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THE MINERALOGICAL RESEARCH OF MANGANESE–PHOSPHATE CRUSTS IN THE REGION OF HODUŠÍN – BOŽETICE AT MILEVSKO

Miroslav BROŽ [1], **Miloslava KOVÁŘOVÁ** [2], **Zdeněk LOSOS** [3]*,
Marcela LINHARTOVÁ [2] **and Václav VÁVRA** [3]

[1] *Geobrick Ltd., Polní 23/25, 639 00 Brno, Czech Republic*
[2] *Czech Geological Survey, Leitnerova 22, 658 69 Brno, Czech Republic*
[3] *Institute of Geological Sciences, Masaryk University, Kotlářská 2, 611 37 Brno, Czech Republic*
**Corresponding author's e-mail*: losos@sci.muni.cz

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ABSTRACT
A mineralogical study of the weathering crusts rich in P and Mn from the locality Hodušín – Božetice at Milevsko is presented. The locality belongs to the central part of the variegated group of Sušice and Votice in the Moldanubian Unit. From the analytical methods used, the IR-spectroscopy yielded satisfactory results. The main crust components subjected to weathering are apatite (of a CarHap B – dahllite type) and Mn-minerals (massive black psilomelane, the needle-aggregates probably comprise a poorly recrystallized psilomelane). Disintegrated rocks consist of a mixture of clay minerals, calcite and relicts of primary minerals (quartz, K–feldspars, albite, pyroxene and rutile). The origin and the source material of these crusts rich in P and Mn can not be unambiguously determined. Apatites without CL-effects indicate that the weathering crusts have originated in a strongly oxidative environment.

Well documented neighbouring occurrences of phosphate minerals in the variegated group of Sušice and Votice are associated with graphitic rocks. Optical and quantitative chemical analyses of the rocks suggest that the source of apatite could possible be calc-silicate rocks (erlans) close to the graphitic rocks. Hypothetically, the metaphosphorite layers in the variegated Moldanubian Unit can also be considered a possible source of phosphorus.

KEYWORDS: Czech Republic, Moldanubicum, Hodušín, Božetice, variegated rock group of Sušice and Votice, apatite, phosphates, weathering crusts, Mn–minerals

1. INTRODUCTION

In the course of geological mappings for a special map - sheet Tábor in the years 1925–1939, V. Čech first discovered manganese–phosphate crusts in the area between Hodušín and Božetice u Milevska in the vicinity of the local kaolin deposits. Chemical qualitative methods and microscopic studies proved the white cryptocrystalline matter of the concretions to be a phosphorite of an undefined composition, in its low refractive index and CO_2 content close to dahllite. The black, spherical to irregular mineral clusters of a semi-metallic gleam and fibre-like structures present in the white substance were classified as psilomelane (Čech and Rost, 1941). At first the authors attributed the origination of the concretions to weathering processes. Nevertheless, Čech also later (1948) suggested that the concretions could have originated by a redeposition of Tertiary sediments. This phenomenon has recently been studied in more detail by Brož in his diploma thesis (1997).

Manganese–phosphate crusts are to be found in the fields along the railroad track Tábor – Ražice close to an unbarred crossing of a field road, about 1 km NW from the Hodušín church. The locality can be accessed from the road going from Tábor to Milevsko, taking the field road which turns in the North towards Božetice (Fig. 1). From the regional-geological point of view, the locality is situated in the central part of a variegated Sušice-Votice group in the Moldanubian Unit. The locality as labelled as the point no. 6 on the Bernartice Sheet of the geological map on a scale 1:25 000 /22-243/ (Suk et al., 1975). There are no outcroppings in the locality. The occurrence of the weathering crusts is limited to a strip which is about 150 m long and 20 m wide. The stretch direction is conformal to the lithological structure of the undersoil (identical to the direction of the intercalations in the Moldanubian Unit).

About 50 m up the slope, yellow to grey clays emerge together with graphitic rocks. These clays probably represent the once mined kaolin deposits mentioned by Čech, Šafránek, Jókely, Kratochvíl and other authors (1957–1964).

The site was subjected to sampling of weathered rock fragments in order to localize the source rock of the manganese–phosphate crusts. Due to the overall weathering, the differentiation among the individual rock types was often possible only in the rock slices. The Moldanibian rocks are represented especially by biotite gneisses, graphitic quartzites, quartzites, erlanes and amphibolites. The rocks of the Central Bohemian Pluton comprise a leucocratic vein granite,

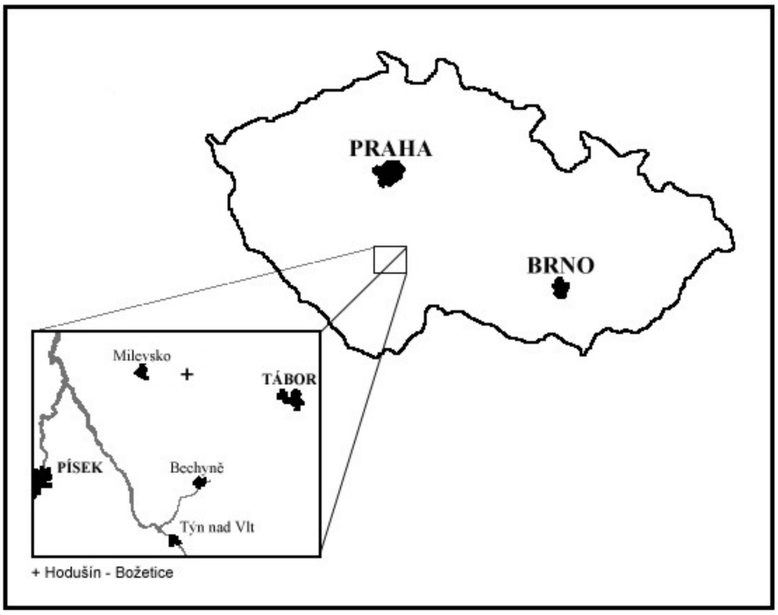

Fig. 1 The location of the occurrence of manganese–phosphate crusts near Hodušín – Božetice at Milevsko.

Table 1 Chemical analyses of rocks from the locality Hodušín – Božetice, 1 – biotite gneiss, 2 - graphitic quartzite, 3 – quartzite, 4 – calc-silicate rock, 5 – amphibolite, 6 – strong cataclased gneiss?, 7 – vein granitic rock. The analyses were performed by P. Kadlec, Institute of Geological Sciences, Masaryk University, Brno.

