

MICHENERITE AND FROODITE, PALLADIUM BISMUTHIDE MINERALS

J. E. HAWLEY AND L. G. BERRY

Queen's University, Kingston, Ontario

ABSTRACT

Two palladium bismuthides from nickeliferous ores of the Frood Mine, Sudbury, Ontario, detected and described by C. E. Michener some years ago, are re-described and named michenerite and froodite. Michenerite is an isometric form of PdBi_2 with a pyrite structure, $a = 6.68 \text{ \AA}$. It is greyish white, soft, brittle, with no cleavage. Froodite is grey, soft, brittle, with one perfect cleavage (100) and one less perfect (001), monoclinic— $C2/m$ with $a = 12.75$, $b = 4.29$, $c = 5.67$, $\beta = 102^\circ 52'$, containing 4 $[\text{PdBi}_2]$. It is identical with synthetic $\alpha\text{-PdBi}_2$ formed at moderate temperatures.

INTRODUCTION

The chief purpose of this paper is the proposal of names for two palladium bismuthides discovered some years ago in nickeliferous ores of the Frood mine, Sudbury district, Ontario.

All who have studied the ores of Sudbury have long been familiar with the problem of the manner of occurrence of palladium, the most abundant platinoid in the ores. Years ago Dr. A. P. Coleman noted that palladium could not possibly be accounted for in the composition of the only platiniferous mineral (sperrylite) known then in these deposits. For some years the senior author, with his students, has been studying the ore minerals of this famous area, both in polished sections and by spectrographic means. Until recently no indication was found of a distinct palladium species, although the erratic occurrence of palladium in both arsenical ores, in some galena, and also in chalcopyrite, and the rather constant association with it of bismuth, gave strong indications of the actual existence of palladium bismuthides.

During the past year a re-study of our collections by the senior author and R. L. Stanton again focussed attention on the palladium problem. An investigation of the literature uncovered the work of Dr. C. E. Michener and associates, results of which are embodied in his doctorate thesis, University of Toronto, 1940. Dr. Michener has been kind enough to place this at our disposal and to permit publication of the data obtained at that time. Subsequent investigations on artificial alloys of palladium and bismuth by Burr & Peacock (1942) have also been of assistance in comparisons of the natural minerals and synthetic products.

The following descriptions are entirely the work of Michener and associates. Results of our own observations are to appear in a later paper on the mineralogy of these ores. Our discussion, however, of the composition of the two species is based on comparisons of x -ray data on artificial PdBi_2 and PtBi_2 with the natural minerals, data not available to Michener at the time his thesis was written.

Two palladium bismuthides, one isotropic and the other anisotropic were found by superpanning mill concentrates from arsenic- and lead-copper-rich ores of the Frood mine. Of the two the isotropic mineral for which the name michenerite is suggested, is reported to be the more abundant.¹ The anisotropic mineral, here named froodite, has been seen only rarely as isolated particles in mill concentrates.

MICHENERITE

This mineral was referred to in the early unpublished reports as Pd_{xx} and later as Pd_2Bi_3 .

The mineral was separated from a few milligrams of 325 mesh precious metal mill-concentrate by immersion in dilute nitric acid and removal of such grains as gave a distinct yellow palladium reaction, by means of a capillary tube.

The mineral is greyish white in colour, has a dull metallic lustre, black streak, with no visible cleavage. It is brittle, has a hardness of B(2.5). Specific gravity is between sperrylite and galena, probably about 9.5

Chemical analyses using the dithizone method on three samples gave an apparent ratio of $\text{Pd}:\text{Bi} = 2:3$. As will be seen later there is reason to believe that the true composition is PdBi_2 .

Optical properties as determined by Michener are as follows: light grey, isotropic.

Etch reactions: HNO_3 —effervesces slowly, blackens; FeCl_3 —slowly stains dark, some negative; Aqua regia—instantly stains black; HCl , KCN , KOH —negative.

With the cooperation of Dr. G. A. Harcourt and E. Cornford the original x -ray film #241, which is reproduced in Michener's thesis as representing " Pd_2Bi_3 ", was located in their files. The envelope bears the identification: " $\#241, \text{Cu}, \text{Pd}_{xx}, \text{Pd}_2\text{Bi}_3$ " together with a note by the late Professor M. A. Peacock "not found in Pd-Bi alloys M.A.P. June '42." This note refers to the fact that the pattern is unlike that of any product found by Burr & Peacock (1942) in their study of the Pd-Bi system.

