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MICHENERITE (PdBiTe) REDEFINED AND FROODITE ($PdBi_2$) CONFIRMED FROM THE SUDBURY AREA *

L. J. CABRI AND D. C. HARRIS

Mineral Sciences Division, Mines Branch, Department of Energy, Mines and Resources, Ottawa, Ontario, Canada. K1A 0G1

AND

R. I. GAIT

Royal Ontario Museum, Toronto, Ontario.

ABSTRACT

Michenerite was found in samples from the Vermilion and Frood Mines, Sudbury area as well as from a sample labeled "Copper Cliff concentrates". Michenerite, as redefined, is PdBiTe. The mineral is cubic, $a = 6.646(5)$ Å. $Z = 4$, $D = \sim 10.0$ g/cm^3, space group is $P2_13$. The strongest x-ray diffraction reflections are 2.97(10) (012), 2.71(8) (112), 2.003(10) (113), 1.778(8) (123), 1.451(7) (124), 1.234(7) (025), and 0.8654(7) (137).

In hand specimens michenerite has the colour and lustre of galena but shows conchoidal fracture. Under reflected light it is creamish white with a tinge of grey in air and in oil. Reflectances at 470, 546, 589, and 650 nm are 58.2, 55.2, 54.3, and 54.7%. VHN_{25}, obtained from two different grains is 320-325 (av. 321) and 304-317 (av. 311) kg/mm^2. The mineral has been synthesized.

Froodite has been confirmed as monoclinic $PdBi_2$, $a = 12.70(2)$, $b = 4.28(1)$, $c = 5.65(1)$ Å, $\beta = 102°\ 32'$ (6). Reflectances at 470, 546, 589, and 650 nm are 57.7-61.3, 57.2-60.3, 56.8-60.4, 56.5-60.2%. $VHN_{25} = 84$ kg/mm^2.

INTRODUCTION

Though palladium is one of the two principal platinum group elements to be produced from the Sudbury area, knowledge of the mineralogy of Sudbury-area palladium minerals is very limited. The only evidence, to date, on the nature of the Sudbury palladium minerals is the unpublished work of Michener (1940) and the proposal of the names michenerite and froodite by Hawley & Berry (1958) for the two palladium minerals discovered by Michener after superpanning mill concentrates from the arsenic- and lead-copper-rich ores of the Frood mine. Michener had described one as Pd_2Bi_3, $a = 6.65$Å ; in reflected light, light grey, isotropic, hardness B, fracture uneven, and no observable cleavage ; colour grey, lustre dull, metallic, and streak black. This mineral was later named michenerite

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by Hawley & Berry and assigned the formula $PdBi_2$ since the x-ray diffraction pattern was very similar to that of synthetic $PtBi_2$. Unfortunately, Michener's material was not available for study as all had been consumed in the analyses.

Michener described the other mineral as $PdBi_3$, monoclinic, and with the cell dimensions (determined from a single crystal by the late Dr. H. Berman of Harvard University) $a = 5.71$, $b = 4.29$, $c = 6.37$Å, $\beta = 102°27'$. The mineral had the following properties: colour grey; streak black; lustre metallic; splendant on fresh cleavage but tarnishes readily; fracture uneven; brittle; hardness 2.5; specific gravity 12.5 (by G. A. Harcourt). Under reflected light: colour, light grey; hardness B; anisotropic, light grey to dark grey. The single crystal examined by Berman was lost but Hawley & Berry (1958) obtained a powder spindle for x-ray diffraction and this was shown to be equivalent to synthetic α-$PdBi_2$. Hawley & Berry named the mineral froodite, the natural equivalent of α-$PdBi_2$.

Genkin *et al.* (1963) reported michenerite from Monchegorsk and obtained the compositions $Pd_{0.44}Pt_{0.18}Bi_{0.81}Te_{1.18}$ and $Pd_{0.72}Pt_{0.21}Bi_{0.98}Te_{1.02}$ from micro-spectrographic analyses and the unit cell $a = 6.654(2)$Å. Genkin *et al.* further reported that the mineral could not be synthesized without Pt and that the best formula was $Pd_{0.75}Pt_{0.25}BiTe$.

