

MINERALOGY OF Fe-ochre deposits formed from acid mine water in the Smolník mine (Slovakia)

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Abstract: When the acid mine drainage water, formed as the result of massive pyrite oxidation in the flooded Smolník mine, mixes with surface water of Smolník Stream, characteristic brown-ochre precipitates are formed. These ochres continue to form in the strong acidic aqueous environment: stream water pH values are in range 3–5, and ochre deposit pore water has a $\text{pH} < 3$. The ochre samples have been studied by X-ray diffraction and electron microscopy methods (TEM, SEM) with elemental microanalysis. Large amounts of the fresh precipitates are X-ray amorphous. The SEM and TEM investigations have shown that there are a few mineral crystalline phases in ochre hardpan samples consisting of crystals some tens to several hundred nm large in size. The Fe-sulphates, jarosite ($\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$) and probably schwertmannite ($\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$) are found in the precipitates and have formed from high SO_4^{2-} and acid solutions. Goethite ($\alpha\text{-FeOOH}$) has also been identified in the ochre deposits, and is the dominate mineral when the pH value increases and the SO_4^{2-} concentration decreases in the water-ochre deposit system. In acid conditions aluminosilicate minerals have been dissolved or degraded and amorphous Si-Al phase and possibly neoformed halloysite have formed as a result.

Key words: oxidation, pyrite, mineral identification, goethite, jarosite, schwertmannite, X-ray diffraction, electron microscopy.

Introduction

The water quality of the Smolník Stream dramatically decreased a short time after drainage of the Smolník mine works, the acid mine waters penetrating through and flowing into the stream. The marked change in the pH value of the stream water can be observed downstream from the Smolník mine works to the confluence of the stream with the Hnilec River (Fig. 1, Jaško et al. 1996). Massive pyrite oxidation and free sulphuric acid production are the major reasons for mine water acidification. It appears, that pyrite oxidation continued intensively after mine works drainage not only in the vadose zone but also in the saturated part of the mine aquifer. Pyrite oxidation in the Smolník mine district has been used for more than seven hundred years to make up so called “cement copper” (Ilavský 1993). Iron-sulphide oxidation processes mainly relating to ore pyrites have been investigated in connection with waste water from abandoned mine workings around the world during recent decades (Singer & Stumm 1970; Nordstrom 1982; Jambor & Blowes 1994; Holub et al. 1993; Šucha et al. 1996). The mine water pH value is about 3 to 4 (Jaško et al. 1996) and the same pH-level is found in the most polluted part of the Smolník Stream (Fig. 1, Tab.1). The mine waters also have a high level of dissolved solids

(TDS 17 to 47 g/l). The ochre precipitates have formed mainly on the mine-side bank of the stream but also in the opposite stream bank, about to 2–3 km downstream from the mine. The ochres have formed thin films to hardpan-like deposits on the rock and cemented stream sediment and plant remains.

The goal of the present study is to characterize the mineralogy and chemistry of the ochre precipitates forming during/after mine and surface waters mixing. The chemical composition of the acid mine and stream waters suggested, that wall rock minerals had been dissolved (Jaško et al. 1996). Some dissolved elements are potential pollutants and may have accumulated in Fe-precipitates (Schwertmann & Cornell 1991; Ruan & Gilkes 1995; Bigham 1994). These precipitates are poorly crystalline or/and extremely fine grained and special methods for their study are required (Bigham 1994; Schwertmann et al. 1982; Schwertmann & Cornell 1991).

Geology and ore deposit characterisation

Smolník is situated in the Southwest part of Spišskogemerské rudohorie Mts. (East Slovakia). The Smolník copper-mine district is one of the most ancient

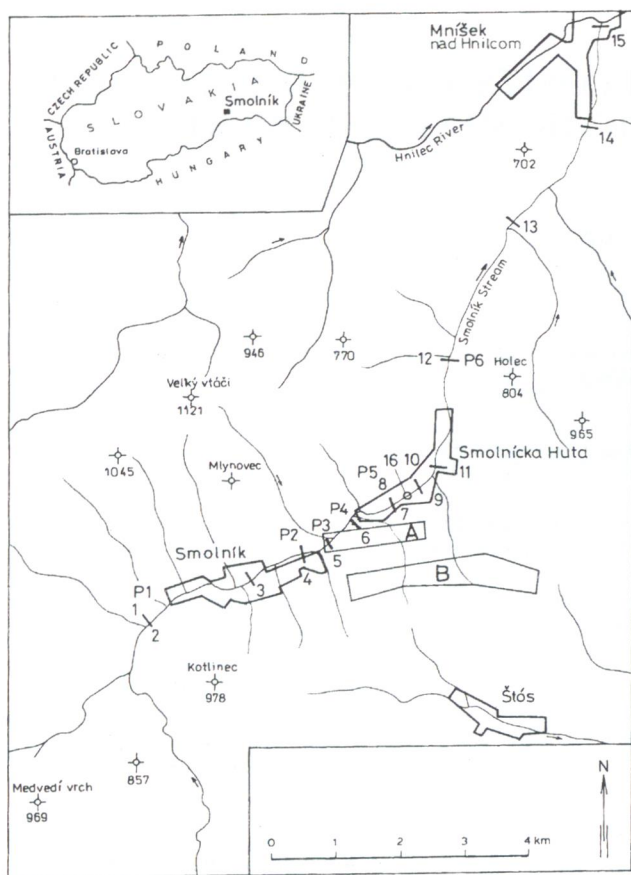


Fig. 1. The studied area and localization of samples. 1 to 15 — samples of stream sediment, 16 — ochre samples. P1 – P6: localization of hydrographic profiles and field stream water pH measurements.

