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Microscopic and microchemical study of iron sulphide weathering in a chronosequence of technogenic and natural soils

Łukasz Uzarowicz *

Department of Soil Environment Sciences, Faculty of Agriculture and Biology, Warsaw University of Life Sciences SGGW, ul. Nowoursynowska 159, building no. 37, 02-776 Warsaw, Poland

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ABSTRACT

Sulphide alterations are among the most important mineralogical aspects of the functioning of soils developed from sulphide-bearing parent materials. In the present study, the processes of iron sulphide weathering were investigated in a system including sulphide crystals and secondary minerals adjacent to oxidised sulphides. Light microscope observations and scanning electron microscope–energy dispersive spectrometry (SEM–EDS) analyses were used in order to examine evidences of iron sulphide decay at a microscopic and submicroscopic scales, as well as to determine the modes and effects of sulphide weathering on an example of a chronosequence of technogenic soils (Technosols) and naturally developed soils (Leptosols and Cambisols) in Poland. The study covered (1) several years old Technosols developed on the dump of the abandoned hard coal mine in Trzebinia town, (2) several dozen of years old Technosols developed on mine spoils of the abandoned pyrite mine in Rudki village, (3) 100–200 years old Technosols developed on dumps of the abandoned pyrite mine in Wieściszowice village, as well as (4) Leptosols and Cambisols developed on natural outcrops of pyrite-bearing schists in the vicinity of the mine in Wieściszowice. Chemical weathering was the most important process involved in the alteration of iron sulphides in the soils studied. The process is expressed by (1) the oxidation of sulphides resulting in a subsequent crystallisation of iron oxides and sulphates from Fe and sulphate ions released to the soil solution, as well as by (2) the development of pseudomorphs after sulphides due to the gradual in-situ transformation of sulphides into secondary minerals (iron oxides mainly). Porous (poorly crystalline) iron oxides predominated across the products of iron sulphide oxidation in "young" technogenic soils from Rudki, in contrast to "old" technogenic and natural soils from Wieściszowice, where massive (well crystallised) iron oxides prevailed. This suggests that the degree of crystallinity of iron oxides increases along with the age of soils. Microstratification was a typical feature of secondary iron oxides occurring in "old" soils from Wieściszowice. The EDS analyses performed along the lines perpendicular to stratified oxides showed that the alternating microlayers differed from each other in terms of contents of oxygen (O-poor layers were alternated with layers rich in this element). This suggests that temporal changes of oxygen concentration in soils may affect the process of iron sulphide transformation. The content of most trace elements (including heavy metals such as Cu, Zn, and Pb) in the examined iron sulphides, analysed by EDS, was low. Furthermore, amounts of these elements in secondary oxide rims were reported to be slightly elevated in comparison with the adjacent sulphides. This suggests that the rims did not constitute places of concentration of high amounts of trace elements in the soils investigated.

1. Introduction

Sulphides rarely occur in naturally developed soils, except for certain coastal areas, peat and periodically flooded soils, as well as soils on outcrops of sulphide-bearing rocks. Iron sulphides (e.g. pyrite, marcasite, and their precursors) are among the most common sulphide minerals present in soils and sediments (e.g. Bush et al., 2004; Doner and Lynn, 1989; Fanning et al., 2002; Pracz and Kwasowski, 2001). The deposition of sulphide-bearing mine wastes, frequently occurring in the vicinity of sulphide, hard coal, and lignite mines, results in the occurrence of iron sulphides on the land surface (e.g. Johnson, 2003). Technogenic soils (Technosols) develop on the superficial parts of such mine waste landfills (e.g. Kostenko and Opanasenko, 2005; Thomas and Jansen, 1985; Uzarowicz and Skiba, 2011).

Weathering of sulphides enormously affects soil properties. One of the most important features of soils containing sulphides is strong acidity caused by the oxidation of sulphides (e.g. Hecht and Kölling, 2002 and references therein), unless neutralising agents (e.g. carbonates) are present. The effect of acidity on soils is manifested by leaching of Ca, Mg, and K from soil profiles (e.g. Golez and Kyuma, 1997; Rosicky et al., 2004; Ross et al., 1985) and an increase in toxic element (e.g. Al) concentrations in the soil solution along with a decrease in pH (Johnston et al., 2010; Parker, 2005; Ross et al., 1988 and references therein).

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* Tel.: +48 22 59 326 10; fax: +48 22 59 326 02.
E-mail address: lukasz_uzarowicz@sggw.pl.

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Weathering of iron sulphides affects the mineral composition of soils. Secondary mineral phases, such as iron oxides and sulphates (mainly gypsum and jarosite), develop at the expense of oxidised sulphide (e.g. Dixon et al., 1982; Hita and Torrent, 2005; Mees and Stoops, 2010; Mermut et al., 1985; Poch et al., 2009; Trafford et al., 1973; Uzarowicz and Skiba, 2011). The decomposition of aluminosilicates and formation of swelling clay minerals at the expense of inherited layer silicates (e.g. chlorite and mica) occurs in strongly acidic soils developed from sulphide-bearing rocks and mine wastes (e.g. Barnhisel and Rotromel, 1974; Dixon et al., 1982; Krasil'nikov, 1997; Uzarowicz and Skiba, 2011; Uzarowicz et al., 2008, 2011).

Weathering of mine wastes, particularly those located in the vicinity of coal and sulphide mines exploiting polymetallic ores, may enrich soils and groundwaters in heavy metals and radioactive elements (e.g. Barnhisel and Massey, 1969; Dang et al., 2002; Johnson, 2003; Uzarowicz, 2011). The identification of the mineral paragenesis occurring in mine wastes with the application of a combination of analytical techniques (e.g. diverse microscopic methods), permits the determination of the course of their weathering, and the assessment of the potential risk related to the release of toxic elements into the environment (Jamieson, 2011 and references therein).

Previous studies concerning microscopic and submicroscopic evidences of iron sulphide weathering in the soil environment were mostly restricted to acid sulphate soils (e.g. Poch et al., 2009; Strawn et al., 2002) and certain inland weathering environments (e.g. Mermut et al., 1985; Miedema et al., 1974; Prakongkep et al., 2012). Inland sulphide-bearing technogenic soils and mine wastes have not yet been examined in detail in terms of the micromorphology and microchemistry of iron sulphide weathering (e.g. Dixon et al., 1982; Lu et al., 2005). The objective of the present study was to examine the modes and effects of iron sulphide decay in a system including sulphide crystals and adjacent secondary minerals based on the example of a chronosequence of technogenic soils (Technosols) and natural soils (Leptosols and Cambisols) developed from sulphide-bearing parent materials.

2. Materials and methods

2.1. Study area and study material

The study covered soil samples taken from technogenic soil (Technosol) profiles developed on mine wastes containing iron sulphides (Table 1). The study areas were located at three abandoned industrial sites in Poland: (1) the “Siersza” hard coal mine in Trzebinia town (the Silesian Upland), (2) the “Staszic” pyrite mine in Rudki village (the Holy Cross Mts.), and (3) the pyrite mines in Wieściszowice village (the Rudawy Janowickie Mts. within the Western Sudetes Mts.). Natural soils (Leptosols and Cambisols) developed on outcrops of metamorphic pyrite-bearing schists located in the vicinity of the former mines in Wieściszowice were also examined (Table 1). All the soils studied developed in well drained locations and were distinguished by udic moisture regime. The detailed location and descriptions of the soil profiles were presented elsewhere (Uzarowicz and Skiba, 2011; Uzarowicz et al., 2011).

Properties of the soils investigated and their mineral composition (Tables 1 and 2) were presented in detail elsewhere (Uzarowicz, 2011; Uzarowicz and Skiba, 2011; Uzarowicz et al., 2011). All the soils studied, except for profile R1 (Tables 1 and 2), were devoid of carbonates. Soil units were described and classified according to the World Reference Base for Soil Resources (IUSS Working Group WRB, 2006).

The technogenic soils investigated developed in the superficial parts of mine spoils. They varied in age and properties of their parent materials (Table 1). Mining exploitation in the “Siersza” hard coal mine ceased in 1999. Therefore, the soils developed on the surface

Table 1
The description of the soils investigated and their parent materials.

Soil profile	Location of soil profiles	Description of the parent materials	Bulk mineralogy of soils determined by XRD and SEM[a], as well as field observations and optical microscope studies
T1	Trzebinia town; the surface of the dump of the abandoned “Siersza” hard coal mine.	A mixture of sulphide- and coal-bearing upper Carboniferous rocks (tonsteins, mudstones, sandstones).	Major minerals inherited from parent material: quartz, feldspars, kaolinite, micas, iron sulphides (pyrite and marcasite), traces of carbonates. Major secondary minerals: gypsum, jarosite.
T2	ditto	ditto	ditto
R1	Rudki village; the surface of the former flotation tank located near the abandoned “Staszic” iron sulphide mine.	A bipartite profile. The subsoil (C2 horizon) comprises the post-flotation sludge originated due to grinding of dolomitic sulphide ore. The topsoil (A and C1 horizon) is built of brown and orange loamy material deposited on the sludge during reclamation works in the 1970s.	Major minerals inherited from parent material (the topsoil): quartz, micas, kaolinite, goethite, hematite, feldspars, iron sulphides (marcasite and pyrite), dolomite. Major minerals inherited from parent material (the subsoil): dolomite, iron sulphides (marcasite and pyrite), quartz, micas, calcite. Major secondary minerals (the whole profile): gypsum, porous Fe oxides.
R2	Rudki village; the surface of the so-called “Serwis” mine waste dump located near the abandoned “Staszic” iron sulphide mine.	Brown and rusty loamy material containing rocks fragments consisting of iron sulphides.	Major minerals inherited from parent material: quartz, feldspars, micas, kaolinite, iron sulphides (marcasite and pyrite). Major secondary minerals: gypsum, jarosite, porous Fe oxides.
W1	Wieściszowice village; the surface of the stony mine waste dump located near the abandoned pyrite mine.	Metamorphic pyrite-bearing schists crushed during the operation of the mine.	Major minerals inherited from parent material: quartz, chlorite, micas, feldspars, low amounts of pyrite. Major secondary minerals: massive Fe oxides, low amounts of gypsum and jarosite.
W2	Wieściszowice village; the surface of the fine earth mine waste dump located near the abandoned pyrite mine.	Metamorphic pyrite-bearing schists crushed and ground during the operation of the mine.	ditto
NS1	Wieściszowice village; natural outcrop of the pyrite-bearing mica schists located near the abandoned pyrite mine.	Metamorphic pyrite-bearing mica schists	Major minerals inherited from parent material: quartz, micas, traces of pyrite. Major secondary minerals: massive Fe oxides, jarosite.
NS2	Wieściszowice village; natural outcrop of the pyrite-bearing chlorite-mica schists located near the abandoned pyrite mine.	Metamorphic pyrite-bearing chlorite-mica schists	Major minerals inherited from parent material: quartz, chlorite, micas, feldspars, traces of pyrite. Major secondary minerals: massive Fe oxides.

