

Mertieite, A New Palladium Mineral from Goodnews Bay, Alaska¹

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Abstract

Precious-metal placer concentrates provided by John B. Mertie, Jr., and obtained from the Goodnews Bay Mining Company carry a new palladium mineral, mertieite, that has the approximate composition $\text{Pd}_5(\text{Sb, As})_2$ and contains 0–2.5 weight percent copper. Mertieite in polished section is brassy yellow, birefractant, and distinctly anisotropic. At 546 nm, in air, R_p' ranges from 50.8 to 56.4 percent and R_g' from 53.6 to 59.0 percent; $\bar{R} = 55.5$ percent $\approx R_m$. $HV_{50} = 561$ – 593 , mean 578. Precession photographs show that mertieite is pseudo-hexagonal, possibly monoclinic, with pseudo-hexagonal $a = 15.04$, $c = 22.41$ Å. Strongest lines in X-ray powder photographs are 2.28 vs, 2.23 *mw-s*, 2.17 *m-vs*, 2.01–2.02 *m*. A total of 43 reflections are indexable according to the pseudo-hexagonal cell. Electron microprobe analysis of eight mertieite grains show Pd 70.8–74.0, Cu < 0.1–2.5, Sb 15.2–25.5, as 2.8–9.4 wt percent, sum 97.8–100.8. The name mertieite is in honor of John B. Mertie, Jr., of the U.S. Geological Survey, who studied the Goodnews Bay, Alaska, platinum placers. The name and the mineral have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association.

An inhomogeneous but stoichiometric compound whose bulk composition is $\text{Pd}_5(\text{Sb, As})_2$ has been synthesized. The X-ray powder pattern of this compound is essentially the same as that of mertieite.

Quantitative microprobe analysis of X-ray stibiopalladinite from the locality of its original description shows that the chemical formula of this mineral should be Pd_5Sb_2 rather than Pd_5Sb . A stable phase corresponding to Pd_5Sb could not be synthesized. Arsenic is not detected in stibiopalladinite but is present in all grains of mertieite. Precession photographs show that stibiopalladinite is different from mertieite and is either hexagonal or perhaps orthorhombic. Powder data for stibiopalladinite can be indexed provisionally according to a cell having $a = 12.80$, $b = 15.04$, $c = 11.36$ Å. If stibiopalladinite is truly orthorhombic, its space group is $P22_2$, but the space group assignment must be regarded as tentative. Optically, stibiopalladinite resembles mertieite but differs in magnitude and sign of birefractance. For stibiopalladinite, at 546 nm in air, R_p' ranges from 51.8 to 54.9 percent and R_g' from 52.3 to 55.4 percent; $\bar{R} = 53.6$ and $R_m' = 54.4$ percent. $HV_{50} = 589$ – 644 , mean 607.

Introduction

Several brassy-colored grains, which range from 0.10 to 0.50 mm in maximum dimensions but are mostly less than 0.25 mm, occur in precious-metal placer concentrates at Goodnews Bay, Alaska. Grains in the concentrates are chiefly alloys of platinum, iridium, and osmium. The palladium mineral, when polished, appears as a brassy yellow phase, exhibits slight birefractance, and is distinctly anisotropic with crossed nicols; in oil its appearance is unchanged. It is the only major palladium mineral observed in the placer concentrates. Its recognition is based on qualitative electron microprobe and X-ray fluorescence

milliprobe analysis of about 250 alloy grains of the precious-metal concentrates of which palladium is only a minor constituent. Palladium constitutes less than 0.5 wt percent of the platinum metals of the district (Mertie, 1969, Table 37). For analyses of concentrates, see Mertie (1940, p. 76–85; 1969, p. 86–87).

Two of the palladium mineral grains contain irregularly distributed intergrown native gold. Silver is the only element alloyed with the gold, and it constitutes about 35 wt percent. Minerals other than gold were not observed in contact with the palladium mineral. The precious metal placer concentrates appear to be derived from ultramafic bedrock, because chromite is a common constituent in the concentrates and also occurs intergrown with platinum-group

¹ Publication authorized by the Director, U.S. Geological Survey.