	1	2	3	4	5	6	7	White colloform crusts with fibered radial structure
H_2O^-	0.3	0.19	0.08	0.97	0.69	1.05	0.17	-
H_2O^+	1.35	1.44	0.02	1.04	1.72	5.57	0.41	0.07
SiO_2	63.89	84.18	98.07	47.92	45.81	47.34	72.61	96.38
TiO_2	2.64	0.06	stopy	0.75	2.8	0.26	0.15	0.01
Al_2O_3	14.65	4.66	0.2	14.4	13.98	12.29	14.38	1.52
Fe_2O_3	1.22	1.67	0.35	1.73	2.6	22.11	0.41	0.07
FeO	4.33		0.14	7.2	8.49	-	1.11	0.21
MnO	0.07	0.04	0.06	0.24	0.19	3.56	0.04	0.01
CaO	2.07	0.33	0.5	18.18	12.78	0.7	1.9	0.22
MgO	2.21	0.26	0.01	4.13	7.26	0.25	0.5	0.07
K_2O	3.43	0.91	-	0.45	0.55	1.51	3.61	1.24
Na_2O	2.61	-	-	1.42	1.49	-	4.01	traces
Li_2O	-	-	-	traces	-	0.01	-	-
S	-	-	-	-	traces	-	-	-
CO_2	0.78	-	0.16	0.75	1.01	4.1	0.4	0.1
P_2O_5	0.09	0.16	0.13	0.69	0.46	0.93	0.02	0.01
C	-	7.16	-	-	-	-	-	-
Total	99.64	101.06	99.72	99.87	99.83	99.68	99.72	99.91

pegmatite, and vein quartz. Chemical analyses of the rock samples are listed in Table 1. The highest P_2O_5 content was found in erlane. This rock contained microscopically abundant apatite crystals.

2. MACROSCOPIC AND MICROSCOPIC DESCRIPTION OF MANGANESE–PHOSPHATE CRUSTS

The size of the collected samples of Mn–phosphate crusts is on average about 10 cm. Their structures are sometimes breccia-like and they comprise a wholly weathered rock, which is glued together by apatite and manganese minerals. The cavities are fringed by a kidney-like coating of apatite and filled by associations of both clastic and newly-formed minerals (Fig. 2). Results of the chemical analyses of the Mn-phosphate crusts samples are shown in Table 2.

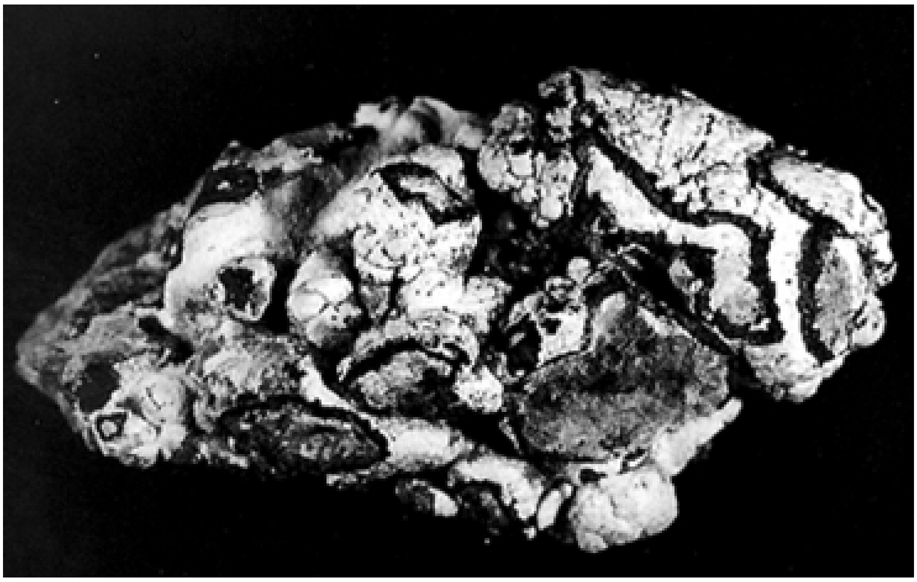

Fig. 2 The sample of manganese–phosphate bulb. White kidney-like aggregates are formed by apatite, massive black aggregates are formed by Mn–minerals. Area of the bulb is about 10 x 6 cm.

Table 2 Partial chemical analyses of manganese–phosphate crusts from the locality Hodušín – Božetice. Note: The analyses are not complete. The CO_2 content was not determined, the content of Mn was recalculated to MnO_2 content and Ba was titrated together with CaO. A significant error could have originated during the determination of the P_2O_5 content (very high concentration) and SiO_2 (Mn-oxides affect the coagulability of SiO_2). The analyses were performed by P. Kadlec, Institute of Geological Sciences, MU, Brno.

	1	2	3	4	5	6	7	8
H_2O^-	1.46	1.73	1.18	1.15	1.3	2.58	1.81	1.68
H_2O^+	2.22	2.35	2.37	2.27	3.13	1.77	2.5	3.17
SiO_2	11.3	24.32	17.67	11.01	5.21	13.03	17.68	10.17
TiO_2	0.18	0.24	0.18	0.09	0.12	0.23	0.15	0.18
Al_2O_3	3.67	6.54	5.45	3.97	3.93	4.29	6.18	4.76
Fe_2O_3	2.29	2.56	2.68	3.16	1	3.77	2.63	2.52
FeO								
MnO_2	5.33	0.26	3.04	10.56	39.68	3.98	1.84	17.78
CaO	40.21	34.57	36.94	37.44	25.86	38.2	37.31	33.22
MgO	0.72	0.93	0.84	0.73	0.46	0.55	1.09	0.94
K_2O	0.98	1.79	1.49	0.36	0.52	1.27	1.34	0.69
Na_2O	0.13	0.13	0.13	0.13	0.1	0.13	0.16	0.1
Li_2O	0.01							
CO_2	4.69							
P_2O_5	28.3	21.55	23.98	24.86	16.27	24.46	24.1	20.74
C						0.8		
Total	101.49	96.97	95.95	95.73	97.58	95.06	96.79	95.95

WEATHERED ROCK

Out of the original rock-forming minerals, only quartz, biotite and locally diopside have been preserved. Quartz forms irregular, rounded fine grains, displays undulose extinction and numerous crack ruptures. Biotite is present only in small relicts and a brownish monoclinic pyroxene is substantially weathered. The feldspars have given rise to sericite and clay minerals.