[a] According to Uzarowicz and Skiba (2011).

Table 2
The selected properties and the WRB classification of the soils investigated.

Depth (cm)	Horizon	Percentage of fraction (in mm)			pH_{H2O}	Content of organic carbon (w/w %) [a]	Content of carbonates (w/w %) [b]
		2.0–0.05	0.05–0.002	<0.002			
profile T1, Spolic Technosol (Toxic, Humic, Skeletic)							
0–10	C1	80	15	5	2.5	–	n
10–35	C2	44	37	19	2.5	10.4	n
Profile T2, Spolic Technosol (Toxic, Humic)							
0–40	C1	–	–	–	2.4	–	n
40–76	C2	50	35	15	3.4	7.4	n
76–98	C3	44	36	20	3.1	14.8	n
98–105	C4	76	14	10	2.4	1.6	n
Profile R1, Spolic Technosol (Calcaric, Toxic)							
0–1	Oi	–	–	–	–	–	–
1–3	A	45	33	22	7.3	5.2	3.0
3–30	C1	40	20	40	7.2	0.9	2.4
30–95	C2	59	37	4	7.4	–	60.3
Profile R2, Spolic Technosol (Toxic)							
0–2	Oi	–	–	–	–	–	n
2–7	A	69	17	14	4.4	2.5	n
7–14	C1	47	29	24	4.3	0.6	n
14–30	C2	51	29	20	3.0	0.3	n
30–60	C3	52	26	22	2.7	0.3	n
60–75	C4	54	28	18	3.3	–	n
Profile W1, Spolic Technosol (Skeletic)							
0–1	Oi	–	–	–	4.8	–	n
1–4	Oe	–	–	–	4.0	–	n
4–9	A1	57	74	15	3.9	9.9	n
9–10	A2	51	71	19	4.0	4.9	n
10–45	C	70	75	17	3.9	0.7	n
Profile W2, Spolic Technosol							
0–1	Oi	–	–	–	–	–	n
1–4	A	75	18	7	4.2	2.6	n
4–15	AC	65	28	7	4.2	1.0	n
15–30	C1	11	68	21	4.3	0.5	n
30–35	C2	86	9	5	4.4	0.9	n
35–86	C3	11	70	19	4.3	0.5	n
86–112	C4	87	8	5	4.3	0.9	n
Profile NS1, Hyperskeletic Leptosol (Hyperdystric)							
0–1	Oi	–	–	–	–	–	–
1–10	A	64	23	13	3.4	0.9	n
10–12	BwC	51	31	18	3.2	0.6	n
12–60	C	–	–	–	2.8	0.3	n
Profile NS2, Haplic Cambisol (Dystric, Skeletic)							
0–1	Oi	–	–	–	4.0 [c]	–	–
1–6	Oe	–	–	–	3.7 [c]	–	–
6–15	A	35	53	12	3.7	9.9	n
15–55	Bw	39	52	9	4.3	2.1	n
55–75	C	56	37	7	4.2	2.4	n

– Not determined.
n — Lack of carbonates.
[a] Content of organic carbon determined using oxidometric Tyurin method.
[b] Content of carbonates determined using volumetric Scheibler method.
[c] pH measured in proportion: weight of soil sample/volume of solution as 1:10.

of the dump were several years old. They were not reclaimed before the completion of the investigation. Land in the area of the "Staszic" pyrite mine was reclaimed after the cessation of mining in the 1970s (Table 1). The soils developed there were approximately 40 years old. Mining exploitation and waste deposition in the Wieściszowice region continued between 1785 and 1925. Therefore, the soils on the dumps may be 100–200 years old. The dumps have not been reclaimed, and the soils most likely developed there due to spontaneous plant succession. The natural soils from Wieściszowice were probably much older than the soils developed on the dumps, as the occurrence of well recognised genetic horizons (A and Bw) was a typical feature of the natural soils (Table 2). This suggests the presence of advanced soil-forming processes in these soils, and indirectly — a prolonged period of development of these profiles. However, it was difficult to assess the exact age of the natural soils studied.

The profiles investigated can be arranged into the sequence of soils from the weakest developed (the youngest) to the best developed (the oldest) in the following order: technogenic soils from Trzebinia (profile T1 and T2) → technogenic soils from Rudki (profile R1 and R2) → technogenic soils from Wieściszowice (profile W1 and W2) → weakly developed natural soils from Wieściszowice represented by profile NS1 → well developed natural soils from Wieściszowice represented by profile NS2.

2.2. Analytical methods

The soil samples were dry-sieved in order to separate the fractions of <1 mm and 2–1 mm. Considering the main objective of the research, i.e. the examination of iron sulphide weathering pathways in a system including sulphides and adjacent secondary phases, the samples of 2–1 mm fraction (i.e. fine earth in which iron sulphides were expected to be more abundant than in finer grain fractions) were saturated with Araldite 2020 epoxy resin. Polished thin sections were subsequently prepared from the impregnated soil material. The thin sections were studied in both transmitted and reflected light using a petrographic microscope in order to find iron sulphide crystals and preliminarily examine the degree of their transformations. The polished thin sections were prepared in the Department of Soil Science and Soil Geography, Institute of Geography and Spatial Management, Jagiellonian University, Kraków, Poland.

The selected air-dried loose soil samples (<1 mm fraction) and thin sections from 2–1 mm fractions were carbon-coated and studied using a field emission scanning electron microscope (SEM) (Hitachi S-4700), equipped with an EDS (Vantage Noran) microanalysis system and a back-scattered electrons detector (YAG BSE). The EDS elemental mapping, as well as line and point analyses (Tables 3 and 4), were performed on the selected oxidised sulphide grains in thin sections. The SEM–EDS studies were performed in the Institute of Geological Sciences, Jagiellonian University, Kraków, Poland.

3. Results

3.1. The modes and effects of iron sulphide weathering in technogenic soils

Iron sulphides from very weakly developed ("young") technogenic soils from Trzebinia (profiles T1 and T2) were represented by pyrite and marcasite (Uzarowicz, 2011; Uzarowicz and Skiba, 2011). The former mineral was recognised macroscopically based on its cubic habit and brass-yellow colour. The typical feature of the latter was the tabular habit and bronze-yellow colour. Iron sulphides were poorly weathered in the soils from Trzebinia. Several centimetre large rock fragments consisting of iron sulphides found in these soils exhibited no macroscale weathering alterations (Uzarowicz, 2011). Observations in SEM, however, revealed the dissolution pits or cracks on the surface of iron sulphides (Fig. 1). The pits were arranged along regular lines. The release of Fe and sulphate ions due to sulphide oxidation resulted in the crystallisation of iron oxides and sulphates, e.g. subhedral prismatic crystals of gypsum and euhedral cubic-shaped jarosite (Uzarowicz and Skiba, 2011).

Iron sulphides (marcasite and pyrite recognised during the field work and by XRD analyses (Uzarowicz and Skiba, 2011)) in Technosols from Rudki (profiles R1 and R2) were poorly to partly weathered (Figs. 2, 3, and 4). Majority of sulphide crystals occurring in these soils comprised incomplete pseudomorphs of iron oxides after iron sulphides. Sulphide crystals enclosed within the polymineral grains of the 2–1 fraction oxidised starting from the external parts of the crystal towards its interior (Fig. 3). These pseudomorphs after iron sulphides, which were partly

Table 3
Chemical composition of the selected Fe sulphides from the soils studied based on point EDS analyses (in weight percent).

Element	The Fe sulphide from:		
	Profile R1	Profile R2	Profile W2
S	53.94	52.72	52.09
Ti	<	<	<
V	0.01	<	0.05
Cr	<	<	0.04
Mn	<	0.01	0.09
Fe	45.49	46.95	46.90
Co	<	<	0.08
Ni	<	<	<
Cu	<	<	0.15
Zn	0.09	0.14	0.12
As	<	<	0.48
Cd	0.19	<	<
Sb	0.28	0.18	<
Pb	<	<	<

< Below detection limit.

exposed to the soil environment, had a thicker layer of iron oxides on the sides exposed to the environment (Fig. 3). The layer of secondary oxides was reported to be thinner on the side of pseudomorph adjoining to the host rock.

The most typical feature of soils from Rudki was the abundance of iron oxides in a form of porous, irregular microaggregates occurring adjacent to oxidised sulphides (Fig. 4). These mineral phases most likely consisted of poorly crystalline iron oxides (e.g. ferrihydrite) which might have developed due to the crystallisation from the soil solution. Porous iron oxides contained certain amounts of sulphur (Table 4). This suggests the occurrence of sulphates co-existing with oxides. Sulphur may also be adsorbed onto secondary iron oxides (Lu et al., 2005). Moreover, sodium and potassium were more abundant constituents in iron oxides from the strongly acidic profile R2 (Table 4). Porous iron oxides from profile R2 were also enriched in Al and Si, as confirmed by EDS point analyses (Table 4) and detailed SEM–EDS investigations in high magnifications (Uzarowicz and Skiba, 2011). On the other hand, secondary oxides in the neutral profile R1 contained more Mg and Ca than the oxides from the acidic profile R2 (Table 4).

