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Soil Mineralogy

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MINERAL TRANSFORMATIONS IN SOILS ON SPOIL HEAPS OF AN ABANDONED PYRITE MINE IN WIEŚCISZOWICE (RUDAWY JANOWICKIE MTS., LOWER SILESIA, POLAND)

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Abstract. Weathering – soil forming processes were studied on the spoil heaps of an abandoned pyrite mine in Wieściszowice (German: Rohnau, Lower Silesia, Poland). These heaps of waste material were formed during the 19th century, with the mining ceasing in 1902. The material was not homogenous texturally (loam and sandy loam layers) and did not show coloured genetic horizons. In the soil formations, the humus horizon was approximately 10 cm deep, and contained approximately 10% of organic matter in various stages of decomposition. The reaction in the whole soil profiles was acidic (pH approx. 4.0), and composition quartz, feldspars, chlorites and micas prevail in the mineral. Pyrite was not observed among the minerals, although secondary sulphate minerals were found such as: gypsum, jarosite, fibroferrite and iron oxides (mainly goethite). Clay minerals included chlorite, illitic material (K-mica and Na-mica), kaolinite and smectite as well as mixed-layered minerals of the mica/smectite type.

Pyrite, like other sulphide minerals, is very rare in natural soils. The occurrence of this mineral in soils, besides those of marshes and coastal acid sulphate soils, is usually related to the industrial activity of man and for this reason it is commonly found in mining waste [10, 11, 15].

The strong acidity in the soil was the result of pyrite weathering sulphur oxidates into sulphuric acid. Strongly acidic soils due to acidulation with the products of the pyrite decomposition and disintegration are considered toxic not only because of the low reaction values (pH 2-4) but also because they contain considerable amounts of toxic elements (Al and heavy metals). As a result they are subject to recultivation and scientific research all over the world [4, 6, 7].

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The purpose of this paper is to show mineral changes in the soil formations formed on the mining spoil heaps of the abandoned pyrite mine in Rudawy Janowickie Mts., Lower Silesia (Wieściszowice) (Fig. 1).

RESEARCH AREA AND METHODS

The study was undertaken in the Rudawy Janowickie ridge area, part of the Western Sudety Mts., and about 6 km NW of the town of Kamienna Góra (Fig. 1). Pyrite mining in the Wieściszowice mine ended in 1902 [3]. Pyrite can be found in the metamorphic pyrite bearing chlorite-sericite schists of the Leszczyniec Unit [16]. Crushed rock fragments containing a quantity of pyrite were transported and deposited on a heap north of the excavation sites.

