

AUROSITIBITE, AuSb_2 ; A NEW MINERAL IN THE PYRITE GROUP¹

A. R. GRAHAM² AND S. KAIMAN³

Mines Branch, Ottawa, Canada.

ABSTRACT

A new mineral identical with the intermetallic compound AuSb_2 has been found in gold ores from the Giant Yellowknife mine, Northwest Territories, and from the Chesterville mine, Larder Lake, Ontario. In the former locality it occurs in dolomitic carbonate and quartz with gold, freibergite, stibnite, jamesonite, chalcostibite, bournonite, arsenopyrite, pyrite, chalcopyrite, and sphalerite; in the latter in quartz with gold, freibergite, galena, tennantite, bournonite, chalcopyrite, sphalerite, arsenopyrite, gersdorffite, and pyrite. In polished section the mineral is galena-like with a slight pinkish tinge; in hand specimen minute anhedral grains show a bornite-like tarnish. The standard etch reactions in the order of reactivity are: HNO_3 , FeCl_3 , HCl , KOH positive; HgCl_2 and KCN negative. The hardness is C-. The composition of the mineral was determined by comparing its x-ray powder pattern with that of the synthetic compound, and was checked by microchemical tests. The crystal structure is pyrite type; the unit cell containing Au_4Sb_8 has $a = 6.646 \pm 0.003$ kX (synthetic 6.644 ± 0.003 kX); the single Sb parameter is 0.386 ± 0.007 . The calculated gravity is 9.91 compared with 9.98 measured on synthetic material.

DISCOVERY

The mineral later identified as the natural counterpart of the artificial compound AuSb_2 was first observed by the senior author in rich gold ore specimens from the Giant Yellowknife mine, N.W.T. which had been submitted for examination to the Mineragraphic Laboratory of the Mines Branch. Rounded anhedral grains less than 200 microns in diameter showing a bornite-like tarnish were noticed on one hand specimen adjacent to hackly masses of native gold. The x-ray powder data obtained from these grains proved to be unlisted in available mineralogical publications. An identical powder pattern was later obtained from galena-like grains of similar dimensions and association noticed by Mr. W. E. White of the Mineragraphic Laboratory, in a polished section of gold ore from the Chesterville mine, Larder Lake, Ontario. The coincidence of two widely separated localities containing the same unidentified mineral in such an interesting association impelled the authors to establish its identity.

¹ Published by permission of the Director-General of Scientific Services, Dept. of Mines and Technical Surveys.

² Mines Scientist, Mineral Dressing and Process Metallurgy Division, Mines Branch, Dept. of Mines and Technical Surveys.

³ Mineralogist, Radioactivity Division, Mines Branch, Dept. of Mines and Technical Surveys.

IDENTIFICATION PROCEDURE

Since insufficient pure material was available for quantitative analysis, even spectrographically, the investigation was pursued on the basis of the *x*-ray data alone. The pattern could be indexed completely on the basis of a simple cubic structure, with cell-edge about 6.6 kX, using the Hull-Davey cubic crystal analyzer. This cell-edge compared most favourably with that listed in the cubic crystal structure tables of Knaggs, Karlik, and Elam (1932) for the artificial compound AuSb₂. Search of metallurgical references located *x*-ray powder data on AuSb₂ given by Bottema and Jaeger (1932) which were identical with those of our mineral. The existence of AuSb₂ as a mineral was consistent with the mineral assemblages in the ores from both localities, which included native gold, and antimony-bearing minerals. Microchemical tests on the mineral confirmed the presence of gold and antimony.

The artificial compound has been well established as the only intermediate compound in the binary system Au-Sb. It was described as a synthetic product by Vogel (1906) during investigations of certain metallic systems. Oftedal (1928), using *x*-ray powder methods, determined its structure as pyrite-type, giving a value of 3/8 for the single Sb parameter. Nial, Almin, and Westgren (1931), Bottema and Jaeger (1932) and Grigorjew (1932), all agreed within experimental error concerning the phase relations in the Au-Sb system, and confirmed the existence of AuSb₂ as an intermetallic compound with distinctive physical properties. This work as summarized in Hansen (1936) shows that in the system Au-Sb an eutectic point exists between Au and AuSb₂ at about 25% Sb, and a temperature of 360° C. A triple point among melt, AuSb₂, and Sb occurs at about 54% Sb and a temperature of 460° C. The compound with stoichiometric composition 55.2% Sb dissociates at the latter temperature to a mixture of gold-rich liquid and solid Sb. Little solid solution of either gold or antimony in AuSb₂ is shown. Bottema and Jaeger gave evidence of three polymorphous modifications of AuSb₂ with inversion temperatures at about 355° C. and 405° C.