mine area of Europe and was exploited for about one thousand years (Ilavský 1993). In the lower Palaeozoic vulcano-sedimentary rock sequences of Gelnica Group accumulated massive, banded and lens shaped ore bodies up to 40 m thick consisting of pyrite-chalcopryrite with sphalerite and galena. The productive horizon attains a thickness of 150 m in the central part of the deposit (Rojkovič 1994; Ilavský 1993). Metamorphic overprinting is a characteristic feature of the Gelnica Group sediments and also of the ore deposit. Tuffaceous and siliceous sediments were metamorphosed to a low degree namely chlorite zone of green-shist facies (Grecula 1982) and mineral veins formed as a result of metamorphic mobilization. These veins contained not only major sulphides (pyrite, chalcopryrite), but also arsenopyrite and sulphosalts of Cu, Sb, As, Bi and native Au and Bi (Onačila & Hurny 1994; Ilavský 1993). Supergene processes were responsible to the well developed oxidation zone with characteristic Fe-oxide minerals.

Economically most important are the stratiform chalcopryrite ores, massive sulphide bodies with Cu contents of more than 10 wt. % and these have been extensively

Table 1: The pH values of stream waters and of the stream sediment sample extracts: $\text{pH}_{\text{H}_2\text{O}}$ — distilled water extract, pH_{KCl} — 1M KCl extract. Values of total Fe content (Fe_{tot}) and field pH stream water are from Jaško et al. (1996).

Samples	$\text{pH}_{\text{H}_2\text{O}}$	pH_{KCl}	Fe_{tot} %	pH stream water
1	6.06	5.55	3.59	6.44–7.54 P1
2	5.67	5.30	3.61	
3	6.15	6.02	5.55	
4	6.47	6.63	3.87	6.47–6.70 P2
5	6.48	6.36	3.81	6.24–7.77 P3
6	6.48	6.43	4.02	6.24–7.77 P4
7	3.98	3.95	8.42	4.62–4.92 P5
8	4.58	4.04	6.52	
9	3.70	3.66	10.71	
10	3.84	3.30	10.67	4.23–4.62 P6
11	3.69	3.62	9.51	
12	3.93	3.86	9.93	
13	3.94	3.92	19.93	4.4
14	4.58	4.24	7.03	
15	4.33	4.07	10.5	
16	2.63	2.33	39	

exploited for some centuries. Until the latter half of the last century only pyrite with a low Cu content (less than 1 wt.%, later less than 0.5%) for sulphur was exploited as raw material. Copper solutions (cemented Cu) were also exploited by directing large amounts of surface waters into the mine and recharging in the Cu-poor parts of deposit. The ore mining was finished in 1990 and the mine works were continually drained. More than 6 mil. tons pyrite ores of various quality have been abandoned in the mine (Ilavský 1993). Short time after mine drainage, strong acid waters start to pollute the Smolník Stream. The evolution of stream and mine water acidification clearly show, that this process will damage the environment for a long time (Jaško et al. 1996).

Materials and methods

Ochre deposits were sampled at point 16 (Fig. 1). We collected six different samples - from soft/fresh precipitates to hardpan materials. Fifteen stream sediment samples from uncontaminated (1 to 6) and contaminated (7–15) parts of the stream bottom were also mineralogically characterized as rock samples and $< 2 \mu\text{m}$ fractions. The $< 2 \mu\text{m}$ fractions were separated from the $< 0.125 \text{ mm}$ fractions of stream sediment samples. The field of pH water values were done by Datasonde DS 3 Hydrolab equipment during different seasons of the year measurements (Jaško et al. 1996). In the laboratory pH measurements of distilled water and 1M KCl extracts were done by standard potentiometric methods. The 10 grams of dry samples were mixed with 25 ml of distilled water or KCl and pH values were measured. Total iron contents were analysed by X-ray-fluorescence meth-

ods (Jaško et al. 1996). Because the samples contain large amounts of iron, X-ray diffraction analyses of samples were performed on Philips PW 1710 equipment with $\text{CoK}\alpha$ radiation. X-ray analyses of untreated samples and samples heated for one hour at 500 and at 900 °C were also made. Transmission electron microscopy (TEM) investigations were done on the JEOL JEM -2000 microscope and elemental X-ray semiquantitative microanalyses using 10 000 AN LINK- energy dispersive analysis system (EDS). TEM investigations were conducted on dozed down finely dispersed suspensions. Hardpan ochre material and shale samples with pyrite and Fe minerals were investigated by scanning electron microscope (SEM). Small pieces of material were simply shadowed by gold and observed using a TESLA BS 300 microscope.

Results

pH measurement

The pH measurements and total Fe contents (Jaško et al. 1996) of the stream sediment and ochre samples are shown in Table 1. It is evident, that Fe content increases in the most acid samples. The stream water and sediment extract pH values are somewhat different. Measurements of water pH have been done a number of times during the year (Jaško et al. 1996) and pH values vary with the flow of the Smolník Stream. It may be suggested, that the lower pH values of sediment extracts reflect the acidity of newly mixed (mine and stream) solutions and/or pore solutions of recently formed ochres. But pH measurement are also sensitive in relation to the electrode type and equipment used.

