

## Stibiopalladinite from the type locality<sup>1</sup>

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### Abstract

Stibiopalladinite from the type locality, Farm Tweefontein, near Potgietersrust, Transvaal, South Africa, is considered to have a composition between  $\text{Pd}_5\text{Sb}_2$  and  $\text{Pd}_6\text{Sb}_3$ . The structural formula may be  $\text{Pd}_{6+x}\text{Sb}_{2-x}$  or  $\text{Pd}_{6-x}\text{Sb}_{3+x}$ , but the former is proposed pending a detailed crystal-structure analysis because of its close relationship with synthetic  $\text{Pd}_{6+x}\text{Sb}_{2-x}$  of El-Boragy *et al.* (1970). The general formula is  $(\text{Pd,Cu})_{6+x}(\text{Sb,As,Sn})_{2-x}$ , where  $x \approx 0.05$  and  $\text{Pd} \gg \text{Cu}$ ,  $\text{Sb} \gg \text{As,Sn}$ . The mineral is hexagonal,  $P6_3/mmc$ ,  $P6_3mc$ , or  $P\bar{6}2c$ ,  $a = 7.598(2)$ ,  $c = 28.112(9)\text{\AA}$ ,  $D(\text{calc}) = 10.8 \text{ g/cm}^3$  for  $Z = 12$ . The cell dimensions vary slightly with Cu, As, and Sn substitutions. Stibiopalladinite is also different crystallographically from synthetic  $\text{Pd}_6\text{Sb}_3$ ,  $\text{Pd}_6\text{Sb}_2$ , and  $\text{Pd}_6\text{Sb}_{1.94}\text{As}_{0.06}$ .

Mertieite II, corresponding to  $(\text{Pd,Cu})_8(\text{Sb,As,Sn})_3$  with a rhombohedral cell, is reported from this locality for the first time.

### Introduction

As part of a research project on the minerals of the platinum group, Cabri *et al.* (1975) outlined the problems relating to the identity of stibiopalladinite. The mineral was originally assumed to be  $\text{Pd}_5\text{Sb}$  (Adam, 1927). Recently, Desborough *et al.* (1973) and Clark *et al.* (1974), analyzing material from the original locality, Potgietersrust, Transvaal, South Africa, suggested that the composition should be  $\text{Pd}_5\text{Sb}_2$ . However, neither of their analyses is precisely stoichiometric, but lie between  $\text{Pd}_5\text{Sb}_2$  and  $\text{Pd}_6\text{Sb}_3$  (Cabri *et al.* 1975), where a synthetic phase,  $\text{Pd}_{5+x}\text{Sb}_{2-x}$ , was reported (El-Boragy and Schubert, 1971).

Desborough *et al.* also reported that mertieite had the general formula  $(\text{Pd,Cu})_{5+x}(\text{Sb,As})_{2-x}$ , where  $x = 0.1 - 0.2$ , but their group II mertieite was reanalyzed by Cabri *et al.* and found to be  $\text{Pd}_6(\text{Sb,As})_3$ . Meanwhile, Razin and Dubakina (1974) reported "mertieite" with compositions  $(\text{Pd,Ag})_{5-x}(\text{Sb,As})_2$  from Noril'sk and  $(\text{Pd,Cu})_{3+x}(\text{Sb,As})$  from Ingali, U.S.S.R.

Successful synthesis of the phases  $\text{Pd}_5\text{Sb}$ ,  $\text{Pd}_6\text{Sb}_3$ ,  $\text{Pd}_{5+x}\text{Sb}_{2-x}$ , and  $\text{Pd}_5\text{Sb}_2$  was reported by El-Boragy and Schubert, though Desborough *et al.* stated that they

could not synthesize a stable phase of  $\text{Pd}_5\text{Sb}$  or  $\text{Pd}_6(\text{Sb,As,Cu})$  composition. The X-ray powder diffraction patterns of these synthetic (Pd,Sb)-phases appear to be similar to each other and are structurally related to that of  $\text{Pd}_5\text{Sb}_2$  (El-Boragy *et al.*, 1970).

