

STIBIOBETAFITE, A NEW MEMBER OF THE PYROCHLORE GROUP FROM VEZNÁ, CZECHOSLOVAKIA

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ABSTRACT

Stibiobetafite occurs with accessory Ti, Nb > Ta, Be, Zr, REE minerals in a pegmatite cross-cutting serpentinite at Věžná, Czechoslovakia. It forms discrete octahedra, or granular aggregates veining and replacing partly disordered columbite and niobian rutile. The mineral is brittle, brownish-black with a vitreous lustre, and with a creamy-white streak. It turns pale orange after heating at 700°C for 1 h in air. It is isotropic with n_{calc} of about 2.2; density is 5.30 (meas.) and 5.19 g/cm³ (calc.). Stibiobetafite is cubic with a 10.356(2) Å, V 1110.6 (7) Å³, $Z=8$, and its space group is $Fd\bar{3}m$. Chemical composition corresponds to $Ca_{1.11}Sb^{3+}_{0.69}Sn^{2+}_{0.04}Mn^{2+}_{0.04}Na_{0.04}O_6[O_{0.76}(OH)_{0.21}F_{0.03}]_{\Sigma=2.01}(Ti^{4+}_{0.89}Nb^{5+}_{0.70}Ta^{5+}_{0.38}Al_{0.04})_{\Sigma=2.01}$. Combination of substantial Ti, Nb (> Ta) and Sb in a pegmatite mineral is a geochemical oddity.

SOMMAIRE

On trouve la stibiobétafite, associée aux minéraux accessoires d Ti, Nb (> Ta), Be, Zr, TR d'une pegmatite intrusive dans une serpentinite, à Věžna (Tchécoslovaquie). Elle se présente en octaèdres ou bien en agrégats granulaires qui recourent et remplacent de la columbite partiellement désordonnée et du rutile niobifère. Elle est cassante, à poussière blanc-crème, d'un brun-noir à éclat vitreux; elle vire à l'orange pâle après une heure de chauffage à 700°C dans l'air. Elle est isotrope, $n_{calc} \sim 2.2$; sa densité est de 5.30 (mes.), 5.19 (calc.). Elle cristallise dans le groupe spatial $Fd\bar{3}m$, a 10.356(2) Å, V 1110.6(7) Å³, $Z=8$. Sa composition correspond à la formule $(Ca_{1.11}Sb^{3+}_{0.69}Sn^{2+}_{0.04}Mn^{2+}_{0.04}Na_{0.04})_{\Sigma=2.01}(Ti^{4+}_{0.89}Nb^{5+}_{0.70}Ta^{5+}_{0.38}Al_{0.04})_{\Sigma=2.01}O_6[O_{0.76}(OH)_{0.21}F_{0.03}]$. La présence de Ti, Nb (> Ta) et de Sb dans un minéral pegmatitique est une curiosité géochimique.

(Traduit par la Rédaction)

INTRODUCTION

Since the 1950s, several minerals of scientific interest have been described from pegmatite localities in the vicinity of Věžná, western Moravia, Czechoslovakia (e.g., Černý 1965).

However, the exact identity of one of these minerals, found by the first author in 1961 and provisionally designated antimonian pyrochlore, has so far remained in question. Emission spectrographic analyses performed in several laboratories gave extremely contradictory results and consumed most of the available material without producing significant information. Only recently did a quantitative microanalytical re-examination of this mineral result in the present definition of a new species.

Stibiobetafite is a member of the pyrochlore group of cubic multiple-oxide minerals, with compositional parameters substantially exceeding the minima recommended by the International Mineralogical Association for naming a new species in this group (Hogarth 1977). The mineral and the name were approved by the Commission on New Minerals and Mineral Names, I.M.A., prior to publication. Type material is preserved in the Mineralogical Museum, Department of Earth Sciences, University of Manitoba (M5233), and a polished section was deposited in the collections of the Royal Ontario Museum, Toronto (M35630).

