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Schwertmannite precipitated from acid mine drainage in the Western Sudetes (SW Poland) and its arsenate sorption capacity

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This paper contains XRD, Mössbauer and IR spectroscopy, chemical composition and thermal analysis results for the mineral schwertmannite present in the weathering zone developed in two abandoned sulphide mines in the Sudetes (SW Poland). In Wieściszowice a pyrite deposit was exploited, and in Radzimowice the deposit consisted of polymetallic mineralization with predominant arsenopyrite. In both localizations schwertmannite is developed as dripstones in underground workings and loose sediments precipitating from the acid mine drainage (AMD) waters. Schwertmannite forms tiny, needle-like crystals 2–3 μm in size, usually grouped in botryoidal aggregations. The chemical composition of schwertmannite from Wieściszowice is typical for this mineral, and in Radzimowice the mineral contains up to 5.20 wt. % of As_2O_5. Due to highly developed specific surface and structural features, schwertmannite has the strongest sorption capabilities among the components of ochres, and takes up the largest amounts of arsenate oxyanion from AMD, as well as considerable amounts of phosphates and heavy metals. About 71–87% of arsenate is sorbed on to the surface of the schwertmannite crystals and may readily be released into solution, 12–30% is bound into the structure of the mineral, and about 1% is an admixture of insoluble ferric arsenates.

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INTRODUCTION

Iron oxyhydroxides, known as ochres, are important products of weathering of sulphide minerals such as pyrite, marcasite, pyrrhotite, chalcopyrite and arsenopyrite. They are common in numerous ore deposits, as well as in some rocks, sediments, soils and industrial wastes. Generally, they form very fine grains with poorly crystalline structure and are a mixture of various phases, usually with an admixture of local material. A stable iron mineral in ochres is goethite, which is easily identifiable by X-ray analysis. In low pH conditions, typical of sulphide-weathering environments, large amounts of deposits, described formerly as amorphous iron hydroxides, are precipitated. A more detailed study of those deposits shows that they are poorly crystalline and demonstrate a short-range structural order. The most important of the minerals of this type distinguished until now are iron oxyhydroxide-ferrihydrite and an iron oxyhydroxysulphate-schwertmannite.

Schwertmannite is one of the main phases precipitating from acid mine drainage (AMD) waters, although problems with its identification meant that, as a mineral species, it was recognized only recently (Bigham *et al*., 1994). At present, it may be understood as a ferric mineral, typical of acid aqueous environments (pH 2–4), rich in sulphates. Schwertmannite seems to be the first mineral formed after oxidation and hydrolysis of Fe(II)-SO_4 solution acidulated up to pH 5–6 (Regenspurg *et al*., 2004). The schwertmannite from Wieściszowice and Radzimowice described herein is the first documented occurrence of this mineral in Poland, but it is probably much more widespread. It may be expected in sediments precipitating from AMD from other abandoned or operating sulphide or coal mines, mine waste dumps, and so on. A suit of selected methods (SEM, XRD, Mössbauer and IR spectroscopy, chemical analyses, thermal analyses, sorption capacity) were employed to verify their usability for schwertmannite identification and study.

AMD, with a chemical composition developed through complex processes of sulphide oxidation and acidic solution — rock interaction, is presently a subject of intense interest of geochemists, hydrogeologists, environment engineers, and microbiologists (Bigham *et al*., 1990; Kawano and Tomita, 2001; Kim *et* *al*., 2002; Baker and Banfield, 2003; Murad and Rojik, 2003; Kim and Kim, 2004). It constitutes a serious hazard for the natural environment by polluting soil, surface and underground waters with considerable amounts of sulphates and various metals, also with toxic heavy metals, aluminium, arsenic, and so on (Garcia-Sanchez and Alvarez-Ayuso, 2003). The chemical composition of AMD is largely controlled by ochreous precipitates, among which the mineral schwertmannite plays a fundamental role. This mineral, due to its high surface area and specific structure with tunnel cavities, is characterized by an exceptionally high sorption capability. It may well scavenge toxic components released in the weathering zone, preventing them from rapidly migrating into surface or underground waters. However, this mineral is metastable, thus its solubility due to dilution of AMD and increase of pH leads to gradual release of sorbed components (Yu *et al*., 1999; Yu *et al*., 2002).

The results of experimental work and field observations show a potentially significant role of schwertmannite in retaining of arsenic within AMD (Fukushi *et al*., 2004; Regenspurg and Peiffer, 2005). Sampling schwertmannite developed in two weathering zones, that are different in their mineral composition, should allow assessment of the role of this mineral in the sorption of arsenic in the natural environment. In Wieściszowice virtually the only weathering sulphide is pyrite. Sulphate minerals are predominant among the products of weathering, with no arsenic present (Parafiniuk, 1996). In the weathering zone of the polymetallic deposit at Radzimowice, where arsenopyrite predominates, numerous weathering arsenate minerals are formed (Siuda, 2004).

GEOLOGICAL SETTING

The pyrite deposit at Wieściszowice is located in the Rudawy Janowickie Complex (Western Sudetes), about 25 km east of Jelenia Góra. In the Wieściszowice area the Rudawy Janowickie Complex comprises metamorphic rocks, belonging to the Leszczyniec Unit (Fig. 1). These are mafic and felsitic rocks metamorphosed under greenschist and epidote-amphibolite facies (Teisseyre, 1973; Kryza *et al*., 1995), dated to around 500 Ma (Oliver *et al*., 1993). This complex is interpreted as a metasedimentary-volcanic succession of the Saxothuringian oceanic basin (Mazur and Aleksandrowski, 2001; Mazur, 2002). Within the Leszczyniec Unit, two formations are distinguished. The older is the Czarnów Schists Formation, made up of various schists, leptynite, quartzites and amphibolites, with subordinate dolomitic marble. The younger is volcanogenic Leszczyniec Formation, made up of metavolcanites, amphibolites, greenstones and schists (Teisseyre, 1973). Pyrite mineralization is present in sericite-chlorite schists, belonging to the Leszczyniec Formation, extending for four kilometres between Wieściszowice and Mount Wielka Kopa. The outcrop width of the schists is about 200 m. The deposit has an exhalative-sedimentary origin, associated with submarine lavas (Jaskólski, 1964). The upper part of the deposit comprises chlorite schists. Below them occur pyrite-bearing sericite-chlorite schists. These are composed of fine-grained quartz, sericite, chlorite and albite, in various proportions. Fine-grained calcite also occurs. The pyrite-bearing schists are underlain by quartz schist. Pyrite forms tiny, up to 0.5 cm in size, euhedral or subhedral crystals, scattered in the rock mass. The richest parts of the deposit contain about 30% of pyrite, and the average is 10%. The deposit is virtually monomineralic; only in the quartz veins some traces of sulphides and sulphosalts of Cu, Pb, and Zn have been found (Piestrzyński and Salomon, 1977).

