PAULKERRITE AND EARLSHANNONITE FROM PEGMATITE NEAR DOLNÍ BORY (WESTERN MORAVIA, CZECHOSLOVAKIA)

PAULKERRIT A EARLSHANNONIT Z DOLNÍCH BORŮ

JOSEF STANĚK

Abstract

Staněk, J., 1988: Paulkerrite and earlshannonite from pegmatite near Dolní Bory western Moravia, Czechoslovakia). *Acta Mus. Moraviae, Sci. nat.*, 73:29—34.

Associated with secondary Fe-Mn phosphates from pegmatite near Dolní Bory, two additional ones — paulkerrite and earlshannonite — were found. In the case of paulkerrite it is the second occurrence in the world and in the case. of earlhannonite it is the third one. Both minerals were formed by alteration of zwieselite. Paulkerrite forms tabular crystals 0.1—0.3 mm in size, beige-white in colour, associated with rockbridgeite I, rockbridgeite II, jahnsite, garnet, pyrite, beraunite, laueite. It is orthorhombic, space group Pbca, a = 10.490 (26), b = 20.685 (101), c = 12.505 (28) Å, V = 2713.42 (13.48) $Å^3$. Earlshannonite forms fine grained aggregates composed of yellow needle-like crystals, 0.1 mm in length, associated with laueite and beraunite. It is monoclinic, space group $P2_1/c$, a = 9.914 (12), b = 9.669 (10), c = 5.468 (6) Å, β = 93.43 (8)^0, V = 523.24 (65) $Å^3$.

Key words: paulkerrite and earlshannonite, phosphates, pegmatite, Dolní Bory, Czechoslovakia.

Josef Staněk, Department of Mineralogy and Petrography, Faculty of Science, J. E. Purkyně University, Kotlářská 2, 611 37 Brno, Czechoslovakia.

Paulkerrite

Paulkerrite, having the idealized formula $KTi(Mg, Mn)_2(Fe^{3+}, Mg, Al, Ti)_2(PO_4)_4(OH)_3 . 15 H_2O$, was described as a new mineral from the locality 7 U 7 Ranch near Hillside, Yavapai County, Arizona, by Peacor et al. (1984a), as an alteration product of triplite associated with bermanite, phosphosiderite, leucophosphite, strengite, and switzerite. It is an orthorhombic mineral with space group Pbca; a = 10.49 (7), b = 20.75 (13), c = 12.44 (2) Å, Z = 4. It forms light yellowish brown, grading to nearly colourless, tabular crystals 0.2 mm in size. It is isostructural with mantienneite $K(Mg, Fe^{2+})_2Al_2Ti(PO_4)_4(OH)_3 . 15 H_2O$ (Fransolet et al. 1984).

An unknown secondary phosphate from "Oldřich" pegmatite vein near Dolní Bory in western Moravia (the type locality of sekaninaite), until recently indicated as "A" phosphate (Staněk 1968, 1970, 1983), has appeared to be identical with paulkerrite. Only the first unpublished paper gives its partial characterization — optical data, d-values of powder X-ray photograph, qualitative spectral analysis, and a brief occurrence characterization; the other two only register it. Only in 1987, a hint was given that the unknown mineral is paulkerrite (Staněk 1987). Dolní Bory is for the present the second surely known occurrence of this mineral.

Paulkerrite from Dolní Bory forms fine, beige-white, grading to colourless, thin tabular up to lamelar crystals 0.1—0.3 mm in size, usually connected

in crystalline aggregates, most frequently crusts. The crystals are of such small sizes that it is not possible to measure them on a goniometer. Very small crystals, nearly black in colour, unidentified more closely, in all probability another secondary phosphate, often grow on them. The form of the crystals examined under a microscope is shown in Figure 1, and under SEM in Figures 2, 3, 4. The crystals are tabular, most probably flattened on {010}, the forms {100} and {111} are very likely present.

Paulkerrite is biaxial negative with 2V near to 80°, strong dispersion $\nu > \upsilon$. Indices of refraction are $\alpha = 1.610$, $\gamma = 1.650$. Orientation is X = c, Z = a. The given data compare well with those of the original paulkerrite, only the indices of refraction are rather higher in the case of the mineral from Dolní Bory, which may be due to the somewhat different content of some of the cations or to the degree of iron or manganese oxidation. The measured density is 2.35 (4) g/cm^3.