Michener noted that the pattern could be indexed on a cubic lattice and is similar to the patterns of gersdorffite-ullmannite. X -ray powder

¹Private communication, September 5, 1939.

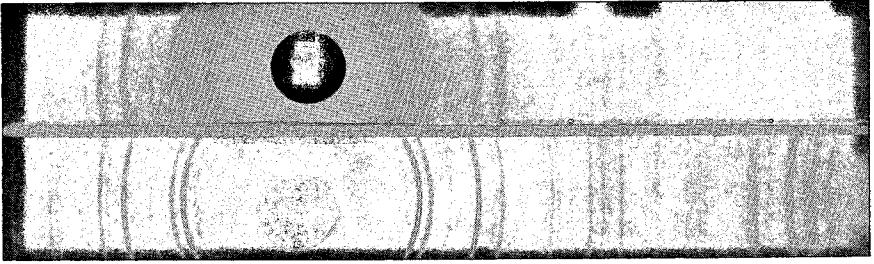


FIG. 1 (*above*). Michenerite—PdBi₂, Frood mine, Sudbury. Contact print of film #241 made by C. E. Michener.

FIG. 2 (*below*). PtBi₂, Synthetic material formed from the elements by fusion and annealing. Contact print of film made by W. O. J. Groeneveld Meijer. (Full size reproduction of *x*-ray powder films; camera 57.3 mm. diameter, CuK α radiation, 1 mm. on film \approx 1 degree θ .)

data on other substances of pyrite structure has become available in recent years. The spacings obtained from Michener's film #241 (Fig. 1), kindly remeasured by E. Cornford, are given in Table 1 together with

TABLE 1. MICHENERITE-PdBi₂, PtBi₂ AND AUROSTIBITE-AuSb₂—X-RAY POWDER DATA

Michenerite—PdBi ₂ Sudbury <i>a</i> = 6.68 Å			PtBi ₂ Wallbaum (1943) <i>a</i> = 6.696 Å		Aurostibite AuSb ₂ Yellowknife, N.W.T. Graham & Kaiman (1952) <i>a</i> = 6.659 Å	
<i>I</i>	<i>d</i> (meas)	<i>hkl</i>	<i>I</i>	<i>d</i> (meas)	<i>I</i>	<i>d</i> (meas)
—	—	111	5	3.85*	10	3.83
10	3.39	002	20	3.35	50	3.33
100	2.99	021	70	2.99	40	2.98
80	2.73	112	70	2.73	30	2.71
15	2.37	022	60	2.364	40	2.34
5	2.11	013?	—	—	—	—
90	2.01	113	100	2.013	100	2.003
5	1.92	222	20	1.938	10	1.918
15	1.86	023	60	1.854	10	1.840
75	1.79	123	80	1.788	20	1.777
10	1.67	004	10	1.675	5	1.524
5	1.50	024	50	1.495	10	1.485
30	1.46	124	70	1.460	10	1.448
10	1.42	233	50	1.427	5	1.417
5	1.37	224	50	1.366	10	1.356
20	1.285	{115 333	100	1.288	30	1.280
25	1.24	{025 234	80	1.241	10	1.233
20	1.22	125	70	1.221	51	1.213
25	1.18	044	100	1.181	20	1.177
—	—	135	—	—	5	1.126

*From Groeneveld Meijer (1954).

TABLE 1—(continued)

