Precipitation and chemical composition of iron ochres in the pyrite and stibnite deposits in the Malé Karpaty Mts.

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Abstract. Exploitation of pyrite ores and hydrothermal Sb deposits in the Malé Karpaty Mts. culminated at the turn of the 20th century. The host rocks of mineralizations are black shales in the actinolitic schists and amphibolites. Intensive weathering occurs mostly on the dumps and outcrops in the pyrite-bearing black shales of the Augustín deposit. Acidofilic lithotrophic bacteria was isolated from mine water with pH 2.5–3, which indicates their partition in weathering processes. As solid secondary phases, gypsum and jarosite occur in weathered black shales. The formation of young iron ochres prevail in drainages with pH 5.5–8. They are collected on the bottom of effluents and sometimes fill extentive marshes. According to chemical composition, several types were recognized: depending on the primary mineralization As-, Si-, Al-, and SO_4-rich ochres are formed. Sb, Zn, Ni, Pb, Cd, Ti, P, Ca, Na and P are accummulated as minor or trace elements. Our research refers to the presence of poorly crystalline goethite, schwertmannite, Fe arsenate-sulphate in precipitates, the occurence of ferrihydrite and Si-phases can not be excluded. Based on our and previous investigations, the ecological problem of the area actually may be toxic metals pollution (As, Sb, Al and SO_4) rather than acidification itself.

Key words: Malé Karpaty Mts., mine drainage, iron oxyhydroxides, sorbtion

Introduction

Economically the most important ore mineralizations in the Malé Karpaty Mts. were emplaced in the lower- to middle Devonian (Planderová & Pahr, 1983) volcano-sedimentary formation, later metamorphosed in the amphibolite facies. According to Chovan *et al.* (1992) two mineralization types occur:

I. Metamorphosed, primarily exhalation-sedimentary pyrite mineralization.

II. Hydrothermal mineralization, which is subdivided into three sub-types:

1 - molybdenum in granitoides;

2 - copper-base metal with silver: (a) Cu-Pb, Ag, (Ni); (b) Pb-Zn; (c) Pb-Ag;

3 - antimony-gold: (a) gold-sulphidic; (b) gold-quartz; (c) stibnite.

Two of these subtypes were subjected to mining. First, the pyrite-pyrrhotite mineralization, which is a product of exhalation and sedimentary processes of submarine volcanism. Pyrite exploitation dates to the late 18th century, flourishing between 1850 and 1896 (Cambel, 1959). Second, the hydrothermal Sb-As-Au mineralization cuts through the pyrite-pyrrhotite one. Dominant ore minerals are arsenopyrite, pyrite, stibnite and gudmundite. Intense carbonatization took place as well. Two Sb deposits bound to this mineralization were exploited: the Pernek deposit (1790 – 1922, Koděra ed., 1990) where several abandoned dumps remained, and the Kolársky Vrch de-posit (1790 – early 1990's). The latter was equipped with flotation processing since 1906 (Cambel, 1959). Waste was deposited in three tailings impoundments. Both of these mineralizations are bound to the lenses of black shales in the actinolitic shists and amphibolites.

Weathering of open deposits, dumps and tailings impoundments is the cause of the following processes:

– pollution of water, soil, and alluvium in the surrounding area, main contaminants being As and Sb (Letko *et al.*, 1992; Veselský *et al.*, 1996);

– local acidification (Šucha *et al.*, 1996; Trtíková *et al.*, 1997);

– precipitation of supergene products – a wide variety of secondary minerals has been reported: allophane, azurite, cervantite, gypsum, halloysite, hyalite, jarosite, kaolinite, kermesite, malachite, Mn oxides and hydroxides, senarmontite, siderite, Sb ochre, schafarzikite, valentinite, limonite (Cambel, 1959; Andráš & Chovanec, 1985; Koděra ed., 1990), chapmanite (Polák, 1983), and scorodite (Uher, 1990);

– local degradation of phytocenoses, especially in close proximity of dumps with black shales (Banásová in Šucha *et al.*, 1996).

The most distinctively pronounced hypergenous process is the precipitation and deposition of iron ochre. Our research deals with these young hypergenous products in the pyrite-pyrrhotite bearing ore district of Augustín and Michal and in the region of Sb - Au deposits of Kolársky Vrch and Pernek. The aim of our study is to identify iron

oxyhydroxides - basic components of iron ochres (Bigham *et al.*, 1996a), to investigate their chemical composition and to specify the conditions of their formation.

