THE SUPERGENE MINERALIZATION OF URANIUM OCCURRENCE RÝŽOVIŠTĚ NEAR HARRACHOV (KRKONOŠE MTS., CZECH REPUBLIC)

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Abstract. The following 14 supergene mineral phases were determined and characterized at the desolated uranium occurrence Rýžoviště near Harrachov in the Krkonoše Mts. (Czech Republic) by X-ray powder diffraction data, calculated unit cell parameters, chemical analyses and IR absorption spectra: bismite, uranosphaerite, bismutite, churchite(Y), metaautunite, metatorbernite, phosphuranylite, atelestite, pharmacosiderite, preisingerite, walpurgite, amorphous Bi–U–As phase, kasolite and uranophane. Three development stages of origin of the supergene zone at Rýžoviště can be distinguished.

■ Rýžoviště, Harrachov, Bohemia, minerals, X –ray study, IR absorption study

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Introduction

The uranium occurrence Rýžoviště near Harrachov is located at the southern slope of the Zadní Plech Mts. (1210 m), 3 km ENE of Harrachov in the Krkonoše Mts., Czech Republic (Pl. 1). The occurrence was discovered by the uranium exploration in the western Krkonoše Mts., in 1952 – 1954. No traces of old mining were found there. The occurrence was verified by 22 surficial test trenches and followed by a gallery (1060 m) of length 326 m. It was desolated in 1957 (Ocman et al. 1985). At the present time, the gallery is entirely overwhelmed and the occurrence is represented only in the remains of the mine dumps (Fig. 1), partly afforested (Pilous 1985).

The first references concerning Rýžoviště minerals are found in the papers of Bradna and Šita (1968) and Šita and Bradna (1972), who described deposits of bismuth, bismutite, walpurgite, sklodowskite, torbernite, autunite, erythrite, zeunerite, tyuyamunite, skutterudite, wad, nickeline and liebigite. Recently, the bismuth minerals from Rýžoviště were studied by Sejkora (1992) and the occurrence was mentioned in the mineralogy description of the Harrachov area (Sejkora 1994).
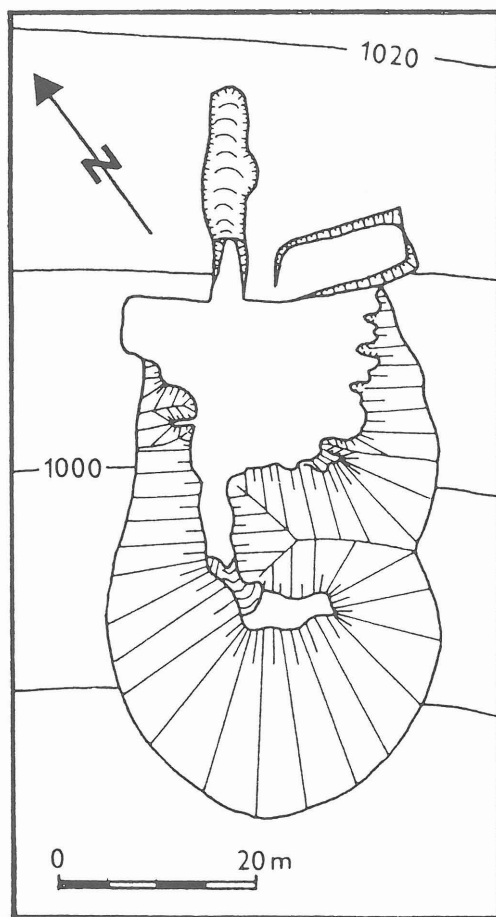
Fig. 1. The map of mine dump at Rýžoviště (Pilous 1985)

The geology of occurrence

The ore veins pass the Krkonoše crystalline complex in exocontact of the Krkonoše – Jizerské hory pluton. This pluton is represented by three main types of granites: porphyric coarse grained biotite granite in the near contact zone; medium–grained biotite and fine grained aplitic granite.

The crystalline complex is composed of the metamorphic group of the Upper Proterozoic: biotite and feldspar grey mica shists with an intercalated hornstone, quartzite and hornblende schist (Ocman et al. 1985). Detailed information about attitude and the character of the ore veins at Rýžoviště are not known. On the analogy of the proximity of the small uranium deposit Medvědín, and a study of mine dump materials there, it is possible to assume some systems of ore veins (at Medvědín there are three systems of ore veins in thef NW, NE and E directions) and thicknesses in the range of 5 – 30 cm (Arapov at al. 1984). The quartz ore veins are short and irregular. The lode rock is represented by fault clay, quartz of some generations and a small share of carbonates, uraninite, pure bismuth, chalcopyrite, arsenopyrite and pyrite. All mining works at Rýžoviště are located in the oxidized zone with great concentrations of the secondary U and Bi minerals.

Rýžoviště is considered representative of *u* association (Bernard et al. 1981) with an atypical

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display of Ag–Bi–Co–Ni mineralization. Silver, cobalt and nickel are suppresed, and only bismuth is exterted widely.

Methods of mineralogical research

The X–ray powder diffraction data of studied minerals were obtained from a handpicked sample using the diffractometer DRON 3 (Czech Geological Survey, Prague, CuKα and CoKα radiation, 32 kV/40 mA, step scanning, analysts J. Sejkora and F. Veselovský) and the diffractometer HZG4/TuR (National Museum, Prague, CuKα radiation, step scanning, 34 kV/25 mA, analyst J. Sejkora). The measured X–ray powder diffraction patterns were worked up by ZDS–system (software for analyses of powder diffraction data, Ondruš, Kovanic, in press) and the precise positions of diffraction were determined by profile fitting. The powder Guinier – de Wolff camera (114.6 mm, CuKα radiation, 80 hours, Charles University, Prague) was used for diffraction study of some minerals. All the diffraction data are set out in Åunits (corresponds with 10^{-10} m).

In order to index the powder diffraction patterns, the information of crystal structures of each minerals phases were used to generate the theoretical powder data by the LAZY PULVERIX program (Yvon et al. 1977). The unit cell parameters were refined from the powder X–ray diffraction data by Burnham's program (1962).

The IR absorption spectra of some phases were recorded with a Pye-Unicam 9512 type apparatus with KBr, TlBr and CsBr tablets in the 200 – 4000 cm^{-1} region (The Institute of Inorganic Chemistry, Czech Academy of Science, Řež, analysts F. Hanousek and E. Večerníková). These spectra were corrected on the background absorption. The IR absorption spectra of other minerals were measured on the FTIR Nicolet 740 type apparatus with DRIFT accessories (The Institute of Chemical Technology, Prague, analysts M. Novotná and J. Vylita). The samples (about 1 mg) were measured in the 4800 – 400 cm^{-1} range in mixture with KBr in the reflexion mode. The measured spectra were recalculated by Fouriers transsformation and corrected on the background absorption and reflection on preparative grains by the PCIR program (Nicolet Co.). The intensity of absorption bands were expresed by Kubelka – Munk units which formally correponded to absorbance. The relative intensity and character of absorption bands were expressed next by symbols: vw = very weak, w = weak, mw = medium weak, ms = medium strong, s = strong, vs = very strong, shr = sharp, br = broken, sh = shoulder.

The chemical composition of minerals was studied by electron microprobe in the energy dispersive mode (TESLA BS 320 apparatus, Czech Geological Survey, Prague, analyst A. Gabašová). Quantitative chemical analyses were performed with a JEOL JXA – 50A electron microprobe (Institute of Geology, Czech Academy of Sciences, Prague, analysts V. Šrein and L. Thin). Operating conditions were 20 kV accelerating voltage, 25 nA beam current, 2m specimen beam size. Standards were used in the following phases: Bi, GaAs, V_2O_5, apatite from Durango and clinoclase from Novoveská Huta. The X–ray intensities of each were measured three times with an exposure of ten seconds. The raw analytical data wase corrected by a version of the program based on conventional ZAF methods of Philibert (1963) and Duncumb and Reed (1968).

The morphology of crystals and crystal aggregates was followed by the electron scanning microscope TESLA BS 340 (National Museum, Prague, I. Čejková and J. Sejkora) with increases in the 100 – 6000 times range.

Description of minerals

Bismite Bi_2O_3

The find of bismuth oxide from Ullesreuth in 1848 was probably the first description of this phase in nature. Lately, samples from Meymac, France and Tazna, Bolivia (not a pure sample) were analysed by Carnot in 1874. Formerly descriptive bismuth oxide (1753) was according to original analyses rather than bismutite (Frondel 1943b). Bismutite was sufficiently defined by Frondel (1943b) who distinguished it from other close mineral phases by X–ray powder diffraction data.
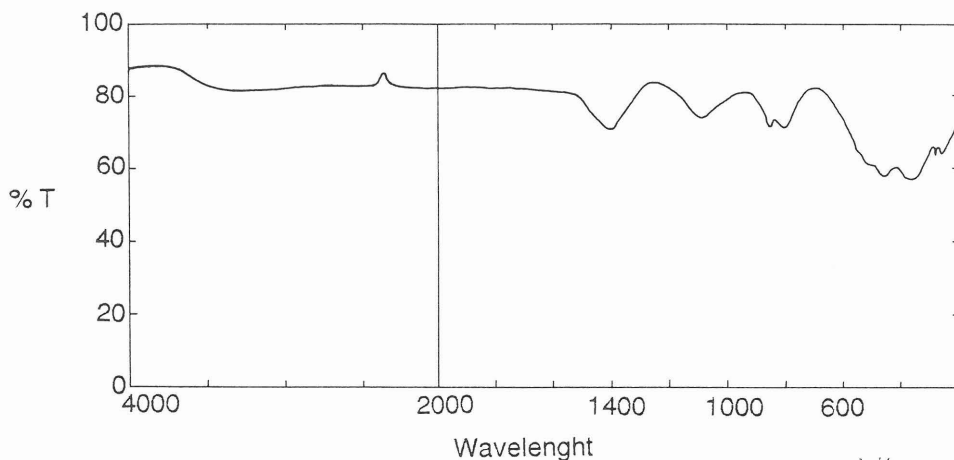
Fig. 2. The IR absorption spectrum of bismite from Rýžoviště

The four polymorphous modifications were discovered by X-ray study of synthetic Bi_2O_3 (Schumb, Rittner 1943, Aurivilius, Sillen 1945):

1) α-Bi_2O_3, monoclinic with space group P 2_1/c, pseudoorthorhombic, stable below 704° C, corresponding to bismite

2) ß-Bi_2O_3, tetragonal, P4b2, stable above 704° C (Gattow, Schütze 1964, Blower 1988)

3) γ-Bi_2O_3, cubic I 23, a=10.25, stable at high temperature, below 700° C stabilization by admixture of Si, Al, Fe, corresponding to sillenite

4) δ-Bi_2O_3, cubic Fm3m with a=5.66 (Gattow, Schröder 1962)

The crystal structure of α-Bi_2O_3 corresponding to mineral bismite was published by Sillén (1941) who discovered that bismite is monoclinic and not orthorombic.

In the Czech Republic, bismite was described from Cínovec, Jáchymov and Horní Slavkov (Kratochvíl 1957, Mach, Korbel 1990), unfortunately the majority of old papers described bismite as Bi-ochre by which bismutite can also be described.

At Rýžoviště, bismite ranks among the relatively common minerals however, it occurs mostly in size aggregates of only a few cm. Bismite forms very fine grained to massive aggregates which are usuallly rimmed by a net of tine crazes in average 5 mm distances. The bismite colour is dark grey with greenish or brownish shade. It has a greasy lustre. The light grey bismutite and waxy yellow amorphous Bi-U-As phase replace bismite on the surface and in the crannies of its aggregates.

The X-ray powder pattern of bismite is shown in Table 1. The crystal structure information of bismite and orthorombic unit cell parameters of Swanson et al. (1964) were used to index the powder diffraction pattern. The calculated lattice parameters for monoclinic (Table 2) and orthorombic (Table 3) symmetry are close to other published data.

The IR absorption spectrum of bismite (Fig. 2) has not been published yet. It is very similar to that of sillenite (Sejkora 1992). The small admixture of bismutite(I) is expressed in the spectrum of bismite (Table 4). This bismutite(I) admixture was not found by X-ray powder diffraction data. The IR spectrum of bismite is close to the spectra of α-Al_2O_3 (corundum), amorphous SiO_2 and partly α-SiO_2 (quartz), as well.

