

STIBIVANITE, A NEW MINERAL FROM THE LAKE GEORGE ANTIMONY DEPOSIT, NEW BRUNSWICK

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ABSTRACT

Stibivanite, an antimony-vanadium oxide, is a new mineral found at the Consolidated Durham Mines and Resources Ltd. antimony deposit, Lake George, New Brunswick. It occurs as very yellow green to deep yellow green radiating fibrous crystals, up to 2 mm in length, associated with native antimony, stibnite, senarmontite and pyrite. Stibivanite is monoclinic, space group is $C2/c$, a 17.989(6), b 4.792(1), c 5.500(2) Å, $\beta = 95.15(3)^\circ$ (Szymański 1980). The strongest lines in the X-ray powder-diffraction pattern are [d_{meas} (I)]: 4.646(6), 3.502(7), 3.173(7), 2.996(10), 2.114(4), 1.870(4), 1.747(4). Electron-microprobe analysis gave the composition: Sb_2O_3 79.31, VO_2 22.01, total 101.32 wt. %, corresponding to $\text{Sb}^{3+}_{2.01}\text{V}^{4+}_{0.98}\text{O}_5$. The ideal formula, Sb_2VO_5 , $Z = 4$, is confirmed by crystal structure (Szymański 1980). Calculated density is 5.264 Mg m⁻³. Stibivanite is optically biaxial negative, $n_a > 1.87$, $n_\gamma < 1.89$, $2V = 85^\circ (\pm 1^\circ)$, $r \gg v$, X is parallel to b , $Z \wedge c \sim 0^\circ$. Extinction is parallel to c . Pleochroism is strong with Y emerald green, Z olive green, X emerald green with olive tint. The mineral is readily synthesized by direct combination of Sb_2O_3 with V_2O_3 or V_2O_4 in vacuum-sealed silica tubes in the temperature range 625–675°C.

Keywords: Stibivanite, antimony-vanadium oxide, Consolidated Durham Mines and Resources Ltd. antimony deposit, Lake George, New Brunswick.

SOMMAIRE

On a découvert un nouveau minéral, la stibivanite, oxyde de Sb et de V, dans le gîte d'antimoine exploité par Consolidated Durham Mines and Resources Ltd. au lac George (Nouveau-Brunswick). Les cristaux, fibroradiés, d'un vert jaune à un vert jaune foncé, atteignent 2 mm de longueur. Antimoine natif, stibnite, senarmontite et pyrite sont les minéraux associés. La stibivanite, monoclinique $C2/c$, a pour maille a 17.989(6), b 4.792(1), c 5.500(2) Å, $\beta = 95.15(3)^\circ$ (Szymański 1980). Les raies les plus intenses du cliché de poudre sont données sous la forme d_{mes}

(I): 4.646(6), 3.502(7), 3.173(7), 2.996(10), 2.114(4), 1.870(4), 1.747(4). Une analyse à la microsonde électronique donne Sb_2O_3 79.31, VO_2 22.01, total 101.32 (% en poids), ce qui correspond à la formule $\text{Sb}^{3+}_{2.01}\text{V}^{4+}_{0.98}\text{O}_5$. La formule idéale Sb_2VO_5 ($Z = 4$) est confirmée par la structure cristalline (Szymański 1980), d'où la densité calculée, 5.264. Optiquement, la stibivanite est biaxe négative, $n_a > 1.87$, $n_\gamma < 1.89$, $2V = 85^\circ (\pm 1^\circ)$, $r \gg v$, X parallèle à b , $Z \wedge c \sim 0^\circ$, d'où extinction parallèle à c ; fortement pléochroïque: Y vert émeraude, Z vert olive, X vert émeraude à teinte olive. On peut facilement synthétiser ce minéral en combinant Sb_2O_3 avec V_2O_3 ou V_2O_4 en tube de silice scellé sous vide, entre 625 et 675°C.

(Traduit par la Rédaction)

Mots-clés: stibivanite, oxyde d'antimoine et de vanadium, Consolidated Durham Mines and Resources Ltd., gîte d'antimoine, lac George, Nouveau-Brunswick.