Analytical Techniques

Places of acid mine effluents were recorded, as well as areas where iron ochres precipitate and settle. The pH of waters was measured and samples of water and solid secondary phases were taken for further analysing.

The sampling methods were chosen according to those described in Bigham *et al.* (1996b). Plastic bottles were filled with material after a wash in the local water. Organic matter (remains of plants) and inorganic detritus were removed by sieving and sedimentation. Solid samples were then air-dried and properly packed to prevent oxidation. The contents of dissolved elements in mine waters was measured by Atomic Absorption Spectrometry (AAS). In the X-ray powder diffraction (XRD), $CoK\alpha$ radiation with a Philips PW1710 goniometer was used and solid samples were scanned from 4 to $80° \, 2\Theta$ with increment of $0.02° \, 2\Theta$ and 0.5-0.8 s per step (Geological Institute of Slovak Academy of Sciences). The total Fe content (Fe_{tot}) in the precipitates was determined using dissolution in concentrated HCl. Oxalate soluble Fe (Fe_o) was determined after dissolution in ammonium oxalate (Schwertmann, 1964). Samples were analysed for Al (atomic emission spectroscopy with inductively coupled plasma), As, Sb (AAS with hydride generation), Fe (AAS with atomization in air-acetylene flame), SO_4 (gravimetry), Cd, Cu, Mn, Pb, Si, Zn, Na and K (AAS) (Laboratories of analytic methods of the Faculty of Natural Sciences, Comenius University, Bratislava and the Slovak Academy of Science, Banská Bystrica). Transmission electron micrographs (TEM) for studying morphology of precipitates (JEOL 2000, Faculty of Nature Sciences, Comenius University, Bratislava) were acquired. Infrared absorption spectra (IR) were obtained with a Nicolet Magna 750 Fourier transform infrared spectrometer equipped with a DTGS detector (Institute of Inorganic Chemistry, Slovak Academy of Sciences, Bratislava). For each sample 256 scans were recorded in the $4000 - 400 \, cm^{-1}$ spectral range with a resolution of $4 \, cm^{-1}$. The KBr pressed disc technique (1 mg of sample and 200 mg of KBr) was used. The acidofilic chemolithotrophic bacteria from mine drainages were identified through isolation tests, where selective nutrient medium after Silverman, Lundgren and Vaksman (Silverman & Lundgren, 1959) was applied (Geotechnical Institute of the Slovak Academy of Sciences, Košice).

Results and discussion

Pyrite deposit Augustín

The pyrite-pyrrhotite deposit of Augustín is situated in the upper part of the Hrubá dolina valley (Fig. 1), 8.2 km NW from Pezinok. The most intensive oxidation, dissolution and acidification occur in the ore-bearing black shales of dumps and outcrops. The sites 1 and 2 were
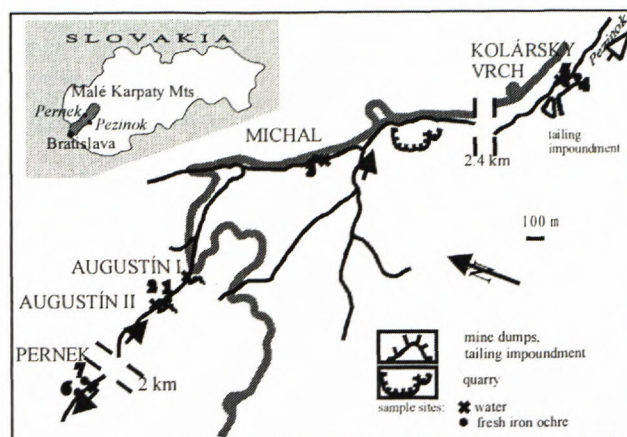

