INTRODUCTION

The mineralogy of the weathering zones of selected ore deposits in the Sudetes raised little attention among scientists from the Warsaw research centre, at least until the end of the 1980s. This resulted on the one hand from the belief that such studies had only marginal significance and on the other hand, from the methodological difficulties in investigating the mineral assemblages that occur in complex mixtures, are finely-crystalline and often unstable. Systematic research, conducted in the Institute of Geochemistry, Mineralogy and Petrology for over 20 years and continued until the present, has resulted in a significant advancement in our understanding of the mineralogy and geochemistry of weathering zones of ore deposits in the Sudetes. The geochemical conditions and peculiarities in the development of weathering zones of particular ore deposits, the influence of weathering processes on the chemical composition of surface water and shallow groundwater, and the role of microorganisms in still active weathering processes have been recognized. The investigations have allowed us to find and describe over forty secondary minerals, mainly sulphates and arsenates, of which a significant part had been so far unknown in the Sudetes, and had not been even noted in Poland (Table 1).

The studies were concentrated on the weathering zones of pyrite deposits from Wieścisowice and polymetallic deposits from Miedzianka–Ciechanowice and Radzimowice (Text-fig. 1). The Wieścisowice pyrite
deposit is likewise located in the eastern metamorphic cover of the Karkonosze pluton, but is related to metamorphosed submarine volcanites. The Miedzianka–Ciechanowice deposit is situated in the eastern metamorphic envelope of the granitoid Karkonosze Massif, with which it is genetically related. The Radzimowice deposit, situated in the southern part of the metamorphic Kaczawa Mountains unit is genetically related with Carboniferous acid volcanism. The material for the investigations was selected to represent the variable types of mineralization, mono- and polymetallic, and the variable chemical environments and duration of the influence of atmospheric factors on the exposed ore minerals.

This paper contains a compilation and overview of the characteristics of the weathering zones of selected ore deposits, with a particular focus on the individual properties of each zone and an inventory of the paragenetic sequences of the secondary minerals. Most attention is drawn to supergene minerals from among the sulphates and arsenates, which are most common in the studied weathering zones. Based on the ore deposits from the Sudetes, an attempt was made to indicate which groups of these minerals may be treated as reliable indicators of the weathering processes in specific ore and climatic conditions. They can also be used in environmental studies to determine the influence of the weathering zones of ore deposits on soils, surface- and groundwater. Additionally, the role of microorganisms in the paths and kinetics of the weathering of ore deposits is also displayed.

WEATHERING ZONE OF THE PYRITE-BEARING SCHIST DEPOSIT IN WIESCISZOWICE

The pyrite deposit at Wieściszowice (Rudawy Janowickie Mts.) is located in a meridional belt of chlorite and chlorite-sericite schists, up to 10 m wide, exposed between the houses of Wieściszowice village and the slopes of the Wielka Kopa Mt. The series of schist mineralized with pyrite display intense small-scale folding and dips at an angle of 50–70° to the east. The schist are composed of quartz, sericite and chlorite laminae. They also contain porphyroblasts of albite, epidote, and actinolite. Locally, aggregates of quartz or calcite occur in the schist. The mineralization is of an impregnated type. Euhedral or subhedral pyrite grains, randomly distributed in the rock, are up to 5 mm in size and the pyrite content in the deposit may be estimated at about 10%. The mineral composition of the ore deposits is very homogeneous. Pyrite is accompanied only by trace amounts of chalcopyrite, sphalerite, and galena. The pyrite deposit is of hydrothermal origin and its formation is related to a submarine basalt flow on the sea bottom (Jaskólski 1964). A later stage of regional metamorphism resulted merely in pyrite recrystallization.
The pyrite deposit in Wieciszowice was exploited in the years 1785–1925. Pyrite was used for the production of vitriol, and in later years of sulphuric acid. Exploitation was conducted with variable intensity by open cast mining and, in some parts of the deposit, also by underground mining. After the mining activities three open pits remain open, of which the largest – the northern excavation of the “Hope” Mine – has a length of 430 m, a width up to 110 m and depth up to 150 m. The bottom of this excavation is filled with the Purple Pond, named after the dark colour of its water. Located above there is the Blue Pond, and above that the Green Pond emerges periodically.