TABLE 1. COMPOSITION AND PHYSICAL PROPERTIES* OF MERTIEITE AND STIBIOPALLADINITE

Composition (weight percent)										
Mertieite							Stibiopalladinite			
Group I				Group II						
Four grains				Four grains (five areas)			Seven grains			
Range	Mean	s ^{1/}		Range	Mean	s ^{1/}	Mean		s ^{1/}	
Pd	70.8-74.0	72.9	1.4	71.5-73.1	72.3	0.8	67.8		±0.5	
Cu	<0.1- 2.5	-1.2	-1.1	<0.1- 0.2	<0.1	-0.1	1.9		±0.1	
Sb	15.2-15.3	15.3	0.06	23.4-25.5	24.7	0.8	31.2		±0.5	
As	9.0- 9.4	9.2	0.2	2.8- 4.2	3.3	0.6	-		-	
	97.6-99.9	-98.6	1.0	99.4-100.8	100.4	0.6	100.9			
Formula (mean)										
[best approximation for mertieite taken as (Pd,Cu) _{5+x} (Sb,As) _{2-x} , where x = 0.1-0.2]										
Mertieite - Group I				Mertieite - Group II			Stibiopalladinite			
(Pd _{5.04} Cu _{0.14})(Sb _{0.92} As _{0.90})				(Pd _{5.13} Cu _{<0.02})(Sb _{1.53} As _{0.33})			(Pd _{4.83} Cu _{0.23})Sb _{1.94}			
Reflectance										
wave-length, nm	Four grains			Four grains			Eight grains			
	470	546	589	470	546	589	470	546	589	
R _g ¹	45.7-54.8	54.6-58.5	57.7-61.4	48.9-55.0	53.6-59.0	55.3-61.4	47.0-51.7	52.3-55.4	55.1-58.2	
R _m ^{2/}	50.3	54.9	57.2	-	-	-	48.4	54.4	57.0	
R _p ¹	45.0-50.8	53.3-54.9	56.2-57.1	48.9-52.2	50.8-56.4	52.7-58.8	45.6-50.3	51.8-54.9	55.1-57.2	
$\frac{R_g + R_p}{2}$	50.2	55.5	58.0	51.2	55.6	57.2	48.6	53.6	56.6	
Vickers hardness, 50-gram load										
	Two grains			Two grains			Seven grains			
Means	570,593			582,584			590-644			
	Five grains--ungrouped data									
	578						607			

*R_g¹ = maximum reflectance for observed orientation of grain; R_m = intermediate principal reflectance; R_p¹ = minimum reflectance for observed orientation of grain; n.d. = not determined.

^{1/} Standard deviation of the sample.

^{2/} R_m of mertieite determined from section of null bireflectance observed in one grain only. R_m¹ of stibiopalladinite determined statistically.

metal alloys as well as with minor laurite (RuS₂) in a nugget (Leonard *et al.*, 1969).

Quantitative Physical Properties of Mertieite

For seven grains of mertieite, the reflectance values measured at 470, 546, and 589 nm with a Reichert photoelectric microphotometer reveal no constant value for any particular wavelength. Thus mertieite cannot be tetragonal or hexagonal. The United States primary germanium standard calibrated by the National Physical Laboratory, Teddington, England, was used as the standard for comparison. Values for the germanium standard are 47.0, 51.3, and 52.0 percent at 470, 546, and 589 nm (nanometers), respectively.

The indentation or Vickers hardness of mertieite, as measured with a Leitz hardness indenter using a 50-gram load (Table 1), is moderately high and comparable to that of magnetite.

