

CLAY-MINERAL FORMATION IN SOILS DEVELOPED IN THE WEATHERING ZONE OF PYRITE-BEARING SCHISTS: A CASE STUDY FROM THE ABANDONED PYRITE MINE IN WIEŚCISZOWICE, LOWER SILESIA, SW POLAND

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Abstract—Intense mineral transformations that produce acid soils from weathering zones of pyrite-bearing rocks, including alterations of layer silicates, are of critical importance to agricultural and environmental interests in various regions of the world. To date, the transformations of layer silicates in these soils have not been studied in detail. The aim of the present investigation was to examine the weathering pathways controlling processes of clay-mineral formation in acidic soils developed near the abandoned pyrite mine in Wieściszowice (Lower Silesia, SW Poland). A sequence of soils, from weakly developed technogenic soils (located on the mine dumps) to well developed natural soils, was selected. Bulk soil material and separated clay fractions were analyzed using X-ray diffractometry, Fourier-transform infrared spectroscopy, and scanning electron microscopy-energy dispersive spectrometry. The profiles analyzed were developed on pyrite-bearing schists containing trioctahedral Mg,Fe-chlorite and dioctahedral micas (muscovite and paragonite). Because of pyrite weathering, all the soils studied were strongly acidic (pH 2.8–4.4). Inherited chlorite and micas (K- and Na-mica) predominated in the clay fractions of soils developed on the mine dumps, whereas clays from natural soils were rich in pedogenic minerals (*i.e.* smectite, vermiculite, and mixed-layer minerals containing hydrated interlayers). The formation of both vermiculite and smectite at the expense of chlorite was observed in the soils studied. The transformation probably led to smectite formation *via* intermediate stages of mixed-layer minerals (*i.e.* chlorite-vermiculite, chlorite-smectite, and/or vermiculite-smectite). The process of chlorite dissolution took place simultaneously with the transformation. Micas were mainly transformed to smectite and mixed-layer mica-smectite. Neoformation of kaolinite occurring in A horizons of the soils investigated was also documented. Metal-hydroxy interlayers in Bw horizons of well developed soils were found. The process of interlayer development appeared to be pH dependent and took place at pH ≥ 4.2 . The processes of clay-mineral formation in soils developed in the weathering zone of a pyrite-bearing schist are similar to those occurring in podzols (Spodosols).

Key Words—Acidic Soils, Acid Sulfate Weathering, Hydroxy Interlayers, Kaolinite, Mixed-layer Minerals, Pyrite Weathering, Schists, Smectite, Vermiculite.

INTRODUCTION

Weathering zones of pyrite-bearing rocks do not occur widely in nature though breakdown of pyrite-bearing rocks has significant local influence. Pyrite oxidizes in weathering zones when exposed to an oxygen-bearing atmosphere. As a result of the oxidation, large amounts of Fe and sulfuric acid are released, leading to acidification of water, saprolites, and soils (Bolan *et al.*, 2005).

In the acid environment of the weathering zones of pyrite-bearing rocks, intense mineral transformations occur. Previous investigations of sulfide weathering zones (*e.g.* Parafiniuk, 1996; Balcerzak *et al.*, 1992; Bigham *et al.*, 1996; Lintnerová *et al.*, 1999; Singh *et*

al., 1999; Šucha *et al.*, 2002; Murad and Rojík, 2003; Siuda, 2003; España *et al.*, 2005; Parafiniuk and Siuda, 2006) focused largely on the determination of weathering products of the sulfides. The transformations of layer silicates in acidic soils developed within sulfide weathering zones or affected by the activity of acidic mine waters have not been studied extensively (*e.g.* De Kimpe and Miles, 1992; Krasil'nikov, 1997; Šucha *et al.*, 2002). In general, transformations of primary layer silicates to swelling minerals, and dissolution of less resistant silicates (*i.e.* chlorite and biotite) were observed in these soils.

The transformations of layer silicates and the formation of secondary clay minerals in podzolic soils and acid Cambisols, which are similar to soils developed on material containing sulfides, in terms of their properties (*i.e.* low pH), have been investigated to a greater extent. In such soils, chlorite and mica are transformed to swelling minerals, *i.e.* vermiculite and smectite, often containing hydroxy interlayers (*e.g.* Bain

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and Russell, 1981; Ross *et al.*, 1982; April *et al.*, 1986; Righi *et al.*, 1993; Carnicelli *et al.*, 1997; Gillot *et al.*, 2000). Moreover, pedogenic kaolinite (Skiba and Skiba, 2005; Skiba, 2007), as well as amorphous and poorly crystalline Al and Si phases, *e.g.* allophane and imogolite (Farmer *et al.*, 1980; Gustafsson *et al.*, 1999), were found to develop in podzolic soils.

The objective of the present paper was to investigate processes controlling layer-silicate transformations and the formation of pedogenic clay minerals, as well as to determine the course of layer-silicate transformations in

acidic soils developed in the weathering zone of pyrite-bearing schists in the area of the abandoned pyrite mine in Wieściszowice (Lower Silesia, SW Poland).

MATERIALS AND METHODS

Site and material description

The study site is located within the abandoned pyrite mine in the village of Wieściszowice in the Rudawy Janowickie Mountains situated within Western Sudety Mountains, SW Poland (Figure 1). Altitudes ranging