APATITE

Apatite, which contributes to the formation of the rock cement, appears to be a compact matter with no visible grains in the rock slices. It is optically pseudoisotropic and cryptocrystalline and it forms white kidney-like coatings of a concentrically-zonal to radial structure in the free cavities.

In the rock slices, the needles of apatite are colorless or slightly turbid and significantly stretched along the z-axis. The character of the zone is negative; the interference figure could not be determined due to the small size of the needles. Refractive index was measured by the immersion method on three samples. Cryptocrystalline character of the apatites allowed only the determination of the mean refractive index, the values of which are almost constant and amount to 1.602 ± 0.0004. Low refractive index values of the apatite from the locality of interest are typical for carbonate apatites (Carap). According to Hewitt (1980), the morphology of the phosphates is determined by their chemical composition. Phosphates close to carbonate fluorapatite (CarFap, francolite) form well-defined small-grained crystals, whereas carbonate hydroxylapatite (CarHap, dahllite) are characterized by a cryptocrystalline evolution of spherical structures like those observed in the case of the apatites from the studied locality.

Mn-MINERALS

Mn-minerals occur in two macroscopically different mineral phases. The first phase forms massive, locally porous and up to several centimeters large black aggregates. The second phase forms radial spinelike to dendritic aggregates, which are only a few millimeters large. The latter phase is most likely formed by a recrystallization of the former one.

THE FILL OF THE CAVITIES

The few-millimeter small cavities are filled by a poorly-defined mixture of clay minerals, sericite, biotite, quartz, feldspars (K-feldspar and plagioclase), broken-apart kidney-like apatite coatings and rock fragments (esp. quartzite).

3. X-RAY DIFFRACTION (XRD)

X-ray powder diffraction data were recorded using a STOE diffractometer (Stadi P system) in a transmission arrangement (CuKα1 and CoKα1 radiation). Diffraction records were evaluated by means of the Visual X^{pow} software, JCPDS tables of diffraction data (1986) and the PDF1 database, Set 46.

APATITE

The native mineral types of apatite are fluorapatite $Ca_{10}(PO_4)_6F_2$, chlorapatite $Ca_{10}(PO_4)_6Cl_2$, hydroxylapatite $Ca_{10}(PO_4)_6OH_2$ and carbonate apatites (carbonate fluorapatite CarFap, carbonate hydroxylapatite CarHap). They differ from each other in the lattice parameters. The parameters of elementary lattice cells of various apatites were given e.g. by Wallaeys and Chaudron (1950), Brasseur (1950) or Altschuler et al. (1953).

Brasseur has developed a method, which allows an approximate identification of individual apatite types based on the c_0/a_0 ratio. A higher c_0/a_0 ratio of the apatite in the manganese–phosphate crusts from the Hodušín – Božetice locality suggests the carbonate character of the apatite (fluorapatite and hydroxylapatite exhibit lower values of the c_0/a_0 ratio). The incorporation of CO_3^{2-} into the apatite structure results in a contraction of the elementary cell, which is demonstrated especially in the decrease in the a_0 parameter (linear dependence), to a lesser extent in the parameter c_0 (LeGeros, 1965). The mutual relations between the degree of C^{4+}/P^{5+} substitution and the size of the lattice parameters were studied by McClellan and Lehr (1969), who proposed the following empirical formula for the determination of the CO_2 content in apatites from the x-ray data: mass % $CO_2 = 1014.66 - 108.25\ a_0$.

Lattice parameters, the ratio of lattice parameters c_0/a_0, and the calculated CO_2 contents of the apatite in the manganese–phosphate crusts from the Hodušín – Božetice locality are listed in Table 3. It is impossible to differentiate between carbonate apatite and fluorapatite just by comparing their diffraction spectra (Table 4). The recorded diffraction spectra best fit the spectrum of fluorapatite, however, the IR analysis (Chapter 4) shows that the apatite from the manganese–phosphate crusts in the Hodušín – Božetice locality is a carbonate hydroxylapatite of type B (dahllite).

Table 3 Lattice parameters of apatites from the manganese–phosphate crusts of the Hodušín – Božetice locality and CO_2 contents calculated from the diffraction data by the method of McClellan and Lehr (1969).

sample	a [10^{-10}m]	c [10^{-10}m]	c/a	mass% CO_2
2 - apt.1	9.347	6.904	0.7386	2.8
3 - apt.2	9.348	6.900	0.7382	2.8
4 - apt.2	9.351	6.896	0.7375	2.4
7 - apt.2	9.337	6.899	0.7389	3.9

Table 4 Diffraction lines of apatite from manganese–phosphate crusts from the locality Hodušín – Božetice and their comparison with JCPDS (1986).

samples								**comparison with JCPDS (1986)**				
2-apt.1		**3-apt.2**		**4-apt.2**		**7-apt.2**		**Fap 15-876**		**CarHap 19-272**		
d [10^{-10}m]	I_r	d [10^{-10}m]	I_r	d [10^{-10}m]	I_r	d [10^{-10}m]	I_r	d [10^{-10}m]	I_r	d [10^{-10}m]	I_r	**hkl**
8.095	9.2	8.095	8.8	8.098	8.4	8.086	8.7	8.121	8.0			100
4.047	8.3	4.048	7.0	4.049	7.2	4.043	7.3	4.055	8.0			200
3.870	7.1	3.870	6.1	3.870	7.3	3.867	6.7	3.872	8.0			111
3.452	46.1	3.450	68.8	3.448	57.5	3.450	54.8	3.442	40.0			002
3.175	14.0	3.174	19.5	3.172	17.2	3.173	18.7	3.167	14.0	3.170	2.0	102
3.060	15.3	3.060	13.9	3.061	15.1	3.056	15.9	3.067	18.0			120
2.797	100.0	2.797	100.0	2.798	100.0	2.794	100.0	2.800	100.0			121
2.777	49.4	2.776	61.1	2.775	50.5	2.774	55.4	2.772	55.0	2.780	100.0	112
2.698	48.7	2.699	49.3	2.699	52.4	2.695	48.9	2.702	60.0			300
2.627	29.9	2.626	34.3	2.625	32.5	2.624	34.0	2.624	30.0	2.622	10.0	202
				2.289	8.6	2.288	8.7	2.289	8.0	2.285	6.0	122
2.245	23.3	2.245	19.7	2.246	22.7	2.243	21.5	2.250	20.0			130
2.065	7.8	2.064	9.1	2.063	8.6	2.063	8.5	2.061	6.0	2.069	2.0	113
		2.000	6.1	1.999	5.3	1.999	6.1	1.997	4.0	2.004	2.0	203
1.935	25.2	1.935	25.3	1.935	26.9	1.933	26.7	1.937	25.0	1.929	16.0	222
1.882	13.4			1.882	15.3	1.880	13.8	1.884	14.0			132
1.839	34.7	1.839	42.1	1.838	38.3	1.838	39.4	1.837	30.0	1.838	16.0	123
1.793	12.4	1.793	14.0	1.794	13.4	1.792	11.8	1.797	16.0			231
1.766	13.2	1.767	11.6	1.767	12.3			1.771	14.0			140
1.746	11.3	1.746	11.5	1.746	13.0	1.744	12.7	1.748	14.0			402
1.726	18.6	1.725	25.0	1.724	22.3	1.725	22.7	1.722	16.0			004
				1.636	6.2			1.637	6.0			232
1.503	7.7			1.502	5.1	1.502	6.5	1.501	4.0			124