Using qualitative spectral analysis the presence of P, Fe, Mg, Mn, Ti, Al, Ca, Zn, Si, in trace amount Bi, As, Cu, Sn but no potassium was found in the mineral.

Using EDX analysis (Dr. J. Siemroth) is loaded with rather big errors and does not make it possible to determine oxygen and hydrogen; the following results were found for the two crystals analysed: K_2O = 4.0, 6.1, FeO = 14.9, 19.3. MnO = 9.3, 17.0, CaO = 3.9, 0.8, TiO_2 = 17.2, 16.6, P_2O_5 = 50.7, 40.3, sum = = 100.0, 100.1 %. Paulkerrite from the type locality gave the following result: K_2O = 4.4, Al_2O_3 = 1.6, Fe_2O_3 = 12.2, MnO = 7.1, MgO = 4.6, TiO_2 = 9.8, P_2O_5 = = 29.4, F = 0.9, [H_2O] = 30.5, sum = 100.4, less O = F = 0.4, sum = 100.0 %. In spite of the fact that the results obtained by us must be taken with caution it is very probable that the chemism of the mineral from Dolní Bory will be somewhat different from that or the original paulkerrite though perhaps in details only.

Table 1. X-ray powder data of paulkerrite.

1		2			1		2		
I	d(obs)	I	d(obs)	hkl	I	d(obs)	I	d(obs)	hkl
9	10.37	90	10.3	020	1	2.370			314
8	7.54	80	7.46	111	2	2.322	5	2.322	314
10	6.30	100	6.20	002	2	2.247			
3	5.23	20	5.22	200	2	2.195	5	2.187	442
2	4.75	1	4.72	211	1	2.135	5	2.117	433
1	4.28	1	4.37	141	3	2.076	10	2.069	006
5	3.97	30	3.95	231	5	1.983	20	1.980	
6	3.76	40	3.75	222	2	1.932			
2	3.45				1	1.873	2	1.864	
3	3.34				3	1.832	2	1.831	
10	3.140	70	3.13	004	2	1.788			
1	3,060	5	3.05	312	2	1.744			
3	3.002	20	2.979	024	3	1.717	5	1.713	
5	2.879	40	2.872	233	0.5	1.689			
3	2.804	10	2.814	341	2	1.663	2	1.633	
1	2.700				0.5	1.634			
1	2.627	20	2.624	400	2	1.611	1	1.608	
2	2.570	10	2.563	323	2	1.568	1	1.566	
3	2.515	10	2.512	411					

1. Paulkerrite, Dolní Bory (Co/Fe radiation, 114.6 mm camera diameter).
2. Paulkerrite, Hillside, Yavapai County, Arizona (Peacor et al. 1984a).

Paulkerrite from Dolní Bory was identified mainly on the basis of powder X-ray photograph. Table 1 gives d-values of paulkerrite from Dolní Bory and compares them with the d-values of this mineral from the type locality, reported by Peacor et al. (1984a). Both paulkerrites are in a very good agreement. Using minimal square method according to programme of Burnham (1962) from 16 unambigously indexible diffractions, the indices of which were adopted from Peacor et al. (1984a) — but in addition diffraction of 2.076 Å indexed 060 was taken —, the following lattice parameters were calculated: a = 10.490 (23), b = 20.685 (101), c = 12.505 (28) Å, V = 2713.42 (13.48) $Å^3$. They are in a good agreement with the lattice parameters of original paulkerrite.

Paulkerrite from Dolní Bory is among the latest secondary Fe-Mn phosphates; it originated as almost one of the last ones. It was relatively frequent in association with other Fe-Mn phosphates. It occurred in several parageneses. It was rare in cavities of rockbridgeite I, associated with rockbridgeite II and jahnsite, furthermore with garnet, pyrite, beraunite, jahnsite, laueite, rockbridgeite II, or quite alone in cavities after leached Fe-Mn phosphates, mainly zwieselite.