**Table 1. Selected supergene minerals from Wieciszowice, Radzimowice and Miedzianka ore deposits**

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Chemical formula</th>
<th>Occurrence</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Agardite (Ce)</td>
<td>[Ca₂(PO₄)₂(OH)₄]</td>
<td>Miedzianka, Seggen Gottes mine dumps</td>
<td>this paper</td>
</tr>
<tr>
<td>Baydinite</td>
<td>[Cu₃Al₆O₁₆(OH)₁₂]</td>
<td>Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, Kruszewski, 2006</td>
</tr>
<tr>
<td>Brochantite</td>
<td>[Cu₃Al₆O₁₆(OH)₁₂]</td>
<td>Radzimowice, old mine galleries; dumps; Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, Kruszewski, 2013</td>
</tr>
<tr>
<td>Bukovskylite</td>
<td>[Fe₃Al₆O₁₆(OH)₁₂]</td>
<td>Radzimowice, old mine galleries</td>
<td>Parafiniuk, 1996</td>
</tr>
<tr>
<td>Chloroaluminate</td>
<td>[Cu₃Al₆O₁₆(OH)₁₂]</td>
<td>Radzimowice, old mine galleries</td>
<td>Studa, Kruszewski, 2013</td>
</tr>
<tr>
<td>Cuprite</td>
<td>Cu₃V₂O₇</td>
<td>Radzimowice, old mine galleries; Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, Kruszewski, 2006</td>
</tr>
<tr>
<td>Cyanotrichite</td>
<td>[Cu₄Al₆O₁₆(OH)₁₂]</td>
<td>Radzimowice, old mine galleries</td>
<td>Studa, 2012</td>
</tr>
<tr>
<td>Devillite</td>
<td>Cu₃(As₂O₄)₂(SO₄)₂</td>
<td>Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, Kruszewski, 2013</td>
</tr>
<tr>
<td>Episomite</td>
<td>Mg₅SO₄·7H₂O</td>
<td>Wieciszowice, open pit</td>
<td>Parafiniuk, 1996</td>
</tr>
<tr>
<td>Ferrihydrite</td>
<td>Fe₂O₃·H₂O</td>
<td>Radzimowice, old mine galleries; Wieciszowice, open pit</td>
<td>Parafiniuk, Studa, 2006</td>
</tr>
<tr>
<td>Föresterite</td>
<td>Fe²⁺·SO₄·9H₂O</td>
<td>Wieciszowice, open pit</td>
<td>Parafiniuk, 1996</td>
</tr>
<tr>
<td>Goethite</td>
<td>FeOOH</td>
<td>Wieciszowice, open pit; Radzimowice, old mine galleries; Miedzianka, Seggen Gottes mine dumps</td>
<td>Parafiniuk, Studa, 2006</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO₄·2H₂O</td>
<td>Wieciszowice, open pit</td>
<td>Parafiniuk, 1996</td>
</tr>
<tr>
<td>Hydroniumjarosite</td>
<td>[H₂Cu₃(PO₄)₂(OH)₆]</td>
<td>Radzimowice, old mine galleries</td>
<td>Studa, 2012</td>
</tr>
<tr>
<td>Karkite</td>
<td>Fe₃(PO₄)₂·1,5H₂O</td>
<td>Radzimowice, old mine galleries</td>
<td>Studa, 2012</td>
</tr>
<tr>
<td>Langite</td>
<td>[Cu₄Al₆O₁₆(OH)₁₂]</td>
<td>Radzimowice, old mine galleries; Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, Kruszewski, 2013</td>
</tr>
<tr>
<td>Leibethinite</td>
<td>[Cu₄Al₆O₁₆(OH)₁₆]</td>
<td>Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, Gołębiewska, 2011</td>
</tr>
<tr>
<td>Malachite</td>
<td>Cu₂CO₃(OH)₂</td>
<td>Radzimowice, old mine galleries; Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, Kruszewski, 2013</td>
</tr>
<tr>
<td>Melanterite</td>
<td>Fe₂O₃·H₂O</td>
<td>Wieciszowice, open pit; Radzimowice, underground mine galleries</td>
<td>Studa, 2012</td>
</tr>
<tr>
<td>Morhinite</td>
<td>[Pb₂Cu₃(PO₄)₂(OH)₆]</td>
<td>Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, Gołębiewska, 2011</td>
</tr>
<tr>
<td>Olivine</td>
<td>Cu₃Fe₂(PO₄)₂·4H₂O</td>
<td>Suda, Kruszewski, 2006</td>
<td>Suda, Kruszewski, 2006</td>
</tr>
<tr>
<td>Pharmacosiderite</td>
<td>KFePO₄·(OH)₆</td>
<td>Radzimowice, old mine galleries</td>
<td>Studa, 2012</td>
</tr>
<tr>
<td>Pickeringite</td>
<td>[M₃Fe₃Mn²⁺Al₄O₁₆(SO₄)₁₀]</td>
<td>Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, Kruszewski, 2006</td>
</tr>
<tr>
<td>Pinitol</td>
<td>Fe₉₃(AsO₄)₉·4H₂O</td>
<td>Wieciszowice, open pit</td>
<td>Parafiniuk, 1996</td>
</tr>
<tr>
<td>Pounjakite</td>
<td>[Cu₃(PO₄)₂(SO₄)₂(OH)₆]</td>
<td>Radzimowice, old mine galleries; Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, Kruszewski, 2013</td>
</tr>
<tr>
<td>Razenite</td>
<td>Fe₂O₃·4H₂O</td>
<td>Wieciszowice, open pit; Radzimowice, old mine galleries</td>
<td>Studa, 2012</td>
</tr>
<tr>
<td>Schwertmannite</td>
<td>Fe₃Al₆O₁₆(SO₄)₂·4H₂O</td>
<td>Miedzianka, Seggen Gottes mine dumps</td>
<td>Parafiniuk, Studa, 2006</td>
</tr>
<tr>
<td>Scoolite</td>
<td>Fe₃Al₆O₁₆(SO₄)₂·4H₂O</td>
<td>Radzimowice, old mine galleries</td>
<td>Studa, 2012</td>
</tr>
<tr>
<td>Sjökilde</td>
<td>Mg₆Fe₃(PO₄)₂·3H₂O</td>
<td>Wieciszowice, open pit</td>
<td>Parafiniuk et al., 2010</td>
</tr>
<tr>
<td>Tyrolite</td>
<td>Ca₂O₃·Al₂O₃·(OH)₆·8H₂O</td>
<td>Radzimowice, old mine galleries; Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, Gołębiewska, 2011</td>
</tr>
<tr>
<td>Woodwardite</td>
<td>Ca₃Al₆O₁₆(OH)₂·3H₂O</td>
<td>Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, Kruszewski, 2013</td>
</tr>
<tr>
<td>Witwenellite</td>
<td>[Ca₃Al₆O₁₆(OH)₂·3H₂O]</td>
<td>Radzimowice, old mine galleries; Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, Kruszewski, 2013</td>
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<tr>
<td>Zykale</td>
<td>Fe₃Al₆O₁₆(SO₄)₂·4H₂O</td>
<td>Radzimowice, old mine galleries; Miedzianka, Seggen Gottes mine dumps</td>
<td>Studa, 2012</td>
</tr>
</tbody>
</table>

* empirical chemical formula of mineral was marked (italic)
Schists with pyrite mineralization exposed on the walls of the excavations have been open to the atmosphere for at least 100 years. The effect has been the formation of a well-developed weathering zone with features typical of the climatic conditions of the Sudetes, characterized by seasonal temperature oscillations and intense rainfall. The monomineralic composition of the ore has resulted in the formation of a natural laboratory, where pyrite oxidation and formation of secondary minerals can be observed. Weathering processes are indicated not only by the crystallization of secondary minerals but also by the chemical composition of waters in the mining excavations. Water from the Purple Pond has a composition typical of acid mine drainage (AMD), with a pH of about 2.5. Water analysis of the Purple Pond has indicated the presence of the following cations: iron 380–540 mg/L, calcium 100–280 mg/L, magnesium 150–210 mg/L, and aluminium 90–130 mg/L. The sodium content is very low, about 5 mg/L. Concentrations of heavy metals, manganese, copper, and zinc, amounted to 1.3 mg/L. The anions are dominated by sulphate ions in concentrations of 2730–3500 mg/L. The content of chlorides is low, at 3.15 mg/L. The variability of the chemical composition of the water results from seasonal oscillations of rainfall.

