Clay Minerals, (2012) **47**, 401–417

The effect of hydrochemical conditions and pH of the environment on phyllosilicate transformations in the weathering zone of pyrite-bearing schists in Wieściszowice (SW Poland)†

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(*Received 15 February 2012; revised 31 May 2012; Editor: John Adams*)

The influence of hydrological conditions and the pH of the environment on chlorite and mica transformations in the acidic weathering zone of pyrite-bearing schists was studied. Phyllosilicate transformations were investigated in the area of the abandoned pyrite open-pit mine in Wieściszowice (Lower Silesia, SW Poland) using X-ray diffractometry (XRD), Fourier transform infrared (FTIR) spectroscopy and chemical methods. (Mg,Fe)-chlorite, micas (muscovite and paragonite), quartz, feldspars and pyrite were reported to be the most abundant minerals occurring in pyrite-bearing schists. Phyllosilicate transformations were significantly stronger in dry conditions than in wet ones. This conclusion was supported by the fact that the inherited phyllosilicates predominated in the clay mineral fraction of waterlogged saprolites, whereas the secondary swelling minerals were minor components. In dry and extremely acidic saprolites ($pH < 3$), trioctahedral chlorite was dissolved and transformed into clay minerals (e.g. smectite and kaolinite), whereas swelling clays (smectite mainly) were formed at the expense of dioctahedral micas. The pH of water is an important factor influencing phyllosilicate transformations in waterlogged conditions. The phyllosilicate alterations under the influence of extremely acidic waters ($pH < 3$) were more advanced than in moderately acidic ones (pH of 4.6), as the secondary clay minerals seemed to be represented exclusively by smectite in the former, whereas HIMs and mixed-layer minerals such as R0 I-S-Ch, R0 I-S, as well as R1 Ch-V and/or R1 Ch-S occurred in the latter.

KEYWORDS: acid mine drainage, hydroxy-interlayered minerals, mixed-layer minerals, smectite, pyrite weathering, vermiculite, XRD pattern modelling, Wieściszowice, Poland.

Pyrite weathering zones are often related to iron sulphide mines occurring all over the world (e.g. Komnitsas *et al.*, 1995; Parafiniuk, 1996; Banks *et al.*, 1997; Lintnerová *et al.*, 1999; España *et al.*, 2005; Wolkersdorfer & Bowell, 2005). Pyrite decays in oxidizing environments according to the simplified reaction (van Breemen, 1982): $4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 16H^+ + 8SO_4^{2-}$. The

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† Presented at the Euroclay 2011 Conference at Antalya, Turkey

DOI: 10.1180/claymin.2012.047.4.01

weathering of pyrite causes a strong acidification of saprolites, soils and waters.

Acidic weathering zones of iron sulphides are places where intense mineral transformations proceed. Most of the previous investigations were aimed at recognition of sulphide alterations leading to the origin of distinctive mineral associations which contain oxides, oxyhydroxides, and sulphates (e.g. Parafiniuk, 1991; Balcerzak *et al.*, 1992; Bigham *et al.*, 1996; Singh *et al.*, 1999; Murad & Rojík, 2003; Parafiniuk & Siuda, 2006). Phyllosilicate transformations in weathering zones of sulphide-bearing rocks (e.g. Dixon *et al.*, 1982; De Kimpe & Miles, 1992; Krasil'nikov, 1997; Uzarowicz *et al.*, 2008, 2011; Uzarowicz & Skiba, 2011), as well as in saprolites and soils influenced by acid mine drainage (e.g. Galan *et al.*, 1999; Dubiková *et al.*, 2002; Šucha *et al.*, 2002), have not been frequently examined. The studies mentioned above revealed that the processes controlling phyllosilicate transformations in such weathering environments are similar to those observed in other acidic soil environments (e.g. in podzols), where the processes like (1) dissolution of less resistant aluminosilicates (e.g. chlorite), (2) formation of secondary swelling minerals and mixed-layer minerals containing swelling interlayers at the expense of chlorite and mica (Carnicelli *et al.*, 1997; Gillot *et al.*, 2000; April *et al.*, 2004; Skiba, 2007), and (3) crystallization of kaolinite (Skiba, 2001, 2007; Skiba & Skiba, 2005) have been documented.

The previous studies performed in the iron sulphide weathering zones paid little attention to the influence of the environmental conditions on phyllosilicate transformations. The objective of this paper is to investigate in more detail the influence of hydrological conditions and the degree of acidification of water on the course of chlorite and mica transformations in saprolites and pond deposits developed in the weathering zone of pyrite-bearing schists located in Wieściszowice (SW Poland).

MATERIALS AND METHODS

Site and material description

The investigated weathering zone is located within the abandoned pyrite mine in Wieściszowice village in the Rudawy Janowickie Mts (Western Sudety Mountains, SW Poland). The geological bedrock of the region is built of pyrite-bearing schists of the Leszczyniec Unit (Mazur *et al.*, 2006). Genesis of the pyrite mineralization in Wieściszowice is believed to be linked to the metamorphosis of sedimentary deposits related to submarine exhalations (Jaskólski, 1964). The pyrite mine in Wieściszowice was in operation between 1785 and 1925. Nowadays, abandoned open pits filled with acid mine drainage (so-called Coloured Ponds, e.g. Purple and Blue Ponds) and mine (excavate) dumps located near the pits are remnants of the former mining activities.

Dry (well drained) and wet (waterlogged) saprolites from the weathering zone were investigated (Table 1). The saprolite samples were always collected along with their parent rock equivalents. Two dry samples (W1 and W2) represented saprolites derived from chlorite schists (sample R1) and mica schists (sample R2) respectively. Hence, it was easier to determine chlorite and mica alterations in dry conditions separately. Two waterlogged samples (W3 and W4) were deposits collected from the extremely acidic Purple Pond

TABLE 1. The description and the pH_{H_2O} of the saprolites investigated.

Saprolite sample	Description	pH_{H_2O}
W1	Greenish and yellowish earthy aggregations occurring on rocky wall built of chlorite schists (rock sample R1)	2.0
W2	Brown loamy saprolite derived from mica schists (rock sample R2)	2.7
W3	Rusty loamy deposit derived from chlorite-mica schists (rock sample R3) taken from the extremely acid Purple Pond	2.6
W4	Brown loamy deposit derived from chlorite-mica schists (rock sample R4) taken from the moderately acid Blue Pond	4.6

TABLE 2. Properties and content of ions in waters of the Purple and the Blue Ponds.

	pH	Conductivity	Content of ions (mg·dm^{-3})										
	pH	(µS cm^{-1})	H^+	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	F^-
Purple Pond	2.7	2690	1.92	242.01	128.67	13.70	8.15	5.75	90.65	1741.91	4.48	<0.0025	2.43
Blue Pond	4.6	202	0.02	19.30	7.51	4.11	0.48	0.41	4.09	79.99	2.37	1.92	0.10

and moderately acidic Blue Pond (Table 2), respectively. Both evolved from the same parent rock, i.e. chlorite-mica schist (samples R3 and R4). This sampling strategy allowed us to determine the transformations of chlorite and mica as dependent on the acidity of pond waters.

Analytical methods

The pH of saprolites was analysed potentiometrically in distilled water, based on air-dried samples of fine earth (<2 mm) using a saprolite/solution ratio of 1:2.5 (Table 1).

Each of the rock and bulk saprolite samples (<2 mm) were ground in an agate mortar and packed into face loading holders. The bulk mineralogy of the rocks and saprolites was determined using the X-ray diffraction (XRD) method.

The clay fractions (<0.2 and 0.2–2 µm) were separated from bulk saprolites according to the Jackson (1975) procedure, including removal of organic matter (using 30% hydrogen peroxide buffered with an acetic acid buffer at pH ~5) and removal of free iron oxides, according to the Mehra & Jackson (1960) method, using a sodium dithionite buffered with citrate-bicarbonate solution. Clay fractions separated by centrifugation were saturated (Na, Mg or K) and dialysed. Oriented mounts on glass slides were prepared by sedimentation. The XRD analyses were performed on the mounts in air-dried (AD) conditions (Na-saturated, Mg-saturated and K-saturated samples) after glycerol or ethylene glycol (EG) saturation (Na-saturated and Mg-saturated samples), and after heating for at least 1 hour at 330ºC and 550ºC (Na-saturated and K-saturated samples).

X-ray diffraction analyses were carried out using a Philips X'Pert diffractometer with PW1870 generator and PW3020 vertical goniometer equipped with a 1º divergence slit, 0.2 mm receiving slit, incident- and diffracted-beam Soller slits, 1º anti scatter slit, and a graphite diffracted-beam monochromator. Cu-*K*α radiation was used (40 kV, 30 mA). Random mounts of the ground rocks and bulk saprolite material, as well as oriented mounts of clay fraction, were scanned from 2 to 64º 2θ at a counting time of 1 s per 0.02º step.

