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BUKOVSKÝITE, $Fe_2^{3+} (AsO_4) (SO_4) (OH) . 7 H_2O$, FROM KAŇK, NEAR KUTNÁ HORA — A NEW MINERAL

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Abstract: Bukovskýite, a recent weathering product of arsenopyrite, occurs in medieval dumps at Kaňk, near Kutná Hora, Central Bohemia. It composes pale yellowish-green to grayish-green microcrystalline aggregates of metacolloidal nature, similar to those of destinezite. Nodules of bukovskýite that reach 30 cm. in maximum dimension are soft, nearly powdery on the surface, with uneven earthy fracture. Streak is yellowish-white. Bukovskýite readily decomposes in HCl. Density is 2,334. Colourless or yellowish needles with average dimensions 0,5 × 0,007 mm. can be distinguished in microscope. The crystals have columnar habit, their symmetry is probably monoclinic-prismatic. Refractive indices are $\beta' = 1{,}570$—$1{,}582$, $\gamma' = 1{,}626$—$1{,}631$, extinction angle is 22°. The morphology and fabric of minute crystals of bukovskýite were studied by aid of electron microscope. Recalculation of four chemical analyses leads to the formula $Fe_2^{3+} (AsO_4) (SO_4) (OH) . 7 H_2O$ which corresponds to the theoretical composition Fe_2O_3 32,60 %, As_2O_5 23,46 %, SO_3 16,35 %, H_2O 27,59 %. The water content slightly varies. Infrared spectra revealed the absorption band of the $(SO_4)^{2-}$ and $(AsO_4)^{3-}$ anions, of crystal water and (OH) groups. Thermogravimetric curves show two distinct weight losses. The first at 50—350 °C is caused by the loss of crystal water and probably also of the (OH) groups, then the dissociation of ferric sulphate and escape of SO_2 take place at 630—760° C. The d. t. a. curve records these reactions as pronounced endothermal effects. Exothermal reactions at 600—660 °C are caused probably by crystallization of complex oxysulphates and arsenates of iron. X-ray investigation proved the crystalline nature of bukovskýite. Strongest X-ray powder lines (in Å): ~ 9,6 (10), ~ 9,2 (10), 5,30 (6—8), 4,47 (6—9), 3,90 (7—9), 3,59 (7—9). Bukovskýite can be regarded as arsenate analogue of destinezite. Both these minerals can be arranged in a separate mineral group, together with sarmientite which has a similar chemical composition as bukovskýite but different structure and crystal water percentage. Pitticite is considered to be an X-ray amorphous colloidal analogue of bukovskýite and sarmientite. Bukovskýite was named in honour of Professor A. Bukovský who analyzed this mineral already in 1914.

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INTRODUCTION AND HISTORY

The nodular, powdery to earthy substance has been known for long time in medieval dumps of Kutná Hora and used by inhabitants, because of the high arsenic content, for poisoning mice. This substance is quoted in literature under various scientific and local names, *e. g.* "arsenite", "arsendestinezite", "arsenic", "the Kaňk powder", "the Kutná Hora earth", "the poisonous earth of Kutná Hora". The mineralogical composition was not well known, however, up to the present. All data on the "Kutná Hora earth" and papers dealing with it were compiled by J. Kratochvíl (1957—1964).

The first chemical analysis of the examined material was done by A. Bukovský (1915), who called it "the poisonous earth of Kutná Hora". Some other data on this substance were published by F. Slavík (1925) who considers it to be an inhomogeneous mixture or a mineral of the pitticite group. F. Slavík examined microscopically the type material of A. Bukovský that was deposited in mineral collection of the secondary school at Kutná Hora. He noted that it is composed of minute needle-like crystals similar to gypsum, and that it resembles destinezite from some Bohemian localities. Later F. Slavík gave a specimen of the "Kutná Hora earth" to F. Ulrich; this author published a short preliminary report on this mineral, based on the chemical analysis by A. Bukovský and on his own optical examination. Ulrich stated that the oxide ratio is identical with that in destinezite, with exception of the $(PO_4)^{3-}$ groups substituted by $(AsO_4)^{3-}$. Since the optical investigation also confirmed the close similarity to destinezite, F. Ulrich gave to this mineral a preliminary name "arzéndestinezit". Unfortunately he did not publish any detailed study on this species. F. Slavík (1932) reported on this Ulrich's article in *Mineralogical Abstracts*; from this source A. N. Winchell and H. Winchell (1951) quoted the name "arsenian destinezite". In later publications the terms "arsendestinezite" and "arsenian destinezite" cannot be located, having been probably forgotten (*e. g.*, Ch. Palache *et al.* 1954, H. Strunz 1966).

New finds made recently in some occasional exposures of medieval dumps at Kaňk[3]) near Kutná Hora brought us to a new detailed study of this mineral. We succeeded in proving again its homogeneity and relatively stable chemical composition on these new specimens. The existence of a new mineral species was undoubtedly established and named bukovskýite in honour of Antonín Bukovský (1865—1950), professor at the secondary school in Kutná Hora. A. Bukovský devoted most of his studies to the mineralogical and chemical investigation of minerals from Kutná Hora. He was the first who analyzed the "poisonous earth of Kutná Hora" (A. Bukovský 1901, 1915).

As to the preliminary proposal "arsendestinezite" by F. Ulrich (1930), we consider it to be unsuitable from the nomenclatoric point of view. The term "arsenian destinezite" should be restricted only to varieties of destinezite with $(PO_4)^{3-}$ still prevailing over $(AsO_4)^{3-}$. In bukovskýite phosphorus is almost completely substituted by arsenic. The other obsolete names are either incorrect ("arsenite", "arsenic") or incompatible with the present rules of the mineralogical nomenclature ("the poisonous earth of Kutná Hora" etc.). Only two minerals are chemically related to bukovskýite among the well-defined species: pitticite and sarmientite. As will be shown below, the properties of both these minerals evidently differ from those of bukovskýite.

Specimens of bukovskýite are deposited in the collection of the Department of Mineralogy, Geochemistry and Crystallography, Charles University, Praha (No. 14240), and in the collection of the Department of Mineralogy, National Museum, Praha (No. 53411).

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[3]) Kaňk is a village 2,5 km north of Kutná Hora, located in the historic part of the Kutná Hora ore district.

OCCURRENCE AND GENESIS

The old dumps at Kaňk, near Kutná Hora, Central Bohemia, represent the type locality of bukovskýite (Photo 1). Nodular aggregates of this mineral are located in them usually about 1—3 m below their surface. Bukovskýite originates here as a weathering product of common sulphides, predominantly of arsenopyrite and pyrite. Unoxidized remnants of arsenopyrite that witness this mode of formation were observed in cores of some nodules already by A. Bukovský (1915). The origin of bukovskýite is recent, the dumps are estimated to be 400—600 years old. The nodular, microcrystalline and metacolloidal character of the examined mineral suggests that it crystallized from gel. Bukovskýite occurs mostly in the northern part of the Kutná Hora ore district whose veins are rich in common sulphides, particularly in arsenopyrite.

DESCRIPTION OF MATERIAL

Bukovskýite composes nodular, pale yellowish-green to grayish-green aggregates whose shape resembles much that of destinezite (Photo 2). The nodules range from 5 up to 30 cm. in size. Fracture is uneven, earthy, the microcrystalline material is rather soft. The surface of some nodules is covered by a powdery coating, coloured in yellowish-white to yellowish-

-brown hues by some ferric iron compounds. In the inner parts of the bukovskýite aggregates small vugs can be observed under binocular microscope whose walls are lined with radiating bunches of needle-like crystals. These are irregularly developed and often taper off to the free ends. Their morphology could not be studied because of the minute size of single crystals. The air-dried bukovskýite matrix turns a bit lighter, at elevated temperatures it acquires a rich yellow to brown colour; material heated at 1000 °C is dark reddish-brown. In central portions of the nodules the bukovskýite matrix is relatively homogeneous, but contains numerous chips of dump material, particularly of the porous vein quartz, near their surface. Streak is pale yellowish-white to dirty yellow. Bukovskýite decomposes only in the boiling HNO$_3$ but is readily soluble in HCl.

OPTICAL PROPERTIES

Some optical properties of bukovskýite published by F. Slavík (1925) and F. Ulrich (1930) were already mentioned above. Both these authors drew attention to the close optical similarity of bukovskýite and destinezite from some Bohemian localities (Litošice, Úvaly, Nučice and Zdice) and to the morphological resemblance of bukovskýite to gypsum crystals. Optical constants of bukovskýite determined by F. Ulrich are quoted in Table 1 and compared with the new data measured by Dr. E. Fediuková on the recently analyzed material. According to F. Ulrich (1930), bukovskýite forms tiny needles about 30 μ long and hardly 10 μ thick, similar to gypsum and optically symmetric with it.