Uranosphaerite $\quad Bi_2U_2O_9 \cdot 3\ H_2O$

Documented natural occurrences of uranosphaerite including type material are orange to red papillate aggregates composed of very tiny spicular crystals from the Walpurgis vein, Weisser Hirsch mine, Schneeberg, Saxony and similar aggregates in association with de-

Table 1. X-ray powder diffraction data for bismite from Rýžoviště

mon	*1		Rýžoviště		mon	romb	romb
h k l	d_{teor}	I_{teor}	dobs	I_{obs}	d_{calc}	d_{calc}	h k l
0 1 1	5.259	2	5.257	4	5.277	5.275	
0 2 0	4.070	2	4.089	8	4.085	4.084	0 2 0
1 0 2	3.608	9	3.609	9	3.618	3.620	1 0 3
0 0 2	3.445	25	3.454	15	3.456	3.455	0 0 4
1 1-1	3.298	11	3.309	5	3.308	3.309	1 1 3
1 1 2	3.298	28	3.309	5	3.308		
1 2 0	3.244	100	3.252	100	3.254	3.255	1 2 1
1 2 1	3.243	47	3.252	100	3.254		
0 1 2	3.172	32	3.183	10	3.183	3.182	0 1 4
2 1 1	2.744	10	–		–	–	
1 2-1	2.700	25	2.709	61	2.708	2.709	1 2 3
1 2 2	2.700	22	2.709	61	2.708		
2 0 0	2.685	45	2.696	61	2.691	2.694	2 0 2
2 0 2	2.685	20	2.696	51	2.690		
0 2 2	2.629	9	–		–	–	0 2 4
2 1 0	2.550	4	2.554	11	2.556	2.558	2 1 2
2 1 2	2.549	12	2.554	11	2.555		
0 3 1	2.525	12	–		–		0 3 2
1 0-2	2.491	6	2.501	4	2.499	2.499	1 0 5
1 3 1	2.422	6	2.431	2	2.430	2.430	1 3 1
1 1-2	2.382	11	2.391	10	2.390	2.390	1 1 5
1 1 3	2.382	5	2.391	10	2.389		
2 2 2	2.241	6	–		–		
1 3-1	2.169	3	2.172	4	2.176	2.176	1 3 3
1 2-2	2.125	9	2.132	6	2.132	2.132	
0 4 0	2.035	2	–		–		0 4 0
0 2 3	2.000	6	2.004	5	2.007	2.006	0 2 6
0 4 1	1.952	29	1.957	16	1.959	1.958	0 4 2
2 3 2	1.908	2	1.919	4	1.914	1.915	
3 1 2	1.873	7	1.872	10	1.876	1.871	
1 0 4	1.865	18	–		–		
1 3-2	1.835	4	1.841	4	1.841	1.841	

Diffractometer DRON 3, CoKα radiation, step scanning, 0.02°/2 s, Si as internal standard.
*1 X-ray powder diffraction data calculated from crystal structure information for bismite by Sillén (1941), I_{calc} ≤1.0 have been omitted.

Table 2. Unit cell parameters for bismite
(orthorhombic cell)

	Rýžoviště	*1	*2
a	5.852(6)	5.850	5.828(8)
b	8.167(5)	8.166	8.133(5)
c	13.820(8)	13.827	13.79(1)
V	660.5(6)	660.53	653.3(8)

*1 Bismite (Swanson et al. 1964)
*2 Bismite from Jáchymov (Sejkora, 1992)

Table 3. Unit cell parameters for bismite
(monoclinic cell, space group P 2_1/c)

	Rýžoviště	*1	*2	*3
a	5.842(6)	5.83	5.848	5.835(8)
b	8.170(6)	8.14	8.166	8.138(6)
c	7.503(6)	7.48	7.510	7.482(8)
ß	67.09(5)°	67.07	67.00°	67.04(8)°
V	329.9(5)	326.9	330.1	327.1(8)

*1 synthetic α-Bi_2O_3 by Sillén (1941)
*2 synthetic α-Bi_2O_3 by Malmros (1970)
*3 bismite from Jáchymov by Sejkora (1992)

Table 4. IR absorption spectrum for bismite from Rýžoviště

Bismite		Sillénite*1		SiO_2*2	Tentative assignment
1464	sh				
1400	ms	1400	vs		v_3 CO_3
1322	sh	1378	sh		
		1161	sh		
		1133	sh		
1084	ms	1101	vs	1095	v Bi-O
846	s	848	s		v_2 CO_3
796	s	800	s	801	v Bi-O-Bi
		751	sh		
		695	ms	695	
532	sh				
500	ms				
452	ms	420	vs	468	δ Bi-O
366	ms				
342	s				

Pye – Unicam 9512
*1 Sillénite from Smrkovec (Sejkora 1992)
*2 amorphous SiO_2 (Pljusnina 1977)

windtite and wölsendorfite from Kersegalac, Lignon (Protas 1959). In the Czech Republic, uranosphaerite was described from Jáchymov but more recently it was determined as ura-nopilite (Kratochvíl 1964). Currently, uranosphaerite is found as orange red spherical ag-gregates (up to 1 mm) growing to uranophane at mine dumps of the small uranium deposit Kladská near Mariánské Lázně (P. Bouše, pers. comm.).

Uranosphaerite was considered as an orthorhombic phase by study of its optical properties but the powder diffraction pattern was not indexed (Berman 1957). Protas (1959) described it on the basis of the study of natural and synthetic uranosphaerite monoclinic unit cell parameters as a=7.65(4), b=7.78(4), c=7.53(4) and ß=93.(1). The proposed chemical com-position for uranosphaerite $BiO(UO_2)(OH)_3$ is close to the published chemical analyses (Table 5). The definitive destination of the chemical formula and the lattice parameters will require a new chemical analyse and monocrystal diffraction study.

At Rýžoviště, uranosphaerite occurs very rarely, only some samples were found. It forms minute thin spicular crystals grouping to spherical aggregates up to 1 mm in size. Its colour is orange yellow to orange red. These aggregates grow on small crannies of rock and in
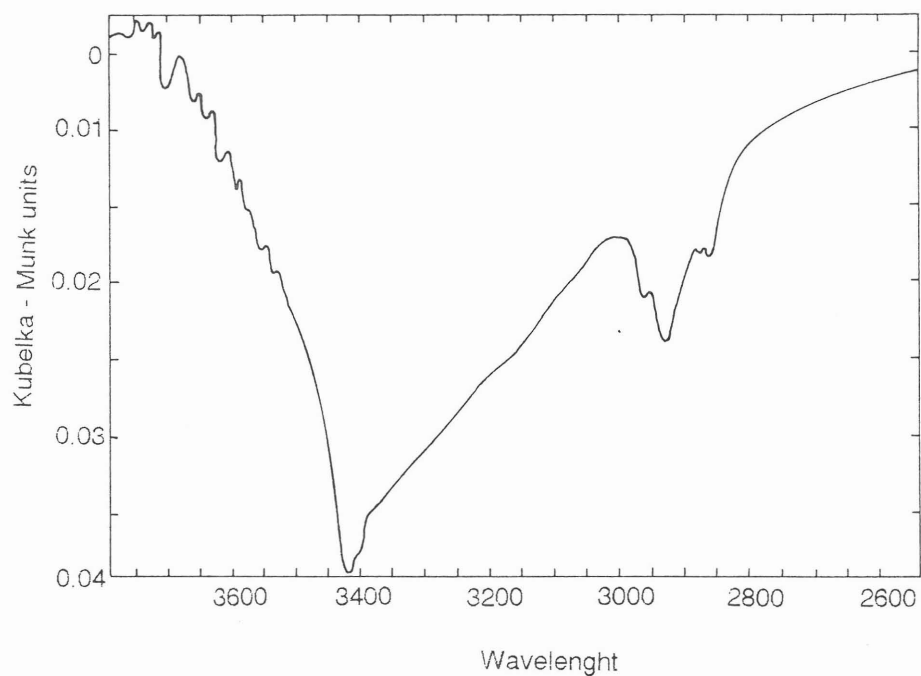
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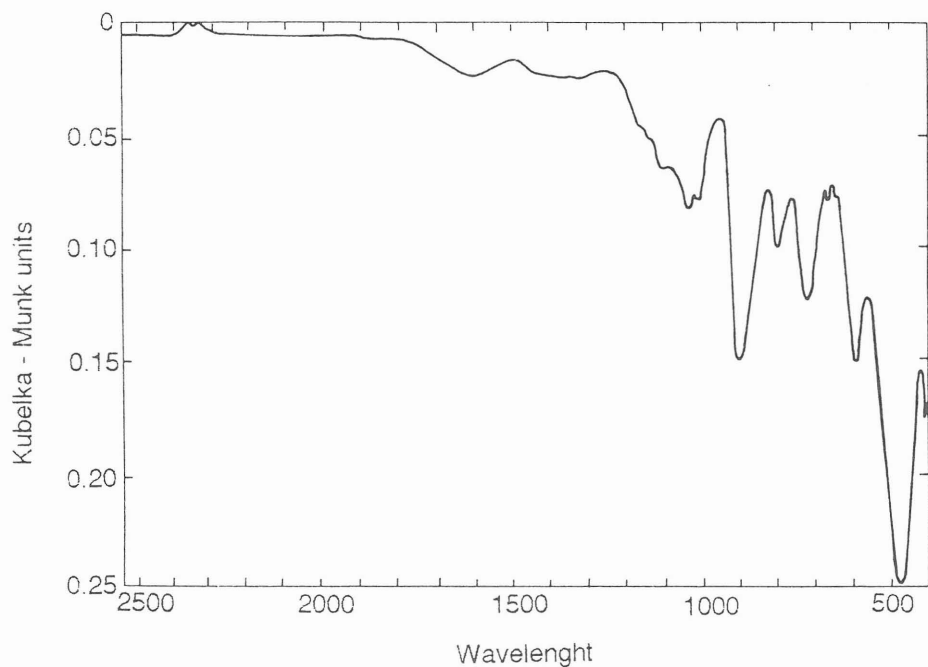**Fig. 3. The IR absorption spectrum of uranosphaerite from Rýžoviště**

Fig. 4. The IR absorption spectrum of uranosphaerite from Rýžoviště

Table 5. Chemical analyses of uranosphaerite

	*1	*2	*3	*4
Bi_2O_3	42.66	44.34	43.46	42.92
UO_3	52.39	50.88	52.62	54.09
H_2O	4.95	4.75	3.59	2.99
	100.00	99.97	99.67	100.00

*1 theoretical composition of uranosphaerite (BiO) (UO_2) $(OH)_3$
*2 uranosphaerite from Schneeberg by Weisbach (1873)
*3 uranosphaerite from Weiser Hirsch, Schneeberg by Protas (1959)
*4 synthetic uranosphaerite by Protas (1959)

Table 6. X-ray powder diffraction pattern for uranosphaerite from Rýžoviště

Rýžoviště		*1		*2	
d	I	d	I	d	I
5.281	93	5.45	ff	5.25	8
		5.17	F		
				4.74	3
4.371	20	4.45	ff	4.37	4
		4.30	mF	4.15	1
3.853	36	3.85	F	3.87	7
		3.79	mF		
3.482	38	3.43	mF	3.47	7
3.356	10	3.34	m		
3.164	100	3.14	F	3.16	10
		3.11	FF		
3.065	53	3.04	m	3.05	3
		3.01	m		
2.740	11	2.70	m	2.71	1
2.607	8	2.57	m	2.60	1
		2.50	m	2.54	1
2.465	14			2.46	1
2.392	16	2.35	m	2.39	2
2.355	14	2.32	mf	2.35	1
		2.29	fff		
		2.15	ff	2.16	2
		2.11	mf		
2.089	17	2.06	m	2.08	2
		2.01	fff	2.03	1
1.98	*	1.959	f	1.97	8
1.890	12	1.864	m	1.90	7
1.832	43			1.83	8
		1.807	mF	1.80	1
1.726	5			1.73	2
1.667	14			1.66	4
1.598	7			1.59	1
				1.56	1
1.532	6			1.52	1

Diffractometer DRON 3, CuKα radiation, step-scanning 0.02°/4 s, NaCl as internal standard.
* coincidence of NaCl; *1 uranosphaerite from Weisser Hirsch mine by Protas (1959); *2 uranosphaerite from Schneeberg by Berman (1957)

small cavities of phosphuranylite and uranophane. Uranosphaerite is associated, as a rule, with phosphuranylite, walpurgite and metatorbernite(II).

The X-ray powder diffraction data of uranosphaerite from Rýžoviště (Table 6) agree well with the data of Berman (1957) and Frondel et al. (1956). The lattice parameters of Protas (1959) were used to calculate the theoretical interplanar distances with correspondence (hkl) but this data is impossible to use to correct indexing of the measured powder diffraction pattern of uranosphaerite from Rýžoviště. The IR absorption spectrum of uranosphaerite (Fig. 3, 4) has not yet been published. The frequency of absorption bands are: 3416, 2957, 2874, 2858, 1607, 1163, 1108, 1034, 1013, 899, 795, 714, 590, 471, 401 cm^{-1}. The absorption bands in the 3416 – 2858 cm^{-1} range are connected to the vibration of the (OH) group, the splitting of this vibration could be caused by the existence of some nonequivalent (OH) groups in the crystal structure of uranosphaerite. The band at 899 cm^{-1} is connected to v_3 vibration of the uranyl group and the bands at 1034, 795 and 471 cm^{-1} probably correspond to the vibration of Bi–O bonds. The chemical composition of uranosphaerite was studied by electron microprobe in the energy dispersive mode, only contents of Bi and U were found.