<i>I</i>	<i>d</i> (meas)	<i>hkl</i>	<i>I</i>	<i>d</i> (meas)	<i>I</i>	<i>d</i> (meas)
10	1.15	{244	50	1.114	10	1.109
		006				
5	1.087	061	50	1.100	—	—
		{116				
20	1.083	235	100	1.085	10	1.080
—	—	026	40	1.058	5	1.050
15	1.02	335	80	1.020	20	1.013
—	—	226	50	1.007	5	1.003
		{063				
20	0.996	245	100	0.997	5	0.991
15	0.985	136	80	0.986	5	0.981
—	—	{117			10	0.934
		155	—	—		
—	—	046	—	—	5	0.923
		{027			10	0.914
25	0.918	146	—	—		
		{127				
25	0.910	255	—	—	10	0.904
—	—	336	—	—		
		246	—	—	20	0.890
40	0.870	{137	—	—	50	0.867
		355	—	—		
20	0.857	065	—	—	10	0.853
		346	—	—		
30	0.850	156	—	—	10	0.846
		237	—	—		
10	0.835	008	—	—	20	0.833
5	0.810	{028	—	—	20	0.808
		446	—	—		
30	0.803	128	—	—	20	0.802
		247	—	—		
5	0.797	356	—	—	5	0.796
—	—	{228	—	—	40	0.785
		006	—	—		
Cu radiation Angstrom units not corrected for film shrinkage			CoK α radiation $\lambda = 1.790$ $\lambda = 1.7889$ for <i>d</i> below 1.25		CuK α radiation converted from kX, units	

powder data on artificial PtBi₂ (Wallbaum, 1943, A.S.T.M. X-ray powder data file #7-373) and on aurostibite, AuSb₂ (Graham & Kaiman, 1952).

Groeneveld Meijer (1954) obtained a low temperature form of α -PtBi₂ by fusion of the elements and annealing for 48 hours at 250°C. The x-ray powder data (Fig. 2) yield $a = 6.701 \text{ \AA}$ and agree closely with that given by Wallbaum (1943). He also obtained a second phase β -PtBi₂, by quenching a fusion of the elements. The x-ray powder pattern of this high temperature phase is not similar to that for any PdBi₂ phase. The agreement in the x-ray powder data is striking, although marked differences are evident in the intensities of corresponding lines in the three patterns. These differences could easily be due to differences in sample preparation and mounting, camera design, and structural factors, since

there is a marked difference in the scattering power of the elements involved. The high absorption of PtBi_2 is clearly the cause of the anomalously high intensities for the low spacings in that material. Indexing of this pattern (michenerite) gives the cubic cell edge $a = 6.68 \text{ \AA}$. Only one weak line, $I = 5$, $d = 2.11$, has no counterpart in the PtBi_2 or AuSb_2 patterns. This line has an index (013) which is incompatible with the pyrite space group.

The x -ray data strongly supports the view that michenerite is a form of PdBi_2 with the pyrite structure. It is possible that the structure is deficient in bismuth and may approach the composition Pd_2Bi_3 found by analysis. On the other hand analyses made on such small samples of uncertain purity may well be subject to a considerable error. The fact that PdBi_2 has not been found to form by cooling of artificial melts, renders it difficult to establish the composition more accurately by laboratory work, but does not preclude the composition PdBi_2 for this mineral.

The mineral is named after Dr. C. E. Michener, presently vice-president, Canadian Nickel Company Limited, Toronto.

FROODITE

This mineral is referred to as PdBi_x or PdBi_3 in the unpublished reports. Flat cleavage fragments and rounded grains of a single, pure palladium-bismuthide were recovered from mill concentrates from the Frood Mine, after which it is named (Fig. 3, 4).

According to Michener this has the following properties: colour—grey, streak—black; lustre—metallic, splendent on fresh cleavage, tarnishes quickly; fracture—uneven, brittle; hardness—2.5; specific gravity—12.6, 12.5 (by G. A. Harcourt).

Single crystal x -ray films were obtained by the late Harry Berman at Harvard University on the cleavage fragment illustrated in figure 1. The films obtained by Dr. Berman were kindly loaned from the Harvard files by Professor C. Frondel. The cleavage fragment is not available for further study.

X-ray study. Rotation and zero-layer Weissenberg films (Berman) on a cleavage fragment rotating about the cleavage edge yielded the following data:² monoclinic; cleavage, (001) very perfect, (100) less perfect; $a = 5.71$, $b = 4.29$, $c = 6.37$, $\beta = 102^\circ 27'$; $a : b : c = 1.33 : 1 : 1.49$.

Burr & Peacock (1942), in their study of the Pd-Bi system, obtained two modifications of PdBi_2 by crystallization from fusion of the elements in various proportions. Material of composition PdBi_2 , cooled in air,

²Personal communication, August 21, 1939.