X-ray diffraction

Ochre precipitates: The rock minerals chlorite, mica (muscovite), quartz and also feldspar (one sample) were identified in the ochre precipitate samples. Jarosite ($\text{KFe}_3(\text{OH})_6(\text{SO}_4)_2$) and probable goethite (FeOOH) were also indicated (Fig. 2), but in relatively low amounts. Goethite increases in the hardpan like samples, but not to any great extent. One ochre sample contains about 39 wt. % Fe, about 61 wt. % as FeOOH . The low goethite content of the ochre samples indicates low goethite stability (Bigham et al. 1992) in strong acid conditions (pH 2.3–2.6). In soft/fresh ochre samples no goethite has been identified and the background of the X-ray profile indicated the presence of poorly crystallized or X-ray amorphous iron (mineral) phases only. The presence of some broad bands (Fig. 2) and also the slight shift of these reflections (Fig. 2A–B) indicated that the samples may contain, in addition to goethite (Fig. 2A), the next oxyhydroxysulphate mineral — schwertmannite (Jambor 1994; Bigham et al. 1990, 1992). The X-ray pattern of the B-sample (Fig. 2) shows no reflection of goethite at 4.18 Å, but there is a broad band of low intensity with a d-value of about 2.55 Å. The X-ray diffraction pro-

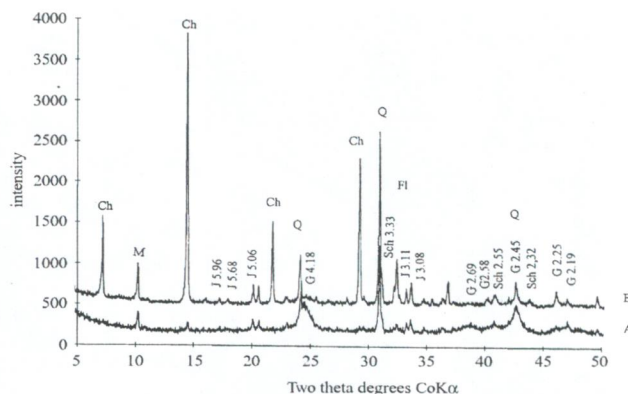


Fig. 2. X-ray diffraction profiles of ochre samples from place 16. A — sample with schwertmannite and jarosite, B — hardpan sample with goethite and jarosite. Ch—chlorite, M—mica, Fl—feldspars, Q—quartz, G—goethite, Sch—schwertmannite, J—jarosite.

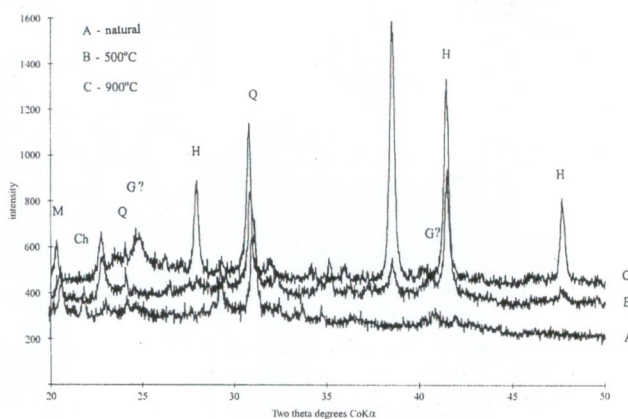


Fig. 3. X-ray patterns of stream sediment sample 10, fraction < 2 μm. A — poorly crystalline Fe minerals, with low intensity and broad X-ray bands at 40–45 °2θ. B — Sample after heating at 500 °C, 1 hour: the beginning of hematite (H) formation can be seen. C — Intensity of hematite reflections after heating samples at 900 °C shows also, that much of the Fe-ochre material is presented in poorly-crystalline or X-ray amorphous forms.

file of schwertmannite — $\text{Fe}_8\text{O}_8(\text{OH})_6\text{SO}_4$ consists of eight broad bands (Bigham et al. 1990; Jambor 1994) but its X-ray identification is complicated in the ochre samples because of the primary mineral presence. The X-ray diffraction peaks for jarosite shown in Fig. 2 are of low intensity, but quite discreet. Jarosite would appear to be stable in this strongly acidic aqueous environment. Pyrite was identified only in a shale sample covered by Fe-ochre minerals. This sample also contains goethite and this neoformed phase was investigated further by SEM (Fig. 4).

Stream sediment: In the stream sediment samples primary minerals quartz, chlorite, mica and feldspars were identified. This mineral assemblage is identical to the composition of the chlorite-mica shale in the Smolník Stream banks. No ore minerals were found in the stream sediment samples.