Materials and Method of Investigation

Samples were obtained from the surface dump outside the abandoned Vermilion mine, Lot 6, Conc. IV, Denison Twp., Sudbury area, Ontario. One sample had visible gold and hauchecornite (ROM 29438), and the other had a large sperrylite crystal (~3 x 6 mm). A polished section containing both michenerite and froodite is preserved at the Royal Ontario Museum (M31189), Toronto; it was prepared from ROM M29438. Cubanite-rich ore from the Frood mine was crushed and the sized fractions passed through a superpanner. Four grains of michenerite were identified in the $-200 + 270$ mesh fraction. A sample of eight crystals labelled "Copper Cliff concentrate", kindly provided by Dr. J. D. Scott, was found to contain three crystals of michenerite.

The minerals were studied by ore microscopy, x-ray diffraction analysis, and by the electron-probe microanalyser. X-ray diffraction powder data were obtained by the film method using 57.3 and 114.6 mm Gandolfi and Debye-Scherrer cameras. Film shrinkage corrections were applied, and the unit cell parameters were refined by a least-squares computer program.

The compositions were determined using a Materials Analysis Company model 400 electron-probe microanalyser, operated at 25kv with a specimen current of about 0.03 microamperes. Corrections were applied using Edition VII of the program by Rucklidge (1967). Synthetic PdBiTe was used as a standard and it was synthesized by reacting high purity elements in evacuated quartz tubes. The elements were initially heated for seven days at 450° C; then the charge was quenched, ground and pelletized. It was melted at 600° C, quenched, then annealed at 400° C for one day. It was quenched again, ground and pelletized, and then heated at 450° C for three days. The unnecessasy number of steps taken reflects the lack of knowledge on the stability of this compound when the investigation was begun.

The samples were mounted in cold-setting plastic, polished on lead laps and lightly buffed on a cloth lap using minus 0.2-μ alumina. The reflectance values were obtained with reference to a silicon standard calibrated by the National Physical Laboratory, Great Britain, using a 16.5:1 objective with a numerical aperture of 0.40. The micro-indentation hardness was measured with a Leitz Durimet tester.

Optical, Physical and Chemical Properties

Michenerite

In hand specimens the mineral has the colour and lustre of galena but shows a conchoidal fracture. Under reflected light the colour in oil and air is creamy white with a tinge of grey. It is isotropic and the reflectances at the four standard wavelengths 470, 546, 589 and 650 nm are 58.2, 55.2, 54.3, and 54.7%, respectively (mean values for four grains). The range and mean micro-indentation hardness values for two grains are : VHN_{25} = 320 − 325 (321) kg/mm² and VHN_{25} = 304 − 317 (311) kg/mm² (5 indentations each).

The michenerite from the Vermilion mine was found associated with gold, bismuthinite and froodite in one section (Figs. 1 and 2). In another sample the mineral is associated with gold and a new unnamed mineral of composition Pd(Te,Sb,Bi) still under study. The michenerite grains from the Frood mine were associated with cubanite, chalcopyrite, hessite, altaite, native bismuth, galena, and sperrylite. The three michenerite crystals from the Copper Cliff concentrates had the highest antimony contents.

The first microanalysis of michenerite, using metal standards, indicated that it had a small Pt content. Later analyses, reported in Table 1, using

synthetic PdBiTe, as well as Pt and Sb metals as standards, shows minor Sb for 5 grains, but no Pt in any of the 8 grains examined in detail.

X-ray diffraction powder data for michenerite were obtained with Ni-filtered Cu-radiation using a 57.3 mm Gandolfi camera (Table 2). The unit cell edge, $a = 6.646(5)$ Å, compares favourably with that obtained for synthetic PdBiTe using a 114.6 mm Debye-Scherrer camera (Ni-filtered Cu-radiation), $a = 6.651(5)$ Å (Table 2). Hulliger & Müller (1963) report $a = 6.656$ Å for synthetic PdBiTe. Single crystal precession photographs of the mineral confirmed the cubic symmetry and suggested that the space group was either $Pm3$ or $P23$. However, during the determination of the crystal structure (J. D. Childs, pers. comm.) only the space group $P2_13$ was found to be consistent with the data. Therefore, the very weak extra reflections on the powder pattern of synthetic PdBiTe are probably due to minor impurities. The density was calculated to be about 10.0 g/cm^3 with $Z = 4$.