Sulphate ions released to soils resulted in the crystallisation of sulphate minerals in the soils from Rudki. Euhedral (or subhedral) prismatic crystals of gypsum were observed in the neutral R1 profile. Subhedral platy crystals of gypsum were found in the strongly acidic profile R2 (not shown). Jarosite in a form of euhedral cubic crystals (Fig. 4) was exclusively detected in the acidic profile R2.

The most common iron sulphide in the Wieściszowice region was pyrite recognised by its habit (i.e. cubic-shaped crystals) and brass-yellow colour. The degree of the advancement of pyrite weathering was high in Technosols from Wieściszowice (profiles W1 and W2). Majority of sulphide crystals observed in these soils were almost totally transformed into secondary minerals, including jarosite forming assemblages of pseudocubic or irregular crystals (Fig. 4), as well as massive Fe oxides (Figs. 2, 4, 5, and 6) with an admixture of sulphates (and/or adsorbed sulphur), as indicated by the presence of S in EDS spectra (Table 4, Fig. 5). Moreover, Fe oxides contained some amounts of Al and Si (Table 4). Secondary oxides occurred as rims within the range of pseudomorphs after sulphide crystals (Figs. 4 and 5). The most typical feature of these rims found in soils from Wieściszowice was microstratification (Figs. 4 and 5). Some of the stratified oxide rims consisted of distinct microlayers. This feature was well visible in the back-scattered electron (BSE) images in SEM (Figs. 4F and 5), where alternating light-grey (O-rich)

Table 4
Chemical composition of the selected secondary Fe oxides from the soils studied based on point EDS analyses (in weight percent).

Element	The Fe oxide from:							
	Profile R1	Profile R1[a]	Profile R2	Profile R2[b]	Profile W2 (oxygen-rich microlayer)[c]	Profile W2 (oxygen-poor microlayer)[c]	Profile NS2 (the internal part of the pseudomorph)[d]	Profile NS2 (the external part of the pseudomorph)[d]
O	27.00	29.89	21.63	27.74	26.42	19.84	25.57	28.95
Na	<	<	0.10	0.67	0.32	0.19	<	<
Mg	0.46	1.00	<	0.01	0.09	0.03	<	<
Al	0.19	0.49	1.47	0.82	0.29	0.72	0.11	2.57
Si	0.03	0.11	0.52	0.46	0.62	0.47	0.61	1.56
P	<	<	<	<	<	<	<	0.25
S	3.94	1.09	1.40	<	1.48	1.84	0.28	0.93
K	<	0.04	0.07	0.32	0.06	<	<	0.02
Ca	0.79	0.62	0.04	0.23	0.13	0.40	0.11	<
Ti	0.01	<	<	0.04	0.08	0.03	<	0.02
V	<	<	0.12	<	0.03	0.04	0.07	<
Cr	0.15	<	0.17	<	0.02	0.02	0.01	<
Mn	1.26	1.33	0.22	0.42	0.16	0.03	<	<
Fe	61.79	62.16	72.78	67.80	69.25	72.16	72.63	64.20
Co	0.19	0.43	<	0.07	0.21	<	<	<
Ni	0.09	<	<	<	<	<	0.25	0.16
Cu	0.23	0.13	0.18	0.09	<	<	<	0.90
Zn	0.27	0.30	0.20	<	0.07	0.27	<	<
As	1.10	<	<	0.42	0.08	<	<	<
Cd	<	<	0.20	<	0.09	0.32	<	0.13
Sn	0.55	0.44	0.30	0.31	0.16	0.36	<	<
Sb	1.09	0.88	0.23	0.56	0.22	0.40	<	0.15
Tl	0.53	0.29	<	0.04	<	1.10	<	<
Pb	<	0.39	<	<	0.22	1.78	0.36	0.15
Th	0.16	0.41	<	<	–	–	–	–
U	0.17	<	0.37	<	<	<	<	<

< Below detection limit.
– Not determined.
[a] The point of EDS analysis is shown in Fig. 4B.
[b] The point of EDS analysis is shown in Fig. 4C.
[c] The point of EDS analysis is shown in Fig. 5.
[d] The point of EDS analysis is shown in Fig. 8B.

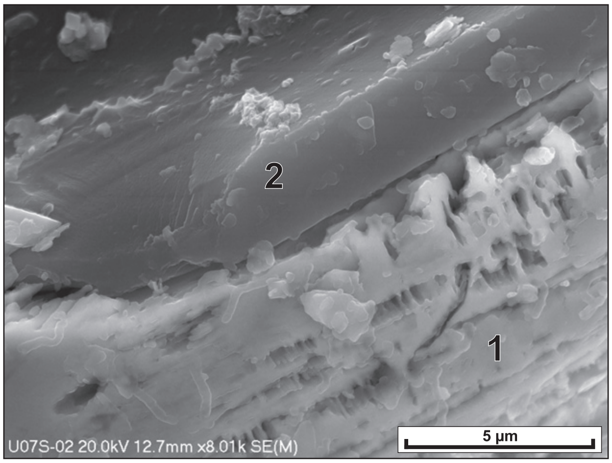

Fig. 1. The secondary electron (SE) image showing dissolution patterns at the surface of iron sulphide (1) occurring in hard coal (2); profile T2, C2 horizon.

and dark-grey (O-poor) layers were recognised. Their occurrence in the soils from Wieściszowice was reported earlier by Uzarowicz and Skiba (2011).

Part of sulphide crystals from Technosols from Wieściszowice were cracked (Fig. 6), most likely due to the technological processes of pyrite exploitation, i.e. crushing and grinding of pyrite-bearing rocks. Crushing the sulphide crystals permitted faster oxidation of sulphides along the cracks. The observations in SEM showed that the opened cracks were partly filled with allochthonous mineral grains (e.g. aluminosilicates), subsequently surrounded by layers of massive and microstratified iron oxides (Fig. 6). Furthermore, the oxides crystallising at the surfaces of sulphides exposed to the soil environment agglutinated adjacent mineral grains. This resulted in the development of characteristic coatings (Fig. 6). Beneath these coatings, the weathering of sulphides proceeded in the manner typical of soils from Wieściszowice, i.e. the formation of stratified rims occurred.

Crystals of sulphate minerals were rarely found in Technosols from Wieściszowice. These minerals were represented by subhedral, prismatic crystal of gypsum (Uzarowicz and Skiba, 2011; Uzarowicz et al., 2008), as well as subhedral and anhedral pseudocubic crystals of jarosite (Fig. 4E).

3.2. The modes and effects of iron sulphide weathering in naturally developed soils

Partly weathered iron sulphides (pyrites) were found in weakly developed Leptosol (profile NS1, Fig. 7). Pellicular alterations (Stoops, 2003) of sulphide crystals were the most commonly observed alteration patterns in that soil (Fig. 7). The external parts of the crystals found were transformed into massive oxides, whereas the internal parts comprised unoxidised sulphide. Such a mode of weathering was typical of iron sulphides enclosed within rock fragments and was also documented in other soils investigated (Figs. 2 and 3). On the other hand, crystals of iron sulphides were very rarely found in relatively well developed (old) Cambisol (profile NS2). Majority of crystals in that soil were complete pseudomorphs of iron oxides after pyrite. Fig. 8B presents such a pseudomorph having two characteristic forms of secondary iron oxides: the first was microstratified oxides occurring in the external part of the pseudomorph and the second was massive and uniform iron oxides present within it. The internal part of the pseudomorph observed in BSE images looked like iron sulphide (Fig. 8B). However, the EDS chemical analysis revealed that the phase mainly consisted of Fe and O (Table 4). The external part of the pseudomorph from profile NS2 (Fig. 8B) was richer in Al and Si than its internal part (Table 4). Sodium and potassium were absent in the entire pseudomorph, however phosphorus was detected exclusively in its external part.

Secondary oxides originating as an effect of pyrite weathering in natural soils from Wieściszowice frequently formed coatings (or infillings) occurring in voids (Figs. 8A and 9). The voids were very often distinguished by straight boundaries and isometric shape, suggesting that they might constitute former iron sulphide crystals. The coatings found in the voids were built of alternating microlayers (Fig. 9) similar to those found in Technosols from Wieściszowice (Figs. 4F and 5). The coatings contained Fe and O as major elements. Lower amounts of S, K, Al, and Si were detected in the coatings (Fig. 9).

Separate crystals of sulphates were not found in either of the natural soils studied, based on the microscopic method used. However, traces of jarosite were detected by XRD in profile NS1 (Uzarowicz et al., 2012), where this mineral had favourable conditions to crystallise (e.g. very low pH, sufficient amounts of sulphates from oxidising pyrite, and availability of K^+ and Na^+ ions released from dissolved micas and feldspars).

3.3. Trace elements in Fe sulphides and secondary Fe oxides

Iron sulphides analysed did not contain high amounts of trace elements. It is confirmed by both studies of EDS elemental maps (Figs. 3, 5, and 7) and EDS point analyses (Table 3). Depending on the specimen studied, the concentrations of five metals (i.e. Cu, Zn, As, Cd, and Sb) only exceeded the value of 0.1% (Table 3). On the other hand, secondary iron oxides adjacent to sulphides did not constitute places of high concentration of trace elements in the soils investigated (Table 4). Contents of majority of trace elements in all of the Fe oxides studied generally did not exceed 0.5%.

