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

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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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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).