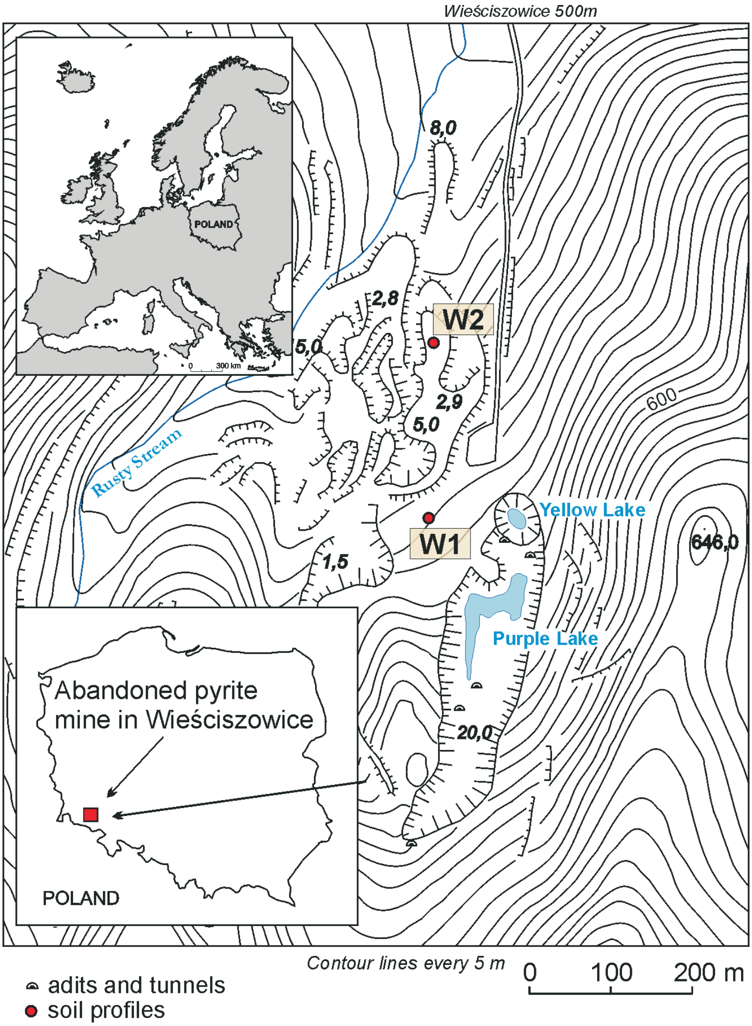

Fig. 1. Location of investigated area.

The study involved two soil profiles (W1 and W2) of the mine spoil heaps (Fig. 1). Soil samples collected were analysed, and a number of soil properties determined:

– texture with the areometric and sieve methods (particles above 2 mm and 1 mm),
– reaction with the use of a potentiometer in water (pH_{H_2O}) and in 1M water solution of KCl (pH_{KCl}),
– organic carbon content with the oxidometric method,
– mineral composition with the XRD (X-ray diffraction) method.

The mineral composition of the parent rock material (metamorphic schists) from the mine was determined, with soil and rock samples being ground in an agate mortar. X-ray diffraction analyses were performed with the use of Philips X'Pert APD diffractometer with PW1870 generator and vertical goniometer PW3020, equipped with a graphite diffraction beam monochromator. CuKα radiation was used, at 40 kV and 30 mA. The mounts were scanned from 2 to 64° 2Θ with a counting time of 1 s per 0.02° step.

Fractions <0.2 and <2 were separated from the studied soils by centrifuging preceded by the Jackson procedure [2]. Carbonates, sulphates and divalent exchangeable cations were removed using an acetic buffer. Organic matter was oxidised using a 30% hydrogen peroxide solution, while free iron oxides were removed using sodium dithionite according to the Mehra and Jackson procedure [5]. The separated fractions were sodium saturated and dialysed. XRD analyses of the oriented slides prepared from the separated fractions were registered in air-dry conditions, after saturation with ethylene glycol vapour and heating at 330 and 550° C.

Rock and soil samples were also analysed by a scanning electron microscope (SEM) equipped with Energy Dispersive X-ray Spectroscopy (EDS) and a backscattered electron detector (BSE). Samples were coated with carbon powder.

Mineralogical analysis and microscope observations were carried out at the Institute of Geological Sciences of the Jagiellonian University in Cracow.

RESULTS AND DISCUSSION

The investigated soil profiles were formed on the at least hundred year old mining spoil heaps. The weathering and soil-forming processes were not particularly advanced, and a slow accumulation of the organic matter could be observed in the O/A surface horizon together with colour changes – red or blue/green coloured lenses that indicate gleyic processes. Selected properties of the investigated soil formations are shown in Tables 1 and 2.

Profile W1 formed on a pebble/rock mine heap now covered with mixed forest (mainly spruce and beech). The parent rock contains a considerable amount of skeleton while the earth parts have a clay texture. The reaction of the soil mass is