INTRODUCTION

In October 1978, Dr. V. Ruzicka of the Geological Survey of Canada brought to the attention of one of us (SK) an occurrence of radioactive mineralization and thucholite in the antimony ore from the Lake George deposit, New Brunswick. An examination of the specimens revealed a bright green mineral as a crust of fine, fibrous to platy crystals on some of the rock surfaces. An X-ray-diffraction pattern of the mineral could not be identified by comparison with known minerals, suggesting a new species. An attempt was made to obtain more of the mineral from the mine, but none was present in the material sent.

A short time later the green mineral was observed by Dr. J.D. Scott (Eldorado Nuclear Ltd.) in specimens from the mine dump that were believed to have originated from the 453 stope. Also, the mineral was observed in samples supplied by Ms. E. Zaleski of Eldorado Nuclear Ltd., collected from the mine 7 m west of plug 263 in the hanging wall of the

*Retired.

vein. More recently, Dr. J. Grice, National Museum of Natural Sciences, provided us with specimens that he had collected from the mine stockpile in June 1976.

Detailed mineralogical studies confirm that the green fibrous material is a new antimony-vanadium oxide mineral. The new mineral *stibivanite* (stib'i van it) is named for the composition; the mineral and name were approved by the Commission on New Minerals and Mineral Names, I.M.A., prior to publication. Type material is preserved in the Systematic Reference Series of the National Mineral Collection, Geological Survey of Canada, Ottawa (61523, 61524, 61525), the Royal Ontario Museum, Toronto (M36642) and the Mineral Sciences Division, National Museum of Natural Sciences, Ottawa.

OCCURRENCE

The Lake George deposit, now being mined by Consolidated Durham Mines and Resources Ltd., is located 40 km west of Fredericton, New Brunswick. The deposit consists of a vein system, in an area of Silurian greywacke and quartzite with associated shale and argillite, about 4 km east of a large granitic mass of Devonian age. Stibnite, the most abundant ore mineral, occupies interstices between quartz and carbonate of the vein. Earlier mineralogical studies by Abbott & Watson (1975) listed arsenopyrite and pyrite as following stibnite in abundance, with several sulfosalt and sulfide minerals in trace amounts: tetrahedrite, chalcostibnite, plagiönite, fülöppite, bournonite and

cubanite. The particular specimens examined in this study contain native antimony as the major constituent, followed by stibnite, senarmontite, pyrite, stibivanite, arsenopyrite and sphalerite. These specimens were selected for their stibivanite contents and are not representative of the ore. St. Pierre & Bourgoin (1978) reported that stibnite is the main ore mineral, with some ore zones also containing 1 to 5% native antimony.

Abbott & Watson (1975) identified three stages of mineralization. The first stage consisted of euhedral pyrite and arsenopyrite, followed by stibnite and various sulfosalts, with the third stage forming cubanite. Our limited observations support those of Abbott & Watson. The evidence suggests that native antimony and stibnite crystallized simultaneously, with stibivanite and senarmontite forming in the same stage of mineralization or shortly thereafter.

PHYSICAL AND OPTICAL PROPERTIES

Stibivanite occurs as radiating fibrous crystals up to 2 mm in diameter. The color is very yellow green (115) (colors and numbers refer to ISCC-NBS Centroid Color Charts) to deep yellow green (118). The mineral is easily split into fine, flexible and elastic lath-shaped fibres (Fig. 1).

The streak of stibivanite is white, and the lustre is adamantine. A sample sufficient for density measurements could not be separated from the hand specimens; however, the calculated density is 5.267 Mg m^{-3} . Micro-indentation hardness, based on nine indentations on

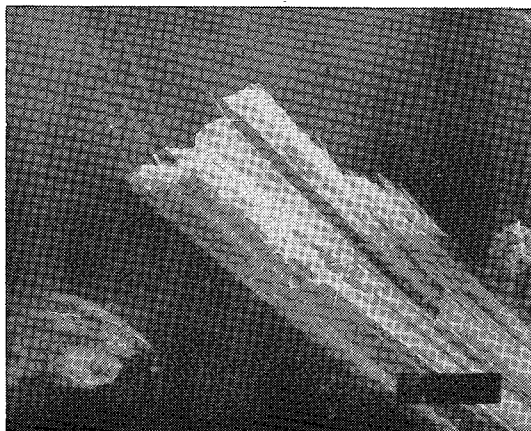


FIG. 1. Scanning electron-microscope image of stibivanite showing its fibrous properties.