Fig.1 Schematic map of the mining area in the Malé Karpaty Mts. showing location of the main sampling sites

situated where the pH of stream and pit water is 2.5-3 (Tab. 1). Chemolithotrophic bacteria, *Thiobacillus ferrooxidans, Th. thiooxidans* and *Leptospirillum ferrooxidans* (Fig. 4) was isolated under these acid conditions. The occurrence of bacterial cells confirms that intensive biooxidation of the sulphides takes place. Stream water in the surroundings of this locality does not contain large amounts of dissolved contaminants (Tab. 1). Secondary phases precipitate from acidic solutions directly in the dump débris, predominantly gypsum and jarosite. Young iron oxyhydroxide precipitates form in very small amount on the bottom of brooks, usually close to the source, i.e. right below the dumps. The phases are poorly ordered, nevertheless, they exhibit features typical for schwertmannite - $Fe_8O_8(SO_4)(OH)_6$ (Fig. 2a, b). Although the conditions are favourable for its precipitation (Bigham *et al.*, 1994; Bigham *et al.*, 1996a; Bigham *et al.*, 1996b) and major part of the material is oxalate-soluble (Tab. 4) it does not contain appropriate amount of SO_3 (Tab. 2 and 4). According to Bigham *et al.* (1994), the Fe_{tot}/S_{tot} mole ratio for schwertmannite can vary from 5 to 8. Other elements and SiO_2 show low or trace contents, too, (Al, Ti, P, Zn, Cu, Pb etc.) in the samples (Tab. 3). Due to the common paucity of precipitates, it was not possible so far to obtain samples for further analyses.