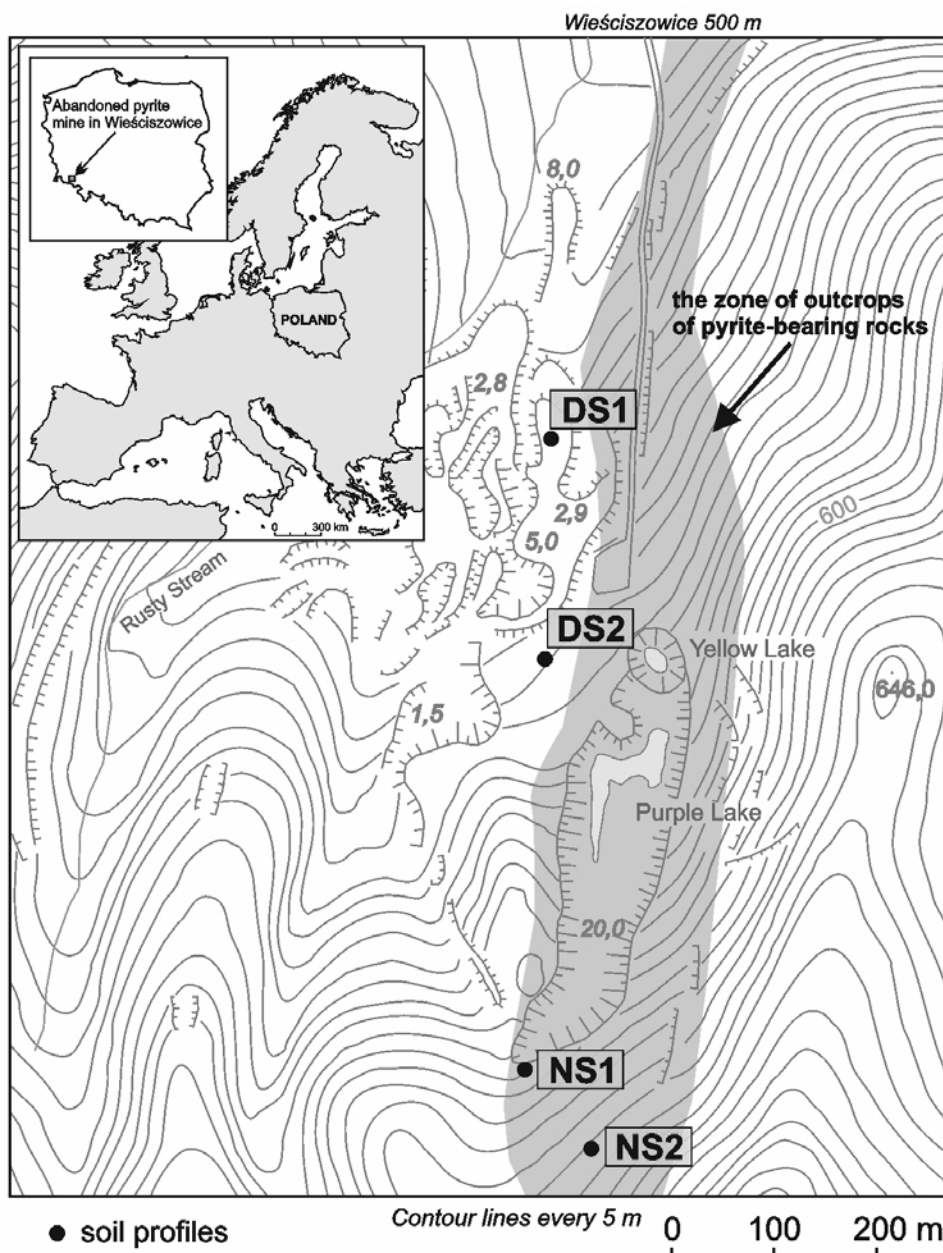


Figure 1. Location of the study area and the soils investigated.

from ~400 to 945 m a.s.l., mean annual temperatures from 7 to 4.5°C, and precipitation from 750 to 1050 mm are typical of this mountain region (Staffa, 1998). Metamorphic chlorite-mica pyrite-bearing schists of the Leszczyniec Unit occur in the bedrock of the area (Mazur *et al.*, 2006). The pyrite mine in Wieściszowice operated between 1785 and 1925 (Jaskólski, 1964). Nowadays, the site is dominated by open abandoned pits filled with acid mine drainage and mine (excavation) dumps located near the pits.

Four soil profiles (Table 1) developed on pyrite-bearing schists were selected for the present study. Profiles DS1 and DS2 were developed on mine dumps and profiles NS1 and NS2 were developed on natural pyrite-bearing schist outcrops in the area of the former mine.

The soil profiles studied are of different ages. The dumps were deposited at the time of the mine operation and so the soils on the dumps are ~100–200 y old. In soils developed on natural rock outcrops, well developed soil horizons were distinguished which indicated the

occurrence of advanced soil-forming processes and, therefore, profiles are of considerable age (hundreds or possibly thousands of years old).

Analytical methods

Basic soil properties (Table 1) were analyzed using common pedological methods (van Reeuwijk, 2002). The texture was determined using the Casagrande method (for the <1 mm fraction) and by dry-sieving (for the 2–1 mm fraction). The pH_{H_2O} was analyzed potentiometrically based on air-dried samples of fine earth using a soil/solution ratio of 1:2.5 (for organic samples the ratio was 1:10). The concentration of organic carbon was determined using dichromate oxidation techniques (modified Tyurin method; digestion reagent: $K_2Cr_2O_7$ and H_2SO_4 ; titrant: $FeSO_4 \cdot 7H_2O$) (Oleksynowa *et al.*, 1991). Soil units were described according to the WRB soil system (IUSS Working Group WRB, 2006).

The bulk mineralogy of the soils and the mineral composition of the clay fractions were analyzed using

Table 1. Locations and selected properties of the soils investigated.

Depth (cm)	Horizon	Percentage of fraction (mm)			pH _{H₂O}	Organic carbon content (wt.%)
		2.0–0.05	0.05–0.002	<0.002		
Profile DS1, Spolic Technosol, located on the surface of a fine earth dump. Geographical position: lat. 50°49'50.1″N, long. 15°58'21.4″E, alt. 550 m a.s.l.						
0–1	Oi	—	—	—	—	—
1–4	A	75	18	7	4.2	2.6
4–15	AC	65	28	7	4.2	1.0
15–30	C1	11	68	21	4.3	0.5
30–35	C2	86	9	5	4.4	0.9
35–86	C3	11	70	19	4.3	0.5
86–112	C4	87	8	5	4.3	0.9
Profile DS2, Spolic Technosol (Skeletal), located on the surface of a stony dump. Geographical position: lat. 50°49'43.6″N, long. 15°58'23.2″E, alt. 555 m a.s.l.						
0–1	Oi	—	—	—	4.8	—
1–4	Oe	—	—	—	4.0	—
4–9	A1	74	15	11	3.9	9.9
9–10	A2	71	19	10	4.0	4.9
10–45	C	75	17	8	3.9	0.7
Profile NS1, Hyperskeletal Leptosol (Hyperdystric), located on a slope of a hill (slope exposure: N; inclination: ~15°). Geographical position: lat. 50°49'32.1″N, long. 15°58'21.3″E, alt. 600 m a.s.l.						
0–1	Oi	—	—	—	—	—
1–10	A	64	23	13	3.4	0.9
10–12	BwC	51	31	18	3.2	0.6
12–60	C	—	—	—	2.8	0.3
Profile NS2, Haplic Cambisol (Dystric, Skeletic), located on a slope of the hill (slope exposure: W; inclination: ~5°). Geographical position: lat. 50°49'24.7″N, long. 15°58'21.8″E, alt. 636 m a.s.l.						
0–1	Oi	—	—	—	4.0*	—
1–6	Oe	—	—	—	3.7*	—
6–15	A	35	53	12	3.7	9.9
15–55	Bw	39	52	9	4.3	2.1
55–75	C	56	37	7	4.2	2.4

* pH measured in proportion: weight of soil sample/volume of solution as 1:10

— not determined

X-ray diffraction (XRD). Small amounts (~5 g) of each of the soil samples were ground in an agate mortar and packed into face-loading holders. The clay fractions were separated from the soil samples according to the Jackson (1975) procedure. Organic matter was removed using 30% hydrogen peroxide buffered with an acetic acid buffer (pH ~5). Free Fe oxides were removed according to the Mehra and Jackson (1960) method using sodium dithionite buffered with citrate-bicarbonate solution. Clay fractions (<2 μm and <0.2 μm) were separated by centrifugation; saturated with Na, Mg, or K; and dialyzed. Oriented mounts on glass slides were prepared by sedimentation. The XRD analyses were performed in air-dry conditions (Na-, Mg-, and K-saturated samples), after glycerol saturation (Mg-saturated samples only), and after heating for at least 1 h at 330°C and 550°C (K-saturated samples only).