One of the trace elements which seemed to clearly concentrate in pseudomorphs after Fe sulphides occurring in technogenic soils from Rudki was Mn (Fig. 3). Secondary oxide rims from the neutral profile R1 are richer in Mn than the rims from the acidic profile R2 (Table 4). The rims from profile R1 occurring in pseudomorphs exposed to the environment were particularly rich in Mn in comparison with the rims enclosed within the mineral grains (Fig. 3). Significant amounts of Mn were also present in aggregations of Fe oxides found in the soils from Rudki (Fig. 4A). Variable contents of other trace elements studied (usually below 0.5%) were typical of the secondary Fe oxide rims from Rudki (Table 4). The highest concentrations (up to approx. 1.1%) were reported for As and Sb. Elevated amounts of Sn and Tl (0.55 and 0.53, respectively) were also present in these oxides. More trace elements were generally found to be concentrated in Fe oxides from the neutral profile R1 in comparison with oxides from the acidic profile R2 (Table 4).

The EDS mapping and line analyses showed that there were no clear differences in amounts of trace elements analysed (e.g. Ti, Mn, Cu, Zn, and others not shown in Fig. 5) between light-grey (oxygen-rich) and dark-grey (oxygen-poor) rims found in stratified Fe oxides from Wieściszowice (Fig. 5). However, EDS point analyses showed that oxygen-poor microlayers were slightly richer in Zn, Cd, Sn, Sb, Tl, and Pb in comparison with oxygen-rich microlayers (Table 4, Fig. 5). On the other hand, oxygen-rich microlayers contained more Ti than oxygen-poor layers (Table 4).

Elevated amounts of Ti were found to be concentrated in secondary iron oxide rims surrounding iron sulphides in natural soils from Wieściszowice (Fig. 7). The thin (several μm thick) layer located in the external part of the iron oxide rim found around the iron sulphide crystal was particularly rich in Ti. Such a feature may be an effect of iron sulphide weathering and subsequent concentration of Ti in the microenvironment enclosed between the iron sulphide and the host rock. The Ti-rich layer shown in Fig. 7 can also be a primary feature (e.g. related to the metamorphic processes involved in the genesis of pyrite-bearing schist from Wieściszowice). Moreover, the iron oxide coatings from natural soils

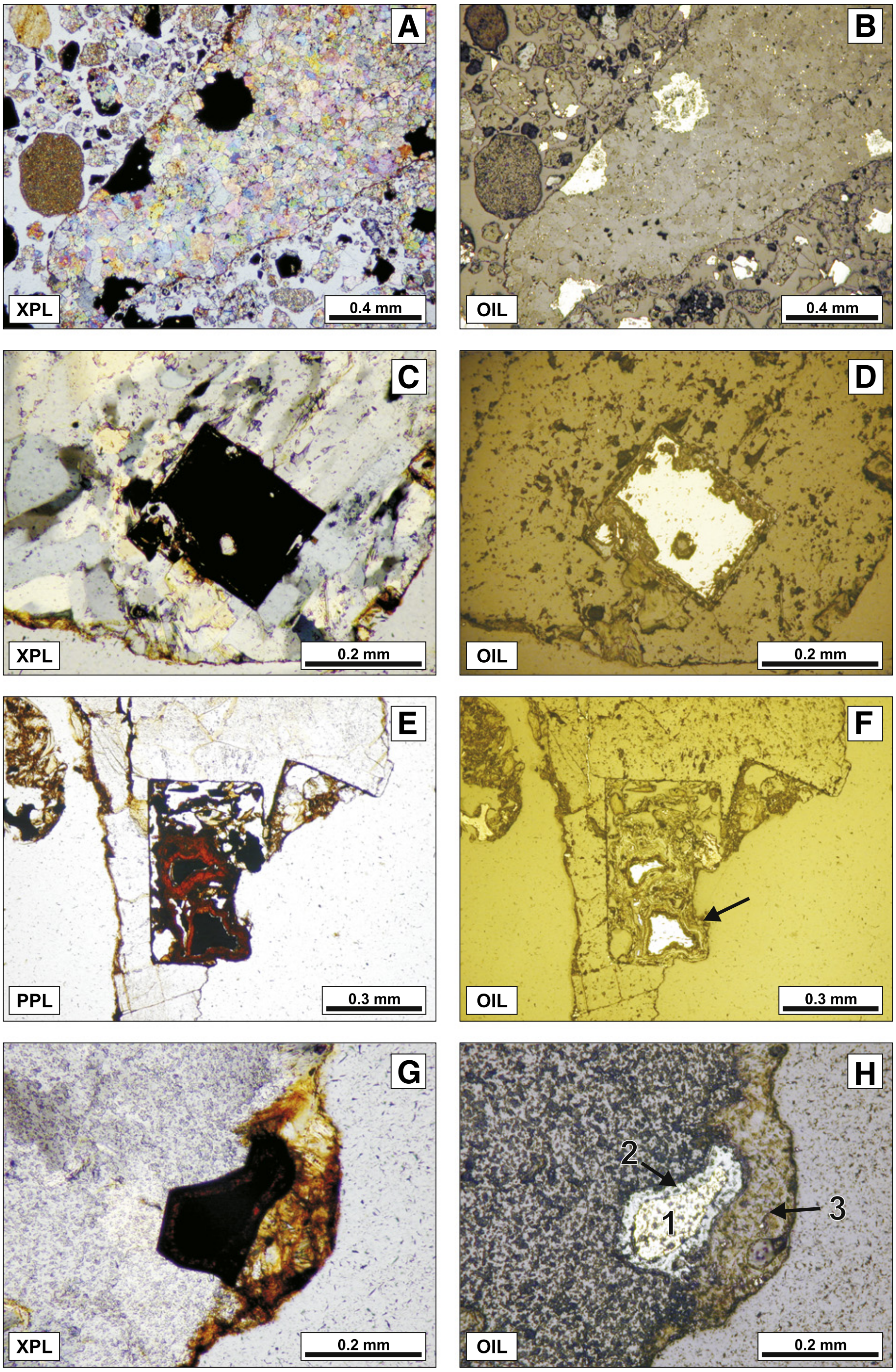

Fig. 2. Typical features of iron sulphide weathering based on petrographic microscope observations. A and B — poorly weathered crystals of iron sulphides occurring both as separate grains and enclosed within dolomite fragments, profile R1, C2 horizon. C and D — partly weathered iron sulphide enclosed within quartz grain, profile W2, C4 horizon. E and F — almost entirely weathered and crushed crystals of iron sulphides partly filled with grains of allochthonous minerals, profile W1, A2 horizon; a fragment of the crystal indicated by the arrow is shown in Figs. 4F and 5; the whole crystal was also shown in Fig. 3 in Uzarowicz and Skiba (2011). G and H — partly weathered iron sulphide (1) surrounded by iron oxides (2) and a coating containing e.g. secondary Fe mineral phases (3), profile NS2, Bw horizon. Symbols in the images: OIL — oblique incident light, PPL — transmitted light, plane polarised light, XPL — transmitted light, crossed polarisers.

from Wieściszowice also contained slightly elevated amounts of Ti in comparison with the adjacent minerals (Fig. 9).

Similarly to the technogenic soils occurring in the area of Wieściszowice, the secondary Fe oxides from natural soils did not contain high amounts of heavy metals (Table 4). The external parts of the pseudomorph from profile NS2 (Fig. 8) contained a little bit more Cu, Cd, and Sb than its internal part.

4. Discussion

Soil parent materials containing iron sulphides were deposited on the land surface in the areas studied (Trzebinia, Rudki, and Wieściszowice) due to human industrial activity. The weathering processes presumably commenced immediately after the deposition of sulphide-bearing mine wastes on landfills. Different time of deposition in all of the areas studied,

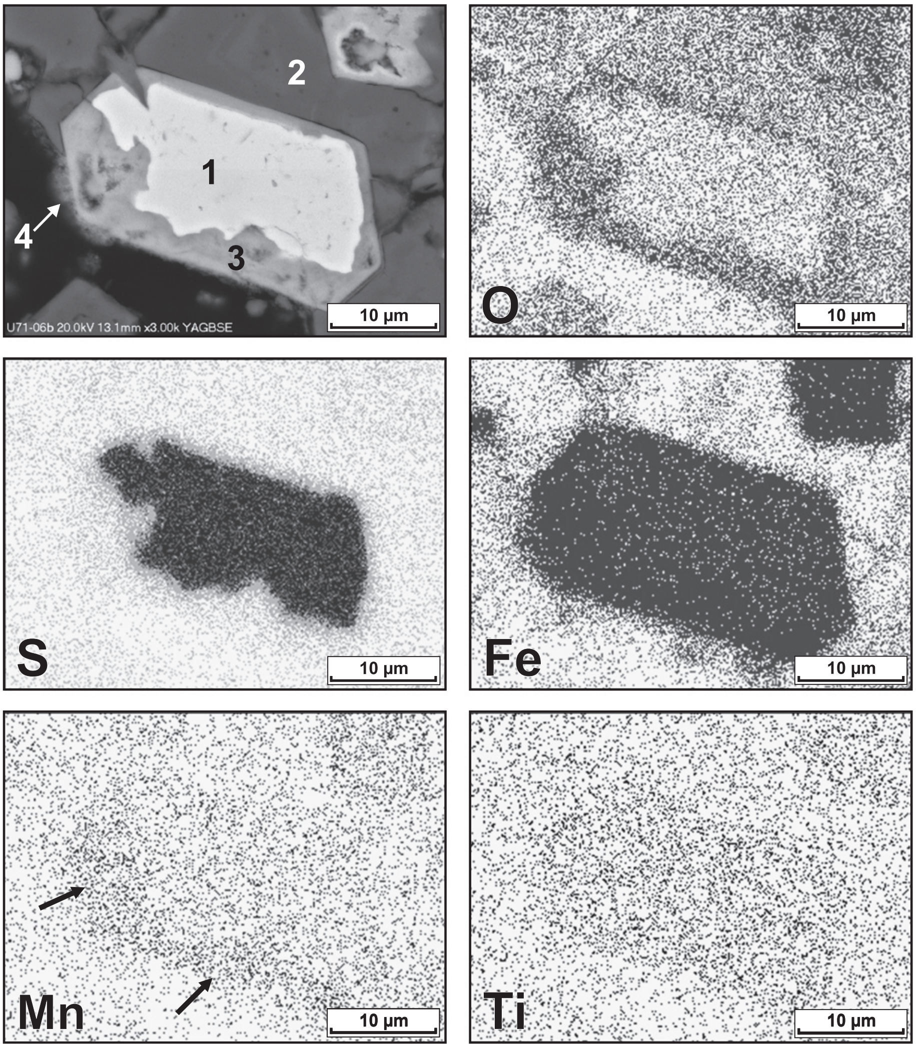

Fig. 3. Partly weathered iron sulphide (1) occurring in mineral grain built of dolomite (2) and surrounded by massive (3) and porous (4) iron oxides; profile R1, C2 horizon, back-scattered electron (BSE) image and elemental maps for the selected elements. The black arrows indicate Mn-enriched iron oxides.

permitted a study on the weathering of iron sulphides in a chronosequence of technogenic soils (Technosols) developed on the surface of the landfills investigated. This chronosequence was further supplemented with natural soils (Leptosols and Cambisols) containing iron sulphides developed from pyrite-bearing metamorphic schists in Wieściszowice. This approach permitted the determination of the progress of iron sulphide weathering and its effects in the soils studied (Table 5). The results obtained may be useful in predicting the alterations of iron sulphides and the fate of elements in sulphide-bearing materials exposed to the weathering environment.