The separated Na-saturated clay fractions were analysed by means of Fourier transform infrared (FTIR) spectroscopy using a BIO-RAD FTS-135 device. The pressed pellet technique was used with pellets prepared as a ground mixture of 300 mg potassium bromide (after 24 h heating at 550ºC) with 0.8 mg of 0.2–2 μm clay (after 12 h drying at 105ºC). The spectra were recorded in the range from 400 to 4000 cm^{-1} at a resolution of 2 cm^{-1}. The XRD and FTIR spectroscopy analyses were performed in the Institute of Geological Sciences, Jagiellonian University, Krakow, Poland.

The pH and conductivity of waters from the Purple and Blue Ponds, as well as their chemical compositions were examined (Table 2). The content of ions in the waters was determined using an ICS-2000 (DIONEX) ion chromatograph. These analyses were carried out in the Hydrological Laboratory of the Institute of Geography and Spatial Management, Jagiellonian University, Krakow, Poland. The contents of the selected elements (Fe, Al, Mn, Zn and Cu), along with the amount of dissolved silica in waters (Table 3), were determined by the ICP-AES method using the "Plasma 40" (Perkin Elmer) apparatus. Analyses were carried out in the Hydrogeochemical Laboratory of the Faculty of Geology, Geophysics and Environment Protection, AGH University of Science and Technology, Krakow, Poland.

Interpretation of XRD patterns and FTIR spectra

X-ray diffraction patterns of the clay fractions were interpreted using criteria given by Brindley & Brown (1980), Moore & Reynolds (1997) and Środoń (2006). The detailed interpretation of chlorite, vermiculite and hydroxy-interlayered minerals was carried out using the recommendations of Barnhisel & Bertsch (1989), Lagaly *et al.* (2006) and Meunier (2007). The XRD patterns were processed using ClayLab (Mystkowski, 1999). Definitions provided by van der Marel & Beutelspracher (1976), Russell & Fraser (1994) as well as Madejová (2003) were used during interpretation of the FTIR spectra.

XRD patterns modelling and peak decomposition

X-ray diffraction patterns of clays (AD and EG-saturated) from sample W4 (i.e. the sample which exhibited the most complex and "problematic" mineral composition) were modelled using the Sybilla© software (Chevron™), which is based on mathematical formalism given by Drits & Sakharov (1976). In this research, the Sybilla© modelling was used to reveal the nature of mixed-layer clay minerals reported in the sample W4. Modelling first included a trial-and-error procedure that yielded optimal clay mineral structural and probability parameters, which enabled the best fit to be obtained between experimental and calculated positions and intensities of basal reflections for each mineral present in the sample. For mixed-layer clay minerals occurring in analysed soils, the number, nature and stacking sequence of different compositional layers were taken as modifiable values (Hubert *et al.*, 2009, 2012). Once the parameters of all the modelled phases had been set, the content of each phase could be adjusted to match the original pattern as far as possible.

The experimental set-up used for modelling the clay minerals found in soils followed recommendations and procedures provided by Hubert *et al.* (2009, 2012). To produce the modelled W4 pattern we introduced three discrete phases (illite, paragonite and chlorite) and two mixed-layer minerals (R0 I-S-S-Ch and R0 I-S-S). The R0 I-S-S-Ch comprised two smectite layers having one and two water (1w and 2w respectively) molecules, as well as one and two ethylene glycol (1g and 2 g respectively) molecules in AD and EG-solvated samples, respectively. The parameter describing the orientation of particles on the mounted X-ray slide (σ^*) was set to ~6 and ~12 for R0 I-S-S-Ch and R0 I-S-S, respectively. Coherent scattering domain sizes expressed in layers in Sybilla© modelling were ~9 and ~20 for R0 I-S-S-Ch and R0 I-S-S, respectively.

TABLE 3. Content of the selected elements and dissolved silica in waters of the Purple and the Blue Ponds.

	Content (mg dm^{-3})					
	Al	Fe	SiO_2	Mn	Zn	Cu
Purple Pond	68.52	134.74	49.10	2.24	0.38	1.79
Blue Pond	1.65	0.08	18.93	0.18	0.03	<0.01

Decomposition of AD and EG XRD patterns for sample W4 was performed using DecompXR software (Lanson, 1993) in the range from 4 to 10º2θ. Lanson & Besson (1992) showed that a minimum difference of 0.3º2θ on peak position and 0.2º2θ on width is necessary for DecompXR to separate the contributions of two phases. Both criteria were greatly fulfilled by decomposition of the composite reflections in the W4 sample. With the backgrounds subtracted, experimental patterns were decomposed by the progressively increasing number of Gaussian elementary curves in order to obtain a good fit using the smallest number of curves. The initial parameters (position and FWHM) were taken from other studies dealing with soil clay parageneses (e.g. Hubert *et al.*, 2009, 2012).

RESULTS

Chemical properties of saprolites and pond waters

Saprolites and waters that occurred in the pyrite weathering zone in Wieściszowice were acidic. The pH_{H_2O} of saprolites ranged from 2.0 to 4.6 (Table 1). The pH of the Purple Pond waters was of 2.7. The conductivity of water was very high in the Purple Pond (2690 μS cm^{-1}) (Table 2) and the water contained large amounts of SO_4^{2-}, Ca^{2+}, and Mg^{2+} ions. It also contained relatively large amounts of Fe, Al, dissolved silica, and trace elements – Mn, Cu, and Zn (Table 3). High acidity and the occurrence of the compounds mentioned are typical features of acid mine drainage (Johnson, 2003). The water of the Blue Pond was less acidic than the Purple Pond; its pH was 4.6. The conductivity and content of the investigated constituents (ions, elements and dissolved silica) were much lower in the Blue Pond than in the Purple Pond (Tables 2 and 3).

Mineral composition of rocks and bulk saprolite samples

The mineral compositions of rocks and bulk saprolite samples (<2 mm) are shown in Figs 1–3. The paragenesis of rock sample R1 defines the rock as a chlorite schist consisting of (Mg,Fe)-chlorite of brunsvigite composition, quartz, albite, calcite and pyrite (Fig. 1). The rock did not contain mica or it was below the XRD detection limit. The main minerals occurring in the bulk saprolite sample W1 derived from chlorite schist were sulphates: slavikite $MgFe[(OH)_3(SO_4)_4]\cdot 18H_2O$, fibroferrite $Fe[(OH)(SO_4)]\cdot 5H_2O$ (both formulae according to Parafiniuk, 1996) and gypsum (Fig. 1). The occurrence of illite (clay-sized K-mica) in this saprolite (Fig. 4), and on the other hand its lack in the respective parent rock R1, might be explained by aeolian deposition or gravitational redeposition of micas from the higher parts of an outcrop, as the fact that saprolite sample W1 was collected from the foothill of an almost vertical rocky wall which, apart from chlorite, might have contained some content of mica as well.

Rock sample R2 was a mica schist composed of micas (muscovite and paragonite) and quartz as predominating minerals (Fig. 2). Albite, chlorite (brunsvigite) and pyrite were present in minor amounts. Bulk saprolite W2 derived from such a defined mica schist contained the same minerals as its parent rock (R2), with the exception of pyrite, which was presumably completely weathered (Fig. 2). Traces of jarosite were found in the sample W2, as indicated by the presence of 3.08, 3.11 and 5.68 Å reflections in the XRD pattern (Fig. 2).

Mineral compositions of rock samples R3 and R4 were more or less the same. These rocks were chlorite-mica schists containing chlorite (brunsvigite), micas (muscovite and paragonite), quartz, albite and pyrite (Fig. 3). The bulk saprolite sample W3 occurring in the strongly acidic (pH 2.7) Purple Pond, as well as bulk saprolite W4 taken from moderately acidic (pH of 4.6) Blue Pond, consisted of the same minerals as their parent rocks (R3 and R4 respectively) (Fig. 3) with the exception of pyrite which was not detected by XRD.