Bismutite $Bi_2(CO_3)O_2$

Bismutite ranks among the most common bismuth supergene minerals, it was found for the first time in Ullersreuth, Saxony. The identity of bismutite with bismutosphaerite, basobismutite, hydrobismutite and normanite was proved by X-ray powder diffraction patterns (Frondel, 1943b). The crystal structure of synthetic bismutite was described by Lagercrantz, Sillén (1947) on the basis of the tetragonal cell (space group I 4/mmm) with paramters a=3.867 and c=13.686. The bismutite crystals from pegmatite in Karelia, Russia, were described by Nefedov (1956), who stated their optical and X-ray data. Nefedov also found the tetragonal cell but ascertained that bismutite is biaxial with 2V = 45° and proved that the tetragonal bismutite cell is possible to transform into orthorhombic by operation with matrix 110/110/001. The proposed orthorhombic cell has parameters a≈ b = 5.44 and space group F mmm. Sahama and Lehtinen (1968) who studied bismutite from Maropino, Mozambique by the X-ray monocrystal method and obtained a known tetragonal cell but by using electron diffraction they confirmed Nefedovs (1956) conclusion about the orthorhombic cell with a b = 5.473.

Bismutite(I) described from many occurrences (Moldava, Cínovec, Jáchymov, Horní Slavkov etc.), where it forms dark grey massive aggregates with submetallic luster (Sejkora 1992) were found at Rýžoviště very rarely as an admixture in massive bismite by the IR absorption spectrum.
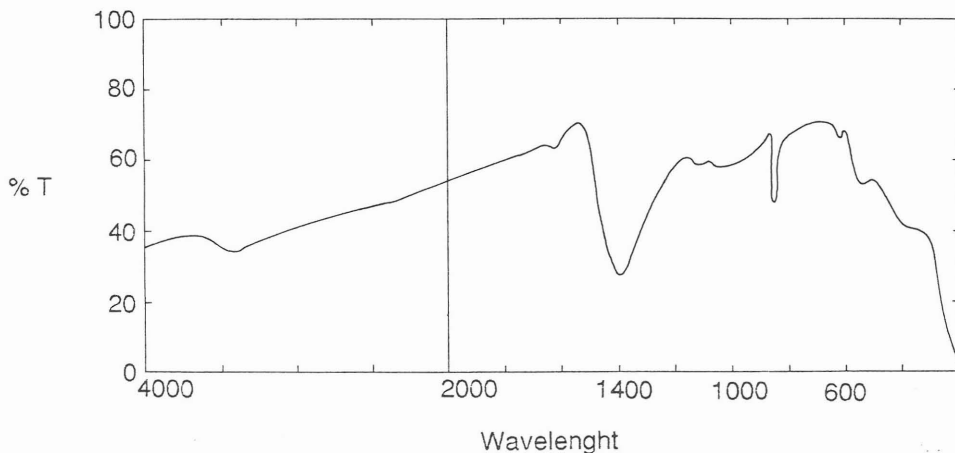

Fig. 5. The IR absorption spectrum of bismutite from Rýžoviště

Bismutite(II) forms at Rýžoviště powder to earthy, white, yellow, yellow grey and sometimes ochreous coatings on quartz gangue and aggregates in minute cavitites of gangue. It rarely occurs as white grey, fine powder to plastic coatings on dark grey massive bismite aggregates, in association with atelestite and walpurgite.

The X–ray powder diffraction data of bismutite from Rýžoviště (Table 7) agrees well with data calculated from the crystal structure information of Lagercrantz, Sillén (1947). The unit cell parameters of bismutite from Rýžoviště is very close to other published data (Table 8). The IR absorption spectrum for bismutite from Rýžoviště (Fig. 5) is very close to other published spectra (Farmer, 1974). The frequency of absorption bands are: 3400, 2944, 1628, 1438, 1392, 1110, 1044, 844, 530, 368 and 264 cm^{-1}. The bands at 3400, 2944 and 1628 cm^{-1} are connected with vibrations of adsorbed water. The vibrations of the $(CO_3)^{2-}$ group are represented in the absorption bands: 1438 and 1392 cm^{-1} (v_3), 1110 and 1044 cm^{-1} (v_1) and 844 cm^{-1} (v_2).

Table 7. X-ray powder diffraction data for bismutite from Rýžoviště

	*1		Rýžoviště		
h k l	d_{teor}	I_{teor}	d_{dobs}	I	d_{calc}
0 0 2	6.843	42	6.889	50	6.834
1 0 1	3.721	44	3.743	60	3.725
0 0 4	3.422	9	3.424	20	3.417
1 0 3	2.950	100	2.957	100d	2.950
1 1 0	2.734	35	2.736	70	2.738
1 1 2	2.539	6	2.547	20	2.542
0 0 6	2.281	10	2.279	30	2.278
1 1 4	2.136	19	2.135	40	2.137
2 0 0	1.934	18	1.942	50	1.938
2 0 2	1.861	6	1.863	10	1.863
1 1 6	1.752	24	1.749	50d	1.751
1 0 7	1.745	11	–		–
2 1 1	1.716	11	1.714	30	1.717
2 0 4	1.683	6	–		
2 1 3	1.617	34	1.618	60	1.619
2 0 6	1.475	11	1.473	30	1.475

Guinier – de Wolff camera, radiation CuKα

*1 calculated X-ray powder diffraction intensities of bismutite from crystal data by Lagercrantz, Sillén (1947). $I_{calc} \leq 5.0$ have been omitted.

Table 8. Unit cell parameters for bismutite (tetragonal, space group I 4/mmm)

occurence	a	c	V
Harrachov	3.871(3)	13.67(2)	204.9(3)
synthetic 1)	3.867(3)	13.683(3)	204.6
Mozambique 2)	3.870(3)	13.697(3)	206.2
Moldava 3)	3.867(3)	13.77(1)	205.9(1)
Cínovec 3)	3.865(3)	13.72(1)	204.9(2)
Smrkovec 3)	3.874(2)	13.69(1)	205.5(2)
Horní Slavkov 3)	3.876(4)	13.73(5)	206.2(5)
Jáchymov 3)	3.871(2)	13.87(1)	207.7(2)

1) synthetic bismutite by Lagercrantz, Sillén (1947)
2) bismutite from granite pegmatite from Mozambique by Sahama, Lehtinen (1968)
3) Sejkora (1992)

Churchite(Y) $Y(PO_4) . 2 H_2O$

Churchite(Y) was originally described by A. H. Church in 1865, and named by C. G. Wiliams in the same year. The specimens were collected from an unnamed locality in Cornwall, Great Britain. In 1922, H. Laubmann described a phosphate of Y from the Nitzelbuch mine, Auerbach, Bavaria, under the name weinschenkite. The identity of churchite(Y) and weinschenkite were described by Clarringbull, Hey (1953). In the Czech Republic, churchite(Y) was found in the cement of the Cenomanian conglomerates at the uranium deposit Stráž pod Ralskem by Scharmová et al. (1993).

Churchite(Y) belongs to the youngest supergene minerals at Rýžoviště, it occurs in minute crannies of rock in association with metatorbernite(II) crystals. Churchite(Y) forms grey white aggregates (up to 1 cm^2) composed by radially arranged minute transparent spicular crystals up to 0.1 mm in length (Pl. 2, fig. 1 and Pl. 3). Its crystals sometimes grow on green dipyramidal metatorbernite crystals (Pl. 4).

The X-ray powder diffraction pattern of churchite(Y) from Rýžoviště (Table 9) shows only slight differences compared with the pattern of Clarringbull, Hey (1953). In indexing the powder diffraction pattern the lattice parameters of Clarringbull, Hey (1953) were used to calculate the theoretical interplanar distance with correspondence (hkl). The refined unit cell parameters show a good agreement with the data of Clarringbull, Hey (1953).

The IR absorption spectrum of churchite(Y) from Rýžoviště (Fig. 6, Table 10) is very close to the weinschenkite spectrum by Moenke (1966). The O–H stretching vibrations of H_2O are represented by an extensive band with a nonsignificant maxima at 3372 and 3140 cm^{-1}. The band at 796 cm^{-1} may be a H_2O librational mode, the two components of the water bending vibration, at 1628 and 1076 cm^{-1} are more widely separated than in the isostructural gypsum itself (Farmer, 1974). The $(PO_4)^{3-}$ group is represented by bands at 1014 and 1068 cm^{-1} (v_3) and 532, 644 cm^{-1} (v_4). The band corresponding to the activated vibration

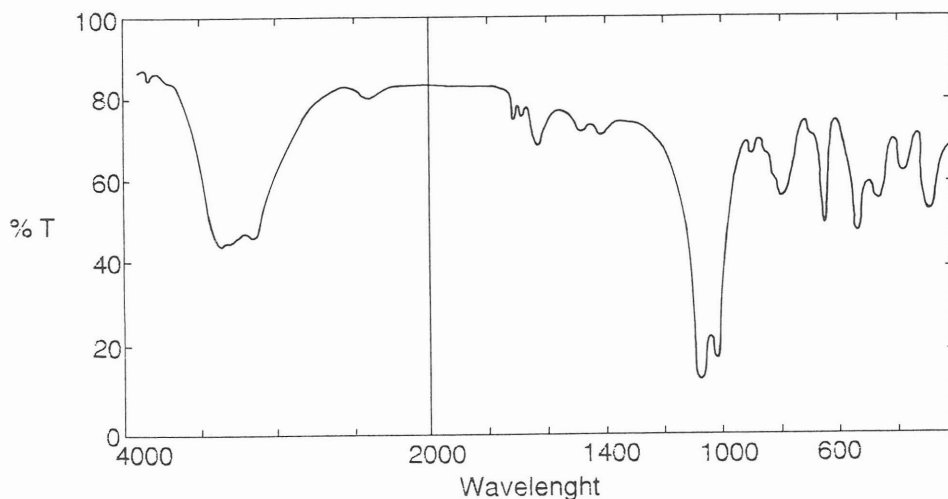

Fig. 6. The IR absorption spectrum of churchite(Y) from Rýžoviště

Table 9. X-ray powder diffraction data from churchite(Y) from Rýžoviště

			Rýžoviště			*1	
h	k	l	d_{obs}	I_{obs}	d_{calc}	d_{obs}	I_{obs}
0	2	0	7.549	92	7.538	7.55	vs
0	1	1	5.232	8	5.232	5.22	w
1	1	−1	4.711	12	4.706	4.70	mw
1	2	0	4.205	100	4.199	4.20	vvs
0	4	0	3.767	38	3.769	3.74	ms
1	4	0	3.023	100	3.022	3.01	vs
1	2	−2	2.837	15	2.837	2.83	m
2	2	−1	2.628	10	2.624	2.61	mw
0	6	0	2.509	15	2.513	2.52	vw
2	0	−2	2.474	6	2.477	2.47	vw
						2.44	vw
2	2	0	2.395	8	2.396	2.37	w
1	5	1	2.176	15	2.173	2.162	mw
0	5	2	2.049	9	2.048	2.059	w
2	0	1	1.999	7	2.001	2.005	vvw
1	7	−1	1.974	11	1.975	1.964	w

$$a = 5.600(5) \qquad a = 5.61$$
$$b = 15.076(8) \qquad b = 15.14$$
$$c = 6.180(8) \qquad c = 6.19$$
$$\text{ß} = 115.47(6) \qquad \text{ß} = 115.3$$
$$v = 470.9(1.0) \qquad v = 475.3$$

Diffractometer HZG 4/TuR, CuKα radiation, step scanning O.O5°/8 s.
*1 weinschenkite, Nitzelbuch mine, Auerbach, Bavaria by Claringbull, Hey (1953). Order of intensities: vvs, vs, s, ms, m, mw, w, vw, vvw.

Table 10. The IR absorption data of churchite(Y) from Rýžoviště

cm^{-1}			*1	Tentative assignment
			3570	v OH
3372	s	br	3400	v OH
3140	s	br	3140	v OH
1706	w		1716	δ H_2O
1628	ms		1640	δ H_2O
1470	w	br		
1402	w	br		
1068	vs		1070	v_3 (PO_4)
1019	vs		1020	v_3 (PO_4)
			978	v_1 (PO_4)
888	w			
796	ms		753	libration H_2O
644	ms		650	v_4 (PO_4)
532	ms		533	v_4 (PO_4)
458	ms			
380	ms			
278	ms			

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*1 weinschenkite from Auerbach, Bavaria (Moenke 1966)

v_1 (978 cm^{-1}, Farmer, 1974) was not found in our spectrum. The chemical composition of churchite(Y) was studied by electron microprobe in the energy dispersive mode, Y and P were found as major elements, Dy, Nd, Sm, Yb, Gd and Ce as minor elements (0.5 – 2 wt. % range). Since the content of Y is greater than that of REE and following Levinson's (1966) rule this mineral should be named churchite(Y).