Pyrite deposit Michal

Pyrite deposit Michal (Fig. 1) is situated 1 km southeast of the Augustín locality. These two deposits are connected by old adits which are inundated by waters containing dissolved metals. The chemical composition of the water is similar, however, with pH of 6.3-6.6 (Tab. 4). The most massive sedimentation of iron ochres takes place in the Michal gallery effluent stream (site 3, Fig. 1), and forms a red-coloured wetland covering the area of about $400 m^2$. Ochres absorb considerable amount of Al_2O_3 and SiO_2 (12 - 13 wt%) but are poor in SO_3 ($Fe_{tot}/S_{tot} = 156.67$, Tab. 4). X-ray diffraction pattern of the sample consists of one broad line at 2.82 A (Fig. 2a) and indicates that the precipitates are very poorly crystallized. The infrared spectra shows the coincidents of
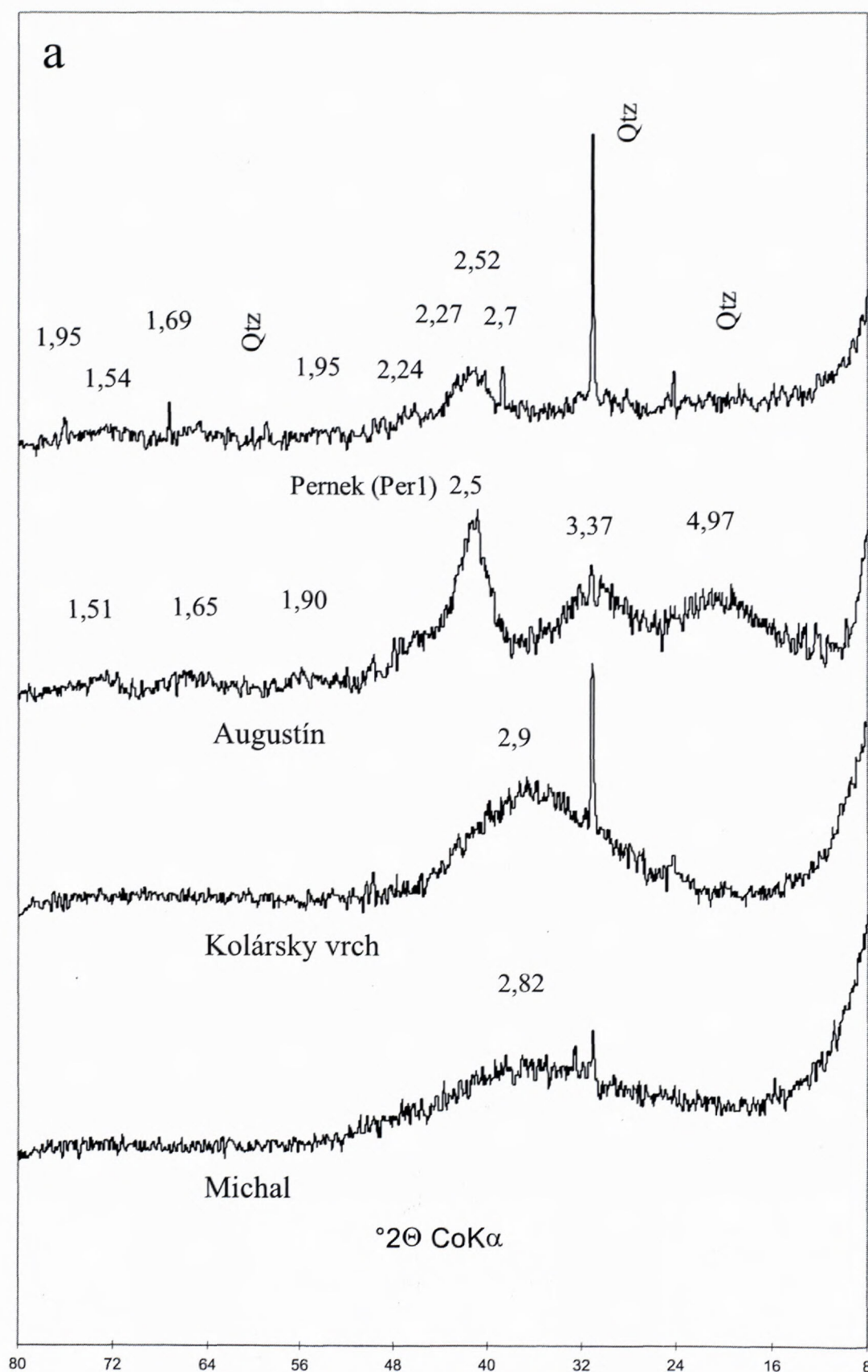
Fig. 2a - X-ray diffractograms of poorly crystalline natural iron ochres from Malé Karpaty Mts.; X-ray diffractograms of Fe oxyhydroxides from acid mine drainages, published data: b - schwertmannite (Sh), c - goethite (Gt) (Bigham et al., 1996b), d - ferrihydrite (6 and 2 lines ferrihydrite) (Schwertmann & Cornell, 1991).
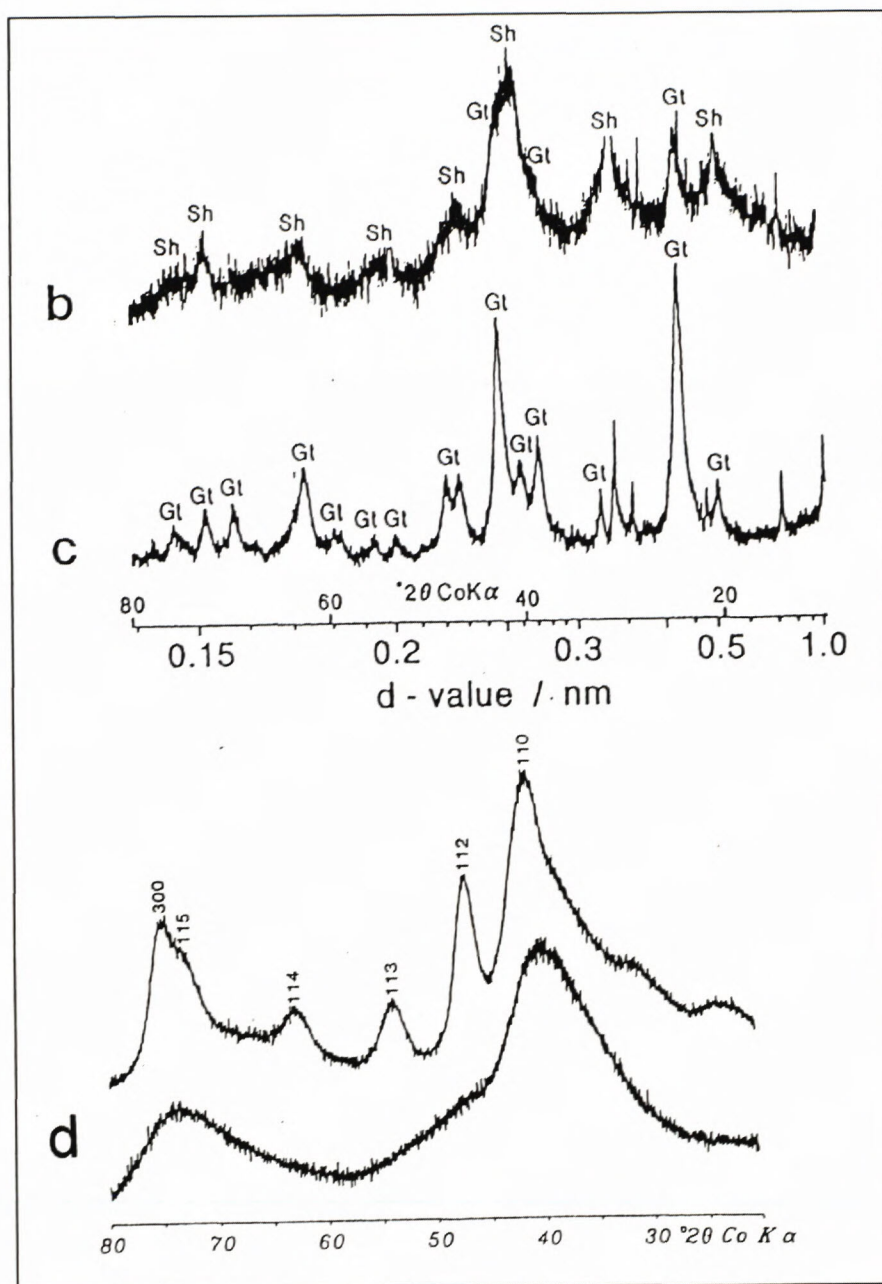
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Fig. 2b-d