Mn-MINERALS

The presence on Mn-minerals, the absence of long-distance order in their structure, and a high background of the diffraction records caused by Mn fluorescence did not allow a reliable identification of the phases by means of X-ray powder diffraction.

4. INFRARED SPECTROSCOPY (IR)

IR absorption spectra were recorded by M. Linhartová on a Perkin – Elmer 783 double-beam dispersion spectrophotometer using standard KBr tablets. 300 mg KBr were homogenized with 1 – 2 mg of the sample in a vibration mill, evacuated, and the tablets were pressed for 5 minutes under pressure of 10 MPa. The recording time was 20 minutes and the range 4000 – 400 cm^{-1}. The obtained spectra were processed according to the reference by Hesse and Bach (1982) and Potter and Rossman (1979).

APATITE

Characteristic absorption bands of OH^-, CO_3^{2-} and PO_4^{3-} functional groups, which are characteristic for apatite, are to be found between 4000 and 400 cm^{-1}. Valent vibrations of OH- groups are situated between 3750 and 3250 cm^{-1}. Deformation vibrations of water molecules can be found between 1640 and 1620 cm^{-1} but they are difficult to resolve (Farmer ed., 1974).

The positions and changes of absorption bands of CarHap type B upon heating were described by Labarthe et al. (1973). The measured IR spectra of apatites from the locality of interest were compared to those of CarHap of urinary concrements given by Hesse and Bach (1982) (Fig. 3, Table 5).

The CO_3^{2-} group can substitute OH^- (Carap A) or PO_4^{3-} (Carap B) groups, or it can be sorbed onto the surface. Doublets of CO_3^{2-} bands between 1450 and 1420 cm^{-1} were found (valence vibrations), as well as a vibration band at 875 cm^{-1} (deformation vibrations), which belong to CO_3^{2-} ions bound in the structure of apatite. The latter bond shifts towards lower frequencies with an increasing degree of fluoridation of apatite (Okozaki, 1983). The IR spectroscopic bands at 1534 and 1465 cm^{-1} indicate a substitution of CO_3^{2-} by OH^- (Carap A) and the bands at 1455 and 1430 cm^{-1} a substitution of CO_3^{2-} by PO_4^{3-} (Carap B) (Bonel and Montel, 1964; Elliot, 1965; Elliot et al., 1985).

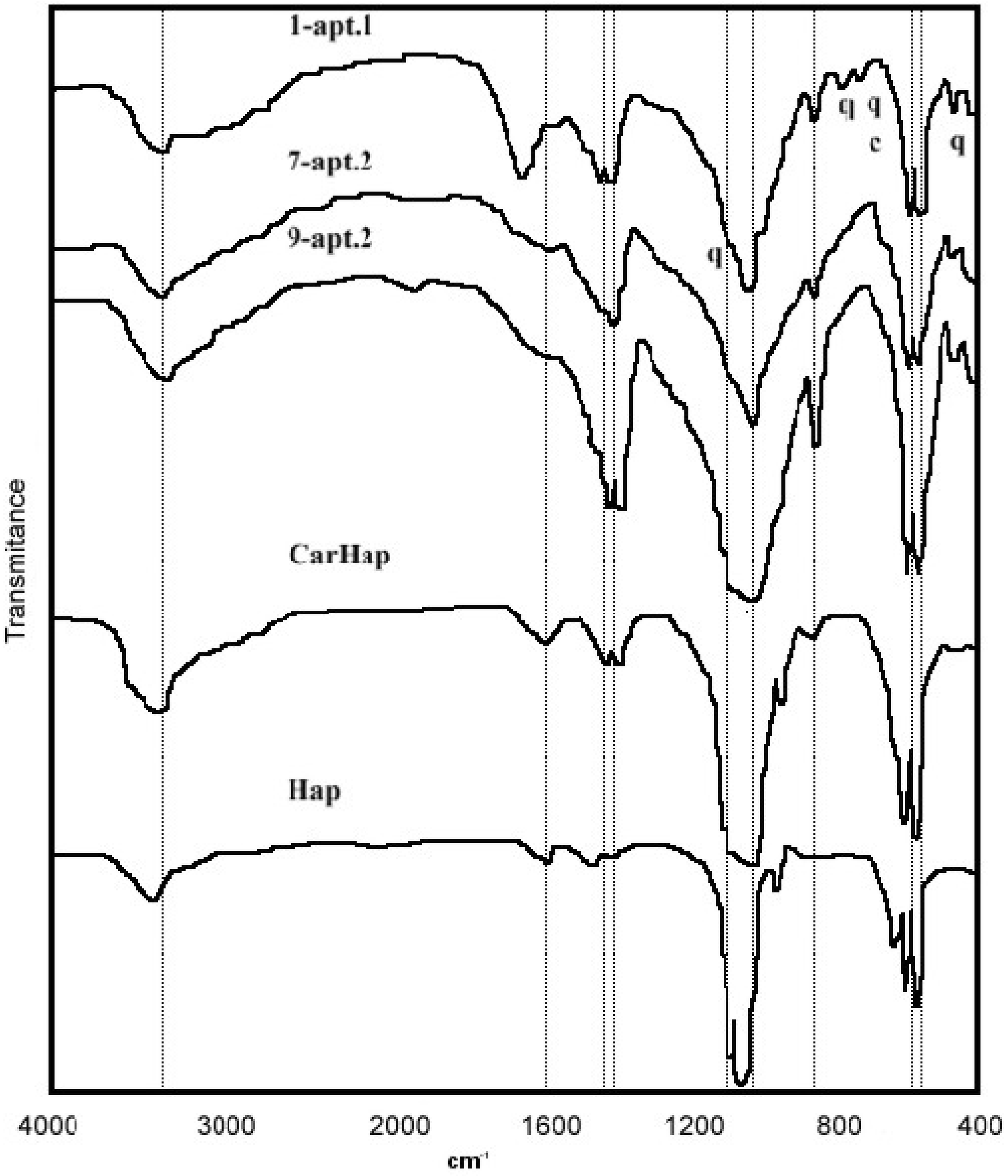

Fig. 3 IR spectra of apatites from the locality Hodušín – Božetice and the spectra of carbonate hydroxylapatite /CarHap / and hydroxylapatite /Hap/ of urinary concrements according to Hesse and Bach (1982). The identification of minerals in the apatite cement was accomplished according to Farmer ed. (1974).
Notes: c – calcite, q – quartz.