Mineral composition of clay fractions based on XRD pattern and FTIR spectra interpretation

Phyllosilicates from the clay fraction of saprolites developed in the weathering zone studied can be divided into two groups: (1) minerals inherited from parent rocks (chlorite and micas) and (2) secondary minerals (smectite, vermiculite, hydroxy-interlayered minerals, as well as mixed-layer phases containing hydrated interlayers) (Figs 4–6). Trioctahedral (Mg,Fe)-chlorite (~14.3 Å basal reflection beginning the rational series and characteristic 3570 cm^{-1} absorption band in the FTIR spectra) and

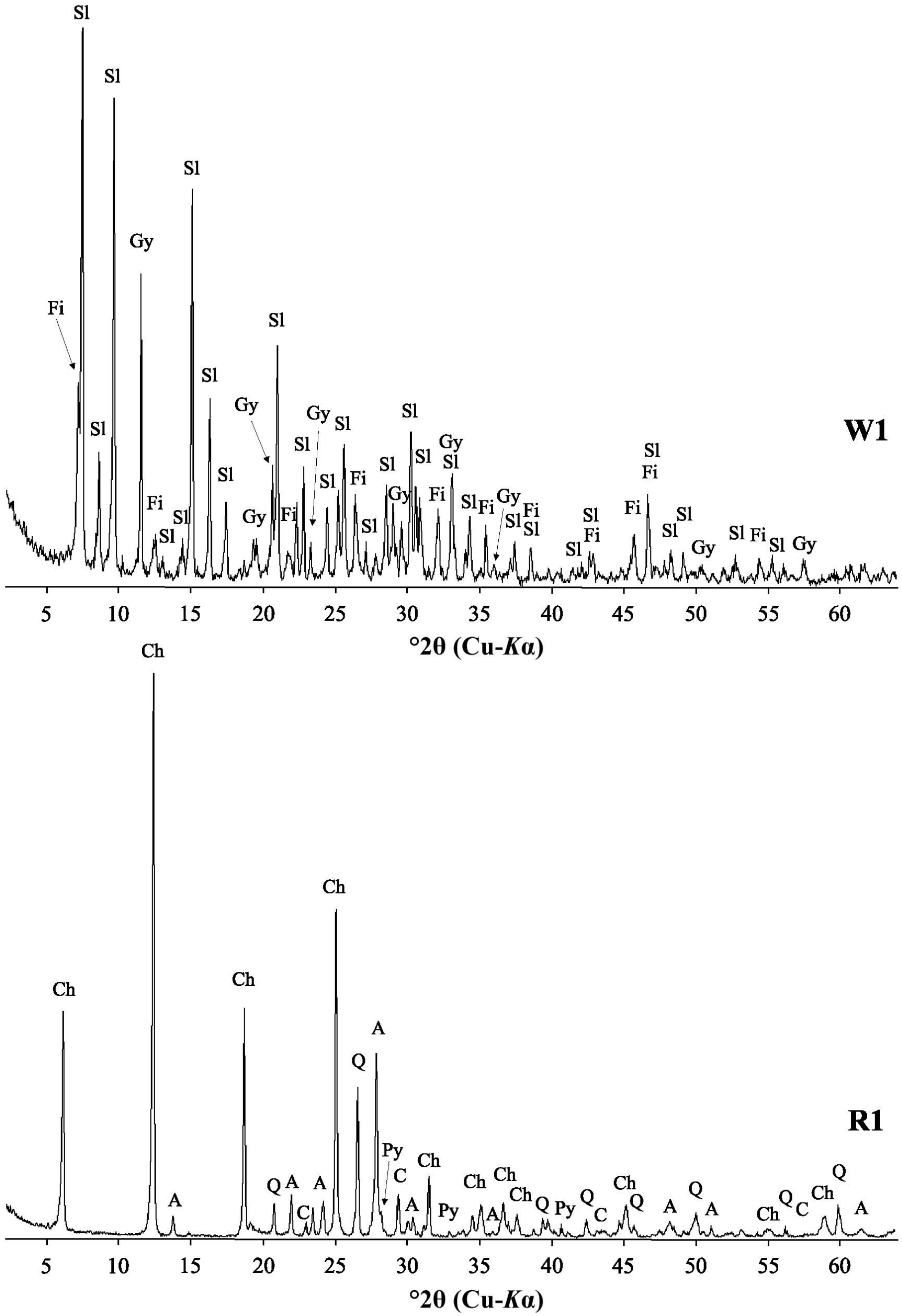

FIG. 1. Mineral composition of chlorite schist (sample R1) and bulk mineralogy of saprolite (sample W1) derived from chlorite schist. Mineral symbols for the Figures 1, 2, and 3: A – albite, C – calcite, Ch – chlorite, Fi – fibroferrite, Gy – gypsum, J – jarosite, Kf – potassium feldspar, M – muscovite, P – paragonite, Py – pyrite, Q – quartz, Sl – slavikite.

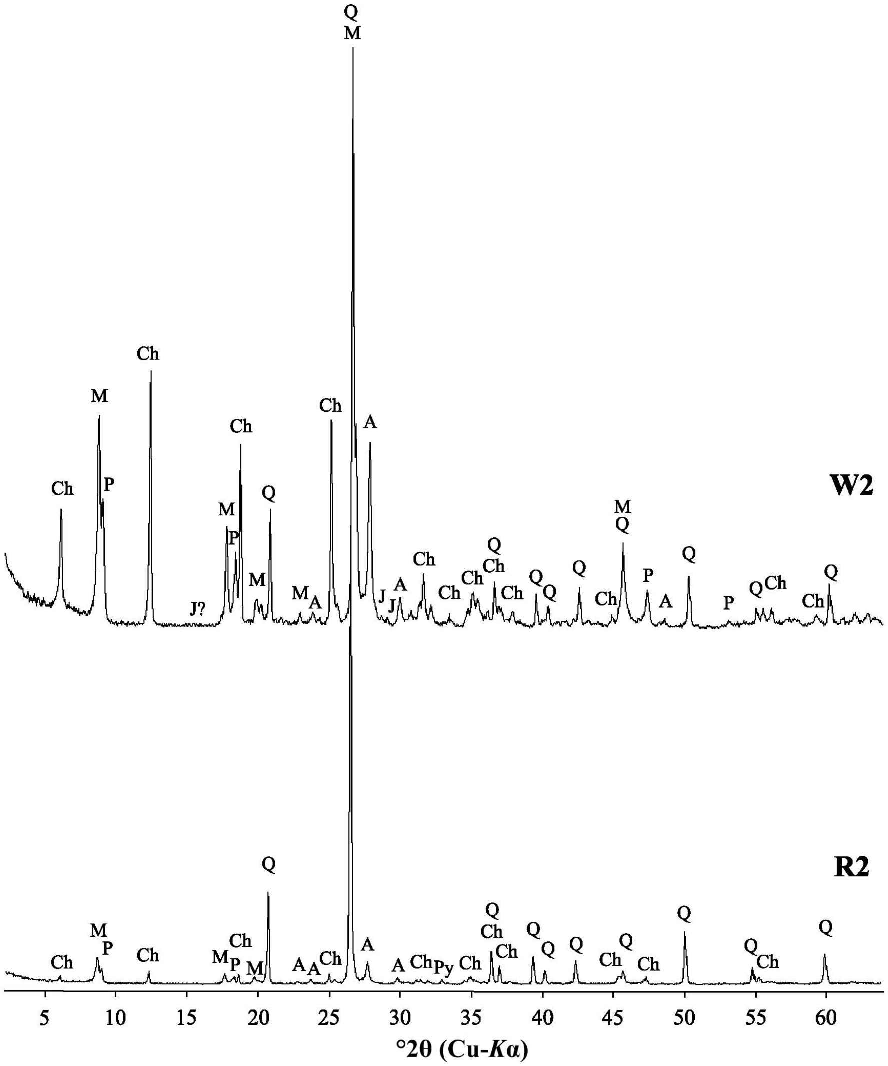

FIG. 2. Mineral composition of mica schist (sample R2) and bulk mineralogy of saprolite (sample W2) derived from mica schist. Mineral symbols as in Fig. 1.

dioctahedral micas – illite (clay-sized K-mica; 10 Å basal reflection) and brammallite (clay-sized Na-mica; 9.7 Å basal reflection) – usually predominated across the mineral composition of the clay fractions studied. The presence of kaolinite has also been found in some of the investigated saprolites (e.g. sample W1). It was confirmed by characteristic reflections in the XRD patterns (~7 Å and 3.58 Å basal reflections, Fig. 4), and absorption bands in the FTIR spectra (e.g. 3697 cm^{-1} band, Fig. 6). Smectite and/or mixed-layer clay minerals containing a smectitic component (17 Å or 18 Å reflections in the EG- or glycerol-solvated clays, respectively) seem to be the most abundant swelling clay reported in the investigated saprolites. The presence of vermiculite was hard to determine because of the 001 basal line interferences of chlorite and vermiculite. Nevertheless, the occurrence of vermiculite was indicated in saprolite W4 by a decrease of intensity of the ~14 Å reflection after heating, along with a simultaneous reinforcement of the 10 Å reflection (Fig. 5).

