

Sulphate and arsenate minerals as environmental indicators in the weathering zones of selected ore deposits, Western Sudetes, Poland

JAN PARAFINIUK*, RAFAŁ SIUDA and ANDRZEJ BORKOWSKI

*Institute of Geochemistry, Mineralogy and Petrology, Faculty of Geology, University of Warsaw, Al. Żwirki i Wigury, 93,
PL-02-089 Warszawa, Poland. *E-mail: j.parafiniuk@uw.edu.pl*

ABSTRACT:

Parafiniuk, J., Siuda, R. and Borkowski, A. 2016. Sulphate and arsenate minerals as environmental indicators in the weathering zones of selected ore deposits, Western Sudetes, Poland. *Acta Geologica Polonica*, **66** (3), 493–508. Warszawa.

The results of a complex investigation of the sulphate and arsenate assemblages forming in the weathering zone of selected ore deposits in the Sudetes are presented. The development of the weathering zone has been characterised in the polymetallic ore deposits at Miedzianka–Ciechanowice and Radzimowice, and the pyrite deposit at Wieściszowice, which differ in the chemical compositions of the ore and barren minerals and the hydrological conditions. Secondary sulphate and arsenate mineral assemblages vary significantly among the ore deposits under study. Their crystallization is discussed, taking into consideration the stability of particular minerals and the paths of their transformation. It is shown that these minerals have great potential as indicators of weathering processes. A significant role for microorganisms in the formation of the weathering zone of the ore deposits under study is also proven.

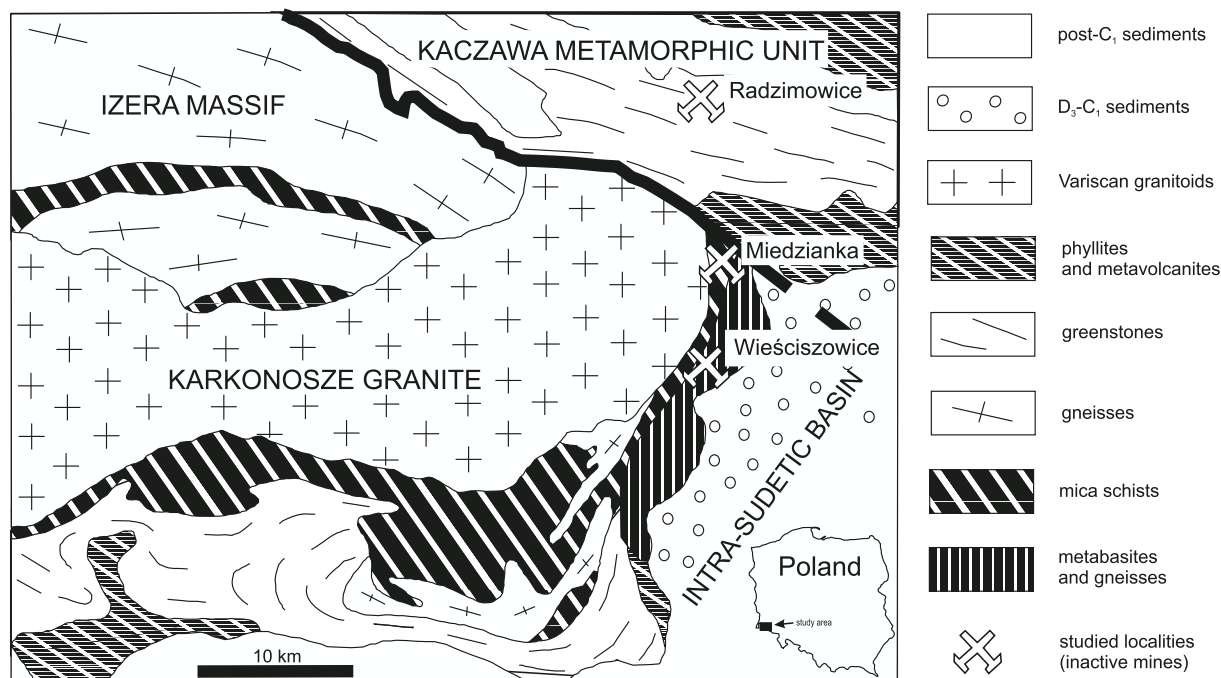
Key words: Sulphates; Arsenates; Slavikite; Zýkaite; Kańkite; Pitticite

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 Wieściszowice and polymetallic deposits from Miedzianka–Ciechanowice and Radzimowice (Text-fig. 1). The Wieściszowice pyrite



Text-fig 1. Locality map of the Wieściszowice, Radzimowice and Miedzianka deposits in the Western Sudetes (modified after Mazur *et al.* 2006)

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 microor-

ganisms in the paths and kinetics of the weathering of ore deposits is also displayed.

WEATHERING ZONE OF THE PYRITE-BEARING SCHIST DEPOSIT IN WIEŚCISZOWICE

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.