The XRD analyses were performed using a Philips X'Pert diffractometer with the PW1870 generator and the PW3020 vertical goniometer, equipped with a 1° divergence slit; a 0.2 mm receiving slit and incident- and diffracted-beam Soller slits; 1° anti-scatter slit; and a graphite diffracted-beam monochromator. CuK α radiation was used with an applied voltage of 40 kV and current of 30 mA. Random mounts of the bulk soil material and oriented mounts of the clay fraction were scanned from 2 to 64°2 θ at a counting time of 1 s per 0.02°2 θ step.

The separated Na-saturated clay fractions were analyzed using a Fourier-transform infrared (FTIR) BIO-RAD FTS-135 spectrometer. The pressed-pellet technique was used. Pellets were prepared as a ground mixture of 300 mg of KBr (after 24 h of heating at 550°C) with 0.8 mg or 3 mg of <2 μm clay (after 12 h of drying at 105°C). Each spectrum was recorded once in the range from 400 to 4000 cm^{-1} at a resolution of 2 cm^{-1} .

The selected air-dried soil samples were carbon coated on the mounts and studied using a scanning electron microscope (SEM). An Hitachi S-4700 field emission scanning electron microscope equipped with a Vantage Noran EDS microanalysis system was used.

Interpretation of XRD patterns and FTIR spectra

The XRD patterns of the clay fractions were interpreted using criteria from Brindley and Brown (1980), Moore and Reynolds (1997), and Srodoń (2006). Detailed interpretation of chlorite, vermiculite, and hydroxy-interlayered swelling minerals was carried out using criteria from Barnhisel and Bertsch (1989), Lagaly *et al.* (2006), and Meunier (2007). The XRD patterns were processed using the *ClayLab* computer program (Mystkowski, 1999). Definitions given by van der Marel and Beutelspacher (1976), Russell and Fraser (1994), and Madejová (2003) were used during the interpretation of the FTIR spectra.

X-ray diffraction pattern modeling using the *SYBILLA* computer program (Chevron, Inc.) based on

the algorithms by Drits and Sakharov (1976), helped to reveal the nature and the compositional ratios of the mixed-layer and hydroxy-interlayered clay phases. Throughout the modeling process, the program changed the amount of the suggested phases continuously in order to achieve the best fit between the model and the experimental pattern which was based on the least-square method. The classification of hydroxy-interlayered minerals (HIMs) provided by Meunier (2007) was used.

RESULTS AND DISCUSSION

Soils from the dumps (profiles DS1 and DS2) were very weakly developed technogenic formations showing little trace of soil-forming processes (oxydo-reduction processes, accumulation of organic matter, and weathering of the soil-mineral substrate were found) (Table 1). Natural soils (profiles NS1 and NS2) were better developed, as genetic soil horizons (the A horizons and Bw horizons) were distinguished in the profiles (Table 1). All of the soil profiles studied had high acidity (pH_{H₂O} between 2.8 and 4.8). Organic matter was concentrated in the upper parts of the profiles, and its largest amount occurred in soils formed under well developed forest communities (profiles DS2 and NS2).

Based on the properties and the degree of development (Table 1), the soil profiles were arranged from the least well developed to the best developed as follows: DS1, DS2, NS1, NS2.

The mineral composition of the bedrock (pyrite-bearing schists) and bulk (<2 mm) mineral composition of soils from the Wieściszowice area were examined in the present study and were described in detail elsewhere (Uzarowicz *et al.*, 2008). The main layer silicates occurring in the parent rock were trioctahedral Mg,Fe-chlorite (with the chemical composition of brunsvigite) and dioctahedral K- and Na-micas. The schists also contained quartz, feldspars (albite and K feldspar), and pyrite. The parent rock of profile NS2 was chlorite dominated, whereas schists with minor amounts of chlorite and predominant mica were the bedrock for profile NS1. The dumps, consisting of ground, pyrite-bearing schists, were the parent material for profiles DS1 and DS2.

The mineral compositions of the soil clay fractions (<0.2 μm and <2 μm) are shown in Tables 2 and 3, and in Figures 2–6. Analysis by XRD of the clays from soils gave more or less the same picture as analysis by FTIR spectroscopy. Layer silicates occurring in clay fractions of acidic soils developed in the weathering zone of the pyrite-bearing schist in Wieściszowice can be divided into minerals inherited from the parent rock and pedogenic phases. These former are: chlorite (~14 Å basal reflection) and micas – K-mica (illite, 10 Å basal reflection) and Na-mica (brammalite, 9.7 Å basal reflection). On the other hand, pedogenic minerals are:

Table 2. Mineral compositions of clay fractions (<0.2 μm) and relative proportions of minerals identified in the soils investigated based on XRD analysis.

Soil profile	Depth (cm)	Horizon	Relative proportions of the mineral phases identified													
			Chlorite	K-mica	Na-mica	Smectite and/or R0	M-S	Vermiculite	Kaolinite	HIV or HIS	R1 M-S	R1 and/or R0 M-V	R1 and/or R0 Ch-S	R1 and/or R0 Ch-V	R1 and/or R0 V-S and K-S	Quartz and feldspars
DS1	0–1	Oi	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	1–4	A	+++	+++	++	+++	—	—	+	—	—	—	—	—	—	+
	4–15	AC	+++	+++	++	+++	—	—	+	—	—	—	—	—	—	—
	15–30	C1	n.a.	n.a.	n.a.	+++	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	30–35	C2	++	++	++	+++	—	—	?	—	—	—	—	—	—	—
	35–86	C3	+++	+++	++	+++	—	—	+	—	—	—	—	—	—	+
DS2	86–112	C4	+++	+++	++	+++	—	—	+	+	—	—	—	—	—	—
	0–1	Oi	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	1–4	Oe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	4–9	A1	+++	+++	++	+++	—	—	++	—	—	—	—	—	—	+
	9–10	A2	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	10–45	C	+++	+++	++	+++	—	—	+	—	—	—	—	—	—	—
NS1	0–1	Oi	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	1–10	A	++	++	++	+++	—	—	+	—	—	—	—	—	—	—
	10–12	BwC	++	++	++	+++	—	—	+	—	—	—	—	—	—	—
	12–60	C	++	++	++	+++	—	—	—	—	—	—	—	—	—	—
NS2	0–1	Oi	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	1–6	Oe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	6–15	A	++	++	++	+++	—	?	+	+++	+++	+++	+++	+++	+++	+
	15–55	Bw	+++	++	++	?	+++	+	+++	—	?	?	—	?	?	—
	55–75	C	+++	++	++	?	?	+	?	—	—	—	—	—	—	+

Mineral symbols as in Figure 2 or in the text.

n.a.: not analyzed; —: not identified; ?; uncertain occurrence; +: present in minor amounts; ++: present in moderate amounts; +++: present in large amounts.