As further confirmation of the identity of the mineral, several attempts were made to synthesize pure AuSb₂ by dry fusion of stoichiometric proportions of Au and Sb. Various techniques were employed in an endeavour to homogenize the product. These included sintering under argon at atmospheric pressure just below the dissociation temperature, and very slow cooling of a melt under the same conditions. The most successful convenient method was found to be repeated fusion and solidification in evacuated and sealed silica glass tubes small enough to prevent condensation of distilled antimony upon unevenly heated walls.

Microscopic examination at high magnification of polished sections of

all products showed evidence of incongruent melting of the compound in narrow selvages of a yellow and white eutectic mixture on the boundaries of coarse white grains of a main phase. Small blebs of unreacted antimony were enclosed in the main phase. The more successful fusions had less than 1% unreacted antimony and eutectic, a proportion insufficient to alter materially the composition of the main homogeneous product. The latter gave an *x*-ray powder pattern identical with that listed for $AuSb_2$ and with that of the mineral under study.

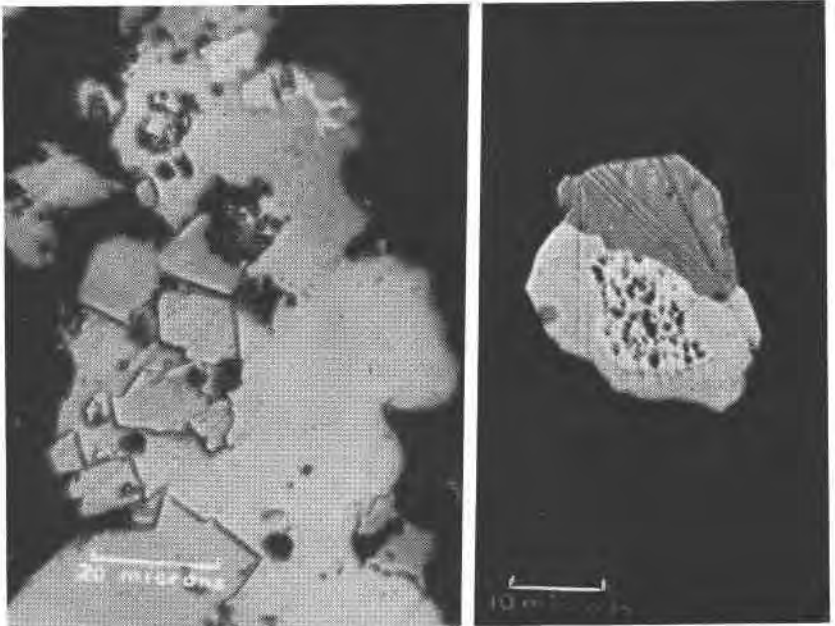
The name "aurostibite" was selected to indicate the composition of the mineral, and a more complete mineragraphic and crystallographic description attempted.

OCCURRENCE AND PHYSICAL PROPERTIES

Search of the available specimens from both the Giant Yellowknife and Chesterville mines located minute amounts of aurostibite in three polished sections and one hand specimen from the former locality, and in one polished section and two hand specimens from the latter. The mineral assemblages from both localities were quite similar. The type specimen from Giant Yellowknife is a two-inch fragment of grayish-white impure vein quartz, somewhat fractured, and containing partly absorbed inclusions of chloritized and silicified wall-rock heavily mineralized with fine euhedral arsenopyrite. The walls of narrow vugs in the vein quartz are coated with minute imperfect rhombohedral crystals of dolomitic carbonate and thin flakes of sericite mica less than $\frac{1}{4}$ mm. across. Among the carbonate crystals in these vugs scattered grains of hackly gold varying in size from about 20 microns up to 1 or 2 mm. occur accompanied by rounded iridescently tarnished separate grains of aurostibite up to about 350 microns in greatest dimension. Certain of the gold grains appeared to be thinly coated with tarnished gray aurostibite; thinner layers of aurostibite may account for rusty-brown tarnish occurring on other gold grains. Occasionally, films of gold appeared to be interleaved between laminae of the mica. From these relationships, it could be inferred that the gold and aurostibite were late in the sequence of mineral deposition, and that the deposition of aurostibite probably continued after that of gold.