Quantitative Chemical Analysis and X-ray Powder Data

Quantitative electron microprobe analysis using the Applied Research Laboratories instrument of the U.S. Geological Survey was carried out at 20 kV and a specimen current of 1.5×10^{-8} amp and constant beam current. The following synthetic materials were used as standards (numbers express wt percent): (1) Pd wire (99.99 percent); (2) Pd_{85.3}Fe_{14.7}; (3) Au_{73.52}Pd_{26.48}; (4) Pt_{88.01}Pd_{11.99}; (5) Sb_{100.0}; Pt_{56.58}As_{43.42}; (7) Ag_{36.72}Sb_{41.45}S_{21.83}; (8) Ag_{59.76}Sb_{22.48}S_{17.76}; (9) Ag_{63.19}Sb_{14.26}S_{22.54}; (10) Fe_{30.48}Cu_{34.62}S_{34.94}; (11) Pd_{60.65}Sn_{39.35}. Selection of these standards was determined by similarity in composition and average atomic number (\bar{Z}) to the unknown. The standard of nearest concentration to the unknown was used for each element determined. Linearity of element concentration versus X-ray line

intensity for the standards precluded use of other corrections. Deviations of X-ray line intensity versus element concentration are included in the "uncertainty" of analysis. Wavelength scans were made on the analyzed grains by means of LiF and ADP crystals for detection of major and minor elements. Simultaneous quantitative analyses for each of three elements were performed with the following analyzing crystals for the indicated spectral lines: (1) ADP for $\text{PdL}\alpha$, LiF for $\text{CuK}\alpha$, and ADP for $\text{SbL}\alpha$; (2) ADP for $\text{SbL}\alpha$, LiF for $\text{AsK}\alpha$, and ADP for $\text{PdL}\alpha$. Results of analysis of eight mertieite grains are given in Table 1. The maximum uncertainty value is based on the reproducibility of analysis at three separate times and on the variations in line intensity attributed to instrument drift or instability, as judged by measurements on the standards both before and after analysis of the Pd mineral. The values listed are the average of determinations of five to ten areas on each of eight grains during two separate periods of analysis. Six of the eight grains are chemically homogeneous within the limits of analysis. Mineragraphic studies show that one of the slightly inhomogeneous grains is composed of several different optical units which correspond to the compositional variations observed.

Data for the eight analyzed grains (Table 1) have been combined into groups, at the editor's suggestion. The grains of group I differ significantly from those of group II in Sb and As content, even when allowance is made for the maximum uncertainty in the microprobe analysis. However, grains of the two groups do not differ significantly in reflectance, microhardness, or X-ray powder data.

Results of microprobe analysis indicate mutual substitution of antimony and arsenic but a fixed ratio of palladium to antimony plus arsenic (Table 1). A general atomic formula of $\text{Pd}_5(\text{Sb,As})_2$ is indicated by the chemical data; however, a more satisfactory expression is $(\text{Pd,Cu})_{5+x}(\text{Sb,As})_{2-x}$, where $x = 0.1-0.2$. Copper may be nonessential in the formula inasmuch as five of the eight grains analyzed contain less than 0.1 wt percent Cu (Table 1).

The formula of mertieite, $\text{Pd}_5(\text{Sb,As})_2$, is similar to the formulas ascribed to stibiopalladinite, Pd_3Sb , to arsenopalladinite, Pd_3As , and to the compound, Pd_5As_2 , synthesized by Raub and Webb (1963). The crystal structure has not been determined, but X-ray powder data show the five strongest lines to be 2.20(10), 2.33(8), 2.365(8), 2.268(4), 2.116(4). Chemical data indicate that mertieite differs from

stibiopalladinite in that 2.8 to 9.4 wt percent arsenic is present in all grains of mertieite. The synthetic compound Pd_3As is tetragonal and has the Fe_3P structure (Schubert *et al.*, 1960). X-ray powder data for stibiopalladinite have been published (Berry and Thompson, 1962; Ramdohr, 1960; Genkin, 1968), but, to our knowledge, the structure has not been determined. The differences in listed d -values and intensities for the X-ray reflections of $\text{Pd}_5(\text{Sb,As})_2$ shown for each mertieite grain sampled (Table 2) are partly the result of spottiness of powder patterns and partly of actual differences in the smallest d -values. Compositional differences in the two different grains are probably responsible for some of the variation in spacings (Tables 1 and 2). Actual differences in the position of the arcs representing highest values of 2θ are evident by overlaying the powder patterns. The X-ray data of mertieite are dealt with more fully in the following comparison of mertieite and stibiopalladinite.