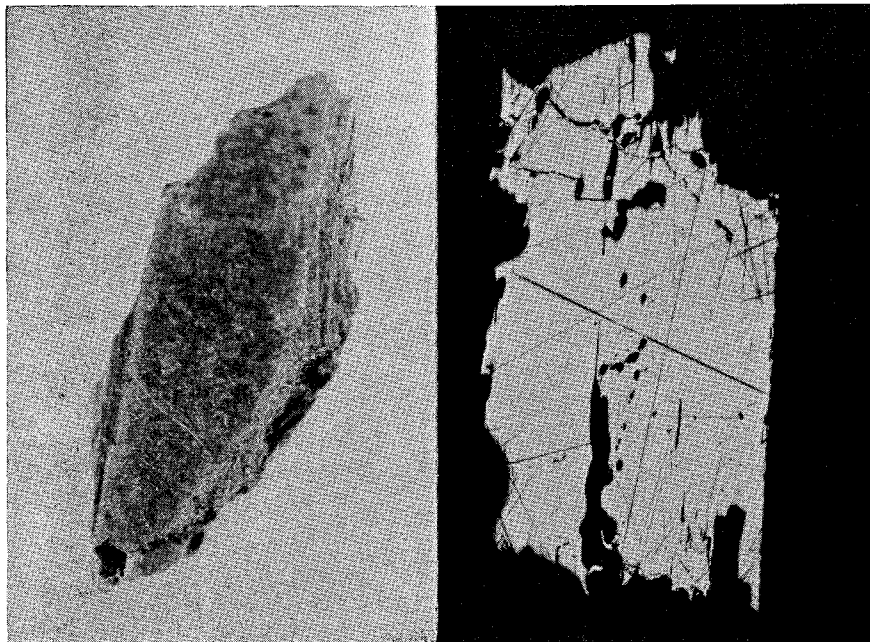


FIG. 3 (left). Froodite—PdBi₂, Frood mine, Sudbury. Crystal fragment showing flat (100) cleavage face x 18. Photo by C. E. Michener.

FIG. 4 (right). Froodite—PdBi₂, Frood mine, Sudbury. Polished surface in bakelite mount x 54. Photo by C. E. Michener.

showed zoned crystals with cores of high temperature β -PdBi₂ and margins of low temperature α -PdBi₂. After annealing in a furnace for 13 days at a temperature below the melting point and cooling slowly in the furnace, homogeneous α -PdBi₂ results.

This artificial α -PdBi₂ has the following properties: monoclinic— $C2/m$; cleavage (100) perfect, poor cleavage ($\bar{1}02$)?; $a = 12.75$, $b = 4.29$, $c = 5.67$, $\beta = 102^\circ 52'$; content 4 [PdBi₂]; specific gravity 11.5 (meas), 11.52 (calc).

Comparison of natural and artificial compounds. No mention was made of the natural palladium bismuthide in the paper by Burr & Peacock, but in his files Peacock has noted that "Michener's PdBi₃" is identical with α -PdBi₂. A comparison of Berman's single crystal films obtained from the natural fragment and Burr & Peacock's films of the artificial α -PdBi₂ reveals that the rotation and zero-level Weissenberg films are indeed identical. The rotation axis is b in both cases. The difference between the two sets of data results from the fact that Berman did not obtain a first-layer Weissenberg film and thus missed the diffractions

which require doubling of one period. The data compare as follows in the setting chosen by Burr & Peacock:

Berman natural froodite	Burr & Peacock α -PdBi ₂
Monoclinic	Monoclinic— $C2/m$
$2c = 12.74 \text{ \AA}$	$a = 12.75 \text{ \AA}$
$b = 4.29$	$b = 4.29$
$a = 5.71$	$c = 5.67$
$\beta = 102^\circ 27'$	$\beta = 102^\circ 52'$
S.G. = 12.5	S.G. = 11.5
Cleavage (100), (001)	Cleavage (100) and $\bar{1}02$
	4 [PdBi ₂]