Froodite

Under reflected light froodite is creamy white, with a pale brown tinge in air. In oil immersion its colour is creamy white with a brownish

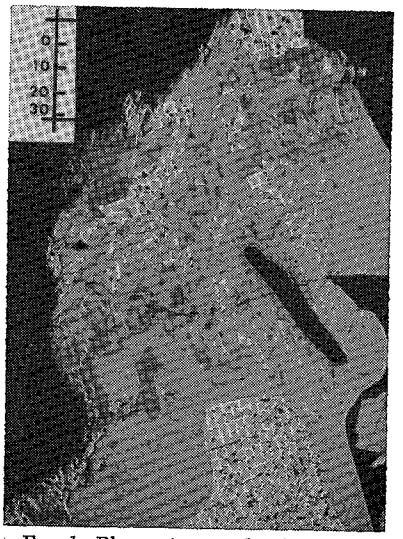

FIG. 1. Photomicrograph of michenerite (light grey) intergrown with bismuthinite (dark grey) and gold (white, pitted). Scale in microns.

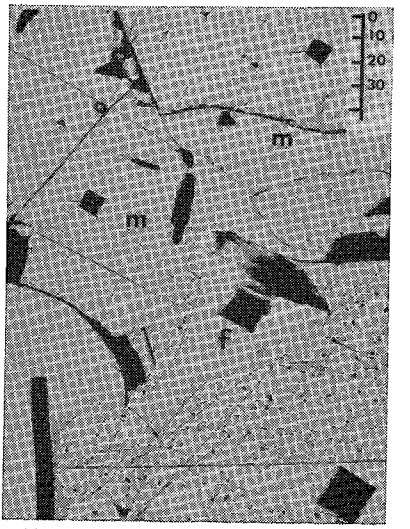

FIG. 2. Photomicrograph showing michenerite (m) in contact with froodite (f) and gold (light grey, pitted). Size of micro-indentations show that gold < froodite << michenerite, in hardness. Scale in microns.

TABLE 1. ELECTRON PROBE ANALYSES OF MICHENERITE

Wt.%	1	2	3	4	5	6
Pd	24.0	24.6	24.1	24.6	24.8	24.8
Te	28.8	28.8	28.5	29.9	29.9	29.6
Bi	46.5	45.8	47.0	43.3	43.0	43.1
Sb	0.4	0.9	n.d. *	3.3	3.3	3.0
Pt	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total	99.7	99.9	99.6	101.1	101.0	100.5

* Not detected.
1 — $Pd_{1.00}(Bi_{0.99}Sb_{0.01})Te_{1.00}$ with Au and froodite, Vermilion Mine.
2 — $Pd_{1.00}(Bi_{0.96}Sb_{0.03})Te_{0.99}$ with Au and unnamed mineral, Vermilion Mine.
3 — $Pd_{1.00}Bi_{1.00}Te_{0.99}$ — average of three grains, Frood Mine.
4 — $Pd_{1.00}(Bi_{0.89}Sb_{0.12})Te_{1.01}$ — crystal No. 2, Copper Cliff concentrate.
5 — $Pd_{1.00}(Bi_{0.88}Sb_{0.11})Te_{1.00}$ — crystal No. 3, Copper Cliff concentrate.
6 — $Pd_{1.00}(Bi_{0.88}Sb_{0.11})Te_{1.00}$ — crystal No. 7, Copper Cliff concentrate.

TABLE 2. X-RAY DIFFRACTION DATA FOR MICHENERITE AND SYNTHETIC PdBiTe

Michenerite $a = 6.646(5)$ Å				Synthetic PdBiTe $a = 6.651(5)$ Å		
I	d(meas.)	d(calc.)	hkl	I	d(meas.)	d(calc.)
			011	0.5	4.708	4.702
1	3.33 *	3.323	002	3	3.321	3.325
10	2.97	2.972	012	10	2.974	2.974
8	2.71	2.713	112	8	2.715	2.715
3	2.35	2.349	022	4	2.350	2.351
1	2.22	2.215	122	2	2.217	2.217
1	2.10	2.101	013	1	2.104	2.103
10	2.003	2.004	113	9	2.000	2.005
2	1.916	1.918	222	2	1.914	1.919
4	1.841	1.843	023	5	1.843	1.844
8	1.778	1.776	123	8	1.773	1.777
3	1.662	1.661	004	4	1.661	1.662
0.5	1.610	1.612	223	1	1.612	1.613
1	1.567	1.566	114	1	1.567	1.567
			133	0.5	1.525	1.525
4	1.486	1.486	024	4	1.485	1.487
7	1.451	1.450	124	7	1.451	1.451
4	1.417	1.417	233	5	1.417	1.417
2	1.357	1.357	224	2	1.356	1.357
1	1.303	1.303	134	1	1.303	1.304
6	1.278	1.279	115	6	1.279	1.279

TABLE 2. X-RAY DIFFRACTION DATA FOR MICHENERITE AND SYNTHETIC PdBiTe (cont'd.)