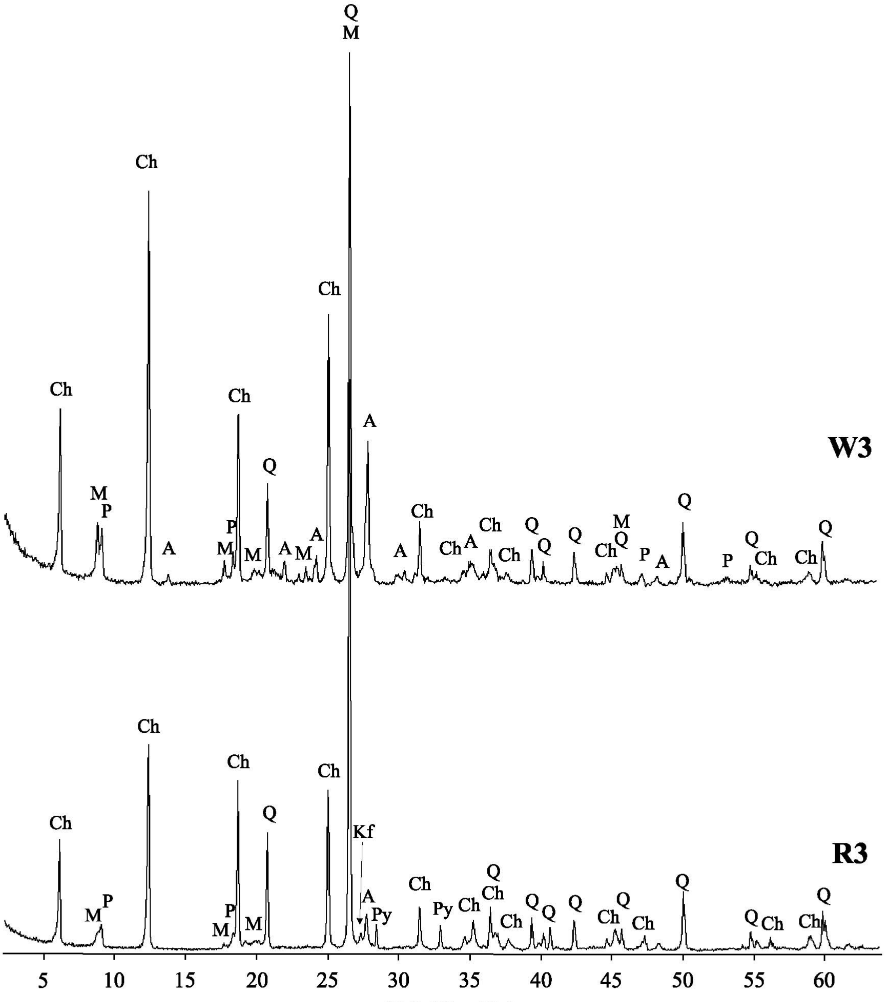

FIG. 3. Mineral composition of chlorite-mica schist (sample R3) and bulk mineralogy of saprolite (sample W3) derived from chlorite-mica schist collected in Purple Pond. Similar mineral composition is typical of rock and saprolite sample collected from Blue Pond (R4 and W4 sample, respectively). Mineral symbols as in Fig. 1.

Mixed-layer clays containing swelling interlayers, most likely illite-smectite-chlorite and/or illite-smectite-vermiculite, developed in deposits from the Blue Pond (W4 sample) (Fig. 5). This is suggested by the 13–12 Å pronounced asymmetry of the 001 chlorite reflection (AD pattern) shifting to the 17–15 Å region as seen for the EG treated sample. Further on, the 13–12 Å asymmetry was found to be completely diminished on heating. Moreover, hydroxy-interlayered minerals (HIMs) were found to occur in sample W4 (Fig. 5). Both hydroxy-interlayered vermiculite (HIV) and hydroxy-interlayered smectite (HIS) were likely to be present, as the 12.8 Å reflection (typical of HIV) and 11–10 Å asymmetry of mica peak (typical of HIS) in the XRD pattern of clay heated at 330ºC appeared (Fig. 5). According to Meunier (2007), these features might indicate the presence of HIMs. Owing to the low intensity of peaks typical of HIMs, it was estimated that HIM participation is modest in sample W4. Furthermore, due to their complex behaviour, HIMs were excluded from further pattern modelling and peak decomposition processes.

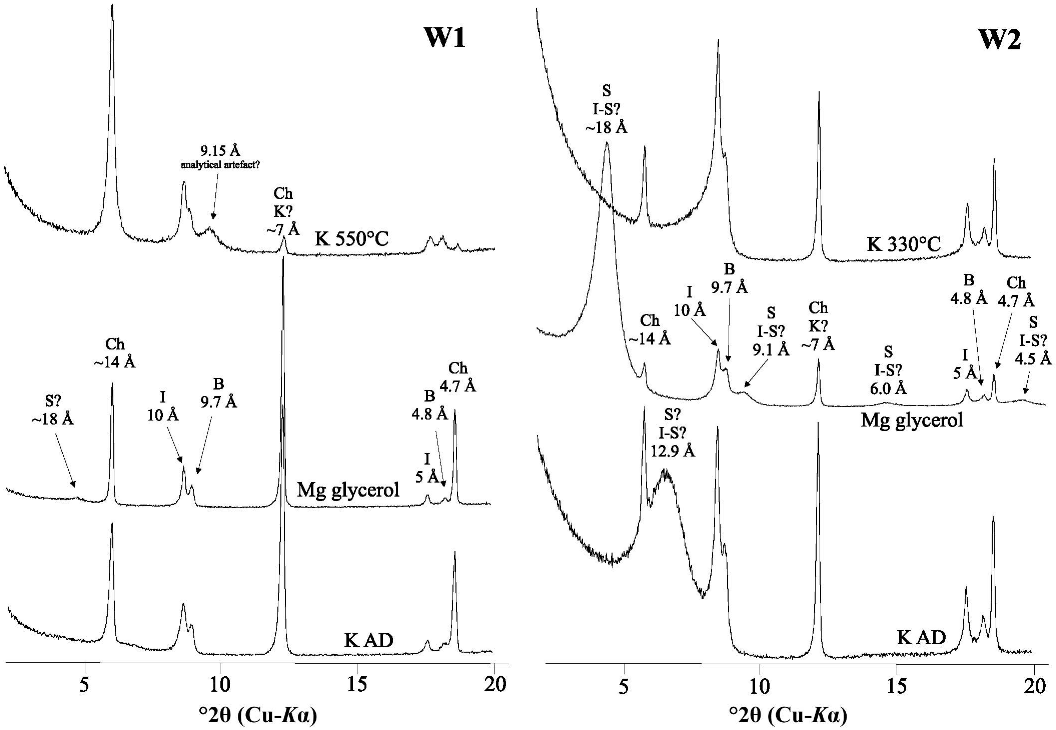

FIG. 4. Mineral composition of clay fractions (<0.2 μm) separated from saprolites derived from chlorite schist (sample W1) and mica schist (sample W2). Mineral symbols for the Figures 4 and 5: B – brammalite (clay-sized Na-mica), Ch – chlorite, HIS – hydroxy-interlayered smectite, HIV – hydroxy-interlayered vermiculite, I – illite (clay-sized K-mica), I-S – illite-smectite, I-S-Ch – mixed-layer illite-smectite-chlorite phase, I-S-V – mixed-layer illite-smectite-vermiculite phase, K – kaolinite, Q – quartz, S – smectite, V – vermiculite.

Pattern modelling and peak decomposition

Major reflections of the experimental pattern (14.3 Å, 10 Å, 9.7 Å, 7.1 Å, 5 Å, 4.8 Å, and 4.7 Å) for sample W4 were modelled by Sybilla© using only discrete phases (illite, paragonite and chlorite) (Fig. 7). However, some residual misfits between the experimental and calculated XRD patterns for Na-saturated samples remained. They pertain to the bulging of chlorite 001 reflections, as well as to the asymmetry of 001 basal reflections of mica (Fig. 7). The composite chlorite basal peak was initially modelled in the sample AD by introduction of mixed-layer R0 illite-smectite-chlorite that displayed a chlorite peak anomaly (~13 Å) in its higher angle domain (Fig. 7). In addition, it satisfactorily reproduced a bulging shift of the chlorite peak anomaly towards the lower degree region (~15.5 Å) that took place upon glycolation (Fig. 7). Lower angle asymmetry of the 001 mica reflection was reproduced by introduction of mixed-layer R0 illite-smectite having a low smectite component. Proportions (in %) between different phase components in mixed-layer phases were I(57)-S2w(29)-S1w(0)-Ch(14) in illite-smectite-chlorite for sample AD and I(41)-S2g(35)-S1g(5)-Ch(18) for sample EG, whereas they were I(85)-S2w(7)-S1w(8) in illite-smectite for sample AD and I(80)-S2g(4)-S1g(16) for sample EG.