(Meta)autunite $Ca(UO_2)_2(PO_4)_2 \cdot 6-8 \ H_2O$

Metaautunite is one from the most common supergene uranyl minerals in nature. It occurs in two forms: as fully hydrated autunite with 12 molecules of H_2O and metaautunite with 6 – 8 H_2O (Čejka and Muck 1985). Both forms occur, as a rule, together distinct from meta torbernite.

Table 11. X-ray powder diffraction data for (meta)autunite from Rýžoviště

Rýžoviště				Autunite *1		Metaautunite *2			
d_{obs}	I_{obs}	d_{calc}	h k l	d_{obs}	I_{obs}	d_{calc}	h k l	d_{obs}	I_{obs}
9.993	100	9.972	0 0 2	10.37	100				
8.478	36					8.463	0 0 2	8.51	100
6.629	2	6.596	1 0 1	6.61	6				
5.402	4					5.386	1 0 2	5.39	70
4.995	33	4.986	0 0 4	5.19	86			4.96	50
4.823	10	4.817	1 0 2	4.91	35				
4.427	5	4.428	1 1 2	4.45	15				
4.244	9					4.264	1 1 2	4.28	60
3.619	15					3.619	1 0 4	3.63	80
3.474	22			3.567	83			3.50	90
3.237	5					3.227	2 0 2	3.24	80
2.932	2					2.929	1 2 2	2.94	40
2.830	3	2.829	2 1 3	2.842	13				
2.700	3					2.693	2 0 4	2.70	30
2.639	8	2.639	1 0 7	2.729	16				
2.615	9					2.616	1 0 6	2.61	30
2.494	6	2.493	0 0 8	2.598	5			2.51	20
2.461	3					2.469	2 2 0	2.47	20
2.400	2	2.399	2 2 2	2.397	7				
2.368	1					2.370	2 2 2	2.38	30
2.209	4			2.203	26			2.21	30
2.158	4	2.158	3 1 2	2.157	16				
2.137	4					2.136	1 3 2	2.14	30
2.111	13			2.146	17			2.10	30
2.025	3			2.080	45			2.04	30
1.995	11	1.995	0 0 10	2.076	45				
1.943	2					1.948	1 1 8	1.941	20
1.850	4	1.850	1 1 10	1.914	10				
		a = 6.989(5)				a = 6.982(5)			
		c = 19.95(1)				c = 16.93(1)			

Diffractometer HZG 4/TuR, CuKα radiation, step scanning 0.05°/10 s.
*1 autunite (Takano 1961), indexing on the basis of the Takano's (1961) paper
*2 metaautunite from Sabugal, Portugal (Frondel et al. 1956), indexing by theoretical powder diffraction data generated from crystal structure information of metatorbernite (Ross et al. 1964) by replacing Ca – Cu.

The (meta)autunite is at Rýžoviště more rare than metatorbernite. It forms two base types: (meta)autunite(I) is earthy as a component of massive uranophane - phosphuranylite pseudomorphs after uraninite. (Meta)autunite(II) forms minute (up to 2 mm in size) table crystals growing on the crannies of rock near the ore veins and on massive phosphuranylite - uranophane aggregates. (Meta)autunite(II)s colour is bright yellow to greenish yellow, it has a perfect cleavage along (001) and glassy luster. The very thin cleavage plates are yellowish, translucent to transparent. In the short wave of UV light metaautunite has a very intensive green yellow fluorescence.

The X-ray powder diffraction pattern for (meta)autunite from Rýžoviště is given in the Table 11. This sample is mixture of metaautunite with prevailing fully hydrated autunite. The autunites unit cell parameter c (19.95) is disticly different to other described parameters (range 20.73 - 20.76, Takano 1961).

Metatorbernite $Cu(UO_2)_2(PO_4)_2 \cdot 8\ H_2O$

Torbernite occurs in two forms: fully hydrated torbernite with 12 molecules of H_2O and as a metaform with 8 H_2O. Torbernite is stable only in damp environment and at low moisture content in the air it changes reversibly to metatorbernite (Čejka et al. 1985). Metaform prevails in nature and additionally, finds of the mixture torbernite and metatorbernite are relatively rare (Mrázek and Novák 1984). The crystal structure of metatorbernite consists on infinite $(UO_2PO_4)_n$ layers isostructural with those of metaautunite. Cu^{2+} cations and water molecules are located in the interlayer space. Each cation is six-coordinated by two oxygen atoms of two different uranyl groups and four water molecules forming thus a distorted tetragonal dipyramid. The four water molecules form squares $Cu(H_2O)_4$ perpendicular to c, with or without Cu atoms at their centers. Successive uranylphosphate layers are interconnected by practically linear chains $-O-U-O-Cu-O-U-O$ (Čejka et al. 1985).

At Rýžoviště, the first description of metatorbernite is the find of Bradna and Šita (1968). It occurs in the two types: metatorbernite(I) forms massive earthy light green aggregates composed together with uranophane, phosphuranylite and (meta)autunite(I) pseudomorphs after uraninite aggregates. Metatorbernite(II) forms thin plates and coatings (from 0.1 mm up to some cm in size) on minute crannies of rock near the ore veins. It occurs more rarely as druses of well-formed dipyramidal crystals up to 7 mm in size growing on quartz in minute cavities of quartz gangue (Pl. 2, fig. 2 and Pl. 5, fig. 1). The perfect cleavage along (001), glassy lustre and lacking fluorescence in UV light are characteristic for this mineral.
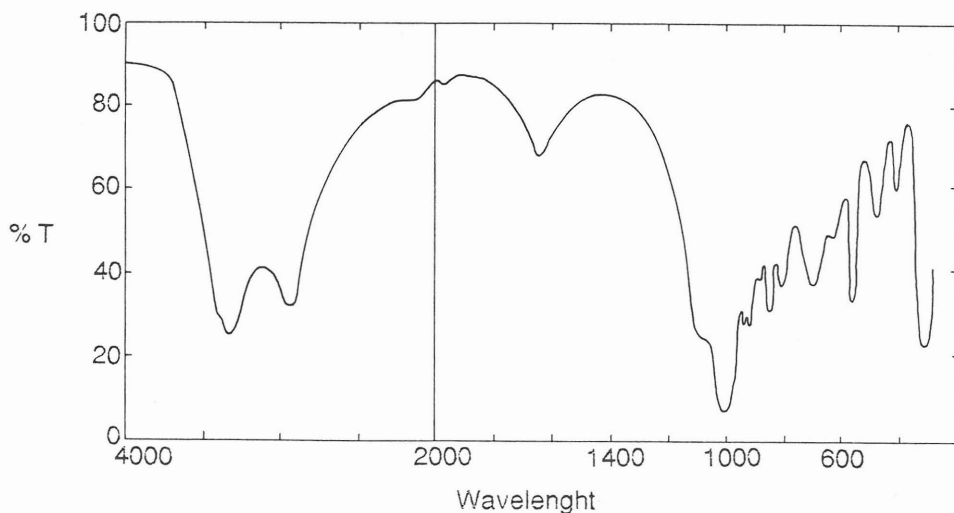

Fig. 7. The IR absorption spectrum of metatorbernite from Rýžoviště

Table 12. X-ray powder diffraction data for metatorbernite from Rýžoviště

h	k	l	d_{teor}	I_{teor}	d_{obs}	I_{obs}	d_{calc}
			*1		Rýžoviště		
0	0	2	8.653	100	8.611	100	8.642
1	0	1	6.465	6	6.446	0	6.451
1	0	2	5.428	41	5.408	11	5.417
1	1	0	4.928	63	4.910	9	4.917
0	0	4	4.327	6	4.313	18	4.321
1	1	2	4.282	21	4.267	6	4.273
1	0	4	3.676	94	3.667	68	3.670
2	0	0	3.485	65	3.474	16	3.477
2	0	2	3.232	45	3.223	13	3.225
1	2	2	2.932	12	2.924	6	2.926
2	1	2	2.932	10	2.924	6	2.926
2	0	4	2.714	5	2.708	3	2.709
1	0	6	2.665	15	2.661	16	2.661
1	2	4	2.529	11	2.523	8	2.524
2	1	4	2.529	15	2.523	8	2.524
1	1	6	2.489	3	2.484	2	2.485
2	2	0	2.464	15	2.457	3	2.458
2	2	2	2.370	16	2.363	5	2.365
3	0	1	2.302	2	2.296	0	2.297
3	0	2	2.244	7	2.238	2	2.239
3	1	0	2.204	15	2.199	6	2.199
1	3	0	2.204	12	2.199	6	2.199
0	0	8	2.163	8	2.161	34	2.160
3	1	2	2.136	5	2.132	5	2.131
1	3	2	2.036	6	2.132	5	2.131
2	1	6	2.117	7	2.113	9	2.113
1	2	6	2.117	8	2.113	9	2.113
1	0	8	2.066	5	2.062	7	2.063
3	0	4	2.047	23	2.043	9	2.042
1	1	8	1.981	14	1.979	12	1.978
3	2	2	1.886	3	1.884	1	1.882
2	3	2	1.886	4	1.884	1	1.882
2	0	8	1.838	8	1.836	5	1.835
3	0	6	1.809	7	1.806	2	1.806
1	2	8	1.777	2	1.774	3	1.774
2	1	8	1.777	2	1.774	3	1.774
3	2	4	1.765	9	1.762	5	1.761
2	3	4	1.765	9	1.762	5	1.761
4	0	0	1.742	9	–		
0	0	10	1.731	2	1.730	7	1.728
4	0	2	1.708	5	1.705	0	1.704

Diffractometer HZG 4/TuR, CuKα radiation, step scanning 0.05°/5 s.
*1 the calculated X-ray powder difraction intensities from crystal data by Ross et al. (1964). $I_{calc} \leq 1.9$ have been omitted.

Table 13. The IR absorption data of metatorbernite from Rýžoviště

cm⁻¹			*1	Tentative assignment
3400	sh			ν OH
3340	s		3350	ν OH
2936	s		2930	ν OH
1636	ms	br	1645	δ H$_2$O
1074	sh		1100	ν_3 (PO$_4$)
994	vs		990	ν_3 (PO$_4$)
931	vw		930	ν_3 (UO$_2$)
916	ms		910	ν_3 (UO$_2$)
842	ms		845	ν_1 (UO$_2$)
800	ms		800	ν_1 (UO$_2$)
690	ms		680	libration mode H$_2$O
612	w		615	libration mode H$_2$O
546	ms	shr	550	ν_4 (PO$_4$)
464	ms		465	ν_4 (PO$_4$)
398	ms		405	ν_4 (PO$_4$)
292	s		295	ν_2 (UO$_2$)
256	s	shr	258	ν_2 (UO$_2$)

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*1 metatorbernite, Abertamy, Czech Republic (Čejka et al. 1985)
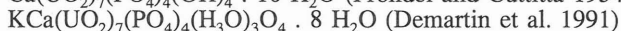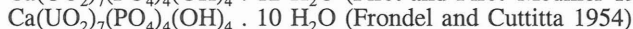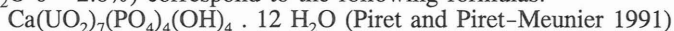
The colour of metatorbernite is bright green and at dipyramidal crystals to emerald green. The minute cleavage tables of metatorbernite are translucent to transparent and have light green colour. Metatorbernite(II) appears to be located with churchite(Y) the youngest secondary minerals. It is associated with churchite(Y), (meta)autunite(II), uranosphaerite and walpurgite.

The X-ray powder diffraction pattern of metatorbernite from Rýžoviště (Table 12) agrees with data calculated from the crystal structure information by Ross et al. (1964) but there is distinctly expressed a preferred orientation of the sample which has an influence on the intensity of some diffractions. The diffraction peaks with (hkl) type (00l) which have distinctly greater intensities. The lattice parameters of metatorbernite from Rýžoviště are a = 6.9533(8), c = 17.283(3) and agree very well with Ross et al.s (1964) parameters a = 6.969, c = 17.306.

The infrared absorption spectrum of metatorbernite from Rýžoviště (Fig. 7) is very close to the metatorbernite spectrum from Abertamy, Czech Republic by Čejka et al. (1985). The tentative assignment of individual absorption bands (Table 13) was carried out on the basis of Čejka et al.'s (1985) paper.

Phosphuranylite   KCa(UO$_2$)$_7$(PO$_4$)$_4$(H$_3$O)$_3$O$_4$. 8 H$_2$O

The analyses published till now (UO$_3$ 77.3 - 79.3%, CaO 1.6 - 1.3%, P$_2$O$_5$ 9.8 - 11.3%, K$_2$O 0 - 2.8%) correspond to the following formulas:

Ca(UO$_2$)$_7$(PO$_4$)$_4$(OH)$_4$. 12 H$_2$O (Piret and Piret–Meunier 1991)

Ca(UO$_2$)$_7$(PO$_4$)$_4$(OH)$_4$. 10 H$_2$O (Frondel and Cuttitta 1954)

KCa(UO$_2$)$_7$(PO$_4$)$_4$(H$_3$O)$_3$O$_4$. 8 H$_2$O (Demartin et al. 1991)

The ratio Ca:UO$_2$:PO$_4$ was identified as 1:7:4. Potassium was identified at first at 4 localities (Sardinia, France, Italy, Zambia – Demartin et al. 1991). Due to its low content (less then 2.8 % K$_2$O) and complications of K analyses besides high U content, potassium was not identified before. The existence of K must definitely be confirmed on material from the original locality of the Flat Rock mine in the U.S.A.