Earlshannonite

Earlshannonite, ideally $MnFe^{3+}{}_2(PO_4)_2(OH)_2 . 4 H_2O$, has been described as a new mineral by Peacor et al. (1984b) from two localities, viz., from Foote Mineral Company spodumene mine, Kings Mountain, North Carolina, and from Hagendorf in Bavaria, West Germany. It is monoclinic, space group $P2_1/c$, with a = 9.910 (13), b = 9.669 (8), c = 5.455 (9) Å, β = 93.95 (9)°, Z = 2. In the first locality it forms reddish-brown crystals arranged in radial aggregates associated with rockbridgeite, laueite, and mitridatite; in the second one it forms radial aggregates of bright yellow crystals coating rockbridgeite-frondelite. It is the Mn-analogue of whitmoreite $Fe^{2+}Fe^{3+}{}_2(OH)_2(PO_4)_2 . 4H_2O$ (Moore et al. 1974).

An unknown phosphate until recently indicated "B" (Staněk 1968, 1970, 1983) from "Oldřich" pegmatite vein near Dolní Bory was identified with earlshannonite. As early as 1968, on the basis of powder X-ray photograph and some of the optical data, it became evident that it was a new mineral. The first indication about earlshannonite from Dolní Bory was given in 1987 (Staněk 1987).

Earlshannonite from Dolní Bory was found, on the one hand, quite alone in a small cavity in quartz and, on the other, in another cavity associated with laueite and beraunite; both cavities are on the same specimen.

Earlshannonite forms fine grain aggregates composed of short prismatic to thin lamellar crystals, 0.1 mm in length at the maximum, coloured green-yellow.

Earlshannonite, observed under a microscope, forms fine needles. (Z = c); it is slightly pleochroic X = light yellow, Z = yellow. Indices of refraction are the following: α = 1.703, γ = 1.772. The density, measured using heavy-liquid techniques, is 2.91 (2) g/cm^3. The given data are in relatively good agreement with those given for the original earlshannonite.

So far, the chemism of earlshannonite from Dolní Bory was checked using qualitative spectral analysis only. Thus the presence of P, Fe, Mg, Mn, Ca, Al, Zn, Ti, and As was determined in it.

Earlshannonite from Dolní Bory was identified mainly on the basis of powder X-ray photograph. Its d-values and their intensities are given in Table 2

Table 2. X-ray powder data of earlshannonite.

1		2			1		2		
I	d(obs)	I	d(obs)	hkl	I	d(obs)	I	d(obs)	hkl
10	9.93	100	9.8	100	1	2.152			
8	6.92	80	6.9	110			1	2.119	312
4b	4.90	40	4.95	200	4	2.096	30	2.089	222
		5	4.82	020	2	2.005	10	2.003	
4	4.40	40	4.38	11$\bar{1}$	1	1.973	10	1.982	
6	4.19	60	4.18	111	3	1.940	10	1.951	
1	3.94				2	1.901			
1	3.66				1	1.888	5	1.882	
3	3.51				2	1.845			
3	3.441	60	3.45	220	0.5	1.805	10	1.807	
1	3.346	2	3.34	121	2	1.706	2	1.715	
1	3.164				3	1.674	5	1.673	
2	3.065	5	3.07	130	2	1.648			
4	2.975	30	2.987	22$\bar{1}$	0.5	1.624			
4	2.874	60	2.856	221	1	1.584	2	1.577	
8	2.779	70	2.789	3[illegible]$\bar{1}$	2	1.553	10	1.551	
6	2.703	40	2.712	320			5	1.533	
1	2.631	2	2.646	131	1	1.528	5	1.527	
2	2.580	30	2.577	102	1	1.487	5	1.488	
0.5	2.507				0.5	1.466	2	1.458	
1	2.441	2	2.451	23$\bar{1}$	1	1.451	1	1.445	
4	2.389	30	2.389	410	1	1.386	2	1.385	
0.5	2.345	2	2.345	140	1	1.369	5	1.373	
		1	2.303	330	1	1.345	2	1.346	
2	2.255	1	2.250	212	1	1.332	5	1.334	
2	2.212	30	2.210	041					