Optical investigation of bukovskýite was performed in oil immersion. The character of its tiny crystals can be well observed in Photo 3. Their shape is sticky to needle-like. The average length of the crystals studied was 0,05 mm., 0,11 mm. in extreme cases, the width averaging about 0,007 mm. reached up to 0,015 mm. Besides isolated crystals, aggregates that suggest a radial arrangement can be also observed in immersion mounts. Crystals of bukovskýite are colourless to yellowish, anisotropic, with low interference colours and inclined extinction 22° (Fig. 1 A). Some crystals display glide bending similar to that characteristic for gypsum. The usual development of bukovskýite crystals is demonstrated in Fig. 1 C. The habit of the usually single terminated crystals suggests the monoclinic-prismatic symmetry.

In Table 1, the optical properties of bukovskýite are compared with the data published for minerals that are chemically or structurally related to this species: destinezite, diadochite, sarmientite and pitticite.

According to V. Angelelli and S. G. Gordon (1941), sarmientite

Mineral	Refractive Indices			Birefringence	J/C	Symmetry	Locality	Author
Bukovskýite	β' 1,582$_0$		γ' 1,630$_6$	> 0,056	22°	Monoclinic or triclinic(?)	Kaňk, near Kutná Hora	E. Fediuková, this paper
Bukovskýite ("Arsendestinezite")	β' 1,570		γ' 1,626	> 0,049	18°		Kaňk, near Kutná Hora	F. Ulrich (1930)
Sarmientite	α 1,628	β 1,635	γ 1,698	0,061	12°		Santa Elena, Alcaparrosa, Argentina	V. Angelelli and S. G. Gordon (1941)
Destinezite	1,615 ±0,005	1,625 ±0,005	1,665 ±0,005	0,050	16°		Visé, Belgium	E. S. Larsen (1921)
Destinezite	β' 1,638$_0$		γ' 1,6658	> 0,028	14°		Chvaletice, Czechoslovakia	F. Ulrich (1922)
Destinezite		1,620 ±0,001	1,668 ±0,003	> 0,048			Blyava, Southern Ural, USSR	L. D. German (1956)
Pitticite	1,615—1,617					isotropic, amorphous	Manhattan, Nevada, USA	Ch. Palache, H. Berman, and C. Frondel (1951)
	1,635						Freiberg, Saxony	
Diadochite	1,618—1,70						various occurrences	

monoclinic and forms tiny prismatic crystals 2—25 μ long. It is biaxial positive. It differs from bukovskýite by evidently higher refractive indices.

Crystals of destinezite from Chvaletice were studied for comparison with bukovskýite. They are mostly short columnar or thick tabular with a rhomboid outline. The largest face can be indexed as (010) by comparison with crystals of gypsum. The rhomboid shape is often converted to pseudohexagonal by cutting off the acute corners by some additional facets.

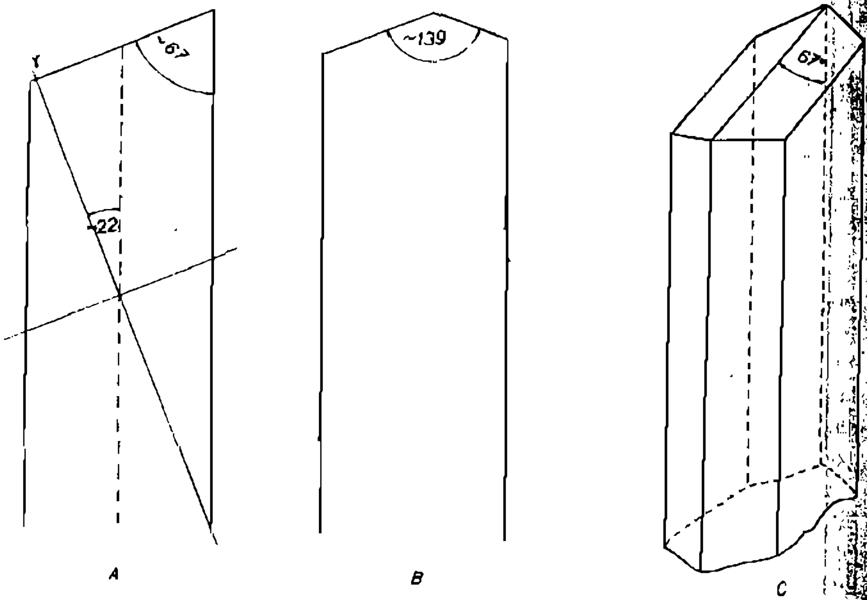

Fig. 1. Cross-section of the bukovskýite crystals (A, B) and their most frequent morphology (C)

V. Bouška *et al.* (1960) describe destinezite from Chvaletice as irregularly developed pseudohexagonal platelets, too. Among the destinezite crystals scarce twins of the swallow-tail type were observed that closely remind of those of gypsum. The general character of destinezite crystals from Chvaletice can be observed in Photo 4. The crystal habit of destinezite considerably differs from that of bukovskýite, despite of the fact that these minerals are probably isostructural. Refractive indices of destinezite are remarkably higher than those displayed by bukovskýite but slightly lower than the values quoted for sarmientite (Table 1). A. N. Winchell and H. Winchell (1951) treat destinezite as monoclinic. Optical measurements made by E. S. Larsen (1921) suggest rather triclinic symmetry.

is is in accord with the results obtained by J. Toussaint and J. Mélon 955). The latter authors indexed the X-ray diffraction patterns as tri-ic. V. Bouška *et al.* (1960) also regard the triclinic symmetry as more obable for destinezite.

Pitticite and diadochite are isotropic — with exception of those that ntain some admixed crystalline phase — and differ substantially in this spect from bukovskýite and destinezite. Refractive indices of the former inerals deviate from those of their crystalline counterparts only negli-bly.

The other minerals that might show some relation to bukovskýite are uite different: refractive indices of scorodite are well above 1,77, those coquimbite do not reach 1,58.

ELECTRON MICROSCOPE STUDY

With regard to the extremely minute size of the bukovskýite crystals he optical investigation in petrographic microscope was completed by lectron microscopic observation. The "Tesla" BS 242 apparatus was used or the investigation of carbon replicas and transparent preparates. A uspension on collodion membrane was applied to the first technique, arbon replicas were obtained by vaporizing the specimen under 30° ngle and dissolving it in HCl. The electron microphotographs illustrate he morphology of bukovskýite (Photos 5 and 6): its well-shaped sticky rystals are not penetrable for electrons. Their respective ranges of length nd width are 3—15 μ and 0,5—3 μ. In carbon replicas the length of rystals reaches 25 μ and the width 7 μ (Photos 7—10). The short and ong columnar crystals are doubly terminated by pyramidal or prismatic aces. Besides crystals and their fragments, a probably amorphous consti-uent of bukovskýite can be observed in photographs of the microcrystal-ine matrix. It forms very fine particles with irregular outline, partially ranslucent, usually accumulated into larger irregular aggregates or dhering to larger bukovskýite crystals. Heterogenous admixtures were ot observed in the studied mounts. Electron microphotographs of carbon eplicas did not reveal any regular orientation of crystals on the fracture urface of microcrystalline aggregates.

SPECTROGRAPHIC ANALYSES

Specimens of bukovskýite collected in 1938 and 1958 were studied by d of qualitative spectrographic analysis. Destinezite from Chvaletice and

Praha—Vysočany was analyzed, too, for comparative purposes. Graphic presentation of the results is demonstrated in Table 2.

Table 2. Qualitative spectrographic analyses of bukovskýite and destinezite

MINERALS	Sample No	Al	As	Ba	Ca	Cd	Cr	Cu	Fe	Li	Mg	Mn	Na	P	Si	Sn	Sr	Ti	V	Zn
Bukovskýite	1	·	■		·	⁝	·	·	■		·	·	·	●	●			·		○
	2	·	■		·	⁝	·	·	■		·	·	·	●	●	·		·		○
Destinezite	3	○	○		·		·	·	■	·	·	○		■	○			·		·
	4	○	○	●	●		·	·	■		○	○		■	○		·	·	⁝	·
	5	●	○	○	●		·	·	■		○	○		■	●		·	·		·
	6	○	○		○			·	■		○	·		■	○			·	⁝	·

■ XO %
▣ X %
● 0.X %
○ 0,0X %
· < 0,0X %
⁝ Problematic element presence

1 — Bukovskýite: Kaňk, specimen found in 1938, microcrystalline aggregate
2 — Bukovskýite: Kaňk, specimen found in 1958, microcrystalline aggregate
3 — Destinezite: Chvaletice, grayish-white to grayish-yellow
4 — Destinezite: Chvaletice, yellowish-brown
5 — Destinezite: Chvaletice, brownish-red
6 — Destinezite: Praha—Vysočany, grayish-white

Analyst: O. Paukner; spectrograph Q 24

Besides the most important components As and Fe, higher admixture of P and Si was found in bukovskýite. Phosphorus substitutes for arsenic in the examined mineral in the form of $(PO_4)^{3-}$ ions. Si stems from the admixture of quartz that was identified in the insoluble residue by X-ray methods. Among other trace elements the presence of Cr, Ti is interesting, as well as the relatively higher admixture of Zn (0,0X %). Both the older and more recently collected specimens display similar contents of trace elements.