TABLE 1. SELECTED PHYSICAL PROPERTIES OF THE INVESTIGATED SOILS

Soil horizon (cm)		Soil colour		Texture (mm)			Soil textural class	Content of rock fragments (wt. %)
		moist	dry	2.0-0.05	0.05-0.002	<0.002		
Profile W1, Umbric Technosol (Skeletic)								
0-1	Of	leaf and needle litter		-	-	-	-	-
1-4	Ofh	leaf and needle litter		-	-	-	-	-
4-9	A1	10YR 2/2	10YR 4/2	73	16	11	sandy loam	57
9-10	A2	10YR 2/3	10YR 5/3	71	19	10	sandy loam	51
10-45	C	10YR 6/6	10YR 7/6	69	21	10	sandy loam	70
Profile W2, Spolic Technosol								
0-1	Ol	grass and leaf litter						
1-4	A	10YR 4/2	10YR 6/3	76	17	7	sandy loam	3
4-15	A/C	10YR 5/6	10YR 7/6	65	28	7	sandy loam	0
15-30	C1	2.5Y 6/8	2.5Y 8/6	11	68	21	silty loam	0
30-35	C2	10YR 5/6	10YR 7/8	88	7	5	sand	1
35-86 (rusty spots)	C3	2.5Y 6/6	2.5Y 8/6	11	70	19	silty loam	0
35-86 (white spots)		2.5Y 7/2	2.5Y 8/1					
86-112	C4	2.5Y 6/6	2.5Y 7/6	88	7	5	sand	0

strongly acidic ($\mathrm{pH}_{\mathrm{H_2O}}$ between 3.88-4.82), while various stages of decomposition can be found in the surface horizon organic matter (conifer needles and leaves).

Profile W2 has developed on the small grain material of the heap. Sand and silty-loam layers occurred alternately, and the heap was covered with young and sparse pine-birch forest. As mentioned above, in the soil mass almost no rock fragments were found. The reaction of the mineral soil mass was also strongly acidic ($\mathrm{pH}_{\mathrm{H_2O}}$ 4.1-4.4) and the organic carbon content in the humus horizon was 2.5%. What is important is the fact that, along the whole soil profile, only very small amounts of organic matter were found.

MINERAL COMPOSITION

Minerals occurring in the investigated soil formations can be divided into two groups: minerals inherited from the parent rock and secondary minerals.

TABLE 2. SOME CHEMICAL PROPERTIES OF THE INVESTIGATED SOILS

Soil horizon (cm)		% C org.	pH	
			H_2O	KCl
Profile W1, Umbric Technosol (Skeletic)				
0-1	Of	-	4.8	4.3
1-4	Ofh	-	4.0	3.4
4-9	A1	9.86	3.9	3.3
9-10	A2	4.88	4.0	3.4
10-45	C	0.72	3.9	3.4
Profile W2. Spolic Technosol				
0-1	Ol	-	-	-
1-4	A	2.57	4.1	3.5
4-15	A/C	0.96	4.1	3.6
15-30	C1	0.52	4.3	3.6
30-35	C2	0.93	4.4	3.9
35-86	C3	0.50	4.3	3.6
86-112	C4	0.85	4.3	4.1

In the area of the abandoned pyrite mine in Wieściszowice, metamorphic pyrite-bearing schists with various petrographic properties occur (Fig. 2). These rocks, fragmented and deposited in the heap are the parent rock for the soil formations found there. In the complex mineral composition were found quartz, trioctahedral chlorites, dioctahedral micas (muscovite and paragonite), albite and orthoclase. Those schists also contain pyrite. Some of the rocks contain large amounts of calcite and epidote and accessorial minerals: titanite, rutile and apatite. This was determined by observation of thin sections using the SEM.

Using bulk samples to assess the mineral composition of the mine heap soil mass (Fig. 3), quartz was found to dominate as well as trioctahedral chlorites and dioctahedral micas (K-mica – muscovite, Na-mica – paragonite), albite and orthoclase, i.e. minerals inherited from the parent rock. Mineralogical analyses together with SEM observations showed the absence of pyrite from the soil material (fraction <1mm), where this material is subject to decomposition (Table 3).