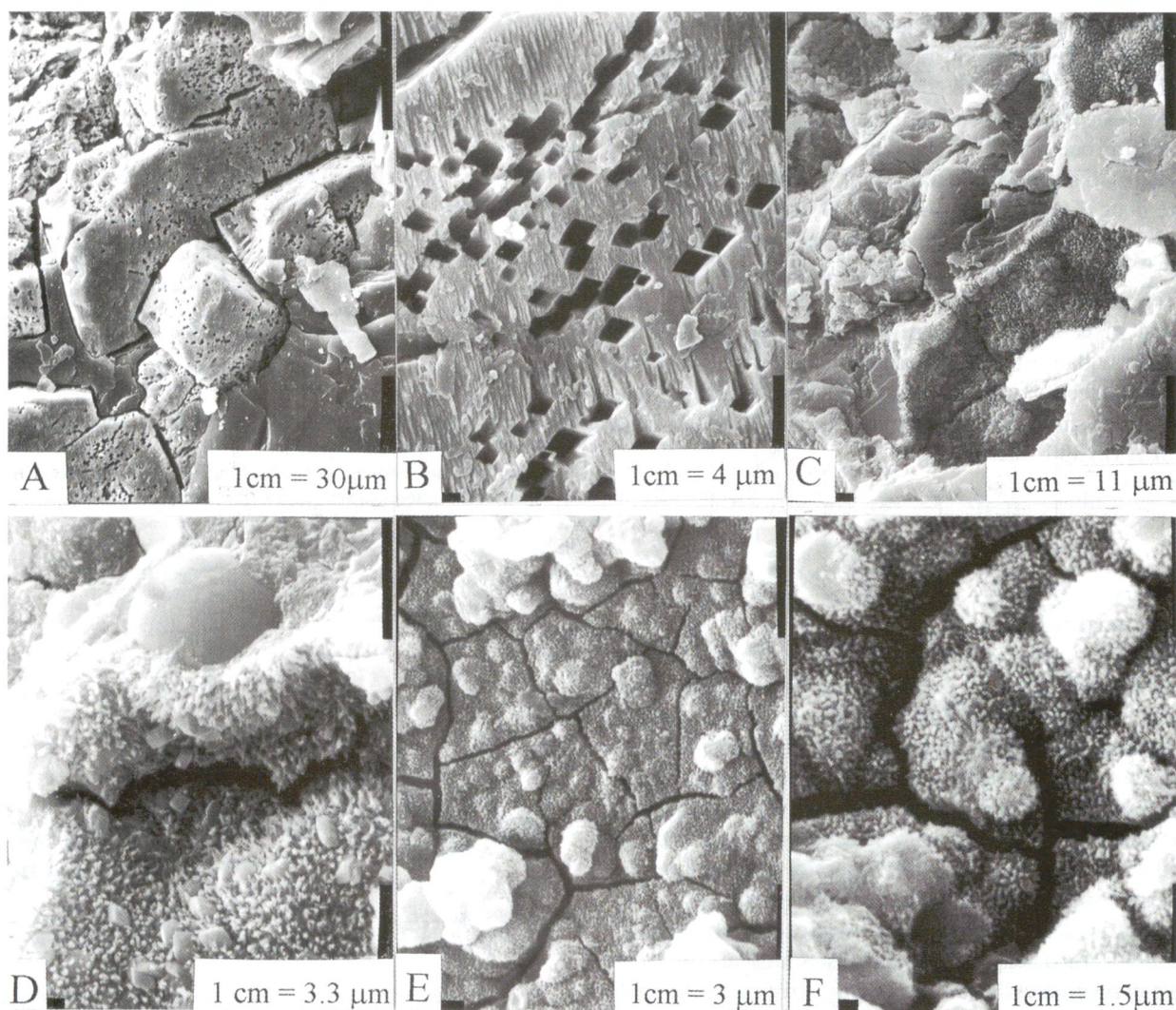
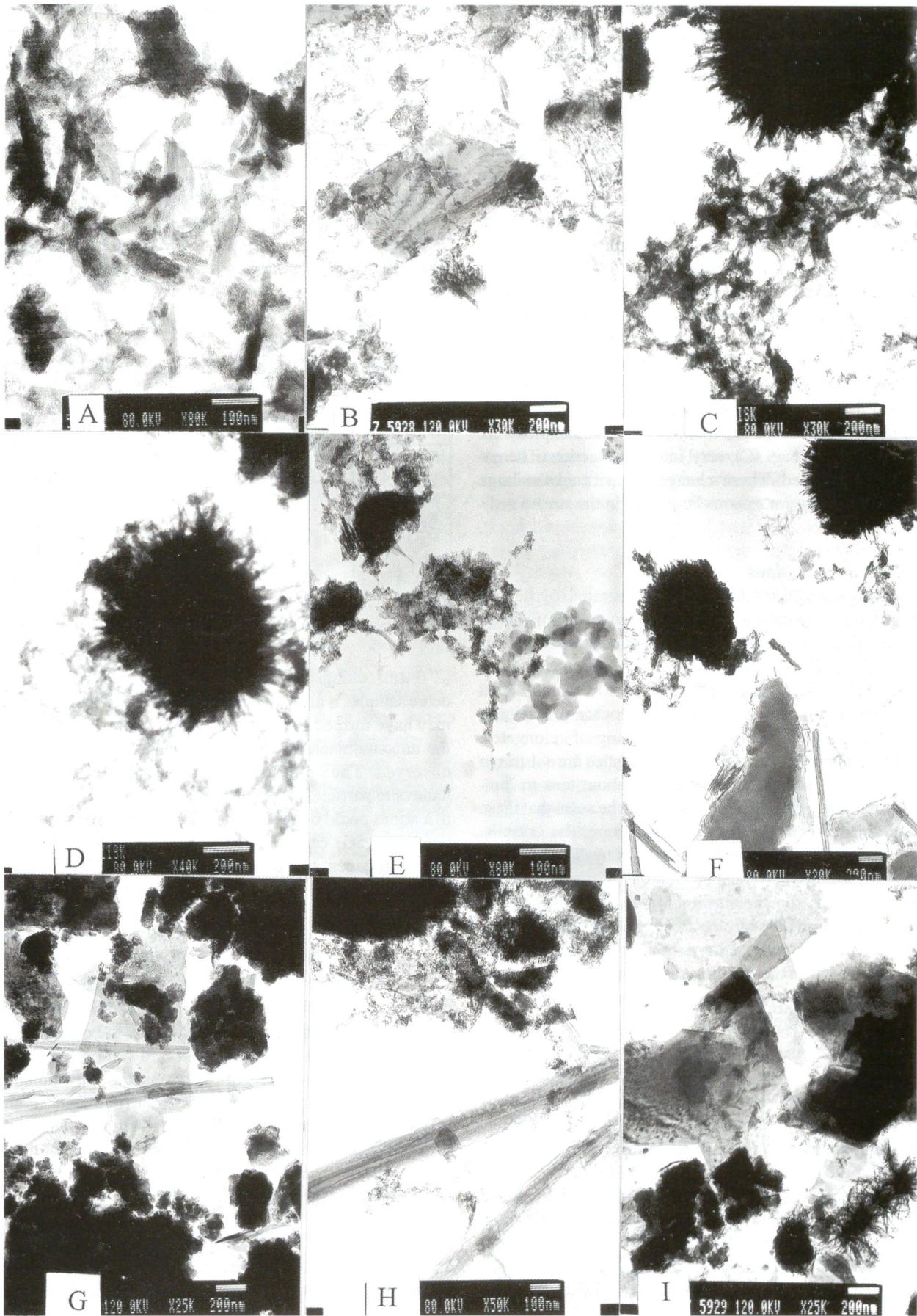