Spectrographic analysis of destinezite yielded similar results; $(AsO_4)^{3-}$ groups are in this case substituted by $(PO_4)^{3-}$ ions but arsenic is also present in very low quantities. Al, Ca, Mg, and Mn is present in larger amounts in destinezite, two specimens contain also Ba and Sr. The majority of these admixtures belongs evidently to heterogeneous impurities.

CHEMICAL COMPOSITION

Quantitative chemical analysis and its recalculation were performed already by A. Bukovský (1915). According to this author, the studied material is a combined hydrous arsenate and hydrous basic sulphate

of ferric iron, $Fe_2(AsO_4)_2 . Fe_2(OH)_2(SO_4)_3 . 16\ H_2O$ with the molecular ratio $Fe_2O_3 : SO_3 : As_2O_5 : H_2O = 2 : 2 : 1 : 17$. Three specimens of bukovskýite were analyzed in the course of present investigation; two pieces of microcrystalline aggregates broken off of the 1938 and 1958 specimens and aggregates of crystals separated from vugs in the microcrystalline matrix. All analyses of bukovskýite that have been made till now (Table 3) indicate that the composition of this mineral is relatively constant; it may be also concluded that the examined material is homogeneous in spite of the fact that the analyzed specimens were collected at various dates. The metacolloidal nature of this mineral causes probably the variations of the water content. The insignificant insoluble residua of large samples reach only 0,1 %; the X-ray investigation proved that quartz is their predominating component.

Table 3. Chemical analyses of bukovskýite

	1	2	3	4
	A. Bukovský (1915)	specimen found in		
		1938	1958	1958
Fe_2O_3	30,84	31,40	30,71	32,42
Al_2O_3		1,43	—	—
SO_3	14,70	14,69	15,68	16,50
As_2O_5	20,81	22,10	21,62	22,10
P_2O_5	0,40	—	—	—
SiO_2	—	0,90	—	—
MgO	—	0,11	—	—
CaO	—	0,17	—	—
H_2O	28,73	29,41	31,61	28,12
Insol.	0,22	—	—	—
Σ	95,70 %	100,21 %	99,62 %	99,32 %

Analysts: 1 — A. Bukovský, 2,3, and 4 — P. Povondra
1,2, and 3 — microcrystalline aggregate
4 — aggregate of needle-like crystals

Because of the variable H_2O content, the crystallochemical formulae were computed for the sum of cations under assumption that $R^{3+} = 2$ (Table 4). As shown by the analysis No. 2, a small amount of Al^{3+} can substitute for Fe^{3+}. The crystallochemical computations indicate that the ratio of the most important components is nearly constant in all analyzed specimens of bukovskýite and leads to the formula $Fe^{3+}_2(AsO_4)(SO_4)(OH) . 7\ H_2O$. The number of crystal water molecules is derived from the analysis No. 4, made of the best crystallized material. In Table 5 the analyses of bukovskýite are compared with its theoretical composition containing 7 and 8 molecules of crystal water; it is evident that the

Table 4. Calculation of crystallochemical formulae of bukovskýite

	Molecular ratios							
	1		2		3		4	
Fe_2O_3	0,193		0,197		0,192		0,203	
Al_2O_3	—		0,014		—		—	
SO_3	0,184		0,184		0,196		0,206	
As_2O_5	0,091		0,096		0,094		0,096	
P_2O_5	0,003		—		—		—	
H_2O	1,595		1,632		1,755		1,561	
	Ions per unit cell							
Fe^{3+}		2,00	1,87	2,00		2,00		2,00
Al			0,13					
$(SO_4)^{2-}$	0,95	1,92	0,87	1,78	1,02	2,00	1,02	1,97
$(AsO_4)^{3-}$	0,94		0,91		0,98		0,95	
$(PO_4)^{3-}$	0,03							
$(OH)^{1-}$		1,00		1,00		1,00		1,00
H_2O	16,51	7,00	15,50	7,00	18,24	7,00	15,38	7,00
H_2O^-*)		2,63 %		0,97 %		2,89 %		0,69 %

*) The water expressed as adsorbed water in %

Crystallochemical formulae:

1 — $Fe_2^{3+}(SO_4, AsO_4, PO_4)_{1,92}(OH) . 7 H_2O$ (2,63 % H_2O^-)
2 — $(Fe^{3+}, Al)_2(SO_4, AsO_4)_{1,78}(OH) . 7 H_2O$ (0,97 % H_2O^-)
3 — $Fe_2^{3+}(SO_4, AsO_4)_{2,00}(OH) . 7 H_2O$ (2,89 % H_2O^-)
4 — $Fe_2^{3+}(SO_4, AsO_4)_{1,97}(OH) . 7 H_2O$ (0,69 % H_2O^-)

analyses of the microcrystalline aggregates approach closely the composition with 8 H_2O. This is caused by the more pronounced metacolloidal nature of these specimens. Calculating formulae the excess of water over 7 molecules was considered to be adsorbed. The X-ray investigation of higher hydrates of both bukovskýite and its phosphate analogue destinezite indicate their lower degree of crystallinity, illustrated on X-ray photographs by low number of reflections and their diffuse character. Besides the above calculations, in Table 5 the chemical composition of bukovskýite is compared with that of the related minerals sarmientite and pitticite. Sarmientite differs from bukovskýite in containing only 5 molecules of crystal water. Some chemical analyses quoted by CH. PALACHE, H. BERMAN and C. FRONDEL (1951) are closely similar to those of bukovskýite and sarmientite. These pitticites (Table 5, Nos. 9 and 10) may be considered to be colloidal equivalents of bukovskýite and sarmientite. Their colloidal character enables frequent deviations of their composition from constant stoechiometric ratios. Some pitticites, for example, contain only wery low percentages of SO_3 and are regarded as impure hydrolyzed scorodites (A. G. BETEKHTIN 1950, F. V. CHUKHROV

955). Microcrystalline scorodite from the medieval dumps at Kaňk was ecently described by Z. TRDLIČKA and V. HOFFMAN (1965).

Table 5. Chemical composition of bukovskýite, sarmientite and pitticite

	1	2	3	4	5	6	7	8	9	10
Fe_2O_3	32,60	31,84	31,71	30,83	32,70	31,90	35,20	36,43	34,85	35,37
Al_2O_3	—	—	1,48	—	—	—	—	—	—	—
SO_3	16,35	15,18	14,79	15,74	16,64	15,98	17,64	18,21	13,91	18,69
As_2O_5	23,46	21,49	22,32	21,70	22,29	22,94	25,32	22,59	26,70	15,12
P_2O_5	—	0,41	—	—	—	—	—	—	—	—
H_2O	27,59	31,08	29,70	31,73	28,37	29,18	21,84	22,77	24,54	30,82
Σ in %	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00	100,00

1 — Theoretical composition: $Fe_2^{3+}(AsO_4)(SO_4)(OH) . 7 H_2O$
2 — Bukovskýite: recalculated to 100 %; A. BUKOVSKÝ (1915)
3 — Bukovskýite: specimen found in 1938; recalculated to 100 % (microcrystalline aggregate)
4 — Bukovskýite: specimen found in 1958; recalculated to 100 %; (microcrystalline aggregate)
5 — Bukovskýite: specimen found in 1958; recalculated to 100 % (aggregates of needle-like crystals)
6 — Theoretical composition: $Fe_2^{3+}(AsO_4)(SO_4) (OH) . 8 H_2O$
7 — Theoretical composition: $Fe_2^{3+}(AsO_4)(SO_4)(OH) . 5 H_2O$
8 — Sarmientite: Santa Elena Mine, Alcaparrosa, Argentina; recalculated to 100 % after deduction of 0,27 % CaO; V. ANGELELLI and S. G. GORDON (1941)
9 — Pitticite: Schwarzenberg, Saxony (in CH. PALACHE *et al.* 1951)
10 — Pitticite: Manhattan, Nevada, USA (in CH. PALACHE *et al.* 1951)

Density of bukovskýite was determined by aid of pycnometer in destilled water at 22 °C. The measured value G = 2,334 is nearly identical with hat already found by A. BUKOVSKÝ (1915) — 2,34. Densities of some similar minerals are quoted in Table 6. These data show that the density of bukovskýite evidently differs from that of sarmientite and scorodite but ranges well among these of pitticite and destinezite.

Table 6. Density of bukovskýite and some related minerals

Mineral	G	Author
Bukovskýite (microcrystalline aggregate)	2,334	this paper
Bukovskýite	2,34	A. BUKOVSKÝ (1915)
Sarmientite	2,58	V. ANGELELLI and S. G. GORDON (1941)
Pitticite	2,2—2,5	CH. PALACHE, H. BERMAN, and C. FRONDE (1951)
Destinezite	2,0—2,4	,,
Scorodite	3,01	,,

INFRARED SPECTRA

Bukovskýite and some other structurally and chemically related minerals were studied by aid of infrared absorption analysis. The curves obtained are demonstrated in Fig. 3. The samples were finely powdered and homogenized with Nujol, with exception of the specimen No. 1 that was mixed with KBr, carefully prepared for infrared analysis. The study by C. J. Brester (1924) can be used as a basis for treatment of our results. The author determined in the range of NaCl-prism four characteristic vibrations for the tetrahedral groups of the XO_4 type that can be applied also to compounds that contain anions of this type in their structure:

1. symetrical valence vibrations A_1, inactive for infrared radiation,
2. triply degenerated valence vibrations F_2 [ν(a)] — bands of highest frequencies in the range below 1300 cm^{-1}, active for infrared radiation,
3. doubly degenerated deformation vibrations E, inactive for infrared radiation,
4. triply degenerated deformation vibrations F_2 [δ (a)] — active for infrared radiation.