A crystal structure of phosphuranylite was studied by Šaskin and Sidorenko (1975), Piret and Piret–Meunier (1991) and Demartin et al. (1991). It is an orthorombic mineral with relatively high cell parameters: a=15.853, b=13.724, c=17.324 (Piret, Piret–Meunier 1991).

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Table 14. X-ray powder diffraction data for phosphuranylite from Rýžoviště

			*1		Rýžoviště		
h	k	l	d_{teor}	I_{teor}	d_{obs}	I_{obs}	d_{calc}
1	1	0	10.393	20	10.413	12	10.356
1	1	1	8.909	6	–		
0	0	2	8.650	5	8.690	14	8.654
2	0	0	7.945	100	7.919	100	7.890
0	2	0	6.870	9	–		
0	2	1	6.385	6	6.395	8	6.379
2	0	2	5.851	41	5.844	25	5.830
2	2	0	5.197	6	5.177	8	5.178
2	2	1	4.977	5	4.965	10	4.961
3	1	1	4.752	14	4.738	14	4.733
0	2	3	4.417	25	4.422	15	4.416
3	1	2	4.291	9	4.269	13	4.272
1	1	4	3.993	10	–		
4	0	0	3.972	41	3.953	67	3.945
2	2	3	3.860	32	3.858	23	3.853
2	0	4	3.799	15	3.797	16	3.794
0	4	0	3.435	19	3.433	16	3.431
3	3	1	3.397	7	–		
4	2	1	3.373	12	3.350	28	3.355
0	4	2	3.193	8	–		
2	4	0	3.153	56	3.148	34	3.147
0	2	5	3.090	43	3.090	29	3.091
5	1	1	3.048	6	3.039	15	3.028
4	2	3	2.954	12	2.945	17	2.942
2	2	5	2.880	51	2.879	30	2.878
4	4	0	2.598	5	2.587	10	2.589
5	3	1	2.582	5	2.570	7	2.569
5	1	4	2.518	6	–		
3	1	6	2.490	7	2.484	12	2.487
4	4	2	2.488	7	2.484	12	2.480
4	2	5	2.439	12	2.431	17	2.433
6	2	1	2.446	6	2.431	17	2.432
4	4	4	2.227	8	2.223	8	2.222
0	0	8	2.163	3	2.167	7	2.163
3	5	4	2.125	6	2.123	9	2.121
6	4	0	2.097	10	2.087	12	2.087
2	0	8	2.087	6	2.087	12	2.086
2	6	3	2.056	11	–		
6	2	5	2.011	7	1.999	11	2.003
8	0	0	1.986	5	1.972	10	1.973
1	5	6	1.974	5	1.972	10	1.973
0	6	5	1.910	11	–		
8	2	1	1.897	10	1.884	11	1.885
2	6	5	1.857	13	1.856	9	1.855
2	4	8	1.783	9	1.781	8	1.783
4	6	5	1.721	8	1.715	11	1.718

Diffractometer HZG 4/TuR, CuKα radiation, step scanning 0.05°/8.5 s.
*1 the calculated X-ray powder diffraction intensities from crystal data by Demartin et al. (1991). I_{calc} ≤ 4.9 have been omitted.

The other published and calculated cell parameters are very close to each other but even a maximal difference of only 1.3 % causes relatively high changes in the interplanar distances (Sejkora 1993).

The water content of phosphuranylite was not determined directly before but only calculated as a rest up to 100 % or according to an ideal chemical formula. The water content is in the range of 4.8–8.6 wt. %, i.e. 8–14 H_2O molecules in its empirical formula. H_3O and OH groups in its structure are questionable. H_3O can not be confirmed by IR absorption spectroscopy because of a coincidence in its absorption belts v_1, v_3 (3375, 3223 cm^{-1}) with those of H_2O a OH, v_4 (1646 cm^{-1}) with H_2O and v_2 (1060 cm^{-1}) with PO_4 groups (Sejkora, 1993).

The chemical composition, X-ray powder pattern, lattice parameters, optical constants and IR absorption spectrum of yingjangite (Zhangru et al. 1990) from the locality Tongibignan in China, $K_{1.3}Ca_{0.7}(UO_2)_6(PO_4)_4(OH)_{2.7}.8\ H_2O$ are practically identical with those of phosphuranylite.

Formerly, phosphuranylite was confused with uranophane, but more recently phosphuranylite samples have been determined from Ruprechtice u Liberce, Novotníky, Chotěboř, Kladská, Předbořice, Horní Slavkov a Rožínka (Sejkora 1993).

At Rýžoviště, phosphuranylite occurs relatively often as yellow powdery aggregates up to some cm in diameter, overgrown both in quartz veins and hydrothermally altered rocks. It occurs sometimes in mixture with uranophane. These two minerals can be distinguished only with the aid of instrumental methods. Metatorbernite(I), (meta)autunite(I) and uranosphaerite are intergrown in phosphuranylite aggregates. The X-ray powder pattern of phosphuranylite (Table 14) are in good agreement with data calculated from the crystal structure published by Demartin et al. (1991). A comparison of calculated lattice parameters and published data are found in Table 15.

Table 15. Unit cell parameters of phosphuranylite
(Orthorhombic, space group Cmcm)

	Rýžoviště	*1	*2	*3	*4
a	15.780(7)	15.889	15.835	15.95	15.99
b	13.725(8)	13.740	13.724	13.75	13.73
c	17.307(8)	17.300	17.324	17.38	17.33
V	3748.(2.)	3777.	3765.	3812.	3805.

*1 phosphuranylite by Demartin et al. (1991)
*2 phosphuranylite by Piret, Piret–Meunier (1991)
*3 phosphuranylite by Šaškin, Sidorenko (1975)
*4 yingjangite by Zhangru et al. (1990)

Table 16. The IR absorption spectrum of phosphuranylite from Rýžoviště

cm^{-1}		Tentative assignment
3479	s	v OH
3207	s	v OH
1633	ms	H_2O
1504	ms	
1367	ms	
1091	s	v_3 (PO_4)
1041	s	v_3 (PO_4)
1006	vs	v_3 (PO_4)
912	vs	v_3 (UO_2)
887	s	v_3 (UO_2)
797	w	v_1 (UO_2)
507	vs	v_1 (PO_4)

Nicolet 740

The chemical composition of phosphuranylite was studied semiquantitatively with an energy dispersive analyser. Ca, U and P were identified as the main elements and Bi, Si in concentration were less than 1 wt. %. K can not be confirmed due to its coincidence with U.

The infrared absorption spectrum of phosphuranylite is given in Fig. 8 (Table 16). The presence of molecular water is manifested by the H_2O vibration with maximum at 1633 cm^{-1}, and the v O–H vibrations in the range 2700 – 3700 cm^{-1} with two maxima: 3207 and 3479 cm^{-1}. The (PO_4) tetrahedron is in the structure partly deformed (Demartin et al. 1991), the P–O bond lengths range from 1.51 to 1.54, the O–P–O angles ranging from 102 – 113°. A decrease of the symmetry of the PO_4 group is manifested specially in a splitting of an antisymmetric vibration v_3 into 3 absorption bends with maxima 1006, 1041 and 1091 cm^{-1}, split absorption bend v_4 (PO_4) with maximum at 508 cm^{-1} and possibly an activation of the v_1 vibration, which is in an area of intensive absoptions v_3 (UO_2). Absorption at 1504 (1006 + 508) and 1367 cm^{-1} are probably combined absorption bends. The uranyl group is manifested by a split vibration v_3 and an absorption bend at 797 cm^{-1}, which correspond to an activation of the v_1 vibration.

On the basis of the modified Badger rule, values of an antisymmetric vibration v_3 (UO_2) were used to calculate R(U–O) bond length in the uranyl group. The used relations are mentioned at walpurgite. We supposed that symmetrical vibration v_1 (PO_4) does not appear in the spectrum. The vibration v_3 (UO_2) is distinctly splitted into two vibration bends: the more intensive bend with maximum 912 cm^{-1} and the shoulder 887 cm^{-1}. Thus, at least two non–equivalent U–O bonds are suggested in phosphuranylite.

The following values of bond lengths were calculated for the belt 912 cm^{-1}: $R_{1,2,3}$(U–O) = 1.76, 1.77, 1.77 and for the belt 887 cm^{-1}: $R_{1,2,3}$(U–O) = 1.78, 1.79, 1.78. Demartin et al. (1991) mentioned 3 nonequivalent coordinates of U in phosphuranylite: pentagonal dipyramid around $U_{(1)}$ with R(U–O) 1.79(1), 1.80(1); hexagonal dipyramid around $U_{(2)}$ with R(U–O) 1.77(1) and tetragonal dipyramid around $U_{(3)}$ with R(U–O) 1.77(1). Considering the bond length of U–O in hexagonal and tetragonal dipyramids which does not differ (1.77(1) in both cases), the results of IR absortion spectroscopy express very good agreement with the crystal structure published by Demartin et al. (1991).
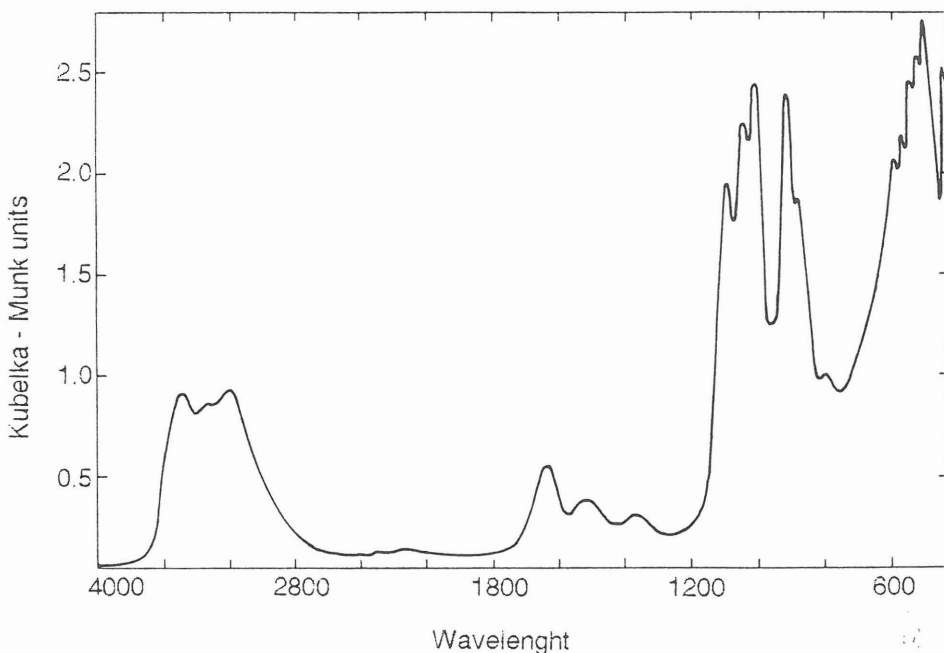

Fig. 8. The IR absorption spectrum of phosphuranylite from Rýžoviště

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Atelestite $Bi_2O(OH)(AsO_4)$

Atelestite was found for the first time in the mine Neuhilfe, in the Schneeberg ore district, Saxony, as small crystals and crystal coatings on quartz gangue, by Breithaupt (1832). Later atelestite was described as rhagit, from the mine Weisser Hirsch, Schneeberg, by Weisbach (1871). Identity of atelestite and rhagite was ascertained by on X-ray powder diffraction study (Frondel, 1943a). The yellow crusts composed of very small crystals of atelestite were found in the Mosrif deposit in association with mixite and scorodite by Timofjeva (1965).