Apart from the minerals inherited from the parent rock, the investigated soils also contain secondary minerals. Sulphates are among the most common secondary minerals: gypsum $CaSO_4\ 2H_2O$, jarosite $KFe^{3+}{}_3(SO_4)_2(OH)_6$ and fibroferrite $Fe^{3+}(SO_4)(OH)\ 5H_2O$ (Figs 4 and 5). Sulphates formation is due to the vast amount of sulphate ions from pyrite weathering. The occurrence of jarosite is

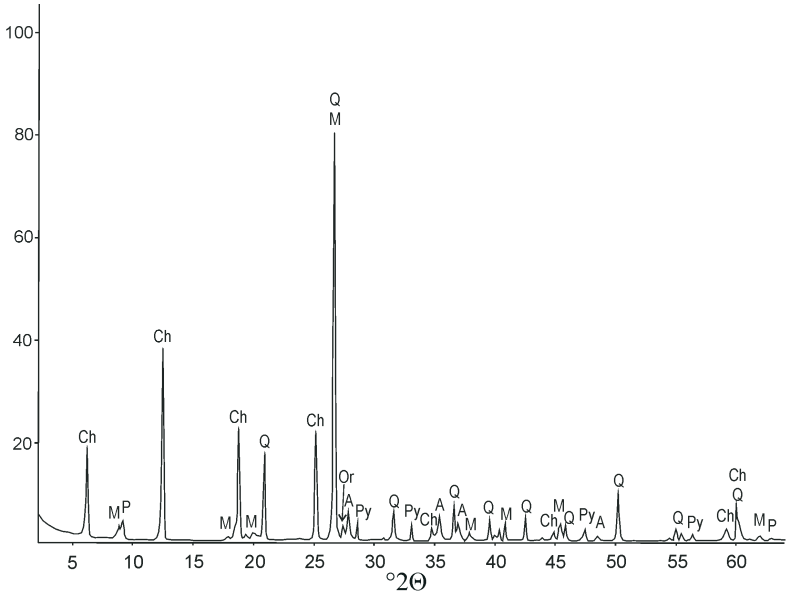

Fig. 2. Mineral composition of chlorite-sericite schist; minerals: Ch – chlorite, M – muscovite, P – paragonite, Q – quartz, Or – orthoclase, A – albite, Py – pyrite.

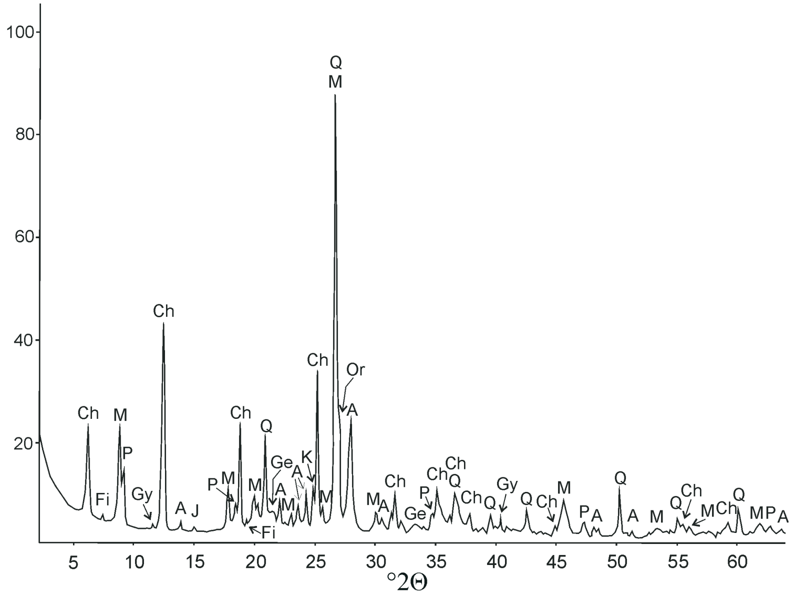

Fig. 3. Mineral composition of bulk soil sample from profile W1, A1 horizon; minerals: A – albite, Ch – chlorite, Fi – fibroferrite, Ge – goethite, Gy – gypsum, J – jarosite, K – kaolinite, M – muscovite, Or – orthoclase, P – paragonite, Q – quartz.