As shown above, the active vibrations sub 2) and 4) are the only significant for the identification by infrared analysis. It must be, however, stressed again, that these conclusions were arrived at and are valid only for free molecules of the described tetrahedral type but the application to compounds containing them is also possible. It must be taken into account that the examined minerals are complex compounds of various anions and cations; the individual vibration frequencies may be shifted and their intensities changed.

By aid of numerous published data and his own experiments, H. Moenke (1962) schematized the positions of absorption bands of some compounds containing XO_4 type anions; we are particularly interested in absorption bands of sulphates, arsenates and phosphates that compose the analyzed minerals. The positions of these bands are demonstrated in Fig. 2 for the wavelengths in the range of NaCl-prism, *i. e.* between 700 and 1800 cm^{-1}. The deformation vibrations of H_2O that occur at 1640 cm^{-1} are also shown in this picture. The absorption band of valence vibrations of the (OH) group is not included; it lays well in the range of LiF-prism, was sought for only in bukovskýite and found as a weak band at 3300 cm^{-1}. According to the analysis described above the following absorption bands can be ascribed to bukovskýite:

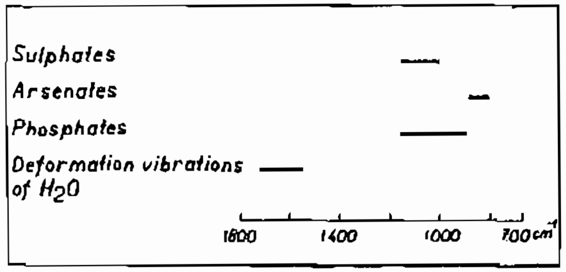

Fig. 2. Location of frequencies of (XO_4) and H_2O links in the range 700—1800 cm^{-1} in the infrared radiation (arranged according to C. J. Brester 1924)

851 cm^{-1}	valence oscillation of	$(AsO_4)^{3-}$
1099 cm^{-1}	valence oscillation of	$(SO_4)^{2-}$
(997) cm^{-1}		
1408 cm^{-1}		
1648 cm^{-1}	deformation oscillation of	H_2O

Following minerals were studied in the infrared for comparison: sarmientite from the type locality Santa Elena, Argentina (HMM[4]) 97719), destinezite from Praha—Vysočany, Bohemia, and pitticite from Olovi, Western Bohemia (Fig. 3). The analyzed specimen of "sarmientite" shows an absorption curve very similar to that of coquimbite. The absorption bands indicate a very low $(AsO_4)^{3-}$ content in sharp contrast with the chemical composition of this species quoted by V. Angelelli and S. G. Gordon (1941). A more detailed discussion of this specimen follows in the chapter dealing with the X-ray examination.

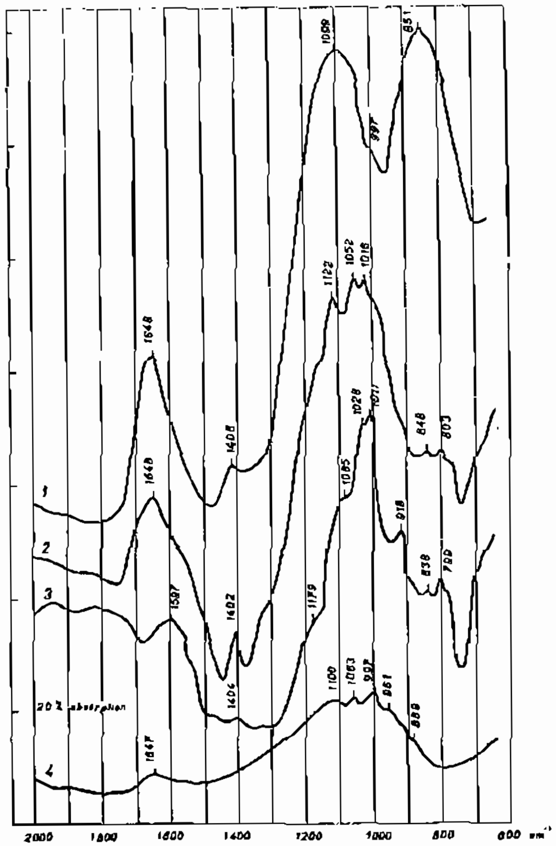

Fig. 3. Infrared absorption curves of bukovskýite and some related minerals: 1 — Bukovskýite: Kaňk (specimen found in 1938); 2 — Destinezite; Praha—Vysočany; 3 — Pitticite: Olovi, Western Bohemia; 4 — "Sarmientite" (= coquimbite): Santa Elena, Alcaparrosa, Argentina (HMM 97719)

Technical conditions: Apparatus IKS 14, NaCl and LiF prisms

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[4]) Harvard Mineralogical Museum

THERMAL INVESTIGATION

Thermal behaviour of bukovskýite in the range 20—1000 °C was studied by aid of classic thermogravimetric and differential thermal apparatus (Figs. 4 and 5), as well as with "Derivatograph" (Figs. 6 and 7). A series of thermal curves obtained from various specimens of this mineral is nearly identical. Two destinezite specimens — from Chvaletice and Praha—Vysočany — were also analyzed (Fig. 5).

Two evident weight losses recorded by the thermogravimetric curve of bukovskýite (Fig. 4) correspond to two strong endothermal maxima of the d. t. a. curve (Fig. 5). The first, larger weight loss takes place in the range 50—350 °C; it agrees well with the loss of crystal water and probably also of the hydroxyl groups, since the total loss equals to all water determined by chemical analysis. In curves obtained at low sensibility of the apparatus (Fig. 5) this loss is recorded as an endothermal doublet. The first reaction culminating at 130 °C correlates probably with the loss of crystal water. The second, shallower endotherm at 180 °C might be caused by dehydroxylation of the specimen, following immediately after the first reaction. The highly sensible arrangement of the apparatures leads to a combined, unresolved broad effect with a common peak at 180 °C. A stepped dehydration was observed also on destinezite. (V. Bouška *et al.* 1960) and can be traced in the d. t. a. curves of this mineral demonstrated here, too (Fig. 5). Doubling of the first, strong endothermal effect is characteristic also for coquimbite and quenstedtite (F. Cesbron 1964).

The second, smaller but sharply limited weight loss occurs at 630—760 °C. It is caused by the escape of gaseous dissociation products of ferric sulphate. In Table 7 the thermogravimetric wight losses are compared with the H_2O and SO_3 contents determined chemically. A similar step illustrative for the decomposition of ferric sulphate and of the

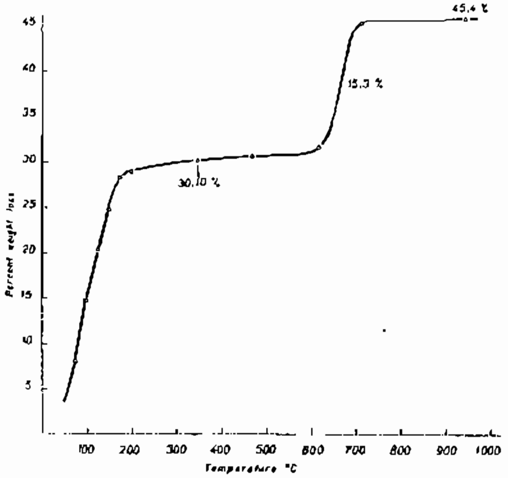

Fig. 4. Thermogravimetric curve of bukovskýite from Kaňk

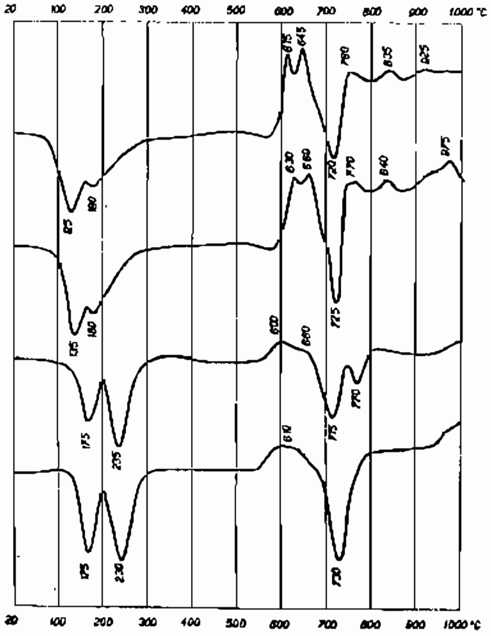

Fig. 5. Differential thermal curves of bukovskýite from Kaňk (1,2) and destinezite from Chvaletice (3) and Praha—Vysočany (4).
1 — Bukovskýite from Kaňk, specimen found in 1938
2 — Bukovskýite from Kaňk, specimen found in 1958
The curves were obtained on an automatic apparatus under following conditions: a Pt—Pt/Rh thermocouple, heating rate 11 °C/1 min., inert standart the ignited Al_2O_3, weight of finely powdered sample 0.2 g