and thus there is no doubt that froodite is the same as α -PdBi₂. There remains however the apparent difference in composition, PdBi₃ for the natural material and PdBi₂ for artificial. The work of Burr & Peacock does not indicate that any appreciable variation from the composition PdBi₂ can be expected. Fusions of composition Pd₃-Bi₉₇ to Pd₃₁-Bi₆₉ all show both α -PdBi₂ and bismuth in polished sections and in *x*-ray powder films. Certainly under these conditions of synthesis no significant variation in the composition of PdBi₂ occurs. The *x*-ray powder data obtained by Michener are compared in Table 2 with the data obtained from a new film made in our laboratories on a powder spindle from M. A. Peacock's files. This spindle is purported to contain Michener's original sample. Also in the table the *x*-ray powder data of α -PdBi₂ given by Burr & Peacock (1942) are reproduced. The powder data confirm the identity of froodite with α -PdBi₂. This being the case, one can only surmise as to the reasons for the results of approximate analyses by Michener which yielded a ratio close to PdBi₃. The possibility still remains of the existence of still another palladium compound in these ores, and is strongly suggested by recent studies by the senior author and R. L. Stanton. These have revealed fine grains, the hardness, reflectivity, and double refraction of which, though similar to froodite are not identical with it. Unfortunately not enough of this substance has been found for *x*-ray analysis, let alone chemical analysis.

Optical properties: light grey, anisotropic—polarization colours—light to dark grey.

Etch reactions: Etch reactions for froodite as determined by Michener, are compared in the following table with those obtained by us on artificial α -PdBi₂ prepared by Burr & Peacock, are as follows:

TABLE 2. FROODITE AND α -PdBi₂—X-RAY POWDER DATA
(CuK radiation, Ni filter, camera diameter 57.3 mm.)

Froodite* C. E. Michener		Froodite†			α -PdBi ₂ ‡ artificial	
<i>I</i>	<i>d</i> (meas)	<i>I</i>	<i>d</i> (meas)	<i>hkl</i>	<i>I</i>	<i>d</i> (meas)
—	—	20	6.24	200	30	6.27
—	—	30	3.14	111,400	30	3.17
—	—	—	—	—	10	3.12
30	2.96	70	2.97	310	60	2.99
80	2.81	20	2.81	311	50	2.82
—	—	100	2.77	{002 202	100	2.77
40	2.50	70	2.48	401, 311	50	2.48
—	—	40	2.35	{112, 402 202	30	2.34
60	2.27	70	2.21	312, 112	80	2.20
60	2.13	50	2.14	{510, 511 020	40	2.14
—	—	50	2.09	601	40	2.08
—	—	10	1.881	—	10	1.883
30	1.70	40	1.689	—	30	1.690
20	1.65	60	1.637	—	40	1.638
—	—	—	—	—	10	1.617
—	—	20	1.590	—	20	1.587
50	1.57	80	1.556	—	70	1.552
20	1.50	40	1.497	—	20	1.494
—	—	10	1.453	—	20	1.450
20	1.43	60	1.419	—	40	1.418
10	1.35	5	1.337	—	5	1.337
—	—	5	1.293	—	5	1.292
—	—	20	2.281	—	10	1.279
—	—	10	1.261	—	10	1.254
—	—	10	1.244	—	10	1.240
—	—	—	—	—	5	1.223
—	—	5	1.199	—	5	1.198
20	1.19	40	1.185	—	40	1.177
—	—	—	—	—	5	1.151
20	1.13	30	1.118	—	30	1.115
30	1.087	30	1.075	—	30	1.073
—	—	5	1.052	—	5	1.048
—	—	10	1.034	—	10	1.030
—	—	5	1.015	—	5	1.014
—	—	20	0.980	—	30	0.978
—	—	5	0.964	—	5	0.962
—	—	5	0.952	—	5	0.950
—	—	5	0.942	—	5	0.942
—	—	10	0.934	—	10	0.932
—	—	10	0.915	—	5	0.912
—	—	10	0.907	—	10	0.906
—	—	10	0.900	—	10	0.898
—	—	—	—	—	5	0.888

*Data given by Michener (1940).

†Data from new film obtained from powder spindle in M. A. Peacock's file, labelled "Michener's PdBi₂" ($\lambda = 1.5418$).

‡Data for α -PdBi₂ from Burr & Peacock (1942) converted to Å.