The chemistry of the weathering zone in Wieściszowice is shaped by the oxidation of pyrite and the impact of acidic products of pyrite oxidation on the other minerals in the pyrite-bearing rocks. As indicated by the results of geochemical modelling based on AMD analyses, the least resistant to the action of sulphuric acid is chlorite (Parafiniuk 1996). Decomposition of chlorite and calcite present in some parts is a factor which, besides pyrite oxidation, largely influences the chemical composition of AMD.

A rich paragenesis of weathering minerals was found on the walls of the open pit at Wieściszowice, making it one of the best developed zones of sulphide weathering in Poland. Due to the type of ore mineralization and the environment of silicate minerals, the zone is dominated by sulphate minerals. One of the most common sulphates in Wieściszowice is fibroferrite Fe\(^{3+}\)SO\(_4\)·5H\(_2\)O, unrecorded from other sites in Poland. It forms grey-greenish crusts with a thickness of several to over a dozen millimetres, covering up to several metres of the weathering schist surfaces. Finger-powdered concentrations of fibroferrite indicate a fibrous habit typical of this mineral. The mineral is rather poorly soluble in water, therefore its concentrations are preserved on the walls of the mining excavations throughout the entire year. Slavikite (H\(_2\)O\(_3\))\(_3\)Mg\(_6\)Fe\(_{15}\)SO\(_{21}\)(OH)\(_{18}\)·98H\(_2\)O is a relatively rare iron and magnesium sulphate that is abundant in Wieściszowice. The described weathering zone is the only locality with this mineral in Poland. It occurs individually or in groups with other sulphates in crusts up to few centimetres thick in some parts of the exposure. Slavikite is distinguished by its intensely green or yellow-green colour. Aggregates are composed of well-developed platy crystals, a fraction of a millimetre in size, with an intense, glassy lustre (Text-fig. 2a).

The specific chemistry of the weathering zone in Wieściszowice reflected in the exceptional deficiency in alkali has, based on the material from this locality, allowed us to determine a new chemical formula for slavikite as a phase lacking sodium and to confirm its structure (Parafiniuk et al. 2010). A rather common weathering sulphate in Wieściszowice is a mineral from the copiapite group, forming rich, sulphur-yellow crusts and botryoidal aggregates in some parts of the weathering zone. Aggregates of this mineral are composed of fan-like, very fine-tabular crystals, recognizable only under the microscope (Text-fig. 2b). The mineral is easily soluble in water and can therefore be found in the dry seasons, whereas in humid seasons it occurs only in sheltered places. It was described earlier from Wieściszowice under the informal name pseudo-copiapite (Kubisz 1964). Chemical analyses have indicated that magnesio-copiapite MgFe\(_2\)(SO\(_4\))\(_3\)(OH)\(_2\)·20H\(_2\)O mainly occurs in Wieściszowice; some samples contained significant admixtures of aluminum, close to the composition of aluminocopiapite Al\(_{0.66}\)Fe\(_4\)(SO\(_4\))\(_9\)(OH)\(_2\)·20H\(_2\)O.

However, members of the copiapite group with composition of ferrous copiapite or ferricopiapite were not found. In sheltered parts of the mining excavations occur crusts of the easily soluble pickeringite MgAl\(_2\)(SO\(_4\))\(_4\)·22H\(_2\)O, with thicknesses reaching up to several centimetres. They are composed of white fibrous crystals with a silky lustre, rarely exceeding 1 mm in length (Text-fig. 2c). Varieties of pickeringite, containing significant substitution of Fe\(^{3+}\) for Al\(^{3+}\), creamy-yellow to dark brown in colour, have also been noted. Pickeringite described here for the first time in Poland (Parafiniuk 1991) also forms common fluffy coatings composed of fine, needle-like crystals growing on aggregates of magnesio-copiapite and other secondary sulphates. Halotrichite, mentioned in the literature (Kubisz 1964), was not encountered. Gypsum CaSO\(_4\)·2H\(_2\)O is a common sulphate of the weathering zone in Wieściszowice, forming typical rosette aggregates of tabular crystals, several millimetres in size. They cover surfaces of the weathering schists several metres wide, typically in more humid places, where other secondary sulphates would be dissolved. Sporadically, in the driest seasons, small amounts of other secondary minerals can be found in Wieściszowice, such as: melanterite FeSO\(_4\)·7H\(_2\)O.
and rozenite FeSO₄·4H₂O formed from its dehydration, epsomite MgSO₄·7H₂O, and alunogen Al₂(SO₄)₃·17H₂O, which disappear immediately after the humidity increases. A characteristic feature of the weathering zone in Wieściszowice is the almost complete lack of minerals of the jarosite group, common in other environments of this type. This probably results from the deficiency of alkali in the pore solutions and in the AMD. A rather common mineral precipitating from AMD is the iron oxyhydroxysulphate schwertmannite Fe₁₀(OH,SO₄)₁₂·₁₃·10-12H₂O. This mineral forms stalactites in the adits and precipitates as soft,
WEATHERING ZONE OF THE POLYMETALLIC ORE DEPOSIT IN RADZIMOWICE