After subtraction of the extremely high background occurring in the range of ~2–5° 2θ (XRD pattern of EG-solvated sample W4, Fig. 5), a peak at ~31 Å became evident (Fig. 7), which might be an indication of the presence of R1 Ch-V and/or R1 Ch-S (e.g. Moore & Reynolds, 1997).

Using a broad band (~1.7 Δ °2θ) along with a sharp maximum (~0.3 Δ °2θ) we fitted the composite chlorite peak at ~14.3 Å, having a pronounced bulge in its higher and lower angle regions, for both AD and EG W4 samples,

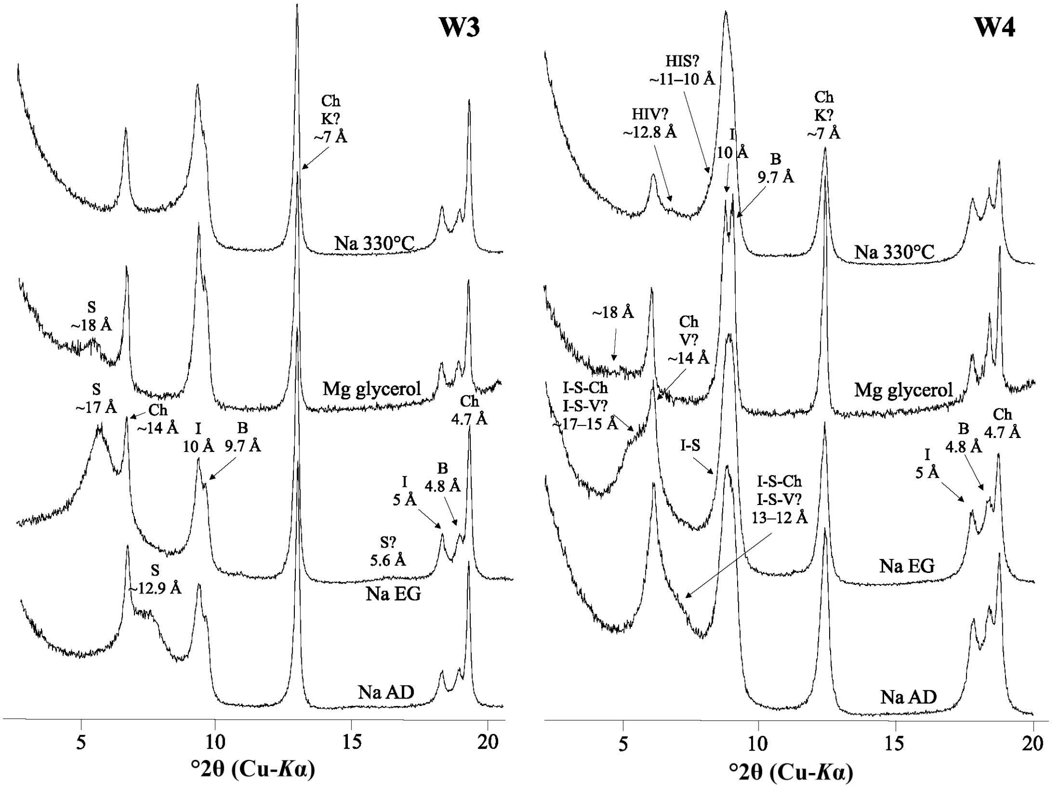

FIG. 5. Mineral composition of clay fractions (<0.2 μm) separated from saprolites derived from chlorite-mica schist collected in the extremely acidic Purple Pond (sample W3) and the moderately acidic Blue Pond (sample W4). Mineral symbols as in Fig. 4.

respectively (Fig. 8). Comparing the decomposition pictures for the AD and EG samples, one is able to trace a migration of the broad peak starting from 13.4 Å towards 15.5 Å (Fig. 8). These peaks can be assigned to mixed-layer R0 illite-smectite-chlorite. The mica reflection was decomposed into two peaks, 10 and 9.7 Å, representing illite and brammallite respectively. A low-angle shoulder of illite arose due to the presence of an I-S mixed-layer mineral, which is represented by the broad reflection at ~10.5 Å (Fig. 8). Peak decomposition procedures fully confirmed the results obtained by pattern modelling.

DISCUSSION

Taking into account generally accepted types of processes involving clay mineral formation in weathering environments (e.g. Wilson, 1999, 2004), the inheritance of phyllosilicates from parent rocks is thought to be one of the most important processes controlling clay mineral formation in the studied area (Table 4). The inherited chlorite and micas were subjected to alteration processes in an acidic weathering environment. The transformation into swelling minerals (smectite and vermiculite) and the dissolution of inherited phyllosilicates, which is the best expressed in the case of chlorite, seem to act as the most significant weathering processes.

Relatively larger amounts of secondary swelling clay minerals were found in well-drained saprolites (W2 sample, Fig. 4) than in waterlogged ones (W3 and W4 samples, Fig. 5), as suggested by intensity differences of the respective mineral peaks. It is known that the processes of clay mineral formation are more advanced in weathering environments where wetting and drying cycles occur alternately (e.g. Rich, 1968; Velde & Meunier, 2008). Furthermore, bearing in mind the generally

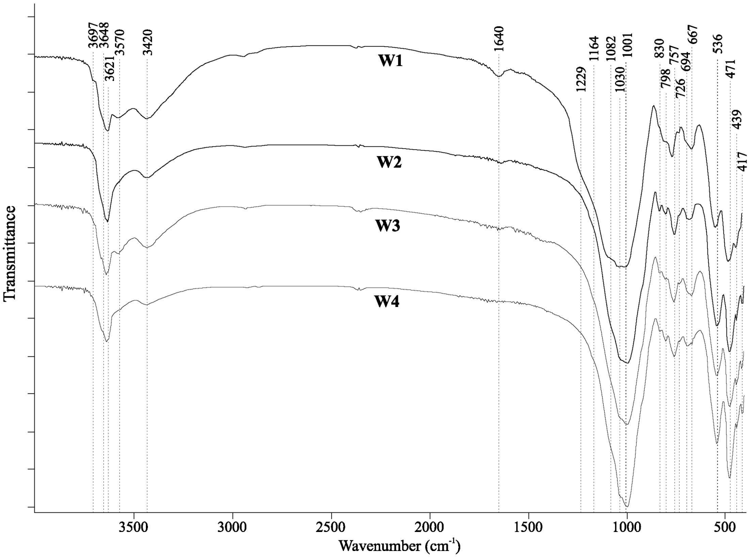

FIG. 6. FTIR spectra of clay fractions (0.2–2 μm) separated from saprolites investigated.

accepted sequence of phyllosilicate weathering which can be simplified to a three-part sequence; initial phyllosilicate (e.g. chlorite or mica) → vermiculite → smectite (e.g. Jackson, 1962), chlorite and mica transformations into swelling clays are more advanced in extremely acidic environments (W3 sample) than in moderately acidic ones (W4 sample, Fig. 5). Therefore, the scale of phyllosilicate transformations and swelling clay formation seems to be inversely correlated with the pH value of the weathering environment. A similar feature was also documented in technogenic soils developed on mine spoils containing iron sulphides (Uzarowicz & Skiba, 2011).

The dissolution of chlorite taking place in the weathering zone studied is a typical feature of this mineral, as the process was observed during the experimental studies (e.g. Ross, 1969; Kodama & Schnitzer, 1973; Parafiniuk, 1996; Brandt *et al.*, 2003; Hamer *et al.*, 2003), as well as in the natural acidic weathering environments (e.g. Bain, 1977; Barnhisel & Bertsch, 1989; Galan *et al.*, 1999). Parafiniuk (1996) investigated the influence of sulphuric acid solutions on dissolution of minerals occurring in pyrite-bearing schists from Wieściszowice. The only mineral that was clearly dissolved during the experiment was chlorite. The effect of the dissolution was a release of Mg, Al, Fe and silica to the solution. The data obtained in the present study (Tables 2 and 3) are consistent with the experiments of Parafiniuk (1996). The ions released in the process of chlorite dissolution crystallize in well drained parts of the weathering zone as secondary minerals, e.g. slavikite, which is one of the most typical minerals occurring in the weathering zone in Wieściszowice (Parafiniuk, 1996). Large amounts of slavikite were observed on the surface of chlorite schists exposed to weathering, as evidenced by observations during the field work and XRD studies (Fig. 1). Moreover, the dissolution (hydrolysis) of chlorite tends to be the most important process responsible for large amounts of Mg, Al and dissolved silica in the acid mine drainages studied (Tables 2 and 3). The presence of Al and dissolved silica in the water may be also linked to the dissolution of other aluminosilicates (e.g. micas and feldspars). The data obtained suggest that the intensity of phyllosilicate dissolution is directly proportional to the increase of weathering environment acidity, in agreement with the results of previous studies (e.g. Parafiniuk, 1996; Brandt *et al.*, 2003). This dependency is corroborated by the presence of larger amounts of cations (e.g. Mg, Na and K), Al, and dissolved silica in strongly acidic water of the Purple Pond than in less acidic water of the Blue Pond (Tables 2 and 3).