Sulphides in the youngest technogenic soils from Trzebinia exhibited little weathering changes. Regular micro-etchings found in these soils on weathered iron sulphide surfaces (Fig. 1) most likely reflect the crystallographic structural planes. This suggests that the process of dissolution of iron sulphide surfaces exposed to the weathering environment starts from mineral domains marked by structural weakness, constituting a common feature of many weathered minerals (e.g. Stoops et al., 1979). Similar etchings on pyrite in soils were documented by Mermut et al. (1985). Moreover, a typical arrangement of etchings suggests that the dissolution of sulphides in soils form Trzebinia is most likely accelerated by microorganisms. It was found (e.g. Edwards et al., 1999) that effects of pyrite oxidation (i.e. dissolution pits and etchings) caused by acidophilus bacteria often occur in crystallographically preferred orientations.

The oxidation of sulphides caused high acidity in Technosols from Trzebinia (Table 2) in spite of the relatively young age of the soils. According to column (lysimetric) studies of sulphide-bearing mine wastes from the Polish hard coal mines (Strzyszcz, 1978), the acid production begins within the first two years after the deposition of wastes on the land surface. Therefore, it can be presumed that within that range of time, first morphological alterations on the surfaces of iron sulphides appear due to dissolution, followed by the crystallisation of the first portion of sulphates and iron oxides from the soil solution (Fig. 1, Table 5).

Diverse reaction of technogenic soils from Rudki permitted the comparison of weathering pathways of iron sulphides depending on the pH of soils. The modes of sulphide weathering itself were very similar both in near neutral and extremely acidic soils from Rudki. It is corroborated by the presence of pseudomorphs after iron sulphides covered by secondary oxide layers, which looked similar both in neutral and acidic soils when observed in a petrographic microscope and SEM (Fig. 4, Uzarowicz and Skiba, 2011). The process of pseudomorph development in these soils is most likely driven by the diffusion of oxygen from the weathering environment towards the internal parts of sulphide crystals.

Acidic and neutral soils from Rudki, however, differ in terms of chemical composition of products formed as an effect of iron sulphide oxidation. Secondary oxide rims in pseudomorphs occurring in the acidic profile R2 generally contained relatively more sodium and potassium

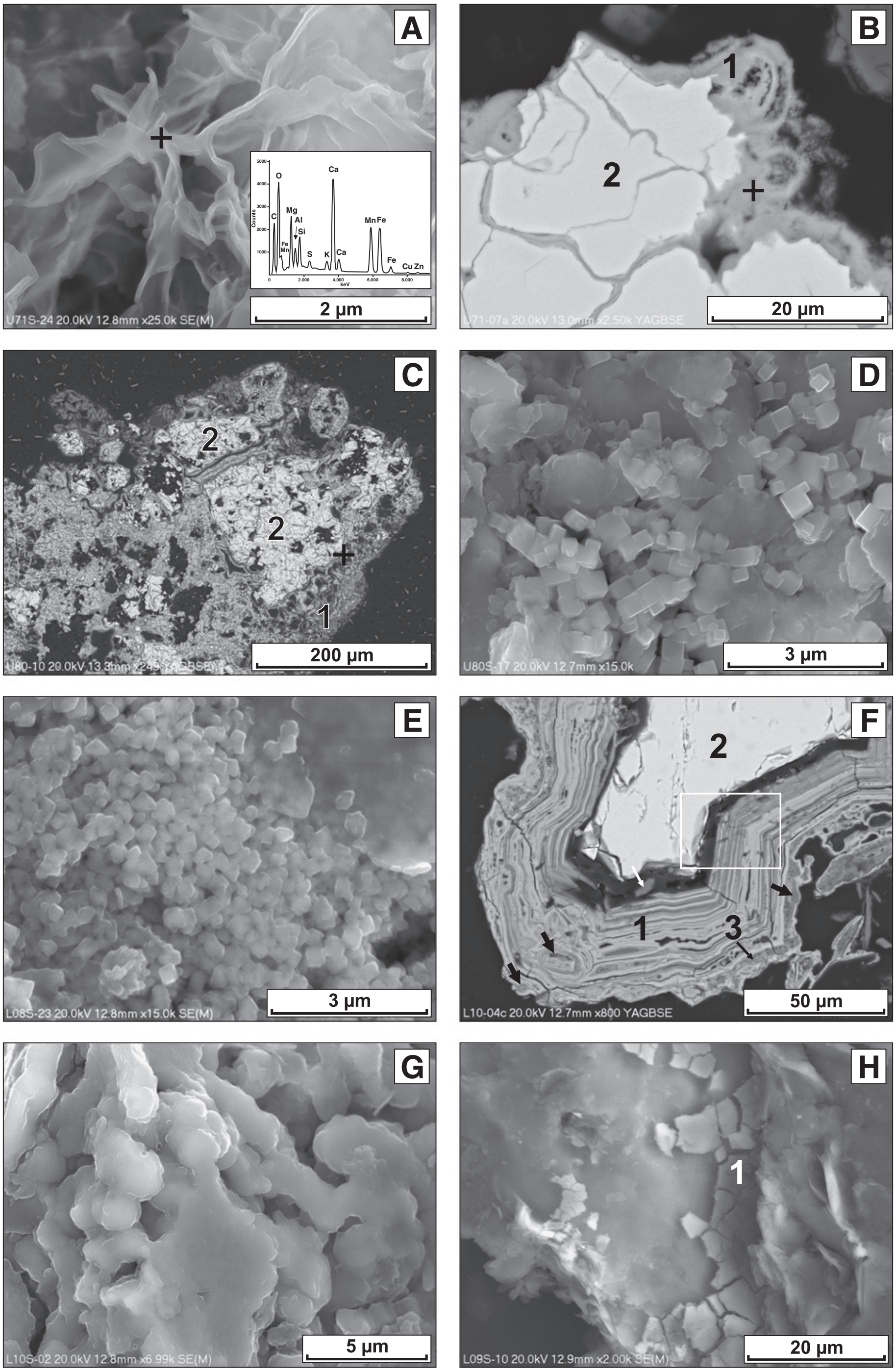

Fig. 4. SEM images showing typical features of iron oxides and sulphates originated in the technogenic soils studied. A — an irregular aggregate of iron and manganese oxides and its EDS analysis, the neutral profile R1, C2 horizon, SE image; the cross indicates the point of EDS analysis; Al, Si, K, Ca, and Mg in the EDS analysis arise from aluminosilicates and dolomite situated beneath the oxides analysed. B — porous iron oxides (1) covering the surface of iron sulphide (2), the neutral profile R1, C2 horizon, BSE image; the cross indicates the EDS analysis shown in Table 4. C — porous iron oxides (1) surrounding iron sulphides (2) from strongly acidic profile R2, C4 horizon, BSE image; the cross indicates the EDS analysis shown in Table 4. D — typical assemblages of euhedral cubic crystals of jarosite group minerals from strongly acidic profile R2, C4 horizon, SE image. E — typical assemblages of subhedral (and anhedral) pseudocubic crystals of jarosite group minerals from acidic profile W2, C3 horizon, SE image. F — a stratified rim (1) consisting of massive iron oxides, developed at the surface of iron sulphide (2), and containing certain amounts of Si and Al (3), profile W1, A2 horizon, BSE image; the fragment in the frame is shown in Fig. 5; the black arrows indicate allochthonous mineral grains (mainly quartz and aluminosilicates) trapped in the iron oxide rim. G — globular iron oxides, profile W1, A2 horizon, SE image. H — a crushed crust (1) consisting of massive iron oxides, profile W1, A1 horizon, SE image.

than those in the neutral profile R1 (Table 4). This suggests that jarosite group minerals may coexist with iron oxides in secondary oxide rims developed in acidic soils. Moreover, jarosite group minerals were commonly found to form separate assemblages of euhedral cubic crystals in profile R2 (Fig. 4D, Uzarowicz and Skiba, 2011). It is known as a common feature in acidic soil environments where iron sulphides weather (Mees and Stoops, 2010; Miedema et al., 1974 and references therein).