The absorption band characteristic for Carap A was not found and there was also no shift of the 875 cm^{-1} band observed. It is therefore obvious that the apatite from the Hodušín – Božetice locality corresponds in its composition to a carbonate apatite type B, CarpHap (dahllite). CO_3^{2-} bands belonging to carbonate apatite are different from the absorption bands of calcite. Calcite itself can only absorb at 719 cm^{-1} (Hesse and Sanders, 1988) and such a band was observed in the spectrum of the sample 1-apt.1.

PO_4^{3-} group is represented by a broad band at 1043 cm-1. With a decrease of CO_3^{2-} content in the apatite structure this band verges into a doublet of PO_4^{3-} bands (1040 and 1090 cm^{-1}). Two characteristic bands are situated in the region between 600 and 570 cm-1. The latter band can, according to Ballo et al. (1977), characterize carbonate apatite. In the IR spectrum of the apatite cement sample 1-apt.1, absorption bands characteristic for calcite and quartz were found (Farmera, 1974).

Table 5 IR spectra of apatites from the Hodušín – Božetice locality and the spectra of carbonate hydroxylapatite /CarHap / and hydroxylapatite /Hap/ of urinary concrements according to Hesse and Bach (1982).

samples						comparison with (Hesse-Bach 1982)			
1-apt.1		7-apt.2		10-apt.2		CarHap		Hap	
cm^{-1}	T%	cm^{-1}	T%	cm^{-1}	T%	cm^{-1}	T%	cm^{-1}	T%
3420	55.0	3420	51.8	3420	57.0	3427	57.2		
3000	57.5								
2920	59.6	2920	59.9	2920	64.2	2924	86.7		
		1995	67.5	1995	70.0				
1670	47.0								
		1620	59.0	1620	64.0	1630	85.3		
1585	57.5								
1450	49.5	1450	45.0	1450	57.0	1450	77.0		
1420	47.0	1420	44.0	1420	55.5	1415	76.4		
1345	63.5								
1305	62.0								
1090	36.2	1090	33.8	1090	45.0			1088	
1040	27.8	1040	25.5	1040	36.0	1043	0.0	1042	
990	40.2								
960	49.5	960	42.0	960	59.5	963	60.0	961	
875	63.0	875	53.0	875	68.0	876	86.9		
860	59.5	860	49.0	860	66.0				
780	66.0								
740	66.5								
719	69.5								
598	44.0	600	37.0	600	53.0	605	15.2	602	
570	44.0	570	37.0	570	53.0	571	10.6	569	
470	62.0	470	58.5	470	67.5	474	81.3		
415	65.0								

Mn-MINERALS

The amorphous character of Mn-minerals favors the IR spectroscopy over the X-ray diffraction. The obtained spectra were compared to the spectra of Mn-minerals published by Potter and Rossman (1979).

The wavenumber interval between 4000 and 1400 cm^{-1} shows the character of H_2O and OH^- bonding in the structure of manganese minerals. The range from 1400 to 200 cm^{-1} is important for the determination of the degree of polymerization of MnO_6 octahedrons. Because of the method of KBr tablet preparation, the spectra could only be compared in the range from 1400 to 400 cm^{-1}. For technical reasons, the narrow range 400–200 cm^{-1} which contains characteristic absorption bands of many Mn-minerals could not be taken advantage of. Besides, the measured absorption spectra are distorted by absorption bands belonging to apatite. The IR spectra are similar to those of romanechite/psilomelane (Fig. 4). According to Fleischer (1960), romanechite is a better-crystallized equivalent of psilomelane. IR spectra of romanechite and psilomelane differ from each other by a presence/absence of two absorption bands at 340 and 270 cm^{-1} (out of the measured range). The shoulder of the band 5 is typical of romanechite/psilomelane, the band 4 is the main absorption band. The bands 2 and 1 are also characteristic of romanechite/psilomelane. Radial to spinelike aggregates of the Mn-mineral (Fig. 4) could not be determined.

5. CATHODE LUMINESCENCE (CL)

The samples of manganese–phosphate crusts were studied on a cathode luminescence microscope HC2-LM/EQN with a hot-cathode with an acceleration voltage of 40 kV at the Institute of Geological Sciences, Masaryk University, Brno.

Cryptocrystalline apatite forming the cement of manganese–phosphate crusts in the locality of interest demonstrates either a very week or no luminescence at all. Small apatite grains contained in this cement (relicts of the original apatites, crystallization cores originating during the catch crystallization) demonstrate a substantial luminescence of a yellow-