The X-ray powder diffraction data for stibiopalladinite (Berry and Thompson, 1962; Genkin, 1968) have not been indexed and are not identical to each other or to the data reported by Desborough *et al.* (1973), but resemble those of some synthetic (Pd,Sb)-phases and "mertieite" (Cabri *et al.*, 1975; Desborough *et al.*, 1973; Razin and Dubakina, 1974). Due to the uncertainty of the chemical composition and crystal data, and the similarity with mertieite, stibiopalladinite was reexamined in detail.

### Material

A stibiopalladinite specimen (ROM M 19388) from the Farm Tweefontein, No. 1033, Potgietersrust district, Northern Transvaal, South Africa, the locality of its original description, was obtained from the Royal Ontario Museum, Toronto, for this study. The specimen (one vial) consists of a heavy-mineral concentrate containing grains of stibiopalladinite, braggite, cooperite, and mertieite II of approximately 0.2-0.3 mm in size. Under reflected light, in air, stibiopalladinite is white, weakly anisotropic and

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shows no bireflectance. The qualitative optical properties are more similar to those reported by Clark *et al.* (1974) than to those given by Desborough *et al.* (1973). A deeply weathered specimen labelled "Palladium Antimonide," also from Farm Tweefontein, 16 miles from Potgietersrust, was also obtained from the Royal Ontario Museum (ROM M 15995). Thirty-six slices were cut from the 5×5×2.5 cm specimen for an exhaustive polished-section examination, but the only metallic minerals found were sperrylite and pyrite.

### Chemical composition

Electron microprobe analyses were performed at 25 kilovolts using the following X-ray lines and (synthetic standards): PdL $\alpha$ , SbL $\alpha$ , CuK $\alpha$  (Pd<sub>4.85</sub>Cu<sub>0.15</sub>Sb<sub>2</sub>); AsK $\alpha$  (Pd<sub>5</sub>As<sub>1.48</sub>Sb<sub>0.51</sub>); and SnL $\alpha$  (PtSn). Bi, Te, and Pt were also searched for but were not detected. The X-ray intensity data were processed by the computer program, EMPADR VII, of Rucklidge and Gasparrini (1969). The homogeneities of the elements in the mineral are generally very good, with homogeneity index (Boyd *et al.* 1969): Pd, 0–1; Sb, 1; Cu, 1–2; As, 3; and Sn, 2. The specimens and synthetic standards were freshly polished immediately prior to probe analysis, since they tarnish rapidly, even under a carbon coating. The results of six analyses are compared in Table 1 with those of the average analyses given by Clark *et al.* (1974) from Potgietersrust (BM Spec. No. 1930,952) and by Desborough *et al.* (1973) from Farm Tweefontein (USNM R6483).

The analyses were calculated to 7 atoms. The aver-

age, corresponding to (Pd<sub>4.85</sub>Cu<sub>0.20</sub>) $\Sigma$ <sub>5.05</sub>(Sb<sub>1.92</sub>As<sub>0.02</sub>Sn<sub>0.01</sub>) $\Sigma$ <sub>1.95</sub>, agrees more closely to a  $\Sigma$ Pd/ $\Sigma$ Sb ratio of 5:2 than 8:3 or 3:1. The composition agrees very well with the mean for seven grains, (Pd<sub>4.88</sub>Cu<sub>0.28</sub>) $\Sigma$ <sub>5.06</sub>Sb<sub>1.94</sub>, reported by Desborough *et al.* (1973), and is also comparable with those given by Clark *et al.* (1974). The total of  $\Sigma$ Pd (*i.e.* Pd + Cu) and  $\Sigma$ Sb (*i.e.* Sb + As + Sn) of each analysis was also calculated to 100 atom percent, and the results show that all the analyses from Potgietersrust fall within the range of Pd 72.3–71.8 atomic percent reported by El-Boragy and Schubert (1971) for synthetic Pd<sub>5+</sub>Sb<sub>2-</sub>. For stibiopalladinite from Potgietersrust, the general formula (Pd,Cu)<sub>5+x</sub>Sb<sub>2-x</sub> with  $x \sim 0.05$  appears to be more favorable than the formula Pd<sub>5</sub>Sb<sub>2</sub> suggested by Desborough *et al.* (1973) or (Pd,Cu)<sub>5</sub>Sb<sub>2</sub> suggested by Clark *et al.* (1974). We consider that Cu substitutes for Pd and that As and Sn substitute for Sb, since those elemental substitutions are not uncommon for such minerals. It is uncertain, however, whether Cu, As, and/or Sn are essential for stibiopalladinite.