OCCURRENCE

The stibiobetafite-bearing pegmatite is exposed in the eastern part of a serpentinite body south of Věžná, 49°26'50"N, 33°56'30"E, located in a migmatitic terrain close to the northeastern outskirts of the Bohemian massif (Svoboda 1966). The pegmatite consists mainly of sodic plagioclase (An_{14-0}) and quartz, commonly in coarse graphic intergrowth; it is separated from the ultrabasic wallrock by banded reaction rims of anthophyllite, talc, tremolite and altered phlogopite. Accessory mineralization includes biotite, tourmaline, beryl, columbite, niobian rutile, cassiterite, zircon, monazite, xenotime and stokesite. Late alteration produced muscovite, chlorite, vermiculite, celadonite, prehnite, thomsonite, natrolite, wellsite, epid-

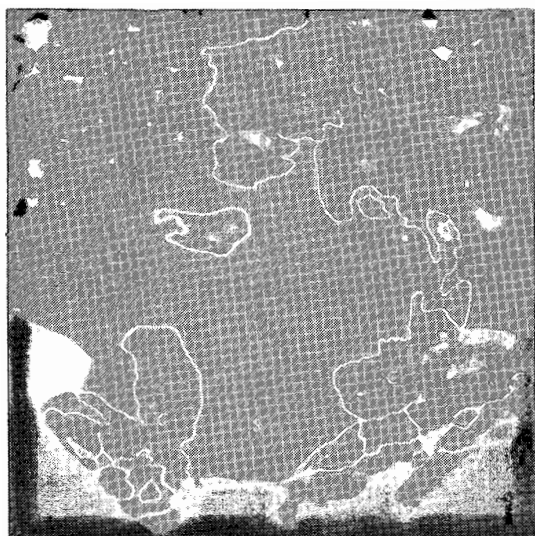


FIG. 1. Stibiobetafite (s) corroding partly disordered columbite (c) with inclusions of an unknown darker phase and niobian rutile (r). The boundary between the first two minerals is outlined in ink. Albite constitutes the dark area along the bottom margin. Polished section, polarized light, linear magnification approximately 170x.

dymite, eudidymite, milarite, bavenite, hydrocalcite, opal, carbonates and disordered hydrated talc-like phases.

Stibiobetafite occurs predominantly in veins and as replacement in aggregates of columbite and niobian rutile (Fig. 1). Intergrowths of columbite, niobian rutile, cassiterite and zircon, penetrated and covered by stibiobetafite and stokesite, occur rarely in miarolitic vugs lined with albite. The columbite-like phase is considerably disordered and its unit-cell dimensions could be adequately refined only on the basis of an ixiolite-type subcell. Its chemical composition is characterized by high Fe/Mn and Nb/Ta ratios, and by appreciable Ti and Sn contents (Table 1). The niobian rutile appears to be homogeneous; compared with other Nb-rich rutiles (Cerny *et al.* 1964), it belongs to samples with intermediate (Fe, Mn, Nb, Ta) contents (Table 1). Zircon is partly metamict and probably somewhat hydrated; it has expanded unit-cell dimensions. Relatively high Hf content, appreciable Y and REE, and virtual absence of P are noteworthy (Table 1).

Alteration of stibiobetafite seems to be rather limited. A dense network of heterogeneous alteration products, with specks of native antimony replacing stibiobetafite but leaving niobian

TABLE 1. CRYSTALLOCHEMICAL CHARACTERISTICS OF MINERALS ASSOCIATED WITH STIBIOBETAFITE

Disordered columbite		Niobian rutile		Zircon***					
wt. %	u.c. content*	wt. %	u.c. content**	wt. %					
Nb ₂ O ₅	59.1	Nb	2.15	Nb ₂ O ₅	14.3	Nb	.20	SiO ₂	29.4
Ta ₂ O ₅	16.0	Ta	.35	Ta ₂ O ₅	13.0	Ta	.11	ZrO ₂	52.5
TiO ₂	4.4	Ti	.27	TiO ₂	64.4	Ti	1.49	HfO ₂	9.2
CaO	.4	Ca	.04	CaO	-	-	-	TiO ₂	.2
FeO	12.8	Fe	.86	FeO	7.5	Fe	.19	CaO	.1
MnO	3.7	Mn	.25	MnO	.1	Mn	.002	Y ₂ O ₃	2.1
SnO ₂	1.1	Sn	.04	SnO ₂	2.4	Sn	.03	Yb ₂ O ₃	1.6
								Er ₂ O ₃	.3
								Ta ₂ O ₅	.4
97.5		101.7		95.8					
a (Å)	4.709(2)	4.622(3)		6.67					
b (Å)	5.718(3)	-		-					
c (Å)	5.110(1)	2.987(7)		6.05					
γ (Å)	137.58(6)	63.81(3)		269.16					

Electron microprobe analyses by J.H.G. Laflamme.