1. Earlshannonite, Dolní Bory (Fe/Mn radiation, 114.6 mm camera diameter).
2. Earlshannonite, Kings Mountain, North Carolina (Peacor et al. 1984b).

and they are compared with the d-values of earlshannonite from the type locality, reported by Peacor et al. (1984b); the agreement is very good. Using minimal square method according to Burnham's programme (1962) the lattice parameters were calculated; 17 unambigously indexible diffractions were used (or calculation. a = 9.914 (12), b = 9.669 (10), c = 5.468 (6) Å, β = = 93.43 (8)°, V = 523.24 (65) Å^3. The values obtained are close to those of earlshannonite from the original locality.

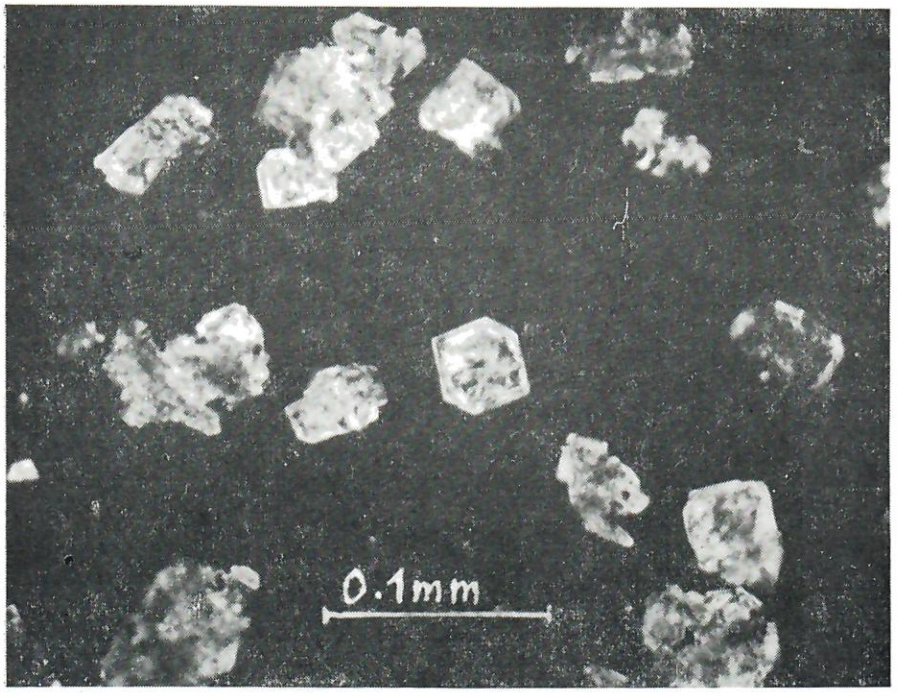
Earlshannonite in Dolní Bory was found on a dump just as the other Fe-Mn phosphates. Therefore it is not easy to make a statement about its formation and successive position, particularly as it was found in one specimen only. But everything suggests that it may belong to the latest-stage secondary formed phosphates.

Besides these two new phosphates from Dolní Bory, some others still remain undetermined or partly determined. A list of all known minerals from the pegmatites in "Hatě" near Dolní Bory is given below in systematic sequence. As to number of minerals, the pegmatites from Dolní Bory are among the foremost pegmatite localities in the world at present.