Tarkian and Stumpfl (1975) reported a stibiopalladinite from the Driekop mine, South Africa, which when recalculated on a basis of seven atoms is (Pd<sub>4.74</sub>Cu<sub>0.16</sub>Pt<sub>0.07</sub>) $\Sigma$ <sub>4.97</sub>(Sb<sub>1.85</sub>As<sub>0.18</sub>) $\Sigma$ <sub>2.03</sub>, corresponding to a  $\Sigma$ Pd of 71 atom percent. The composition is very close to Pd<sub>5</sub>(Sb,As)<sub>2</sub> or Pd<sub>5-</sub>(Sb,As)<sub>2+</sub>. However, no X-ray data were given to prove the identity of the mineral, but they noted the close agreement of their reflectance data with those reported for stibiopalladinite by Desborough *et al.* (1973) and Clark *et al.* (1974).

TABLE 1. Electron-probe analyses of stibiopalladinite and mertieite II

Grain no.	Weight percent						Total	Atomic proportions							
	Pd	Cu	Sb	As	Sn	Pd		Cu	$\Sigma$ Pd	Sb	As	Sn	$\Sigma$ Sb	$\Sigma$ Pd+ $\Sigma$ Sb=100	
													$\Sigma$ Pd	$\Sigma$ Sb	
1.	68.0	1.6	30.5	0.2	0.2	100.5	4.87	0.19	5.06	1.91	0.02	0.01	1.94	72.29	27.71
2.	67.2	1.7	30.3	0.2	0.2	99.6	4.85	0.21	5.06	1.91	0.02	0.01	1.94	72.29	27.71
3.	67.7	1.7	30.7	0.2	0.1	100.4	4.85	0.20	5.05	1.92	0.02	0.01	1.95	72.14	27.86
4.	67.0	1.6	30.6	0.2	0.3	99.7	4.84	0.19	5.03	1.93	0.02	0.02	1.97	71.86	28.14
5.	67.6	1.6	30.6	0.2	0.2	100.2	4.86	0.19	5.05	1.92	0.02	0.01	1.95	72.14	27.86
6.	67.1	1.6	30.4	0.2	0.2	99.5	4.85	0.20	5.05	1.92	0.02	0.01	1.95	72.14	27.86
7.	66.9	1.7	30.9	-	-	99.5	4.80	0.20	5.00	1.94	-	-	1.94	72.05	27.95
8.	67.8	1.9	31.2	-	-	100.9	4.83	0.23	5.06	1.94	-	-	1.94	72.29	27.71
9.	70.8	0.1	25.1	3.4	n.d.	99.4	7.97	0.02	7.99	2.47	0.54	-	3.01	72.61	27.39
10.	71.9	n.d.	25.7	3.2	n.d.	100.8	8.00	-	8.00	2.50	0.50	-	3.00	72.70	27.30
11.	68.9	1.8	27.4	1.9	0.3	100.3	7.67	0.34	8.01	2.66	0.30	0.03	2.99	72.77	27.23
12.	68.8	1.8	27.9	1.8	0.2	100.5	7.65	0.34	7.99	2.71	0.28	0.02	3.01	72.59	27.41
1-6.	Stibiopalladinite														
7.	Clark <i>et al.</i> (1974). Average of 6 grains.														
8.	Desborough <i>et al.</i> (1973). Average of 7 grains.														
9-12.	Mertieite II														
n.d.	not detected														

## X-ray data

Two of three grains of stibiopalladinite (Gr. 1 and Gr. 4), preanalyzed by electron probe and Gandolfi camera, were studied by the precession method using MoK $\alpha$  radiation. The diffraction aspect,  $P1/**c$ , corresponds to space groups  $P6_3/mmc$ ,  $P6_3mc$ , or  $P62c$ . The cell parameters, refined by a least-squares method, are listed in Table 2.