Mineral	Chemical formula*	Occurrence	References
Agardite-(Ce)	$[(Ce_{0.18}La_{0.15}Nd_{0.11}Y_{0.10})_{20.54}Pb_{0.36}Bi_{0.21}Ca_{0.03}]_{21.14}Cu_6[(AsO_4)_{2.43}(PO_4)_{0.45}(SiO_4)_{0.22}]_{23.10}(OH)_{5.50} \cdot 3H_2O$	Miedzianka, Seggen Gottes mine dumps	this paper
Aluminocopiapite	$(Al_{0.42}Mg_{0.27}Fe^{2+}_{0.20}Ca_{0.02}Cu_{0.02})Fe^{3+}_{3.83}Al_{0.07}[(OH)_2(SO_4)_6] \cdot 20,14H_2O$	Wieściszowice, open pit	Parafiniuk, 1996
Alunogen	$Al_2(SO_4)_3 \cdot 18H_2O$	Wieściszowice, open pit	Parafiniuk, 1996
Bayldonite	$Cu_{3.12}Pb_{1.00}Fe_{0.06}Ca_{0.01}[(AsO_4)_{1.92}(PO_4)_{0.05}(VO_4)_{0.01}]_{1.98}(OH)_{1.40}$	Miedzianka, Seggen Gottes mine dumps	Siuda, Kruszewski, 2006
Brochantite	$(Cu_{3.95}Fe_{0.04})_3.99(SO_4)_0.84(OH)_{6.22}$	Radzimowice, old mine galleries, dumps; Miedzianka, Seggen Gottes mine dumps	Siuda, Kruszewski, 2013
Bukovskýite	$Fe_{2.00}[(AsO_4)_{0.98}(SO_4)_{0.83}(PO_4)_{0.02}]_{2.81}(OH)_{1.36} \cdot 7,19H_2O$	Radzimowice, old mine galleries	Siuda, 2012
Chalcoalumite	$CuAl_2SO_4(OH)_{12} \cdot 3H_2O$	Radzimowice, old mine galleries	Siuda, Kruszewski, 2013
Chrysocolla	$Cu_{2-x}Al_xFe^{3+}_xH_{2-x}Si_2O_5(OH)_4 \cdot nH_2O$	Miedzianka, Seggen Gottes mine dumps	Siuda, Gołębiowska, 2011
Clinoclase	$(Cu_{2.9}Zn_{0.02}Pb_{0.01})_{33.00}[(AsO_4)_{0.77}(PO_4)_{0.26}(VO_4)_{0.02}(SiO_4)_{0.04}]_{21.11}(OH)_{2.63}$	Miedzianka, Seggen Gottes mine dumps	Siuda, Gołębiowska, 2011
Conichalcite	$Ca_{1.04}Cu_{0.96}(AsO_4)_{1.04}OH_{0.88}$	Miedzianka, Seggen Gottes mine dumps	this paper
Copper	Cu	Radzimowice, old mine galleries	Siuda, Kruszewski, 2013
Cornwallite-pseudomalachite	$(Cu_{4.96}Zn_{0.03}Pb_{0.01})_{25.00}[(AsO_4)_{1.88}(PO_4)_{0.05}(SiO_4)_{0.03}]_{21.96}(OH)_{4.01} - (Cu_{4.96}Zn_{0.03}Pb_{0.03})_{25.00}[(PO_4)_{1.44}(AsO_4)_{0.43}(VO_4)_{0.01}(SiO_4)_{0.05}]_{21.93}(OH)_{4.16}$	Miedzianka, Seggen Gottes mine dumps	Siuda, Kruszewski, 2006
Cuprite	$Cu_2O \cdot Fe_{0.02}O$	Radzimowice, old mine galleries; Miedzianka, Seggen Gottes mine dumps	Siuda, Kruszewski, 2013
Cyanotrichite	$Cu_3Al_2SO_4(OH)_{12} \cdot 2H_2O$	Radzimowice, old mine galleries	Siuda, 2012
Devilline	$Ca_{1.00}(Cu_{3.96}Al_{0.04})_{24.00}[(SO_4)_{1.99}(SiO_4)_{0.05}]_{22.04}(OH)_{6.0} \cdot 6,1H_2O$	Radzimowice, old mine galleries; Miedzianka, Seggen Gottes mine dumps	Siuda, Kruszewski, 2013
Epsomite	$MgSO_4 \cdot 7H_2O$	Wieściszowice, open pit	Parafiniuk, 1996
Ferrihydrite	$Fe^{3+}_5O_3(OH)_9$	Radzimowice, old mine galleries; Wieściszowice, open pit	Parafiniuk, Siuda, 2006
Fibroferrite	$Fe^{3+}SO_4 \cdot OH \cdot 5H_2O$	Wieściszowice, open pit	Parafiniuk, 1996
Goethite	FeOOH	Wieściszowice, open pit; Radzimowice, old mine galleries; Miedzianka, Seggen Gottes mine dumps	Parafiniuk, Siuda, 2006
Gypsum	$CaSO_4 \cdot 2H_2O$	Wieściszowice, open pit	Parafiniuk, 1996
Hydroniumjarosite-jarosite	$(H_3O^{+}_{0.53}K_{0.47})_{21.00}(Fe_{2.82}Al_{0.02})_{22.84}[(SO_4)_{1.95}(AsO_4)_{0.05}(PO_4)_{0.02}]_{22.00}(OH)_{6.38}$	Radzimowice, old mine galleries	Siuda, 2012
Kaňkite	$Fe[(AsO_4)_{0.73}(SO_4)_{0.18}(PO_4)_{0.13}]_{21.04} \cdot 3,5H_2O$	Radzimowice, old mine galleries, dumps	Siuda, 2012
Langite	$(Cu_{3.96}Al_{0.04})_{24.00}(SO_4)_{1.00}(OH)_{6.0} \cdot 1,90H_2O$	Radzimowice, old mine galleries; Miedzianka, Seggen Gottes mine dumps	Siuda, Kruszewski, 2013
Libethenite	$(Cu_{1.68}Pb_{0.02})_{22.00}[(PO_4)_{0.68}(AsO_4)_{0.08}(SiO_4)_{0.04}]_{20.80}OH_{1.56}$	Miedzianka, Seggen Gottes mine dumps	Siuda, Gołębiowska, 2011
Magnesiocopiapite-aluminomagnesiocopiapite	$(Mg_{1.18}Al_{0.08}Fe^{2+}_{0.03}Cu_{0.03}Ca_{0.01}Mn_{0.01})Fe^{3+}_{3.78}Al_{0.23}[(OH)_2(SO_4)_6] \cdot 23,11H_2O - (Al_{0.43}Mg_{0.56}Fe^{2+}_{0.07}Ca_{0.03}Cu_{0.01})Fe^{3+}_{3.95}Al_{0.05}[(OH)_2(SO_4)_6] \cdot 20,69H_2O$	Wieściszowice, open pit	Parafiniuk, 1996
Malachite	$Cu_2CO_3(OH)_2$	Radzimowice, old mine galleries, old dumps; Miedzianka, Seggen Gottes mine dumps	Siuda, Kruszewski, 2013
Melanterite	$FeSO_4 \cdot 7H_2O$	Wieściszowice, open pit, Radzimowice underground mine galleries	Siuda, 2012
Mottramite	$(Pb_{0.80}Ca_{0.15}Cu_{0.05}Zn_{0.01}Fe_{0.01})_{22.00}[(VO_4)_{0.45}(AsO_4)_{0.40}(PO_4)_{0.09}(SiO_4)_{0.05}]_{20.99}(OH)_{1.02}$	Miedzianka, Seggen Gottes mine dumps	Siuda, Gołębiowska, 2011
Olivenite	$Cu_{2.19}Fe_{0.02}Al_{0.01}Zn_{0.01}Pb_{0.01}[(AsO_4)_{0.63}(PO_4)_{0.23}(SiO_4)_{0.05}]_{20.91}(OH)_{1.02}$	Miedzianka, Seggen Gottes mine dumps	Siuda, Kruszewski, 2006
Pharmacosiderite	$KFe^{3+}_4(AsO_4)_3(OH)_4 \cdot 6 \cdot 7H_2O$	Miedzianka, Seggen Gottes mine dumps	Siuda, Gołębiowska, 2011
Phillipsburgite	$Cu_{5.04}Zn_{0.93}(AsO_4)_{1.40}(PO_4)_{0.70}(VO_4)_{0.01}Fe_{8.00} \cdot 1,29H_2O$	Miedzianka, Seggen Gottes mine dumps	Siuda, Kruszewski, 2006
Pickeringite	$(Mg_{1.37}Mn_{0.04}Fe^{2+}_{0.01}Al_{1.95}(SO_4)_4 \cdot 29,04H_2O - (Mg_{1.18}Fe^{2+}_{0.13}Mn_{0.03}Ca_{0.03}Cu_{0.02})Al_{1.09}Fe^{3+}_{0.65}(SO_4)_4 \cdot 21,36H_2O$	Wieściszowice, open pit	Parafiniuk, 1996
Pitticite	$Fe^{3+}_{20}(AsO_4)_4(SO_4)_{13}(OH)_{24} \cdot 9H_2O (?)$	Radzimowice, old mine galleries, dumps	Siuda, 2012
Posnjakite	$(Cu_{3.97}Al_{0.03})_{24.00}[(SO_4)_{0.95}(SiO_4)_{0.05}]_{21.00}(OH)_{6.0} \cdot 1,95H_2O$	Radzimowice, old mine galleries; Miedzianka, Seggen Gottes mine dumps	Siuda, Kruszewski, 2013
Rozenite	$FeSO_4 \cdot 4H_2O$	Wieściszowice, open pit, Radzimowice, old mine galleries	Siuda, 2012
Schwertmannite	$Fe_{15.92}Al_{0.08}[(SO_4)_{2.54}(SiO_4)_{0.20}(AsO_4)_{0.05}]_{2.76}(OH)_{10}O_{16} \cdot 10H_2O$	Wieściszowice, open pit; Radzimowice, old mine galleries	Parafiniuk, Siuda, 2006
Scorodite	$(Fe_{0.98}Al_{0.01}Cu_{0.01})_{21.00}[(AsO_4)_{0.87}(SO_4)_{0.05}(SiO_4)_{0.01}]_{20.94} \cdot 2H_2O$	Radzimowice, old mine galleries, dumps	Siuda, 2012
Slavikite	$(H_3O^{+})_3Mg_6Fe_{18}(SO_4)_{21}(OH)_{18} \cdot 98H_2O$	Wieściszowice, open pit	Parafiniuk et al., 2010
Tyrolite	$CaCu_5(AsO_4)_2CO_3(OH)_4 \cdot 6H_2O$	Miedzianka, Seggen Gottes mine dumps	Siuda, Gołębiowska, 2011
Woodwardite	$Cu_5Al_2SO_4(OH)_{16} \cdot 2 \cdot 3H_2O$	Radzimowice, old mine galleries	Siuda, Kruszewski, 2013
Wroewolfeite	$(Cu_{3.95}Fe_{0.04}Al_{0.01})_{24.00}[(SO_4)_{0.84}(SiO_4)_{0.01}]_{20.85}(OH)_{6.0} \cdot 1,63H_2O$	Radzimowice, old mine galleries	Siuda, Kruszewski, 2013
Zykaite	$(Fe_{3.81}Al_{0.06}K_{0.10}Ca_{0.03})_{24.00}[(AsO_4)_{3.08}(SO_4)_{0.56}(PO_4)_{0.02}]_{2.66}(OH)_{1.35} \cdot 15,46H_2O$	Radzimowice, old mine galleries	Siuda, 2012