The polymetallic ore deposit in Radzimowice is located in the southern part of the Kaczawa Metamorphic Complex, about 15 km to the west of Jelenia Góra. The deposit is composed of over a dozen ore veins, of which six were exploited for gold, copper, lead, and arsenic. The mining of these ores took place with breaks from the 13th to the mid-20th century. Since the mid-19th century, the ore deposit was exploited in the underground Wilhelm Mine, with excavations reaching a depth of over 140 m below the surface (Dziekoński 1972). At present, they are accessible to a depth of about 100 m. These ore veins cut both the metamorphic (quartz-sericite shales, phyllites) and Carboniferous – Permian igneous rocks (rhyolites, kersantites). They run more or less parallel along the E–W direction. The dips of the veins are steep (ca. 60–90º) and directed mainly to the north. The thickness of the veins varies from a few centimetres to more than 1 m. The longest vein – “Miner’s Consolation” – is ca. 2 km long and up to 1.4 m thick. The most common primary ore minerals include pyrite, arsenopyrite, and chalcopyrite. These minerals are accompanied by variable amounts of sphalerite, galena, marcasite, tetrahedrite, boulangerite, bournonite, meneghinite, gold, bismuth, and tellurium minerals (Manecki 1965; Zimnoch 1965; Mikulski 2005, 2007).

Typical minerals of the weathering zone in the Radzimowice ore deposit are the sulphates and arsenates. They occur in the iron cap, which was almost completely exhausted between the 13th and 18th centuries, on dumps of mining waste, and have also been formed recently in the abandoned mining galleries. Several secondary copper minerals have been noted in the underground excavations of the Wilhelm Mine, formed mainly from chalcopyrite oxidation. Brochantite Cu₄SO₄(OH)₆·H₂O is a common secondary sulphate in Radzimowice. It forms green crusts covering the surfaces of weathering rocks, and coarser crystalline aggregates in sinters of Fe oxyhydroxides. This mineral is rarely found on dumps. Aggregates of brochantite are composed of fine crystals up to 1 mm in size with a tabular habit. Langite Cu₄SO₄(OH)₆·2H₂O occurs also in similar places as brochantite. The mineral occasionally covers many square metres of the walls of the mining excavations. The dark-blue crystals of langite reach 2 mm in size. They have a tabular habit and are multiply twinned along wall {001} (Text-fig. 2d). On the faces of langite crystals traces of dissolution and replacement by posnjakite are commonly observed. On the sidewalls of the abandoned mining galleries, posnjakite (Cu₄SO₄(OH)₆·3H₂O) forms light blue, dendritic aggregates composed of thin tabular crystals with sizes up to 1 mm. Much rarer in Radzimowice is devilline CaCu₄(SO₄)₂(OH)₁₀·3H₂O. It occurs as thin needle crystals with lengths up to 2 mm, forming irregular, green-coloured aggregates with a nearly lustre.

One of the typical sulphates occurring in the abandoned mine galleries at the Wilhelm Mine is woodwardite Cu₆Al₂SO₄(OH)₁₆·2-3H₂O. It occurs as light blue, soft covers, up to several centimetres thick, covering the walls of the mining galleries over areas of several square metres (Text-fig. 3a). It also forms small, up to 2–3 cm long, stalactites and unconsolidated sediments on the bottom of stagnant small pools of mine water. Accumulations of woodwardite are composed of oval or spherulitic aggregates with a cryptocrystalline structure. The mineral can be found only in places where fresh meteoric waters are mixed with AMD. A similar composition has a much rarer mineral, chalcoalumite Cu₅Al₃SO₄(OH)₁₁·2H₂O. It forms fine, up to 5 cm long stalactites and draperies with a characteristic dark blue colour. They are built of fine, up to 200 μm in size, spherical aggregates. Chalcoalumite occurs also in the empty voids of goethite stalactites. The presence of small admixtures of cyanotrichite Cu₃SO₄(OH)₁₂·2H₂O, forming fine, acicular crystals up to 0.5 mm long, was also noted in the dripstone aggregates of chalcoalumite. The list of secondary copper sulphates in Radzimowice is supplemented by the rare wroeolfite Cu₅SO₄(OH)₁₂·2H₂O. It occurs as thin tabular, light grey crystals up to 0.2 mm in size. Other secondary copper minerals occurring with the copper sulphates include the most common malachite Cu₂CO₃(OH)₂, cuprite Cu₂O, and native copper Cu.