Table 3. Mineralogical compositions of clay fractions (<2 µm) and the relative proportions of the minerals identified in the soils investigated based on XRD analysis.

Soil profile	Depth (cm)	Horizon	Relative quantity of the identified mineral phases												
			Chlorite	K-mica	Na-mica	Smectite and/or R0 M-S	Vermiculite	Kaolinite	HIV or HIS	R1 M-S	R1 and/or R0 M-V	R1 and/or R0 Ch-S	R1 and/or R0 Ch-V	R1 and/or R0 V-S and K-S	Quartz and feldspars
DS1	0–1	Oi	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	1–4	A	+++	+++	+++	++	–	+	–	–	–	–	–	+	+
	4–15	AC	+++	+++	+++	++	–	+	–	–	–	–	–	+	+
	15–30	C1	+++	+++	+++	++	–	+	–	–	–	–	–	+	+
	30–35	C2	+++	+++	+++	++	–	+	–	–	–	–	–	–	–
	35–86	C3	+++	+++	+++	++	–	+	–	–	–	–	–	–	–
DS2	86–112	C4	+++	+++	+++	++	–	+	–	–	–	–	–	+	+
	0–1	Oi	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	1–4	Oe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	4–9	A1	+++	+++	+++	+	–	++	–	–	–	–	–	+	+
	9–10	A2	+++	+++	+++	++	–	++	–	–	–	–	–	+	+
	10–45	C	++	+++	+++	++	–	+	–	–	–	–	–	–	–
NS1	0–1	Oi	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	1–10	A	++	+++	+++	+++	–	+	–	–	–	–	–	–	–
	10–12	BwC	++	+++	+++	+++	–	+	?	–	–	–	–	+	+
	12–60	C	++	+++	+++	++	–	–	–	–	–	–	–	+	+
NS2	0–1	Oi	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	1–6	Oe	n.a.	n.a.	n.a.	+++	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	6–15	A	+++	+++	+++	+++	?	+	–	+++	+++	+++	+++	+	+
	15–55	Bw	+++	++	++	?	+++	–	+++	–	–	–	–	+	+
	55–75	C	+++	++	++	–	?	?	++	–	–	–	–	+	+

Mineral symbols as in Figure 2 or in the text.

n.a.: not analyzed; —: not identified; ?; uncertain occurrence; +: present in minor amounts; ++: present in moderate amounts; +++: present in large amounts.

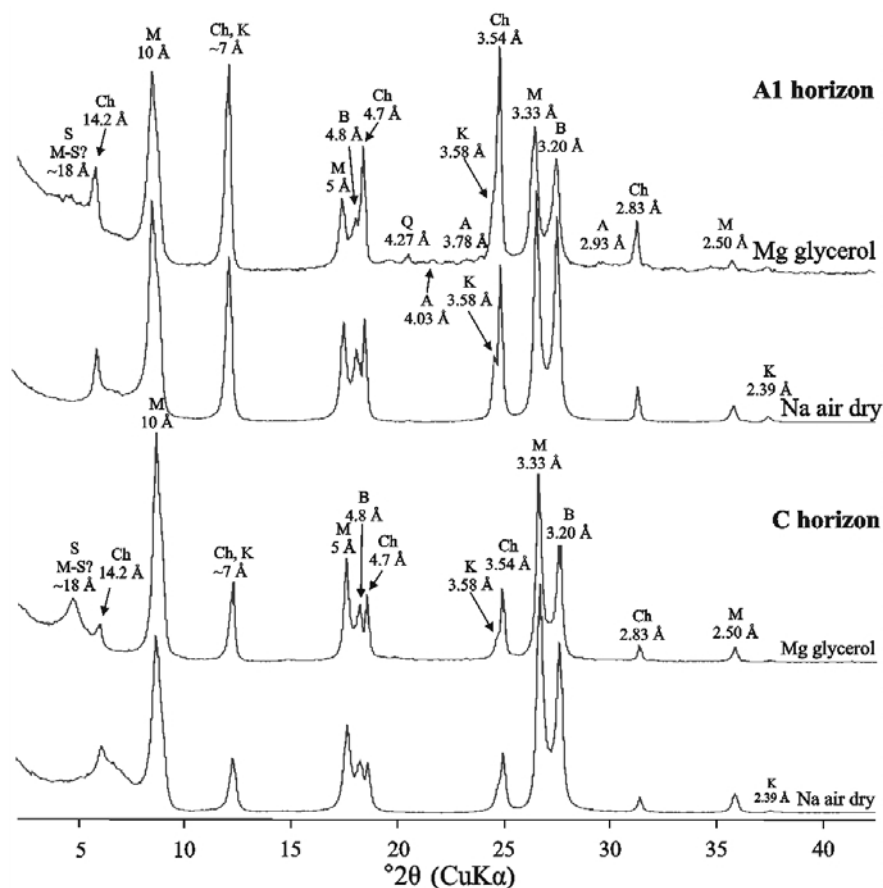


Figure 2. XRD patterns of oriented mounts of the soil clay fraction (<2 μm) from selected horizons of profile DS2. Mineral symbols for all XRD patterns: A – albite, B – Na mica (so-called brammalite), Ch – chlorite, HIS – hydroxy-interlayered smectite, HIV – hydroxy-interlayered vermiculite, K – kaolinite, Kf – K feldspar, M – K mica (so-called illite), M-S – mixed-layer mica-smectite, Q – quartz, S – smectite, V – vermiculite.