* empirical chemical formula of mineral was marked (*italic*)

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

The pyrite deposit in Wieściszowice 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.

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 ores 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.

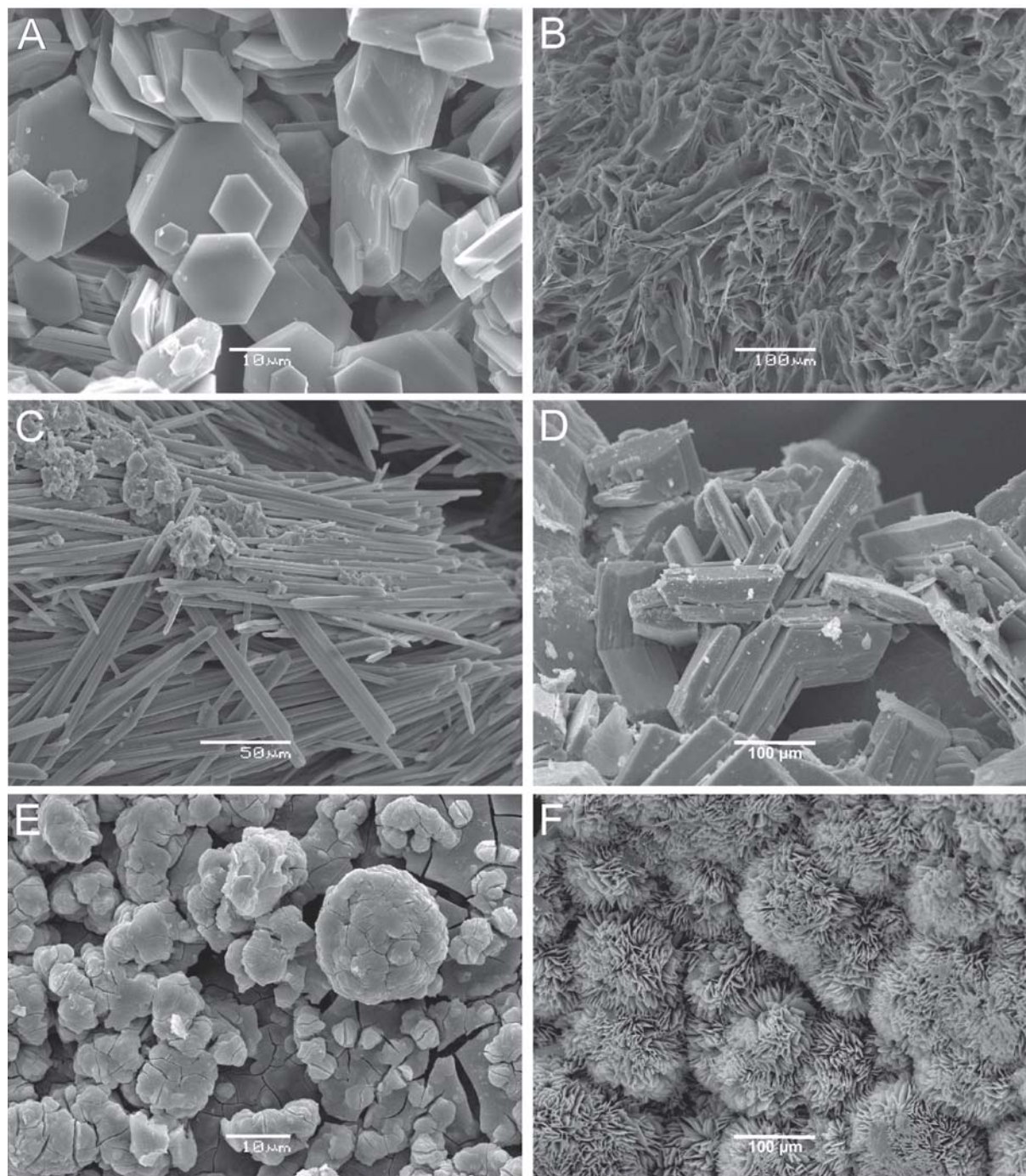
A rich paragenesis of weathering minerals was found on the walls of the open pit at Wieściszowice, making it one of the best developed zones of sulphide weathering in Poland. Due to the type of ore mineralization and the environment of silicate minerals, the zone is dominated by sulphate minerals. One of the most common sulphates in Wieściszowice is fibroferrite $\text{Fe}^{3+}\text{SO}_4 \cdot 5\text{H}_2\text{O}$, 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 $(\text{H}_3\text{O}^+)_3\text{Mg}_6\text{Fe}_{15}(\text{SO}_4)_{21}(\text{OH})_{18} \cdot 98\text{H}_2\text{O}$ 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 pseudocopiapite (Kubisz 1964). Chemical analyses have indicated that magnesiocopiapite $\text{MgFe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$ mainly occurs in Wieściszowice; some samples contained significant admixtures of aluminum, close to the composition of aluminocopiapite $\text{Al}_{0.66}\text{Fe}_4(\text{SO}_4)_6(\text{OH})_2 \cdot 20\text{H}_2\text{O}$.