Although chlorite is not resistant to weathering in acidic conditions, paradoxically, large amounts of chlorite were found in the clay fraction of saprolites

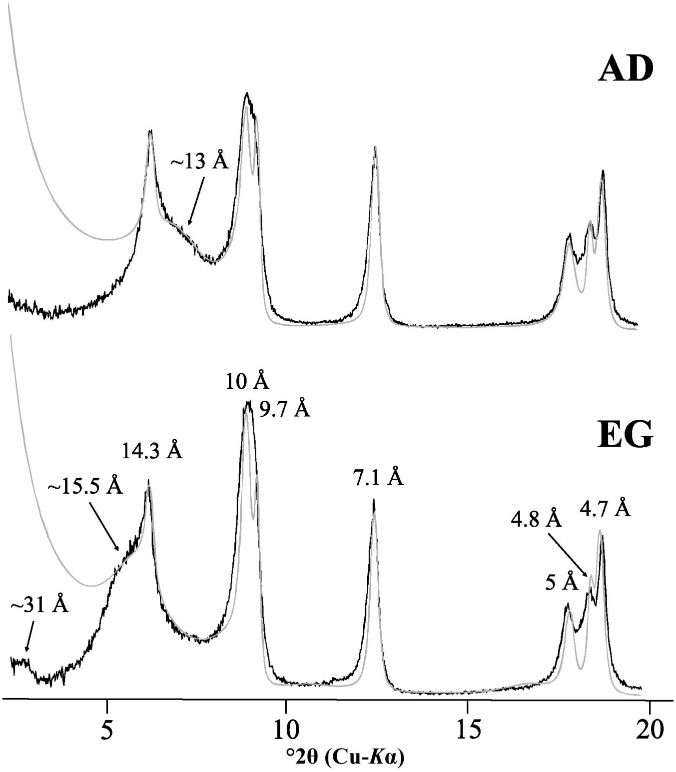

FIG. 7. Comparison between experimental (black) and calculated (grey) XRD patterns for Na-saturated <0.2 µm clay fraction from the sample W4: AD and EG-solvated clay. The settings of the analysis are described in the text.

from weathering zone in Wieściszowice (Figs 4 and 5). The emergence of chlorite in saprolites, following its intense dissolution, may result from the intense physical weathering of the parent rocks. This process most likely occurs simultaneously with the processes of chemical weathering of chlorite

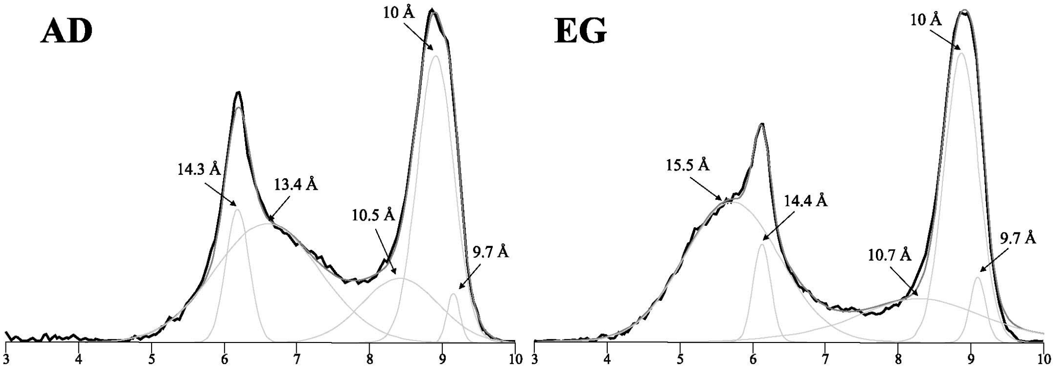

FIG. 8. Decomposition of XRD patterns for Na-saturated <0.2 µm clay fraction from the sample W4: AD and EG-solvated clay. The experimental XRD patterns are black, the best fits are dark grey and elementary Gaussian curves are light grey. The settings of the analysis are described in the text.

TABLE 4. The most important weathering processes affecting chlorite and mica with respect to hydrological conditions and the degree of acidification of weathering environment in the area of the abandoned pyrite mine in Wieściszowice.

Hydrological conditions	Degree of acidification of weathering environment	Type of phyllosilicate	The most important processes of mineral transformations and clay formation
Wet (waterlogged)			
	extremely acidic (pH <3)	chlorite	inheritance from parent rock dissolution and release of Mg, Fe, Al, and dissolved silica to waters
		mica	inheritance from parent rock partial dissolution and release of K and Na to waters transformation into smectite
	moderately acidic (pH of 4.6)	chlorite and mica*	inheritance from parent rock transformation into interstratified clays containing swelling layers formation of HIMs as a result of chlorite and/or mica transformation
Dry (well drained)			
	extremely acidic (pH <3)	chlorite	inheritance from parent rock dissolution and subsequent crystallization of sulphates (e.g. slavikite) transformation into swelling clays and kaolinite?
		mica	inheritance from parent rock intense transformation into smectite partial dissolution and subsequent crystallization of jarosite
	moderately acidic (pH 4.2–4.3)**	chlorite and mica*	inheritance from parent rock formation of vermiculite and HIMs as a result of chlorite and/or mica transformation

* it was hard to examine mica and chlorite transformations separately; ** the data concern phyllosilicate transformations in subsurface horizons (i.e. Bw and C horizons) from natural soils developed in the weathering zone in Wieściszowice, according to Uzarowicz *et al.* (2011)

(i.e. transformation to secondary minerals and dissolution).

Chlorite is likely to have been transformed into smectite and kaolinite, as the XRD reflections and absorption bands in FTIR spectra typical for the latter minerals, were reported in clay fraction of saprolite derived from chlorite schist (W1 sample, Fig. 4 and Fig. 6). This observation is consistent with the results obtained by other authors (e.g. Bain & Russell, 1981; Cho & Mermut, 1992; Murakami *et al.*, 1996; Carnicelli *et al.*, 1997), which documented the formation of swelling clays and kaolinite at the expense of chlorite in weathering environments.

Vermiculite is considered to be one of the most common products of chlorite and mica transformation in weathering zones, and its formation proceeds with the participation of mixed-layer minerals (e.g. chlorite-vermiculite and illite-vermiculite respectively) acting as transitional phases (e.g. Ross & Kodama, 1976; Barnhisel & Bertsch, 1989; De Kimpe & Miles, 1992; Banfield & Murakami, 1998; Wilson, 1999, 2004). The results obtained in the present study showed that vermiculite and/or some mixed-layer phase containing vermiculite interlayers was present only in the least acidic (pH of 4.6) saprolites investigated (W4 sample, Table 2, Fig. 5). Therefore, one may conclude that the pH of the weathering environment comprises a more important factor influencing the process of vermiculite formation than the kind of initial phyllosilicate (i.e. chlorite or mica). Moreover, the process of hydroxy interlayer formation seems to be a pH-dependent phenomenon (i.e. it takes place at pH >4), which is in agreement with the generally accepted view (e.g. Rich, 1968; Churchman, 1980; Barnhisel & Bertsch, 1989; Bain *et al.*, 1990; Meunier, 2007; Skiba, 2007). HIMs (i.e. HIV and HIS) were found exclusively in moderately acidic saprolite W4 (Fig. 5).

Larger amounts of smectite occurred in the saprolites that are typically reported to be strongly acidic (pH <3, Table 1, Figs 4 and 5). Exceptions are saprolites derived from chlorite schist (sample W1), where the main operating mechanism controlling a chlorite transformation is its dissolution rather than transformation into swelling clays. The results obtained indicate that smectite in extremely acidic conditions (e.g. in samples W2 and W3) develops mostly at the expense of micas. Moreover, the data presented in this paper suggest that very high acidity (pH <3) favours the formation of discrete smectite. This is consistent with the studies of Šucha *et al.* (2002), where the influence of acid mine drainage on mineral composition of soils was investigated. They stated that larger amounts of smectite were likely to occur in more acidic soils (pH_{H_2O} 2.3–2.4), rather than in the less acidic ones (pH_{H_2O} 5.2–5.3). Furthermore, smectite is rather a minor component of the moderately acidic W4 sample (Fig. 5). The XRD pattern modelling (Fig. 7) and decomposition (Fig. 8) showed that mixed-layer I-S-Ch, I-S, HIV and HIS are likely to form in the clay fraction from sample W4 instead of discrete smectite.