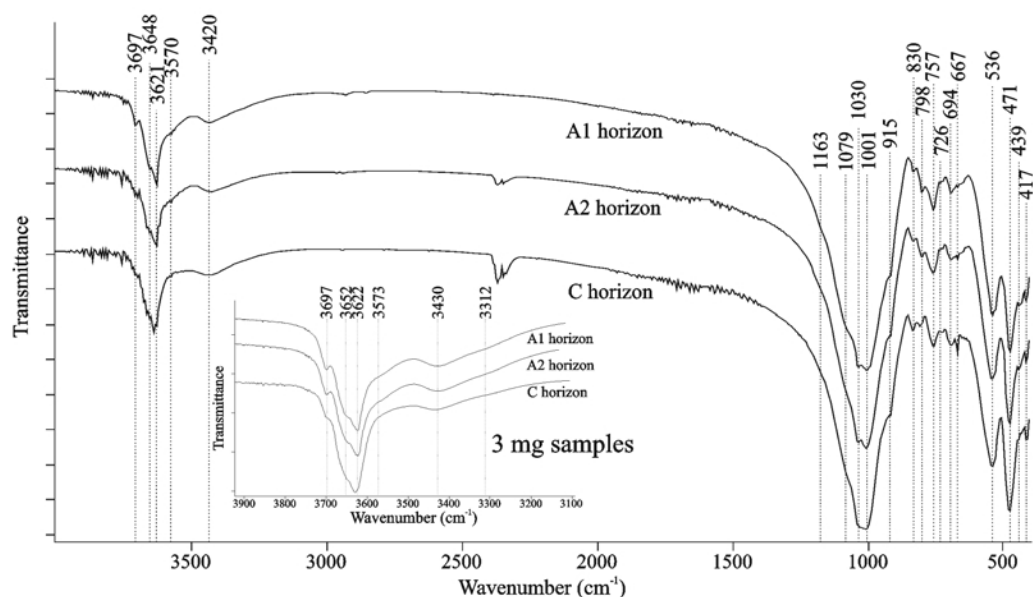


Figure 3. FTIR spectra of separated clay fractions (0.8 mg samples for the whole spectrum and 3 mg samples for the OH-stretching region) of profile DS2.

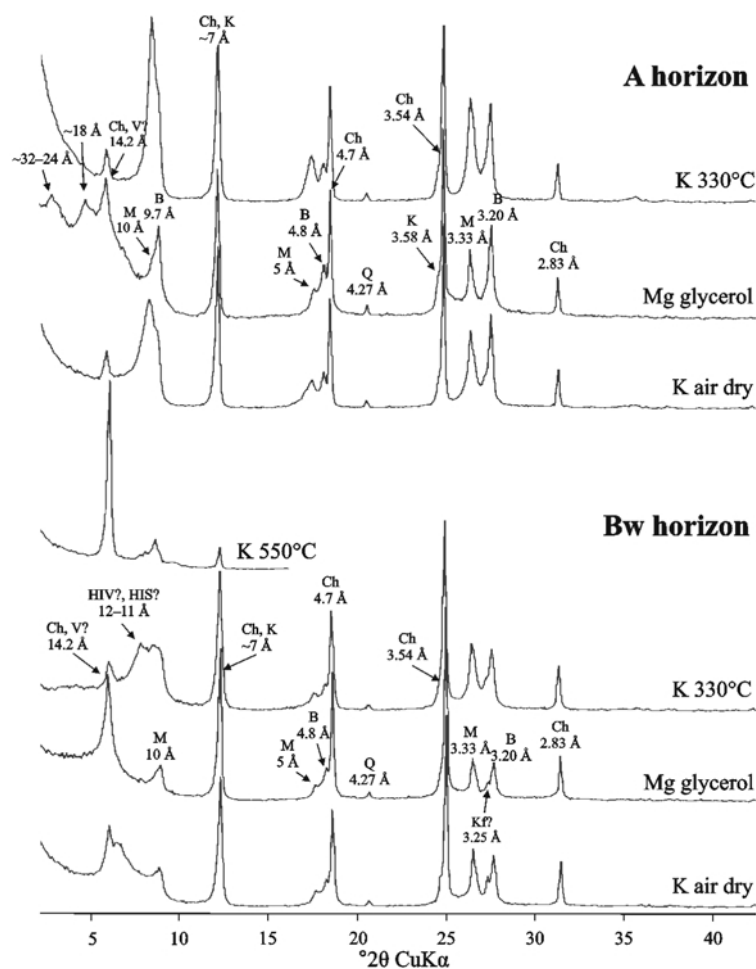


Figure 4. XRD patterns of oriented mounts of the soil clay fraction (<2 μm) from profile NS2; mineral symbols as in Figure 2.

smectite (broad ~ 18 Å reflection in the glycerol-treated Mg-saturated samples); vermiculite (~ 14.5 Å reflection in the glycerol-treated Mg-saturated samples; its identification was sometimes difficult due to the overlapping 001 reflections of chlorite and vermiculite); hydroxy-interlayered vermiculite, and/or smectite (incomplete collapse to 10 Å in the heated clay samples); kaolinite (~ 7 Å and 3.58 Å basal reflections in air-dried samples); and a number of mixed-layer minerals (mica-smectite, mica-vermiculite, chlorite-vermiculite, chlorite-smectite, vermiculite-smectite, and kaolinite-smectite), both R0 and R1 types, for which a broad ~ 18 Å reflection, the background hump between ~ 18 Å and ~ 14 Å, and the broad superstructure reflection (~ 32 – 24 Å) visible in the XRD patterns of glycerol-treated, Mg-saturated samples are characteristic. Soil profile NS2 was particularly rich in the mixed-layer minerals (Figure 4, Tables 2, 3).

In soils developed in the weathering zone of pyrite-bearing schists in Wieściszowice, a chronosequence of layer-silicate transformations was documented (Figure 7). The sequence studied consists of three

parts. The starting points are parent rocks containing trioctahedral chlorite and dioctahedral micas. Another part of the sequence consists of soils on the dumps ~ 100 – 200 y old, represented by profiles DS1 and DS2, and by the weakly developed natural soil profile (NS1). The clay fraction of the soils contains minerals inherited from bedrock and pedogenic minerals (kaolinite, smectite, and/or mixed-layer minerals of the R0 mica-smectite type, as well as vermiculite) (Figures 2, 3, and Tables 2, 3). Differences between soils on the dumps and the NS1 profile are related to relative amounts of smectite, occurring in larger amounts in the latter (Tables 2, 3). The final parts of the sequence are well developed natural soils represented by profile NS2. Aside from the above-mentioned clay minerals, the soil contains a number of R1 mixed-layer minerals and hydroxy-interlayered vermiculite. The profile contains a relatively large amount of fine (<2 μm) quartz and feldspars, as indicated by the presence of relatively intense 1164, 1082, 800, and 780 cm^{-1} bands typical of quartz (Figure 6). The amounts are significantly greater