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 $\text{MgAl}_2(\text{SO}_4)_4 \cdot 22\text{H}_2\text{O}$, 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 magnesiocopiapite and other secondary sulphates. Halotrichite, mentioned in the literature (Kubisz 1964), was not encountered. Gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ 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 $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

and rozenite $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$ formed from its dehydration, epsomite $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and alunogen $\text{Al}_2(\text{SO}_4)_3 \cdot 17\text{H}_2\text{O}$, 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 $\text{Fe}_{16}(\text{OH},\text{SO}_4)_{12-13} \cdot 10-12\text{H}_2\text{O}$. This mineral forms stalactites in the adits and precipitates as soft,



Text-fig. 2. SEM images of secondary minerals; A – tabular crystals of slavikite from Wieściszowice. B – crystals of copiapite from Wieściszowice. C – Prismatic pickeringite crystals from Wieściszowice. D – langite twin parallel to {110} from Radzimowice. E – scorodite aggregates from Radzimowice. F – kańkite crystals from Radzimowice

rusty concentrations from the mine drainage. It is accompanied by ochre concentrations of ferrihydrite $\text{Fe}_{10}\text{O}_{14}(\text{OH})_2$ and goethite FeOOH , which is the final product of the transformation of both the unstable nanominerals.

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. 60–90°) 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 (Maneck 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 $\text{Cu}_4\text{SO}_4(\text{OH})_6$ 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 $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ 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 ($\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$) forms light blue, dendritic aggregates composed of thin tabular crystals with sizes up to 1 mm. Much rarer in Radzimowice is devilline $\text{CaCu}_4(\text{SO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$. It occurs as thin needle crystals with lengths up to 2 mm, forming irregular, green-coloured aggregates with a pearly lustre. One of the typical sulphates occurring in the abandoned mine galleries at the Wilhelm Mine is woodwardite $\text{Cu}_6\text{Al}_2\text{SO}_4(\text{OH})_{16} \cdot 2 \cdot 3\text{H}_2\text{O}$. 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 $\text{CuAl}_4\text{SO}_4(\text{OH})_{12} \cdot 3\text{H}_2\text{O}$. 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 cyanotrychite $\text{Cu}_4\text{Al}_2\text{SO}_4(\text{OH})_{12} \cdot 2\text{H}_2\text{O}$, 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 wroewolfeite $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$. 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 $\text{Cu}_2\text{CO}_3(\text{OH})_2$, cuprite Cu_2O , 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 $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ 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, kańkite $\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$ is one of the most common iron arsenates. It occurs as earthy, monomineralic accumulations up to 40 cm in diameter. At natural humidity, kańkite 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 zýkaite $\text{Fe}_4(\text{AsO}_4)_3\text{SO}_4\text{OH} \cdot 2\text{H}_2\text{O}$ 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 $\text{Fe}_2\text{AsO}_4\text{SO}_4\text{OH} \cdot 7\text{H}_2\text{O}$. 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 $\text{Fe}^{3+}_{20}(\text{AsO}_4, \text{SO}_4)_{13}(\text{OH})_{24} \cdot 9\text{H}_2\text{O}$ (?). 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% Fe_2O_3 . It is accompanied by small amounts of aluminium (up to 0.74 wt% Al_2O_3), manganese (up to 0.10 wt% MnO), calcium (up to 0.13 wt% CaO), sodium (up to 1.53 wt% Na_2O), and potassium (up to 1.13 wt% K_2O). The As content in the analysed samples of pitticite varies widely, from 16.29 to 54.75 wt% As_2O_5 . It is negatively correlated with sulphur (from 0.59 to 7.80 wt% SO_3) and phosphorus (up to 5.04 wt% P_2O_5). The highest concentrations of phosphorus have been noted in the dripstones of beige coloured pitticite, on which bacterial colonies had developed.

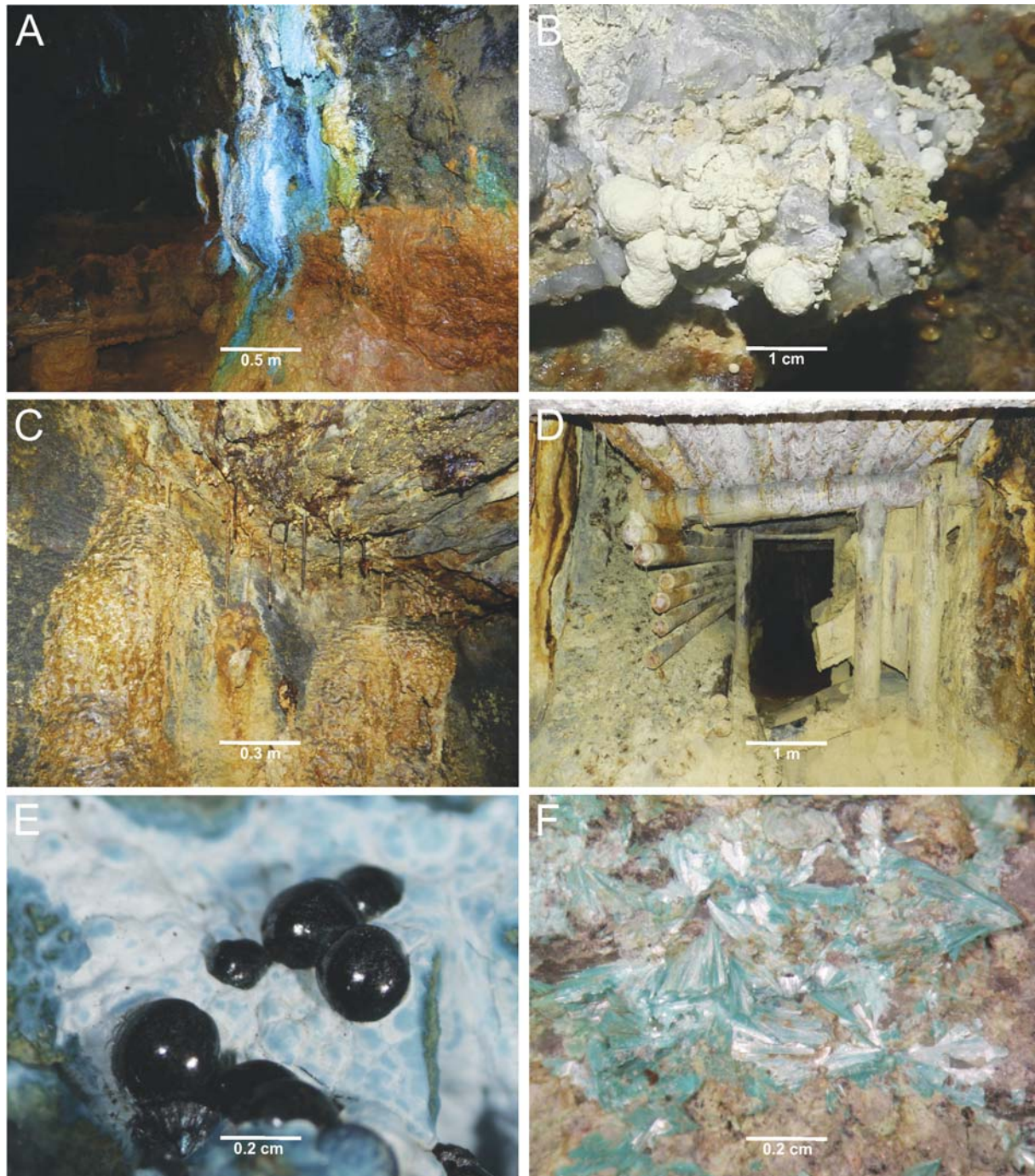
In contrast to Wieściszowice, the most common

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 $(\text{H}_3\text{O}, \text{K})\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ isomorphic 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 As_2O_5 wt %. The presence of melanterite $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ 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