absorption bands of oxyhydroxides with more intensive bands of kaolinite (Fig. 3a). But the occurrence of Al and Si in the solution after selective dissolution (Tab. 2) is due to sorption of elements on oxyhydroxides. Ochres consist mainly of oxalate-soluble phase (Fe_o/Fe_{tot} = 0.95) and ferrihydrite - $Fe_5HO_8 \cdot 4H_2O$ then could be their main component.

Sb deposit Kolársky vrch

The Sb deposit with tailings impoundment is situated 3.5 km northwest of Pezinok (Fig. 1). Increased contents of metals in the mine waters of this area refer to intensive oxidation (Letko *et al.*, 1992). The pH of this water is 7.5-8 (Tab. 4) because the acidity here is buffered by the high content of carbonates in the tailings impoundment. The concentrations of SO_4, As, Sb, Mn, Na and K (Tab. 1) in the water of seepages (site 4) and tailing effluent (site 5) are significantly higher than in other deposits. The contents of As_2O_5 and SO_3 in iron ochres is very high (Tab. 2), sum of As_2O_5 and SO_3 is higher than Fe_2O_3 contents, Fe_{tot}/S_{tot} mole ratio is 2.53–2.86 (Tab. 4). The material which consists of colloid-size particles (Fig. 5) is poorly crystalline, an X-ray diffractogram shows a wide maximum at 2.9 Å, in the region of Fe oxyhydroxides (Fig. 2a). This sample is highly soluble in ammonium oxalate (Tab. 4). The infrared spectra of a precipitates (Fig. 3a) show a sharp feature at 814 cm^{-1}, which is

Tab. 1 Water chemistry of the district (location of sample sites 1 - 7 are shown on Fig. 1). Former data (*) are from Šucha et al. (1996).

Sample site	Fe_{tot}	SO_4	Al	As	Sb	Cu	Zn	Mn	Ca	Na	K
						ppm					
Augustín II*	*3.38	*295.30	*2.11	*0.00	*0.00	*0.13	*0.14	*0.41	-	-	-
Augustín II	0.75	-	-	-	-	4.15	1.90	0.75	9.02	6.35	0.80
Augustín I	*28.61	*761.70	*31.03	*0.00	-	*0.77	*1.27	*0.79	-	-	-
Michal *	*10.44	*280.20	*2.84	*0.01	*0.00	*0.06	*0.37	*0.42	-	-	-
Michal	0.00	-	-	-	-	0.00	0.10	0.20	12.17	8.40	0.80
Kolársky vrch	0.08	2349.60	<0.10	3.35	2.51	0.10	0,10	3.15	24.19	23.20	22.40
Pernek	0.03	662,50	<0.10	0.00	0.31	0.08	0.00	0.08	107.50	4.93	0.90

Tab. 2 Chemical composition of iron ochres, main major components, 1 and 2 - Augustín deposit, 3 - Michal deposit, 4 and 5 - Kolársky vrch deposit, 6 and 7 - Pernek deposit, (location of sample sites 1 - 7 are shown on Fig. 2).