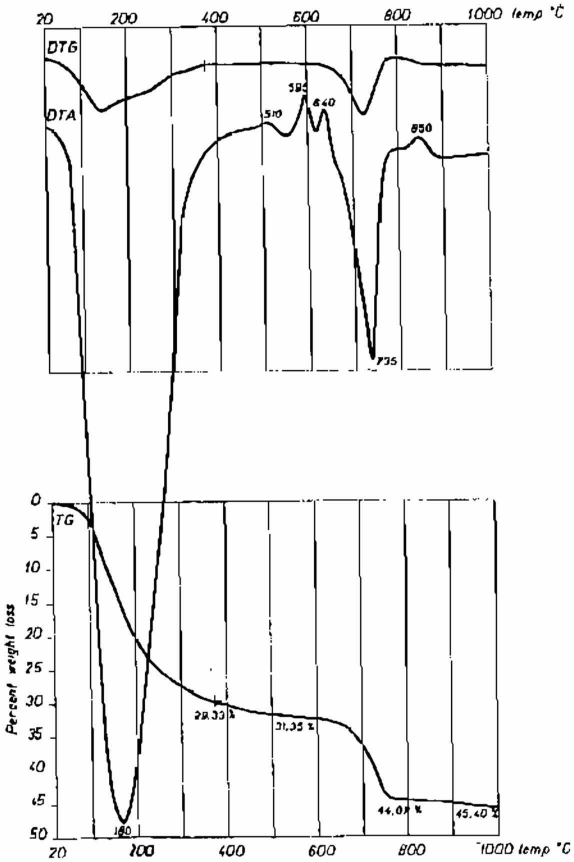

Fig. 6. Thermal data for bukovskýite from Kaňk, specimen found in 1958. DTG — first derivative curve of the thermobalance curve; DTA — differential thermal curve; TG — thermobalance curve
Thermal analyses were performed in the fully automatic "Derivatograph" produced by ORION, Budapest. Weight of sample 750 mg, inert substance 750 mg. Al_2O_3, DTA sensibility 1/5 — 500, DTG 1/10 — 100, 110 V. Temperature measured in the sample. The same thermal data give the specimen of bukovskýite found in 1938.

SO_3 escape can be observed also on thermogravimetric curves of destinezite (V. Bouška *et al.* 1960).

Discussion of the d. t. a. curves of bukovskýite is a little more complicated and needs further study. The endothermal effects were already commented above. In the range 600—660 °C sharp endothermal effects occur at 615 and 645 °C (Fig. 5, No. 1) and at 630 and 660 °C (Fig. 5, No. 2). These reactions might be ascribed to the crystallization of complex oxysulphates and arsenates of iron; the final reaction product is probably Fe_2O_3. $FeAsO_4$ is decomposed presumably at temperatures higher than 1000 °C. In the range 800—1000 °C small and diffuse exothermal reactions can be observed with maxima centered at 840 °C (crystallization of Fe_2O_3?), 925, and 975 °C.

The d. t. a. curves of destinezite (Fig. 5, Nos. 3 and 4) agree closely with those of bukovskýite. The most important difference is in the first endothermal trough. This is shifted to higher temperatures for destinezite and evidently doubled; peaks culminate at 170 and 230—245 °C.

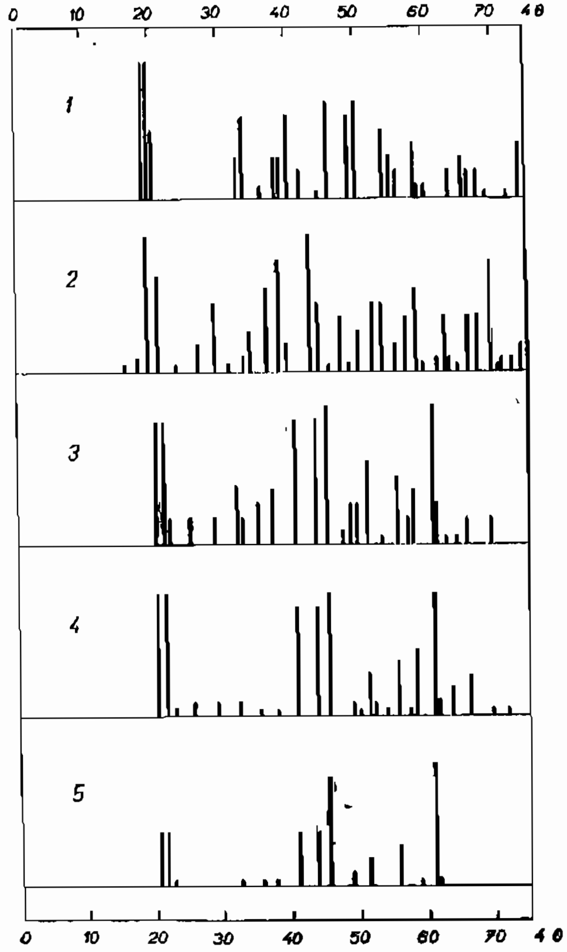

Fig. 7. Diagrammatic X-ray powder patterns of bukovskýite, sarmientite and destinezite:
1 — Bukovskýite: Kaňk; 2 — Sarmientite: Santa Elena Mine, Alcaparrosa, Argentina; 3 — Destinezite, grayish-white to yellowish-gray: Chvaletice; 4 — Destinezite, reddish-brown with yellowish-brown surface: Chvaletice; 5 — Destinezite, reddish-brown: Chvaletice.
Technical conditions: Specimens Nos. 1,3,4 and 5 were photographed by aid of Cu-radiation in the Guinier — de Wolff camera, No. 2 with Fe-radiation in the 114,59 mm. diameter camera.

The second reaction is more pronounced in destinezite; this may be caused by its lower content of crystal water.

Thermal behaviour of scorodite differs from that of bukovskýite. Its d. t. a. curve displays a strong endotherm in the 200—300 °C range and a medium exothermal effect at 500—600 °C (V. P. Ivanova 1961, Z. Trdlička and V. Hoffman 1965). Thermal properties of sarmientite and pitticite have not been studied up to the present.

Table 7. Comparison of weight losses derived from thermogravimetric curves with the H_2O and SO_3 contents found chemically

Loss of weight on the thermobalance record		Chemical analysis (No. 3)		
t °C	%	%		
0—340	31,58	31,61		H_2O
340—730	15,62	15,68		SO_3
Σ	47,20	47,29		Σ
		Chemical analysis (Nos. 1 and 2)		
0—380	29,33	29,41	30,10	H_2O
380—800	14,74	14,69	14,70	SO_3
Σ	44,07	44,10	44,80	Σ

The d. t. a. curves of diadochite from Banská Belá, Slovakia, and from Chlum, near Benešov, Central Bohemia (J. Jarkovský and B. Čîčel 1958, V. Bouška *et al.* 1960) are similar to those of destinezite, with exception of the second endothermal reaction that is rather ill-defined or completely absent. In our opinion this is caused by the colloidal nature of this mineral. We observed a considerable decrease of this second endotherm also on destinezite with lower crystallinity and higher content of colloidal phase. Our examination proved that diadochite from Chlum is quite X-ray amorphous. Diadochite from Banská Belá shows some diffuse reflections in X-ray records (J. Jarkovský and B. Čîčel 1958) that might be correlated with the strongest reflections of destinezite; they indicate the presence of a small amount of crystalline phase.

X-RAY POWDER DATA

With regard to the microcrystalline character of bukovskýite the X-ray investigation was performed only by aid of powder methods, using the cylindrical cameras with 57,3 and 114,59 mm. diameters and the Guinier-de Wolff camera (Tables 8 and 9). The latter camera was used also for comparison of bukovskýite with the chemically and structurally related minerals, particularly with destinezite, diadochite, sarmientite and pitticite.