Comparison of Mertieite and Stibiopalladinite

For direct comparison, stibiopalladinite was obtained from the U.S. National Museum (USNM specimen No. R6483). This specimen is from Farm Tweefontein, 16 miles from Potgietersrust, Transvaal, South Africa, and is the same as that used for X-ray diffraction by Berry and Thompson (1962, p. 32). In the Tweefontein specimen subhedral grains of stibiopalladinite less than 0.5 mm in diameter are disseminated along one side of a mafic silicate rock which appears to be hortonolite dunite. Several grains were removed for X-ray diffraction studies and electron microprobe analysis.

Two separate powder spindles of stibiopalladinite were prepared from fragments of several different grains. The resulting X-ray diffraction data (Table 2) differ somewhat from those reported for stibiopalladinite by Ramdohr (1960), Berry and Thompson (1962), and Genkin (1968, Table 17). The X-ray reflections listed by Ramdohr (1960) as the strongest for stibiopalladinite are in poor agreement with those given by Berry and Thompson (1962). Possibly these discrepancies result from compositional differences.

The distinctive but rather inconspicuous differences in the powder data of mertieite and stibiopalladinite (Table 2) were confirmed by precession photographs, for which even minute single crystals were difficult to obtain. Mertieite is pseudo-hexagonal, monoclinic(?), with pseudo-hexagonal $a = 15.04$,

TABLE 2. X-RAY POWDER DATA* FOR MERTIEITE, ITS SYNTHETIC ANALOGUE, AND STIBIOPALLADINITE

Synthetic analogue** of mertieite		Mertieite-Pd ₅ (Sb,As) ₂						Stibiopalladinite, Pd ₅ Sb ₂					
		Group I				Group II		USNM R6483					
Cu/Ni d(obs.)Å		Spindle #8 Cu/Ni d(obs.)Å	I	Spindle #9 Cu/Ni d(obs.)Å	I	Spindle #6 Fe/Mn d(obs.)Å	I	d(obs.)Å	I	Cu/Ni d(obs.)Å	I	Cu/Ni d(obs.)Å	I
-----		-----		-----		-----		-----		3.88	w	3.82	w
-----		-----		3.65	w	-----		-----		3.50	vw	3.53	vw
-----		-----		3.34	vw	-----		-----		3.35	mw	3.36	w
-----		-----		-----		-----		3.01	mw	3.13	vw	3.18	vw
2.786	w	2.783	w	2.779	w	2.770	vw	-----		2.95	vw	2.96	vw
-----		-----		-----		-----		-----		2.84	mw	2.83	vw
2.597	w	2.592	w	2.589	w	2.586		2.600	w	2.78	vw	-----	
2.516	w	2.522	w	2.518		2.505	vw	-----		2.55	w	2.55	w
2.456	m	-----		2.452	mw	-----		2.456	w	2.48	mw	2.47	mw
2.382	s	2.395	w	2.392	w	2.391	vw	2.400	w	2.40	w	2.40	w
-----		2.359	w	2.365	w	-----		-----		-----		-----	
-----		-----		-----		2.316	w	-----		2.33	vw	2.34	vw
2.278	s	2.281	vs	2.278	vs	2.279	vs	2.279	vs	2.270	vs	2.273	vs
2.231	m	2.232	mw	2.232	m	2.230	s	2.233	ms	-----		-----	
2.180	vs	2.171	vs	2.171	vs	2.169	vs	2.172	m	2.194	vs	2.194	vs
-----		-----		2.135	vw	2.132	m	-----		-----		2.126	vw
2.058	mw	2.076	vw	2.078	vw	-----		2.078	mw	-----		-----	
2.016	m	2.014	m	2.017	m	-----		2.019	m	2.015	mw	1.966	mw
1.920	mw	1.920	mw	1.918	m	1.920	m	1.923	ms	1.954	w	1.956	w
1.879	mw	1.861	mw	1.861	m	1.864	w	-----		1.880	w	1.872	w
1.826	m	-----		1.816	vw	-----		1.811	w	1.860	w	-----	
1.732	vw	-----		1.798	vw	-----		-----		1.820	vw	1.823	vw
1.608	w	-----		-----		-----		1.675	m	1.791	vw	-----	
1.573	w	1.573	m	1.572	m	1.573	m	1.576	w	1.577	m	1.579	m
1.544	mw	-----		1.491	vw	1.491	w	-----		1.507	vw	1.511	w
-----		1.477	mw	1.477	m	1.476	w	1.481	m	1.480	w	1.485	w
1.456	w	-----		1.449	vw	1.453	mw	1.456	w	-----		1.431	w
-----		1.435	mw	1.434	w	1.429	w	-----		1.427	w	1.406	vw
-----		1.413	w	1.411	w	1.410	m	1.416	mw	1.385	vw	1.388	w
-----		1.341	m	1.340	mw	1.343	w	1.343	w	1.359	w	1.363	w
-----		-----		-----		1.317	w	-----		1.335	vw	1.336	vw
1.261	mw	1.272	w	1.272	mw	1.272	w	1.273	w	1.316	w	1.318	vw
-----		1.254	w	1.252	w	1.254 ₀₁	m	-----		1.282	mw	1.284	mw