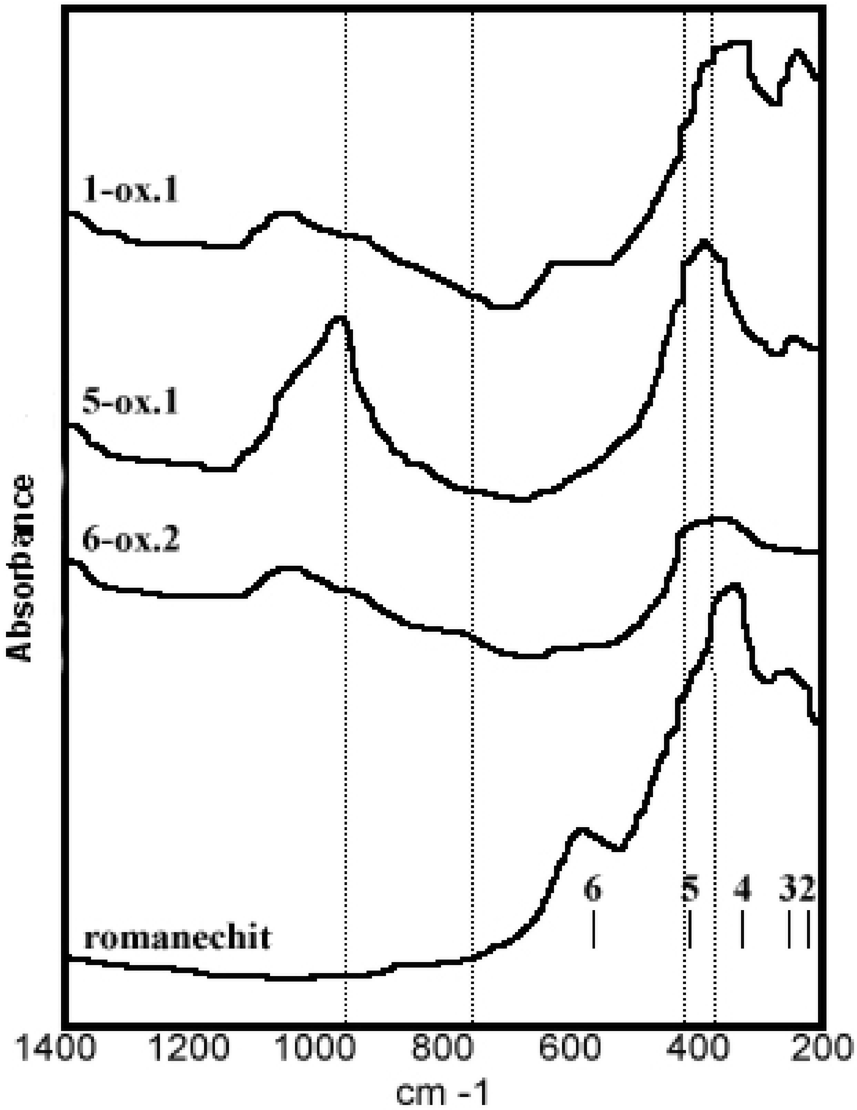

Fig. 4 IR spectra of manganese minerals from the Hodušín – Božetice locality and IR spectra of romanechite/psilomelane according to Potter and Rossman (1979).

green color. Concentrically-zonal apatites with radial structure, which fill the cavities of the weathering crusts, luminesce differently depending on the growth zones, with the youngest growth zones exhibiting no luminescence.

Yellow and green color of the apatite luminescence belongs to the Mn^{2+} activator (576 nm). Non-luminescent apatites are rare since most of the apatites contain an amount of Mn^{2+} or REE, which is sufficient for the activation and even relatively pure apatites demonstrate luminescence already with contents of 0.0x mass %. Non-luminescent apatites were discovered e.g. in the supergene mineralization of a porphyric Cu-ore bed in Safford, Arizona. The absence of luminescence was in this particular case caused by the oxidation of Mn^{2+} to Mn^{4+} and its exclusion from the structure during the crystallization together with REEs. The luminescence of apatite can also be quenched by the presence of Fe^{2+} if the concentration of these ions reaches values around 1 mass % (Marshall et al., 1988). Poor detectability of colophanite in phosphate iron ores is often caused by the dispersion of very fine hematite grains in its crystals (Hagni in Marshall et al., 1988).

The dominance of the Mn^{2+} activator in the studied samples corresponds to crystalline rocks, granites and aplites, which are present in the subsoil. The variable luminescence might be a consequence of changing oxidative conditions and of the different character of washing, which determine the amount of Mn^{2+} and REE in the apatite structure. EDX microanalyses of apatite did not reveal any Fe^{2+}; the increased amount of Mn results from the detection of elements on the boundaries of the intergrowing mineral phases (Brož, 1997).

Table 6 Results of the point EDX analyses of manganese–phosphate crusts from the locality Hodušín – Božetice. Results of the point analyses were affected by the detection of elements at the interface between mineral phases.

Figure	**5**	**6**	**6**	**5**	**5**	**5**	**5**	**5**	**6**	**6**
Mineral phase	**Mn - needles**			**Concentrically zonal aggregates of a Mn-mineral**				**White colloform crusts with fibered radial structure**		
Defined	**not defined**			**psilomelane**				**CarHap B - dahllite**		
oxides %	**2**	**4**	**5**	**8**	**9**	**10**	**11**	**1**	**3**	**6**
MnO_2	70.47	73.95	72.56	76.41	76.16	75.99	74.30			
MnO								0.38	5.72	4.93
CaO	1.36	1.73	2.16	0.94	0.92	0.87	0.90	53.07	48.27	49.18
MgO	1.53	2.09	1.91	0.54	0.63	0.48	0.87			0.30
BaO	5.10	5.16	4.35	10.95	11.08	10.90	10.52		0.48	0.77
K_2O	0.95	1.05	1.11	0.00	0.73	0.89	0.63			
SiO_2	0.00	0.61	0.48	0.51	0.60	0.45	0.47			
NiO	0.82	0.52	0.00	0.00	0.00	0.00	0.00		0.25	
Al_2O_3	0.92	0.85	0.88	0.63	0.62	0.90	0.86	0.30	0.60	0.92
Fe_2O_3	0.00	0.00	0.00	0.46	0.83	0.63	0.49			
SO_3	0.61	0.39	0.42	0.00	0.00	0.00	0.00			
P_2O_5	0.30	0.29	0.52	0.00	0.41	0.34	0.39	35.96	32.32	33.17
Total	82.06	86.64	84.39	90.44	91.98	91.45	89.43	89.71	87.64	89.27

Table 7 Calculation of empirical formula units of dahllite based on the analysis No. 1 (Table 6). Formula CarHap: $Ca_{10-x+u}(PO_4)_{6-x}(CO_3)_x(OH)_{2-x+2u} * n\,H_2O$.

	oxides %	**mol. quant.**	**quant. metal**	**quant. O,OH**	**26 O,OH**	**number of cations and anions in the formula**		
MnO	0.35	0.0054	0.0054	0.0054	0.056	Mn^{+2}	0.056	9.942
CaO	53.07	0.9463	0.9463	0.9463	9.886	Ca^{+2}	9.886	
Al_2O_3	0.30	0.0029	0.0058	0.0087	0.061	Al^{+3}	0.061	6.000
P_2O_5	35.96	0.2534	0.5068	1.2670	5.294	P^{+5}	5.294	
CO_2	3.91	0.0888	0.0888	0.1776	0.928	C^{+4}	0.928	
						C^{+4}	0.283	2.034
H_2O^+	1.51	0.0838	0.1676	0.0838	1.751	OH^{-1}	1.751	
H_2O^-	0.47							
Total	95.57			2.4888				

6. ENERGY DISPERSIVE X-RAY ANALYSES (EDX)

Point EDX analyses with ZAF correction were performed by V. Vávra and accomplished using a scanning electron microscope CAMSCAN 4DV with an attached energy dispersive analyzer LINK AN 10000 at the Institute of Geological Sciences at Masaryk University.