Sample site	Fe_2O_3	SiO_2	SO_3	Al_2O_3	As_2O_5
			wt %		
1.	50.34	1.84	1.12	0.68	0.05
2.	46.33	2.52	0.82	0.59	0.02
3.	37.18	12.88	0.23	12.47	0.02
4.	34.68	2.57	13.31	0.32	24.07
5.	36.56	6.91	12.51	1.08	21.40
6.	51.19	19.17	3.31	8.88	0.06
7.	55.63	10.10	2.32	3.74	0.06

Tab. 3 Chemical composition of iron ochreous precipitations, minor and trace elements, 1 and 2 - Augustín deposit, 3 - Michal deposit, 4 and 5 - Kolársky vrch deposit, 6 and 7 - Pernek deposit, (location of sample sites 1 - 7 are shown on Fig. 2).

Sample site	Sb	Cu	Zn	Pb	Cd	P	Ti	Mn	Ca	Na	K
						ppm					
1.	239	80	400	25	13	3200	2800	0	396	600	40
2.	236	80	600	18	4	2700	2500	0	136	640	80
3.	191	720	840	24	12	2000	2400	80	4352	640	80
4.	527	0	606	19	5	2900	2300	1980	2832	727	323
5.	490	0	825	16	4	1600	1800	412	10837	701	124
6.	322	523	243	37	0	1200	1100	597	1800	467	131
7.	320	516	536	39	0	1000	600	1231	0	318	60

Tab. 4 Properties of natural Fe ochreous precipitations. (*) – mole ratio, Fe_o – Fe extractable in oxalate, Fe_{tot} - Fe extractable in HCl, 1 and 2 - Augustín deposit, 3 - Michal deposit, 4 and 5 - Kolársky vrch deposit, 6 and 7 - Pernek deposit, (location of sample sites 1 - 7 are shown on Fig. 2).

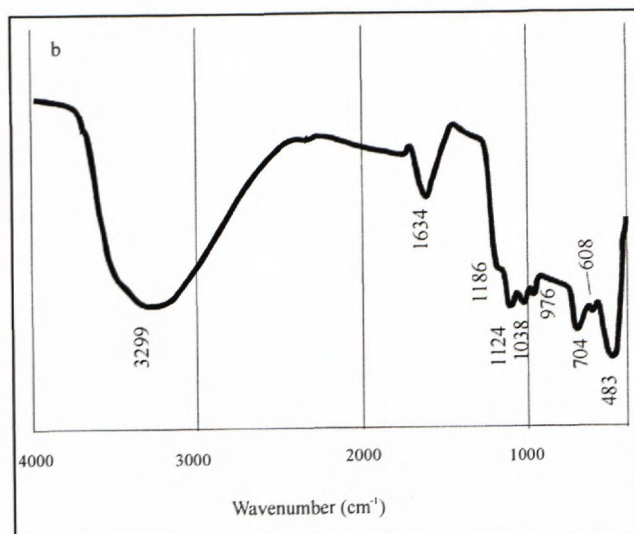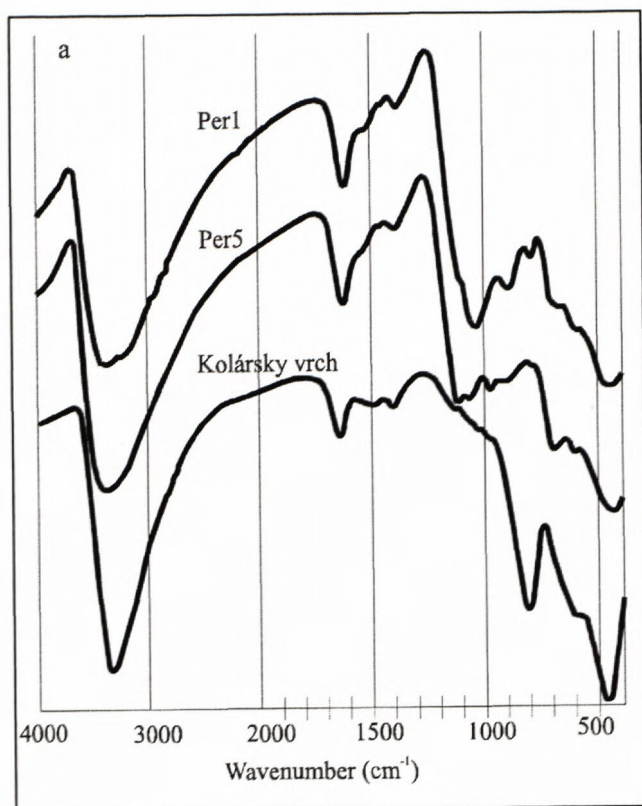| Sample site	pH	Fe_{tot}	Feo	SO_3	Fe_o/Fe_{tot}*	Fe_{tot}/S_{tot}*
			wt %			
1.	2.5-3	35.20	34.16	1.12	0.97	45,00
2.	2.5-3	32.40	29.28	0.82	0.90	58.00
3.	6.3-6.6	26.00	24.75	0.23	0.95	156.67
4.	7.8-7.9	24.24	24.36	13.31	1.00	2.53
5.	7.5	25.57	24.19	12.51	0.95	2.86
6.	6.3	35.80	32.83	3.31	0.92	16.00