$c = 22.41$ Å. Stibiopalladinite seems to be hexagonal or perhaps orthorhombic. Pseudohexagonal a and c of mertieite correspond to hexagonal a and c of stibiopalladinite, but c of stibiopalladinite is some multiple of c of mertieite. The $h0l$ reflections of stibiopalladinite are streaked where $h \neq 3n$; this suggests disordering along c of stibiopalladinite. Qualitatively at least, the precession photographs of mer-

tieite and stibiopalladinite support the findings from probe analyses and X-ray powder photography that the two minerals are different. The pseudohexagonal, rather than truly hexagonal, symmetry shown by precession photographs of mertieite confirms the deduction from optical study that the symmetry of mertieite must be lower than tetragonal or hexagonal.

The interplanar spacings of mertieite, averaged

TABLE 2, Continued

Mertieite-Pd ₅ (Sb,As) ₂						Stibiopalladinite, Pd ₅ Sb ₂					
Group I			Group II			USNM R6483					
Spindle #8 Cu/Ni d(obs.)Å	I	Spindle #9 Cu/Ni d(obs.)Å	I	Spindle #6 Fe/Mn d(obs.)Å	I	d(obs.)Å	I	Cu/Ni d(obs.)Å	I	Cu/Ni d(obs.)Å	I
1.222	m	1.222	mw	1.222 α_1	m	1.225	w	1.265	mw	1.268	mw
1.196	m	1.197	mw	1.197 α_1	m	1.200	m	1.241	vw	1.245	vw
1.181	mw	1.180	mw	1.180 α_1	m	-----	-----	1.227	mw	1.227	mw
-----	-----	1.170	vw	-----	-----	1.171	mw	1.194	mw	1.194	mw
1.148	vw	1.142	vw	-----	-----	-----	-----	1.182	mw	1.181	mw
-----	-----	-----	-----	-----	-----	1.103	m	1.097	vw	1.097	mw
-----	-----	-----	-----	-----	-----	1.089 α_1	m	-----	-----	-----	-----
-----	-----	-----	-----	-----	-----	1.081 μ	m	-----	-----	-----	-----
-----	-----	-----	-----	1.061 α_1	m	-----	-----	-----	-----	-----	-----
-----	-----	-----	-----	1.052 α_1	m	1.055 α_1	w	1.051	vw	1.049	mw
1.0404	w	1.0392 α_1	mw	1.0400 α_1	m	1.0433 α	m	-----	-----	-----	-----
-----	-----	-----	-----	1.0289 α_1	m	-----	-----	-----	-----	-----	-----
0.9988	w	1.0000	mw	1.0001 α_1	s	1.0017 α_1	s	-----	-----	1.004	vw
-----	-----	-----	-----	-----	-----	0.9920 α_1	mw	-----	-----	0.9874	vw
-----	-----	-----	-----	-----	-----	0.9826 α_1	m	0.9618	vw	0.9629	w
-----	-----	0.9568	mw	-----	-----	-----	-----	0.9483	vw	0.9488	vw
0.9270	mw	0.9277	m	-----	-----	-----	-----	0.9235 α_1	vw	0.9383	vw
0.9097	w	0.9098	w	-----	-----	-----	-----	0.9089 α_1	vw	0.9176	vw
-----	-----	0.8981 α_1	w	-----	-----	-----	-----	-----	-----	0.9110	vw
-----	-----	0.8913 α_1	w	-----	-----	-----	-----	-----	-----	0.8993	w
-----	-----	0.8827 α_1	w	-----	-----	-----	-----	0.8826 α_1	w	0.8819 α_1	w
0.8756 α_1	m	0.8753 α_1	m	-----	-----	-----	-----	-----	-----	0.8749	vw
0.8668 α_1	m	0.8670 α_1	m	-----	-----	-----	-----	-----	-----	0.8621	vw
0.8528 α_1	m	0.8531 α_1	m	-----	-----	-----	-----	-----	-----	-----	-----
-----	-----	0.8398 α_1	w	-----	-----	-----	-----	-----	-----	-----	-----
0.8214 α_1	w	0.8208 α_1	w	-----	-----	-----	-----	0.8295 α_1	mw	0.8286 α_1	mw
-----	-----	0.8187 α_1	mw	-----	-----	-----	-----	0.8186 α_1	mw	-----	-----
0.8146 α_1	w	0.8150 α_1	mw	-----	-----	-----	-----	-----	-----	-----	-----
0.8123 α_1	mw	0.8122 α_1	w	-----	-----	-----	-----	-----	-----	-----	-----
0.7994 α_1	mw	0.7997 α_1	w	-----	-----	-----	-----	0.8077 α_1	mw	0.8078 α_1	mw
0.7942 α_1	ms	0.7942 α_1	m	-----	-----	-----	-----	-----	-----	-----	-----
0.7879 α_1	w	0.7878 α_1	mw	-----	-----	-----	-----	-----	-----	-----	-----
0.7805 α_1	ms	0.7804 α_1	m	-----	-----	-----	-----	-----	-----	-----	-----