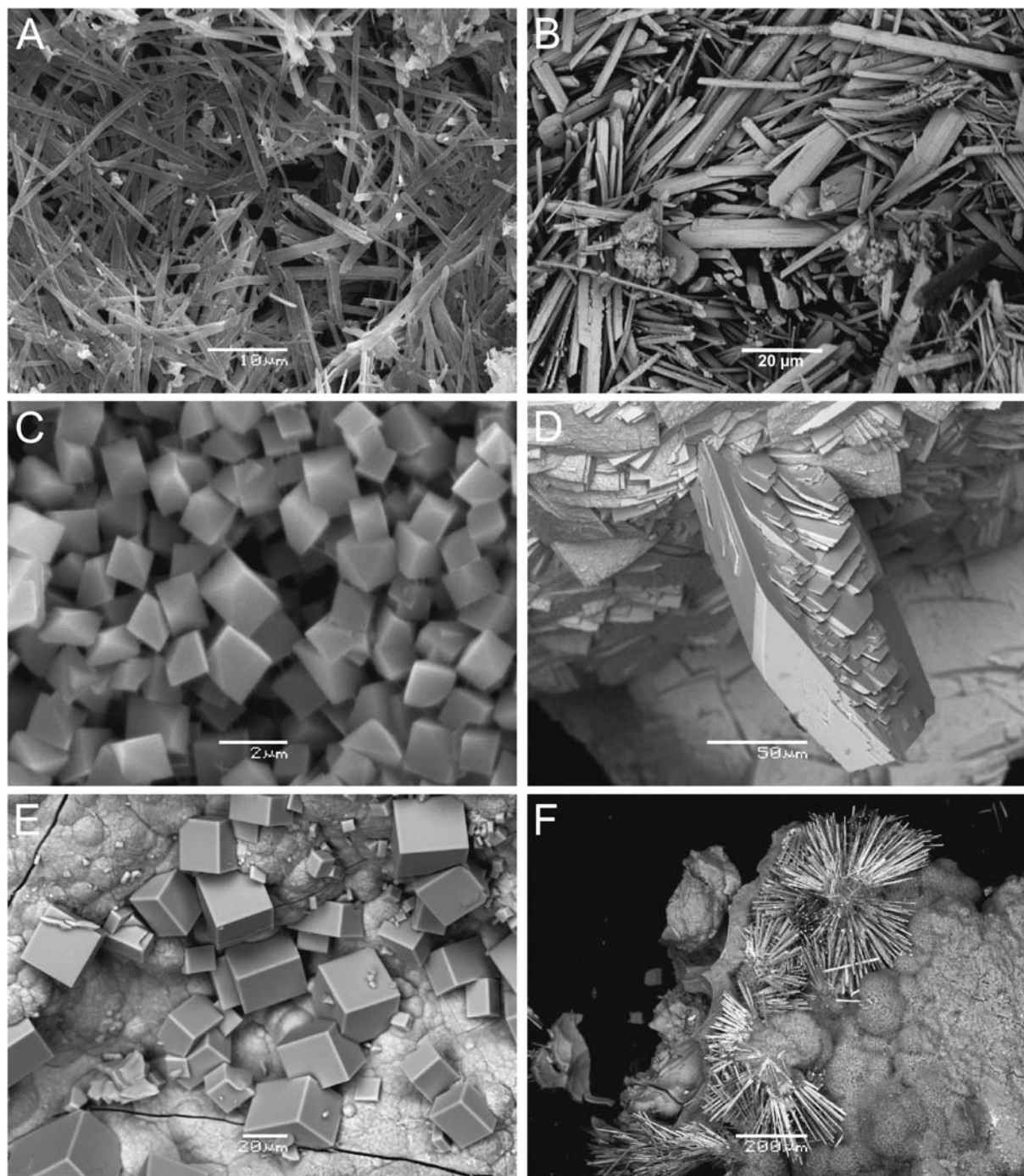
The polymetallic ore deposit in Miedzianka–Ciechanowice, today of historical significance, is situated in the eastern part of the metamorphic envelope of the Karkonosze granitoid massif. Ore mineralization occurs mainly in amphibolites, amphibolite or quartz-sericite schists, and skarns. Exploited from 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-



Text-fig. 3. A – blue dropstones of woodwardite from Radzimowice. B – puff-ball like aggregates of zýkaite from Radzimowice. C – dropstones of pitticite from Radzimowice. D – yellow accumulations of hydroniumjarosite from Radzimowice. E – dark green botryoidal aggregates of cornwallite-pseudomalachite on chrysocola surface (“Seggen Gottes” mine dump, Miedzianka). F – green aggregates of tyrolite from “Seggen Gottes” mine dump, Miedzianka

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



Text-fig. 4. SEM images of secondary minerals; A – prismatic zýkaite crystals from Radzimowice. B – acicular crystals of bukovskýite from Radzimowice. C – crystals of hydroniumjarosite from Radzimowice. D – aggregate of philipsburgite tabular crystals from “Seegen Gottes” mine dump, Miedzianka. E – a group of pseudocubic crystals of pharmacosiderite from “Seegen Gottes” mine dump, Miedzianka. F – acicular agardite-(Ce) crystals on chrysocolla from “Seegen Gottes” mine dump, Miedzianka

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, nickeline, löllingite, safflorite, 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: “Geseegener 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 ($\text{Cu}_{2-x}(\text{Al,Fe})_x\text{H}_{2-x}\text{Si}_2\text{O}_5(\text{OH})_4 \cdot n\text{H}_2\text{O}$ (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, to 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 $\text{Cu}_5(\text{AsO}_4, \text{PO}_4)_2(\text{OH})_4$ series (Holeczek and Janeczek 1991). They form botryoidal aggregates composed of short-prismatic, dark green crystals with sizes up to 3 mm (Text-fig. 3e). Aggregates of cornwallite–pseudomalachite 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 philipsburgite $(\text{Cu,Zn})_6(\text{AsO}_4, \text{PO}_4)_2(\text{OH})_6 \cdot \text{H}_2\text{O}$ 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 $\text{Cu}_2\text{AsO}_4\text{OH}$ 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 min-

erals form small, millimetre-sized aggregates. Spherulitic accumulations of bayldonite $\text{PbCu}_3(\text{AsO}_4)_2(\text{OH})_2$ and olivenite infill fractures in the amphibolites or overgrow chrysocolla. In the dumps of the “Seegen Gottes” Mine, clinoclase $\text{Cu}_3\text{AsO}_4(\text{OH})_3$ forms platy, dark blue crystals with sizes up to 5 mm, assembled in radial aggregates. Pharmacosiderite $\text{KFe}_4(\text{AsO}_4)_3(\text{OH})_4 \cdot 6-7\text{H}_2\text{O}$ 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 $\text{CaCuAsO}_4\text{OH}$ and tyrolite $\text{Ca}_2\text{Cu}_5(\text{AsO}_4)_4\text{CO}_3(\text{OH})_3 \cdot 11\text{H}_2\text{O}$. 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) $\text{CeCu}_6(\text{AsO}_4)_3(\text{OH})_6 \cdot 3\text{H}_2\text{O}$. 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 $\text{Cu}_2\text{PO}_4\text{OH}$ and yellow-green crusts of mottramite $\text{Pb}(\text{Cu,Zn})\text{VO}_4\text{OH}$ 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 co-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 Wieściszowice, 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-