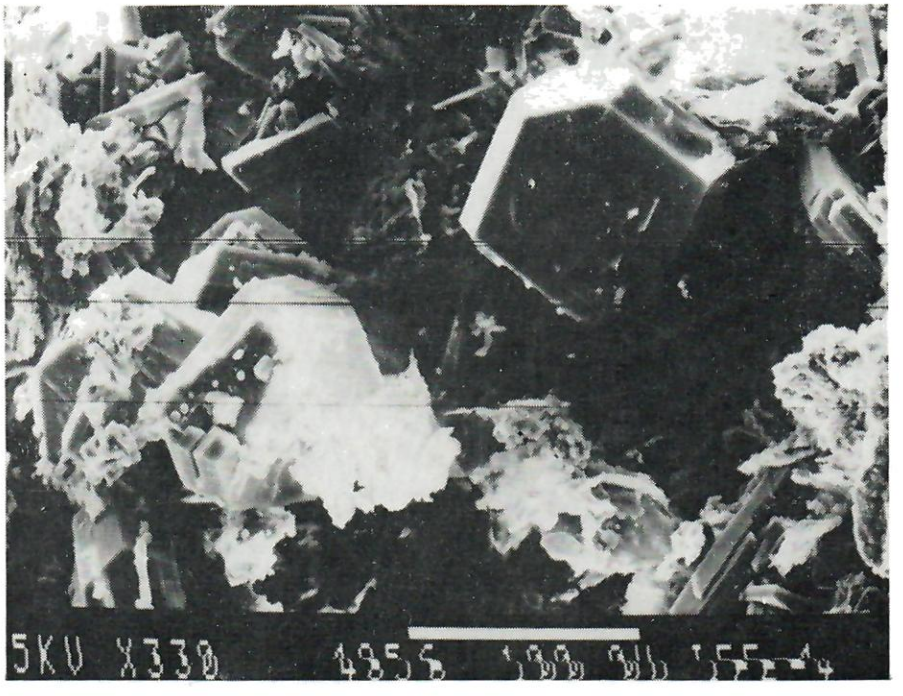
Minerals from pegmatites near Dolní Bory

Elements: bismuth

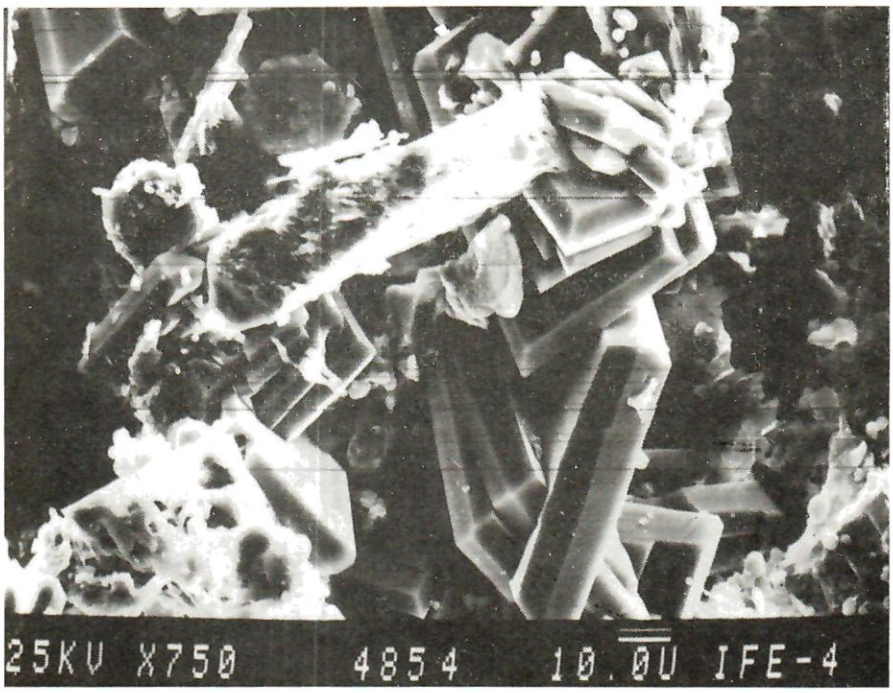
Sulfides: sphalerite, chalcopyrite, pyrrhotite, covellite, bismuthinite, pyrite, marcasite, loellingite, arsenopyrite, molybdenite, bournonite