Besides the diverse paragenesis of the sulphate minerals, numerous arsenates, particularly iron arsenates, are formed in the weathering zone of the Radzimowice ore deposit. These minerals usually appear in the relatively narrow, up to 30 m wide, parts of the deposit containing dispersed ore mineralization composed of arsenopyrite, pyrite, and small amounts of löllingite. The most common iron arsenate in Radzimowice is scorodite FeAsO₄·2H₂O which originated due to arsenopyrite oxidation. In the lower exploitation level of the Wilhelm Mine, scorodite crystallizes as bunch-like, grey-green aggregates with diameters up to a dozen centimetres, covering the sidewalls of the mining galleries. Strong fracturing of scorodite aggregates, which probably resulted
from their dehydration, is visible under the microscope (Text-fig. 2e). The mineral is common in post-mining dumps, where it covers fragments of weathered arsenopyrite. In Radzimowice, kakhtite FeAsO₄·3.5H₂O is one of the most common iron arsenates. It occurs as earthy, monomineralic accumulations up to 40 cm in diameter. At natural humidity, kakhtite is soft and plastic, and characterized by a bright, green-yellow colour. It also forms on mining dumps as cryptocrystalline, green-yellow dripstones and crusts with thicknesses up to 3 mm. Thin tabular crystals of this mineral can be observed by SEM (Text-fig. 2f). The presence of zykait Fe₄(AsO₄)₃·SO₄OH·2H₂O was noted in abandoned mining galleries of the Radzimowice mine and on the dumps. The mineral occurs as whitish, porous, spherical aggregates up to 4 cm in size (Text-fig. 3b). They grow on the surface of rhyolites containing the weathering arsenic ores. At natural humidity they are plastic, whereas after drying they become brittle. Thin needle crystals of this mineral can be seen at high magnifications (Text-fig. 4a). The rarest arsenate in Radzimowice is bukovskýite Fe₂AsO₅SO₄·OH·7H₂O. Its occurrence was observed only in the excavations of the Wilhelm Mine. The mineral forms ochre-yellow, earthy aggregates, reaching up to several millimetres in diameter, composed of fine acicular crystals up to 10 μm in length (Text-fig. 4b). On the lowest exploitation level of the Wilhelm Mine occur considerable amounts of pitticite Fe₃₋₂₀(AsO₄,SO₄)₁₃(OH)₂₄·9H₂O (?). This is a poorly known, amorphous sulphate-arsenate of iron with a variable chemical composition (Dunn 1982; Filippi et al. 2004; Gieré et al. 2003; Frost et al. 2011; Langmuir et al. 2006). In Radzimowice, pitticite mainly forms stalactites and stalagmites with lengths up to 20 cm (Text-fig. 3c). Their colour varies from light grey, through brown, to black. Some are covered by mucous colonies of microorganisms. Pitticite occurs also on mining dumps, where it forms brown to almost black crusts on the surfaces of arsenopyrite. Chemical analyses of pitticite from Radzimowice have indicated its very variable composition. The content of iron changes from 33.71 to 39.12 wt% Fe₂O₃. It is accompanied by small amounts of aluminium (up to 0.74 wt% Al₂O₃), manganese (up to 0.10 wt% MnO), calcium (up to 0.13 wt% CaO), sodium (up to 1.53 wt% Na₂O), and potassium (up to 1.13 wt% K₂O). The As content in the analysed samples of pitticite varies widely, from 16.29 to 54.75 wt% As₂O₅. It is negatively correlated with sulphur (from 0.59 to 7.80 wt% SO₃) and phosphorus (up to 5.04 wt% P₂O₅). The highest concentrations of phosphorus have been noted in the dripstones of beige coloured pitticite, on which bacterial colonies had developed.

In contrast to Wiesiószowice, the most common weathering iron sulphate at Radzimowice is a member of the jarosite group. It forms light yellow, clayey crusts composed of fine rhombohedral crystals, up to 1.5 μm in size (Text-fig. 4c). Jarosite aggregates usually cover the sidewalls of the mining galleries, on which AMD flow down (Text-fig. 3d). They are often covered by mucous colonies of microorganisms. In the floors of the galleries with ponds of low-pH water, unconsolidated accumulations of these minerals with thicknesses up to 0.5 m were deposited. Small amounts of jarosite are also present on mining dumps. Chemical analyses have indicated that jarosite from Radzimowice belongs to the hydroniumjarosite – jarosite (H₂O,K)Fe₃(SO₄)₂(OH)₆ isomorphous series. The presence of high concentrations of the arsenate ion in the weathering environment, manifested in the crystallization of iron arsenates, means that jarosite from Radzimowice is characterized also by an elevated content of arsenic, reaching up to 2.39 As₂O₅ wt %. The presence of melanterite FeSO₄·7H₂O was also noted in the underground excavations of the Wilhelm Mine. This mineral forms green crusts and irregular aggregates, with dimensions up to 10 cm. Accumulations of melanterite are composed of strongly curved fibrous crystals. The mineral appears only in places where fine-grained pyrite-arsenopyrite intergrowths undergo weathering. In some cases the surface of melanterite is covered by earthy, white aggregates of rozenite that have formed from the dehydration of the earlier formed melanterite.

A relatively common mineral noted in the abandoned mining galleries of the Radzimowice Mine is schwertmannite (Parafiniuk and Siuda 2006). It occurs as soft stalactites and stalagmites reaching lengths of tens of centimetres. In some cases it occurs as a thin film floating on the surface of stagnating AMD. The accumulations of schwertmannite are built of characteristic aggregates of fine needle crystals.

WEATHERING ZONE OF THE POLYMETALLIC ORE DEPOSIT IN MIEDZIANKA–CIECHANOWICE

The polymetallic ore deposit in Miedzianka–Ciechanowice, today of historical significance, is situated in the eastern part of the metamorphic envelope of the Karkonosze granitoid massif. Ore mineralization occurs mainly in amphibolites, amphibolite or quartz-sericite schists, and skarns. Exploited from the Middle Ages till the 1950s, the deposit is sub-divided into four mining fields: Western, to the west of Miedzianka; along the contact of the metamorphic cover with the Karkonosze granitoid; Central, located to the south-west of Miedzianka; Eastern, situated to the west of Ciechanowice; and Northern, encom-
passing the Lead Mountains, located to the north of the Bóbr River. The Western mining field is dominated by a magnetite-sphalerite-pyrite ore genetically connected with skarns (Zimnoch 1978; Mochnacka 1982). Ore veins in it are built mainly of chalcopyrite and bornite, accompanied by uraninite mineralization. In the remaining mining fields only polymetallic mineralization occurs. Veins of the Central field are
generally composed of chalcopyrite, sphalerite, bornite, chalcocite, arsenopyrite, tennantite, and Co and Bi ore minerals. These minerals are accompanied by small amounts of barite, fluorite, and chlorite. Veins of the Eastern field contain the most diverse mineral associations. Their main ore minerals include: chalcopyrite, bornite, chalcocite and tetrahedrite–tennantite, sometimes accompanied by arsenic bismuth, sil-
ver, silver amalgamates, nickelaite, löllingite, salflorette, and other minerals (Siuda 2012). In the Northern field occur quartz-barite veins with galena, pyrite, chalcopyrite, and sphalerite.