cavations 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_{tot} 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 bukovskýite. On the basis of field observations conducted in New Zealand (Mains and Crow 2005) and thermodynamic data (Gas’kova *et al.* 2008), it can be assumed that after crystallization, melanterite reacts with arsenate ions and forms bukovskýite. Thermodynamic calculations of Majzlan *et al.* (2012), conducted for bukovskýite from Kaňki near Kutná Hora, confirm the observations from Radzimowice and indicate that the formation of bukovskýite takes place at high activity of sulphate and arsenate ions and over a narrow pH range (about 2.0–3.5). Zýkaite and kaňkite appear under similar conditions. Minerals of the jarosite group are also typical of the AMD environment (Baron and Palmer 1996; Norlund *et al.* 2010). In the abandoned mine galleries of the Wilhelm Mine, hydroniumjarosite and the members of the hydroniumjarosite–jarosite series mark the zone of waters with lowest pH. Crystals of hydroniumjarosite are also formed within the colonies of mi-

croorganisms dwelling in places of AMD drainage. With increasing distance from the AMD outflow, a gradual decline of hydroniumjarosite is observed in favour of schwertmannite. This mineral is a characteristic component precipitating from AMD at pH = 3–4 and containing high concentrations of sulphate ions, around 1.3 g/L (Bigham *et al.* 1996; Knorr and Blodau 2007; Yu *et al.* 2002; Regensburg *et al.* 2004; Aloune *et al.* 2015). Bukovskýite and zýkaite are also sensitive to pH increase, which causes a rapid decrease in the stability of these minerals in comparison to scorodite or kaňkite and in relation to pitticite (Majzlan *et al.* 2015). Scorodite forms beyond the zone dominated by hydroniumjarosite, in which a gradual pH increase to about 3.5 is observed. This corresponds to the data of Paktunc and Bruggeman (2010) and Krause and Ettl (1989) who indicated the high solubility of scorodite under conditions of low and high pH (i.e. <2 and > 6), with minimal solubility at about pH = 3–4. In the proximity of the scorodite accumulations occur also dripstones composed of amorphous 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 ferrihydrite with low crystallinity (e.g. Dove and Rimstidt 1985; Langmuir *et al.* 2006, Bluteau and Demopoulos 2007). Ferrihydrite is a phase that appears in larger amounts at pH exceeding 5.5 (Murad and Rojík 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 brochantite 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 (Malley *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 chalcocopyrite aggregates. Chrysocolla was formed next, intergrowing with massive malachite and pseudomalachite–cornwallite. These minerals are accompanied by inclusions of philipsburgite, bayldonite, and libethenite. 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 chalcocopyrite 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 chalcocopyrite 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

SULPHATE AND ARSENATE MINERALS AS ENVIRONMENTAL INDICATORS

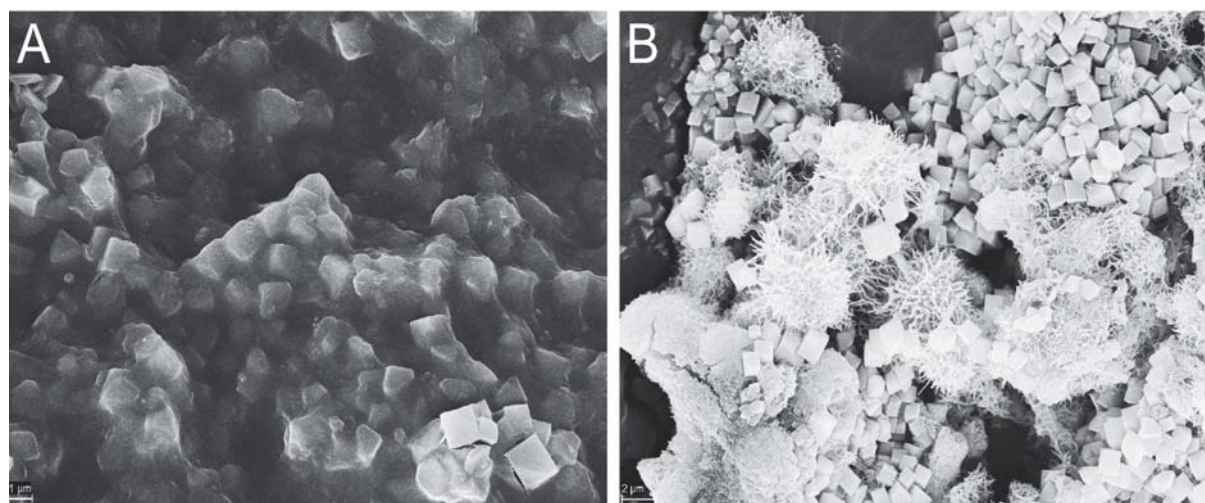
main role of sulphur microorganisms under oxidizing conditions is a significant acceleration of the oxidation processes. A clear example is the oxidation of Fe^{2+} in acidic solutions. Although this process is thermodynamically favoured, it occurs very slowly. Enabling enzyme-catalysed reactions in 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 $0.3 - 3 \times 10^{-9}$ mol/m²/s, respectively. For comparison, the biological rate of Fe^{2+} oxidation and pyrite were 5×10^{-7} mol/L/s and 8.8×10^{-8} 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 Fe^{2+} 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 Fe^{3+} . 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

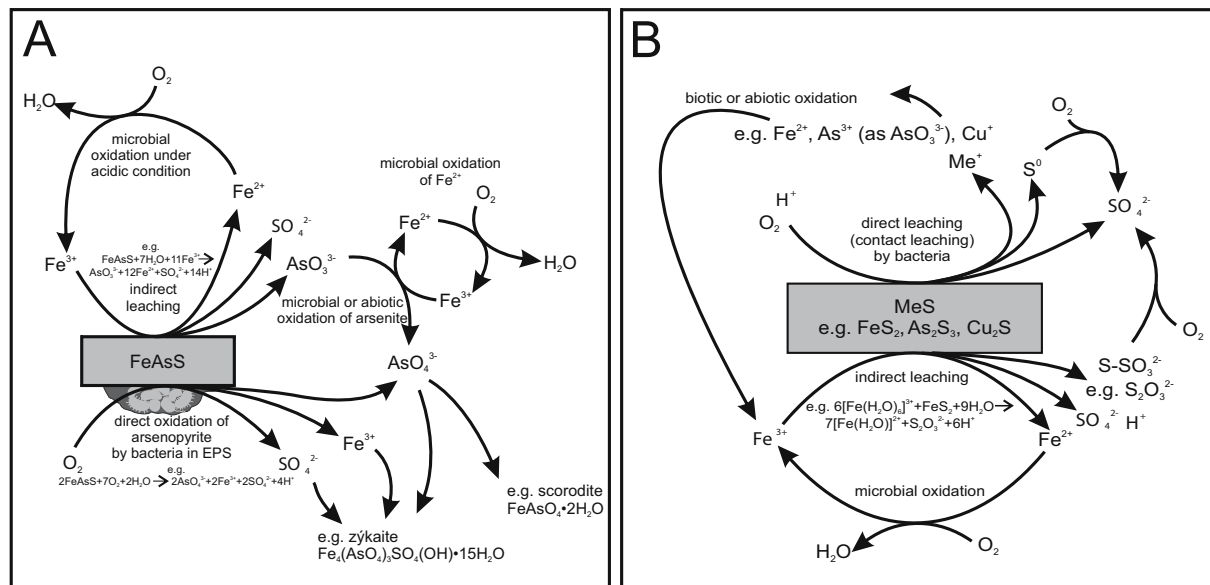
and the supergene mineral phases. In SEM pictures there can be found microbial cells embedded in EPS which may be produced in large quantities and can build the structure of microbial mats. On SEM images of the slime streamers from Radzimowice (Text-fig. 5a, b) can be seen the presence of mineral phases (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 Fe^{2+} . 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 SO_4^{2-} and Fe^{3+} . 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



Text-fig. 5. Microbial slime streamers from "Wilhelm" mine in Radzimowice. A – hydroniumjarosite suspended in EPS. B – hydroniumjarosite and schwertmannite on the EPS surface of microbial community



Text-fig. 6. The most important reactions associated with the oxidation of sulphide minerals (A) and biotransformation of arsenic minerals (B) taking place under hypergene conditions

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 CO_2 . 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 Fe^{3+} ions (Text-fig. 6b). As a result of these processes in acidic environments the typical assemblages of arsenic minerals containing AsO_4^{3-} 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.