A chosen sample was subjected to a series of point analyses. The obtained results were partially affected by the intergrowing of the recrystallized components. Nevertheless, the association of the minority elements with the individual mineral phases is still evident (Table 6).

APATITE

Mn contents in the colloform radial apatite aggregates are somewhat overestimated due to their weak luminescence. Detected Al can substitute P in the lattice of apatite. High CaO/P2O5 ratio, 1.475, is typical for carbonate apatites. Hydroxylapatites have a value of this ratio around 1.317 and this ratio increases with the substitution of PO_4^{3-} in the structure by CO_3^{2-}. The content of CO_2 was calculated from the

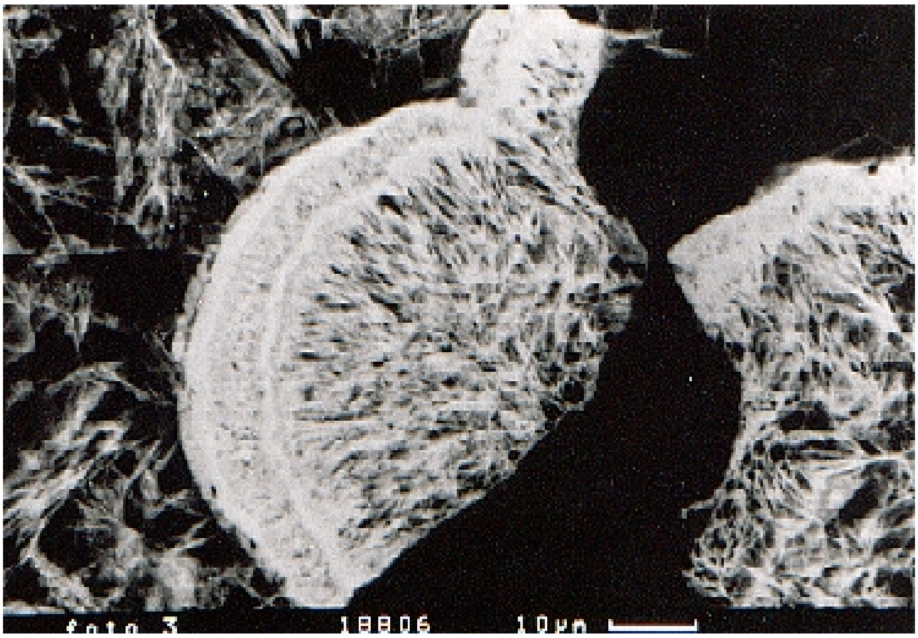

Fig. 5 Concentrically zoned aggregates of a manganese mineral psilomelane.

lattice parameters (Chapter 3, Table 3), H_2O^+ and H_2O^- contents were determined by quantitative chemical analyses of 4 samples. The results of the analyses were recalculated to the total amount of anions (26 O + OH) – Table 7.

Mn-MINERALS

Under microscope, the seemingly massive psilomelane aggregates show a concentrically zonal spongy texture (Fig. 5); recrystallized radial aggregates of Mn-minerals intergrow through apatite like needles (Fig. 6).

Both macroscopically and microscopically distinguishable mineral phases of Mn-oxides-hydroxides differ from one another especially in the contents of Ba and H_2O (Tables 6 and 8). Low sums of chemical analyses of Mn-minerals are due to low water contents. Point analyses indicate a relationship among Ba and Ni and Mn-minerals. The results of psilomelane EXD-analysis were recalculated to the total number of anions (10 O) – Table 9.

The cement of the analyzed sample contained also other minerals (empirical formulas are inferred from the EDX point analyses):

K–feldspar:

$(K_{0.948}\ Na_{0.069}\ Ba_{0.01})_{1.027}\ (Al_{1.009}\ Si_{2.984})_{3.993}\ O_8$

Albite:

$(Na_{0.983}\ Ca_{0.009})_{0.992}\ (Al_{1.023}\ Si_{2.982})_{4.005}\ O_8$

Rutile:

$(Ti_{0.977}\ Fe_{0.011}\ Ca_{0.003}\ Si_{0.006}\ Al_{0.006})_{1.003}\ O_2$

Table 8 Average water content in the detected phases of manganese oxides and hydroxides determined by quantitative chemical analyses. The analyses were performed by P. Kadlec, Institute of Geological Sciences, MU, Brno.

mass %	**psilom.**	**Mn - needles**
H_2O^+	6.22	4.29
H_2O^-	2.87	1.43
Total	9.09	5.72

7. CONCLUSIONS

The work summarizes the results of a complex study of weathering crusts rich in P and Mn from the locality Hodušín – Božetice situated approximately 7 km west of the city of Milevsko. The locality of interested was surveyed employing mineralogical, chemical, IR-spectroscopic, XRD-diffraction and cathode luminescence analyses.

The locality belongs to the central part of the Sušice and Votice group in the variegated Moldanubian unit. The field locality contains numerous bulbs and crusts consisting mainly of Mn- and P-mineral phases.