The concentration of Mg and Ca in secondary oxides from the neutral profile R1 (Table 4) may be explained by the release of these elements due to the weathering of carbonates (dolomite and calcite) and subsequent adsorption of these elements onto iron oxides. Carbonates (in particular dolomite) are one of the most abundant minerals in profile R1 (Table 1, Uzarowicz and Skiba, 2011). Moreover, calcium was found to be bound in subhedral (rarely euhedral), prismatic

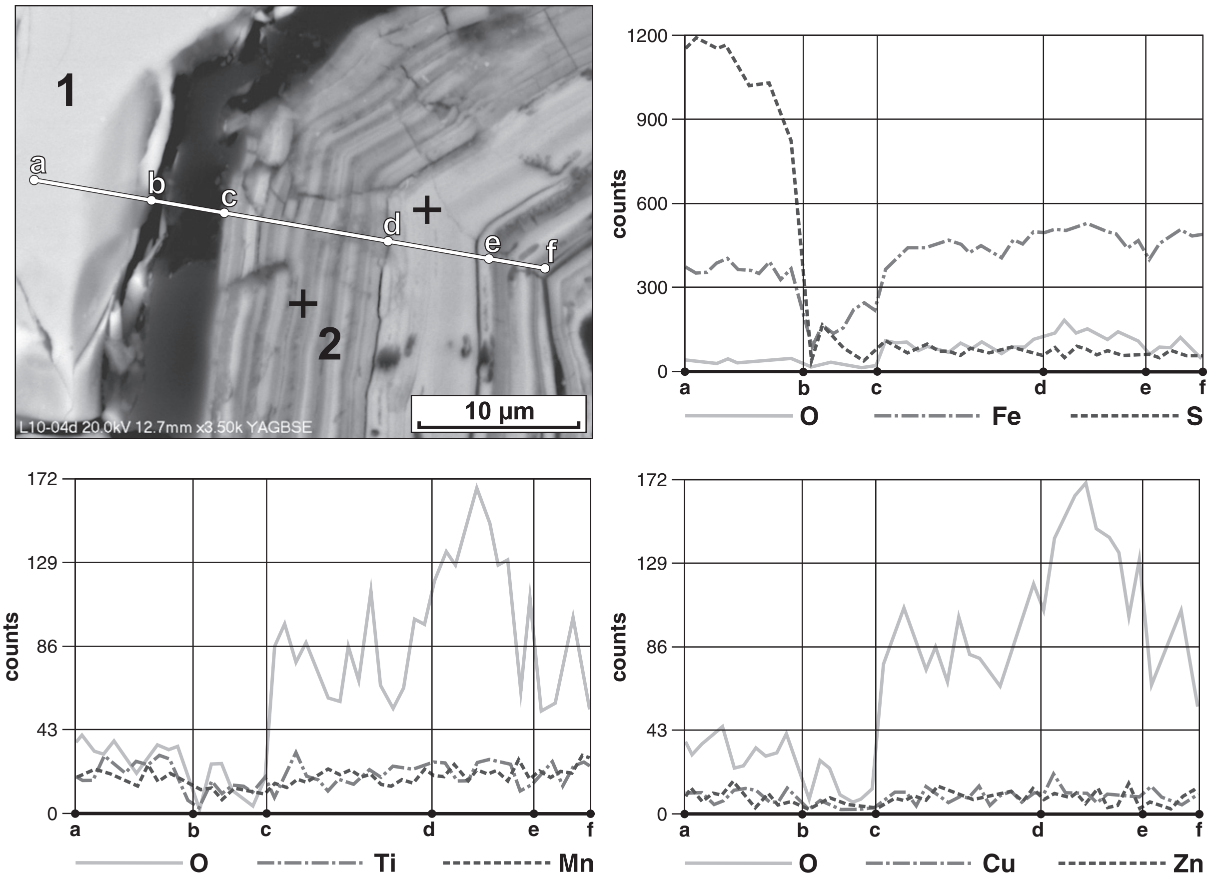

Fig. 5. Contents of the selected elements along the line (from points "a" to "f") crossing iron sulphide (1) and stratified weathering rim built of iron oxides (2); profile W1, A2 horizon, BSE image and elemental profiles for the selected elements with reference to oxygen content. The crosses indicate the EDS analyses shown in Table 4.

crystals of gypsum (not shown). Magnesium, in turn, might also be present in the soils studied as Mg sulphates (e.g. epsomite), although these minerals were not detected in the soils studied, based on the research methods used.

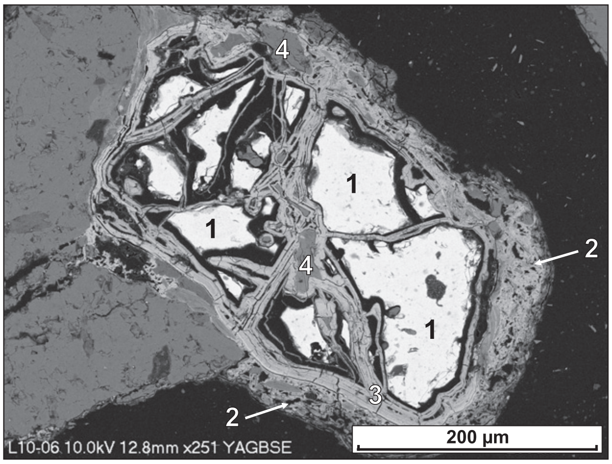

Fig. 6. A crushed iron sulphide crystal; profile W1, A2 horizon, BSE image. Weathered iron sulphide (1) is surrounded by an external layer containing aluminosilicates agglutinated by iron oxides (2), and an internal layer of stratified iron oxides (3). The cracks are partly filled with allochthonous quartz and aluminosilicates (4).

The most intriguing finding in Technosols from Wieściszowice, where massive iron oxides predominated across the products of iron sulphide oxidation, is microstratified oxide rims around sulphides (Figs. 4F and 5). The chemical composition of these rims (Table 4, Fig. 5) suggests that the dark-grey layers (poor in oxygen) observed in BSE images originated in the conditions of oxygen deficiency in the weathering environment. On the other hand, the light-grey (oxygen-rich) layers developed when more oxygen was available in the soil. It was found earlier by Uzarowicz and Skiba (2011) that the oxido-reduction processes play an important role in the functioning of Technosols from Wieściszowice. This thesis can be corroborated by the fact that the occurrence of greyish (soil colour of 2.5Y 7/2 for moist sample) and brown (soil colour e.g. of 2.5Y 6/6 for moist sample) irregular zones and spots constituted a feature typical of the morphology of soil profiles developed on mine dumps in Wieściszowice (Uzarowicz and Skiba, 2011). It is very likely that the temporarily appearing and alternating periods of availability and deficiency of oxygen in the soil profile may affect the processes of weathering of iron sulphides and formation of iron oxides in the soils investigated.

The best developed microstratified oxide rims around sulphides (Figs. 4F and 5) were found in humic (A) horizons of profile W1 from Wieściszowice. The A horizons are supposed to be these parts of a soil profile where microbial activity is the highest in comparison with the horizons located below in the profile (e.g. Agnelli et al., 2004). This leads to another possible explanation of the development of microstratified oxide rims. The rims might be a product of periodically alternating microbial activity in soils resulting in variable amounts of oxygen in the A horizons. Rigby et al. (2006) proved that bacterial activity and/or organic matter play an important role in pyrite oxidation by consumption of available oxygen and retardation of sulphide oxidation rate.

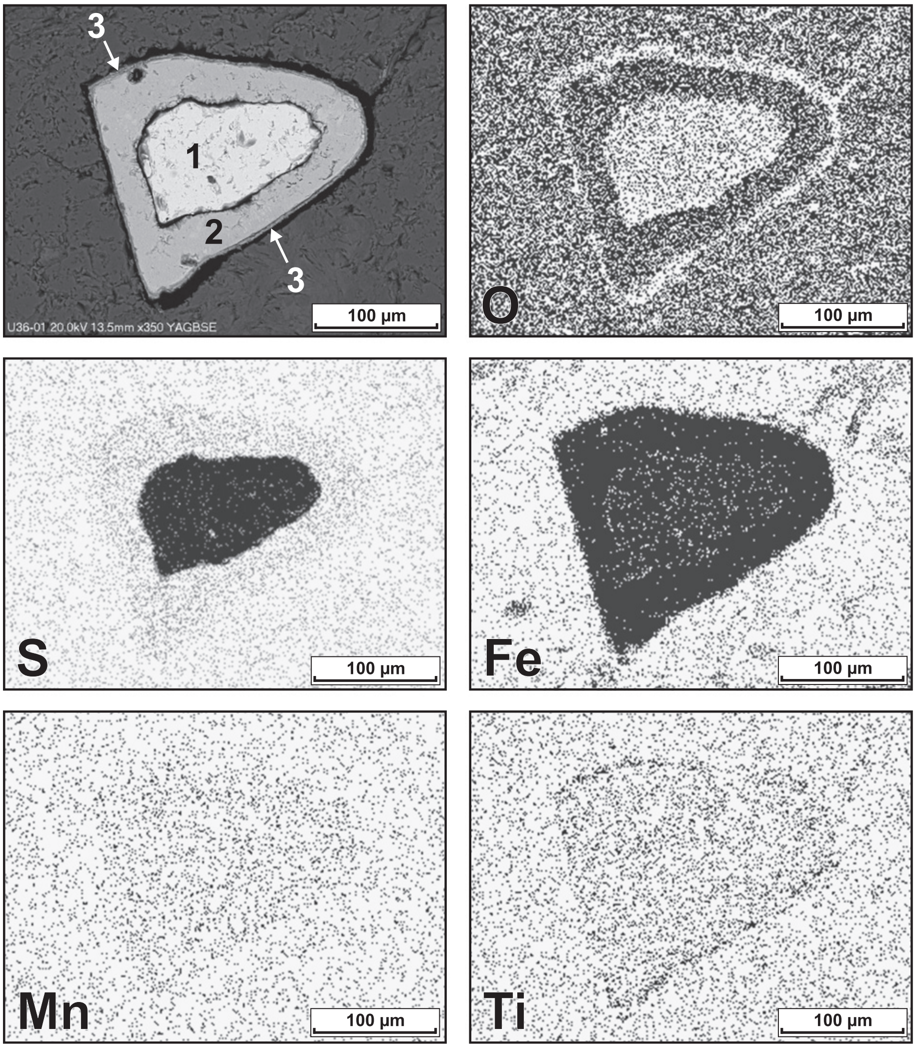

Fig. 7. The remnant of iron sulphide (1) enclosed within quartz and aluminosilicates, surrounded by a layer consisting of massive iron oxides (2), and an external layer enriched in Ti (3); profile NS1, BwC horizon, BSE image and elemental maps for the selected elements.