Pyrite exploitation in Wieściszowice started in 1785 and continued, with interruptions, until 1925, first by quarrying, followed by underground mining. The mine remains includ three open pits, buried mine shafts and short adits starting at the bottom of the open pits. The bottom of the largest excavation

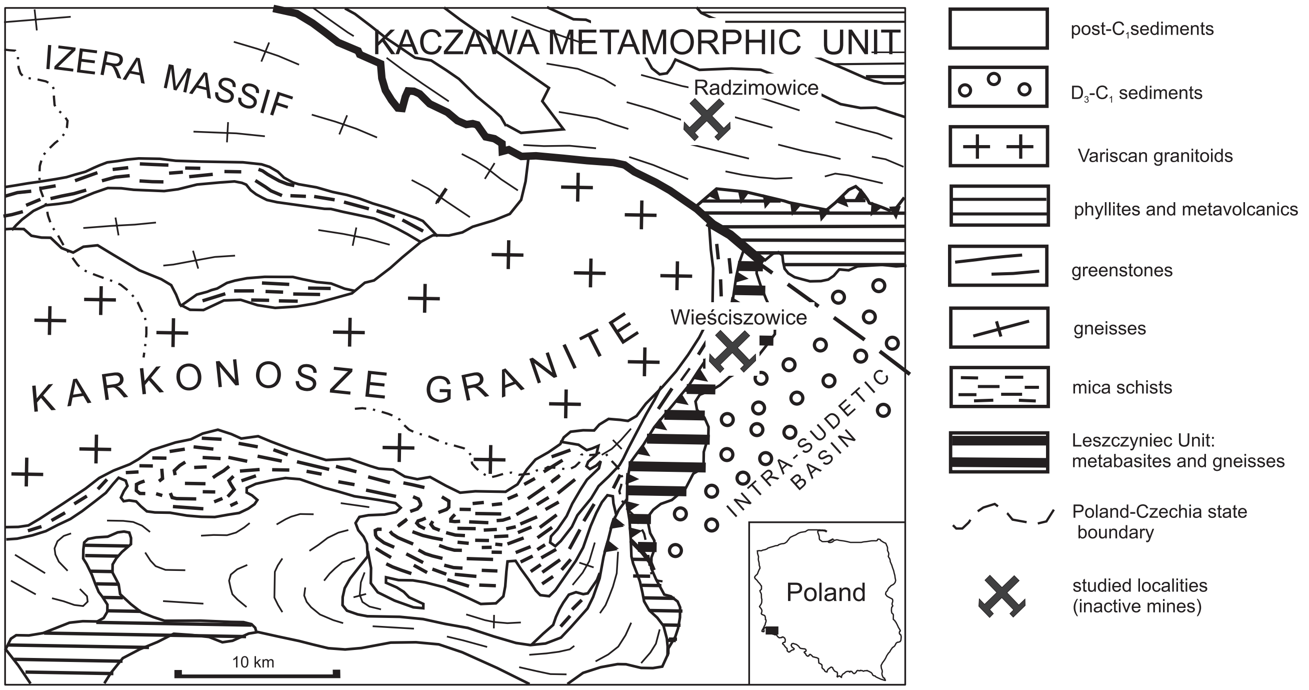

Fig. 1. Locality map of the Wieściszowice and Radzimowice deposits in the Western Sudetes (modified after Mazur *et al*., 2006)

holds a "Purple Pond", with characteristic red-brown coloured water, accumulating the soluble products of weathering of the deposit. Just below the pit large mine-waste dumps of reworked rock material are present. The area of the abandoned pyrite mine constitutes probably the best-developed weathering zone of sulphide ore in Poland. As a result of pyrite oxidization and of interaction of acid mine drainage with chlorite-sericite schists, a paragenesis of supergene sulphate minerals of Fe, Mg, Al and Ca has arisen (Parafiniuk, 1996). In numerous places ochreous sediments, produced by hydrolysis of ferric sulphate, have accumulated.

The polymetallic deposit of Radzimowice, also known as "Stara Góra" lies about 25 km to the NE of Jelenia Góra, within the Radzimowice Unit belonging to the Kaczawa Metamorphic Complex (Western Sudetes; Fig. 1). The Radzimowice Unit is built mainly of Lower Palaeozoic quartz-sericite and quartz-sericite-graphite schists, which were produced by metamorphism of shaly flysch-type sedimentary rocks at greenschist facies (Baranowski *et al*., 1990; Kryza and Muszyński, 2003). The schists are crosscut by Early Carboniferous volcanic rocks building up dykes and subvolcanic intrusions. The largest of these is the volcanic complex of Żelaźniak Hill covering around 3 km^2, built up of rhyolites and related volcanic rocks. It is probably a remnant of a lava dome with the volcano vent uncovered by erosion (Muszyński and Machowiak, 2000; Mikulski, 2005). Within the rhyolite of Żelaźniak and Bukowinka Hills a fine- and medium-grained granite body is present. The Radzimowice schists and rhyolites are crosscut by lamprophyres (kersantites), which form small dykes and veins 2.5 to 8 m thick (Manecki, 1965).

The "Stara Góra" deposit at Radzimowice is built up of a set of six more or less parallel major ore veins crosscutting Radzimowice schists and volcanic rocks and trending E–W. Their thickness varies from few centimetres up to about 1.5 metres and they are 300–350 m long on average, through the "Miners Consolation" vein is about 2 km long. The veins show a diverse mineral composition. The most common minerals present are arsenopyrite, chalcopyrite, pyrite, marcasite, galena and sphalerite, while bournonite, boulangerite, tetrahedrite, bismuth, gold, löllingite, stibnite and cobaltite have also been reported (Manecki, 1965; Zimnoch, 1965; Mikulski *et al*., 2003; Mikulski, 2005).

The deposit was exploited from the middle of 15th century up until 1925. The main subject of exploitation was the gold-bearing arsenopyrite and chalcopyrite. The prospecting carried out in the 1950s revealed very limited reserves of the deposit. The remains of the mining activity are an extended system of adits and shafts of the "Stara Góra" mine, presently accessible down to 120 m below the ground level, mine dumps and remnants of an arsenic smelter.

Weathering processes have been accelerated by exposure of the ore veins in the mine workings. In the 60 years since the last mining activity a considerable array of secondary minerals of Fe, Cu, Pb, Zn, Ca and Mg have developed (Siuda, 2001, 2004). The most rapidly accumulated ochreous precipitates in the underground workings locally are up to several metres thick.