The polished sections of Giant Yellowknife ore confirm the occurrence of aurostibite and gold closely related to a late period of carbonate, quartz and sericite deposition in a series of fractures cutting clear quartz. The clear quartz itself has apparently filled fractures in an earlier milky quartz, which has been largely absorbed and recrystallized. The latter now appears as irregular grayish-white blocks floating in the clear quartz matrix. Both the early grayish and the later clear quartz contain irregu-

lar masses of bournonite, chalcopyrite, sphalerite, and bladed and fibrous masses of jamesonite and chalcostibite, more or less closely associated with masses and strings of arsenopyrite and pyrite crystals. The wall-rock inclusions appear to be mineralized exclusively with disseminated euhedral crystals of pyrite and arsenopyrite. Single grains of gold and aurostibite occur scattered in quartz and carbonate immediately adjacent to fractures in the clear quartz. Small areas and elongated masses



FIGS. 1, 2. Aurostibite, AuSb_2 . Fig. 1, (left) $\times 800$: Polished section of ore from Giant Yellowknife Mine, N.W.T. Light gray euhedral crystals with high relief are arsenopyrite; the light gray groundmass is aurostibite slightly etched with 1:1 HCl; white areas in upper right hand corner are native gold; black areas are holes in the section, and carbonate and quartz gangue. Fig. 2, $\times 1200$: Polished section of ore from Chesterville Mine, Ontario. The stippled area is native gold; the white smooth-polished area is aurostibite; the medium gray area is freibergite; the black field is quartz gangue.

of aurostibite up to 350 microns in size lying in carbonate-filled fractures enclose or partly armour gold grains and euhedral arsenopyrite (Fig. 1). Grains of freibergite, sphalerite, and minute areas of a highly anisotropic gray-white mineral resembling stibnite were observed close to aurostibite, but without direct evidence of deposition sequence. The observed relationships in the polished sections agree with those in the hand specimen. Deposition of gold and aurostibite must have begun ap-

proximately simultaneously, while partial armouring and inclusion of gold by aurostibite indicates persistence of deposition of the latter.

In the two hand specimens from the Chesterville locality, the aurostibite occurs sparsely as minute grains embedded in clear dark quartz near and attached to small hackly masses of bright yellow gold. Where gold is undisturbed below the surface of clear quartz, coatings of light gray aurostibite and darker gray freibergite partly armour some of the extremities of the irregular gold grains. Deformation of the gold during excavation of samples with a needle point usually caused rupture and loss of the brittle coatings. The aurostibite from Chesterville did not show the bornite-like tarnish characteristic of that from Giant Yellowknife: the grains in hand specimen were difficult to distinguish visually from the other gray minerals present.

The polished section of Chesterville ore reveals sparse grains of aurostibite up to 250 microns in diameter in clear quartz closely associated with gold, freibergite, chalcopyrite, jamesonite, and galena. This clear quartz, as in the Giant Yellowknife specimen, has largely absorbed and recrystallized an older, less transparent, milky-white quartz which is now mineralized with pyrite, arsenopyrite, gersdorffite, chalcopyrite, sphalerite, and tetrahedrite. An elongated body of dark impure quartz traverses the length of the sectioned fragment, containing coarse (up to 3 mm.), fractured, subhedral pyrite, euhedral arsenopyrite, and euhedral to anhedral gersdorffite, which have been partly replaced by minor chalcopyrite, sphalerite, and tetrahedrite, and seamed by veinlets of gold. On both sides of this body, which might represent a nearly absorbed fragment of mineralized wall-rock, irregular areas of the later quartz carry quantities of free gold, aurostibite, freibergite, jamesonite, galena, chalcopyrite, and tennantite.