Fig. 4. A: Oxidation and dissolution of pyrite grains in chlorite shale sample. **B:** The pyrite grain surface (detail from A) is covered by oriented dissolution traces. Middle portion of crystal is dissolved preferentially, and shape of crystal is suffered. **C:** Surface of shale sample covered by ochre mineral particles. Fe-minerals are very fine grained, formed as spherical aggregates with spike like minerals. Different degrees of crystallization and some mineral phases can be distinguished. **D:** Spike like minerals are the first generation of crystals formed in precipitate, respective from smooth spheres. Crystallization of the new mineral generation on the tops of spikes — flat crystals, probable goethite. **E:** Ochre mineral in hardpan deposits after drying (characteristic mudcracks). The minerals again formed globular aggregates composed of spike like minerals. **F:** Fine grained spike-like minerals some tens of nm in size.

Fig. 5. A: Crystal morphology in ochre deposits. There are lath-like and short-rod like particles, tens to hundreds of nm in size. The smallest ones form aggregates and are probably X-ray amorphous. Microanalyses of these particles show a high content of Fe (Tab. 2A, analyses 1, 2). These particles are probably goethite. **B:** The size of Fe-mineral aggregates is comparable with that of rock-mica and chlorite grains. Fe-particles also covered surface of mica/chlorite crystals. (Tab. 2A, analyses 3-5). **C, D:** Ochre mineral with pin-cushion morphology of schwertmannite. Microanalyses (Tab. 2A, 7,8) show dominant Fe with relatively high contents of S. Sulphur is also (Tab. 2A) found in aggregate particles without clear pin-cushion morphology (mixed mineral particles in aggregates, adsorbed sulphate ions on the e.g. goethite surface) but in lower/variable concentrations. **E:** Anhedra pseudocubic or pseudo-hexagonal particles of neoformed phases — jarosite, silica, kaolinite? **F:** Elongated tube-like particles probably of halloysite in ochres. Microanalyses (Tab. 2B., analyse 10, 11) show high content of Al and Si. **G:** Halloysite in stream sediment sample 10, fraction < 2 µm (Tab. 2B, analyse 12). **H:** Surface of halloysite crystal. These crystals yield no electron diffraction pattern. **I:** Mica and/or chlorite crystals are differentially altered in acid condition. Some crystals are dissolved at the grain borders. There are also thin (one layer?) crystals yielding no electron diffraction pattern (grain in the top of micrographs). The grain is transformed to polygons or flakes. In the lower part of micrographs there are characteristic morphologies of Fe-aggregate grains.



The samples with high contents of Fe (Tab.1) contained poorly crystalline or amorphous material. The X-ray powder patterns showed broad bands, with d-values about 2.45 and 2.55 Å. Again, Fe-oxyhydroxides or oxyhydroxysulphates are probably present in these samples.

< 2 µm fraction: This fraction of samples contains quartz, mica and chlorite. Goethite was identified in the two samples (2 and 6) from the uncontaminated part of the stream (Tab. 1). These samples have low contents of Fe, and sample extracts are only weakly acid with pH >6, which is similar to regional water acidity. These conditions are suitable for goethite formation. Samples with a high Fe content showed only low amounts of crystalline Fe-minerals (Fig. 3 A). After the samples were heated at 500 °C, the pattern changed (Fig. 3B) and indicated that poorly crystalline Fe-oxyhydroxide (probable goethite-composition) started to recrystallize to hematite (Brown 1980). The change was only observed in the < 2 µm fraction. After the samples were heated at 900 °C (Fig. 3C), very intense reflection of hematite was observed. These changes confirmed the large amounts of X-ray amorphous Fe-phases in the stream sediment samples.

SEM-investigations

SEM investigations have clearly illustrated pyrite oxidation, and dissolution and the neoformation of ochral minerals (Fig. 4). Pyrite in chlorite-mica shale sample being dissolved (Fig. 4 A, B) and this is a major source of acidity. The shale contains large amounts of disseminated pyrite which is covered by neoformed ochre precipitates formed of spherical aggregates consisting of elongated, needle or spike-like crystals. The aggregates are < 1 µm in diameter and individual crystals are about tens to hundreds of nm long (Fig 4, C, F). It can also be seen, that these fine-grained crystals may grow into large, flat crystals. Goethite was identified in these samples by X-ray diffraction. Fine grained spherical or globular aggregates are the dominant forms on the surface of ochres precipitates in hardpan samples (Fig. 4 E, F). Precipitates are still poorly crystallized and contained large content of water as shown by „mudcracks” in the hardpan surface.