* 114.6-mm-diameter powder camera. Film shrinkage corrections made where necessary. Intensities are visual estimates. w = weak, m = medium, s = strong, v = very, ----- = not observed, Cu/Ni = nickel-filtered copper radiation, Fe/Mn = manganese-filtered iron radiation

** Range: Pd_{70.3-73.8}, Sb_{19.8-25.8}, As_{4.0-7.0}, inhomogeneous but one product

from the powder data reported in Table 2, can be indexed according to the pseudohexagonal cell having $a = 15.04$, $c = 22.41$ Å (Table 3).

Reflectivity Data

Nineteen fragments from seven grains of stibiopalladinite were mounted and polished. Determination

of Vickers hardness of stibiopalladinite with a 50-gram load for seven grains gave an average value of 607 with a range of 589–644, which is similar to but slightly higher than that of mertieite (Table 1). Qualitative optical properties of the Tweefontein stibiopalladinite are also similar to those of mertieite, according to examination under a comparison microscope.

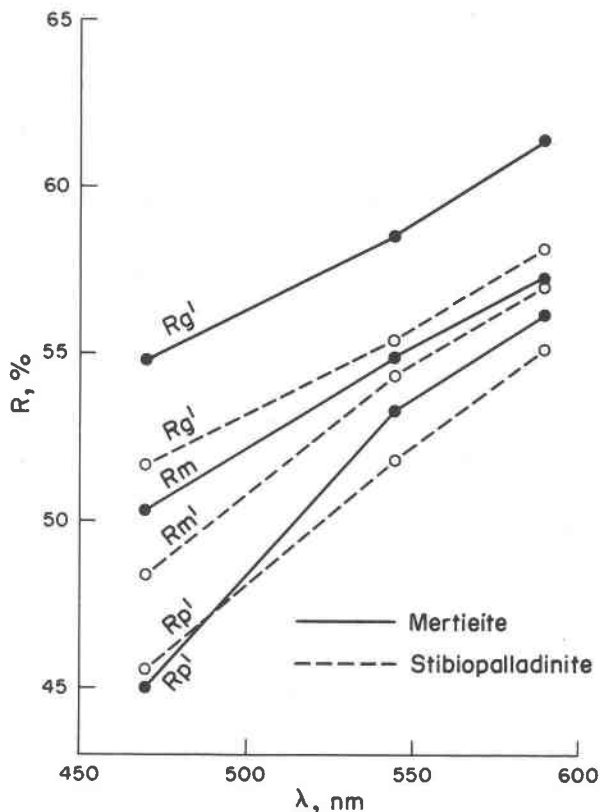


FIG. 1. Dispersion of the reflectance of mertieite (corresponding to analyses of group I) and of stibiopalladinite. The least value of R_p' and the greatest value of R_g' are assumed to approximate R_p and R_g . For mertieite, R_m was determined on sections of null bireflectance. For stibiopalladinite, R_m' was determined statistically by the method of minimum overlap.

Stibiopalladinite is yellowish white in air; in oil, it is very slightly darker and slightly richer yellow. Reflection pleochroism in air is weak, pale yellow to yellowish white. In some orientations, the yellow shows a very faint greenish, pinkish, or lavender tint. In oil, bireflectance is slightly enhanced, but reflection pleochroism is diminished and the pinkish and lavender tints are suppressed. Anisotropism is distinct in air and in oil. Color effects are generally lacking, though some grains are purplish gray to greenish gray in the position of maximum illumination. Internal reflection is absent. Conoscopically, stibiopalladinite shows some dispersion of the ellipticity, the effect approximating that of several native metals. Stibiopalladinite has three microscopic partings, two whose traces are mutually perpendicular and a third oblique thereto. Replacement by a gray alteration product favors one of the cleavage traces.