After the initial fracturing or shearing, the sequence of events appears to have begun with a primary surge of mineralization, consisting of milky quartz accompanied by pyrite, arsenopyrite, gersdorffite, chalcopyrite and sphalerite, which silicified and mineralized the inclusion of wall-rock. Fracturing later permitted the entry of the clear quartz, accompanied by more chalcopyrite and tetrahedrite, bournonite, jamesonite, and tennantite. This age of quartz re-crystallized and partly absorbed the fractured blocks of early white quartz. Further fracturing shattered the clear quartz, and further chalcopyrite, with sphalerite, galena, freibergite, gold, and aurostibite were deposited in and near these fractures as fillings and replacements.

Gold appears to have been deposited in the wall-rock inclusion sparingly in and around the fractured pyrite, arsenopyrite and gersdorffite, while in larger quantities it forms an interlocking stockwork generally

following the late fractures in the clear quartz. Freibergite and gold in the clear quartz show mutual boundaries indicating contemporaneity. Several grains of freibergite attached to gold grains are surrounded and partly replaced by aurostibite, which also partly armours adjacent gold grains (Fig. 2). Where aurostibite and gold occur with chalcopyrite, both send apophyses into it. No aurostibite was recognized in the area of the wall-rock inclusion.

The tests usually employed for identification of minerals in polished section reveal interesting diagnostic properties for aurostibite. The visual reflectivity and colour closely resemble those of galena. A slight pinkish tinge was noticeable on direct comparison with neighbouring galena in the Chesterville sections, but without such direct comparison, the colour may be described as galena-white. Its hardness, estimated by needle scratch, is C-, slightly harder than gold. As polished with magnesia, using a variation of the Sampson-Patmore technique, little relief is evident among gold, aurostibite, and freibergite, although the white, smooth-polishing aurostibite contrasts well with the stippled surface produced upon the yellow gold, and with the medium-gray, smooth-polishing freibergite. Aurostibite is quite brittle, in contrast to the soft-

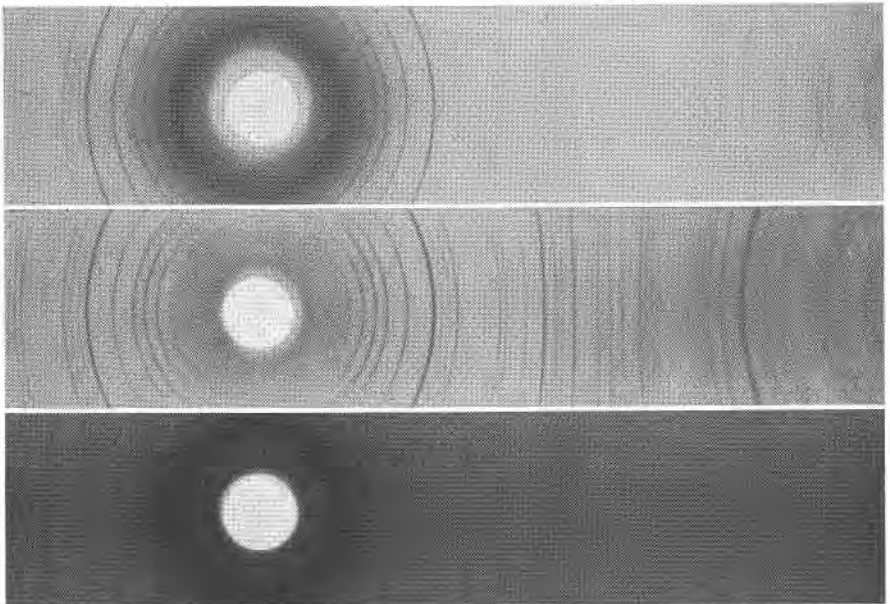


FIG. 3. Powder photographs, $\text{CuK}\alpha$ -radiation, Ni filter. Full size contact prints. ($1^\circ = 1$ mm. in film.) 1. Aurostibite, Giant Yellowknife Mine, N.W.T. 2. Artificial AuSb_2 . 3. Pyrite, Lynn Lake, Manitoba.

ness and malleability shown by many of the tellurides often associated with gold. There is no apparent cleavage.