Both stibiopalladinite grains have the same unit cell ( $a \sim 7.6$ ,  $c \sim 28.1 \text{ \AA}$ )<sup>2</sup> and a relatively pronounced subcell with  $a' = a/3$  and  $c' = c/2$ . However, the diffraction spots of Gr. 4 crystal are sharp, while those of Gr. 1 show streaking along  $c^*$  when  $h - k \neq 3n$ . The streaking is interpreted as arising from stacking(?) disorder along the  $c$  direction. The relative intensities of the reflections from these two crystals are not exactly the same, for example, (207), (208), (507), (508), and (509) are fairly strong in Gr. 4 in contrast to the relatively weak intensities in Gr. 1. The difference is probably due to the slight variation in composition, from  $(\text{Pd,Cu})_{5.03}(\text{Sb,As,Sn})_{1.97}$  of Gr. 4 to  $(\text{Pd,Cu})_{5.06}(\text{Sb,As,Sn})_{1.94}$  of Gr. 1. The calculated density for Gr. 4 of  $10.8 \text{ g/cm}^3$ , with  $Z = 12$ , is not unreasonable for this type of mineral.

Desborough *et al.* (1973) reported that stibiopalladinite was either hexagonal ( $a \sim 15.04$ ,  $c \sim n \times 22.41 \text{ \AA}$ ) or orthorhombic ( $P22_12$ ,  $a \sim 12.80$ ,  $b \sim 15.04$ ,  $c \sim 11.36 \text{ \AA}$ ) with  $a_{\text{orth}} = \cos 30^\circ \cdot a_{\text{hex}}$ ,  $b_{\text{orth}} = b_{\text{hex}}$ , and that due to the optical properties of the mineral, the orthorhombic symmetry was considered more likely. The  $a$  axis,  $7.60 \text{ \AA}$ , obtained in the present study is about half of their orthorhombic  $b$  axis. The cone-axis and single-crystal photographs taken in the present study do not show doubling of the  $a$  axis. Nor can the  $c$  axis be  $\sim 11.36$  or  $n \times 22.41 \text{ \AA}$ . Thus the "orthorhombic" symmetry of stibiopalladinite from Tweefontein might have been due to twinning which they observed in their single-crystal photographs. Also their material has a different length of  $c$  on either a hexagonal or an orthorhombic cell from that of our stibiopalladinite ( $\sim 28.1 \text{ \AA}$ ). There are integer (or near integer) ratios between our and Desborough *et al.*'s cell:  $28.1/22.4 \approx 5/4$  and  $28.1/11.36 \approx 5/2$ . Therefore the possibility of polytypism in stibiopalladinite should not be excluded.

The X-ray powder diffraction data obtained by the Gandolfi camera were indexed by comparison of the

TABLE 2. Crystal data of stibiopalladinite, synthetic Pd<sub>5</sub>Sb<sub>2</sub> and Pd<sub>5</sub>(Sb,As)<sub>2</sub>

Space Group	Stibiopalladinite		Synthetic	Synthetic
	Gr. 1	Gr. 4	Pd <sub>5</sub> Sb <sub>2</sub>	Pd <sub>5</sub> Sb <sub>1.94</sub> As <sub>0.06</sub>
	$P6_3/mmc, P6_3mc, P62c$		$P6_3cm$	$P6_3cm$
$a$	7.607(2)	7.598(2)	7.603(1)	7.595(1)
$c$	28.220(6)	28.112(9)	13.853(4)	13.880(4)
$Z$	12	12	6	6

observed  $d$  values with the calculated values obtained from single-crystal data: only the strong reflections on single-crystal photographs being used to index the patterns. The results are listed in Table 3 in comparison with those given by Desborough *et al.* and with those of the synthetic phase Pd<sub>5</sub>Sb<sub>2</sub>. Although variations of intensities are present in these two stibiopalladinite crystals (Gr. 1 and Gr. 4), in general the powder patterns of these two crystals are similar, and are similar to those reported by Berry and Thompson (1962) (HMM 90667) as well as to those obtained on a specimen from Tweefontein (USNM R6483) by Desborough *et al.*, except that the latter show more weak lines which probably resulted from the better resolution of the Debye-Scherrer camera. The small differences in  $d$  values are assumed due to the small variations in composition and cell dimensions.