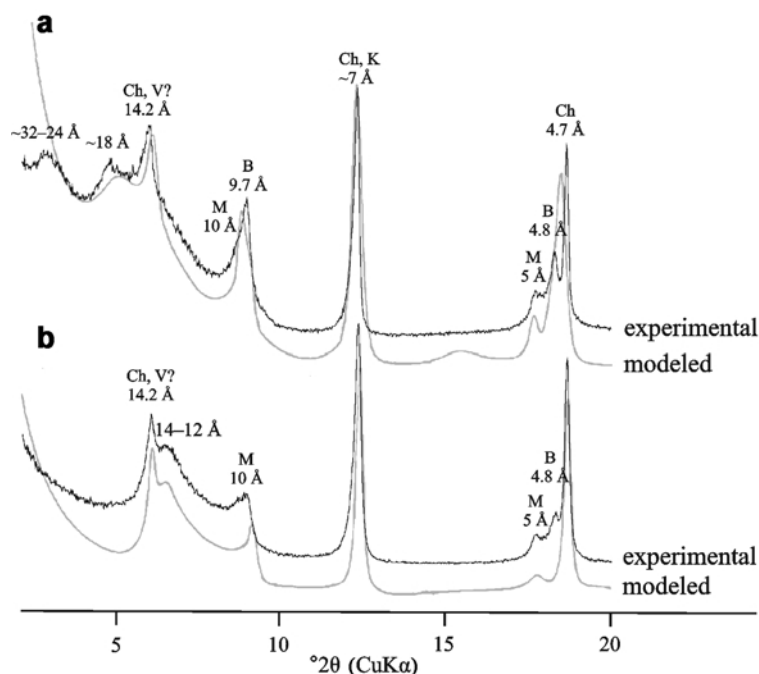


Figure 5. Experimental XRD patterns of clay fractions (<2 μm) from the selected soil horizons of profile NS2 and patterns modeled using *SYBILLA*. (a) Experimental pattern: Mg-saturated, glycerol-treated pattern from the A horizon. Input phases for the computer program: chlorite, K-mica (illite), disordered paragonite-smectite, having more than 95% of the paragonite component, and mixed-layer clay minerals – disordered mica-smectite and disordered kaolinite-smectite. To achieve the best model, the two mixed-layer phases were taken in the ratio of ~3:1. (b) Experimental pattern: pattern for K-saturated, air-dried sample from the Bw horizon. Input phases for the computer program: chlorite₆₀-disordered mixed-layer mineral, chlorite, K-mica (illite), disordered paragonite-smectite, having more than 95% of the paragonite component, and kaolinite.

than those in more weakly developed profiles, suggesting that during soil-forming processes, enrichment of the clay fraction in quartz and feldspars occurs. This process

is probably a result of intense weathering in an acidic soil environment, as the minerals are evenly arranged in the soil profile and the amounts of the minerals do not

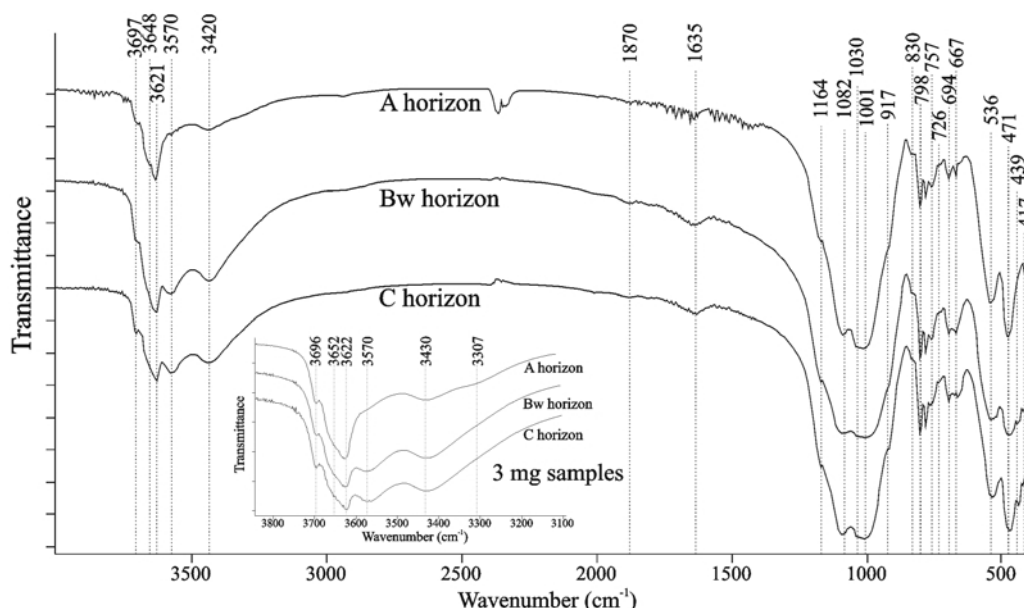


Figure 6. FTIR spectra of separated clay fractions from profile NS2 (0.8 mg samples for the whole spectrum and 3 mg samples for OH-stretching region).

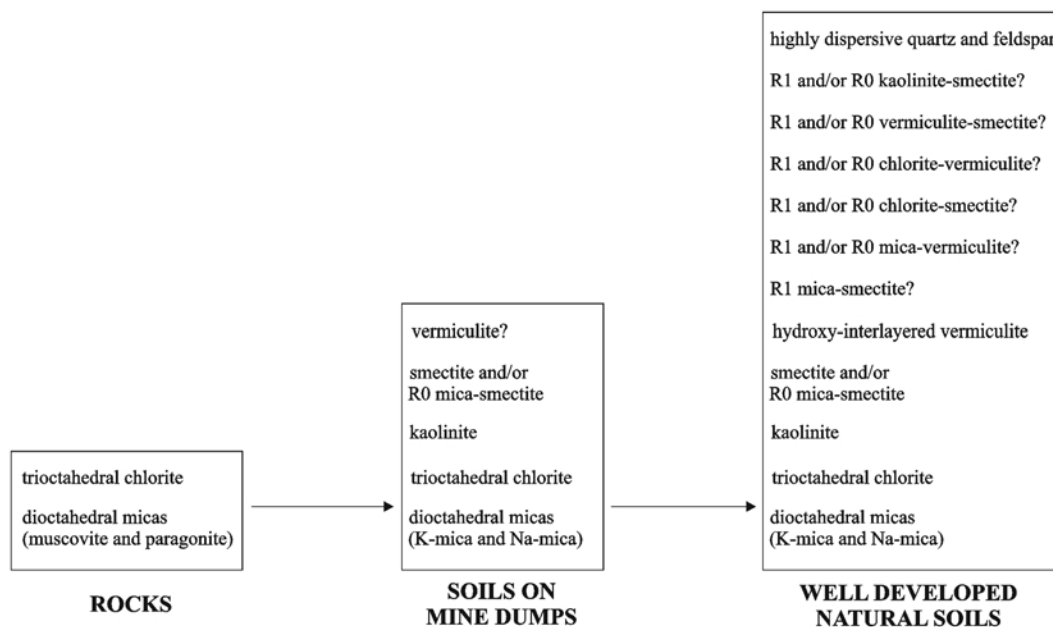


Figure 7. Sequence of silicate transformations along with the advancement of soil-forming and weathering processes in the area investigated.

increase toward the topsoil (Figure 6), which might indicate eolian deposition of the minerals.

Trioctahedral chlorites and dioctahedral micas usually predominated in the soil clay fraction of the study area (Tables 2, 3). Inheritance of layer silicates from bedrock, controlled by physical weathering (*e.g.* disintegration) of primary layer silicate crystals, was, therefore, considered to be one of the most important processes controlling the mineral composition of the soil-clay fraction. Such inheritance is particularly important in ‘young’ soils developed on the dumps (profiles DS1 and DS2). The inherited chlorite and micas in the soil environment were subject to changes resulting from chemical weathering processes.