Etch reactions according to the technique used by Short (1940) place aurostibite in a sub-group not listed in his tables. HNO_3 (1:1) reacts rapidly to form an iridescent coating. HCl (1:1) gives a dark-brown stain; on the synthetic compound the reagent drop "sweats," forming an aureole of lesser drops, which produce a brown to iridescent halo. The reaction on the mineral may be negative when the drop also covers adjacent carbonate gangue. $FeCl_3$ (20%) immediately forms an iridescent coating. KOH (40%) slowly forms a light brown coating and accentuates polishing scratches. $HgCl_2$ (5%) and KCN (20%) give no reactions. These etch reactions were essentially the same on both natural and synthetic material.

No gravity measurements were made on natural material; that measured on synthetic $AuSb_2$ is 9.98.

CRYSTALLOGRAPHY

The close analogy in relative spacings and intensities of x -ray diffractions registered on the powder photograph with those of pyrite left no doubt that the crystallographic description of aurostibite is pyrite-type, class $2/m\bar{3}$, space group $Pa\bar{3}$, with a unit-cell content of Au_4Sb_8 . The cell-edge of the natural material, calculated from the measurements of six back reflections, is 6.646 ± 0.003 kX. Our artificial product gave $6.644 \pm .003$ kX by the same method. These values are included in the table of old and new values of the cell-edge of $AuSb_2$ (Table 1).

TABLE 1. CELL-EDGE OF $AuSb_2$

Investigators	Cell-edge (kX)
Oftedal (1928)	6.636 ± 0.001
Nial, Almin, and Westgren (1931)	6.647 ± 0.005
Bottema and Jaeger (1932)	6.636
Graham and Kaiman (1951)	6.644 ± 0.003
Graham and Kaiman, on aurostibite (1951)	6.646 ± 0.003

The Sb parameter was refined from the approximate value of $3/8$ obtained by Oftedal (1928) on his artificial product, to 0.386 ± 0.007 in the natural mineral. The method employed to obtain this value was the usual one of calculating relative intensities (neglecting temperature and absorption factors) over a generous range of parameter values, comparing them with those observed, and selecting the best fit. The final calculated and observed relative intensities are listed with the powder diffraction

TABLE 2. AUROSTIBITE—AuSb₂: X-RAY POWDER PATTERN IN kX
Cubic, *Pa*3; *a* = 6.646 kX; *Z* = 4

θ (Cu)	<i>d</i> (meas)	<i>d</i> (calc)	hkl	I (obs)	I (calc)	θ (Cu)	<i>d</i> (meas)	<i>d</i> (calc)	hkl	I (obs)	I (calc)
11.60	3.82	3.837	111	1	1.9	50.20	1.001	1.002	226	$\frac{1}{2}$	0.6
13.375	3.32	3.323	002	5	6.5	51.00	0.989	0.991	{063 245}	$\frac{1}{2}$	0.4
15.00	2.97	2.972	021	4	4.8	51.73	0.979	0.980	136	$\frac{1}{2}$	0.4
16.48	2.71	2.713	112	3	4.2	55.58	0.932	0.931	{117 155}	1*	0.4
19.14	2.34	2.350	022	4*	3.9	56.56	0.921	0.922	046	$\frac{1}{2}$	1.3
22.62	1.999	2.004	113	10	9.0	57.46	0.912	0.913	{027 146 127}	1*	0.7
23.67	1.914	1.919	222	1	1.4	58.265	0.904	0.904	{255 336}	1	0.8
24.75	1.836	1.843	023	1	1.9	59.94	0.888	0.888	246	2	1.5
25.70	1.773	1.776	123	2	2.3	62.65	0.865	0.865	{137 355 065}	5	3.5
30.355	1.521	1.525	133	$\frac{1}{2}$	1.0	64.65	0.851	0.851	{346 237 156}	1	0.7
31.26	1.482	1.486	024	1	1.3	65.55	0.844	0.844	246	1	0.8
32.14	1.445	1.450	124	1	0.9	67.71	0.831	0.831	008	2*	0.9
32.94	1.414	1.417	233	$\frac{1}{2}$	0.4	72.52	0.806	0.806	{028 446}	2	1.7
34.615	1.353	1.357	224	1	1.3	73.92	0.800	0.800	{128 247}	2	1.8
37.02	1.277	1.279	{115 333 025 234}	3	3.3	75.45	0.794	0.794	356	$\frac{1}{2}$	0.9
38.65	1.231	1.234	125	$\frac{1}{2}$	0.6	78.95	0.783	0.783	{228 066}	4*	3.0
39.39	1.211	1.213	135	$\frac{1}{2}$	0.5						
40.86	1.175	1.175	044	2*	1.9						
43.16	1.124	1.123	{006 244 116 235}	1	1.0						
43.97	1.107	1.108	244	1	1.0						
45.52	1.078	1.078	116	1	0.8						
47.17	1.048	1.051	026	$\frac{1}{2}$	0.6						
49.47	1.011	1.014	335	2*	1.1						

