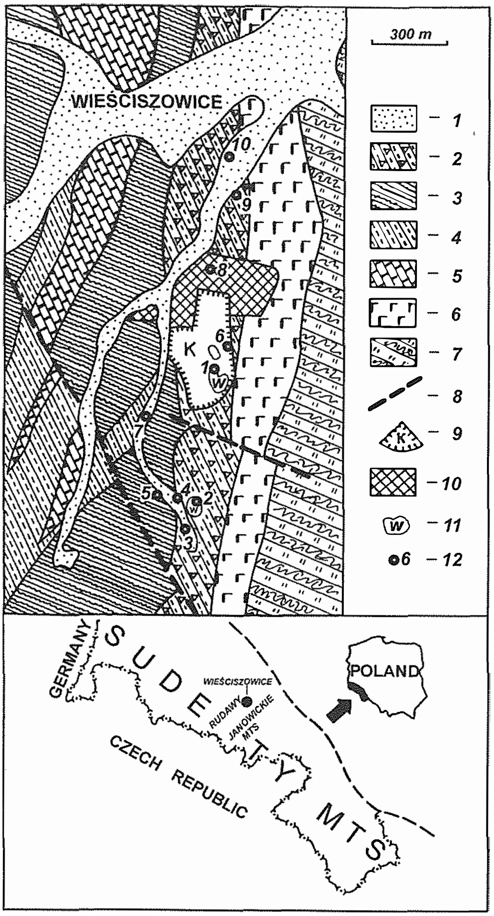

Figure 1. Geological sketch-map of the study area with location of Wieściszowice region within Sudetes Mts. 1 - alluvial deposit (Holocene); Early Paleozoic: 2-pyrite-bearing schist, 3-quartz-chlorite-albite schist, 4-chlorite schist with carbonate intercalations, 5-actinolite schist, 6-diabase, 7-gneiss and amphibolite, 8 –fault, 9-quarry, 10-dump, 11- sample location.

and alunogen. Isotope composition of sulphur in pyrite indicates hydrothermal origin of the deposits and hypogene source of sulphur. High concentration of Fe is caused by vital activity of the bacteria *Thiobacillus ferrooxidans* (Parafiniuk, 1996).

The pyrite-bearing schists are strongly deformedand dip steeply (60-80^{o}) to the NE and E (Szałamacha, 1979). The ore mineral is pyrite with inclusions of chalcopyrite, blende and galenite. No marcasite was determined. The spectra measurements revealed also the presence of Cu and As as well as of lower amounts of Co, Ni, Mn, Pb and Zn (Jaskólski, 1964). Pyrite is dispersed in the chlorite-sericite schists in the form of idiomorphic crystals or idioblastic aggregates with a size ranging from 0,1 to 6,0 mm.

The occurrence of groundwater in metamorphic formations of Rudawy Janowickie Mts. is similar to those in other hard rock areas of the Sudetes Mts. (Marszałek, 1996). The main near-surface aquifer is connected chiefly with fissured rocks down to 20-30 m with a thin weathered cover and alluvial deposits. Precipitation and water from melting snow recharge the groundwater. Springs draining hard rocks discharge mostly from 0,1 to 1,0 L/s.

4 CHEMICAL COMPOSITION OF WATERRESULTS AND COMMENTS

The Wieściszowice pyrite deposit strongly influences the chemical composition of ground- and surface waters. Waters draining the deposit are of the SO_4-Ca-Mg type with a very high content of sulphates (over 4400 mgL) making up for more than 90 % of anions (Fig. 2). Almost no HCO_3 - the anion typical of the waters present outside of the deposit area – was observed. These waters have very low pH and high electrical conductivity reaching 5,8 mS/cm. The major cations are calcium and magnesium.