Froodite		α -PdBi ₂
HNO ₃ (1:1)	Effervescence slow, turns brown with production of granular surface.	Effervescence, etches and leaves brown stain.
HNO ₃ (Conc.)		Vigorous etch with eff. stains brown.
HCl (1:1)	negative	negative
HCl (conc.)		stains faint brown to negative
KCN	slowly stains dark	negative
FeCl ₃	instantly stains black	instantly stains brown to iridescent, brings out grain boundaries, and lamellar twinning
KOH	negative	negative
HgCl ₂	negative	negative to slight roughening of surface.

The slight differences noted in etch reactions, as with KCN and FeCl₃ may be due to slight differences in composition (or impurities) in the natural mineral and the artificial product, and are not regarded as significant.

SUMMARY AND CONCLUSIONS

Two palladium bismuthides discovered in the arsenic- and lead-copper-rich ores of the Frood mine, Sudbury district of Ontario some years ago by C. E. Michener, and reported in his doctorate thesis (University of Toronto, 1940) are re-described and named Michenerite and Froodite. On the basis of *x*-ray data these appear to be two crystalline modifications or phases of PdBi₂, the former isometric, the latter monoclinic, although approximate analyses of the natural materials formerly suggested compositions of Pd₂Bi₃ and PdBi₃. A third modification, β -PdBi₂, prepared by Burr & Peacock, is not yet known to have a natural counterpart.

Michenerite is a greyish white, soft, brittle mineral with no cleavage. The comparison of *x*-ray powder data with that for PtBi₂ and AuSb₂ (aurostibite) indicates that michenerite is isometric with a pyrite structure, $a = 6.68 \text{ \AA}$ and the composition PdBi₂. Burr & Peacock (1942) did not obtain this phase in their study of the Pd-Bi system.

Froodite, found in fragments and rounded grains, is also grey in colour, soft, brittle but with one perfect cleavage (100) and one less perfect (001). *X*-ray study of the natural fragment by the late Dr. Harry Berman and of artificial material by Burr & Peacock (1942) indicates that froodite is monoclinic—C2/m, with $a = 12.75$, $b = 4.29$, $c = 5.67$, $\beta = 102^\circ 52'$, containing 4[PdBi₂], S.G. = 12.5 (mineral, meas), 11.5 (artificial, meas), 11.52 (calc). The data by Burr & Peacock (1942) were obtained on the low temperature phase, α -PdBi₂, found in their study of the system Pd-Bi. The *x*-ray powder data further support the identity of froodite with α -PdBi₂.

While early analyses on small quantities of these minerals may be somewhat in error, the ratios obtained for palladium to bismuth of 2:3 and 1:3, respectively, may in part be explained by the presence with the former of PdBi (known in artificial preparations) along with PdBi₂, and with the latter of still another palladium bismuth mineral detected recently in minute amounts but in too small quantities for either x-ray or chemical study.

It seems clear that much of the palladium in the Sudbury ores may be accounted for by minute disseminations of these minerals in various sulphides or arsenides. This is supported by spectrographic data, not included here, which usually indicates the presence of bismuth with palladium. In other cases it still seems possible that several of the platinum metals including palladium, may be present in solid solution in the common sulphides of these ores.

REFERENCES

- BURR, S. V. & PEACOCK, M. A. (1942): A preliminary study of the alloys of palladium and bismuth, *University of Toronto Studies, Geol. Series*, **47**, 19-20.
- COLEMAN, A. P. (1905): The Sudbury nickel field, *Rept. Ont. Bureau of Mines*, **14**, Part III, 155.
- GRAHAM, A. R. & KAIMAN, S. (1952): Austrobitite, AuSb₂, a new mineral in the pyrite group, *American Mineral*, **37**, 461.
- GROENEVELD MEIJER, W. O. J. (1954): The geochemistry of the platinum metals with respect to their occurrence in nickeliferous sulphide deposits, *Doctorate thesis, Queen's University, Kingston*.
- MICHENER, C. E. (1940): Minerals associated with large sulphide bodies of the Sudbury type, *Doctorate Thesis, University of Toronto*.
- WALLBAUM (1943): *Zeits. Metallkunde* **35**, 200, Quoted from *X-ray powder data file*, card 7-373, American Society for Testing Materials, Philadelphia.