* based on 8 oxygens of an ixiolite-type unit-cell:
(Fe_{0.86}Mn_{0.25}Ca_{0.04}Ti_{0.27}Sn_{0.04}Nb_{2.15}Ta_{0.35})_Z = 3.96₀₈

** based on 4 oxygens of the rutile unit cell:
(Ti_{1.49}Fe_{0.19}Nb_{0.20}Ta_{0.11}Sn_{0.03})_Z = 2.02₀₄

Unit-cell dimensions by least-squares refinement of X-ray powder diffractograms calibrated with annealed CaF₂ (a = 5.462 Å)

*** unit-cell dimensions by precession (V. Kupčfk, priv. comm. 1964); low total probably due to hydration.

rutile intact, has been observed in only one specimen (Fig. 2).

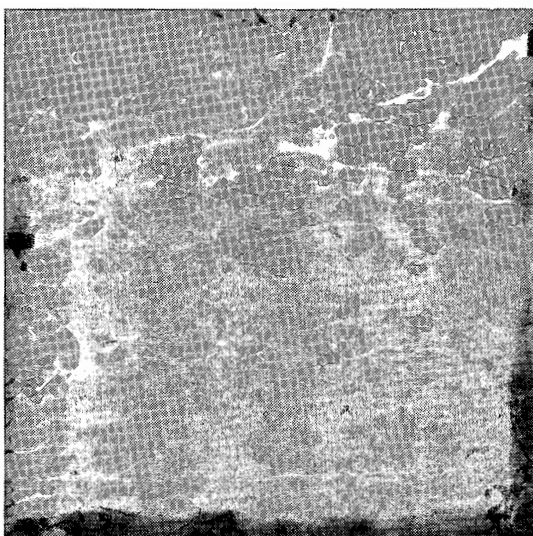


FIG. 2. Stibiobetafite (s) replaces the columbite-like phase (c) and niobian rutile (r), and is in turn replaced by inhomogeneous alteration products (x). Polished section, polarized light, linear magnification approximately 100x.

MORPHOLOGY AND PHYSICAL PROPERTIES

Stibiobetafite is generally anhedral in granular veins and replacement aggregates. Poorly developed octahedra with corners blunted by small cube faces occur in open vugs, where they may reach 8 mm in size. Stibiobetafite is dark-brown to black-brown in the natural state, but it turns pale orange after heating at 700°C for 1 h in air. The streak is pale brownish to creamy, and the lustre is vitreous. Hardness is ~ 5 but the mineral is brittle. The measured density 5.30 g/cm³ is somewhat higher than the calculated value of 5.19 g/cm³, most probably because of inclusions of the columbite-like precursor.

In transmitted light, stibiobetafite is isotropic, with $n_{\text{obs}} > 1.78$ and with n_{calc} of about 2.2, using k values of Mandarino (1976). In immersion mounts, its fragments display various shades of brown. In reflected light, stibiobetafite is medium grey, distinctly darker than columbite and niobian rutile. Its reflectance is close to that of cassiterite, which can be distinguished by anisotropic effects. Also, the polishing hardness of stibiobetafite is much lower than that exhibited by cassiterite, niobian rutile and columbite (in order of decreasing difference) but the quality of its polish is better.

CHEMICAL COMPOSITION

Electron-microprobe analyses of stibiobetafite were performed on a MAC Model 400 electron microprobe, operated at 25 kV with a specimen current of 0.03 μ A and using the following X-ray lines and standards: Ca $K\alpha$, Ti $K\alpha$ (titanite); Fe $K\alpha$, Mn $K\alpha$ (biotite); Al $K\alpha$ (gehlenite); Sb $L\alpha$, Sn $L\alpha$, Nb $L\alpha$, Ta $L\alpha$ (metals). Corrections were applied by using a slightly modified version of the EMPADR VII computer program of Rucklidge & Gasparini (1969). The ARL Ion Microprobe Mass Analyzer was used with a primary ion beam of ¹⁶O⁻ at 20 kV and 12 na, mass resolution 220, and with a vacuum at sample $< 5 \times 10^{-7}$ Torr. Data reduction followed the model of Andersen & Hinthorne (1973) for all elements except F and H, for which a modification of the method presented by Hinthorne & Andersen (1975) was used. A representative analysis by both electron- and ion-microprobe techniques was complemented by electron-microprobe checks of several grains to establish variation ranges of major components (Table 2).