* Observed intensities probably increased by coincident diffractions from free gold.

data in Table 2. The value 0.386 is identical with that quoted by Parker and Whitehouse (1932) for the *S* parameter in pyrite. Multiplying their calculated distances of closest approach, Fe—S = 2.26 kX, S—S = 2.14 kX, by the ratio of the cell-edges of aurostibite and pyrite (6.646/5.405) gives the theoretical values Au—Sb = 2.78 kX, Sb—Sb = 2.63 kX. Calculated geometrically from the cell-edge of aurostibite using 0.386 as the *Sb* parameter, the actual distances of closest approach are Au—Sb = 2.78 kX, Sb—Sb = 2.62 kX, in good agreement with the above values. The Sb—Sb distance in the structure is considerably less than the shortest Sb—Sb distance 2.87 kX in the structure of the element (Strukturbericht, 1, 27). This fact is probably the result of partial covalent bonding between the *Sb* atoms in the pairs.

DISCUSSION

As well as being of scientific interest as another member of the pyrite group of minerals, aurostibite has economic significance as a gold mineral relatively insoluble in cyanide solution. Antimony-bearing gold ores have

often proved refractory to ordinary ore-dressing methods in the past. It is possible that aurostibite is widespread in such ores, minutely subdivided, but perhaps in important quantities. In a personal communication Dr. Frank Stillwell of the University of Melbourne, Australia, states that a gold and antimony-bearing mineral which he suspects to be identical with aurostibite occurs in an antimonial gold ore from Costerfield, Australia. Armouring of gold by aurostibite would certainly cause losses in the ordinary cyanide mill-circuit out of all proportion to the amount of gold actually present in the mineral itself. The behaviour of aurostibite under the roasting conditions often employed in treating such ores is as yet unknown. The ease of its formation from metallic antimony and gold could undoubtedly cause trouble in improperly controlled roasting processes.

REFERENCES

- BARRETT, C. S. (1943): *Structure of Metals*, Metallurgy and Metallurgical Engineering Series, McGraw-Hill, N. Y.
- BOTTEMA, J. A. & JAEGER, F. M. (1932): *Proc. Kon. Akad. Wetensch., Amsterdam*, **35**, 916-928.
- BRAGG, W. L. (1914): *Proc. Roy. Soc. London*, Series A, **89**, 468.
- BUERGER, M. J. (1941): Numerical Structure Factor Tables. *Geol. Soc. Amer.*, Special Papers, **53**.
- GRIGORJEW, A. T. (1932): *Zeits. anorg. allg. Chem.*, **209**, 289-294.
- HANSEN, M. (1936): *Der Aufbau der Zweistofflegierung*, Springer, Berlin.
- Internationale Tabellen zur Bestimmung von Kristallstrukturen*, Bornträger, Berlin (1935).
- KNAGGS, I. E., KARLIK, B., & ELAM, C. F. (1932): *Tables of Cubic Crystal Structure*, London, Adam Hilger.
- LONSDALE, K. (1936): *Simplified Structure Factor and Electron Density Formulae, for the 230 Space-Groups of Mathematical Crystallography*, G. Bell and Sons, London.
- NIAL, O., ALMIN, A., & WESTGREN, A. (1931): *Zeits. phys. Chem. B*, **14**, 81-82.
- OFTEDAL, I. (1928): *Zeits. phys. Chem.*, **135**, 291-299.
- PARKER, H. M., & WHITEHOUSE, W. J. (1932): *Phil. Mag.*, **14**, 939-961.
- SHORT, M. N. (1940): Microscopic determination of the ore minerals, *U. S. Geol. Surv. Bull.* **914**.
- VOGEL, R. (1906): *Zeits. anorg. allg. Chem.* **50**, 151-157.