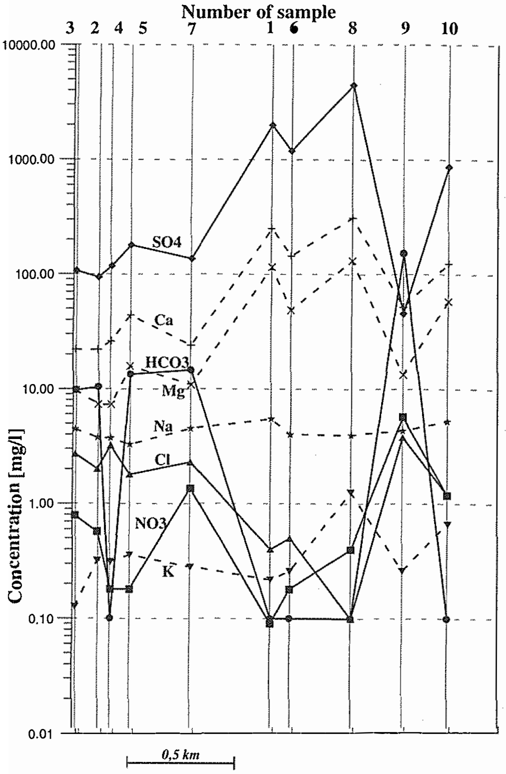

Figure 2. Hydrochemical cross-section.

Concentration of the latter can reach as much as 132 mgL (sample no 8, Fig. 1). Sodium concentrations are rather constant, while those of potassium are very low. The composition of waters collected outside of the deposit area is entirely different. These are HCO_3-SO_4-Ca-Mg or SO_4-HCO_3-Ca-Na type waters. The electrical conductivity of these waters ranges most frequently from 0,08 - 0,20 mS/cm, and rarely exceeds 0,40 mS/cm. The waters pH is mainly weakly acidic or neutral (Fig. 3). The analysis of distribution of the basic chemical composition of waters indicates a presence of a zone of hydrogeochemical anomaly in Wieściszowice area. The anomaly is the best expressed with regard to heavy metal content (Fig. 3).

The waters of the ore deposit series have the highest TDS values as well as concentrations of iron, aluminium and elements like: Cu, Zn, Cr and Co.

They are acidic waters, with pH reaching 2,48. These waters are represented by samples of waters from the abandoned excavation pit, that have a red-brown colour from Fe compounds (sample no 1 from so-called 'Purple Pond'; Fig. 1) or its close vicinity (no 6) as well as by samples of waters that drain old mine dumps (no 8). The latter contained extremely high concentrations of iron (up to 675 mgL), aluminium (up to 54 mgL) and sulphates (up to 4470,0 mgL; Fig. 3).

The concentrations of As and Pb were relatively low: As below 0,012 mgL, and lead 0,014 mgL in the Purple Pond. The highest concentrations of arsene (max. up to 0,072 mg AsL; Fig. 3) were measured in the waters with low (below 10 mgL) iron content (samples no 2,3,5,7; Fig. 1). In every sample of the deposit waters, there were certain components exceeding the Polish standards for potable waters (Fig. 3).

In the deposit zone there is almost no silver in the water, while mercury is present in amounts much lower than the acceptable concentration (0,001mgHgL).

In the waters outside of the deposit zone, contents of the metals mentioned earlier are much lower (Fig. 3). This confirms the existence of a regional hydrogeochemical anomaly in the pyrite occurrence area.

The waters of the deposit zone, those that come from the groundwater drainage (shallow or deeper) and from waters that collect in the excavation pits ('Coloured Ponds', samples no 1,2) strongly influence the quality of the surface waters. The deposit waters chemistry is reflected in the composition of water downstream the deposit (sample no 10; Fig. 1). In these waters, above-standard concentrations of the following elements were measured: Fe (up to almost 53 mgL), lead (Pb=0,04 mgL), arsene (approx. 0,03 mgL) and over19 mgL of Al. So high concentrations of metals in surface exclude them as a potential source for water supply.