METHODS

For this study 12 samples of schwertmannite were taken from the underground workings of the "Stara Góra" abandoned mine in Radzimowice. All the available levels of the mine were sampled. In the Wieściszowice abandoned mine 8 samples were collected from adits, the open pit and the bed of the Rusty Stream that drains the mine area. To avoid humidity changes, the mineral samples were collected into tightly-sealed plastic containers. The samples transported to the laboratory were stored at a temperature of about +5°C. The samples of schwertmannite analyzed were centrifuged to separate them from associated liquid, subsequently dried at room temperature, and then ground in a mortar. The mineral composition of 16 samples selected for wet chemical analysis was examined by X-ray diffraction. Subsequently, they were dissolved in 1:1 nitric acid. AMD waters (20 samples) were filtered through a membrane pore diameter of 0.45 μm and acidified with nitric acid. They were stored in plastic containers at a temperature of +5°C.

X-ray powder diffraction patterns were recorded using a *PHILIPS X`PERT* diffractometer with CuKα source and graphite monochromator, with step increments of 0.02 2 theta/s (AGH University of Science and Technology, Kraków). Chemical analysis of the ochre and AMD water samples were carried out by ACP-MS methods (Faculty of Chemistry, Warsaw University). The chemical composition of the schwertmannite was analyzed at the Inter-Institute Analytical Complex for Minerals and Synthetic Substances, Warsaw University, with a *Cameca SX-100* electron microprobe operating in the WDS mode. Fe_2O_3 (Fe), chalcopyrite (Cu), galena (Pb), orthoclase (K, Al), diopside (Ca, Si), GaAs (As), ZnS (S) were used as reference minerals. The accelerating voltage was 15 kV, the beam diameter 10 μm. Thermal analysis was carried out with a Paulik-Paulik-Erdey derivatograph at a heating rate of 10°/min in air with 200 mg of sample and Al_2O_3 as an inert reference material. A *PHILIPS XL 20* scanning microscope, coupled with *EDS EDAX SYSTEM DX 4.1* a spectrometer , was used for observations of crystal morphology of the schwertmannite, at an accelerating voltage of 25 kV (Faculty of Geology, Warsaw University). IR absorption spectra were recorded with a *Nicolet Magna 550* spectrometer from 4000 to 400 cm^{-1}, using KBr pellets (Faculty of Chemistry, Warsaw University). Mössbauer spectra were recorded from samples mixed with two parts sugar using a 57Co in Rh matrix source (Institute of Nuclear Chemistry and Technology in Warsaw). The spectra were recorded at room temperature (293 K) and at the temperature of liquid nitrogen (77 K). The specific surface of ochreous precipitates was determined with an argon sorption method using a Brauner-Emmett-Teller apparatus (AGH University of Science and Technology, Kraków).

For comparison a synthetic schwertmannite was prepared by hydrolysis of iron chloride with an admixture of sodium sulphate according to the method of Schwertmann and Cornell (2000).

MODE OF OCCURRENCE OF SCHWERTMANNITE

In Radzimowice schwertmannite is abundant in a relatively narrow weathering zone developed ore veins that are composed of pyrite and marcasite. The width of these zones ranges to a maximum of several metres. In the surface streams, draining the vicinity of the Radzimowice abandoned mine, schwertmannite does not precipitate due to rapid neutralization through dilution. At Wieściszowice schwertmannite is a widespread mineral, occurring in exposed parts of the deposit and in the workings of the abandoned mine. Its formation is triggered by intense processes of pyrite oxidization and a significant decrease in the pH of the mine waters. It can also be found on waste dumps of reworked rock material, and at outflows of AMD water. Schwertmannite has also precipitated on the bed of the Rusty Stream, just below the place were AMD waters mix with neutral surface waters. Here large amounts of ochreous sediments have formed (Fig. 2).

In the underground workings of Radzimowice and Wieściszowice schwertmannite creates cryptocrystalline, soft stalactites. The largest of these forms found at Radzimowice is 70 cm long but they usually do not exceed 20 cm. On their surface, transparent, gelatinous masses of microbial colonies often occur. This indicates a specific role of iron bacteria in the formation of the mineral. In places schwertmannite coatings and dripstones have covered the walls of the mine workings. Schwertmannite is also a component of loose ochreous sediments, to 2 metres thick, which were deposited in some parts of the underground workings. In the adits

Fig. 2. Field occurrences of studied AMD and mineralization

A — Purple Pond filling the bottom of the abandoned mine excavation at Wieściszowice; **B** — the Rusty Stream with ochreous precipitates at Wieściszowice; **C** — schwertmannite stalactite (30 cm long) in an old adit (Radzimowice); **D** — schwertmannite accumulation developed near an oxidised pyrite vein (Radzimowice); **E** — loose schwertmannite deposits in the mine gallery floor (Radzimowice); **F** — microbial colonies (pale) on the schwertmannite stalactites (Radzimowice)