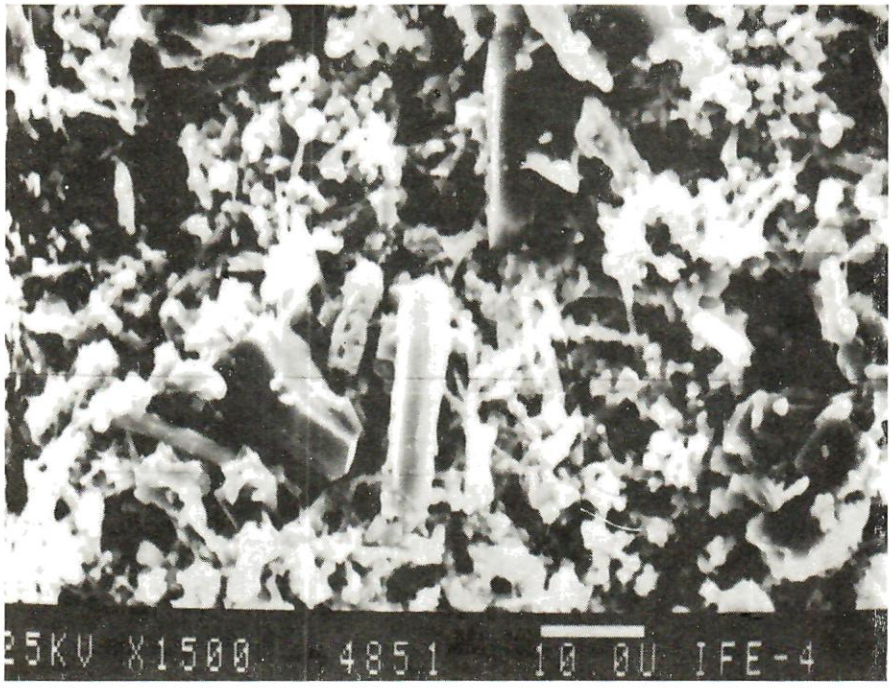
1. Tabular paulkerrite crystals from Dolní Bory. Photomicrograph, crossed nicols.



2. Equant paulkerrite crystal from Dolní Bory. SEM photograph.



3. Tabular paulkerrite crystals from Dolní Bory. SEM photograph.



4. Paulkerrite crystals from Dolní Bory. SEM photograph.

Oxides and hydroxides: corundum, hematite, ilmenite, quartz, chalcedony, opal, rutile, manganomelane, anatase, wolframite, diaspore, goethite, limonite

Carbonates: siderite, calcite, dolomite

Sulfates: halotrichite, gypsum

Phosphates and arsenates: triphylite, graftonite, sarcopside, alluaudite, xenotime, monazite, wagnerite, zwieselite, triplite, scorzalite, rockbridgeite, augelite, apatite, scorodite, vivianite, parasymplesite, ferrisymplesite, fairfieldite, earlshannonite, laueite, cacoxene, beraunite, pitticite, jahnsite, paulkerrite, pharmacosiderite, torbernite, autunite, meta-torbernite, meta-autunite

Silicates: almandine-spessartine, oyamalite, andalusite, dumortierite, sekaninaite, tourmaline-schorl, gedrite, pyrophyllite, muscovite, biotite, hydromuscovite, stilpnomelane, montmorillonite, nontronite, cookeite, chlorite, strigovite, kaolinite, palygorskite, pollucite, K-feldspar, albite, oligoclase

Acknowledgements

The author is indebted to Dr. J. Siemroth, of the Department of Inorganic Chemistry, Halle a. S., for providing SEM photographs and EDX analysis of paulkerrite, and to Prof. Dr. F. Čech, of Charles University in Prague, for calculation of the lattice parameters of both minerals.

SOUHRN

Paulkerrit, idealizovaného vzorce $KTi(Mg, Mn)_2(Fe^{3+}, Mg, Al, Ti)_2(PO_4)_4(OH)_3 \cdot 15\,H_2O$, byl popsán jako nový minerál z pegmatitové lokality 7 U 7 Ranch u Hillside v Arizoně (Peacor et al. 1984a). Je kosočtverečný, prostorová grupa Pbca. S paulkerritem se ukázal být identický neznámý sekundární fosforečnan z pegmatitové žíly „Oldřich" u Dolních Borů, donedávna označovaný jako fosfát „A" (Staněk 1968, 1970, 1983, 1987). Dolní Bory jsou druhým známým výskytem tohoto minerálu.