X-ray powder diagrams of bukovskýite indicate that this species is an independent, homogeneous and crystalline mineral. This is shown by very similar X-ray records of specimens that were collected at various dates (Table 8). The X-ray powder diagrams are characterized especially by the very strong doublet at around 9,6 and 9,2 Å. Diffractograph records of bukovskýite (Fig. 9), show in addition, a doubling of the latter line with a strong 9,31 Å peak and a weak 9,03 Å reflection. It is very difficult to

Table 8. X-ray powder diffraction data for bukovskýite from Kaňk¹)

1		2	
I	d(Å)	I	d(Å)
10	9,56	10	9,60
10	9,16	10	9,21
5	8,84	8	8,84
3	5,48	6	5,48
6	5,30	8	5,30
1 b	4,792	3	4,805
3	4,667	7	4,667
3	4,583	7	4,607
6	4,458	9	4,480
2	4,267	5	4,287
		0,5	4,168
0,5	4,019	1	4,028
7	3,897	9	3,914
6	3,660	8	3,679
7	3,587	9	3,601
5	3,312	8	3,318
3	3,264	7	3,270
2	3,206	7	3,212
4	3,066	7	3,066
1 b	3,040	4	3,046
		4	3,020
1	2,981	5	2,991
		0,5	2,933
2 b	2,820	4	2,829
3	2,740	7	2,749
2	2,712	7	2,724
2	2,653	7	2,661
0,5	2,608	1	2,616
0,5	2,449		
4	2,443	7	2,543
		5	2,434
1	2,393	4	2,402
1	2,363	4	2,363
		2	2,333
1	2,288	2	2,296
1	2,258	5	2,263
1	2,239	4	2,241
1	2,174	0,5	2,179
		0,5	2,159
		0,5	2,142
1	2,116	1	2,118
1	2,083	2	2,090
		6	2,063
1 b	2,045	6	2,045
1	2,002	0,5	2,009
1	1,982	3	1,984
1	1,963	0,5	1,967
1	1,943	2	1,947
		0,5	1,928
1	1,918		
1	1,898		
1	1,883		
2	1,849	4	1,854
1	1,797	1	1,806
1	1,773	2	1,778
		0,5	1,767
1	1,742	0,5	1,743
1	1,726	4	1,728
1	1,705	3	1,710
1	1,685	0,5	1,688
3	1,660	6	1,661
1	1,646		
1 b	1,609		
1 b	1,550		
1	1,529	0,5	1,529
1 b	1,511		
2 b	1,463	5	1,462

¹) Guinier — de Wolff camera, Cu-radiation
1 — specimen found in 1938
2 — specimen found in 1958
b = broad line

deduce the symmetry of bukovskýite from its X-ray powder data, since this species belongs probably to the monoclinic or triclinic system. Certain similarity may be observed between the X-ray tracings of bukovskýite and destinezite. Graphic demonstration of the powder diagrams of bukovskýite, sarmientite and destinezite was used to enable an easier comparison of these minerals (Fig. 7). The doublet of lines with the lowest 2Θ angles is shifted towards higher angles in destinezite diagrams. J. Toussaint and J. Mélon (1955) index the first strong line of this species with $d = 8{,}8$ Å as 010 and consider its unit cell to be triclinic:

$$a_0 = 9{,}61\ \text{Å} \qquad b_0 = 10{,}27\ \text{Å} \qquad c_0 = 7{,}36\ \text{Å}$$
$$\alpha = 81°45' \qquad \beta = 108°1' \qquad \gamma = 121°14'$$

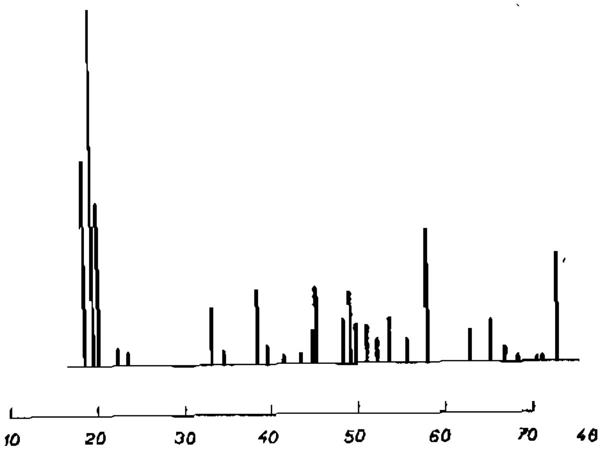

Fig. 9. Graphic demonstration of the diffractometer record of bukovskýite from Kaňk (Cu-radiation).

Assuming that bukovskýite is isostructural with destinezite and triclinic, its unit cell dimensions are evidently larger as shown by the present X-ray powder diffraction data. This expansion of the unit cell of bukovskýite is connected with the higher percentage of crystal water and probably also with the substitution $(PO_4)^{3-}$ — $(AsO_4)^{3-}$.

Three X-ray powder diffraction photographs of destinezite from Praha—Vysočany and four diagrams of this species collected at Chvaletice (Table 10) are nearly identical, differing only in absence or low intensity of some lines. This phenomenon may be explained by the variable crystallinity of the examined specimens. From this point of view, specimen No. 7

Table 9. Comparison of the X-ray powder diffraction data for bukovskýite from Kaňk and sarmientite from Santa Elena, Alcaparrosa, Argentina

Bukovskýite Kaňk, near Kutná Hora				Sarmientite USNM 105682		"Sarmientite" HMM 97719	
1		2		3		4	
I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)
				1	11,1	0,5	11,0
				1	10,0		
10	9,9	10	9,6				
						1	9,34
10	9,1	10	9,1	10	9,2		
				7	8,43	0,5	8,56
0,5	7,7			0,5	7,68	0,5	7,68
0,5	6,5			2	6,59		
				5	6,06	2	6,19
				0,5	5,66	5	5,87
3	5,40					5	5,52
5	5,22	4	5,29	1	5,29		
				3	5,15		
0,5	4,98					10	4,987
				6	4,817	4	4,737
3	4,57	4	4,565	8	4,602		
						0,5	4,621
5	4,43	1	4,440	2	4,440	5	4,423
1	4,23	3	4,258	10	4,210	1	4,258
		0,5	4,127				
2	4,05					4	4,090
				5	4,990	1	3,990
8	3,88	7	3,882	0,5	3,869		
				4	3,730		
6	3,69	3	3,671			1	3,693
				0,5	3,636	7	3,602
8	3,57	5	3,569	3	3,547		
		0,5	3,542			2	3,472
0,5	3,36			5	3,401		
1	3,31	2	3,322	5	3,304		
0,5	3,27	0,5	3,247	2	3,203	6	3,230
		1	3,186			7	3,169
				4	3,118	9	3,126
10	3,07	8	3,069	6	3,037	5	3,069
2	3,00	3	2,960	0,5	2,998	1	2,974
				1	2,901	2	2,908
				4	2,839	2	2,853
2	2,81	2	2,806	1	2,812		
3	2,73	2	2,737	0,5	2,760	1	2,772
1	2,67			4	2,697	0,5	2,673
1	2,62	0,5	2,655	4	2,649		
		0,5	2,591	8	2,575	4	2,586
				0,5	2,536		
1	2,50	1	2,500	1	2,515	8	2,505
				1	2,474		
10	2,44	9	2,442	2	2,420		
2	2,38			0,5	2,386	4	2,396
Al	2,336	Al	2,336	2	2,336	4	2,340
				1	2,300		
0,5	2,26			2	2,254	4 b	2,266
				2	2,214		
0,5	2,18			0,5	2,174	1	2,170
0,5	2,11			2 vb	2,119	0,5	2,126

Table 9. *(Continued)*

Bukovskýite Kaňk, near Kutná Hora				Sarmientite USNM 105682		"Sarmientite" HMM 97719	
1		2		3		4	
I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)
1	2,05	1	2,051	1	2,051	2	2,030
Al	2,02	Al	2,024	2	2,024	2	2,007
1	1,98	0,5	1,980	0,5	1,998	3	1,983
				2	1,970		
0,5	1,95	1	1,940	0,5	1,949	1	1,952
0,5	1,91	0,5	1,909			4	1,934
0,5	1,89	0,5	1,885			0,5	1,897
2	1,85	3	1,850	2	1,858	2	1,868
						6	1,846
0,5	1,81	0,5	1,810	1	1,816	4	1,801
				1	1,792		
0,5	1,77	0,5	1,769			0,5	1,761
1	1,74			1 b	1,750	0,5	1,748
0,5	1,72	1	1,729	1	1,722	1	1,732
		2	1,710	0,5	1,706	3	1,712
				0,5	1,687		
3	1,67	0,5	1,666	2	1,664	4	1,668
1	1,64	0,5	1,632	0,5	1,654	4	1,642
		1	1,610	2	1,622	4	1,617
0,5	1,59			0,5	1,584	3 b	1,582
1	1,56	0,5	1,560	1	1,554	1	1,564
4	1,53	2	1,527	0,5	1,530	2	1,540
0,5	1,51	0,5	1,515	0,5	1,525	0,5	1,518
		1	1,500			1	1,505
				1 b	1,479	2	1,487
3	1,47	2	1,465	1 b	1,459	1vb	1,457
Al	1,432	Al	1,432	1	1,437	1vb	1,432
		1	1,413			0,5	1,410
						0,5	1,404
				0,5	1,387	2	1,376
				1	1,360	2	1,364

1 and 2 — Fe/Mn-radiation, Al internal standard; No. 1—57,3 mm. camera, No. 2 — 114,59 mm. camera.
3 and 4 — Wilson technique, Fe/Mn-radiation, intensities according to a Straumanis-type photograph.
b = broad line, vb = very broad line

is to be regarded as that with lowest degree of crystallinity; only the 3,93 and 2,94 Å lines retain a higher intensity. The same features can be observed also on X-ray records of bukovskýite. The earthy and powdery forms of this mineral yield much poorer X-ray photographs; their higher water content is caused most probably by the presence of some amount of colloidal phase.