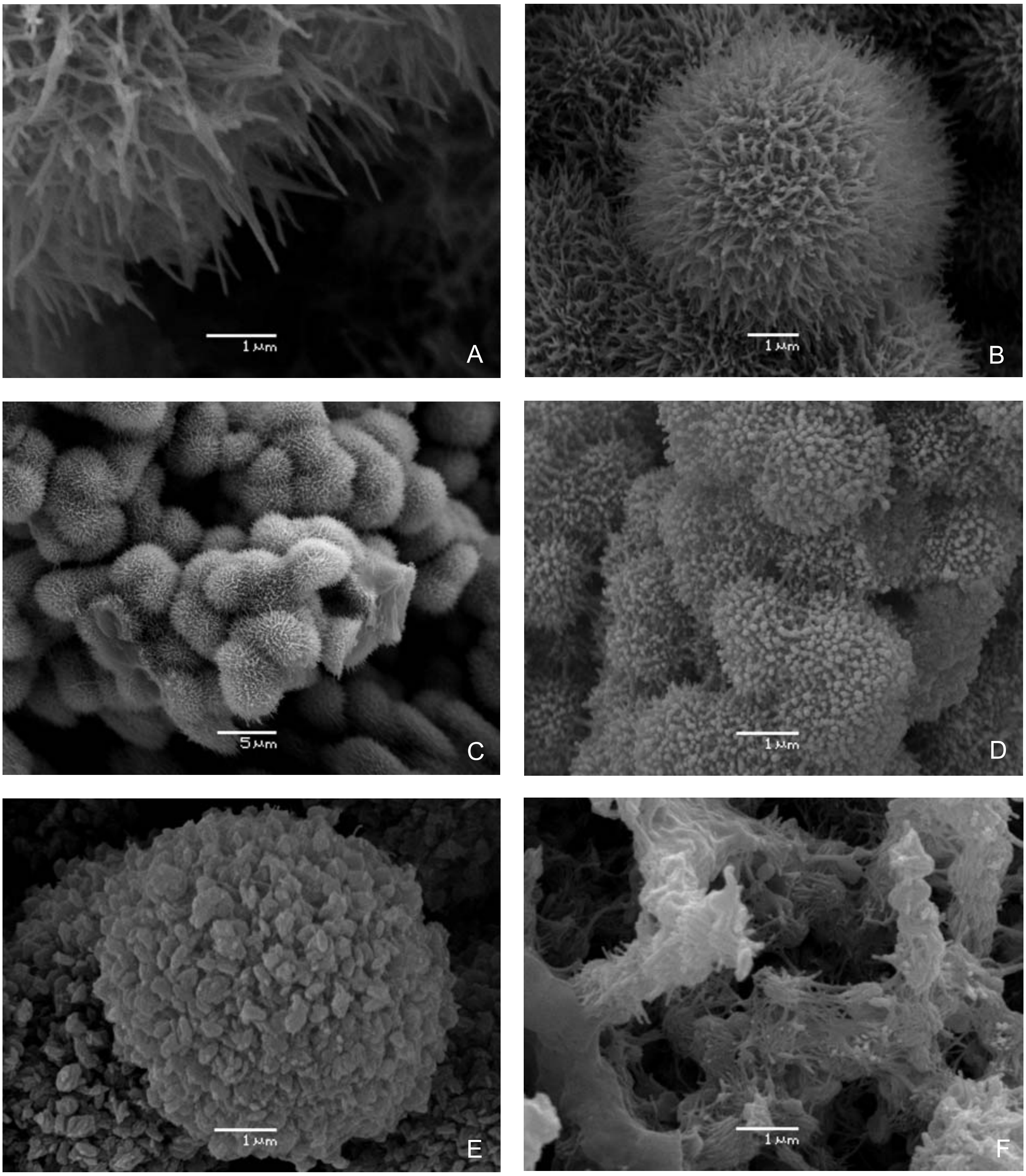

Fig. 3. SEM micrographs of schwertmannite

A — needle-like crystals of schwertmannite; **B**, **C** — spherical aggregates of schwertmannite; **D** — short rod-like crystals forming globular aggregates; **E** — web-like schwermannite aggregates; **F** — schwertmannite impregnation of microbial colonies

schwertmannite occurs also in the form of thin, brittle films, floating on the surface of stagnant water. Schwertmannite is pale orange to dark brown. Commonly within one sample of the mineral a variation of colour is present. The darker the colour, the more consolidated parts is the deposits. Where wet, the ochreous sediments composed of schwertmannite are greasy and soft to the touch. After drying out they become brittle and may be ground with fingers. The speleothem forms are usually more consolidated and a little harder.

Contrary to most of the poorly crystalline phases, the characteristic morphology of schwertmannite crystals on the SEM images (Fig. 3) may be a diagnostic feature of the mineral. Schwertmannite from Radzimowice and Wieściszowice creates typical thin needle-like crystals, that are about 2–3 µm long. Usually they are grouped into spherolitic, "hedgehog" aggregates that form botryoidal accumulations. Locally schwertmannite crystals have atypical, mamillary or granular habits (Fig. 3), grains being about 1 µm across. Similarly to the needle-like crystals, they are grouped in spheroidal forms. The presence of such irregular crystals is interpreted as a result of partial solution of earlier crystallized schwertmannite (Dold, 2003). Schwertmannite covers and impregnates also the filamentous colonies of microorganisms, that played an active role in mineral formation.

The poor crystallinity and small size of the schwertmannite crystals are substantiated by its feature structure. The structure of the mineral is similar to that of akaganeite ß-FeO(OH,Cl) (Bigham *et al.*, 1990). It consists of double chains of $Fe_2O_3(OH)$ octahedra connected by corners. They produce tunnel-shaped structures that are square in cross-section, elongated along the z-axis. In empty tunnels inside the octahedra chains, groups of SO_4^{2-} are located, while two of the sulphate oxygen atoms belong both to the sulphate groups and to the Fe octahedra ($-Fe-O-SO_2-O-Fe-$) (Bigham *et al.*, 1990). Probably the presence of sulphate groups stabilizes the structure of schwertmannite, just as chlorine ions stabilize the structure of akaganeite, but the slightly larger size of the sulphate ion causes distortions in the octahedra chains, and results in small sizes of crystals and poor crystallinity. Loan *et al.* (2004), basing on electron nanodiffraction, questioned the structural similarity between schwertmannite and akaganeite, while suggesting the presence of structural components of ferrihydrite in schwertmannite.

XRD IDENTIFICATION OF SCHWERTMANNITE

The basic method of identification of schwertmannite remains XRD, although the poor crystallinity of the mineral causes some difficulties. The peaks on X-ray powder diffraction patterns of schwertmannite are often diffuse and of low intensity. Especially as regards mixtures of more crystalline phases, this makes distinguishing the peaks from the background of the pattern difficult. In such cases good results may be obtained by differential X-ray diffraction (DXRD), based on subtracting from the patterns produced by a raw sample those produced after extraction with acid ammonium oxalate. Poorly crystalline phases, such as schwertmannite and ferrihydrite, dissolve in a solution of oxalate, but goethite, lepidocrocite, jarosite and other crystalline phases of Fe (III) remain in the residue. As an effect, a readable pattern of schwertmannite can normally be acquired. Only the presence of ferrihydrite, especially of the 6-line variety of this mineral, may cause coincidences. The powder diffraction pattern of schwertmannite is made up of 8 broad peaks. The most intense one is the 0.254 nm peak (Fig. 4). The most intense peak of 6-line ferrihydrite can be found at a similar wavelength , though it is much less symmetrical than that produced by schwertmannite. The set of peaks: 0.495, 0.331, 0.232, 0.194, 0.164, 0.151, and 0.146 nm, is diagnostic of this mineral, with the exception of the peak at 0.151 nm that is also found on the ferrihydrite pattern. The last peak is the second characteristic one, allowing identification of the 2-line ferrihydrite variety.