Paulkerrit z Dolních Borů vytváří 0,1—0,3 mm velké, béžově bílé až bezbarvé, tence tabulkovité, případně lupínkovité krystaly, obvykle pospojované v drobné krystalické agregáty. Krystaly jsou tak malých rozměrů, že se je nepodařilo změřit na goniometru. Jejich vzhled pod mikroskopem ukazuje obr. 1, ze scanového elektronového mikroskopu obr. 2, 3, 4. Krystaly jsou tabulkovité nejspíše podle {010}, přítomny jsou pravděpodobně tvary {100} a {111}.

Opticky je paulkerrit z Dolních Borů dvojosý, negativní, s úhlem optických os blízkým 80°, silnou disperzí $\nu > \upsilon$. Jeho indexy lomu $\alpha = 1{,}610$, $\gamma = 1{,}650$ jsou o něco vyšší než u originálního paulkerritu. Rovina optických os leží v (010), X = c, Y = b, Z = a. Menší rozdíly v indexech lomu mohou být ovlivněny poněkud jiným zastoupením kationtů či odchylným stupněm oxidace Fe^{2+} nebo Mn^{2+} než je tomu u paulkerritu z původní lokality. H = 2,35 (4) g/cm^3.

Ze spektrální analýzy dolnoborského fosfátu „A" nebylo zřejmé, že by minerál mohl mít vysoký obsah titanu (jeho obsah byl uveden v kategorii 0,1—1 %) a také draslíku, jejž nezjistila vůbec (Staněk 1968). Proto když se objevil nový minerál paulkerrit — fosforečnan s podstatným obsahem titanu a draslíku — nebyl brán dolnoborský fosfát „A" vůbec v úvahu, že by se s ním mohl shodovat. Teprve energiově disperzní rentgenová analýza, provedená v r. 1986, v něm zjistila podstatné obsahy titanu a draslíku. Dvě orientační analýzy, nestanovující obsah H_2O, daly tyto výsledky: K_2O 4,0, 6,1, FeO 14,9, 19,3, MnO 9,3, 17,0, CaO 3,9, 0,8, TiO_2 17,2, 16,6, P_2O_5 50,7, 40,3, $\sum$ 100,0 %, 100,1 %. Z nich vyplynulo, že fosfát „A" je svým složením prakticky totožný s paulkerritem. Arizonský paulkerrit obsahuje: K_2O 4,4, Al_2O_3 1,6, Fe_2O_3 12,2, MnO 7,1, MgO 4,6, TiO_2 9,8, P_2O_5 29,4, F 0,9, H_2O 30,5, $\sum$ 100,4, —O = F 0,4, Σ 100 %.

Paulkerrit z Dolních Borů byl jednoznačně určen na základě práškového rentgenogramu. Hodnoty d jež byly zjištěny pro fosfát „A" (Staněk 1968) se zcela shodují s hodnotami d paulkerritu publikovanými Peacorem et al. (1984a), viz tab. 1. Také mřížkové parametry a = 10,490(26), b = 20,685(101), c = 12,505(28) Å, V = 2713,42

(13,48) Å^3 jsou v dobré shodě s mřížkovými parametry originálního minerálu (a = = 10,49(7), b = 20,75(13), c = 12,44(2) Å).

Paulkerrit se v Dolních Borech vyskytuje ve společnosti mladšího rockbridgeitu II, beraunitu, jahnsitu a laueitu. Vznikl, podobně jako ony, hypergenní přeměnou rockbridgeitu I, jenž se vytvořil hydrotermálním přepracováním primárního zwieselitu či vzácnějšího triplitu.

Earlshannonit $MnFe^{3+}{}_2(OH)_2(PO_4)_2 . 4 H_2O$ byl popsán jako nový minerál Peacorem et al. (1984b) z pegmatitových lokalit Kings Mountain v Severní Karolině a z Hagendorfu v Bavorsku. Je monoklinický s prostorovou grupou $P2_1/c$. S earlshannonitem se podařilo ztotožnit neznámý fosfát „B" z pegmatitové žíly „Oldřich" u Dolních Borů, jenž byl donedávna takto označován (Staněk 1968, 1970, 1983, 1987).