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Fig. 3 Infrared spectra of the mine precipitates: a: IR spectra of natural schertmannite (Per1) and goethite (Per5) from Sb deposit Pernek and Fe arsenate-sulphate from Sb-Au deposit Kolársky vrch; b - IR pattern of schwertmannite (Bigham et al., 1994)

assigned to AsO^{3-} or AsO^{4-} compounds. The weak absorption bands at 606 and 982 cm^{-1} and in the 1060-1180 cm^{-1} range likely are attributed to SO_4. The spectrum is dominated by a very intensive feature at 486 cm^{-1}, which can be attributed to Fe-O stretch. It is likely that this material is composed of a mixture of Fe arsenate with Fe sulphate. The infrared spectrum of this sample is comparable to the infrared pattern of synthetic and natural precipitates described by Carlson & Bigham (1992). According to them, AsO_4^{2-} displaces SO_4^{2-} from the surface of oxyhydroxysulphates under acidic conditions.

Sb deposit Pernek

The Pernek-Krížnica locality (Fig. 1) is the oldest Sb deposit in the Malé Karpaty Mts. and it is situated about 3 km northeast of Pernek. No distinct acidification in the surface water was recorded and mine effluents did not exhibit consequential pollution (Tab. 1). Inundated groves where pH varies between 5.0-6.5 (Tab. 4) „produce„ a huge amount of iron ochres rich in SiO_2 and Al_2O_3 (Tab. 2). X-ray diffraction analyses consist of weak and broad lines and of distinct peaks due to detrital quartz (Fig. 2a). The infrared spectrum of sample PER 1 (site 6, Fig. 1) is likely due to the presence of schwertmannite and is comparable with one described by Bigham *et al.* (1994) (Fig. 3b). The spectrum is dominated by bands at 420-460 cm^{-1} (Fig. 3a) and together with broadened feature at 695 cm^{-1}, it can be attributed to Fe-O stretch. Absorption bands at 978 cm^{-1} are likely due to v_1 (SO_4) and at 603 cm^{-1} are due to v_4 (SO_4), which belong to structual SO_4. Features at 1118 and 1074 cm^{-1} can be assigned to the splitting of the v_3 (SO_4), due to the fornmation of the bidendate bridging complex between SO_4 and Fe (Bigham *et al.*, 1994). A band at 1186 cm^{-1} is not present in spectrum of the sample and it is likely coincided. The promi-

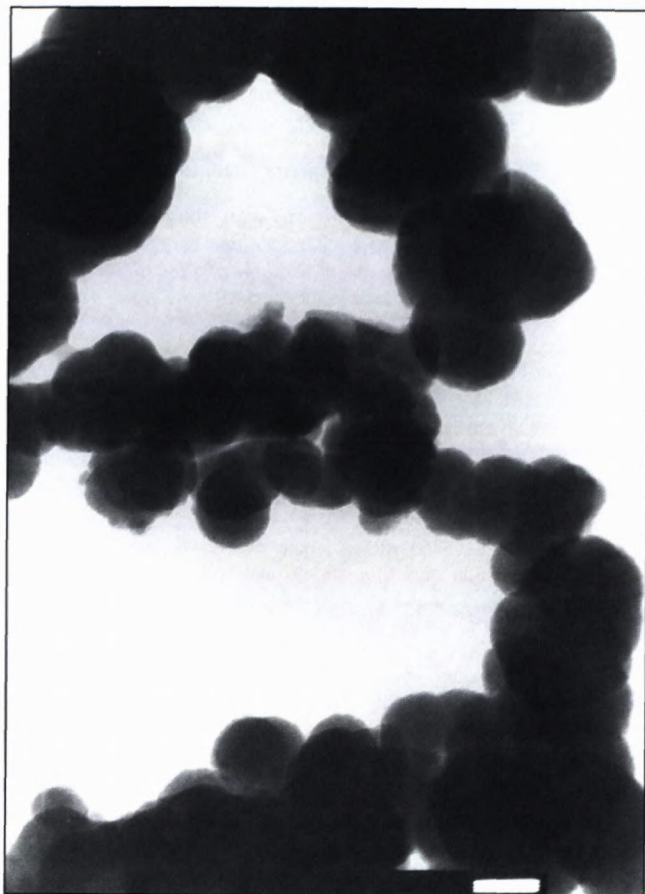Fig. 4 Cells of acidofilic bacteria identified in acid mine water, Augustin deposit.