An attempt to determine the valency of Sb from Mössbauer spectra failed because of insuf-

TABLE 2. CHEMICAL COMPOSITION OF STIBIOBETAFITE

	Selected grain, wt. %	range, wt. %	1/8 unit cell content based on (O,OH,F) ₇	trace contents* <1000 ppm
Nb ₂ O ₅	21.6	20.4-26.3	Ca 1.11	Li 100
Ta ₂ O ₅	19.3	9.0-20.0	Sb .69	K 360
TiO ₂	16.5	14.5-21.9	Sn .09	Be <.1
Al ₂ O ₃ *	.49	.2-.5	Fe .04	Mg 260
Sb ₂ O ₃	23.2	22.6-27.6	Mn .04	Sr 40
PbO*	.13		Na .04	B 2.1
SnO	2.9	2.7-3.8	Pb .002	Cr 6.0
FeO	.6	.5-.7	Ti .89	Y 190
MnO	.6	.5-.8	Nb .70	Si 550
CaO	14.5	14.2-14.9	Ta .38	Zr 20
Na ₂ O*	.30		Al .04	Th 6.0
H ₂ O*	.44		(OH) .21	U 230
F ₂ *	.15		F .03	P <10
			O 6.76	V <10
	100.71			Cl <50
-O=F ₂	-.06			1764.1
	100.65			

Electron microprobe analysis, J.H.G. Laflamme.
*Ion microprobe, J.R. Hinthorne and D.J. Comaford.

ficient material. Nevertheless, the trivalent state can be safely assumed as the analysis shows a good total with Sb₂O₃, and the derived formula conforms well with $A_2B_2X_7$, the general formula of the pyrochlore group with Sb³⁺ in the A group of large cations. Also, Sb³⁺ is known to enter the A sites of synthetic pyrochlore-type compounds (Piffard *et al.* 1978) as well as natural isostructural minerals (stibiconite: Mason & Vitaliano 1953). Geochemically, Sb³⁺ is well documented in stibiotantalites-stibiocolumbites that crystallize in similar stages of pegmatite evolution as stibiobetafite, indicating a favorable $f(\text{O}_2)$. Tin, iron and manganese are assumed to be divalent. In the case of Sn, this choice is supported by the composition of stannomicrolite Sn²⁺₂Ta⁵⁺₂O₇ (described originally as sukulaite: Vormá & Siivola 1967). The nature of the H-bearing species could not be determined, and all hydrogen is assumed to be present as (OH) groups. Possible errors in any of these assignments would have but negligible effect on overall cation contents and site populations. Recalculation of the analysis given in Table 2 on the basis of 7 (O,OH,F) yields a balanced formula $(\text{Ca}^{2+}_{1.11}\text{Sb}^{3+}_{0.69}\text{Sn}^{2+}_{0.09}\text{Fe}^{2+}_{0.04}\text{Mn}^{2+}_{0.04}\text{Na}^{+}_{0.04})_{\Sigma=2.01}(\text{Ti}^{4+}_{0.89}\text{Nb}^{5+}_{0.70}\text{Ta}^{5+}_{0.38}\text{Al}^{3+}_{0.04})_{\Sigma=2.01}[\text{O}_{6.76}(\text{OH})_{0.21}\text{F}_{0.03}]$, in agreement with the general formula of the pyrochlore group $A_{2-m}B_2O_6(\text{O,OH,F})_{1-m} \cdot p\text{H}_2\text{O}$.