Sarmientite was the object of our particular interest since this species is crystalline, chemically close to bukovskýite, and has not been studied by X-rays. From Dr. Mary E. Mrose, U.S. Geological Survey, Washington, we obtained by the courtesy of Dr. F. Čech the type specimen of yellow

Table 10. X-ray powder diffraction data for destinezite from Praha—Vysočany and Chvaletice

1		2		3		4		5		6		7	
I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)	I	d(Å)
7	8,75	8	8,75	9	8,75	8	8,75	9	8,75	9	8,79	4	8,75
8	8,22	8	8,26	9	8,26	8	8,30	9	8,22	9	8,22	4	8,26
2	7,86	0,5	7,93	3	7,89	1	7,86	2	7,89	0,5	7,82	0,5	7,89
1	7,43												
2	6,91	1	6,96	2	6,99	0,5	6,96	2	6,96	1	6,99		
3	6,08	2	6,12	4	6,13	2	6,15	2	6,10	1	6,15		
1	5,86												
4	5,47	3	5,48	5	5,50	3	5,54	4	5,50	1	5,52	0,5	5,52
2	5,35	1	5,40	4	5,42	2	5,40	2	5,37				
2	5,02	1	5,04	3	5,02	1	5,04	3	5,04	0,5	5,04	0,5	5,02
1	4,870												
3	4,704	2	4,741			3	4,729	4	4,729	2	4,716	0,5	4,754
1	4,607	0,5	4,619	1	4,631	0,5	4,619						
8	4,360	8	4,371	9	4,371	8	4,371	9	4,360	8	4,360	4	4,371
1	4,101												
7	4,064	9	4,073	9	4,083	8	4,083	9	4,064	8	4,073	4	4,083
10	3,914	10	3,922	10	3,922	10	3,922	10	3,914	9	3,922	8	3,931
1	3,720	0,5	3,735	0,5	3,735	0,5	3,751	1	3,735				
2	3,638	2	3,645	4	3,652	2	3,660	3	3,638	1	3,638	1	3,645
1	3,559	0,5	3,566	1	3,573	1	3,573	3	3,573	0,5	3,573		
4	3,470	4	3,377	5	3,483	5	3,483	6	3,470	3	3,483	2	3,483
										1	3,424		
1	3,324							0,5	3,330	0,5	3,324		
1	3,252												
4 b	3,201	5	3,206	6	3,206	5	3,206	5	3,206	4	3,218	3	3,218
2	3,108	0,5	3,124	2	3,124	1	3,118	2	3,118	0,5	3,124		
3	3,071	3	3,071	4 b	3,082	2	3,076	4 b	3,076	5 b	3,076	0,5	3,076
1	3,046												
10	2,928	8	2,938	10	2,943	10	2,938	10	2,938	9	2,938	9	2,943
2	2,896	1	2,914	3	2,910	1	2,910	2	2,910	1 b	2,910	0,5	2,919
2	2,833	1	2,846	2	2,846	1	2,838	3	2,846	2 b	2,825		
2	2,769					1	2,773	0,5	2,782				
2 b	2,704			1	2,716	1 b	2,704	1 b	2,720	3	2,720		
2	2,587	1	2,594	2	2,601	1	2,597	3	2,597	0,5	2,597		
1	2,558												
2	2,513			1	2,523					0,5	2,516		
1	2,453			0,5	2,463								
2	2,412			1	2,415			2	2,412				
2	2,354			0,5	2,360								
2	2,305	0,5	2,310	2	2,313			2	2,316				
2	2,271			0,5	2,277								
3	2,249	1	2,258	1	2,255	0,5	2,258	2	2,258				
1	2,225												
1	2,187												
1	2,162												
1	2,118			0,5	2,120								
1	2,092												
3	2,074	1	2,072	2	2,074	1	2,072	2	2,072				
2	2,039	0,5	2,041	1	2,039	0,5	2,032	1	2,039				
3	2,000	1	1,996	2	1,998	1 b	1,998	2	1,998				
1	1,959												
1	1,916												
1	1,901							0,5	1,907				
2	1,861							1	1,861				
2	1,826							1	1,823				
1	1,796												
2	1,748							1	1,745				
2	1,713												
1	1,692												
1	1,675												

*) Guiner de-Wolff camera, Cu-radiation

1,2, and 3 — Destinezite: Praha—Vysočany, grayish-white, microcrystalline

5,6, and 7 — Destinezite: Chvaletice (5 — grayish-white to yellowish-gray, 6 — reddish-brown with yellowish-brown surface, 7 — brick reddish-brown)

Specimens Nos. 2 and 4 are those used in the study of V. Bouška *et al.* (1960).

b = broad line

to orange-yellow sarmientite from the collection of the Harvard Mineralogical Museum (HMM No. 97719). As demonstrated in Table 11 and Fig. 8, *d*-spacings of this specimen show a distinct relation to those of coquimbite (ASTM 1953[5])). The infrared absorption curve and qualitative spectrographic analysis suggest also the identity with coquimbite. Fe was the only substantial element found, Si is present in subordinate amount; As and Al, Cd, Cu, Mg, Mn occur in this specimen only in minor quantities. These facts indicate that the specimen under study is not sarmientite described by V. ANGELELLI and S. G. GORDON (1941) but probably predominantly coquimbite. Therefore Dr. Mary E. Mrose was asked for some other specimens. Two X-ray powder photographs were sent to us, both taken with the Fe/Mn radiation in the 114,59 mm. diameter camera (Table 9). The diagram of sarmientite from the Harvard Mineralogical Museum (HMM No. 97719) yields *d*-spacing that are very close to those obtained in the course of our study; the phase prevailing in the examined material is probably again coquimbite. The second X-ray photograph of sarmientite from the collection of the U.S. National Museum, Washington (No. 105682) gave an entirely different results. This specimen corresponds probably with the actual type sarmientite (Table 9, No. 3). Some strong lines on this record — *e. g.*, 9,2, 4,21 and 3,04 Å — are present also on X-ray photographs of bukovskýite, but the general character of these patterns is definitely different. Refractive indices, density, X-ray powder data, and some other properties indicate that the difference in water content of bukovskýite and sarmientite is sufficient for distinguishing them as independent mineral species.

Table 11. Comparison of X-ray powder diffraction patterns of "sarmientite" from Santa Elena, Argentina¹) and coquimbite

"Sarmientite" (HMM 97719)		Coquimbite ASTM (1945)		"Sarmientite" (HMM 97719)		Coquimbite ASTM (1945)	
I	d(Å)	*I*	d(Å)	*I*	d(Å)	*I*	d(Å)
1	6,21			2	2,336		
3	5,84	3	5,96	1	2,263	7	2,26
0,5	5,52	4	5,65	1	2,162		
10	4,993	9	5,09	1	2,070		
1	4,741			0,5	2,026		
1	4,436			1	2,002		
1	4,083			1	1,971	8	1,98
1	3,690	4	3,67	0,5	1,945		
4	3,601	2	3,53	1	1,930	5	1,93
2	3,235			0,5	1,866	5	1,88
3	3,201			3	1,843	8	1,83
5	3,156			2	1,794	1	1,77
7	3,118	10	3,12	1	1,732	1	1,74
1	3,076	9	3,06	1	1,708	2	1,72
1	2,914	4	2,99	1	1,667	1	1,69
1	2,842	5	2,83	1	1,639		
		3	2,70	1	1,612	4	1,62
1	2,576	5	2,54	1 b	1,576	4	1,59
4	2,496			1 b	1,561	4	1,56

¹) Guinier — de Wolff camera, Cu-radiation b = broad line

Specimens of pitticite from Freiberg, Saxony, and Příbram, Bohemia, were loaned for X-ray investigation from the collection of the National Museum, Praha. No distinct reflections could be observed on the dark background of their X-ray

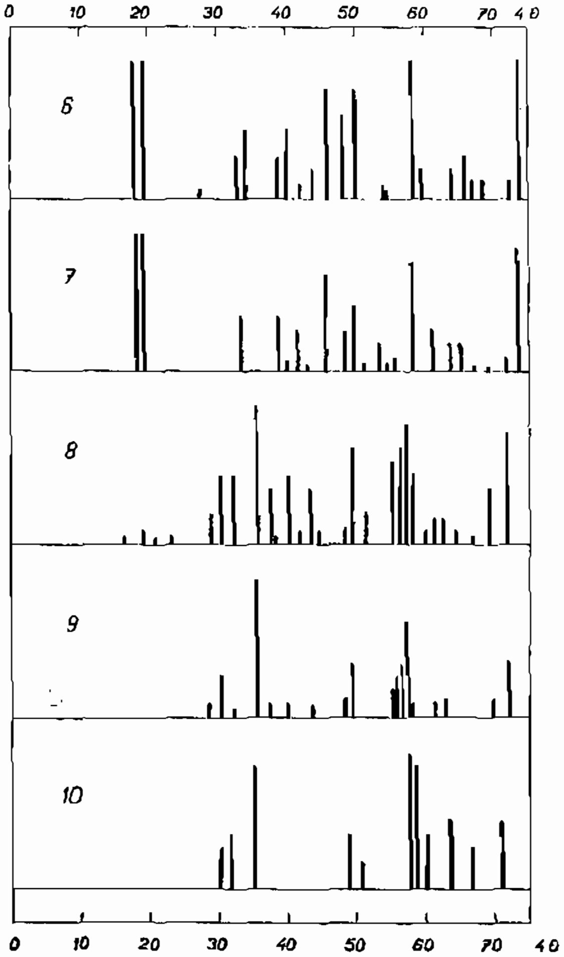

Fig. 8. Diagrammatic X-ray powder patterns of bukovskýite and coquimbite. 6—7 — Bukovskýite: Kaňk; 8—9 — Coquimbite (?) labelled as "sarmientite" in the collection of HMM: Santa Elena Mine, Alcaparrosa, Argentina; 10 — Coquimbite: ASTM 1953

Technical conditions: Specimen No. 6 — Debye-Scherrer method, Fe-radiation, Specimens Nos. 7 and 8 — Debye-Scherrer method, Fe-radiation, 114.59 mm. diameter camera, Specimen No. 9 — Guinier — de Wolff camera, Cu-radiation.