## Synthetic palladium antimonides

Two synthetic compounds, Pd<sub>5</sub>Sb<sub>2</sub> and Pd<sub>5</sub>(Sb<sub>1.94</sub>As<sub>0.06</sub>), synthesized at  $710^\circ\text{C}$  and quenched (Cabri *et al.*, 1975), were studied by the X-ray single-crystal method. Each shows diffraction aspect  $P6/**c$ , corresponding to the space group  $P6_3cm$  determined by structure analysis (El-Boragy *et al.* 1970). The crystal data (Table 2) suggest that the As-bearing compound is part of the Pd<sub>5</sub>Sb<sub>2</sub> solid solution. The  $c$  parameter of this Pd<sub>5</sub>Sb<sub>2</sub> s.s. phase is approximately half of the  $c$  parameter of stibiopalladinite. However, the X-ray powder diffraction patterns of this phase show significant differences in intensities from those of the stibiopalladinite (Table 3), although the indices of each reflection may be related to those of stibiopalladinite by  $100/010/00\frac{1}{2}$ . The calculated densities of Pd<sub>5</sub>Sb<sub>2</sub> and Pd<sub>5</sub>Sb<sub>1.94</sub>As<sub>0.06</sub>, for  $Z = 6$ , are both  $11.1 \text{ g/cm}^3$ .

The synthetic compound Pd<sub>4.85</sub>Cu<sub>0.15</sub>Sb<sub>2</sub> was examined with a  $114.6 \text{ mm}$  Gandolfi camera and has the same powder pattern as synthetic Pd<sub>5</sub>Sb<sub>2</sub>. Therefore Cu is non-essential for synthetic (Pd,Cu)<sub>5</sub>Sb<sub>2</sub>. This also suggests that the difference between stibiopal-

<sup>2</sup> A composite grain from Potgietersrust (BM Spec. No. 1930, 951) was determined to be hexagonal with  $a = 7.6$ ,  $c = 28.0 \text{ \AA}$  for the principal constituent (R. J. Davis, personal communication, 1976).

TABLE 3. X-ray powder diffraction data of stibiopalladinite and synthetic Pd<sub>5</sub>Sb<sub>2</sub>

h k l*	d <sub>calc</sub> **	Gr. 4		Stibiopalladinite		USNM R6483***		Synth Pd <sub>5</sub> Sb <sub>2</sub>	
		d <sub>obs</sub>	I <sub>est</sub>	d <sub>obs</sub>	I <sub>est</sub>	d <sub>obs</sub>	I <sub>est</sub>	d <sub>obs</sub>	I <sub>est</sub>
0 1 6	3.817					3.82	W		
0 0 8	3.514					3.53	VW	3.461	½
1 1 4	3.342					3.36	W	3.328	1
0 1 8	3.100					3.18	VW	3.057	1
0 2 4	2.980					2.96	VW	2.965	1
0.0.10	2.811					2.83	VW	-	
1 1 8	2.580					2.55	W	2.559	1
1 2 0	2.487	2.487	½	2.470	1 ½	2.47	MW	-	
1 2 2	2.449	-						2.449	3
0 2 8	2.402	2.397	1			2.40	W	2.385	3
0.0.12	2.343	2.338	½			2.34	VW	2.339	½
0 2 9	2.265	2.263	10	2.269	10	2.273	VS	2.240	10
1.1.10	2.260							2.191	10
0 3 0	2.194	2.194	10	2.193	9	2.194	VS		
1 2 7	2.115	-				2.126	VW	-	
1 2 8	2.030	2.029	½	2.032	1	-		2.020	3
1.1.12	1.994	1.992	1	2.000	1	-		1.973	3
1 2 9	1.946	1.943	½	1.948	½	1.966	MW	-	
0.2.12	1.908	-				1.956	W	1.888	1
0 3 8	1.861	1.858	1	1.864	2	1.872	W	1.855	1½
1 3 1	1.821	-				1.823	VW	-	
1 3 2	1.810	-						1.808	1
2.2.10	1.574	1.576	4	1.576	4	1.579	M	1.567	5
2 3 1	1.507	-		1.510	½	1.511	W	-	
2 3 2	1.501	-						1.501	1
2.2.12	1.476	1.474	1	1.480	1	1.485	W	1.469	2
1.3.12	1.440	-						1.433	1½
1 4 2	1.429	1.429	2	1.429	2	1.431	W	-	
0.0.20	1.406	1.405	1	1.411	1	1.406	VW	-	
2 3 8	1.387	1.386	2	-		1.388	W	1.385	4
0.1.20	1.375	-						1.357	1
2 3 9	1.359	1.360	2	-		1.363	W	-	
2.3.10	1.330	-				1.336	VW	-	
1.1.20	1.318	1.317	2	1.320	1	1.318	VW	1.301	2
1.4.10	1.279	1.279	5	1.282	4	1.284	MW	1.277	4
0.0.22	1.279	1.267	3	1.268	2	1.268	MW	1.267	4
3 3 0	1.266	-		1.245	½	1.245	VW	-	
0.2.21	1.240	-						-	
0 5 8	1.233	1.228	5	1.230	3	1.227	MW	1.231	1
1.4.12	1.224	-						1.220	3
0 5 9	1.213	1.212	1	-		-		-	
3 3 8	1.191	1.192	1	1.193	2	1.194	MW	1.189	1½
0.3.20	1.184	1.183	5	1.187	3	1.181	MW	1.171	3