The predomination of porous Fe oxides in "young" soils from Rudki, and, on the other hand, the occurrence of high amounts of massive forms of iron oxides in "old" soils from Wieściszowice (Fig. 4), suggest that well crystallised iron oxides become more abundant with the increasing degree of advancement of the weathering (soil-forming) processes in the chronosequence of soils studied (Table 5). Such a feature is typical of soils and weathering zones occurring in the temperate climate zone (e.g. Cornell and Schwertmann, 2003; Schwertmann, 2008). The results of the SEM–EDS analyses presented in this paper seem to be consistent with the results of selective extractions of Fe forms from the soils investigated (Uzarowicz and Skiba, 2011), which showed that the older the technogenic soil, the higher the $\mathrm{Fe_{dithionite}/Fe_{oxalate}}$ ratio. This suggests the course of iron oxide transformations from poorly crystalline into well crystallised phases with the increasing age of soils. Poorly crystalline iron oxides initially developed in soils can be subsequently transformed into well crystallised oxides not only due to "ageing", but also by dehydration e.g. related to changes of soil moisture regime (Mees and Stoops, 2010 and references therein). This process is typical of acid sulphate soils in which water table dropped (e.g. Miedema et al., 1974). In the soils studied, the duration of weathering seems to be a factor influencing iron oxide transformations more importantly than dehydration. It is corroborated by the facts that (1) good drainage was typical of all the soils investigated (i.e. the drainage type was similar in all the soils studied) and (2) the soil moisture regime seems to be the same in each study area both nowadays and at the moment of commencement of pedogenesis (weathering), i.e. immediately after the deposition of the last portion of mine waste and/or emergence of plant cover on the landfills studied.

The predominance of porous (poorly crystalline) Fe oxides in soils from Rudki may also be a consequence of high amounts of carbonates (Table 2) (released from weathered dolomite) and sulphate ions. The concentrations of the latter ions were higher in soils from Rudki than in soils from Wieściszowice (Uzarowicz, 2011). Carbonates and sulphates are supposed to be one of the inhibitors of poorly crystalline Fe oxide transformation into more crystalline phases (e.g. Isaacson et al., 2009 and references therein).

The chemical composition of secondary iron oxides developed in natural soils (Leptosols and Cambisols) (Table 4), relatively older than the Technosols studied, suggests that they are a mixture of massive aluminium- and silicon-containing iron oxides and sulphates (e.g. jarosite) (Fig. 9). Crystallisation of such mineral phases is typical of strongly acidic soil environments, for instance of acid sulphate soils (e.g. Ross et al., 1988), soils affected by acid mine drainage (e.g. Šucha et al., 2002), technogenic soils developed on mine dumps containing iron sulphides (Uzarowicz and Skiba, 2011), and natural soils developed on outcrops of pyrite-bearing rocks, as shown in the present study. The process of Al-substitution in Fe oxides is common in weathering environments

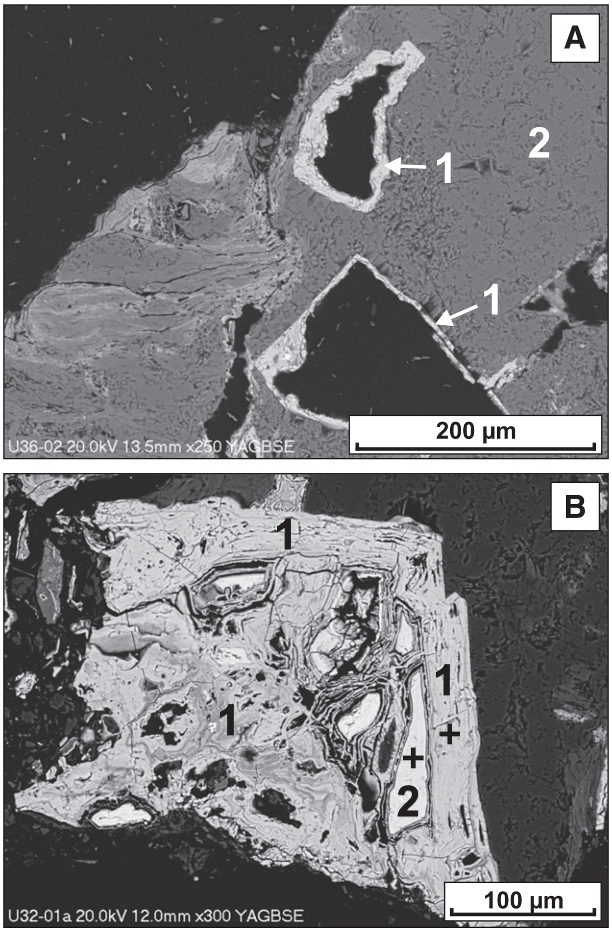

Fig. 8. BSE images showing typical features of iron oxides originated in the natural soils studied. A — coatings built of iron oxides (1) occurring within the voids in quartz (2); profile NS1, BwC horizon. B — former iron sulphide crystal entirely transformed into iron oxides; profile NS2, Bw horizon; two types of Fe oxide structures are visible in the pseudomorph: (1) stratified iron oxides and (2) massive iron oxides. The crosses indicate the EDS analyses shown in Table 4.

(Cornell and Schwertmann, 2003). The formation of iron oxide-silica coatings on the surface of pyrite was also documented by Zhang and Evangelou (1998) during experimental studies.

The contents of Al and Si seem to be higher in iron oxides from old natural soils than younger technogenic soils (Fig. 9, Table 4). This suggests that the older the soil, the higher the amounts of Al and Si in Fe oxides.

Sulphate minerals were rare components of old technogenic and natural soils from Wieściszowice in comparison with young Technosols from Trzebinia and Rudki (Table 5). This finding correlates with the amounts of sulphate sulphur in the soils studied (Uzarowicz, 2011). The data obtained in the present study suggest that the production of sulphate ions in soils depends on the availability of unweathered sulphides, and it may decrease in the course of sulphide weathering. Consequently, the pool of released sulphates may be, at least partly, adsorbed on Fe oxides and/or leached out from soil profiles. The adsorption and leaching reduce the amounts of sulphate ions in the soil solution, therefore limiting the crystallisation of sulphates. Due to lack of favourable conditions to crystallise (e.g. insufficient amounts of sulphate ions in soil solution), sulphate crystals may undergo degradation along with the age of soils. This thesis can be corroborated by the fact that well developed (euhedral) cubic crystals of jarosite were found in younger soils from Trzebinia and Rudki (Fig. 4), whereas subhedral and anhedral pseudocubic crystals of this mineral were typical of older soils from Wieściszowice (Fig. 4). Corrosion of sulphate crystals (e.g. dissolution of gypsum in irrigated soils) was observed in soil environment (e.g. Poch et al., 2010 and references therein).

Another issue investigated in the present study, apart from the weathering pathways of iron sulphides, was the behaviour of trace elements during the weathering of sulphides. The finding that secondary oxides adjacent to Fe sulphides in the soils studied do not constitute places of high concentration of trace elements (Tables 3 and 4) is not in accordance with the studies by Ross et al. (1988), Strawn et al. (2002), and McGregor and Blowes (2002). Ross et al. (1988) found, for example, that an elevated portion of As becomes associated with iron oxides during the weathering of iron sulphides. Moreover, according to Strawn et al. (2002), As and Se were found to be preferentially associated with iron oxide aggregates in the acid sulphate soil studied by the authors. McGregor and Blowes (2002), in turn, found that the cemented layers in mine tailings containing products of iron sulphide weathering (i.e. iron oxides and sulphates) showed enrichment relative to the surrounding uncemented tailings with respect to trace elements (As, Cd, Co, Cu, Ni, and Zn). The explanation for the results of the present study is that iron sulphides in the soils investigated contained low amounts of heavy metals (Table 3). This might be the main reason why adjacent iron oxides were not rich in heavy metals as well (Table 4). A similar finding was documented by Dixon et al. (1982) from pyrite-containing overburdens and wastes coming from lignite mines. Nevertheless, it cannot be excluded that heavy metals may accumulate in the soils studied in microstructures other than pseudomorphs after iron sulphides. High total amounts of heavy metals and radioactive elements documented in these soils (Uzarowicz, 2011) may support this thesis. The recognition of metal containing host minerals, as well as pedogenic minerals and structures in which trace metals may be accumulated requires more detailed micromorphological and microchemical studies.

Temporal changes of oxygen concentration in the soils from Wieściszowice, which probably caused the formation of Fe oxide stratification, are supposed to slightly influence the behaviour of trace elements in these soils. Slightly higher amounts of some trace elements (Zn, Cd, Sn, Sb, Tl, and Pb) in oxygen-poor microlayers (Table 4) suggest that these elements were bound in Fe oxides in the periods of lower concentration of oxygen in the soils.

The comparison of chemical composition of secondary iron oxides from the neutral and acidic soil from Rudki (Table 4) shows that soil pH influences the concentrations of trace elements (e.g. Mn, Co, As, Sn, Sb, and Tl) in iron oxides originating adjacent to iron sulphides. It is consistent with the generally accepted view that majority of trace elements are less mobile in near neutral soils, where they may be, for example, adsorbed on Fe oxides, or incorporated into the Fe oxide structure (Cornell and Schwertmann, 2003; Kabata-Pendias, 2010). The coexistence of Fe and Mn, observed in the neutral profile R1 from Rudki, is a common feature in weathering environments (including soils), as the chemical behaviour of these elements in weathering zones is similar (Cornell and Schwertmann, 2003; Gambrell, 1996; Kabata-Pendias, 2010). Moreover, high pH in soils permits the crystallisation of Mn oxides (Gambrell, 1996). This explains why relatively high amounts of Mn occurred in secondary oxide rims formed around iron sulphides in profile R1 (Fig. 3) with near neutral reaction (Table 4).