Chlorite occurring in the soils studied probably transformed to smectite *via* intermediate stages (vermiculite, hydroxy-interlayered vermiculite or smectite, and mixed-layer minerals, *e.g.* chlorite-vermiculite and chlorite-smectite) and dissolved. The occurrence of mixed-layer minerals indicates that vermiculite and smectite probably formed as a result of partial dissolution of the interlayer octahedral sheet of chlorite in an acidic soil environment, in good agreement with the generally accepted view (*e.g.* Ross and Kodama, 1974; Dixon *et al.*, 1982; Barnhisel and Bertsch, 1989; Wilson, 1999; Wilson, 2004).

The characteristic corrosion gulfs and dissolution pits found (though not shown, using SEM) on the chlorite surfaces confirmed intense dissolution of chlorite in natural conditions. The intensity of the process depends on the progress of soil-forming processes; the most evident traces of dissolution are visible in chlorites from

the well developed soil profile NS2, rather than in ‘young’ soils formed on mine dumps.

Chlorite dissolution occurred most extensively in the uppermost part of the best developed soil profiles as seen not only by SEM, but also by FTIR spectroscopy: the intensity of the ~ 440 , ~ 660 , and ~ 3570 cm^{-1} bands in FTIR spectra, which belong to trioctahedral chlorite, decreased toward the upper part of soil profile NS2 (Figure 6). Such a feature makes these soils similar to podzols in which a decrease in the chlorite content, or even the entire decomposition of chlorite in A horizons was observed (*e.g.* Gjems, 1960; Kodama and Brydon, 1968; Bain, 1977; Ross *et al.*, 1982; Righi *et al.*, 1999). The process occurs because, in an acidic weathering environment, chlorite is unstable and is easily dissolved (Brandt *et al.*, 2003). Decomposition of chlorite and other layer silicates is particularly influenced by the presence of organic acids (*e.g.* Vicente *et al.*, 1977; Hamer *et al.*, 2003) of which large amounts occur in A horizons. The process of dissolution is probably simultaneous with the transformation of chlorite to secondary minerals.

In the soils studied, vermiculite was probably the product of both chlorite and mica mineral transformations. Chlorite and mica were the main layer silicates inherited from bedrock occurring in the soils studied and one cannot assume, based on the methods used, that vermiculite is the weathering product of just one mineral (chlorite or mica) exclusively.

Using the fitting procedure confirmed the presence of hydroxy-interlayered minerals (HIMs) in the clay fraction from the Bw horizon of the NS2 profile (Figure 5).

Furthermore, the relative phase proportions within the clay fractions were determined from the calculated patterns, suggesting a dominance of chlorite (~50%), with the amounts of ~10 Å mica-like phases and HIMs being practically identical (~25%). Heating showed that the expandable layers of the HIMs were sensitive to K-saturation suggesting relatively high-charge layers of vermiculite composition (HIV). Interlayers in the soils studied are likely to be Al-hydroxy interlayers. The formation of hydroxy interlayers in vermiculite (and/or smectite) seem to be pH dependent, as described in the literature (e.g. Churchman, 1980; Barnhisel and Bertsch, 1989; Bain *et al.*, 1990). Interlayers in the soils studied develop at pH 4.2–4.3. At a lower pH, metal-hydroxy interlayers are dissolved and removed from between vermiculite (smectite) layers (Bain *et al.*, 1990), explaining their absence in the NS1 profile (not shown) which has a $\text{pH}_{\text{H}_2\text{O}}$ between 2.8 and 3.4 (Table 1).

The strong acidity in profile NS1 influences not only the formation of interlayers, but also seems to control the formation of specific types of swelling minerals (vermiculite *vs.* smectite). The results obtained showed that vermiculite, often recognized as the intermediate stage in mica (chlorite) to smectite transformations (e.g. Jackson, 1962; Churchman, 1980; Righi *et al.*, 1997; April *et al.*, 2004), probably does not develop in the NS1 profile with $\text{pH}_{\text{H}_2\text{O}}$ of ~3 (Tables 1–3). This suggests that in strongly acidic soils of the pyrite-bearing schist weathering zone studied, as represented by profile NS1, mica (chlorite) probably transformed directly to smectite, without or with little participation by vermiculite as the intermediate stage. The degree of acidification (in the acidic pH range) seems to influence the formation of specific swelling phases (smectite *vs.* vermiculite). Such a feature was suggested for soils developed on mine wastes containing iron sulfides (e.g. Uzarowicz and Skiba, 2011).

Smectite – the main product of layer silicate transformation in the soils studied – like vermiculite is probably the result of transformation of both chlorite and mica minerals. The formation of mixed-layer minerals (*i.e.* R0 and R1 M-S, Ch-S, and K-S) probably takes place in the soils studied (Figure 4). Fitting the experimental XRD patterns showed that M-S predominates across disordered (R0) mixed-layer phases of clay fraction from the A horizon (NS2 profile), along with a minor amount of K-S and probably also Ch-S (Figure 5). Mica to smectite transformations are typical of acidic soil environments (e.g. Churchman, 1980; Righi and Meunier, 1991; De Kimpe and Miles, 1992; Righi *et al.*, 1999; April *et al.*, 2004). The formation of low-charge expandable minerals in acidic soils at the expense of chlorite has also been documented (e.g. Carnicelli *et al.*, 1997). Larger amounts of smectite occur in the <0.2 µm fractions than in <2 µm fractions of all of the soils studied (Tables 2, 3). The mineral probably developed

after physical weathering (strong disintegration) of mica and chlorite crystals along with chemical transformations (e.g. partial dissolution of chlorite or other aluminosilicates and neoformation by crystallization from soil solution, loss of interlayer cations, and the decrease of layer charge) in the acidic soil environment, in accordance with the generally accepted view (e.g. t'Serstevens *et al.*, 1978; Aoudjit *et al.*, 1996).

The type of ordering within mixed-layer minerals resulting from layer-silicate transformations seems to depend on the degree of the development (age) of the soil profile. Dump soils DS1 and DS2 and weakly developed soils on natural rock outcrops (NS1) contain, almost exclusively, discrete smectite and/or R0 mixed-layer minerals containing smectite layers, as indicated by the lack of superstructure reflections in the XRD patterns of clay fractions (Figure 2) in contrast to well developed natural soil (profile NS2), where a number of R1 mixed-layer minerals (*i.e.* mica-smectite, mica-vermiculite, chlorite-vermiculite, chlorite-smectite, and vermiculite-smectite) were likely to occur (Figure 4).