114.6 mm Gandolfi camera; CuK $\alpha$  radiation ( $\lambda = 1.5418\text{\AA}$ ).

\* Indexed on stibiopalladinite cell. Indices for synthetic Pd<sub>5</sub>Sb<sub>2</sub> can be derived by 100/010/00½ from those of stibiopalladinite.

\*\* Calculated from  $a = 7.598$ ,  $c = 28.112\text{\AA}$  (Gr. 4)

\*\*\* Desborough et al. (1973). 114.6 mm Debye-Scherrer camera, CuK $\alpha$  radiation.

ladinite (Pd,Cu)<sub>5+</sub>Sb<sub>2-</sub> and Pd<sub>5</sub>Sb<sub>2</sub> is not due to the presence of Cu.

In addition to Pd<sub>5</sub>Sb<sub>2</sub>, El-Boragy *et al.* (1970) and El-Boragy and Schubert (1971), on the basis of X-ray powder data, reported that the phase Pd<sub>5+</sub>Sb<sub>2-</sub>, with composition ranging from Pd<sub>72.3</sub>Sb<sub>27.7</sub> to Pd<sub>71.9</sub>Sb<sub>28.2</sub>, was synthesized at 500–800°C. The X-ray powder pattern of this quenched phase was reported to have the Pd<sub>5</sub>Sb<sub>2</sub>-type structure, and its pattern was indexed with rhombohedral symmetry,  $a = 7.613$  and  $c = 42.240\text{\AA}$ . However, the powder data of this phase are not close to those of the Pd<sub>5</sub>Sb<sub>2</sub>, nor identical with those of the stibiopalladinite, although the three

strongest lines (2.265, 2.200, 1.580Å) are correlatable with those of Pd<sub>5</sub>Sb<sub>2</sub> (2.240, 2.191, 1.567Å) and of stibiopalladinite (2.263, 2.194, 1.576Å).

El-Boragy and Schubert (1971) and Cabri *et al.* (1975) reported synthesis of the phase Pd<sub>5</sub>Sb<sub>3</sub> at 610–700°C, which was indexed rhombohedrally with cell dimensions  $a \sim 7.6$ ,  $c \sim 42.8\text{\AA}$ . The X-ray powder diffraction data of this phase are different to those of the Pd<sub>5+</sub>Sb<sub>2-</sub> phase and those of stibiopalladinite.

Desborough *et al.* (1973) were unable to synthesize Pd<sub>5</sub>Sb, although El-Boragy and Schubert (1971) reported that the same phase was synthesized at 500–800°C. The composition of this phase was later

reported by Cabri *et al.* (1975) to be approximately  $\text{Pd}_{2.9}\text{Sb}$ . The X-ray powder data of this  $\text{Pd}_{2.9}\text{Sb}$  give three strongest lines at 2.20, 1.94, and 1.56Å, in contrast to the strongest lines of the other synthetic (Pd,Sb) phases or stibiopalladinite.

### Related minerals

Desborough *et al.* (1973) described a new mineral mertieite, with general formula  $(\text{Pd,Cu})_{5+x}(\text{Sb,As})_{2-x}$  where  $x = 0.1-0.2$ , with pseudo-hexagonal symmetry, possibly monoclinic, and pseudo-hexagonal axes,  $a = 15.04$ , and  $c = 22.41\text{Å}$ . The mineral was reported to be structurally related to stibiopalladinite, and the ideal formula  $\text{Pd}_5(\text{Sb,As})_2$  was suggested. Arsenic was considered to be essential for mertieite.