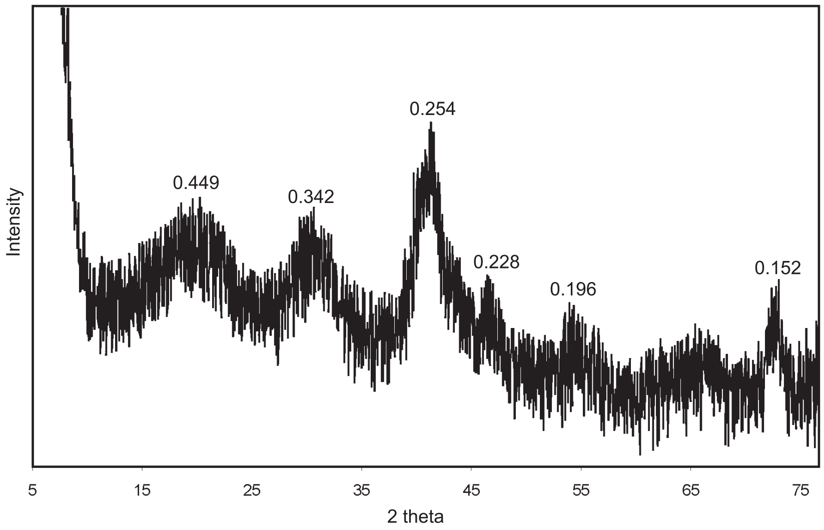

Fig. 4. X-ray powder diffraction pattern of schwertmannite from Radzimowice

MÖSSBAUER SPECTROSCOPY

One of the most useful methods of studying schwertmannite is Mössbauer spectroscopy (Bigham *et al.*, 1990). This method shows that in the structure of the mineral only trivalent Fe is present and in octahedral coordination. Mössbauer spectra recorded at room temperature for schwertmannite originating at Wieściszowice and Radzimowice present a quadrupole doublet, consisting of two broad lines (Fig. 5). This doublet is asymmetrical. The low-velocity line has a higher dip and a lower one than the high-velocity line. The asymmetry is not caused by the presence of Fe^{2+}, because the spectrum is limited to the velocity span of ±5 mm/s. The quadrupole shift is 0.63 mm/s, and the isomer shift 0.31 mm/s. At a temperature of 77 K there is a quadrupole sextet noticeable in the spectra (quadrupole shift 0.64 mm/s, isomer shift 0.24 mm/s), indicating the process of magnetic rearrangement of schwertmannite. The magnetic rearrangement is not induced by the presence of sulphate ion in the structure, hence the asymmetry of the spectrum. Some of the samples of schwertmannite from Wieściszowice and Radzimowice do not show signs of magnetic rearrangement at a temperature of 77 K. The Mössbauer spectra recorded from them at 77 K essentially do not show splitting into the quadrupole sextet, which may be explained by a major influence of sulphate and arsenate ions on the process and temperature of the magnetic rearrangement of schwertmannite.

CHEMICAL COMPOSITION OF SCHWERTMANNITE

In respect to its chemical composition, schwertmannite is a hydrated oxyhydroxysulphate of Fe (III). Its chemical formula

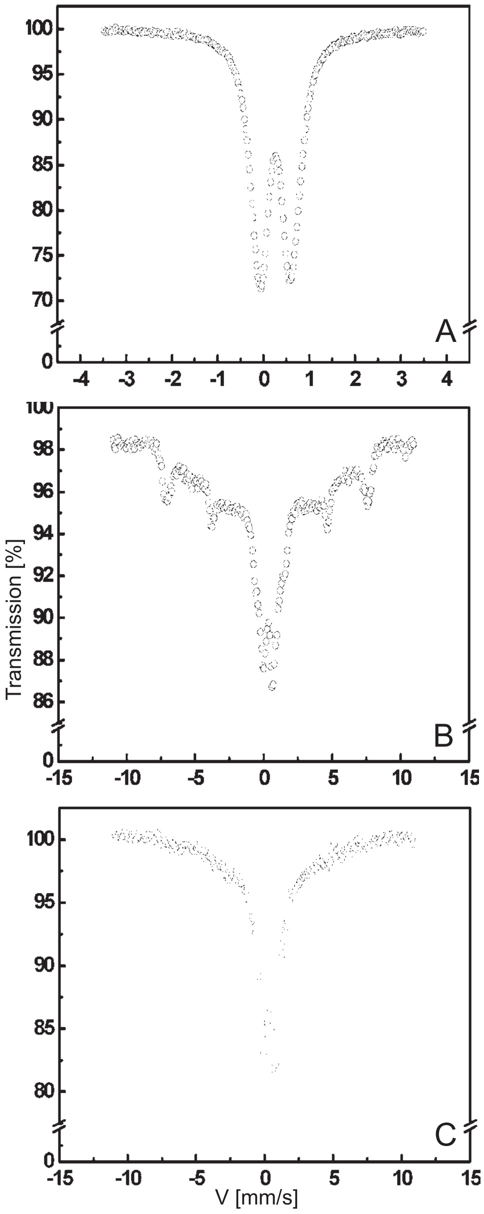

Fig. 5. Mössbauer spectra of schwertmannite from Radzimowice at: A — 297 K, B — 77 K and C —77 K for schwertmannite with the highest As content

is given as: $Fe_{16}O_{16}(OH)_{10}(SO_4)_3 \times 10H_2O$. Chemical data available both for the natural and synthetic samples of schwertmannite shows that the sulphate content in the mineral may significantly differ, hence a more general formula is used: $Fe_8O_8(OH)_{8-2x}(SO_4)_x \times nH_2O$, where $1 \leq x \leq 1.75$ (Bigham and Nordstrom, 2000). The variation in sulphate content is caused by sulphate ion in schwertmannite being bound both into the structure in the tunnel cavities, as well as adsorbed at the surface, usually in the ratio of *ca.* 3:1. The iron content is also variable, which may an effect of inhomogeneous composition of the material analyzed. The results of chemical analyzes of selected samples of schwertmannite from Wieściszowice and Radzimowice are shown in Table 1. The iron content in schwertmannite from Wieściszowice varies significantly with a relatively constant, high sulfur content, which corresponds well with the sulphate abundance in the AMD of this mine. In the schwertmannite samples from Radzimowice the iron content varies less. Significant variations are noticeable in case of sulfur. Arsenic was detected only in samples from Radzimowice. Varieties of schwertmannite, containing smaller amounts of sulfur, are usually characterized by an elevated arsenic content, however no explicit linear relation between sulphate and arsenate contents was noticed. The arsenic content in our samples varied from 0.84 to 5.20 wt. % of As_2O_5 and depends on where schwertmannite crystallized in the weathering zone. The samples richest in As are the ones collected near weathering veins, containing arsenopyrite. The farther from oxidizing sulphates, the lower the arsenic content in the schwertmannite. Such high arsenate contents have not been recorded before in natural samples of this mineral. Regenspurg and Peiffer (2005) found up to 6740 ppm As (2.38 wt. % As_2O_5) in schwertmannite from the silver mine “Prybyslav”, Czech Republic. Fukushi *et al.* (2003) reported 60.9 mg/g As (2.15 wt. % As_2O_5) for ochreous precipitates from Japan. Synthetic schwertmannite may be enriched in arsenate up to 10.3 wt. % without detectable structural changes (Regenspurg and Peiffer, 2005). Some of our analyses also show small amounts of calcium, aluminium and amorphous silica.

THERMAL BEHAVIOUR OF SCHWERTMANNITE

The thermal decomposition of schwertmannite recorded with a derivatograph is a good complement to microprobe analyzes for determining the water content and independently the sulphate (and other substituting oxyanions) content. Figure 6 shows results of thermal analysis of two selected samples of schwertmannite. The Wieściszowice sample (no. wp 8) represents a typical schwertmannite containing no arsenate, and the Radzimowice sample (no. rs 222) contains about 4.5 wt. % of As_2O_5. The DTA,TG and DTG curves of the two types of schwertmannite are very similar. The first DTA endothermic peak at about 160–170°C is connected with dehydration and dehydroxylation. This reaction leads to weight loss of 24.0 and 25.0%, respectively. The exothermic peak at 530–550°C is an effect of recrystallization of the anhydrous phase (Schwertmann *et al.*, 1995). This phase undergoes slow decomposition at 655–680°C, releasing sulphur trioxide (Wieściszowice) or sulphur and arsenic oxides (Radzimowice), registered as an endothermic peak. Final decomposition results in mass loss of 11.0 and 11.5 wt. %, respectively.