TABLE 3. MINERAL COMPOSITION OF THE INVESTIGATED SOIL SAMPLES; THE ORDER SHOWS THE RELATIVE, SEMI-QUANTITATIVE ABUNDANCE OF MINERALS (FROM THE MOST TO THE LEAST ABUNDANT)

Soil horizon (cm)		Mineral composition	
		Bulk soil samples	Clay fraction (<2 μm)
Profile W1, Umbric Technosol (Skeletic)			
0-1	Of	-	
1-4	Ofh	-	
4-9	A1	Q, Ch, A, M, Pa, K, Ge, Or, J, Gy, Fi	Ch, IM, K, S, I/S, Q, A
9-10	A2	Q, Ch, M, A, Pa, K, Or, Ge	IM, Ch, K, S, I/S, Q
10-45	C	Ch, M, Q, A, Pa, Or, K, J	IM, S , Ch, I/S, K, Q
Profile W2, Spolic Technosol			
0-1	Ol	-	-
1-4	A	Q, Ch, A, M, Pa, Or, K	Ch, IM, S, K, Q
4-15	A/C	Q, Ch, A, M, Pa, Or, K	Ch, IM, S, K, Q
15-30	C1	Q, Ch, A, M, Pa	IM, Ch, S, Q, A
30-35	C2	Q, Ch, A, M, Pa	Ch, IM, S, K, Q, A
35-86 (white spots)	C3	Q, Ch, A, M, Pa, K, J	IM, Ch, S, K, Q, A
35-86 (rusty spots)		Ch, Q, A, M, Pa, K, J, Ge	IM, Ch, S, K, Q, A
86-112	C4	Q, Ch, A, M, Pa, K, Gy	IM, Ch, S, K, I/S, Q, A

Minerals: A – albite, Ch – chlorite, Fi – fibroferrite, Ge – goethite, Gy – gypsum, IM – illitic material (K-mica and Na-mica), I/S – mixed-layered mica/smectite mineral, J – jarosite, K – kaolinite, M – muscovite, Or – orthoclase, Pa – paragonite, Q – quartz, S – smectite.

evidence of the long-term acidic reaction of the soils, as this mineral forms when pH is in the range 2-5 [1]. Fibroferrite is a mineral only very rarely found in the natural environment, and was first observed in Poland in Wieściszowice [8]. Gypsum was found only in some samples (Table 3), and is a product of calcite weathering (the source of the Ca^{2+} ions) or of the weathering of other minerals containing calcium (e.g. epidote) that occur in some pyrite bearing schists.

Kaolinite was found in the bulk samples, and it is a common weathering mineral in the tropics, where it forms a dominating mineral in weathering environments [18] although it can also be found in acidic soils of moderate climatic zones [12-14].

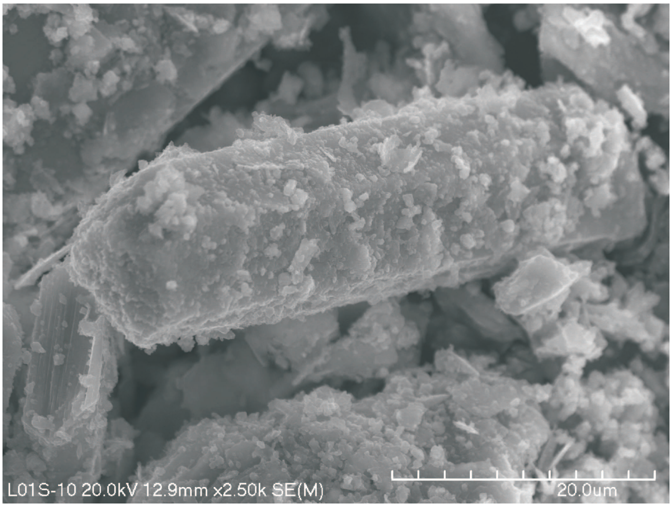

Fig. 4. Crystal of gypsum covered by illitic material and iron oxides, bulk soil material from profile W2, C4 horizon, secondary electron image (SE).