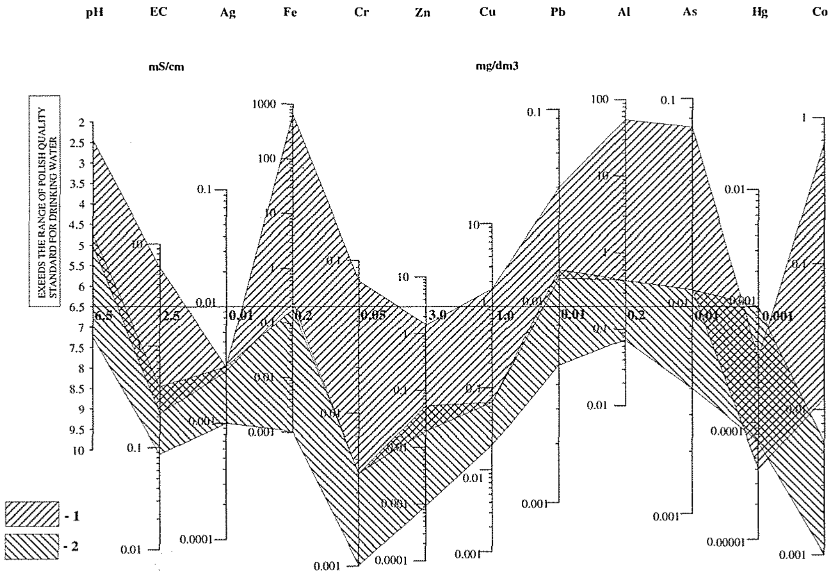

Figure 3. Chemical composition of water in mine area (1) and outside deposit zone (2).

The waters have many properties typical of waters occurring in the zones of sulphide ore deposits oxidation zones, that was already stressed by other authors (Balcerzak et al., 1992). The major factor influencing the water chemistry is the mineral composition of rocks. Oxidation of pyrite results in a strong decrease in water pH, which intensifies metal migration processes and limits concentrations of bicarbonates HCO_3. Decomposition of carbonates controls concentrations of Ca ion, while chlorite decomposition influences Mg content in the water. Very high concentrations of iron result from pyrite oxidation. This process may be intensified by *Thiobacillus* bacteria, and in particular by *T. Ferrooxidans* widespread in acidic mine environments (Parafiniuk,1996).

The decomposition of minerals composing the ore series, like chalcopyrite, sphalerite, galenite, chlorite or pickeringite is the cause of the presence of copper, zinc, lead and aluminium in the waters.

Statistical calculations carried out for selected major ions and trace components indicated a high correlation of SO_4 and Fe with other ions present in waters of pyrite zone (Tab. 1).

Table 1 Result of statistical calculations carried out for selected major ions

	pH	EC	Co	Zn	Cu	Pb	A l	As	Fe	HCO_3	SO_4	Ca	Mg
pH	*****	-0.6655	-0.5373	-0.4340	-0.5949	-0.2283	-0.7305	0.7596	-0.4381	0.6773	-0.5852	-0.6662	-0.6705
EC	-0.6655	*****	0.9705	0.9208	0.9195	-0.0429	0.9468	-0.4779	0.9295	-0.3110	0.9884	0.9740	0.9548
Co	-0.5373	0.9705	*****	0.9865	0.8797	-0.0604	0.8580	-0.3857	0.9862	-0.2749	0.9914	0.9116	0.8977
Zn	-0.4340	0.9208	0.9865	*****	0.8414	-0.1196	0.7787	-0.3340	0.9956	-0.2289	0.9649	0.8468	0.8367
Cu	-0.5949	0.9195	0.8797	0.8414	*****	-0.1808	0.9562	-0.4386	0.8384	-0.2566	0.9169	0.9617	0.9770
Pb	-0.2283	-0.0429	-0.0604	-0.1196	-0.1808	*****	-0.0529	-0.0573	-0.1622	-0.1377	-0.1042	-0.0466	-0.0161
A l	-0.7305	0.9468	0.8580	0.7787	0.9562	-0.0529	*****	-0.4939	0.7877	-0.3431	0.9084	0.9854	0.9833
As	0.7596	-0.4779	-0.3857	-0.3340	-0.4386	-0.0573	-0.4939	*****	-0.3533	0.2054	-0.4316	-0.4744	-0.4511
Fe	-0.4381	0.9295	0.9862	0.9956	0.8384	-0.1622	0.7877	-0.3533	*****	-0.2171	0.9719	0.8525	0.8325
HCO_3	0.6773	-0.3110	-0.2749	-0.2289	-0.2566	-0.1377	-0.3431	0.2054	-0.2171	*****	-0.2887	-0.2521	-0.2945
SO_4	-0.5852	0.9884	0.9914	0.9649	0.9169	-0.1042	0.9084	-0.4316	0.9719	-0.2887	*****	0.9471	0.9308
Ca	-0.6662	0.9740	0.9116	0.8468	0.9617	-0.0466	0.9854	-0.4744	0.8525	-0.2521	0.9471	*****	0.9917
Mg	-0.6705	0.9548	0.8977	0.8367	0.9770	-0.0161	0.9833	-0.4511	0.8325	-0.2945	0.9308	0.9917	*****