The underground excavations of the mine are almost inaccessible and studies of the weathering zone can be conducted only within numerous, randomly distributed mine dumps. The dumps selected for the analyses are located several hundred metres from the village of Miedzianka in the Central mining field. They belong to the “Seegen Gottes” Mine, established in 1714 by the fusion of two much older mines: “Geseegneter Georg” and “Gute Hoffnung”, dating back to the 16th century (Siuda and Borzęcki 2014; Makuch and Stolarczyk 2013). Based on the mining tools found in these dumps, and the recognized methods of rock processing, it can be assumed that the waste material accumulated in the dumps was deposited in the 18th century.

The most common secondary mineral of the dumps is chrysocolla (Cu2-x(Al,Fe)xH2-xSi2O5(OH)4·nH2O where x<1), forming massive accumulations with a conchoidal fracture. In some cases chrysocolla with a strongly porous, spongy structure also occurs. It is usually blue to white-blue in colour. Yellow, brown, and almost black varieties have also been found. Such atypical colours of this mineral are related to strongly dispersed iron oxide-hydroxides. Chrysocolla is accompanied by malachite, sometimes cuprite and various secondary copper arsenates. Among them the most common are aggregates of the cornwallite – pseudomalachite Cu5(AsO4,PO4)(OH)4 series (Holeczek and Janeczek 1991). They form botryoidal aggregates of pseudomalachite – cornwallite usually infill fractures across amphibole schists, in some cases covering surfaces of over ten square centimetres. Alternating intergrowths of pseudomalachite – cornwallite, malachite, and chrysocolla have often been noted. A relatively common arsenate in the dumps is phillipsburgite (Cu,Zn)x(AsO4,PO4)2(y(OH))2·xH2O occurring as emerald-green, thin platy crystals up to 3 mm in size (Text-fig. 4d). The crystals form spherical or radial aggregates, up to several square centimetres in size. Olivenite Cu2AsO4OH occurs in several morphological varieties. The first variety forms white, green-shaded, fibrous aggregates, over ten square centimetres in size. They are built of needle-like, olive-green crystals up to 2 mm long. Grey-olive, massive aggregates of olivenite with diameters up to 3 mm, overgrown by thin, needle-like, white crystals of this mineral have also been encountered. The remaining arsenate minerals form small, millimetre-sized aggregates. Spherolithic accumulations of bayldonite PbCu4(AsO4)2(OH)2 and olivenite infill fractures in the amphibolites or overgrow chrysocolla. In the dumps of the “Seegen Gottes” Mine, clinoclase Cu3AsO4(OH)3 forms platy, dark blue crystals with sizes up to 5 mm, assembled in radial aggregates. Pharmacosiderite KFe4(AsO4)3(OH)4·6-7H2O is uncommon. The mineral forms euhedral crystals up to 2 mm in size with a green-yellow colour (Text-fig. 4e). Rare dump minerals include conichalcite CaCuAsO4OH and tyrolite Ca2Cu4(AsO4)4CO3(OH)3·6H2O. Conichalcite forms green crusts up to 2 mm thick, and tyrolite thin platy, blue-green crystals with sizes up to 5 mm (Text-fig. 3f). They occur with other copper arsenates. A rare mineral in the described dumps is agardite-(Ce) CeCu6(AsO4)3(OH)6·3H2O. It forms fine, light green euhedral crystals up to 2 mm long, intergrown in the porous chrysocolla (Text-fig. 4f). Up to 2 mm in size, small aggregates of libethenite Cu2PO4OH and yellow-green crusts of mottramite Pb(Cu,Zn)VO4OH cover fractures in the amphibolite schists or overgrow chrysocolla.

Secondary copper sulphate minerals in the mine dumps in Miedzianka are rarer than the arsenates and usually occur in small amounts. Brochantite occurs as thin, up to 2 mm thick, emerald-green crusts covering the weathering fragments of chalcopyrite. Langite occurs with brochantite. It usually forms crystalline aggregates with sizes up to 2 mm. In some cases idiomorphic crystals of this mineral with a platy habit and a typical blue colour are sometimes visible. The rarest copper sulphate is devilline. It occurs as thin-platy, bluish crystals with sizes up to 2 mm or forms cryptocrystalline covers on weathering chalcopyrite.

CONDITIONS OF THE FORMATION OF SECONDARY MINERALS

The crystallization conditions of secondary sulphates and arsenates in the weathering zones of selected ore deposits in the Sudetes display a local variability depending on the composition of the ore minerals, the barren rocks and the water regimes. In Wieścisowice, due to the monomineralic composition of the ores, the only paragenesis is composed of secondary sulphates crystallizing from AMD. They crystallize from evaporating AMD in exposures and in mine drainage, and their formation strictly depends on the weather conditions and shows cyclic annual changes. In Radzimowice, the products of weathering of the polymetallic ore deposit were formed not only in mine dumps but also in the underground mining ex-
cavitations with specific hydrological conditions. In Miedzianka–Ciechanowice, the composition of the secondary paragenetic sequences is more diverse, due to the polymetallic character of ore composed of sulphides and sulphosalts being subject to weathering. The weathering processes can be traced only in dumps.

A very dynamic hydrochemical system has developed in the mining galleries of the abandoned “Wilhelm” Mine. Significant annual variations in the amount of groundwater inflowing to the excavations can be observed. The largest amounts are supplied in spring, causing almost complete flooding of the deepest mine galleries, whereas in early autumn and in winter the supply is at its lowest. Moreover, the chemical composition of the mining waters is strongly variable.