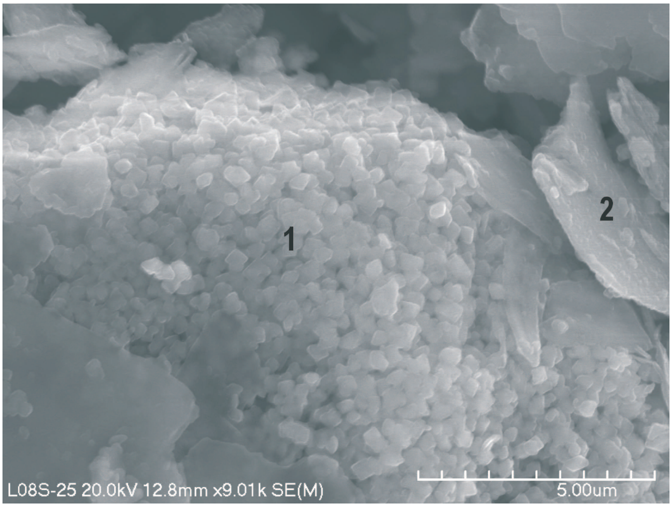

Fig. 5. Crystals of jarosite (1) and micas (2), bulk soil material from profile W2, C3 horizon, secondary electron image (SE).

Other secondary minerals observed include iron oxides and iron oxide-hydroxides such as goethite, but also probably ferrihydrite and lepidocrocite. Those minerals are very common in the area of the abandoned mine in Wieściszowice [9].

Minerals found in the clay fraction (<2 μm) as minerals forming the bulk samples can be divided into inherited (chlorites) or inherited in a transformed form (micas, known as illitic materials) and minerals that are probably secondary (smectite, kaolinite and mixed-layered mineral) (Figs 6 and 7).

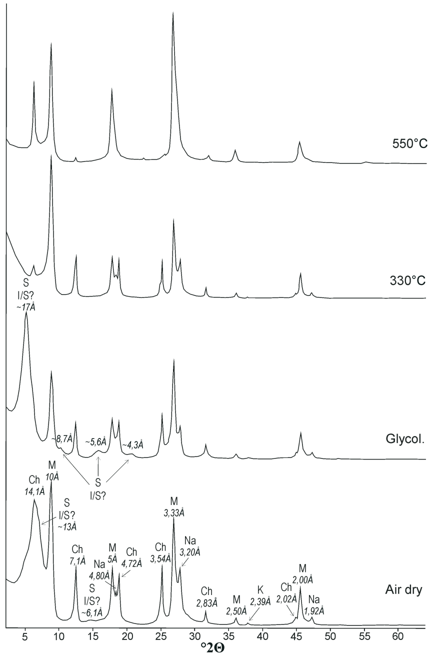

Fig. 6. Mineral composition of fine clay fraction (<0.2 μm), profile W1, C horizon; minerals: Ch – chlorite, M – K-mica, Na – Na-mica, S – smectite, K – kaolinite, I/S – mixed-layered mica/smectite mineral.

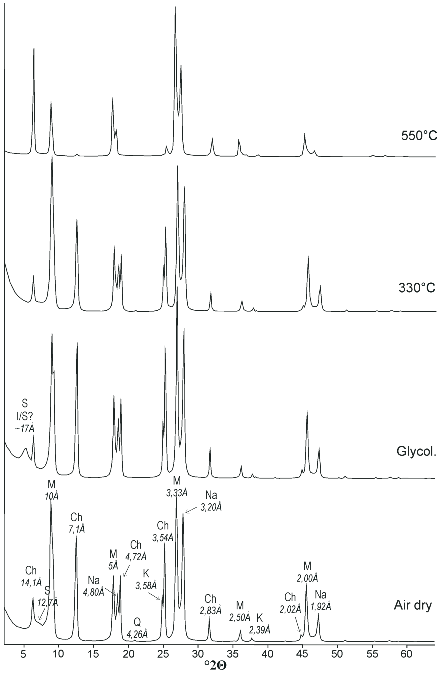

Fig. 7. Mineral composition of coarse clay fraction (<2 μm), profile W1, A1 horizon; minerals as in Fig.6.