Table 17. X-ray powder diffraction for atelestite from Rýžoviště

			*1		Rýžoviště		
h	k	l	d_{teor}	I_{teor}	d_{obs}	I_{obs}	d_{calc}
1	0	0	6.691	27	6.654	9	6.656
0	1	1	6.036	21	6.040	5	6.031
0	1	2	4.247	30	4.255	14	4.244
2	0	0	3.345	8	3.340	1	3.328
2	0	-2	3.284	72	3.266	53	3.267
1	1	2	3.249	55	3.241	47	3.243
1	2	0	3.248	9	–		–
1	2	-1	3.234	100	3.230	100	3.227
1	1	-3	3.178	7	3.179	2	3.173
0	1	3	3.130	65	3.125	45	3.128
2	1	0	3.051	4	–		–
0	2	2	3.018	5	3.017	11	3.015
2	1	1	2.734	39	2.721	16	2.724
2	1	-3	2.668	5	2.660	2	2.658
2	2	-1	2.545	7	–		–
1	1	-4	2.534	18	2.530	12	2.530
2	2	0	2.486	5	2.480	1	2.478
0	3	1	2.409	4	2.409	1	2.406
1	3	0	2.323	6	2.320	2	2.319
3	0	-2	2.310	8	–		–
2	1	-4	2.301	6	2.298	7	2.295
1	3	1	2.219	7	–		–
1	0	4	2.206	11	2.203	13	2.203
1	3	-2	2.205	6	2.203	13	2.201
3	1	0	2.136	15	2.123	6	2.126
0	2	4	2.123	3	–		–
2	2	2	2.071	3	–		–
1	3	2	2.043	18	2.036	13	2.040
2	1	3	2.032	3	2.026	1	2.027
1	3	-3	2.025	6	2.020	2	2.022
2	3	-1	2.021	3	–		–
0	3	3	2.012	4	–		–
2	1	-5	1.977	16	1.970	11	1.972
3	2	-1	1.971	3	1.960	1	1.963
2	3	1	1.894	5	–		–
3	2	-3	1.886	19	1.878	9	1.879
3	0	2	1.860	3	1.855	2	1.852

Diffractometer DRON 3, Cuα radiation, step scanning

*1 the calculated X-ray powder diffraction intensities from crystal data by Mereiter and Preisinger (1986).

Table 18. Unit cell parameters of atelestite

	Harrachov	*1	*2
a	6.961(4)	6.98	7.000
b	7.422(5)	7.42	7.430
c	10.820(9)	10.88	10.831
ß	107.01(5)°	107.22°	107.08°
V			

*1 atelestite from Schneeberg, Saxony by Culver and Berry (1963)
*2 atelestite from Schneeberg, Saxony by Mereiter (1981)

Table 19. Chemical analyses for atelestite from Rýžoviště

	Rýžoviště			
	*1	*2	*3	*4
Bi_2O_3	78.99	79.10	80.45	82.01
As_2O_5	19.48	16.70	14.23	12.14
P_2O_5	–	1.07	3.99	5.04
V_2O_5	–	0.08	0.09	0.33
SiO_2	–	0.00	0.00	0.00
H_2O	1.53	1.50	1.58	1.60
	100.00	98.45	100.34	101.12
Bi *	1.9997	2.0458	1.9578	1.9790
As *	0.9998	0.8757	0.7020	0.5939
P *	–	0.0908	0.3187	0.3992
V *	–	0.0053	0.0056	0.0204
Si *	–	0.0000	0.0000	0.0000
H *	1.0018	1.0035	0.9955	0.9955

electron microprobe JEOL JXA–50 A
* number of ions on the basis 6 (O,OH)
*1 theoretical composition of atelestite ($Bi_2O(OH)$ (AsO_4))
*2 centrum of aggregate *3 medium zone *4 margin of aggregate

Originally the proposed formula of atelestite $Bi_3(AsO_4)O_2(OH)_2$ was adapted to $Bi_8(AsO_4)_3O_5(OH)_5$ by Culver and Berry (1963). Fischer (1956) on the basis of a new chemical analysis and Mereiter (1981) on the basis of a study of atelestites structure proposed formula $Bi_2O(OH)(AsO_4)$ is adopted.

The atelestite was found at Rýžoviště very rarely, was white, white yellow, grey, grey yellow, light green and yellow green hemispherical massive aggregates in size up to 2 mm. Atelestite has fat to glassy lustre and no cleaveability. It is associated with bismite, walpurgite crystals, bismutite and amorphous Bi–U–As phase. The X–ray powder diffraction pattern of atelestite is shown in Table 17. The crystal structure data of atelestite by Mereiter (1981) were used to index the measured powder pattern. The calculated lattice parameters (Table 18) are in agreement with other published data. The chemical compositon of atelestite from Rýžoviště was carried out by electron microprobe (Table 19). For atelestite from Harrachov, a zoning structure of hemispherical aggregates is characteristic. The centre of the aggregates are composed of relative pure atelestite (88 molar per cent of the atelestite – arsenian component), middle zone (70 per cent) and the margin of aggregates are composed of atelestite with only 59 molar per cent of the arsenian component. The thin cover section of the atelestite aggregates are formed by a phosphate analogue of atelestite, a new proposed mineral CNMMN IMA no. 93–040. Analyses recalculated on the basis of six (O,OH), yeilded to the empirical formula (average from three points):

$Bi_{1.99}$ O (OH) $(As_{0.72}P_{0.27}V_{0.01})_{1.00}$ O_4
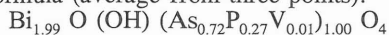
Pharmacosiderite $KFe_4(AsO_4)_3(OH)_4 . 6-7\ H_2O$

Pharmacosiderite was found only rarely in small cavities in quartz veins as small cubic crystals of green colour and glassy luster. The X–ray powder diffraction pattern of pharmacosiderite from Rýžoviště (Table 20) is similar to the data calculated from the crystal structure information by Buerger et al. (1967). The unit cell parameter of pharmacosiderite from Rýžoviště a = 8.009(1) is close to the parameter of Cornwall (a = 7.98) and Horní Slavkov (a = 7.965(1)) pharmacosiderite (Buerger et al. 1967, Korbel 1991).

Table 20. X-ray powder diffraction data for pharmacosiderite from Rýžoviště

h	k	l	*1		Rýžoviště		
			d_{teor}	I_{teor}	d_{obs}	I_{obs}	d_{calc}
1	0	0	7.980	100	8.091	100	8.009
1	1	0	5.643	1	5.681	6	5.663
1	1	1	4.607	20	4.634	9	4.624
2	0	0	3.990	9	3.992	27	4.004
2	1	1	3.258	20	3.268	32	3.270
2	2	0	2.821	15	2.838	20	2.832
3	0	0	2.660	3	2.660	13	2.670
2	2	1	2.660	3	2.660	13	2.670
3	1	1	2.406	14	2.408	5	2.415
2	2	2	2.304	4	2.310	3	2.312
3	2	1	2.133	2	2.133	1	1.140
4	0	0	1.995	1	2.012	1	2.002
4	1	0	1.935	2	1.935	3	1.942
4	1	1	1.881	4	1.899	1	1.888
4	2	0	1.784	5	1.783	6	1.791
4	2	1	1.741	2	1.756	1	1.748
3	3	2	1.701	1	1.707	4	1.708

Diffractometer HZG 4/TuR, CuKα radiation, step scanning 0.05°/9 s.

*1 the calculated X-ray powder diffraction intensities from crystal data by Buerger et al. (1967). I_{calc} ≤ 1.0 have been omitted.

Preisingerite $Bi_3O(OH)(AsO_4)_2$

Preisingerite was first found in the weathering zones of the deposits of San Francisco de Los Andes and Cerro Negro de la Aguadita in San Juan Province, Argentina, by Bedlivy and Mereiter (1982). Preisingerite occurs there in the form of porous aggregates of tiny tabular crystals. It ussually occurs together with rooseveltite and infrequevently with bismutite and mixite. Preisingerite and rooseveltite are pseudomorphous after bismuthinite. The crystal structure of preisingerite consists of a cluster of six Bi atoms which are connected by two OH groups and two oxygen atoms. These $Bi_6O_2(OH)_2$ groups are linked by the AsO_4 tetrahedra to form a framework (Bedlivy and Mereiter, 1982). This structure is very close in structure to monoclinic $Bi_2O(OH)(AsO_4)$, atelestite (Mereiter 1981). The unnamed minerals described

Table 21. X-ray powder diffraction data for preisingerite from Rýžoviště.

h	k	l	d_{teor}	I_{teor}	d_{obs}	I_{obs}	d_{calc}
			*1		Rýžoviště		
−1	1	0	6.688	10	6.714	2	6.699
0	0	1	6.229	17	6.222	3	6.220
0	−1	1	4.951	9	4.957	5	4.950
1	1	0	4.527	35	4.513	21	4.525
−2	1	0	4.391	12	4.385	4	4.393
2	0	0	4.190	3	–		–
1	−1	1	4.130	10	4.133	4	4.125
−2	0	2	3.283	100	3.283	100	3.285
−2	2	1	3.258	93	3.243	91	3.254
1	1	1	3.199	47	3.186	84	3.188
0	−2	1	3.187	55	3.186	84	3.182
0	0	2	3.115	14	3.118	2	3.110
−1	1	2	3.094	17	3.084	51	3.095
2	1	0	3.090	49	3.084	51	3.087
2	−1	1	3.087	32	3.084	51	3.082
−3	1	0	3.017	49	3.008	12	3.016
−3	2	1	2.861	12	–		–
−2	−1	2	2.796	8	–		–
0	1	2	2.701	13	2.701	3	2.698
1	−1	2	2.613	28	2.612	8	2.609
1	0	2	2.574	6	–		–
−3	−1	1	2.514	14	–		–
−4	1	1	2.491	19	2.494	5	2.493
−3	−1	2	2.365	3	–		–
−2	0	3	2.306	3	–		–
−1	3	1	2.267	13	–		–
3	0	1	2.212	14	–		–
−1	−1	3	2.175	6	2.118	7	2.117
−2	−1	3	2.147	3	–		–
−1	1	3	2.118	12	–		–
2	0	2	2.097	4	–		–
0	−1	3	2.066	4	2.059	11	2.063
−1	−3	1	2.059	7	2.059	11	2.060
0	3	1	2.055	11	2.059	11	2.056
1	3	0	2.016	4	–		–
−4	−1	2	1.969	19	1.970	17	1.969
3	−3	1	1.967	17	1.970	17	1.968
−5	1	2	1.965	11	1.970	17	1.968

Diffractometer DRON 3, CuKα radiation, step scanning 0.02°/1 s. Quartz as internal standard.
*1 the calculated X-ray powder diffraction intensities from crystal data by Bedlivy and Mereiter (1982).

Table 22. Unit cell parameters for preisingerite (triclinic space group P –1)

	Rýžoviště	Argentina *1	Moldava *2	Smrkovec *2
a	9.97(1)	9.993(3)	10.01(1)	10.01(2)
b	7.392(7)	7.404(3)	7.433(6)	7.418(7)
c	6.930(7)	6.937(3)	6.940(6)	6.937(8)
α	87.84(8)	87.82(2)	87.65(6)	87.69(7)
ß	115.07(6)	115.01(2)	115.03(5)	115.20(8)
	111.09(7)	111.07(2)	111.22(6)	111.19(8)
V	428.(1)	430.05	432.(1)	430.(1)

*1 preisingerite from San Francisco de Los Andes, Argentine by Bedlivy, Mereiter (1982).
*2 Sejkora (1992)

Table 23. Chemical analyses for preisingerite from Rýžoviště

	Rýžoviště		*1	*2
Bi_2O_3	75.06	75.81	74.53	75.81
Fe_2O_3	0.22	0.20	–	–
SiO_2	0.07	–	–	–
As_2O_5	19.47	19.84	24.51	23.01
P_2O_5	3.03	3.00	–	0.72
V_2O_5	–	0.02	–	–
H_2O	0.97	0.97	0.96	1.10
Σ	98.82	99.84	100.00	100.64
Bi *	3.012	3.014	3.000	3.027
Si *	0.011	–	–	–
As *	1.158	1.599	2.000	1.862
P *	0.399	0.392	–	0.094
V *	–	0.002	–	–
H *	1.000	1.000	1.000	1.136

electron microprobe JEOL JXA 50A
* number of ions on the basis 10 (O, OH)
*1 theoretical composition of preisingerite
*2 preisingerite, Argentina by Bedlivy and Mereiter (1982)

by Frondel (1943a), which appear to be identical to preisingerite, have been found in samples originating from Mammoth Mine, Tintic district, Utah and at Tazna, Bolivia.

The samples originating from Schneeberg, Saxony, Germany (Frondel 1943a) appropriate for schumacherite (Walenta et al. 1983). Schumacherite forms minute triclinic crystals which frequently are tabular parallel to (010) in association with pucherite, in crusts on quartz–bearing gangue. At the occurrences of Gadernheim and Reichenbach in Odewald and from the mine dumps of Pucher mine at Schneeberg, Saxony a phosphate analoque of preisingerite, the new mineral petitjeanite (Krause et al. 1993), was also described.

At Rýžoviště, preisingerite occurs very rarely and only a few samples were found. It forms thin fine grained to powder coatings on quartz gangue (Pl. 5, fig. 2) in association with yellow and yellow grey bismutite. The preisingerite colour is yellow to ochreous in view of an admixture of iron hydroxides.