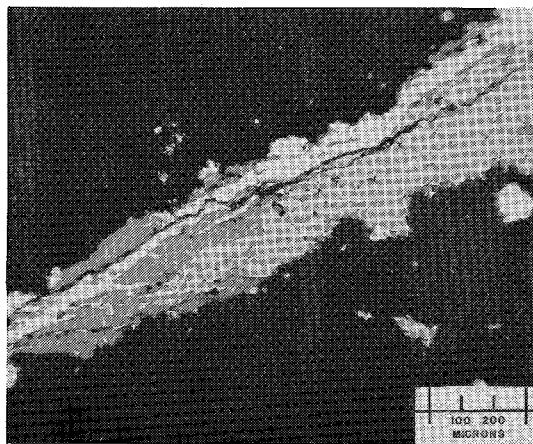


FIG. 2. Optical photomicrograph of a fracture filled with stibivanite (medium grey), stibnite (light grey) and native antimony (white).

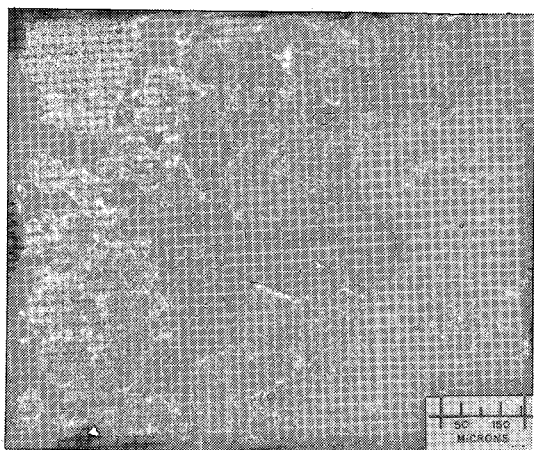


FIG. 3. Photomicrograph of stibivanite with inclusions of native antimony (white) and senarmonite (dark grey) interstitial to quartz.



FIG. 4. Photomicrograph of homogeneous euhedral stibivanite associated with carbonate and quartz.

several grains, gave $VHN_{50} = 232$ (148–286), equivalent to a Mohs hardness of 4.3(2).

Optically, stibivanite is biaxial negative with $2V = 85^\circ (\pm 1^\circ)$. The indices of refraction are $n_\alpha > 1.87$, $n_\gamma < 1.89$. The orientation of the fragments, relative to the lath-shaped habit (elongated c), is $b = X$; angle between c and Z is about 0° , and thus extinction parallel to c . Dispersion is strong with $r \gg v$. Optical sign is length slow (+). The pleochroism is strong with Y emerald green, Z olive green and X emerald green with olive tint.

Seen in polished section, stibivanite occurs in veins and as fracture fillings closely associated with native antimony, stibnite and senarmonite (Fig. 2). It also occurs as isolated crystals, interstitial to quartz (Figs. 3, 4), some of which are completely free of inclusions. The maximum size of these crystals is about 100 μm . The mineral is moderately anisotropic, ranging from light to dark grey with some green to yellowish internal reflections. The mineral is not soluble in cold concentrated HCl or HNO_3 , but dissolves readily in aqua regia.

COMPOSITION

Stibivanite was chemically analyzed with a MAC 400 electron microprobe. The data were corrected using a modified version of the EMPADR VII computer program of Rucklidge & Gasparini (1969). Energy-dispersive and wavelength analyses indicated only antimony and vanadium, suggesting that the mineral is essentially an oxide. Infrared analysis revealed the absence of OH or H_2O . With synthetic V_2O_5 (for V) and stibnite (for Sb) as standards, the analysis gave two choices: Sb_2O_3 79.31, V_2O_5 19.89, total 99.20 wt. % corresponding to $\text{Sb}^{3+}_{4.03}\text{V}^{3+}_{1.97}\text{O}_9$ (basis O = 9) or Sb_2O_3 79.31, VO_2 22.01, total 101.32 wt. % corresponding to $\text{Sb}^{3+}_{2.01}\text{V}^{4+}_{0.98}\text{O}_5$ (basis O = 5). Subsequent crystal-structure analysis (Szymaniński 1980) confirmed Sb_2VO_5 .