Smectite is a more abundant mineral phase in fine clay (<0.2 μm) than in the coarse clay fraction (0.2–2 μm) from all of the saprolites studied. Such a feature was also observed in soils developed in the weathering zone in Wieściszowice (Uzarowicz *et al.*, 2011). It suggests that smectite formation is likely to be controlled by strong disintegration of mica (and/or chlorite) accompanied by chemical transformations in acidic environment consisting of (1) partial dissolution and hydration of chlorite and micas as well as (2) release of K and Na from the interlayer position of micas and subsequent decrease of layer charge (e.g. Barnhisel & Bertsch, 1989; Aoudjit *et al.*, 1996; Wilson, 1999; Velde & Meunier, 2008). The release of K and Na during the transformation of micas permits the crystallization of minerals of the jarosite group (Fig. 2) which has been documented in sulphide weathering zones (e.g. De Kimpe & Miles, 1992).

CONCLUSIONS

Five conclusions have been drawn.

(1) The most important processes controlling phyllosilicate transformations and clay mineral formation in saprolites from the pyrite weathering zone in Wieściszowice are: inheritance of chlorite and micas from parent rock, transformation of chlorite and micas to secondary swelling minerals, and dissolution of phyllosilicates. All these processes most likely occur simultaneously.

(2) Dissolution is the most likely weathering process influencing chlorite in the strongly acidic (pH <3) saprolites investigated. The dissolution of chlorite in the area studied is followed by the release of Mg, Fe, Al and dissolved silica, to superficial waters, and the crystallization of secondary Mg-containing sulphates (e.g. slavikite) in dry conditions. Chlorite is also likely to

transform into secondary clay minerals (e.g. vermiculite, smectite and kaolinite).

(3) The most important weathering process influencing micas seems to be their transformation to swelling clay minerals. Partial dissolution of micas and/or loss of interlayer cations in dry conditions followed by release of K and Na to the environment permits the crystallization of minerals of the jarosite group in dry conditions.

(4) The course of phyllosilicate transformations is influenced, apart from the type of the initial mineral, by hydrological conditions and the pH of the environment in which saprolites weather. Phyllosilicate transformations seem to be more advanced in dry (well-drained) saprolites than in wet (waterlogged) ones. On the other hand, phyllosilicate transformations are more advanced in extremely acidic environments than in moderately acidic ones.

(5) The formation of swelling clay minerals in the acidic range of pH seems to be dependent on the degree of acidification of the weathering environment. In strongly acidic conditions (pH <3) discrete smectite develops almost exclusively, whereas HIMs (i.e. HIVs and HISs) and mixed-layer clays containing swelling layers (R0 I-S-Ch and R0 I-S, as well as R1 Ch-V and/or R1 Ch-S) originate in moderately acidic ones (pH 4.6).

ACKNOWLEDGMENTS

The present investigation was supported financially by the Polish Ministry of Science and Higher Education, grant no. N N305 3251 33. The authors thank Mrs Anna Łatkiewicz (Institute of Geological Sciences, Jagiellonian University, Krakow, Poland) for technical assistance with mineralogical research. Mrs Barbara Jaszczyńska (Institute of Geography and Spatial Management, Jagiellonian University, Krakow, Poland) is acknowledged for the determination of properties and content of ions in waters. Mr. Wiesław Knap (AGH University of Science and Technology, Krakow, Poland) is acknowledged for the determination of elements and dissolved silica in waters. Łukasz Uzarowicz thanks the Mineralogical Society of Poland for the Polish Clay Group Award, which enabled him to present a part of this study during the EUROCLAY 2011 conference (Antalya, Turkey). The authors would like to thank to Dr Bruno Lanson (Institut des Sciences de la Terre, Grenoble) for providing us with the new version of his decomposition software DecompXR and his kind help with technical difficulties. Chevron ETC and Dougal McCarty are acknowledged for permission to use the proprietary Sybilla© software. Professor Rafael Ferreiro Mählmann (Technische Universität Darmstadt, Germany), Professor John M. Adams (Editor) and two anonymous reviewers are acknowledged for their valuable suggestions and comments.

REFERENCES

Aoudjit H., Elsass F., Righi D. & Robert M. (1996) Mica weathering in acidic soils by analytical electron microscopy. *Clay Minerals*, **31**, 319–332.

April R.H., Keller D. & Driscoll T. (2004) Smectite in Spodosols from the Adirondack Mountains of New York. *Clay Minerals*, **39**, 99–113.

Bain D.C. (1977) The weathering of ferruginous chlorite in a podzol from Argyllshire, Scotland. *Geoderma*, **17**, 193–208.

Bain D.C. & Russell J.D. (1981) Swelling minerals in a basalt and its weathering products from Morvern, Scotland: II. Swelling chlorite. *Clay Minerals*, **16**, 203–212.

Bain D.C., Mellor A. & Wilson M.J. (1990) Nature and origin of an aluminous vermiculitic weathering product in acid soils from upland catchments in Scotland. *Clay Minerals*, **25**, 467–475.

Balcerzak E., Dobrzyński D. & Parafiniuk J. (1992) Wpływ przeobrażeń mineralnych na skład wód w strefie wietrzenia łupków pirytonośnych w Wieściszowicach, Rudawy Janowickie, Sudety Zachodnie, Polska. *Annales Societatis Geologorum Poloniae*, **62**, 75–93 (Polish with English abstract).

Banfield J.F. & Murakami T. (1998) Atomic-resolution transmission electron microscope evidence for the mechanism by which chlorite weathers to 1:1 semi-regular chlorite-vermiculite. *American Mineralogist*, **83**, 348–357.

Banks D., Younger P.L., Arnesen R., Iversen E.R. & Sheila B.B. (1997) Mine-water chemistry: the good, the bad and the ugly. *Environmental Geology*, **32**, 157–174.

Barnhisel R.I. & Bertsch P.M. (1989) Chlorites and Hydroxy-Interlayered Vermiculite and Smectite. Pp. 729–788 in: *Minerals in Soil Environments* (J.B. Dixon & S.B. Weed, editors). Soil Science Society of America, Madison, WI.

Bigham J.M., Schwertmann U., Traina S.J., Winland R.L. & Wolf M. (1996) Schwertmannite and the chemical modeling of iron in acid sulphate waters. *Geochimica et Cosmochimica Acta*, **60**, 2111–2121.

Brandt F., Bosbach D., Krawczyk-Bärsch E., Arnold T. & Bernhard G. (2003) Chlorite dissolution in the acid pH-range: A combined microscopic and macroscopic approach. *Geochimica et Cosmochimica Acta*, **67**, 1451–1461.

Brindley G.W. & Brown G., editors (1980) *Crystal Structures of Clay Minerals and their X-ray*

Identification. Mineralogical Society, Monograph no. 5, London.

Carnicelli S., Mirabella A., Cecchini G. & Sanesi G. (1997) Weathering of chlorite to a low-charge expandable mineral in a Spodosol on the Apennine Mountains, Italy. *Clays and Clay Minerals*, **45**, 28–41.

Cho H.D. & Mermut A.R. (1992) Evidence for halloysite formation from weathering of ferruginous chlorite. *Clays and Clay Minerals*, **40**, 608–619.

Churchman G.J. (1980) Clay minerals formed from micas and chlorites in some New Zealand soils. *Clay Minerals*, **15**, 59–76.

De Kimpe C. & Miles N. (1992) Formation of swelling clay minerals by sulfide oxidation in some metamorphic rocks and related soils of Ontario, Canada. *Canadian Journal of Soil Science*, **72**, 263–270.

Dixon J.B., Hosser L.R., Senkayi A.L. & Egashira K. (1982) Mineralogical properties of lignite overburden as they relate to mine spoil reclamation. Pp. 169–191 in: *Acid Sulfate Weathering* (J.A. Kittrick, D.S. Fanning & L.R. Hossner, editors). *Soil Science Society of America Special Publication*, no. 10, Madison, WI.

Drits, V.A. & Sakharov B.A. (1976) *X-ray Structural Analysis of Mixed-layer Minerals*. Nauka, Moscow (in Russian).

Dubiková M., Cambier P., Šucha V. & Čaplovičová M. (2002) Experimental soil acidification. *Applied Geochemistry*, **17**, 245–257.

España J.S., Pamo E.L., Santofimia E., Aduvire O., Reyes J. & Barettino D. (2005) Acid mine drainage in the Iberian Pyrite Belt (Odiel river watershed, Huelva, SW Spain): Geochemistry, mineralogy and environmental implications. *Applied Geochemistry*, **20**, 1320–1356.

Galan E., Carretero M.I. & Fernandez-Caliani J.C. (1999) Effect of acid mine drainage on clay minerals suspended in the Tinto River (Río Tinto , Spain). An experimental approach. *Clay Minerals*, **34**, 99–108.