TEM investigations

Morphology: The ochre precipitates are largely formed of very small crystalline grains (Fig. 5A) of lath-like or short, rod-like, or needle-like appearance some tens to hundreds of nm in size. More precise grain size determinations are complicated by aggregate formations. The electron-dense aggregates are about the same size as phyllosilicate crystals in the samples. Tiny Fe-mineral grains frequently covered mica and chlorite grains (Fig. 5B). In the same ochre samples a unique “pin-cushion” morphology can be seen (Figs. 5 C, D, F), which is characteristic of the mineral schwertmannite, crystallized from acid mine drainage solutions (Bigham 1994). The presence of relatively large

Table 2: Semiquantitative element microanalyses of Fe-grains of ochre minerals (A: 2 – 5, goethite and 7,8 schwertmannite, 1,6,9 — mixed aggregate grains), of neoformed halloysite (B: 10,12) and partly transformed/degraded mica /chlorite grains (B: 13–18) in wt.%. Symbol < is used when concentration of element is less than twice of determination limit.

A		1	2	3	4	5	6	7	8	9
SiO ₂	8.6	6.3	7.1	8.6	31	23.2	1.8	1.5	<	
Al ₂ O ₃	<	<	5.6	6.4	11.2	<	<	<	<	
Na ₂ O	<	<	<	<	<	<	<	<	<	
K ₂ O	<	1.2	<	<	<	<	<	<	<	
MgO	<	<	<	<	<	<	<	<	<	
CaO	<	1.6	<	<	<	<	<	<	<	
P ₂ O ₅	<	<	<	<	<	12.9	<	<	<	
SO ₃	8.5	<	<	<	<	7.3	14.4	15.3	9.7	
MnO	<	1.8	<	<	1.9	<	<	<	<	
Fe ₂ O ₃	81.8	89.4	84.8	83.2	54.1	56.6	81.9	80.7	88.9	

B		10	11	12	13	14	15	16	17	18
SiO ₂	56.5	57.5	66.2	66.1	62.9	72.2	77.9	57.3	54.3	
Al ₂ O ₃	45.9	36.8	23.9	20.2	15.9	13.2	16.1	23.1	24.7	
Na ₂ O	<	<	<	<	<	<	<	<	<	
K ₂ O	<	<	<	3.2	<	<	<	0.9	<	
MgO	<	4.1	<	<	<	<	<	3.4	<	
CaO	<	<	2.9	<	<	<	<	<	<	
SO ₃	<	<	<	<	2.5	<	<	<	5.13	
MnO	<	<	<	<	<	<	<	5.1	<	
Fe ₂ O ₃	<	<	2.1	13.1	19.1	8.5	6.63	7.6	13.1	

(2–3 µm) elongated tube-like crystals (Figs. 5 F, G, H) in ochre samples is also interesting. It is possible that halloysite may have formed in this acid regime. In the samples from the uncontaminated part of the stream, no halloysite was observed. The electron diffraction patterns of these halloysite particles were very pure, so that no precise identifications could be made. The surface of an elongated particle (Fig. 5G) can be seen to be partly leached or dissolved. Adjacent to neoformed iron minerals are slightly bordered, or some poorly crystallized globular to pseudo-hexagonal grains (Fig. 5E). These occur in ochre hardpan samples and could be jarosite, kaolinite or silica, but, no further information about the grains was obtained. Many chlorite or mica particles are corroded or partly dissolved and different stages of phyllosilicate transformations have been observed. Commonly the outer part of the grains has been gradually split into sub-particles and sometimes the inner parts of the grains are incompletely dissolved. Some crystals are very thin (one layer?), and may be divided into polygonal flakes (Fig 5F). However, no electron diffraction patterns could be obtained for them. These crystals have been observed in the < 2 µm fraction of the stream sediment samples with a high content of Fe-minerals (sample 16, 10).

Microanalyses: More precise Fe mineral differentiation and identification was made by elemental grains microanalysis. Grains with pin-cushion morphology besides

dominant Fe also have high sulphur contents (Tab. 2A, samples 7,8). High contents of iron, with no or low sulphur contents are associated with short rod-like or platy morphology (samples 2 to 5). Many very fine Fe-aggregate grains contain sulphur, but in low amounts and with variable Fe : S ratios (sample 6 to 8). It is possible, that these very fine grained Fe-mineral phases bind or adsorb sulphate ions in varying extents. The microanalyses of Fe-phases (Tab. 2A) proved a compositional differentiation of identified minerals in natural samples. The presented results cannot prove that the identified Fe-minerals (e.g. goethite) contained aluminium or other elements originating from sulphides. The analyses showed that Al has been combined with silica in grain, sometimes in unusual or various ratios (Tab. 2 A, B). These changes suggest alteration of micas and/or chlorites in acid mine waters. Some elements, like K, Na, Ca, Mg and Al are leached to the acid water. The analyses of halloysite grains showed, that grains were composed of Al and Si, and in some of them the Si : Al ratios were close to 1. The range of Si and Al contents in leached or partly dissolved phyllosilicate grains is shown in Tab. 2B.

Discussion

Oxidation and weathering of pyrite by mine waters recharge from the surface, result in strongly acidic mine drainage waters and is a major water-pollution process in this ancient ore-mining area. Mine-drainage ochre precipitates have formed after mixing of acid mine waters with the nearly neutral stream waters and these precipitates can fix large quantities of other pollutant metals. Pyrite oxidation is a very complicated process and an important role in this process may be played by acidophilic, iron oxidizing bacteria (Nordstrom 1982; Blowes & Jambor 1994; Bigham et al. 1990).