In some underground parts of the “Wilhelm” Mine excavations, the mining waters have features of AMD. They are characterized by low pH (1.91–2.75) and a high content of the sulphate (727–1165 mg/L) and arsenate (1500–2023 μg/L) ions, at a low concentration of the chloride ion (2.6–3.46 mg/L). The waters contain also very high concentrations of iron (Fe_{aq} 140–294 mg/L) and ions of heavy metals (e.g., Cu^{2+} 1340–28720 μg/L, Zn^{2+} 885–1144 μg/L, Co^{2+} 313–470 μg/L). They occur in the weathering zones of ore veins composed of the mixture of fine-grained pyrite, arsenopyrite, and löllingite. Oxidation of arsenopyrite and löllingite is less intense than that of pyrite. It can be enhanced by the high activity of Fe^{3+} ions formed from pyrite oxidation. Microorganisms, whose colonies commonly occur in these zones, actively participate in pyrite oxidation. A characteristic assemblage of sulphate and arsenate minerals crystallizes from AMD. Directly on the surface of the oxidized pyrite appears melanterite and its dehydrated form, rozenite. They are accompanied by aggregates of chlorides and arsenates of iron oxyhydroxides and arsenic-rich hydrous ferric oxides. The occurrence of scorodite with these phases may indicate a pH increase of the groundwater (e.g., due to an increased supply during the humid seasons), which may lead to incongruent dissolution of this mineral with precipitation of amorphous iron oxyhydroxides and ferricydrates with low crystallinity (e.g., Dove and Rimstidt 1985; Langmuir et al. 2006, Bluteau and Demopoulos 2007). Ferricydrates are a phase that appears in larger amounts at pH exceeding 5.5 (Murad and Rojik 2003; Kim and Kim 2004). Its presence confirms a periodic pH increase in the environment of scorodite crystallization, which may be linked to oscillations in the supply of meteoric waters. The precipitation of pitticite is related to an environment of diluted AMD with increased pH but with high concentrations of arsenate ions. The decrease of this concentration results in the dissolution of pitticite, which is decomposed more easily than crystalline scorodite (Robins 1987; Chukhlantsev 1956; Langmuir et al. 2006). The occurrence of pitticite is separated from the zones of hydroniumjarosite occurrence, which results from the fact that this phase is not stable also at very low pH levels.

Mine waters, whose composition is shaped by the weathering of chalcopyrite veins, have a chemically different character. In comparison to pyrite and arsenopyrite, the oxidation rate of chalcopyrite is very slow (Moncur et al. 2009) and leads to a relatively slight pH decrease. Mine waters in these zones are weakly acid or neutral (pH from 6.37 to 6.97) and contain high amounts of copper (2521–5244 μg/L), calcium (140–254 mg/L), and also the bicarbonate ion (79–171 mg/L) besides the sulphate ion (480–705 mg/L).
The crystallization of basic copper sulphates and carbonates is linked with these zones. Langite and posnjakite are stable at a relatively high activity of sulphate ions and relatively high pH (from 6.0 to 7.5). A decrease of SO$_4^{2-}$ and Cu$^{2+}$ concentrations promotes the crystallization of brochantite, which is the most stable basic copper sulphate. This mineral crystallizes at a pH in the range 4.0–7.5 (Marani et al. 1995). Therefore, dilution of mining water due to an influx of fresh meteoric water causes etching, whose traces are visible on the surfaces of langite crystals, and the formation of pseudomorphs of malachite after langite. It seems that, generally, the pH of solutions, from which basic copper sulphates crystallized, did not fall below 3–4, because in such conditions very fast dissolution of brochantite and crystallization of antlerite could be observed (Maley et al. 2009; Pollard et al. 1992). A decrease in the content of sulphate ions and simultaneous presence of bicarbonate ions lead to the crystallization of malachite and the formation of pseudomorphs of malachite after langite. Based on the model results of Alwan and Williams (1979) for a langite/brochantite–malachite assemblage from Cornwall, it may be assumed that the process took place at pH 6.0–7.5 and depended on the concentrations of CO$_3^{2-}$ ions in the solution. The crystallization of woodwardite and other copper–aluminum sulphates occurs in zones of mixing of mine water (with the above mentioned properties) with AMD containing elevated aluminium contents. The presence of langite in the concentrations of woodwardite indicates that these minerals crystallized from solutions at pH about 6.0–7.5, which corresponds with the values noted by Marini et al. (2003) for woodwardite from the weathering zones of the Vigonzano and Libiola regions in Italy. Our field observations are confirmed by the results of hydrogeochemical modelling by Tumiati et al. (2008), which indicate that woodwardite crystallizes at pH 7.39–7.55 from solutions with a rather low CO$_2$ content, i.e. in which CO$_2$ concentration is below 10$^4$ mol/L. Higher concentrations of CO$_2$ in the solution cause crystallization of malachite and other carbonate minerals.

Secondary minerals occurring in Miedzianka in the "Seegen Gottes" mine dump can be subdivided into two paragenetic sequences formed in different conditions and at different times. The first developed in a naturally formed weathering zone of the ore deposit that at present cannot be observed in the inaccessible mine excavations. Its main components are chrysocolla and copper arsenates. Based on the observed paragenetic relationships, an attempt has been made to determine the order of crystallization. The oldest weathering products are the outgrowths of cuprite and the so-called black copper ore composed of amorphous phases rich in Cu, which form pseudomorphs after chalcopyrite aggregates. Chrysocolla was formed next, intergrowing with massive malachite and pseudomalachite–cornwallite. These minerals are accompanied by inclusions of philippsburgite, bayldonite, and lilethenite. The assemblage composed of conichalcite, clinoclase, chrysocolla, malachite, mottramite, olivenite, tyrolite, conichalcite, pharmacosiderite, and agardite–(Ce) may be of the same age or slightly younger. Data of Magalhães et al. (1988) indicate that olivenite is a mineral stable at relatively low pH. Increase of pH values causes the crystallization of cornwallite, followed by clinoclase. Such an assemblage of coexisting copper arsenates may indicate crystallization over a relatively wide pH range (from about 4.5 to 7). The occurrence of copper arsenates with malachite may also indicate an enhanced activity of carbonate ions relative to arsenate ions. This increase may be related with the much advanced decomposition process of primary arsenic sulphosalts in the subsurface part of the weathering zone.