5 CONCLUSION

The specific chemical composition of ground waters in the abandoned pyrite mine area in Wieściszowice is the effect of water-rock interactions influenced by microorganisms activity. The composition is typical of waters in sulphide weathering zones. This is expressed by high concentrations of sulphates (up to 4,5 gL), iron (over 670 mgL) and toxic heavy metals in the waters. The zone of higher concentrations of chemical components in the groundwaters is limited to the closest vicinity of the pyrite deposit.

Therefore, it forms a distinct regional hydrogeochemical anomaly. Uncontrolled seepage of waters from the deposit area recharge the surface waters and thus leads to the increase of the hydrogeochemical changes.

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REFERENCES

Banks, D., Younger, P.L. & Dumpleton, S. 1996. The historical use of mine-drainage and pyrite-oxidation waters in central and eastern England, United Kingdom. *Hydrogeology Journal* 4 (4): 55-68. Hannover: Verlag Heinz Heise.

Balcerzak, E., Dobrzyński, D. & Parafiniuk, J. 1992. The effects of mineral alterations on the chemical composition of waters in the weathered zone of pyrite-bearing schists in Wieściszowice, Rudawy Janowickie Mts., Poland. *Ann. Soc. Geol. Polon.*, 62 (1):75-93. Kraków (in Polish).

Jaskólski, S. 1964. On the origin of pyrite schists at Wieściszowice (Lower Silesia). *Ann. Soc.Geol. Polon.*, 34 (1-2):29-63. Kraków (in Polish).

Marszałek, H. 1996. Hydrogeology of the upper part of the Kamienna River catchment in the Western Sudetes. *Acta Universitatis Wratislaviensis* 1881. Wrocław (in Polish).

Marszałek, H. & Wąsik, M. 2000. Influence of arsenic-bearing gold deposits on water quality in Złoty Stok mining area (SW Poland). *Environmental Geology* 39 (8):888-892. Springer-Verlag.

Parafiniuk, J. 1996. Sulfate minerals and origin in the weathering zone of the pyrite-bearing schists at Wieściszowice (Rudawy Janowickie Mts., Western Sudetes). *Acta Geologica Polonica* 46 (3-4):353-414. Warszawa.

Piestrzyński, A. & Salamon, W. 1977. New data on polymetallic mineralization of quartz veins in pyrite deposit from Wieściszowice (Lower Silesia). *Kwart. Geol.* 21:25-37. Warszawa (in Polish).

Rubinowski, Z. 1990. Deposits of pyrite.In E.Osika, (ed.) *Geology of Poland.* VI (219-220). Warszawa: Wydawnictwo Geologiczne.

Szałamacha, J. 1979. Pyrite-bearing schists. In Kazimierz Dziedzic (ed.), *Mineral deposits of Lower Silesia*: 205-206. Wrocław: Ossolineum (in Polish).