Fig. 5 Colloid particles of As bearing poorly crystalline precipitates, Sb deposit Kolársky vrch (sites 4 and 5, Fig. 1). Bar scale corresponds to 100μm.

Fig. 6 Aggregates of schwertmannite from ochreous precipitates, Sb deposit Pernek (sites 6, Fig. 1). Bar scale corresponds to 100 μm.

nent absorption band at 3382 cm^{-1} is attributed to the OH stretching band and the feature at 1625 cm^{-1} to the H$_2$O deformation. The Fe$_{tot}$/S$_{tot}$ mole ratio of a mixture with probable schwertmannite is 16 (Tab. 4) and it occurs in more acidic mine effluents. This mineral consists of globular aggregates (Fig. 6), that are a typical feature of schwertmannite. The infrared spectum of sample PER5 (Fig. 3a) is due to the presence of goethite. The characteristic goethite bands with wavenumbers 899 and 800 cm^{-1} are assigned to the OH deformation (Farmer, 1974). The position of these features is shifted to the higher wavenumbers related to Al-Fe substitution (Schwertmann & Cornell, 1991). The intensive band centered at 3382 cm^{-1} may be assigned to the OH stretching band. The occurrence of ferrihydrite and Si-phases or SO$_4$ compound is not excluded from this sample.

Conclusions

Generally speaking, the environmental impact of the acidification is not very pronounced in the study area. Acidity there is buffered by carbonates of hydrothermal origin in the Sb deposits. Contamination of mine drainages in the surroundings of deposits is low except for the Sb deposit of the Kolársky vrch region, where high concentration of SO$_4$, As and Sb in mine water was determined.

The presence of chemolithotrophic bacteria (*Thiobacillus ferrooxidans, Th. thiooxidans* and *Leptospirillum ferrooxidans*) in the acid mine drainages with a pH of 2.5–3 indicates their contribution to the oxidation and precipitation processes. The formation and deposition of young iron ochres along the bottom of streams prevails in mine waters with a pH of 5.0–8 (Kolársky vrch, Michal and Pernek deposits).

The chemical and mineral composition of the precipitates varies widely as well, as a consequence of different formation conditions and the type of deposit. Considerable sorption of Al and Si in the ochres was registered in the old pyrite and Sb deposits. Ochres, precipitating at the tailing impoundment of the Sb deposit are highly enriched in As and SO$_4$. The Sb contents in the mine drainage precipitates never exceeded 530 ppm, even not in the stibnite deposits. Relatively homogeneous is the concentration of Zn and Pb – hundreds and tens ppm. All the samples exhibit a certain sorption of Ti and P (600-3200 ppm), in some samples Na, K, Mn, and Cu also were recorded.

This study refers to the occurrence of poorly crystalline goethite, schwertmannite, and Fe arsenate and Fe sulphate compounds in the mine ochreous precipitates. The formation of ferrihydrite and Si-phases can not be excluded. For more accurate identification of the mineral phases further analytical techniques will be used, such as

thermogravimetric analysis and Mössbauer spectroscopy as described by Carlson & Schwertmann (1981); Carlson & Bigham (1992); Bigham *et al.* (1996a); Bigham *et al.* (1996b); Bigham *et al.* (1990); Bigham *et al.* (1994) etc.

The investigation also revealed that iron ochres might be a latent stock of dangerous pollutants, such as As, Al, Sb. This reservoir is growing and constantly supplied with these toxic metals.

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