The low refractive index value (1.602), the higher ratio of lattice parameters c_0/a_0 and the high CaO/P_2O_5 ratio (1.475) classify the apatite component of the Mn-phosphate crusts as carbonate apatite. The IR analysis indicated the carbonate apatite is of type B and the colloform texture of the studied apatites is

Table 9 Calculation of empirical formula units of psilomelane based on the illustrative EDX-analysis No. 8 was employed (Table 6). Theoretical formula of psilomelane: (Ba, H_2O)$_2$ Mn_5O_{10} (Fleischer, 1960).

	oxides in wt.%	**mol. quotients**	**quotients of cations**	**quotients of O**	**calc. on 10 O**	**number of cations and anions in the formula**		
CaO	0.94	0.0168	0.0168	0.0168	0.070	Ca^{+2}	0.070	
MgO	0.54	0.0133	0.0133	0.0133	0.055	Mg^{+2}	0.055	
SiO_2	0.51	0.0084	0.0084	0.0168	0.035	Si^{+4}	0.035	
Al_2O_3	0.63	0.0062	0.0124	0.0186	0.051	Al^{+3}	0.051	1.855
Fe_2O_3	0.46	0.0029	0.0058	0.0087	0.024	Fe^{+3}	0.024	
BaO	10.95	0.0714	0.0714	0.0714	0.297	Ba^{+2}	0.297	
H_2O^-	2.87	0.1593	0.3186	0.1593	1.323	H_2O	1.323	
MnO	76.41	0.8789	0.8789	1.7578	3.650	Mn^{+4}	3.650	3.650
H_2O^+	6.22	0.3453	0.6906	0.3453	2.868	OH^{-1}	2.868	2.868
Total	99.53			2.4080				

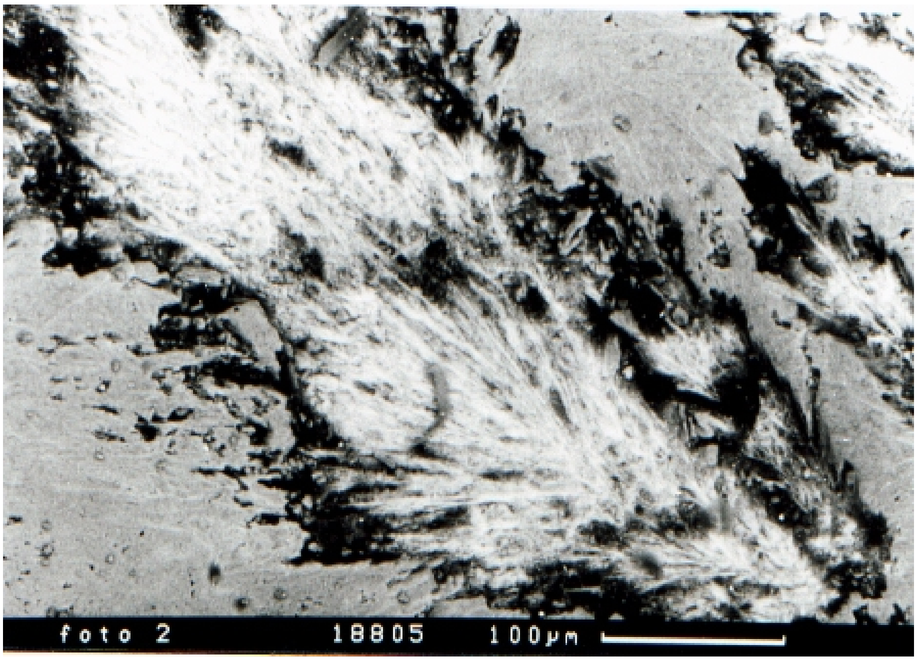

Fig. 6 Needles of an undefined Mn-mineral intergrowing through apatite.

characteristic of CarHap – dahllite. This inference is in agreement with the conclusions of Rost (Čech and Rost, 1941).

Both macroscopically and microscopically distinguishable mineral phases of Mn-minerals differ from one another in the contents of Ba and H_2O. X-ray diffraction spectra were of little use for the identification of the apatite due to the low crystallinity of the studied aggregates and a strong fluorescence of the present manganese. IR spectroscopy yielded better results. The primal non-recrystallized phase was determined as psilomelane. The term "psilomelane" is used in two different meanings in the mineralogical literature. It can be used either as a general name for manganese oxides and hydroxides or it can refer to a poorly crystallized equivalent of romanechite (Fleischer, 1960). In this work, the term is used in the latter sense.

Čech and Rost (1941) attribute the origin of the Mn-phosphate crusts to weathering processes. The stretch direction seems to be conformal to the direction of the intercalations of the Moldanubian Unit. Nonetheless, the source rock of the Mn-phosphate crusts was not found in the locality of interest. The site is covered by a thick layer of hillside soils and the vast majority of the collected samples were considerably weathered.

The literature describes numerous occurrences of phosphates associated with the top wall of graphite-bearing localities in the broader vicinity of the locality of interest (Koloděje nad Lužnicí, Oltyně, Olší, Řepeč). An insignificant content of P_2O_5 found in the sample of graphitic quartzite from the region of Božetice could result from an uneven distribution of apatite in the local rocks. Lime silicate rocks represent another potential source of P_2O_5 in the manganese–phosphate crusts. Chemical analysis of an erlan sample demonstrated a small but increased (relative to other analyzed rocks) content of P_2O_5 – 0.69 %. A formation of the manganese–phosphate crusts by weathering of vein rocks of the Central Bohemian Pluton, which also emerge in the locality, is rather unlikely, i.a. because of the low degree of weathering. Hypothetically, the metaphosphorite layers in the variegated Moldanubian Unit can also be considered a possible source of phosphorus.

The CL results show the manganese–phosphate crusts originated under extreme oxidative conditions with an efficacious washing regime. The predominant Mn^{2+} activator corresponds to the rocks forming the subsoil. The sources of Mn^{4+} in the weathering crusts could have been the dark minerals in the original rocks, Ba could have come from the rock-forming feldspars.

8. SUMMARY

Mineralogical study of weathering crusts rich in P and Mn from the locality Hodušín – Božetice situated approximately 7 km westwards from Milevsko is presented. The locality belongs to the central part of the variegated group of Sušice and Votice of the Moldanubian unit. Weathering crusts were studied by optical methods: X–ray powder spectroscopy, infrared spectroscopy (IR), cathode luminescence (CL) and EDX-analysis. The major components of the weathering crusts are apatite and Mn–minerals. Apatite belongs to the group of CarHap B (dahllite). Massive black Mn–mineral was classified as psilomelane. The aggregates of another Mn–mineral, which is forming needles, probably represent a poorly recrystallized psilomelane. Disintegrated rocks consist of a mixture of clay minerals, calcite and relicts of primary minerals (quartz, K–feldspars, albite, pyroxene and rutile).

The origin and source material of these crusts rich in P and Mn cannot be unambiguously determined. Apatites without CL-effects indicate the weathering crusts have originated in a strong oxidation environment. Known neighboring occurrences of phosphate minerals in the variegated group of Sušice and Votice are associated with graphite rocks. Optical and quantitative chemical analyses of the rocks suggest that the source of apatite could possible be calc-silicate rocks (erlans) close to the graphitic rocks. Hypothetically, the metaphosphorite layers in the variegated Moldanubian Unit can also be considered as possible sources of phosphorus.

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