Larger kaolinite contents in well developed A horizons in comparison with horizons located below in the soil profiles were found in the DS2 and NS1 soil profiles (Figures 2, 3, Tables 2, 3), as the 3697 cm^{-1} OH stretching band, typical of kaolinite, exhibited the greatest intensity in the spectra of clay fractions from A horizons. Moreover, white clay aggregations, enriched in kaolinite, occurring in the upper part of profile NS1 (the A and Bw horizons) were found during the field study. Such data suggest the neoformation of kaolinite in horizons containing soil organic matter, in agreement with the results obtained e.g. by Bain (1977) and Carnicelli *et al.* (1997). Pseudohexagonal kaolinite crystals found in a well developed humus horizon of profile DS2 (Figures 8 and 9, Table 4) seem to confirm this thesis. Kaolinite in the A horizons of the soils

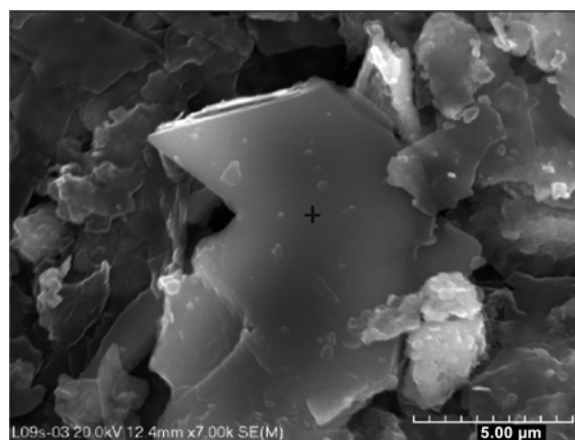


Figure 8. SEM image of pseudohexagonal kaolinite crystal from the A1 horizon of profile DS2. The cross indicates the point of EDS analysis.

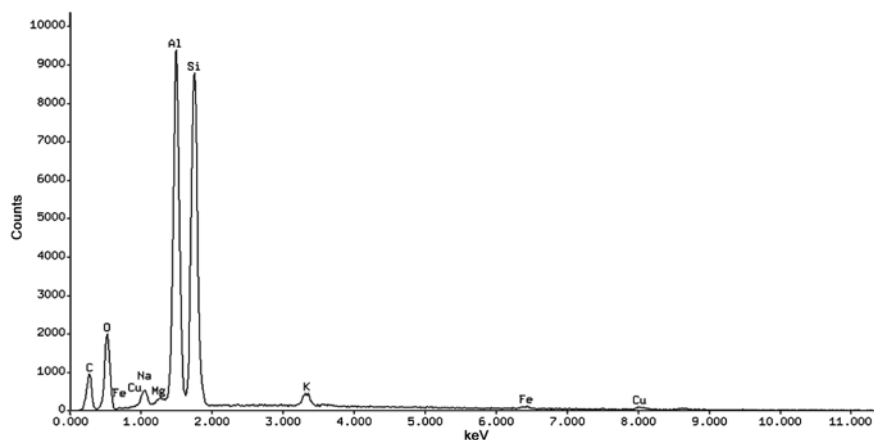


Figure 9. EDS spectrum for the point indicated in Figure 8.

studied may crystallize from Si and Al released during the dissolution of aluminosilicates (e.g. chlorite). A similar process of kaolinite formation *via* crystallization from a soil solution rich in Si and Al was documented in albic horizons of podzols from the Tatra Mountains (Skiba, 2007).

The study revealed that the acidic soils containing micas and chlorite developed in the pyrite-bearing schist weathering zone in Wieściszowice are similar to podzolic soils in terms of transformations of the layer silicates. The results obtained are in accord with studies by other authors (e.g. Vicente *et al.*, 1977; Righi and Meunier, 1991; Righi *et al.*, 1999) who stated that in the B horizons of acid soils, chlorite is transformed to hydroxy-interlayered minerals, and in the humus-rich A horizons chlorite is mainly decomposed (Figure 6), whereas the most advanced mica transformations occur in A horizons, where micas are transformed to swelling minerals (smectite and vermiculite) or mixed-layer minerals containing swelling layers. The data presented here support the thesis that the interpretation of clay-mineral formation in soils should always be performed with reference to soil properties (e.g. the age of soils

expressed in their morphology, the pH, and the soil organic matter content), as these factors influence strongly the course and the intensity of layer-silicate transformations, as well as the effects of silicate weathering (e.g. Righi *et al.*, 1999).

CONCLUSIONS

(1) The most important processes controlling the mineral composition of the clay fraction of soils developed in the acidic weathering zone of pyrite-bearing chlorite-mica schists in Wieściszowice are: inheritance of chlorite and mica from bedrock, transformation of chlorite and mica to swelling minerals (smectite, vermiculite, and mixed-layer minerals containing swelling layers), dissolution of less resistant layer silicates (e.g. chlorite), and neoformation of kaolinite in A horizons. These processes probably take place simultaneously.

(2) Variety in the mineral composition of the clay fraction increases with the age of soils. In 'young' soils on the dumps, minerals inherited from bedrock (chlorite and micas) predominate, along with a relatively small

Table 4. EDS data for the point indicated in Figure 8.

Element	K ratio (calc.)	ZAF	Atom (%)	Element (wt.%)	Wt.% err. (1σ)	Compound formula	Compound (wt. %)	No. of cations*
Na-K	0.0066	2.829	1.66	1.86	±0.05	Na ₂ O	2.50	0.637
Al-K	0.1289	1.631	16.02	21.02	±0.12	Al ₂ O ₃	39.71	6.146
Si-K	0.1340	1.852	18.17	24.82	±0.14	SiO ₂	53.09	6.972
K-K	0.0095	1.298	0.65	1.23	±0.05	K ₂ O	1.48	0.248
Fe-K	0.0040	1.204	0.18	0.49	±0.05	Fe ₂ O ₃	0.70	0.069
Cu-K	0.0067	1.253	0.27	0.84	±0.16	CuO	1.05	0.104
Zn-K	0.0065	1.257	0.26	0.81	±0.10	ZnO	1.01	0.098
Mg-K	0.0013	2.040	0.23	0.27	±0.04	MgO	0.45	0.089
O-K	—	3.177	62.56	48.67**	—	—	—	—

* The number of cations is based on 24 oxygen atoms.

** Wt.% calculated by stoichiometry.

amount of pedogenic smectite (and/or R0 mica-smectite), kaolinite, and vermiculite. All of the minerals mentioned occur in well developed ('old') natural soils, along with a number of mixed-layer minerals (both R0 and R1 types) and hydroxy-interlayered phases.

(3) Changes of disordered (R0) mixed-layer minerals to well ordered (R1) minerals are likely to be a result of progressive development of soils during pedogenesis.

(4) The kind of processes controlling layer-silicate transformations and the set of pedogenic clay minerals differ within the profiles studied, and depend on the properties of the soil horizons (e.g. the pH and the soil organic matter content). The most advanced alterations occur in humus-rich A horizons, where dissolution of chlorite, neoformation of kaolinite, and development of mixed-layer minerals occur. In Bw horizons of the well developed soil profiles, where less organic matter content is present, the main products of mineral transformations in the clay fraction are hydroxy-interlayered minerals, the development of which is pH dependent. Interlayers are formed at pH 4.2–4.3.

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