Chlorite, smectite, micas, kaolinite and the mixed-layered minerals are present in different relative concentrations in both clay <0,2 μm, and <2 μm fractions separated from all the studied soil profiles. The studied samples contain chlorite (reflection ~14 Å after heating the mount to 550°C), micas (K-mica and Na mica gave reflections ~10 and ~9.7Å, respectively), kaolinite (identified by the presence of reflection ~3.57 Å in air dry conditions) and smectite (gave reflection ~17Å after EG saturation) [17]. Broad reflections 8.7, 5.6, and 4.3 Å suggest the presence of mixed-layered minerals (e.g. mica-smectite). In the 060 region of the X-ray diffraction patterns, collected for the bulk samples, several reflections can be distinguished: 1.538 Å reflection indicates the presence of quartz and trioctahedral chlorites, ~1.50Å reflection indicates presence of dioctahedral K-mica and Al-smectite and kaolinite, and the 1.48 Å reflection indicates Na-mica.

This interpretation of the 060 region is supported by the results of the chemical analyses obtained for individual particles of chlorite, smectite and micas, using the energy dispersive spectrometer during observations using the SEM.

Chlorite and micas are most likely inherited from the parent rocks. Smectite, mixed-layered clay minerals and kaolinite are the product of the transformation or neoformation which takes place in a weathering environment.

CONCLUSIONS

1. In the mineral composition of the acidic soil formations on the at least one hundred year old heaps of the abandoned pyrite mine in Wieściszowice silicates were found, which are considerably resistant to weathering, including: quartz, trioctahedral chlorites and dioctahedral micas (muscovite and paragonite) as well as albite and orthoclase. These are minerals inherited form the metamorphic pyrite-bearing schists.
2. In the investigated soils the occurrence of sulphates was determined (gypsum, jarosite, fibroferrite). Jarosite and fibroferrite are minerals characteristic for pyrite weathering. Iron oxide-hydroxides that were found in the soils were mainly goethite.
3. In the clay fraction of the investigated soils chlorite, illitic materials (K-mica, Na-mica) together with secondary clay minerals were found (kaolinite, smectite and probably mixed-layered minerals of the mica/smectite type). Small amounts of quartz and albite were also found.
4. The formation of secondary minerals, including secondary clay minerals, is evidence of active weathering – soil-forming processes.

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PRZEMIANY MINERALNE W UTWORACH GLEBOWYCH NA HAŁDACH NIECZYNNEJ KOPALNI PIRYTU W WIEŚCISZOWICACH (RUDAWY JANOWICKIE, DOLNY ŚLĄSK, POLSKA)

Prowadzono badania procesów wietrzeniowo-glebotwórczych zachodzących na hałdach nieczynnej kopalni pirytu w Wieściszowicach (niem. Rohnau, Dolny Śląsk, Polska). Hałdy te tworzone były w ciągu XIX wieku, a eksploatację górniczą zakończono w 1902 r. Złożony materiał ziemisty nie jest jednorodny pod względem uziarnienia (przewarstwienia piaszczysto-gliniaste i pylasto-gliniaste) i nie wykazuje barwnego zróżnicowania na poziomy genetyczne. W utworach glebowych występuje poziom humusowy o miąższości tylko ok. 10 cm zawierający ok. 25% materii organicznej w różnym stadium dekompozycji. Odczyn w całym profilu jest kwaśny (pH ok. 4,0).

W składzie mineralnym gleb dominuje kwarc, skalenie, chloryty i miki. Wśród minerałów w materiale glebowym nie obserwowano pirytu, który występuje pierwotnie w skałach podłoża, natomiast oznaczono wtórne minerały siarczanowe, takie jak gips, jarosyt i fibroferryt, a także tlenki żelaza (głównie goethyt). Wśród minerałów ilastych występuje chloryt, tzw. materiał illitowy (K-miki i Na-miki) oraz kaolinit i smektyt, jak również minerały mieszanopakietowe typu mika/smektyt.