Gillot F., Righi D. & Elsass F. (2000) Pedogenic smectites in podzols from central Finland: an analytical electron microscopy study. *Clays and Clay Minerals*, **48**, 655–664.

Hamer M., Graham R.C., Amrhein C. & Bozhilov K.N. (2003) Dissolution of ripidolite (Mg,Fe-chlorite) in organic and inorganic acid solutions. *Soil Science Society of America Journal*, **67**, 654–661.

Hubert F., Caner L., Meunier A. & Lanson B. (2009) Advances in characterization of soil clay mineralogy using X-ray diffraction: from decomposition to profile fitting. *European Journal of Soil Science*, **60**, 1093–1105.

Hubert F., Caner L., Meunier A. & Ferrage E. (2012) Unraveling complex <2 μm clay mineralogy from soils using X-ray diffraction profile modeling on particle-size sub-fractions: Implications for soil pedogenesis and reactivity. *American Mineralogist*, **97**, 384–398.

Jackson M.L. (1962) Interlayering of expansible layer silicates in soils by chemical weathering. *Clays and Clay Minerals*, **11**, 29–46.

Jackson M.L. (1975) *Soil Chemical Analysis – Advanced Course*. Published by the author, Madison, WI.

Jaskólski S. (1964) Złoże łupków pirytonośnych w Wieściszowicach na Dolnym Śląsku i próba wyświetlenia jego genezy. *Annales de la Société géologique de Pologne (Annales Societatis Geologorum Poloniae)*, **34**, 29–63 (Polish with English summary).

Johnson D.B. (2003) Chemical and microbiological characteristics of mineral spoils and drainage waters at abandoned coal and metal mines. *Water, Air and Soil Pollution*, **3**, 47–66.

Kodama H. & Schnitzer M. (1973) Dissolution of chlorite minerals by fulvic acid. *Canadian Journal of Soil Science*, **53**, 240–243.

Komnitsas K., Xenidis A. & Adam K. (1995) Oxidation of pyrite and arsenopyrite in sulphidic spoils in Lavrion. *Minerals Engineering*, **8**, 1443–1454.

Krasil'nikov P.V. (1997) Transformation of phyllosilicates in the course of oxidation of sulfide-containing soil-forming rocks. *Eurasian Soil Science*, **30**, 1117–1126.

Lagaly G., Ogawa M. & Dékány I. (2006) Clay mineral organic interactions. Pp. 309–377 in: *Handbook of Clay Science* (F. Bergaya, B. Theng & G. Lagaly, editors). Elsevier.

Lanson B. (1993) DECOMPXR, X-ray diffraction pattern decomposition program. Poitiers, France, ERM, 48 pp.

Lanson B. & Besson G. (1992) Characterization of the end of smectite-to-illite transformation: decomposition of the X-ray patterns. *Clays and Clay Minerals*, **40**, 40–52.

Lintnerová O., Šucha V. & Streško V. (1999) Mineralogy and geochemistry of acid mine Fe-precipitates from the main Slovak mining regions. *Geologica Carpatica*, **50**, 395–404.

Madejová J. (2003) FTIR techniques in clay mineral studies. *Vibrational Spectroscopy*, **31**, 1–10.

Mazur S., Aleksandrowski P., Kryza R. & Oberc-Dziedzic T. (2006) The Variscan Orogen in Poland. *Geological Quarterly*, **50**, 89–118.

Mehra O.P. & Jackson M.L. (1960) Iron oxide removal from soils and clays by dithionite-citrate system buffered with sodium bicarbonate. *Clays and Clay Minerals, Proceedings of 7th National Conference*, Pergamon Press, Oxford, UK, 317–327.

Meunier A. (2007) Soil hydroxy-interlayered minerals: a re-interpretation of their crystallochemical properties. *Clays and Clay Minerals*, **55**, 380–388.

Moore D.M. & Reynolds R.C. (1997) *X-Ray Diffraction* *and the Identification and Analysis of Clay Minerals*. Oxford University Press, New York.

Murad E. & Rojík P. (2003) Iron-rich precipitates in a mine drainage environment: Influence of pH on mineralogy. *American Mineralogist*, **88**, 1915−1918.

Murakami T., Isobe H., Sato T. & Ohnuki T. (1996) Weathering of chlorite in a quartz-chlorite schist: I. Mineralogical and chemical changes. *Clays and Clay Minerals*, **44**, 244−256.

Mystkowski K. (1999) ClayLab, a computer program for processing and interpretation of X-ray diffractograms of clays. *Conference of European Clay Groups Association, EUROCLAY 1999*. Book of abstracts, Krakow, Poland, pp. 114−115.

Parafiniuk J. (1991) Fibroferrite, slavikite and pickeringite from the oxidation zone of pyrite-bearing schists in Wieściszowice (Lower Silesia). *Mineralogia Polonica*, **22**, 3−16.

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

Parafiniuk J. & Siuda R. (2006) Schwertmannite precipitated from acid mine drainage in the Western Sudetes (SW Poland) and its arsenate sorption capacity. *Geological Quarterly*, **50**, 474−486.

Rich C.I. (1968) Hydroxy interlayers in expansible layer silicates. *Clays and Clay Minerals*, **16**, 15−30.

Ross G.J. (1969) Acid dissolution of chlorites: release of magnesium, iron and aluminum and mode of acid attack. *Clays and Clay Minerals*, **17**, 347−354.

Ross G.J. & Kodama H. (1976) Experimental alteration of a chlorite into a regularly interstratified chlorite-vermiculite by chemical oxidation. *Clays and Clay Minerals*, **24**, 183−190.

Russell J.D. & Fraser A.R. (1994) Infrared methods. Pp. 11−67 in: *Clay Mineralogy: Spectroscopic and Chemical Determinative Methods* (M.J. Wilson, editor). Chapman & Hall.

Singh B., Wilson M.J., McHardy W.J., Fraser A.R. & Merrington G. (1999) Mineralogy and geochemistry of ochre sediments from acid mine drainage near a disused mine in Cornwall, UK. *Clay Minerals*, **34**, 301−317.

Skiba M. (2001) The origin of kaolinite from the Tatra Mts. podzols. *Mineralogia Polonica*, **32**, 67−76.

Skiba M. (2007) Clay mineral formation during podzolization in an alpine environment of the Tatra Mountains, Poland. *Clays and Clay Minerals*, **35**, 618−634.

Skiba M. & Skiba S. (2005) Chemical and mineralogical index of podzolization of the granite regolith soils. *Polish Journal of Soil Science*, **38**, 153−161.

Środoń J. (2006) Identification and quantitative analysis of clay minerals. Pp. 765−787 in: *Handbook of Clay Science* (F. Bergaya, B. Theng & G. Lagaly, editors). Elsevier.

Šucha V., Dubiková M., Cambier P., Elsass F. & Pernes M. (2002) Effect of acid mine drainage on the mineralogy of a dystric cambisol. *Geoderma*, **110**, 151−167.

Uzarowicz Ł. & Skiba S. (2011) Technogenic soils developed on mine spoils containing iron sulphides: Mineral transformations as an indicator of pedogenesis. *Geoderma*, **163**, 95−108.

Uzarowicz Ł., Skiba S., Skiba M. & Michalik M. (2008) Mineral transformations in soils on spoil heaps of an abandoned pyrite mine in Wieściszowice (Rudawy Janowickie Mts., Lower Silesia, Poland). *Polish Journal of Soil Science*, **41**, 183−193.

Uzarowicz Ł., Skiba S., Skiba M. & Šegvić B. (2011) 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. *Clays and Clay Minerals*, **59**, 581−594.

van Breemen N. (1982) Genesis, morphology, and classification of acid sulfate soils in coastal plains. Pp. 95−108 in: *Acid Sulfate Weathering* (J.A. Kittrick, D.S. Fanning & L.R. Hossner, editors). *Soil Science Society of America Special Publication*, no. 10, Madison, WI.

van der Marel H.W. & Beutelspracher H. (1976) *Atlas of Infrared Spectroscopy of Clay Minerals and their Admixtures*. Elsevier.

Velde B. & Meunier A. (2008) *The Origin of Clay Minerals in Soils and Weathered Rocks*. Springer.

Wilson M.J. (1999) The origin and formation of clay minerals in soils: past, present and future perspectives. *Clay Minerals*, **34**, 7−25.

Wilson M.J. (2004) Weathering of primary rock-forming minerals: processes, products and rates. *Clay Minerals*, **39**, 233−266.

Wolkersdorfer C. & Bowell R., editors (2005) Contemporary reviews of mine water studies in Europe, Part 2. *Mine Water and the Environment*, **24**, 2−37.

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