Compositional variation seems to be rather restricted for Na_2O , CaO , FeO , MnO , SnO and Sb_2O_3 . In contrast, more extensive range is shown by TiO_2 , Nb_2O_5 , Ta_2O_5 and by the $\text{Nb}_2\text{O}_5/\text{Ta}_2\text{O}_5$ ratio. Nevertheless, the principal characteristics of the representative analysis are retained in all compositions studied: major TiO_2 , $\text{Nb}_2\text{O}_5 > \text{Ta}_2\text{O}_5$, high Sb_2O_3 .

X-RAY CRYSTALLOGRAPHY

X-ray powder diffraction patterns of natural stibiobetafite are partly obscured by the admixed columbite-like phase, as the two minerals are difficult to distinguish. Gandolfi photographs are of poor quality because of strong absorption. However, after the heat-induced color change, stibiobetafite can be easily hand-picked. The pattern of the heated material shows slight sharpening of high-angle reflections and insignificant reduction of the unit-cell edge (Table 3). The unit-cell volume, composition and measured density indicate the number of simple formula units $A_2B_2O_6(\text{O},\text{OH},\text{F})$ per unit cell to be 8.

Single-crystal precession photographs exhibit cubic symmetry with systematic absences hkl : $h+k=2n+1$; hhl : $h+l=2n+1$; Okk : $k,l=2n+1$, $k+l=4n+1$, consistent with the space

TABLE 3. X-RAY POWDER DIFFRACTION DATA FOR STIBIOBETAFITE

natural*			heated**			
I.	d_{calc}	$d_{\text{meas.}}$	hkl	I	d_{calc}	$d_{\text{meas.}}$
$\frac{1}{2}$	5.977	6.05	111	3	5.975	5.94
	3.661		022	$\frac{1}{2}$	3.659	3.65
$\frac{1}{2}$	3.122	3.11	113	2	3.120	3.11
10	2.989	(2.992)	222	10	2.987	2.988
3	2.589	2.585	004	4	2.587	2.581
	2.114		224	1	2.113	2.116
$\frac{1}{2}$	1.993	1.994	333,115	2	1.992	1.991
4	1.830	1.830	044	6	1.829	1.829
	1.750		135	1	1.749	1.754
	1.726		244	$\frac{1}{2}$	1.725	1.729
4	1.561	1.560	226	5	1.560	1.561
1	1.494	1.494	444	3	1.493	1.495
$\frac{1}{2}$	1.450	(1.451)	117,155	2	1.449	1.449
$\frac{1}{2}$	1.348	1.347	137,355	2	1.347	1.348
	1.294		008	2	1.294	1.294
	1.220		065,228	$\frac{1}{2}$	1.220	1.219
	1.188		266	3	1.188	1.187
1	1.158	1.158	048	3	1.158	1.158
$a = 10.356(2)\text{\AA}$				$a = 10.351(1)\text{\AA}$		
$V = 1110.6(7)\text{\AA}^3$				$V = 1109.0(3)\text{\AA}^3$		

* 114.6 mm camera, $\text{Cu K}\alpha$ radiation, corrected for film shrinkage; sample contaminated by columbite; reflections in brackets from Gandolfi films, with intensities adjusted by comparison with the reflections registered in both powder and Gandolfi patterns.

** 700°C/1 hr. in air; 114.6 mm camera, $\text{Cu K}\alpha$ radiation, glass-rod powder mount, corrected for film shrinkage.

group $Fd3m$ characteristic of the pyrochlore group. An additional extinction with $h,k=4n$ and $l=2n$ was observed in the unheated mineral. This is consistent with reflection limitations imposed by all 4 atomic sites in the pyrochlore structure (type E8 in the *Strukturbericht*). However, for the heated powder, a faint reflection was observed at $d = 1.729 \text{\AA}$ which may be indexed as 442.

DISCUSSION

Species and name

Selection of the name follows the chemical basis of nomenclature recommended by the I.M.A. Subcommittee on Nomenclature of the Pyrochlore Group, ratified by the I.M.A. Commission on New Minerals and Mineral Names (Hogarth 1977). In the stibiobetafite formula given above, 2Ti ($=1.78$) exceeds $\text{Nb}+\text{Ta}$ ($=1.08$); such population of the B sites classifies the mineral as a member of the betafite subgroup. Judging from Figure 1 in Hogarth (1977), the Ti content of stibiobetafite is one of the highest ever recorded in bona fide betafites. In the A position, Sb^{3+} constitutes 34.3 at.% of the population, well above the minimum of 20% required for establishing a new mineral. This gives stibiobetafite a hitherto unoccupied species status in the betafite subgroup.