The concentration of Mn and Ti in secondary oxide rims both in soils from Rudki and soils from Wieściszowice is most likely a result of the presence of relatively high total amounts of Mn in the former and Ti in the latter soils (Uzarowicz, 2011). These metals are originally bound with certain host minerals, not recognised in detail during the present study. The results obtained suggest that Mn and Ti might be released to the soil solution in the process of weathering of these minerals, and can be subsequently adsorbed or incorporated into the structure of crystallising secondary iron oxides. It seems that a long period of weathering may be sufficient for Ti-enriched iron oxides to be formed, as shown based on the example of natural soils from Wieściszowice (Figs. 7 and 9), even though Ti is considered to be a relatively immobile element in weathering environments (Kabata-Pendias, 2010).

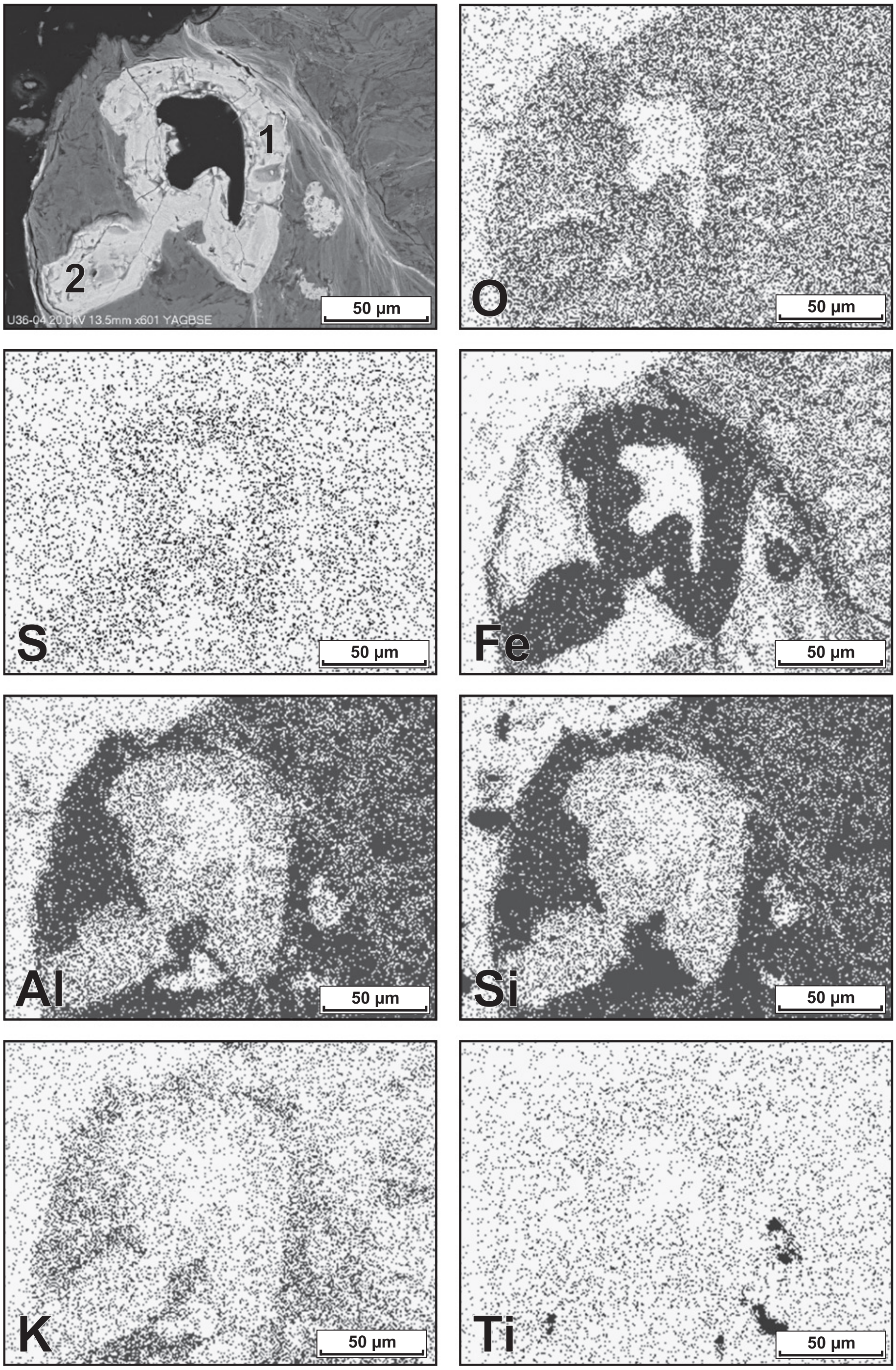

Fig. 9. Coatings (1) and infillings (2) consisting of stratified iron oxides occurring within a void surrounded by aluminosilicates and quartz; profile NS2, Bw horizon, BSE image and elemental maps for the selected elements.

5. Conclusions

1. Iron sulphides in the soils investigated were affected by the processes of both physical weathering (mainly attributed to crushing of sulphide-bearing rocks during technological processes in the mines), as well as chemical weathering expressed by (1) the decay of sulphides followed by the crystallisation of secondary mineral (e.g. Fe oxides and sulphates) from Fe and S released to the soil solution, as well as (2) the development of pseudomorphs in the process of in situ sulphide oxidation.
2. The degree of the advancement of iron sulphide chemical weathering in the chronosequence of soils studied increased along with the increasing age of soils. The weathering of iron sulphides in the chronosequence studied starts from the partial dissolution of sulphide crystal surfaces, most likely driven by microbial activity and expressed by crystallographically preferred etchings. In older soils, sulphides exposed to the environment were covered with coatings composed of either porous (several dozen of years old soils from Rudki) or massive iron oxides (100–200 year-old soils from Wieściszowice). Sulphides enclosed within mineral (rock) grains, regardless of the age of the soils, exhibited pellicular alteration starting at the surface of the crystal and proceeding towards its centre.
3. Weathering of iron sulphides in technogenic soils from Wieściszowice seems to be dependent on temporal changes of oxygen concentration

Table 5
The most common features of weathered Fe sulphides and the main products of Fe sulphide weathering in the chronosequence of soils investigated.

Soils	The approximate age of soils	Typical features of weathered Fe sulphides	The main products of Fe sulphide weathering in soils
Technogenic soils from Trzebinia town (T1 and T2 profile)	Several years old	Macroscopically unaltered Fe sulphides (the dissolution patterns on the surfaces of Fe sulphide crystals formed due to microbial activity are visible at the microscopic scale)	• Fe oxides, gypsum (subhedral prismatic crystals), and jarosite group minerals (euhedral cubic crystals)
Technogenic soils from Rudki village (R1 and R2 profile)	Several dozen of years old	Poorly to partly weathered Fe sulphides	• Porous (poorly crystalline) Fe oxides at the surfaces of Fe sulphides exposed to weathering environment • Partial pseudomorphs of Fe oxides after Fe sulphides (in case of crystals enclosed within mineral/rock fragments) • Sulphates: gypsum (euhedral and subhedral, prismatic and tabular crystals) and jarosite group minerals (euhedral cubic crystals)
Technogenic soils from Wieściszowice village (W1 and W2 profile)	100–200 years old	Almost totally weathered Fe sulphides	• Massive (well crystallized) Fe oxides stratified most likely due to temporal changes of oxygen concentration in soils • Pseudomorphs of Fe oxides after Fe sulphides (in case of crystals enclosed within mineral (rock) fragments) • Small amounts of sulphates: gypsum (subhedral prismatic crystals) and jarosite group minerals (subhedral and anhedral pseudocubic crystals)
Natural soils from Wieściszowice village (NS1 and NS2 profile)	The "old" soils (the exact age is difficult to determine)	Rarely encountered Fe sulphides occurring mostly within mineral (rock) fragments	• Complete pseudomorphs of Fe oxides after Fe sulphides • Stratified Fe oxide coatings (infillings) within the voids • Trace amounts of sulphates; jarosite was exclusively found in strongly acidic profile NS1 using XRD method[a]

[a] According to Uzarowicz et al. (2012).

in the soil environment. The products of sulphide weathering in these soils were stratified iron oxides consisting of oxygen-rich microlayers alternated with layers containing lower amounts of oxygen.

4. The oxidation of sulphide itself, leading to the development of pseudomorphs, seems to proceed in a similar manner both in acidic and near neutral soils. However, there were differences in chemical composition of secondary oxide rims developed in the process of sulphide oxidation. Oxide rims from acidic soils contained more Na, K, Al, and Si, whereas the rims from nearly neutral soils were enriched in Ca and Mg.
5. Sulphate minerals in the soils studied were represented mainly by gypsum and jarosite. Subhedral (rarely euhedral) prismatic crystals of gypsum were the most common habit observed. Subhedral tabular crystals of gypsum were also found. Euhedral cubic crystals of jarosite group minerals were found in younger technogenic soils from Trzebinia and Rudki, whereas subhedral and anhedral pseudocubic crystals of these minerals were typical of old Technosols from Wieściszowice. The development of sulphate parageneses depended on soil pH. Jarosite was exclusively found in strongly acidic soils, whereas gypsum crystallised both in acidic and neutral soils.
6. Secondary iron oxides did not contain significantly higher amounts of trace elements in comparison with the adjacent iron sulphides. As, Sb, Sn, and Tl were the trace elements which elevated amounts were found in secondary oxide rims. Moreover, Mn and Ti were concentrated in secondary oxides occurring in Technosols from Rudki and Wieściszowice, respectively. Mn and Ti were most likely adsorbed by iron oxides and/or incorporated into the structure of Fe oxides from soil solutions rich in these elements.

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