IR SPECTROSCOPY

IR spectroscopy gives additional useful information about the chemical composition of schwertmannite. The comparison of absorption bands obtained for schwertmannite from Wieściszowice and Radzimowice is shown in Table 2, and spectra at the range of 400–2000 cm^{-1} are additionally shown in Figure 7. The broad band with a maximum in the range of 3322–3424 cm^{-1} results from stretching of the O-H bond, and the band with a maximum at 1633 cm^{-1} from bending of the bonds in the H_2O molecule. The

Table 1

Microprobe analyses [wt. %] for selected schwertmannite samples from Wieściszowice and Radzimowice

Localisation and type of occurrence	Fe_2O_3	Al_2O_3	CaO	SO_3	As_2O_5	SiO_2	total
Wieściszowice — stalactite in abandoned mine adit, sample no. w 8	75.13	0.00	0.00	10.89	0.00	0.39	86.41
	76.33	0.00	0.00	10.35	0.00	0.00	86.68
	75.72	0.00	0.01	10.08	0.00	0.00	85.82
	75.91	0.00	0.00	12.61	0.00	0.00	88.52
	74.21	0.00	0.00	12.17	0.00	0.00	86.38
	76.09	0.00	0.00	12.37	0.00	0.00	88.46
	74.87	0.00	0.00	11.92	0.00	0.00	86.79
	76.01	0.00	0.00	11.22	0.00	0.00	87.23
	69.97	0.00	0.00	11.14	0.00	0.00	81.12
Wieściszowice — thin film on the water surface, sample no. w 1	63.56	0.00	0.00	11.63	0.00	0.00	75.19
	66.14	0.00	0.03	10.68	0.00	0.49	77.34
	66.93	0.00	0.00	10.65	0.00	0.49	78.08
	67.24	0.00	0.00	10.70	0.00	0.58	78.53
	66.60	0.00	0.00	10.84	0.00	0.49	77.93
	66.37	0.00	0.07	10.31	0.00	0.49	77.25
Radzimowice — stalactite in abandoned mine adit, sample no. rs 60	68.34	0.00	0.08	8.48	1.30	0.09	78.30
	68.85	0.00	0.04	11.51	1.36	0.01	81.77
	69.43	0.00	0.00	11.16	0.95	0.03	81.57
	69.43	0.00	0.00	12.46	1.10	0.08	83.06
	68.09	0.00	0.00	11.96	0.84	0.00	80.89
Radzimowice — film on the water surface, sample no. 67	67.54	0.21	0.01	8.47	4.14	0.00	80.36
	69.00	0.23	0.07	8.92	2.42	0.00	80.64
	66.83	0.09	0.03	8.40	4.59	0.00	79.94
	69.32	0.22	0.08	9.08	1.77	0.00	80.47
	68.59	0.23	0.05	10.04	1.03	0.02	79.96
Radzimowice — stalagmite in abandoned mine adit, sample no. rs 222	64.32	0.00	0.00	8.24	3.23	0.37	76.16
	63.63	0.00	0.00	8.80	5.20	0.42	78.05
	65.13	0.00	0.00	8.14	2.86	0.44	76.56
	64.56	0.00	0.00	9.61	3.41	0.41	78.00
	64.36	0.00	0.00	8.66	3.33	0.35	76.70

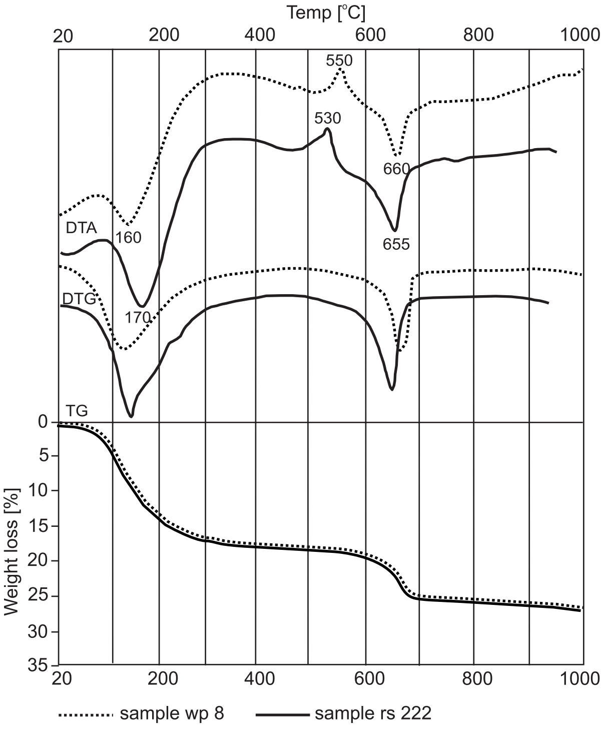

Fig. 6. DTA, TG and DTG curves for schwertmannite from Wieściszowice (wp 8) and Radzimowice (rs 222); derivatograph

presence of a number of oscillations resulting in splitting of bands connected with ν_3 oscillations within the sulphate ion indicates a lowering of symmetry of the SO_4^{2-} group as a result interaction with the Fe^{3+}. For the unidentate complex (C_{3v} symmetry) there are two bands, and for the bidentate complex (C_{2v} symmetry) three characteristic bands of absorption are present (Powers *et al.*, 1975). This complex may be produced both by the incorporation of sulphate ion into the tunnel cavities of the mineral structure, and by its sorption placement on the mineral surface. A very similar geometry and bond energy of the bonds Fe-(SO_4^{2-}) within the structure of schwertmannite and on its surface, make it impossible to determine their position unambsigsuously (Bigham *et al.*, 1990, 1994). The lowering of the symmetry of the sulphate groups is indicated also by the presence of absorption bands in the 979–988 cm^{-1} range (ν_1). The bands 604–612 cm^{-1} are interpreted as ν_4 oscillations of sulphate groups (Nakamoto, 1986). The presence of ν_1 and ν_4 oscillations suggests rather the existence of sulphate groups embedded in the schwertmannite structure, present in the tunnel cavities of the crystals, rather than adsorbed on its surface (Bigham *et al.*, 1994). In contrasty to synthetic material, two absorption bands resulting from the δ deformation of OH groups are strongly reduced or absent for schwertmannite from Radzimowice and Wieściszowice. Their absence is connected most probably with significant substitution of OH groups by sul-

Table 2

IR absorption bands of schwertmannite

Synthetic material	Wieściszowice			Radzimowice				Vibration mode
rs 96	w 8	w 1	w 12	rs 65	rs 60	rs 67	rs 222	
3377	3329	3340	3322	3418	3424	3373	3342	ν O-H
1631	1633	1633	1632	1631	1632	1633	1631	H_2O
1196 sh* 1129 1054	1196 sh* 1124 1075 sh*	1196 sh* 1125 1075 sh*	1123 1055	1180 sh* 1120 1053	1185 sh* 1122 1054	1190 sh* 1123 1055 sh*	1125 1055	ν_3 SO_4^{2-}
980	980	983	980	988	988	981	979	ν_1 SO_4^{2-}
880	878 weak	877 weak						δ OH
				825 weak	820 weak	820	828	ν_3 AsO_4^{3-}
796	798 weak	806 weak	805					δ OH
667	700 668 weak	700 668 weak	697 668 weak	692 668 weak	697 667	699 668 weak	699 669 weak	Fe-O stretch
604	611	604	611	607	606	612	608	ν_4 SO_4^{2-}
460 427	427	427	453	426 420 408	435, 426	465, 459 435 421	452 435, 429 423 402	Fe-O stretch and ν_2 SO_4^{2-} (?)