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The X-ray powder diffraction pattern of preisingerite from Rýžoviště (Table 21) is very close to the data calculated from the crystal structure information by Bedlivy and Mereiter (1982). The unit cell dimensions of preisingerite from Rýžoviště agree well (Table 22) with other published data. The chemical composition of preisingerite from Rýžoviště was carried out with an electron microprobe (Table 23). The Rýžoviště's preisingerite has the characteristic content of a phosphate (petitjeanite) component – about 19 – 20 molar %. This certain content of a phosphate component is described also for preisingerite from Argentina by Bedlivy and Mereiter (1982). The following empirical formula are calculated on the basis 10 (O,OH), H_2O content was recalculated by the ideal formula:

$Bi_{3.01}$ [$(AsO_4)_{1.59}(PO_4)_{0.40}(SiO_4)_{0.01}]_{2.00}$ O (OH).
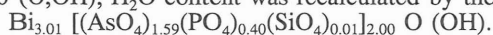
Table 24. X-ray powder diffraction data for walpurgite

h	k	l	d_{teor}	I_{teor}	d_{obs}	I_{obs}	d_{calc}
0	1	0	10.244	100	10.205	86	10.193
1	0	0	6.072	14	6.677	80	6.658
−1	1	0	5.698	27	5.693	29	5.686
1	1	0	5.479	14	5.477	14	5.469
0	2	0	5.122	7	5.092	6	5.096
−1	0	1	4.953	29	4.942	21	4.947
−1	2	0	4.148	5	4.132	6	4.132
0	−2	1	4.015	17	4.004	8	4.008
1	−1	1	3.455	15	3.456	19	3.454
0	3	0	3.415	8	–		–
−2	0	1	3.389	17	3.386	23	3.385
−2	−1	1	3.309	7	–		–
−1	2	1	3.297	15	–		–
0	2	1	3.275	59	3.268	52	3.264
−2	1	1	3.133	47	3.133	100	3.126
1	1	1	3.133	8	3.133	100	3.126
2	1	0	3.129	39	3.133	100	3.129
1	−2	1	3.111	54	3.108	57	3.107
−1	−3	1	3.058	58	3.046	41	3.049
−1	−1	2	2.740	29	2.737	21	2.738
2	2	0	2.740	12	2.737	21	2.735
0	3	1	2.593	9	2.583	6	2.583
0	0	2	2.515	9	2.514	5	2.514
−1	4	0	2.425	23	2.414	19	2.414
2	−1	1	2.416	7	2.414	19	2.415
−1	2	2	2.209	9	–		–
−3	1	0	2.190	9	2.187	15	2.181
−2	−3	2	2.184	8	2.187	15	2.188
1	0	2	2.117	9	2.116	3	2.116
−3	2	0	2.070	8	2.068	5	2.067
−3	−2	2	2.010	11	2.006	9	2.007
1	5	0	1.935	12	1.925	11	1.926
−3	3	0	1.899	10	1.896	6	1.896
−2	3	2	1.863	11	1.857	7	1.857

Diffractometer DRON 3, step scanning 0.02°/1 s. $Pb(NO_3)_2$ as internal standard.
*1 the calculated X-ray powder diffraction intensities from crystal data by Mereiter (1982). $I_{calc} \leq 7.0$ have been omitted.

Walpurgite $(UO_2)(BiO)_4(AsO_4)_2 \cdot 2\ H_2O$

Walpurgite was found for the first time in the Walpurgis vein, Weisser Hirsch mine, Schneeberg, Saxony, by Weisbach (1871). It was found in association with the autunite group minerals (troegerite, zeunerite and uranospinite) and uranosphaerite at the location of a rich occurrence of pure bismuth and uraninite. The mineral waltherite described as bismuth carbonate from Jáchymov (Kratochvíl 1964) was identified by X-ray powder data as walpurgite (Fischer 1955).

Walpurgite at Rýžoviště forms as thin tabular crystals – gyps–like twins, the size of crystals are ussualy up to 2 mm and occasionally up to 4 mm. It forms most commonly in thin coatings on qaurtz – bismite gangue. The wax yellow colour is characteristic of walpurgite, the luster of crystal is glassy to adamantine. The crystals have a eminent cleaveage by (010). Walpurgite from Rýžoviště has no fluorescence in the long or short UV radiation. Walpurgite occurs usually in minute cavities of quartz gangue in association with metatorbernite, bismite, uranosphaerite and atelestite.

The X–ray powder diffraction data of walpurgite (Table 24) agree well with the theoretical powder diffraction pattern calculated from crystal structure information by Mereiter (1982). Unit cell parameters of walpurgite from Rýžoviště are very close to other published data (Table 25). Chemical analyses of walpurgite were carried out by electron microprobe in the energy dispersive mode, Bi, U and As were found as major elements. The phosphorus content was studied by electron microprobe in the energy dispersive mode for the majority of the walpurgite samples in view of the possible presence of being imperfect, described as phosphate analoque of walpurgite – phase phosphowalpurgite (Soboleva, Pudovkina 1957). All walpurgite samples from Rýžoviště are a pure arsenate member. The essential content of phosphorus was not found.

The IR absorption spectrum of walpurgite from Rýžoviště (Fig. 9) is close to the spectrum by Čejka and Urbanec (1990). The tentative assignment of absorption bands was carried out by Farmer (1974), Mereiter (1982) and Čejka et al. (1985). The assignment of the absorption band at 1028 cm^{-1} which is expressed as a majority of the natural arsenates is in question. Farmer (1974) considered the possible admixture of phosphate or the very improbable display of the OH in-plane bending mode (Table 26).

On the basis of Badgers rule being modified, the spectroscopic data were used for the evaluation of R(U–O) bond length. The bond length was calculated from the frequency of v_3 (UO$_2$) vibration (888 cm^{-1}) of walpurgite using the following equations:

$R_1(U–O) = 0.895 + 81.2\ v_3^{-2/3}$ (Weal et al. 1975)
$R_2(U–O) = 0.975 + 74.75\ v_3^{-2/3}$ (Glebov 1981)
$R_3(U–O) = 1.236 + 50.02\ v_3^{-2/3}$ (Serjožkin, Serjožkina 1984)

The following results at walpurgite from Rýžoviště were obtained: R_1=1.774, R_2=1.784, R_3=1.777. The calculated bond length R_2 (Glebov 1981) agrees very well with the bond length R_s = 1.784 which was calculated from the crystal structure information of walpurgite by Mereiter (1982).

Table 25. **Unit cell parameters for walpurgite (triclinic, space group P –1)**

	Rýžoviště	*1	*2	*3
a	7.128(3)	7.13	7.135(2)	7.098(7)
b	10.414(4)	10.44	10.426(4)	10.37(1)
c	5.492(3)	5.49	5.494(1)	5.479(6)
α	101.58(3)°	101.66°	101.47(2)°	101.52(9)°
ß	110.78(3)°	110.82°	110.82(2)°	110.81(8)°
	88.15(3)°	88.28°	88.20(2)°	88.04(7)°
V	373.0(3)	373.70	374.04	369.1(7)

*1 Schneeberg by Fischer (1995)
*2 Schneeberg by Mereiter (1982)
*3 Jáchymov by Sejkora (1992)

Table 26. IR absorption spectra for walpurgite from Rýžoviště

cm⁻¹		Tentative assignment
3520	w	ν OH
3380	ms	ν OH
1604	w	δ H2O
1028	ms	ν (OH) in-plane ?
888	ms	ν_3 UO_2
796	s	ν_1 UO_2, ν_3 AsO_4
778	s	ν_1 UO_2, ν_3 AsO_4
560	w	ν Bi-O
432	ms	ν_4 AsO_4
370	w	ν_2 AsO_4
306	w	ν Bi-O, ν_2 UO_2
245	w	ν_2 UO_2

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Fig. 9. The IR absorption spectrum of walpurgite from Rýžoviště

Amorphous   Bi–U–As phase

Thin, no–large (up to $1 - 3$ cm²), coatings of mineral phase the first taking for walpurgite, were found on the same samples of grey massive bismite with relics of bismuth in association with white grey earthy bismutite(II). These coatings have light to wax yellow colour, non–level surface and fat to glassy luster.

This mineral phase is X–ray amorphous. Its chemical composition was studied by electron microprobe in the energy dispersive mode. Bi, U and As were found as the main elements. The IR absorption spectra of this phase (Fig. 10) is very close to the walpurgite spectrum (Table 27). The absorption bands in the $700 - 900$ cm⁻¹ range (corresponding to vibrations of (AsO_4) and (UO_2) groups) have low intensities and characteristics oder than walpurgite bands. This phenomenon is probably caused by a disorder in the crystal structure of the amorphous phase.

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Table 27. The IR absorption data for amorphous Bi-U-As mineral phase

cm⁻¹			*1	Tentative assignment
3428	vw		3520	ν OH
			3380	ν OH
1618	w	br	1604	δ H$_2$O
1550	w	br		δ H$_2$O
1014	s		1028	ν (OH) in-plane ?
872	w		888	ν_3 UO$_2$
792	w	br	796	ν_1 UO$_2$, ν_3 AsO$_4$
			778	ν_1 UO$_2$, ν_3 AsO$_4$
528	ms		560	ν Bi-O
464	ms		432	ν_4 AsO$_4$
			370	ν_2 AsO$_4$
294	w		306	ν Bi-O, ν_2 UO$_2$
			245	ν_2 UO$_2$

Pye-Unicam 9512
*1 walpurgite from Rýžoviště (this paper)
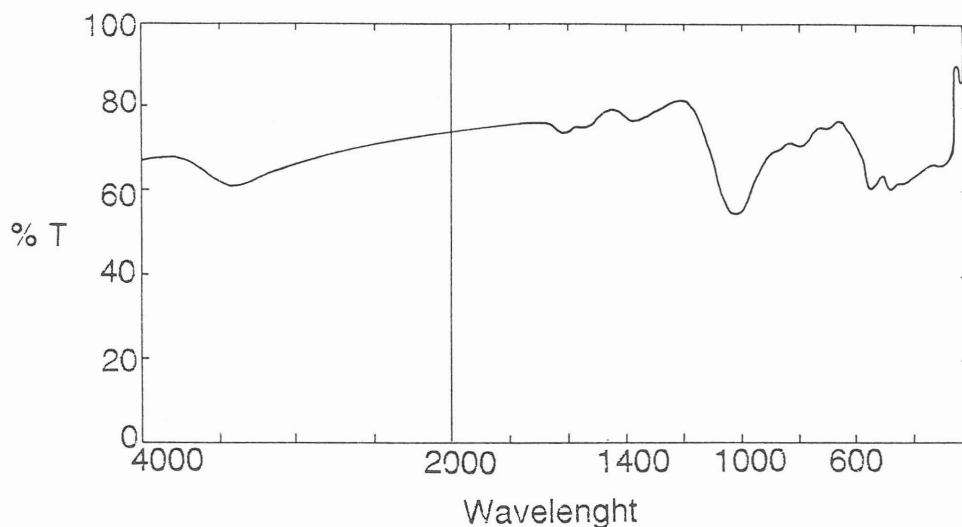
Fig. 10. The IR absorption spectrum of amorphous Bi–U–As phase from Rýžoviště

Kasolite   Pb(UO$_2$)(SiO$_4$) . H$_2$O

Kasolite occurs at Rýžoviště very rarely, only a few samples were found. It forms massive to earthy aggregates up to 1 cm as filling in cavities of strongly supergene altered quartz – uraninite gangue. It is associated with metatorbernite(I) and uranophane.

The X-ray powder diffraction pattern (Table 28) of kasolite are in a good agreement with data calculated from the crystal structure information by Rosenzweig, Ryan (1977). The refined unit cell parameters are close to data of Rosenzweig, Ryan (1977). The chemical composition of kasolite from Rýžoviště was studied by electron microprobe in the energy dispersive mode, Pb, U and Si were found as main its components.