SYNTHESIS

Various synthesis investigations were carried out to elucidate the valence states of antimony and vanadium, the possible compositional variations as well as general reaction rates and volatilities that could be of use in determining the genesis of the mineral. The various oxides employed for the synthesis work were weighed, mixed in a mortar and either pelletized or spread lightly in silica boats. The mixtures were then vacuum-sealed in silica tubes and subjected to various temperature–time heating programs. The final products were examined microscopically, by X-ray-diffraction and electron-microprobe analyses and by scanning electron microscopy. The results showed that the new mineral can be synthesized readily by direct combination of Sb_2O_3 with V_2O_3 or V_2O_4 , but not with combinations of either Sb_2O_4 or V_2O_5 . High temperatures favor the formation of homogeneous crystal tufts. The optimum temperature range is $625\text{--}675^\circ$, and extensive crystal development occurs on the walls of the tubing re-

TABLE 1. X-RAY POWDER-DIFFRACTION DATA FOR STIBIVANITE

I	d meas	d calc	hkl	I	d meas	d calc	hkl
2	9.01	8.959	200	3	2.031	2.032	711
6	4.646	4.630	110	1	1.942	1.944	421
1/2	4.486	4.479	400	4	1.870	1.869	620
1/2	3.730	3.738	310	1/2	1.818	1.815	802
1/2	3.579	3.577	111			1.792	10.0.0
7	3.502	3.496	111	4	1.787	1.789	222
7	3.173	3.172	311			1.788	911
10	2.996	3.010	311	1/2	1.751	1.748	222
		2.986	600	3	1.714	1.712	113
1/2	2.875	2.870	510	3	1.701	1.701	911
1/2	2.738	2.739	002	1/2	1.687	1.685	113
1/2	2.682	2.688	202	1	1.661	1.662	802
1	2.618	2.621	511	1	1.639	1.640	422
1/2	2.556	2.556	202			1.597	821
1/2	2.474	2.470	511	1	1.594	1.593	513
1/2	2.436	2.436	402	1/2	1.567	1.565	10.0.2
2	2.394	2.396	020	1	1.545	1.543	330
2	2.314	2.315	220	1/2	1.525	1.525	131
1/2	2.151	2.150	221			1.494	331
4	2.114	2.115	602	3	1.494	1.493	12.0.0
		2.113	420			1.493	513
1/2	2.059	2.057	512	(28 more lines below $d = 1.494$)			

114.6 mm Debye-Scherrer camera, Fe-filtered Co radiation, $\lambda = 1.7902$. Values of d meas were obtained on material from type locality; values of d calc are based on cell dimensions from structure analysis of synthetic crystal. a 17.989(6), b 4.792(1), c 5.500(2) Å, β 95.15(3)°. Space Group C2/c.

mote from the charge. Although variations in the ratio of $Sb_2O_3:VO_2$ were observed in massive products, the euhedral crystals were consistently very near $2Sb_2O_3 \cdot V_2O_4$ in stoichiometry. Although the mineral apparently contains V^{4+} , the best crystals were obtained starting with V_2O_5 . During reaction the vanadium was oxidized to the tetravalent state, and some of the Sb_2O_3 was reduced to the metallic state. Darriet *et al.* (1976) also found that this compound was best prepared starting with V_2O_5 but with equivalent proportions of Sb_2O_3 and Sb_2O_4 .

X-RAY CRYSTALLOGRAPHY

The X-ray powder-diffraction pattern of stibivanite, given in Table 1, is in reasonable agreement with that of Darriet *et al.* (1976) for synthetic Sb_2VO_5 . Single-crystal studies of the natural and synthetic materials gave identical results. A structure analysis, using a synthetic crystal, is reported separately by Szymański

(1980). The results show that stibivanite is monoclinic, space group C2/c, a 17.989(6), b 4.792(1), c 5.500(2) Å, $\beta = 95.15(3)^\circ$. The structural analysis confirms that the ideal formula is $Sb^{3+}_2V^{4+}O_5$, $Z = 4$. Along a , the structure is characterized by bonded groups of $(SbO_3-VO_5SbO_3)$ units, which do not bond to adjacent units along a . These units form continuous ribbons in the c direction, but are not bonded in the b direction. This accounts for the fibrous acicular form of the crystals, with c being the needle axis, and for the perfect cleavage in the $a-c$ and $b-c$ planes.

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