Michenerite $a = 6.646(5)$ Å				Synthetic PdBiTe $a = 6.651(5)$ Å		
I	d(meas.)	d(calc.)	hkl	I	d(meas.)	d(calc.)
7	1.234	1.234	025	7	1.234	1.235
6	1.213	1.213	125	5	1.213	1.214
6	1.173	1.174	044	6	1.174	1.175
0.5	1.156	1.157	225	0.5	1.157	1.157
0.5	1.124	1.123	135	0.5	1.123	1.124
2	1.106	1.107	244	2	1.108	1.108
3	1.092	1.092	061	3	1.093	1.093
5	1.078	1.078	116	5	1.078	1.078
1	1.050	1.050	026	0.5	1.052	1.051
1	1.037	1.038	126	0.5	1.037	1.038
3	1.013	1.013	335	3	1.014	1.014
2	1.001	1.002	226	2	1.002	1.002
5	0.9909	0.9908	245	5	0.9916	0.9914
4	0.9801	0.9800	136	4	0.9810	0.9806
2	0.9596	0.9594	444	2	0.9602	0.9600
0.5	0.9494	0.9495	236	0.5	0.9510	0.9501
1	0.9399	0.9400	345	0.5	0.9410	0.9406
5	0.9130	0.9130	146	4	0.9139	0.9135
6	0.9045	0.9045	127	5	0.9057	0.9050
3	0.8882	0.8882	246	3	0.8886	0.8887
7	0.8654	0.8653	137	7	0.8668	0.8658
4	0.8510	0.8510	346	5	0.8525	0.8515
6	0.8442	0.8441	237	6	0.8453	0.8446
4	0.8310	0.8308	008	4	0.8316	0.8313
1	0.8243	0.8244	256	0.5	0.8248	0.8249
1	0.8190	0.8181	118	0.5	0.8190	0.8186
0.5	0.8120	0.8120	337	0.5	0.8130	0.8125
3	0.8062	0.8060	028	3	0.8063	0.8065
6	0.8003	0.8001	128	6	0.8004	0.8006
4	0.7947	0.7944	356	5	0.7950	0.7949
4	0.7836	0.7833	228	4	0.7840	0.7838
1	0.7780	0.7779	166	1	0.7785	0.7784
3	0.7731	0.7726	138	3	0.7737	0.7731

Intensities visually estimated.

* Measured from a 114.6 mm film, Gandolfi camera.

N.B. Four extra very weak reflections were observed on the pattern of synthetic PdBiTe at 2.031(0.5), 1.960(1), 1.365(0.5), and 1.343(0.5) which could not be indexed. The extra reflection at 6.518(0.5) can be indexed as (001) but is forbidden by space group $P2_13$.

grey tinge. It shows weak bireflection in air and in oil and is moderately anisotropic. In air, the polarization colours are dark grey to very pale brown or light grey. In oil immersion, the polarization colours are pale brownish grey to dark bluish grey. The minimum and maximum reflectances at 470, 546, 589 and 650 nm are 57.6 and 61.3, 57.2 and 60.3, 56.8 and 60.4 and 56.5 and 60.2%. These values were obtained from two series of measurements on one grain. The second grain of froodite was observed to be twinned. Only one microhardness indentation was possible and gave $VHN_{25} = 84$ kg/mm^2. This indentation is seen in Figure 2 where it can be compared to the slightly larger indentations for gold and the much smaller indentations for michenerite.

The electron microprobe was used to compare the composition of froodite with that of synthetic $PdBi_2$; they were found to be identical.

The x-ray powder diffraction pattern of froodite was found to agree with that reported by Hawley & Berry (1958) and the cell dimensions $a = 12.70(2)$, $b = 4.28(1)$, $c = 5.65(1)$Å, $\beta = 102°32'$ (6) compare favourably with the cell dimensions determined by Berman (in Hawley & Berry). The cell dimensions for synthetic α-$PdBi_2$, $a = 12.700(2)$, $b = 4.267(1)$, $c = 5.657(3)$Å, $\beta = 102°29'$ also agree well with those reported by Burr & Peacock (1942), except that they reported $\beta = 102°52'$.