Although the synthetic compound  $\text{Pd}_5(\text{Sb,As})_2$  was reported to give X-ray powder data similar to those of mertieite (Desborough *et al.* 1973), X-ray single-crystal study of synthetic phases along the  $\text{Pd}_5\text{As}_2$ - $\text{Pd}_5\text{Sb}_2$  join (Cabri *et al.* 1975) showed these to possess different unit cells from those of mertieite or stibiopalladinite.

On the basis of X-ray powder diffraction data and probe analyses, Desborough *et al.* (1973) divided their mertieite into two groups: mertieite I,  $(\text{Pd}_{5.04}\text{Cu}_{0.14})(\text{Sb}_{0.92}\text{As}_{0.80})$ , and mertieite II,  $(\text{Pd}_{5.13}\text{Cu}_{0.02})(\text{Sb}_{1.53}\text{As}_{0.33})$ . The published data of mertieite I show a  $\Sigma\text{Pd}$  of 74 atom percent which is very close to  $\text{Pd}_5\text{Sb}$ . Two grains of their mertieite II were reexamined by Cabri *et al.* (1975) and found to have the stoichiometric composition  $\text{Pd}_6(\text{Sb,As})_3$ , with diffraction aspect  $R^{**}$  and cell dimensions  $a = 7.55$ ,  $c = 43.18\text{Å}$ .

In addition to the six stibiopalladinite grains, four grains of mertieite II from Farm Tweefontein (ROM M19388) were also quantitatively analyzed (Table 1). The analyses, with  $\Sigma(\text{Pd,Cu})$  from 7.99 to 8.01 on the basis of total atoms = 11, correspond well with the 8:3 stoichiometry suggested by Cabri *et al.* (1975) and range in Cu content from not detected, *i.e.* about 0.03 weight percent, to higher than those reported by Desborough *et al.* (1973). Sn is reported for the first time. Two of the four grains (see analyses No. 10 and 11 in Table 1) were also confirmed to be mertieite II by X-ray powder diffraction with a Gandolfi camera.

Razin and Dubakina (1974) reported two "mertieites" with composition  $(\text{Pd,Ag})_{5-x}(\text{Sb,As})_2$  from Noril'sk and another "mertieite" from Ingali as  $(\text{Pd,Cu})_{3+x}(\text{Sb,As})$ . The minerals were reported to have similar X-ray powder patterns as those of stibiopalladinite and to the mertieite pattern of Desborough *et al.* The compositions of the Noril'sk

"mertieites" are more As-rich than the "stibiopalladinite,"  $(\text{Pd}_{4.74}\text{Cu}_{0.16}\text{Pt}_{0.07})_{\Sigma=4.97}(\text{Sb}_{1.85}\text{As}_{0.18})_{\Sigma=2.03}$ , from Driekop reported by Tarkian and Stumpfl (1975) and all are 5:2 compounds. The Ingali "mertieite," however, has a different stoichiometry. These minerals should be reexamined by single-crystal methods.

### Conclusions

Stibiopalladinite from the type locality has space group symmetry  $P6_3/mmc$ ,  $P6_3mc$  or  $P\bar{6}2c$ , with cell dimensions  $a \sim 7.60$ ,  $c \sim 28.1\text{Å}$ . These cell dimensions may be related to those of mertieite II (Cabri *et al.*, 1975) by the relationship  $a_{\text{stib}} = a_{\text{mert II}}$  and  $c_{\text{stib}} = 2/3 c_{\text{mert II}}$ . This relationship may have structural implications which would require that the structural formula of stibiopalladinite be written as  $\text{Pd}_{8-x}\text{Sb}_{3+x}$ , with  $x \approx 0.065$ . This can only be established by a detailed crystal-structure analysis. For the present, however, we shall refer to stibiopalladinite as  $(\text{Pd,Cu})_{5+x}\text{Sb}_{2-x}$  because of its close relationship with the  $\text{Pd}_{5+x}\text{Sb}_{2-}$  of El-Boragy *et al.* (1970).