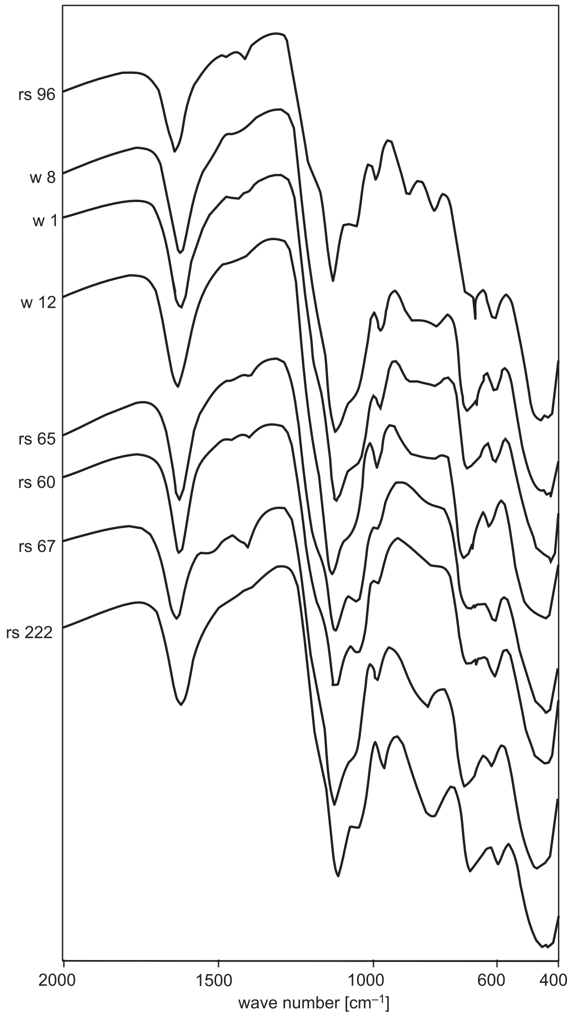

Fig. 7. Infrared spectra of schwertmannite between 2000–400 cm^{-1}

phate ions (for Wieściszowice) or with the presence of new absorption bands associated with the arsenate ion (for Radzimowice). Absorption bands of 820–828 cm^{-1} were recorded only for the Radzimowice schwertmannite. They correspond to ν_3 deformations of the AsO_4^{3-} group, and indicate partial substitution of the sulphate by arsenate. The intensity of these bands increases with the increase in the arsenate content of the schwertmannite. In the case of scorodite ($FeAsO_4 \times 2H_2O$) the absorption band, derived from ν_3 oscillations of AsO_4^{3-}, is assigned to the As-OFe bond (Myneni *et al*., 1998). Lumsdon *et al*. (1984) interpreted the presence of a similar band as originating from arsenate ions absorbed by goethite.

SORPTION CAPACITY

The poor crystalline ferric oxyhydroxide minerals making up the ochreous precipitations, due to their strongly developed proper surface, have high sorption properties. They are capable of scavenging a number of elements released during weathering (Bowell and Bruce, 1995; Hudson *et al*., 1999; Lintnerova *et al*., 1999; Berger *et al*., 2000; Ardau, 2002). The ochres precipitating from AMD waters become one of the major factors controlling their chemical composition.

The chemical composition of the AMD of the areas studied is shown in Table 3. The AMD of Wieściszowice generally have lower pH, higher concentrations of sulphates, aluminium, and magnesium, but are lower in iron, copper and other heavy metals by comparison with the AMD of Radzimowice. Only the Radzimowice AMD waters contain detectable concentrations of arsenic, hence further study of the ochreous precipitates sorption was limited to these. To specify the significance of schwertmannite in arsenate sorption from the AMD, ten ochre samples were selected with different mineral composition

Table 3

Chemical composition of the selected samples of AMD from Radzimowice and Wieściszowice [mg/l]

	Radzimowice				Wieściszowice		
Sample	s 14w	s 10w	s 17w	s 8w	II/1/A	X/A	VII/A
pH	3.0	3.6	4.23	4.65	2.59	2.72	2.89
$Fe_{tot.}$	2669	1151	217	398	389	218	668
Ca	220.17	217.15	170.22	32.94	212	173	160
Mg	140.34	113.82	50.05	12.54	177	177	345
Al	2.44	11.56	2.42	0.22	90.6	65.7	50.9
Na	3.16	5.09	6.33	4.07	4.9	5.6	5.1
K	0.29	3.99	3.43	1.82	0.13	0.6	2.6
Mn	140.34	113.82	50.05	12.54	3.08	3.48	10.3
Cu	38.30	34.26	3.89	3.82	3.16	2.02	2.30
Zn	3.18	1.07	0.24	0.32	0.60	0.49	1.12
Ni	0.07	0.41	0.11	0.05	0.35	0.24	0.37
Co	1.12	0.44	0.21	0.11	0.49	0.40	0.76
SiO_2	1.26	2.63	1.22	1.37	77.5	73.3	62.6
SO_4^{2-}	2260	421	246	500	2734	2389	3759
AsO_4^{3-}	24.02	1.12	18.01	0.90	nd.	nd.	nd.
PO_4^{3-}	0.67	0.09	0.09	0.21	0.60	0.20	0.35

nd. — not detected; s 14w, s 10w, s 17w, s 8w water samples from level 3 of old mine, II/1/A — Purple Pond, X/A — large seepage from the dump, VII/A — small seepage from the dump

ranging from schwertmannite through ferrihydrite to goethite. Results of their ACP-MS analyses, together with mineral compositions and specific surface determinations are shown in Table 4.