Fe-oxide/hydroxide minerals in natural materials are frequently visible because of their characteristic ochre colours, but the identification of these minerals is more complicated. Ochre minerals are very fine grained, even more than phyllosilicates and other common rock minerals. Simple X-ray identification of mineral phases may be obtained only after using selective dissolution techniques (Bigham 1994; Bigham et al. 1990; Murad et al. 1994) but mineral separation is often impossible in most field samples. The field samples are complicated systems and contained more minerals with same dissolution features or phases with a wide range of crystallinity (Bigham 1994). Investigated ochre precipitates are polyminerals systems and also contain rock minerals such as feldspars and chlorite. These mineral phases are more soluble in acid realms and might be transformed to amorphous compounds and/or poorly crystalline (neoformed) minerals. The most important results have been obtained using mainly TEM with element

microanalyses. Microanalysis is not very precise but in a complicated polyminerals system can inform on the element distribution between the mineral phases. Such information will also enable the use of selective dissolution techniques in future investigations (Bigham 1994).

The ochre acid mine drainage minerals are a potential (stored) source of field acidification. Fe-sulphates are easily soluble in surface conditions and after dissolution release free sulphuric acid, iron and other pollutants back into the waters. Large concentrations of Al and Mg as well as metals like Cu, Mn, As, Zn have been found in the Smolník mine and stream water. The sulphate ion concentration of water was increased to more than 12000 mg/l in the upper portal of the mine and was about twice this value in the deeper portal (Jaško et al. 1996). The pH values of mine waters are less variable probably because of the buffering effects of more soluble minerals like chlorite in the mine wall rocks. Under low-pH conditions the dissolution of aluminosilicate minerals becomes an important acid-neutralization mechanism (Blowes & Ptacek 1994). Detailed monitoring of Smolník mine water will show only whether dissolution minerals processes are congruent or not. The greatly increased amounts of total dissolved solids in the nearsurface water (17 g/l) compared with the mine water in 1994 (about 7 g/l) indicated intensive dissolution. It is also important to distinguish the ochre minerals which store pollutant elements like Cu, As, Zn, but especially Al, because these elements are often the source of soil-acidity (Thomas & Hargrove 1984; Cornell 1991).

The results suggest the presence of jarosite, schwertmannite and goethite in the ochre precipitates. These minerals could form very quickly as a result of the oxidation of Fe^{2+} , hydration and neutralization reactions in the mixing waters. Strong acidity and high SO_4^{2-} concentration are favourable (Bigham et al. 1990; Bigham 1994) for the formation of jarosite ($\text{pH} < 3$, $\text{SO}_4^{2-} > 3000$ mg/l) and schwertmannite ($\text{pH} 3\text{--}4$, $\text{SO}_4^{2-} > 1000$ mg/l). Strong acid conditions in the systems could be the result of *Thiobacillus ferrooxidans* activity in the mine water (Nordstrom 1982) and microbiological studies are currently under way. Goethite is present in ochre hardpan samples in large amounts and also in two samples from the uncontaminated part of the stream. The increase in goethite formation results from gradual crystallization of goethite following transformation of sulphate-bearing phases after decreasing acidity and SO_4^{2-} concentration in the surface environment. The influence of meteoric CO_2 and water would be critical factors for these alteration processes. Smolník receives heavy precipitation and large amount of meteoric waters flow into the mine so that the „mine acidity reactor” is recharged continually throughout the year.

The mine waters contain not only high Fe concentrations (e.g. lower portal water: 4068 mg/l) but also Al, Mg and Si (same water: Al—1620, Mg—4962, Si as H_2SiO_3 —144 mg/l, Jaško et al. 1996). These values clearly indicate

that aluminosilicate minerals have been dissolved and the presence of jarosite suggests leaching of K^+ from mica. The major portion of dissolved Al^{3+} must partition into the solid phase through precipitation, sorption and coprecipitation reactions (profile P6: 16 mg/l, Jaško et al. 1996). These processes can remove other elements from solutions to the ochre precipitates. Theoretically Al can replace about 33 mol% of the Fe in goethite (Schulze & Schwertmann 1984; Schwertmann & Cornell 1991; Ruan & Gilkes 1995) by coprecipitation from solutions. The present results cannot confirm this process. Al and Si probably formed halloysite, or some electron amorphous phases in the strong acid environments (Gorbačev 1977; Huang 1974). Neoformed minerals like kaolinite have been described as secondary minerals in the mine tailings (Jambor 1994) and rock minerals weathering in acid soils may altered and soils may contained allophane and halloysite (Romero et al. 1992) following dissolution of common phyllosilicate minerals. The investigation of phyllosilicate acid dissolution would be important to assess the neutralization capacity of rocks in the Smolník mine.

Conclusions

1. Ochre precipitates are formed of fine grained Fe^{3+} minerals typically some tens to several hundred nm in diameter and aggregates usually $< 1 \mu m$.

2. Jarosite, probably schwertmannite and goethite have been identified in the ochre deposits. The crystallization of sulphate-bearing minerals is controlled by low acidity and high SO_4^{2-} concentration in the solutions. Decreasing SO_4^{2-} concentration and acidity in the solution – precipitation system are favourable to goethite crystallization or transformation from sulphate-bearing minerals. In hardpan ochre deposits goethite is more dominant than in soft/fresh deposits.

3. The formation of such minerals as jarosite and halloysite (or amorphous Si-Al compounds) indicate dissolution of aluminosilicate rock minerals in contact with acid mine waters. Halloysite can attract only a small portion of dissolved Al^{3+} in the mine water but Fe^{3+} - Al^{3+} substitution in neoformed minerals (e.g. formation Al-goethite) has not yet been confirmed.