Table 28. X-ray powder diffraction data for kasolite from Rýžoviště (monoclinic, space group % 21/c)

			*1		Rýžoviště		
h	k	l	d_{teor}	I_{teor}	d_{obs}	I_{obs}	d_{calc}
1	0	0	6.499	22	6.493	46	6.505
0	0	2	6.423	21	6.431	41	6.419
0	1	1	6.100	66	6.086	14	6.100
1	0	-2	5.260	17	5.254	20	5.257
1	1	0	4.741	6	4.743	16	4.744
1	1	-1	4.732	9	4.743	16	4.732
0	1	2	4.711	9	–		
1	1	1	4.210	49	4.207	49	4.212
1	1	-2	4.190	63	4.189	40	4.189
1	0	2	4.093	28	4.092	28	4.096
1	1	2	3.524	69	3.529	52	3.526
1	1	-3	3.506	34	3.508	48	3.503
0	2	0	3.466	11	3.465	5	3.466
0	2	1	3.346	26	3.336	24	3.346
2	0	0	3.249	58	3.255	100	3.253
2	0	-2	3.237	54	3.241	53	3.238
0	0	4	3.212	31	3.208	45	3.210
1	0	-4	3.209	10	3.208	9	3.206
1	2	0	3.058	100	3.063	46	3.059
0	2	2	3.050	13	3.063	46	3.050
0	1	4	2.914	60	2.911	67	2.913
1	1	-4	2.912	46	2.911	67	2.910
1	2	-2	2.894	23	–		
2	1	1	2.738	10	2.735	11	2.741
2	1	-3	2.724	15	2.719	12	2.724
0	2	3	2.694	7	2.696	9	2.693
2	0	2	2.649	6	2.656	5	2.652
2	0	-4	2.630	9	2.627	11	2.628
1	1	4	2.462	9	2.460	16	2.462
2	1	-4	2.459	6	2.460	16	2.458
2	2	-1	2.410	14	2.405	12	2.410
0	1	5	2.409	10	2.405	12	2.408
2	2	0	2.371	6	2.372	11	2.372
1	2	3	2.363	13	2.361	16	2.363
0	2	4	2.356	6	2.350	9	2.355
1	2	-4	2.355	8	2.350	9	2.354
1	0	-6	2.201	6	2.204	4	2.198
0	3	2	2.174	51	2.178	26	2.174
3	0	0	2.166	7	–		
3	1	-1	2.121	6	2.130	13	2.122
2	2	2	2.105	6	2.102	12	2.106
1	1	5	2.106	8	2.102	12	2.106
1	2	4	2.097	6	2.102	12	2.097
3	1	0	2.068	8	2.074	5	2.070
3	1	-3	2.061	7	2.057	4	2.061
0	1	6	2.046	9	2.044	18	2.045
0	0	3	2.034	5	2.034	9	2.033

			*1		Rýžoviště		
h	k	l	d_{teor}	I_{teor}	d_{obs}	I_{obs}	d_{calc}
2	0	-6	2.032	10	2.034	9	2.030
2	1	4	1.963	18	1.967	21	1.964
3	1	-4	1.960	17	1.957	15	1.960
2	1	-6	1.950	14	1.944	11	1.948
2	2	-5	1.922	8	1.923	4	1.921
3	0	2	1.915	6	1.916	2	1.917
1	0	6	1.900	15	1.901	9	1.899
2	3	0	1.883	9	1.886	17	1.884
2	3	-2	1.881	12	1.879	21	1.881

a = 6.704(2)	a = 6.709(4)
b = 6.932(2)	b = 6.932(4)
c = 13.252(7)	c = 13.240(7)
ß = 104.22(3)	ß = 104.15(4)
V = 596.98	V = 597.1(6)

Diffractometer HZG 4/TuR, CuKα radiation, step scanning 0.05°/9 s.

*1 the calculated X-ray powder diffraction intensities from crystal data by Rosenzweig, Ryan (1977). $I_{calc} \leq 5.0$ have been omitted.

Uranophane $Ca(UO_2)_2(SiO_3OH)_2 . 5 H_2O$

Uranophane is one of the earliest known uranium minerals. It was first described by Websky (1853) from Kupferberg, Silesia and since then has been identified in nearly all the major, and most of the minor, uranium deposits in the world. It is a mineral of secondary origin, ussually resulting on alteration of uraninite or coffinite (Smith et al. 1957). The structure of uranophane consists of uranylsilicate chains formed by edge sharing of uranyl pentagonal dipyramids and silicate tetrahedra. The chains are interconnected by oxygen atoms to form uranyl–silicate layers of the $[(UO_2)(SiO_4)]_n^{-2n}$. Ca^{2+} cations and molecular water participate in the connection between two successive layers (Čejka et al. 1986). The location of the hydrogen atoms could not be determined in any of the structure determinations. It is, therefore, derived only from the oxygen positions using Browns (1981) bond–valence method. The presence of hydroxonium ions, H_3O^+ in the structure of uranophane given e. g. by Smith et al. (1957) has never been confirmed experimentally, hydrogen atoms are more probably connected with the apical oxygens of silicate tetrahedra forming thus $(SiO_3OH)^{-3}$ groups (Čejka 1993).

At Rýžoviště, uranophane occurs commonly, it forms yellow massive, powder to earthy aggregates up to 5 cm in size, sometimes with uraninite relics. Uranophane is associatied with phosphuranylite, metatorbernite(I) and (meta)autunite(I). The X–ray powder diffraction pattern of uranophane (Table 29) agrees well with the calculated data from crystal structure information of uranophane by Ginderow (1988). The IR absorption spectrum of uranophane from Rýžoviště (Fig. 11) is very close to the uranophane from Kasolo, Zaire (Čejka et al. 1986). The tentative assignment of individual absorption bands (Table 30) was carried out on the basis of Čejka et al.s (1986) paper.

Table 29. The X-ray powder diffraction data for uranophane from Rýžoviště

h	k	l	d_{teor}	I_{teor}	d_{obs}	I_{obs}	d_{calc}
			*1		Rýžoviště		
2	0	0	7.891	100	7.937	100	7.922
0	0	1	6.611	19	6.625	26	6.628
1	0	1	5.840	9	–		
2	0	-1	5.416	20	5.428	19	5.426
0	1	1	4.807	27	4.811	27	4.821
2	1	-1	4.284	8	4.287	18	4.294
2	1	1	3.947	13	3.960	59	3.963
4	0	0	3.945	29	3.960	59	3.961
4	0	-1	3.594	12	3.604	19	3.603
0	2	0	3.501	20	3.511	18	3.512
2	2	0	3.200	24	3.210	25	3.211
1	2	-1	3.071	12	3.089	13	3.079
0	1	2	2.989	28	2.996	30	2.997
4	1	1	2.920	8	2.942	11	2.933
2	2	-1	2.940	7	2.942	11	2.948
2	1	-2	2.908	17	2.918	31	2.914
2	1	2	2.695	14	2.701	22	2.705
6	0	0	2.630	8	2.634	24	2.641
4	2	0	2.619	7	2.634	24	2.628
6	0	-1	2.558	4	2.555	15	2.565
4	1	-2	2.526	6	2.531	15	2.531
6	1	-1	2.402	2	2.407	11	2.410
4	1	2	2.261	5	2.270	12	2.271
6	1	1	2.223	3	2.229	13	2.232
0	3	1	2.204	3	2.206	19	2.208
0	0	3	2.201	4	2.206	19	2.209
2	0	-3	2.196	3	–		
6	2	0	2.103	6	2.113	15	2.111
0	1	3	2.102	2	2.109	20	2.108
2	3	1	2.097	3	2.104	11	2.104
6	1	-2	2.097	4	2.104	11	2.102
2	1	-3	2.095	5	2.097	15	2.099
6	2	-1	2.065	2	2.076	9	2.071
2	0	3	2.056	3	2.066	14	2.063
4	0	-3	2.037	2	2.041	11	2.040
3	3	1	2.001	2	2.001	13	2.008
8	0	0	1.973	5	1.984	19	1.981
8	0	-1	1.959	4	1.965	24	1.966
4	3	-1	1.957	2	1.964	20	1.963
4	1	-3	1.956	3	1.960	11	1.959
1	3	-2	1.910	4	1.915	8	1.915
0	3	2	1.907	6	1.911	16	1.912
2	3	-2	1.885	5	1.891	16	1.890
0	2	3	1.865	2	1.872	7	1.870
2	2	-3	1.860	2	1.863	13	1.864
4	0	3	1.828	2	1.836	5	1.835
2	3	2	1.823	4	1.829	6	1.829

Diffractometer HZG 4/TuR, CuKα radiation, step scanning 0.05°/9 s.
*1 the calculated X-ray powder diffraction intensities from crystal data of uranophane by Ginderow (1988). $I_{calc} \leq 1.9$ have been omitted.

a = 15.909	a = 15.968(9)
b = 7.002	b = 7.024(3)
c = 6.665	c = 6.680(3)
ß = 97.27°	ß = 97.12(5)°

Table 30. The IR absorption data of uranophane

cm⁻¹			*1	Tentative assignment	
3436	s	br	3435	v OH	
3255	sh		3160	v OH	
1680	sh		1670	δ H$_2$O	
1624	ms		1640	δ H$_2$O	
			1625	δ H$_2$O	
1095	w		1140	v_3 (SiO$_4$)	
1000	s		999	v_3 (SiO$_4$)	
940	ms		934	v_3 (SiO$_4$)	v_3 (UO$_2$)
860	s		858	v_1 (SiO$_4$)	v_3 (UO$_2$)
789	w		773	v_1 (UO$_2$)	
556	ms		557	v_4 (SiO$_4$)	
468	ms		480	v_2 (SiO$_4$)	
302	ms			v_2 (UO$_2$)	
260	ms			v_2 (UO$_2$)	

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*1 uranophane from Kasolo, Zaire (Čejka et al. 1986)
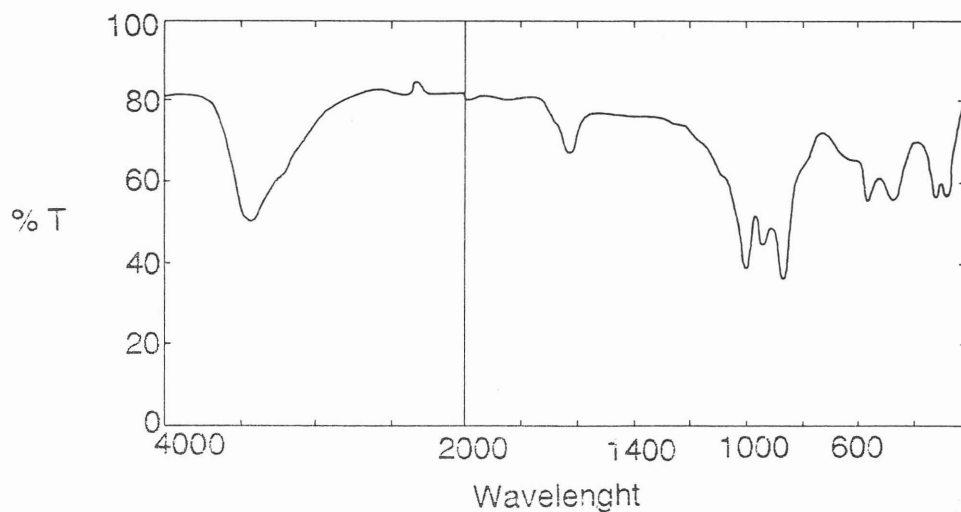
Fig. 11. The IR absorption spectrum of uranophane from Rýžoviště

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Recently nonverified minerals

The following secondary minerals described by Bradna and Šita (1968) from Rýžoviště have not recently been confirmed: sklodowskite, zeunerite, liebigite, erythrite and tyuyamunite.

Genesis of supergene mineralization

The primary minerals conditioning the origin of a relatively rich association of bismuth and uranyl secondary minerals at Rýžoviště are native bismuth, uraninite and a small content of chalcopyrite. At Rýžoviště, three developmental stages of supergene mineralization can be distinguished (Table 31).

The first developmental stage of the supergene zone started most probably during the last traces of the hydrothermal process. Then, at least a part of bismite can originate from the hydrotheramal stage. The alteration was a result of the action of solutions with elementary O and $(CO_3)^{2-}$ anion, under the conditions of pH 6 when the mobility of Bi ions is minimal. Bismite and bismutite(I) form massive pseudomorphs as the first products of native bismuth alteration.

During the second stage they passed to oxidation, decay and hydration of uraninite and its reaction with surroundings on contact with rock. There originated uranyl silicates and phosphates as uranophan, kasolite, phosphuranylite, metatorbernite(I), (meta)autunite(I) in direct proximity of altered uraninite (Ca, Si and P as a contribution from rock).

The mobility of uranyl ions is characteristic for the third stage, they passed trough distinct changes of concentration and chemical content of solutions, and the solutions were generally acidified. This accelerated the activity of AsO_4 and PO_4 anions. The acid solutions with contents of Bi, (UO_2), Ca and Cu ions were relatively mobile and the supergene minerals originated at relatively distant places from the primary mineralization. To be considered as well are solutions with pH less than 4 (Ondruš et al. 1994). This stage is represented by crystals of walpurgite, atelestite, uranosphaerite, churchite(Y), metatorbernite(II) and (meta)autunite(II) in small cavitites of quartz gangue and on rock crannies, and origins of powder to earthy coatings of bismutite(II), presingerite and the amorphous Bi–U–As phase.

Acknowledgements

Table 31

	I.	II.	III.
bismite	▬		
bismutite	▬		▬
uranophane		▬	
kasolite		▬	
phosphuranylite		▬	
metatorbernite		▬	▬
(meta)autunite		▬	▬
walpurgite			▬
uranosphaerite			▬
pharmacosiderite			▬
preisingerite			▬
churchite(Y)			▬
atelestite			▬
amorphous Bi-U-As			▬

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EXPLANATION OF PLATES

PLATE 1.

1. The remains of the mine dumps at Rýžoviště (photo Sejkora, 1994)
2. The remains of the mine dumps at Rýžoviště (photo Sejkora, 1994)

PLATE 2.

1. SEM photo of churchite(Y) aggregates (Rýžoviště)
2. SEM photo of dipyramidal metatorbernite crystal (Rýžoviště)

PLATE 3.

1. SEM photo of churchite(Y) spicular crystals (Rýžoviště)

PLATE 4.

1. SEM photo of dipyramidal metatorbernite crystal with churchite(Y) spicular crystals (Rýžoviště)

PLATE 5.

1. SEM photo of metatorbernite crystals (Rýžoviště)
2. SEM photo of preisingerite aggregates (Rýžoviště)