The formation of the second paragenesis, comprising brochantite, langite, and devilline takes place already in the mine dump with remnants of the chalcopyrite ore. The rock material from the studied mine dump was mined in the 18th century and has been exposed to atmospheric factors since that time. The products of chalcopyrite oxidation are dissolved in meteoric waters, from which basic copper sulphates crystallize. The copper minerals found within the dump indicate that the pH of the primary porous solutions was 6.0 – 6.5; therefore AMD are not formed here. The small amounts of secondary sulphates found within the dumps indicate the rather low dynamics of sulphide weathering processes.

ROLE OF MICROORGANISMS IN THE OXIDATION OF SULPHIDE AND ARSENIC MINERALS

There is no doubt that the formation of some of the mentioned supergene minerals can be affected by bacteria belonging to chemolithoautotrophs. These groups are not homogenous and include microorganisms taxonomically and phylogenetically distinct. Simplifying the issue, it can be assumed that the key process in the formation of the weathering zone is the oxidation of sulphur, sulphide and ferrous ions. The activity of sulphur and „iron“ bacteria can lead to AMD generation in such environments, such as the weathering zone at Wieściszowice (Borkowski et al. 2013) or Radzimowice. These environments can be characterized by pH levels lethal to most living organisms. The
main role of sulphur microorganisms under oxidizing conditions is a significant acceleration of the oxidation processes. A clear example is the oxidation of Fe²⁺ in acidic solutions. Although this process is thermodynamically favoured, it occurs very slowly. Enabling enzyme-catalysed reactions in bacteria may accelerate the rate of iron oxidation by orders of magnitude. Comparison of the rate of abiotic oxidation of pyrite with enzyme-catalysed processes is perhaps the best illustration of the problem. Nordstrom and Alpers (1999) reported an example of the rate of abiotic oxidation of iron and pyrite, finding 3×10⁻¹² mol/L/s and 0.3–3×10⁻⁹ mol/m²/s, respectively. For comparison, the biological rate of Fe²⁺ oxidation and pyrite were 5×10⁻⁷ mol/L/s and 8.8×10⁻⁴ mol/m²/s, respectively.

Ferric ions under acidic conditions play a key role as powerful oxidants. These ions are responsible for the so-called indirect biological leaching of metals via oxidation of mineral ores. This process results in a reduction of iron and Fe²⁺ production, which is then oxidized via microbial activity (Rimstidt et al. 1994; Sand and Gehrke 2006). Thus, in the process the role of the sulphur bacteria is reduced primarily for oxidation of ferrous ions. Sand et al. (1995) described a model of bacterial leaching mainly through the mechanism of an indirect one initiated by Fe³⁺. The other important process is the direct (or contact) leaching of metals and it is assumed that bacteria growing on the surface of minerals are responsible for direct damage of the mineral structure. The effect of both processes that can be observed in situ is a development of the microbial communities (e.g. biofilms or so-called slime streamers) consisting of bacteria with specific extracellular polymeric substances (EPS). Such structures can be closely associated with both primary minerals and the supgene mineral phases. In SEM pictures, there can be found microbial cells embedded in EPS which may be produced in large quantities and can build the structure of microbial mats. On SEM images of the slime streamers from Radzimowice (Text-fig. 5a, b) can be seen the presence of mineral phases (hydroniumjarosite and schwertmannite) related to, or even embedded within, the substance produced by microorganisms.

In the weathering zone, the important sulphur-oxidizing microorganisms living in acidic conditions are Acidithiobacillus thiooxidans, A. ferrooxidans, Leptospirillum ferrooxidans, and thermophilic Archaea belonging to the genus Sulfolobus. Their activity can significantly contribute to lowering of the pH and ferric ion production, leading to the strong oxidizing environment convenient for the weathering of the ore minerals. It should be noted that a large part of the sulphur oxidizing microorganisms can also oxidize Fe²⁺. It seems, therefore, that the most important indicators of the presence of a sulphur microbial consortium in these environments are a low pH and the presence of SO₄²⁻ and Fe³⁺. In Figure 6a, the main reactions associated with the sulphur cycle taking place under the oxidation conditions are presented. The diagram presents the processes related to direct (or contact) leaching and indirect leaching. In the first case, the key roles are played by the microorganisms directly colonizing the mineral ore. In the second case, the ferric ions as a product of bacterial metabolism can oxidize minerals but bacteria have no contact with the leached material. In both cases, typical products of AMD environments are generated.

As in the case of sulphur, arsenic compounds may also undergo biotransformation via direct leaching and
the oxidation by ferric ions under acidic conditions. It seems that indirect leaching can play a crucial role, and the microbial oxidation of iron is the driving force of the arsenic biotransformation process. Arsenic compounds may be significantly more toxic for biochemical activity than the other metal compounds; however, under specific conditions the chemolithoautotrophs can utilize the oxidation of arsenic (III) as a source of energy for the binding of CO₂. The effect of the microbial oxidation of arsenopyrite may be sulphate and arsenite ions, which can be further oxidised to arsenates. Oxidation of arsenates can also take place by both direct microbial activity and as a result of the reduction of Fe³⁺ ions (Text-fig. 6b).

As a result of these processes in acidic environments the typical assemblages of arsenic minerals containing AsO₄³⁻ ions (e.g. scorodite, zýkaite) can be developed.

CONCLUSIONS

Diversified assemblages of secondary sulphate and arsenate minerals, found in the weathering zones of the discussed ore deposits in the Sudetes, have significant potential as indicators of the process of their weathering. By using them, it is possible to recognize the directions of transformation and the dynamics of the weathering process. Recognition of the inventory of secondary minerals, and knowledge of the conditions and range of their stability, allow the determination of the oscillations in the chemical composition and pH of mine water or dump leachates. The minerals are of key significance in the retention of many, often toxic components released during oxidation, such as heavy metals, arsenic compounds, etc. They are bound in the weathering zone and released to surface- or ground-water along with the decomposition or dissolution of relevant sulphate and arsenate minerals. It is obvious that at some stages of the weathering of an ore deposit and in the crystallization of part of the sulphates and arsenates, an important role is played by specialized microorganism colonies, whose life activities should be treated as significant mineral forming factors.

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