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References

- Bigham J.M., 1994: Mineralogy of ochre deposits formed by sulfide oxidation. In: Blowes D.W. & Jambor J.L. (Eds.): *The environmental geochemistry of sulfide mineral-wastes*. Mineral. Assoc. Canada, Waterloo, 22, 103–132.
- Bigham J.M., Schwertmann U. & Carlson L., 1992: Mineralogy of precipitates formed by the biogeochemical oxidation of Fe(II) in mine drainage. In: Skinner H.C. W & R.W. Fitzpatrick (Eds.): *Biomineralization processes of iron and manganese: modern and ancient environments*. Catena Verlag, Cremlingen-Destedt, 219–232.
- Bigham J.M., Schwertmann U., Carlson L. & Murad E., 1990: A poorly crystallized oxyhydroxysulfate of iron formed by bacterial oxidation of Fe(II) in acid mine waters. *Geochim. Cosmochim. Acta*, 54, 2743–2758.
- Blowes D.W. & Ptacek C.J., 1994: Acid-neutralization mechanisms in inactive mine tailings. In: Blowes D.W. & Jambor J.L. (Eds.): *The environmental geochemistry of sulfide mineral-wastes*. Mineral. Assoc. Canada, Waterloo, 22, 271–292.
- Brown G., 1980: Effect of heat on the hydroxides, oxyhydroxides and oxides of aluminium and iron. In: Brown G. & Bridley G.W. (Eds.): *Crystal structures of clay minerals and their X-ray identification*. Mineral. Soc. London, Monograph. 5, 370–376.
- Cornell R.M., 1991: Simultaneous incorporation of Mn, Ni and Co in the goethite ($\alpha FeOOH$) structure. *Clay Minerals*, 26, 427–430.
- Gorbačev B.F., 1977: The comparative stabilities and formation conditions of kaolinite and halloysite. *Litologia i poleznye iskopaemye*, No. 6, 105–112 (in Russian).
- Grecula P. 1982: The Gemericum - a segment of riftogenous basin of Paleothethys. *Miner. slovac, Monograph.*, Bratislava, 1–263.
- Holub Z., Šimonovičová A. & Banášová V., 1993: The influence of acidification on some chemical and microbiological properties of soil, those determining plant variability. *Biologia, Bratislava*, 48/6, 671–675.
- Huang W.H., 1974: Stabilities of kaolinite and halloysite in relation to weathering of feldspars and nepheline in aqueous solution. *Amer. Mineralogist*, 59, 365–371.
- Ilavský J.(Ed.), 1993: The Smolník — the town of copper-ore mines. *Miner. slovac, Monograph*. Bratislava 1–368 (in Slovak, German abstract).
- Jambor J. L., 1994: Mineralogy of sulfide-rich tailings and their oxidation products. In: Jambor J.L. & Blowes D.W. (Eds.): *Environmental geochemistry of sulfide mine-wastes*. Mineral. Assoc. Canada, Waterloo, 22, 59–102.
- Jambor J.L. & Blowes D.W., 1994: Environmental geochemistry of sulfide mine-wastes. *Mineral. Assoc. Canada*, Waterloo, 22, 1–438.
- Jaško V., Cicmanová S., Bajtoš P., Pramuka S., Šesták P., Bašita J., Gajdoš V., Rozimant K., Lintnerová O., Hornung L. & Galajda J., 1996: Smolník — the complete hydrogeological and hydrochemical study of Cu-Fe deposit. *Administrative report*, Aquipur Com. Bratislava, 1–124 (in Slovak).
- Murad E., Schwertmann U., Bigham, J.M. & Carlson L., 1994: Mineralogical characteristic of poorly crystallized precipitates formed by oxidation of Fe^{2+} in acid mine sulfate waters. In: Alper C.N. & Blowes D.W. (Eds.): *Environmental geochemistry of sulfide oxidation*. Amer. Chem. Soc. Symposium, Ser. 550, 190–200.

- Nordstrom D.K., 1982: Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In: *Acid sulfate weathering. Soil Science Soc. of America*, 37–46.
- Onačič D. & Hurny J., 1994: The Smolník Deposits. In: Chovan M., Háber M., Jeleň S. & Rojkovič I. (Eds.): *Ore textures in the Western Carpathians. Slovak Academic Press*, Bratislava, 47–48.
- Rojkovič I., 1994: The stratiform mineralization. In: Chovan M., Háber M., Jeleň S. & Rojkovič I. (Eds.): *Ore textures in the Western Carpathians. Slovak Academic Press*, Bratislava, 45–47.
- Romero R., Robert M., Elsass F. & Garcia C., 1992: Evidence by transmission electron microscopy of weathering microsystems in soil developed from crystalline rocks. *Clay Minerals*, 21, 21–33.
- Ruan H.D. & Gilkel R.J., 1995: Acid dissolution of synthetic aluminous goethite before and after transformation to hematite by heating. *Clay Minerals*, 30, 55–56.
- Schulze D.G. & Schwertmann U., 1984: Influence of aluminium on iron oxides X. The properties of Al substituted goethites. *Clay Minerals* 19, 521–529.
- Schwertmann U. & Cornell R.M., 1991: Iron oxides in the laboratory. VCH Weinheim, N.Y.-Basel- Cambridge, 1–137.
- Singer P.C. & Stumm N., 1970: Acid mine drainage: The rate determining step. *Science*, 67, 1121–1123.
- Šucha V., Kraus I., Zlocha M., Streško V., Gašparovičová M., Lintnerová O. & Uhlík P., 1996: The occurrence and the reasons of the field acidification in the Šobov area (Štiavnické vrchy Mts., Slovakia) *Miner. slova*, in press (in Slovak).
- Thomas G.W. & Hargrove W.L., 1984: The chemistry of soil acidity. In: Adams F. (Ed): *Soil acidity and liming. Agronomy*, 12, Madison, Wisconsin, 4–55.