Discussion

Michenerite

The redefinition of michenerite as cubic PdBiTe was accepted by the Commission on New Minerals and Mineral Names, IMA by a vote of 16 to 0 with 1 abstention. The abstainer, as well as 4 members who voted YES, felt that since the type material is lost there may be a cubic mineral with composition $PdBi_2$.

The Bi-Pd system has been carefully studied by Brazier & Hume-Rothery (1959) and by Zhuravlev & Zhdandov (1953) and they have shown that monoclinic α-$PdBi_2$ is stable up to about 380° C. Above that temperature it transforms to tetragonal β-$PdBi_2$, which melts at about 485° C. Since α-$PdBi_2$ is identical to froodite (β-$PdBi_2$ has not been found in nature) and because the michenerite of Michener (1940) and our mineral give identical x-ray diffraction powder patterns we must conclude that the latter two are the same. The suggestion by Hawley & Berry (1958) that michenerite is $PdBi_2$ was made strictly on the basis of the similarity of its x-ray diffraction powder pattern to that of synthetic $PtBi_2$ and not on any compositional grounds since Michener had actually

reported Pd_2Bi_3. The (013) reflection reported as doubtful by Hawley & Berry apparently is not due to an impurity and therefore the proposed similarity can no longer be true since this reflection is forbidden by the pyrite space group of $PtBi_2$. Correspondence with Dr. C. E. Michener, kindly made available by Professor L. G. Berry, shows that confidence in the Pd_2Bi_3 composition was not high; therefore it seems reasonable that the mineral's composition is that which we report.

We have made an exploratory study of the Pd-Bi-Te system and found that Pd-Bi-Te melts at $489 \pm 2°$ C to two liquids of approximate compositions $Bi_{2.2}Te$ and $Pd_3(Te,Bi)_4$. The analyses of natural michenerite show no deviation from the stoichiometric composition but suggest a small replacement of Sb for Bi and no substitution of Te for Bi in our samples. Experiments at 450° C show limited substitution of Te for Bi (up to about $Pd_{1.00}Bi_{0.82}Te_{1.18}$) but no substitution of Bi for Te. Deviation of Pd : (Te, Bi) from 2.0 by more than 0.0001 along the $PdTe_2$-$PdBi_2$ join for weighed compositions resulted in two phases. The wider variation of (Pd,Pt):(Te, Bi) from 2.0, reported by Genkin *et al.* (1963) for one determination, may be due to the limitations of the method of analysis (microspectrographic). The compositions $Pd_2Bi_2Te_3$ and $(Pd,Pt)_2Bi_3Te_3$ reported by Yushko-Zakharova *et al.* (1970) are harder to evaluate since no details of the microanalytical conditions and treatment of raw data are given. Cabri (1972) suggests that these minerals are both michenerite, PdBiTe.

Froodite

Froodite from the Sudbury area has been confirmed and new data on the optical and physical properties are given. The only other mineral similar to froodite, in the literature, is "palladium bismuthinide" described by Chernyaev & Yushko-Zakharova (1968) from Monchegorsk. They reported a wide range in analyses ($Pd_{1.0}Bi_{2.6\text{-}3.4}$) and assigned the composition $PdBi_3$. No details of analytical procedures are given, so it is impossible to evaluate this proposed composition. $PdBi_3$ is unknown in the Pd-Bi system; there are no compounds known between $PdBi_2$ and Pd. We have confirmed this and, therefore, suggest that "palladium bismuthinide" is froodite ($PdBi_2$).

Summary

The source of palladium from the Sudbury area deposits has been shown to come from at least four minerals — michenerite (PdBiTe), froodite ($PdBi_2$), palladian melonite $(Ni,Pd,Pt)(Te,Bi)_2$ (Rucklidge 1969), and a new unnamed mineral Pd(Te,Sb,Bi). Further study is required to

determine the principal palladium minerals, their associations, and their distribution. Such a study may result in a better understanding of some of the ore-forming events and probably will also lead to the discovery of other new or unreported platinum group minerals. Phase-equilibrium data in ternary systems of the platinum group elements are limited. Studies in these systems would help in understanding such minerals.

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Appendix

ADDENDUM : After acceptance of our paper we read the contribution of Genkin *et al.* (1972) for michenerite from the Oktyabrskoe deposit which is in good agreement with our data except for 1.8 wt.% Ag, not previously reported in michenerite. This silver content may be questionable due to the interference between Pd$L\beta_1$ ($\lambda = 4.146$) and Ag$L\alpha_1$ ($\lambda = 4.154$) which the authors did not discuss.

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