Acknowledgements

The remarks and comments by the journal referees, Justyna Ciesielska, Ray MacDonald, and an anonymous one, helped to improve the final version of the present paper.

REFERENCES

- Aloune, S.H. Hiroyoshi, N. and Ito, M. 2015. Stability of As(V)-sorbed schwertmannite under porphyry copper mine conditions. *Minerals Engineering*, **74**, 51–59.
- Alwan, A.K. and Williams P.A. 1979. Mineral formation from aqueous solution, Part II. The stability of langite, $\text{Cu}_2\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$. *Transition Metal Chemistry*, **4**, 319–322.
- Baron, D. and Palmer C.D. 1996. Solubility of jarosite at 4–35 °C. *Geochimica et Cosmochimica Acta*, **60**, 185–195.
- Bigham, J.M., Schwertmann, U., Traina, S.J., Winland, R.L. and Wolf, M. 1996. Schwertmannite and the chemical

- modeling of iron in acid sulfate waters. *Geochimica et Cosmochimica Acta*, **60**, 2111–2121.
- Bluteau, M.-C. and Demopoulos, G.P. 2007. The incongruent dissolution of scorodite – Solubility kinetics and mechanism. *Hydrometallurgy*, **87**, 163–177.
- Borkowski, A., Parafiniuk, J., Wolicka D. and Kowalczyk P. 2013. Geomicrobiology of Acid Mine Drainage in the weathering zone of pyrite-bearing schists in the Rudawy Janowickie Mountains (Poland). *Geological Quarterly*, **57**, 601–612.
- Chukhlantsev, V.G. 1956. The solubility products of a number of arsenates. *Journal of Analytical Chemistry of the USSR*, **11**, 565–571.
- Dove, P.M. and Rimstidt, J.D. 1985. The solubility and stability of scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$. *American Mineralogist*, **70**, 838–844.
- Dunn, P.J. 1982. New data for pitticite and a second occurrence of yukonite at Sterling Hill, New Jersey. *Mineralogical Magazine*, **46**, 261–264.
- Dziekoński, T. 1972. Wydobywanie i metalurgia kruszców na Dolnym Śląsku od XIII do połowy XX wieku. Ossolineum; Wrocław.
- Filippi, M., Goliáš, V. and Pertold, Z. 2004. Arsenic in contaminated soils and anthropogenic deposits at the Mokrsko, Roudný, and Kašperské Hory gold deposits, Bohemian massif *Czech Environmental Geology*, **45**, 716–730.
- Frost, R.L., Xi, Y., Palmer, S.J. and Tan, K. 2011. Molecular structural studies of the amorphous mineral pitticite $\text{FeAsO}_4 \cdot \text{SO}_4 \cdot \text{H}_2\text{O}$. *Journal of Molecular Structure*, **1005**, 78–82.
- Gas'kova, O.L., Shironosova, G.P. and Bortnikova, S.B. 2008. Thermodynamic Estimation of the Stability Field of Bukovskýite, an Iron Sulfoarsenate. *Geochemistry International*, **46**, 85–91.
- Gieré, R., Sidenko, N.V. and Lazareva, E.V. 2003. The role of secondary minerals in controlling the migration of arsenic and metals from high-sulfide wastes (Berikul gold mine, Siberia). *Applied Geochemistry*, **18**, 1347–1359.
- Holeczek, J. and Janeczek, J. 1991. Pseudomalachite from Radzimowice and some comments on its occurrence in Miedzianka (Sudetes Mts.). *Mineralogia Polonica*, **22**, 17–26.
- Jaskólski, S. 1964. On the origin of pyrite schists at Wieściszowice (Lower Silesia). *Annales Societatis Geologorum Poloniae*, **34**, 29–64. [In Polish]
- Kim, J.J. and Kim, S.J. 2004. Seasonal factors controlling mineral precipitation in the acid mine drainage at Dongha coal mine, Korea. *Science of the Total Environment*, **325**, 181–191.
- Knorr, K.-H. and Blodau, C. 2007. Controls on schwertmannite transformation rates and products. *Applied Geochemistry*, **22**, 2006–2015.
- Krause, E. and Ettl, V.A. 1989. Solubilities and stabilities of ferric arsenate compounds. *Hydrometallurgy*, **22**, 311–337.
- Kubisz, J. 1964. Studies on supergene sulphate minerals occurring in Poland. *Prace Geologiczne Komisji Nauk Geologicznych PAN*, **26**, 1–76. [In Polish]
- Langmuir, D., Mahoney, J. and Rowson, J. 2006. Solubility products of amorphous ferric arsenate and crystalline scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and their application to arsenic behavior in buried mine tailings. *Geochimica et Cosmochimica Acta*, **70**, 2942–2956.
- Magalhaes, M.C.F., Pedrosa de Jesus, J.D. and Williams, P.A. 1988. The chemistry of formation of some secondary arsenate minerals of Cu(II), Zn(II) and Pb(II). *Mineralogical Magazine*, **52**, 679–690.
- Mains, D. and Crow, D. 2005. Composition and mineralogy of historic gold processing residues, east Otago, New Zealand. *New Zealand Journal of Geology and Geophysics*, **48**, 641–647.
- Majzlan, J., Łazić, B., Armbruster, T., Johnson, M.B., White, M.A., Fisher, R.A., Plášil, J., Loun, J., Škoda, R. and Novák, M. 2012. Crystal structure, thermodynamic properties, and paragenesis of bukovskýite, $\text{Fe}_2(\text{AsO}_4)(\text{SO}_4)(\text{OH}) \cdot 9\text{H}_2\text{O}$. *Journal of Mineralogical and Petrological Sciences*, **107**, 133–148.
- Majzlan, J., Amoako, F.Y., Kindlova, H. and Drahotka, P. 2015. Thermodynamic properties of zykaite, a ferric sulfoarsenate. *Applied Geochemistry*, **61**, 294–301.
- Maley, M., van Bronswijk, W. and Watling, H.R. 2009. Leaching of a low-grade, copper-nickel sulfide ore. 3. Interactions of Cu with selected sulfide minerals. *Hydrometallurgy*, **98**, 73–80.
- Marani, D., Patterson, J.W. and Anderson, P.R. 1995. Alkaline precipitation and aging of Cu(II) in the presence of sulfate. *Water Research*, **29**, 1317–1326.
- Marini, L., Saldi, G., Cipolli, F., Ottonello, G. and Zuccolini, M.V. 2003. Geochemistry of water discharges from the Libiola mine, Italy. *Geochemical Journal*, **37**, 199–216.
- Makuch, M. and Stolarczyk, T. 2013. Miedzianka 700 lat dziejów górniczego miasta, pp. 1–149. Legnica.
- Maneck, M. 1965. Mineralogical and petrographical study of ore veins of the vicinity of Wojcieszów (Lower Silesia). *Prace Mineralogiczne*, **2**, 1–90. [In Polish]
- Mazur, S., Aleksandrowski, P., Kryza, R. and Oberc-Dziedzic, T. 2006. The Variscan Orogen in Poland. *Geological Quarterly*, **50**, 89–118.
- Mikulski, S.Z. 2005. Geological, mineralogical and geochemical characteristics of the Radzimowice Au-As-Cu deposit from the Kaczawa Mountains (Western Sudetes, Poland): an example of the transition of porphyry and epithermal style. *Mineralium Deposita*, **39**, 904–920.
- Mikulski, S.Z. 2007. The late Variscan gold mineralization in the Kaczawa Mountains, Western Sudetes. *Polish Geological Institute Special Papers*, **22**, 1–162.