Earlshannonit byl nalezen v Dolních Borech jen v jediné ukázce, tvořené pouze křemenem a fosfáty. Vyskytl se v ní jednak zcela sám v malé dutince po vyluhovaném primárním Fe-Mn fosforečnanu, jednak v jiné dutince ve společnosti laueitu a beraunitu. Vytváří jemně zrnité agregáty složené z úzkých sloupečkovitých až jehlicovitých, maximálně 0,1 mm dlouhých krystalů, majících jasně žlutou barvu.

V práškovém preparátu pod mikroskopem je minerál jehlicovitý až jemně vláknitý. Je slabě pleochroický, X = světle žlutá, Z = žlutá. Z = c. Indexy lomu jsou α = 1,703, γ = 1,772. Pro jemnost jehlic se nedaly zjistit další optické údaje. H = 2,91(2) g/cm^3.

Kvalitativní spektrální analýza dolnoborského earlshannonitu prokázala, že minerál obsahuje vedle fosforu, železa a manganu jako hlavních komponent v menším množství ještě vápník a hořčík, nepatrně pak hliník, křemík, titan a zinek. V earlshannonitu z původní lokality Kings Mountain bylo mikrosondou stanoveno: Al_2O_3 0,1, Fe_2O_3 33,8, FeO 4,6, MgO 0,8, CaO 0,6, MnO 8,2, P_2O_5 30,0, [H_2O] 21,9, Σ 100,0 %.

Dolnoborský earlshannonit byl bezpečně určen na základě práškového rentgenogramu. V tab. 2 jseou uvedeny jeho hodnoty d a porovnány s hodnotami d earlshannonitu z původní lokality; jejich shoda je velmi dobrá. Pro výpočet mřížkových parametrů bylo použito 17 jednoznačně indexovatelných difrakcí. a = 9,914(12), b = 9,669 (10), c = 5,468(6) Å, β = 93,43(8)°, V = 523,24(65) Å^3. I tyto hodnoty jsou blízké hodnotám mřížkových parametrů earlshannonitu z Kings Mountain (a = 9,910(13), b = = 9,669(8), c = 5,455(9) Å, β = 93,95(9)°).

Earlshannonit je jedním z nejmladších dolnoborských sekundárních železnato-manganatých fosforečnanů, vzniklých již v podmínkách hypergeneze.

REFERENCES

BURNHAM, CH. W., 1962: Lattice constant refinement. *Carnegie Inst. Washington Year Book,* 61:132—135.

FRANSOLET, A. M., OUSTRIÈRE, P., FONTAN, F., PILLARD, F., 1984: La mantiennéite, une nouvelle espèce minérale du gisement de vivianite d'Anloua, Cameroun. *Bull. Minéral.,* 107:737—744.

MOORE, P. B., KAMPF, A. R., IRVING, A. J., 1974: Whitmoreite, $Fe^{2+}Fe^{3+}{}_2(OH)_2(H_2O)_4[PO_4]_2$, a new species: its description and atomic arrangement. *Amer. Mineralogist,* 59:900—905.

PEACOR, D. R., DUNN, P. J., SIMMONS, W. B., 1984a: Paulkerrite, a new titanimu phosphate from Arizona. *Mineral. Rec.,* 15:303—306.

PEACOR, D. R., DUNN, P. J., SIMMONS, W. B., 1984b: Earlshannonite, the Mn analogue of whitmoreite, from North Carolina. *Canad. Mineralogist,* 22:471—474.

STANĚK, J., 1968: Železnato-manganaté fosfáty západomoravských pegmatitů. MS, katedra mineral. a petrogr. přír. fak. Univ. J. E. Purkyně. Brno.

STANĚK, J., 1970: Kakoxen und Xanthoxen von Dolní Bory. *Acta Mus. Moraviae, Sci. nat.,* 55:5—12.

STANĚK, J., 1983: Iron-manganese phosphate minerals from the Dolní Bory pegmatite. *Acta Mus. Moraviae, Sci. nat.,* 68:7—22.

STANĚK, J., 1987: Nejvýznamnější mineralogické objevy na Moravě v rozmezí let 1981 až 1986. Sbor. příspěvků z II. celostát. konference mineralogů a petrologů „Úkoly československé mineralogie a petrologie po XVII. sjezdu KSČ": 118—121. Brno—Blansko.