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[5] It must be stressed on this occasion that X-ray powder data for coquimbite quoted in literature display considerable differences, *e.g.*, *d*-spacings in tables ASTM (1953) with those by K. OMORI and P. KERR (1964). Coquimbite from Copiapo, Chile, studied in the X-ray laboratory of the Institute of Mineral Raw Materials, Kutná Hora, gave also different results (Dr. Z. Trdlička, personal communication).

photographs. The same is true for diadochite from Chlum, near Benešov, Bohemia. Therefore pitticite and diadochite may be considered to be X-ray amorphous, colloidal equivalents of bukovskýite, sarmientite and destinezite.

Sumarizing the results of the X-ray powder study we may state that destinezite, bukovskýite and sarmientite are definitely crystalline and can be distinguished by their different X-ray powder patterns. Pitticite and diadochite are X-ray amorphous and represent probably the colloidal analoga of the above minerals. The specimen deposited in the collection of the Harvard Mineralogical Museum and labelled "sarmientite" is most probably coquimbite. The X-ray patterns of bukovskýite, sarmientite and destinezite show some similarities. A doublet of strong lines between 8—10 Å is characteristic for bukovskýite and destinezite. Destinezite and sarmientite were regarded as monoclinic till now; the results of recent investigation indicate rather triclinic symmetry.

POSITION OF BUKOVSKÝITE IN THE MINERALOGICAL SYSTEM

It is difficult to find a place for bukovskýite in the mineralogical system, since no separate group was established for compounds of this type. H. Strunz (1966) arranges similar minerals destinezite and pitticite preliminarly to the strunzite-beraunite group. The main obstacle for classification of bukovskýite and related minerals is the unfinished structural investigation of these species.

The chemical and X-ray study of bukovskýite and destinezite indicates that both minerals are crystalline and well-defined from the chemical point of view. Bukovskýite is chemically analogous to destinezite, differing mainly in the anionic position: $(PO_4)^{3-}$ groups are substituted by $(AsO_4)^{3-}$ ions. It contains also a higher percentage of crystal water. The microcrystalline to metacolloidal character of both these minerals influences only the varying amount of molecular water in these compounds. The presence of $(PO_4)^{3-}$ groups in bukovskýite and pitticite and, on the contrary, the admixture of $(AsO_4)^{3-}$ ions in the destinezite-diadochite series suggests a possibility of isomorphous mixing between these two mineral groups. This might be an analogous case of the diadochic $(AsO_4)^{3-}$ and $(PO_4)^{3-}$ substitution as for example the scorodite group. A phosphorus-rich member of this series was described that contains 16,03 % P_2O_5 (phospho-scorodite of T. N. Shadlun and Ju. S. Nesterova 1947). Since destinezite and bukovskýite are the relatively best defined and examined members of this mineral group, we propose to establish a new separate destinezite — bukovskýite group, as shown in the following schema:

Sarmientite $Fe_2(AsO_4)(SO_4)(OH) . 5 H_2O$ monoclinic (?) microcrystalline	Destinezite $Fe_2(PO_4)(SO_4)(OH) . 5 H_2O$[a] monoclinic or triclinic (?) microcrystalline, metacolloidal
Bukovskýite $Fe_2(AsO_4)(SO_4)(OH) . 7 H_2O$ monoclinic (?) microcrystalline, metacolloidal	?
Pitticite $Fe_2(AsO_4)(SO_4)(OH) . n H_2O$ X-ray amorphous colloidal	Diadochite $Fe_2(PO_4)(SO_4)(OH) . n H_2O$ X-ray amorphous colloidal

[a] F. Slavík (1948) ascribes 6 molecules of crystal water to destinezite.

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BUKOVSKÝIT, $Fe_2(AsO_4)\,(SO_4)\,(OH)\,.\,7\,H_2O$ z KAŇKU U KUTNÉ HORY — — NOVÝ MINERÁL

František Novák, Pavel Povondra, Jiří Vtělenský

Bukovskýit se vyskytuje ve středověkých haldách v Kaňku u Kutné Hory (foto 1). Vzniká recentně jako produkt zvětrávání arzenopyritu. Jeho výskyt je omezen pouze na severní část kutnohorského rudního obvodu, kde jsou rudní žíly velmi bohaté obecnými kyzy, zejména pyritem, arzenopyritem a pyrhotinem. Tvoří obyčejně hlízovité, až 30 cm velké světle žlutozelené až šedozelené mikrokrystalické agregáty podobné destinezitu (foto 2). Agregáty bukovskýitu jsou měkké, na povrchu až práškovité a mají nerovný, zemitý lom. Vryp je žlutobílý. Snadno se rozkládá v HCl. Místy jsou v bukovskýitu uzavřeny rozložené úlomky hornin a žiloviny. V dutinkách je možno pozorovat chomáčky jehličkovitých krystalků s náznaky radiálně paprsčitého uspořádání. Hustota je 2,334. V procházejícím světle má bukovskýit charakter bezbarvých nebo nažloutlých jehliček průměrné velikosti 0,05 × 0,007 mm (foto 3). Krystalky mají sloupečkovitý habitus a pravděpodobně monoklinicko-prizmatickou souměrnost. Index lomu $\beta' = 1{,}582$ a $\gamma' = 1{,}631$, úhel zhášení = 22°. Morfologie a uspořádání jemných krystalků bukovskýitu bylo studováno v elektronovém mikroskopu metodou průsvitu i pomocí uhlíkových replik. Charakter bukovskýitu v elektronovém mikroskopu demonstrují mikrofotografie 5—10. Z rozpočtu čtyř chemických analýz nerostu vyplývá následující vzorec $Fe_2(AsO_4)\,(SO_4)\,(OH)\,.\,7\,H_2O$. Tomuto vzorci odpovídá teoretické složení: $Fe_2O_3 = 32{,}60\ \%$, $As_2O_5 = 23{,}46\ \%$, $SO_3 = 16{,}35\ \%$, $H_2O = 27{,}59\ \%$. Určité kolísání jeví obsah H_2O, což je způsobeno zčásti metakoloidní povahou nerostu. Na infra-red křivce byly prokázány absorpční pásy iontů (SO_4) a (AsO_4), dále krystalová voda a skupiny OH (obr. 3). Na GTA-křivce jsou dva výrazné úbytky na váze (obr. 4, 6 a 7). Prvý v rozmezí 50—350 °C představuje únik krystalové vody a pravděpodobně též OH-skupin. Druhý méně intenzívní úbytek na váze v rozmezí 630—760 °C představuje disociaci síranu železitého a únik SO_2. Na DTA-křivkách (obr. 5, 6 a 7) se tyto úbytky na váze projevují silnými endotermními poklesy. Dále se na nich objevují exotermní efekty v rozmezí 600—660 °C, které představují pravděpodobně krystalizaci komplexních oxysíranů a arzeničnanů železa. Rentgenografickým výzkumem bylo potvrzeno, že bukovskýit má krystalickou povahu a jeho práškové rentgenové snímky (tab. 8) charakterizují tyto nejintenzívnější linie (v Å): ~9,6 (10), ~9,2 (10), 5,30 (6—8), 4,47 (6—9), 3,90 (7—9), 3,59 (7—9). Bukovskýit je možno považovat za arzeničnanový analog destinezitu a oba tyto pravděpodobně izostrukturní nerosty lze vyčlenit jako samostatnou minerální skupinu, kam patří též chemicky bukovskýitu velmi blízký sarmientit. Sarmientit se však od bukovskýitu odlišuje menším podílem krystalové vody a strukturně. Pitticit je možno považovat za rentgenamorfní koloidní ekvivalent bukovskýitu a sarmientitu, podobně jako tomu je v případě destinezitu a jeho amorfního ekvivalentu diadochitu. Název bukovskýit byl novému nerostu dán na počest prof. A. Bukovského, který studovaný minerál chemicky analyzoval již v roce 1914. Bukovským byl studovaný minerál popsán pod názvem „jedová hlinka kutnohorská“.