Crystal chemistry

Stibiobetafite is rather exceptional among natural members of the pyrochlore group, not only by virtue of its unique Sb^{3+} content but also by its overall crystallochemical constitution: (a) all cationic and anionic sites are fully occupied; (b) the anionic composition is close to O_7 ; (c) both A and B sites have mixed-valence populations, mainly ($R^{2+}+R^{3+}$) and ($R^{3+}+R^{4+}$), respectively. This combination of characteristics departs considerably from the two most stable configurations in the pyrochlore structure derived by Pyatenko (1966) from bond-strength considerations, namely, $A^{1.56+2}B^{4.49+2}O_6(\text{OH},\text{F})$ and $A^{3.12+2}B^{3.88+2}O_6\text{O}$. These characteristics correspond closely to the most common natural and synthetic phases (e.g. microcline $\text{NaCa}(\text{Nb},\text{Ta})_2\text{O}_6(\text{OH},\text{F})$, synthetic $\text{La}_2\text{Zr}_2\text{O}_7$, and also, by introducing vacancies in the A sites, bismuthomicrocline $\text{BiTa}_2\text{O}_6\text{F}$). Stibiobetafite recalculated in this manner yields the formula $A^{2.33+2.02}B^{4.53+2.00}O_6\text{O}_{0.76}(\text{OH},\text{F})_{0.24}$. According to Pyatenko, such a composition in-

volving multiple heterovalent substitutions should be less stable than the compounds quoted above. It should be stressed, however, that stibiobetafite does not approach hypothetical compounds of the $A^{2+}_2B^{4.5+}_2O_6(OH,F)$ type [e.g., $Ca_2NbTiO_6(OH,F)$], which are geochemically possible but, in Pyatenko's analysis, crystallochemically improbable in the pyrochlore structure.

Genetic considerations

In granitic pegmatites, minerals of the pyrochlore group most commonly occur in late stages of evolution, simultaneous with or shortly after columbite-tantalite and related complex oxides. This is also the case for stibiobetafite paragenesis at its type locality. From the viewpoint of the overall geochemistry of its parent pegmatite, however, the occurrence of stibiobetafite is quite anomalous. The parent body and nearby related pegmatites carry a Ti, Nb > Ta, Be, Zr, B, Sn and REE mineralization, which is normally devoid of mineralogically noticeable quantities of Sb.

Antimony is most commonly encountered in Li,Rb,Cs-enriched pegmatites which are also distinguished by substantial B, Be, Ta > Nb and Sn mineralization with negligible, if any, Ti and REE. Sb is present in two contrasting assemblages that appear in different stages but generally late in their consolidation. Stibiotantalite-stibiocolumbite minerals are typical of late metasomatic assemblages or vug linings, post-dating columbite-tantalite but preceding microlite (Ginzburg 1956, Cerny & Harris 1973a, Foord 1977). Native antimony, stibarsen and sulfantimonides crystallize with native bismuth, sulfides and other sulfosalts as the last constituents of their parent pegmatites (Volborth 1960, Quensel 1956, Cerny & Harris 1973b, 1978).

Pyrochlore-group minerals, both pegmatitic and nonpegmatitic, do not seem to be common Sb-carriers. No Sb-bearing pyrochlores have been described to date. Similarly, betafites lack Sb, although a possible Sb-bearing Mn-member occurs in Iveland, Norway (preliminary description only: Bjørlykke 1937). Microlites are Sb-poor even where replacing stibiotantalite (Safiannikov & van Wambeke 1961, Cerny & Harris 1973b, Eid & von Knorring 1976, Foord 1977), although electron-microprobe data are lacking for most occurrences (Sofoulis 1952, Ginzburg 1956, Quensel 1956, von Knorring & Hornung 1963).

All these features of antimony behavior in granitic pegmatites, i.e., preference for rare-alkali enriched types, characteristic mineral forms and "avoidance" of the pyrochlore-microlite structure, support the contention that the described occurrence of stibiobetafite is accidental and the mineral is not likely to be found at other pegmatite localities.

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