The results obtained show a distinct dependence between the mineral composition of the ochres and the amounts of the elements contained. The sediments composed of schwertmannite are generally characterized by the highest sulphur (SO_4^{2-}) and arsenic (AsO_4^{3-}) contents, and increased levels of heavy metals. In the case of ochres composed of ferrihydrite, a remarkable drop in arsenate content is associated with high concentrations of phosphate and some heavy metals such as copper, zinc, nickel and cobalt. The arsenate content of ferrihydrite is generally lower than of schwertmannite, but locally it may reach similar levels. Ochres composed of goethite contain practically no sulphate and arsenate. The heavy metal content in them is lower than, or reaches level close to that of ferrihydrite. Furthermore, a significant manganese content was detected for goethite. Analytically determined sulphate, arsenate and other oxyanion contents of ochres may be fixed in different ways. They may be loosely sorbed onto the surface of iron oxyhydroxide phases,

Table 4

Chemical composition [wt. %] of the selected samples of ochreous precipitates from Radzimowice

Sample	s 14	s 10	s 17	s 19	s 13	s 11	s 11a	s 18	s 16	s 9
Mineral composition	sch	gt + fr	sch	sch +gt	sch + am	fr	fr	fr	fr	gt
Specific surface [m^2/g]	123	106	197	203	181	207	184	165	269	85
Ca	0.02	0.03	0.03	1.32	0.01	0.01	0.04	0.37	1.29	0.00
Al	0.00	0.08	0.06	0.00	0.00	0.02	0.04	0.00	0.00	0.00
Na	0	0	0	0	79×10^{-4}	0	15×10^{-4}	0	47×10^{-4}	0
K	6.9×10^{-4}	0	5.6×10^{-4}	29×10^{-4}	21×10^{-4}	0	50×10^{-4}	2×10^{-4}	25×10^{-4}	54×10^{-4}
Mn	0.00	0.00	0.00	0.18	0.00	0.01	0.00	0.05	0.10	0.20
Cu	0.01	0.10	0.03	0.00	0.02	0.07	0.46	0.00	0.00	0.00
Zn	0.00	0.00	0.00	0.13	0.00	0.00	0.00	0.22	0.33	0.27
Ni	0.2×10^{-5}	0.6×10^{-5}	1×10^{-4}	175×10^{-4}	0.8×10^{-5}	0.4×10^{-5}	0.3×10^{-5}	135×10^{-4}	143×10^{-4}	153×10^{-4}
Co	0.7×10^{-5}	0.7×10^{-5}	1×10^{-4}	82×10^{-4}	2×10^{-4}	0.5×10^{-5}	0.6×10^{-5}	125×10^{-4}	81.3×10^{-4}	144×10^{-4}
Si	0.00	0.01	0.01	0.05	0.00	0.00	0.01	0.07	0.16	0.12
S	4.05	0.04	4.73	3.95	4.00	0.44	0.14	0.00	0.09	0.04
As	0.34	0.68	1.09	1.21	1.03	0.00	0.01	0.02	1.73	0.01
P	0.01	0.29	0.09	0.10	0.06	0.01	0.03	0.00	0.13	0.00

sch — schwertmannite, gt — goethite, fr — ferrihydrite, am — amorphous phase

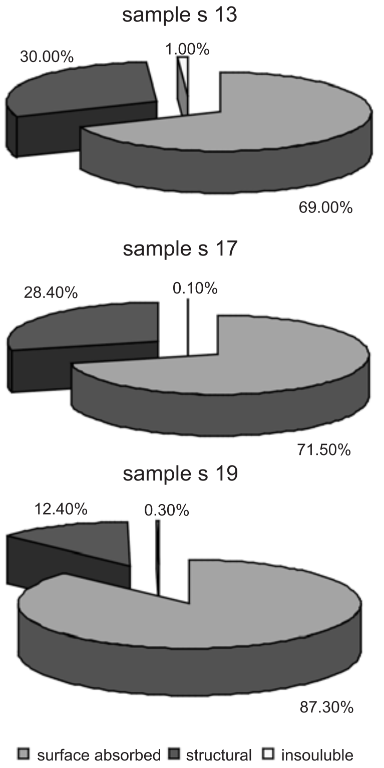

Fig. 8. Ratios of different arsenate bonding forms determined in Radzimowice schwertmannite

be bound in the structure of iron oxyhydroxide minerals or be they may included as an admixture of foreign phases (Manceau, 1995; Waychunas *et al*., 1995; Fukushi *et al*., 2003, 2004). In order to obtain quantitative estimation of the forms of arsenate uptake in schwertmannite, sequential extraction was used, as proposed by Daus *et al*. (1998). This consists of two extraction steps with sodium oxyhydroxide and an oxalic buffer solution. In the first step the arsenate adsorbed on the mineral surface is released into the solution. Next, the iron oxyhydroxides are dissolved in an oxalic buffer that releases the arsenate bond within their structure. The remaining residue contains insoluble iron arsenates. The results obtained for three selected samples are shown in Figure 8. They show that the main form of arsenic in schwertmannite from Radzimowice is the arsenate ion adsorbed on the strongly developed surfaces of the mineral crystallites. This constitutes between 71.5 and 87.3% of the total arsenate content in the mineral, and may easily be removed. The arsenic bond in the structure of the schwertmannite, probably substituting the sulphate ion, makes up to 12.4 to 30% of the arsenate. The lowest amount of arsenic, up to 1%, is present in the form of an admixture of insoluble arsenates. The results obtained indicate that schwertannite may act as a good natural filter for arsenate produced in the weathering zone in the underground workings at Radzimowice, but As may easily be released into meteoric waters as a result of an increase in the pH of AMD waters. Recrystallization of metastable schwertmannite to stable goethite also leads to a release of arsenate. Such a process in the conditions of the abandoned mine at Radzimowice is relatively slow and does not constitute a major hazard for the natural environment of the region.

CONCLUSIONS

The ferric oxyhydroxysulphate, schwertmannite, is one of the major phases that precipitate from acid mine drainage (AMD) waters. This mineral, not previously noted from Poland, was recorded in significant amounts in the weathering zone developed in two abandoned sulphide mines at Wieściszowice and Radzimowice (Sudety Mts.). It is present in underground workings in a form of covers, dripstones and loose sediments at the bottoms of adits. It is also produced at the surface in the open pit, waste dumps and mine drainages. The masses of schwertmannite typically are orange to brown in colour and are made up of crystallites up to several micrometres long with a characteristic needle-like habit.

The chemical composition of schwertmannite strongly reflects the geochemical character of the weathering zone where it is formed. In contrast to schwertmannite from Wieściszowice, which contains only the sulphate group, the mineral formed at Radzimowice mine always contains the arsenate group. In the schwertmannite from Radzimowice we have found up to 5.20 wt. % of As_2O_5, which is one of the highest concentrations recorded in natural material. The presence of the arsenate group in schwertmannite was confirmed by spectroscopic methods. With sequential extraction it has been found that about two-thirds of the arsenate content is adsorbed onto the surface of schwertmannite crystallites, one third is arsenate bound in the structure of the mineral, probably substituting the sulphate group, and about 1% is an admixture of ferric arsenate phases.

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