The material studied by Desborough *et al.* (1973), having the same chemical composition and similar X-ray powder diffraction pattern, probably has the same unit cell as observed in this study. Judging from the variations of intensities of the X-ray powder diffraction lines due to the changes in chemical composition, the synthetic phase  $\text{Pd}_{5+x}\text{Sb}_{2-}$  reported by El-Boragy *et al.* (1970) may have the same space-group symmetry as stibiopalladinite, though the justification can only be made by X-ray single-crystal data. The material studied by Tarkian and Stumpfl (1975) and the Noril'sk "mertieites" reported by Razin and Dubakina (1974), having general compositions very close to  $\text{Pd}_5(\text{Sb,As})_2$ , may show crystal data either like those of synthetic  $\text{Pd}_5\text{Sb}_2$ , or  $\text{Pd}_5(\text{Sb}_{1.61}\text{As}_{0.39})$ , or  $\text{Pd}_5(\text{Sb}_{1.40}\text{As}_{0.60})$  (Cabri *et al.*, 1975). In any case, they would be a different mineral species to stibiopalladinite. However, the possibility that a solid solution extends from  $\text{Pd}_{5+x}\text{Sb}_{2-x}$  to  $\text{Pd}_5(\text{Sb,As})_2$  should not be excluded. The identification of these minerals can only be made by X-ray single-crystal work.

### Preservation of material studied

To our knowledge, no true type material is known to exist, since the material analyzed by Adam (1927) was consumed by chemical analysis. The three specimens at the British Museum (BM 1930, 950-2) were donated by H. R. Adam in 1930 and may represent type material or at the worst are topotypic. Stibiopalladinite from the type locality, Gr. 1 and Gr. 6 (Table

1), X-rayed and probed by us are preserved in the Royal Ontario Museum (M 34299) and Smithsonian Institution (USNM 135408), respectively. The remainder of the vial of concentrate (M 19388) is also at the Royal Ontario Museum, while Gr. 4 is kept in our Crystal Structure Laboratory and a polished section containing Grs. 2, 3, and 5, plus mertieite II and other PGM is kept in our Mineralogical Laboratory.

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### References

- ADAM, H. R. (1927) Note on a new palladium mineral from Potgietersrust platinum field. *J. Chem. Met. Min. Soc. S. Africa*, **27**, 249–250.
- BERRY, L. G. AND R. M. THOMPSON (1962) X-ray powder data for ore minerals—The Peacock atlas. *Geol. Soc. Am. Mem.* **85**, 281 p.
- BOYD, F. R., L. W. FINGER AND F. CHAYES (1969) Computer reduction of electron probe data. *Carnegie Inst. Wash. Year Book*, **67**, 210–215.
- CABRI, L. J., J. H. G. LAFLAMME, J. M. STEWART, J. F. ROWLAND AND T. T. CHEN (1975) New data on some palladium arsenides and antimonides. *Can. Mineral.* **13**, 321–335.
- CLARK, A. M., A. J. CRIDDLE AND E. E. FEJER (1974) Palladium arsenide-antimonides from Itabira, Minas Gerais, Brazil. *Mineral. Mag.* **39**, 528–543.
- DESBOROUGH, G. A., J. J. FINNEY AND B. F. LEONARD (1973) Mertieite, a new palladium mineral from Goodnews Bay, Alaska. *Am. Mineral.* **58**, 1–10.
- EL-BORAGY, M., S. BHAN AND K. SCHUBERT (1970) Kristallstruktur von  $Pd_5Sb_2$  und  $Ni_5As_2$  und einigen Varianten. *J. Less-Common Metals*, **22**, 445–458.
- AND K. SCHUBERT (1971) Über einige Varianten der NiAs-Familie in Mischungen des Palladiums mit B-Elementen. *Z. Metallkde.* **62**, 314–323.
- GENKIN, A. D. (1968) Minerals of the platinum metals and their association in the copper-nickel ores of the Noril'sk deposits. *Akad. Nauk SSSR, Inst. Geol. Rud. Mestorozhd., Petrogr. Mineral. Geokhim.*, 106 p. (in Russian).
- RAZIN, L. V. AND L. S. DUBAKINA (1974) New findings of arsenoantimonides and arsenostannides of palladium in the platinum deposits in the U.S.S.R. *Zapiski Vses. Mineralog. Obshch.* **103**, 581–594 (in Russian).
- RUCKLIDGE, J. C. AND E. L. GASPARRINI (1969) Electron microprobe analytical data reduction, EMPADR VII. Dept. Geol. Univ. Toronto.
- TARKIAN, M. AND E. F. STUMPFEL (1975) Platinum mineralogy of the Driekop mine, South Africa. *Mineral. Deposita*, **10**, 71–85.

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