- Mochacka, K. 1982. Polymetallic mineralization of the eastern metamorphic cover of the Karkonosze Granite and its connection with the geologic evolution of the area. *Biuletyn Instytutu Geologicznego*, **341**, 273–289. [In Polish]
- Moncur, M.C., Janbor, J.L., Ptacek, C.J. and Blowes, D.W. 2009. Mine drainage from the weathering of sulfide minerals and magnetite. *Applied Geochemistry*, **24**, 2362–2373.
- Murad, E. and Rojtk, P. 2003. Iron-rich precipitates in a mine drainage environment: Influence of pH on mineralogy. *American Mineralogist*, **88**, 1915–1918.
- Nordstrom, D.K. and Alpers, C.N. 1999. Geochemistry of acid mine waters. In: Plumlee G., Logsdon M. (Eds), *The Environmental Geochemistry of Mineral Deposits. Part A. Processes, methods and health issues. Reviews in Economic Geology*, **6**, 133–160.
- Norlund, K.L.I., Baron, C. and Warren, L.A. 2010. Jarosite formation by an AMD sulphideoxidizing environmental enrichment: implications for biomarkers on Mars. *Chemical Geology*, **275**, 235–242.
- Paktunc, D. and Bruggeman, K. 2010. Solubility of nanocrystalline scorodite and amorphous ferric arsenate: Implications for stabilization of arsenic in mine wastes. *Applied Geochemistry*, **25**, 674–683.
- Parafiniuk, J. 1991. Fibroferrite, slavikite and pickeringite from the oxidation zone of pyritebearing schists in Wieściszowice (Lower Silesia). *Mineralogia Polonica*, **22**, 3–15.
- Parafiniuk, J. 1996. Sulfate minerals and their origin in the weathering zone of the pyrite-bearing schists at Wieściszowice (Rudawy Janowickie Mts, Western Sudetes). *Acta Geologica Polonica*, **46**, 353–414.
- Parafiniuk, J. and Siuda R. 2006. Schwertmannite precipitated from acid mine drainage in the Western Sudetes (SW Poland) and its arsenate sorption capacity. *Geological Quarterly*, **50**, 475–486.
- Parafiniuk, J., Dobrzycki, Ł. and Woźniak, K. 2010. Slavikite – Revision of chemical composition and crystal structure. *American Mineralogist*, **95**, 11–18.
- Piestrzyński, A. and Salamon, W. 1977. New data on polymetallic mineralization of quartz veins in pyrite deposit from Wieściszowice (Lower Silesia). *Kwartalnik Geologiczny*, **21**, 27–35.
- Pollard, A.M., Thomas, R.G. and Williams, P.A. 1992. The stabilities of antlerite and $\text{Cu}_3\text{SO}_4(\text{OH})_4 \cdot 2\text{H}_2\text{O}$: their formation and relationship to other copper(II) sulphate minerals. *Mineralogical Magazine*, **56**, 359–365.
- Regensburg, S., Brand, A. and Peiffer, S. 2004. Formation and stability of schwertmannite in acid mining lakes. *Geochimica et Cosmochimica Acta*, **68**, 1185–1197.
- Rimstidt, J.D., Chermak, J.A. and Gagen, P.M. 1994. Rates of reaction of galena, sphalerite, chalcopyrite and arsenopyrite with Fe(III) in acidic solutions. *ACS Symposium Series: Environmental Geochemistry of Sulfide Oxidation*, **1**, 2–13.
- Robins, R.G. 1987. Solubility and stability of scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$: Discussion. *American Mineralogist*, **72**, 842–844.
- Sand, W. and Gehrke, T. 2006. Extracellular polymeric substances mediate bioleaching/biocorrosion via interfacial processes involving iron (III) ions and acidophilic bacteria. *Research in Microbiology*, **157**, 49–56.
- Sand, W., Gehrke, T., Hallmann, R. and Schippers, A. 1995. Sulfur chemistry, biofilm and the (in)direct attack mechanism – a critical evaluation of bacterial leaching. *Applied Microbiology and Biotechnology*, **43**, 961–966.
- Siuda, R. 2012. Silver minerals from Friederike Juliane Mine at Ciechanowice (Sudety Mts, Poland). *Biuletyn Państwowego Instytutu Geologicznego*, **448**, 315–324.
- Siuda, R. and Gołębiowska, B. 2011. Nowe dane o minerałach wietrzeniowych złoża Miedzianka-Ciechanowice w Rudawach Janowickich (Dolny Śląsk, Polska). *Przegląd Geologiczny*, **59**, 226–234.
- Siuda, R. and Kruszewski, Ł. 2006. New data on bayldonite, cornwallite, olivenite and philipsburgite from Miedzianka (Rudawy Janowickie Mts., Sudetes, Poland). *Mineralogia Polonica Special Papers*, **28**, 202–204.
- Siuda, R. and Kruszewski, Ł. 2013. Recently formed secondary copper minerals as indicators of geochemical conditions in an abandoned mine in Radzimowice (SW Poland). *Geological Quarterly*, **57**, 583–600.
- Siuda, R. and Borzęcki, R. 2014. Relikty górnictwa i hutnictwa rejonu złoża Miedzianka-Ciechanowice jako obiekty geoturystyczne. *Przegląd Geologiczny*, **62**, 397–402.
- Tumiati, S., Godard, G., Masciocchi, N., Martin, S. and Monticelli, D. 2008. Environmental factors controlling the precipitation of Cu-bearing hydroxalcalite-like compounds from mine waters. The case of the “Eve verda” spring (Aosta Valley, Italy). *European Journal of Mineralogy*, **20**, 73–94.
- Yu, J.Y., Park, M. and Kim, J. 2002. Solubilities of synthetic schwertmannite and ferrihydrite. *Geochemical Journal*, **36**, 119–132.
- Zimnoch, E. 1965. New data about ore mineralization in Stara Góra deposit. *Biuletyn Geologiczny Wydziału Geologii UW*, **5**, 3–38. [In Polish]
- Zimnoch, E. 1978. Ore mineralization of the Miedzianka deposit in the Sudetes. *Biuletyn Instytutu Geologicznego*, **308**, 91–134.