A faint wedge- or flame-like structure, presumably twinning, is barely detectable in one grain. Sector twinning was sought but not found. Its presence in Rietfontein stibiopalladinite led Ramdohr (1969) to note that orthorhombic or lower symmetry might be inferred for the mineral. The ubiquitous twinning shown in single-crystal X-ray photographs of our stibiopalladinite is evidently a submicroscopic feature, though one of several grains etched with HCl conc. + $KClO_3$ showed a few twin lamellae 1 to 10 microns wide.

The reflectance of 8 grains of stibiopalladinite is shown in Table 1, together with the microhardness of 7 grains. Stibiopalladinite is only a little harder than mertieite, but the reflectance curves (Fig. 1) are significantly different. The mean reflectance of the two minerals is close, but mertieite has stronger bireflectance. For both minerals, the bireflectance is signless at 470 nm, within the limits of measurement. However, at 546 and 589 nm the sign of the bireflectance is (+) for mertieite but (-) for stibiopalladinite. Like mertieite, stibiopalladinite has no constant value of R , at each of the measured wavelengths, for one extinction position of each grain and therefore cannot be tetragonal or hexagonal. The red-light reflectance of the minerals could not be reliably determined, owing to the insensitivity of the apparatus for measuring very small areas at 650 nm.

Composition

Analysis of 19 polished grain fragments of the Tweefontein stibiopalladinite for arsenic, using the same standards and conditions listed previously, demonstrates that, unlike mertieite, stibiopalladinite contains no arsenic. However, all the grains contain 1.9 ± 0.1 wt percent copper, indicating that copper may be an essential constituent of stibiopalladinite. The Tweefontein stibiopalladinite contains only Pd, Sb, and perhaps Cu as essential elements. Other elements (Bi, S, Sn, Fe, T, Rh, Ni, Au, Pt, Ru, Os, Ir, Co) were sought but not detected. Quantitative microprobe analysis of 10 grain fragments for Pd, Sb, and Cu gives the following results in weight percent with indicated standard deviations: Pd = 67.8 ± 0.5 , Sb = 31.2 ± 0.5 , and Cu = 1.9 ± 0.1 . This does not correspond to Pd_3Sb where Pd = 72.42 and Sb = 27.58, but rather to the formula $Pd_{4.85}Cu_{0.15}Sb_2$ where Pd = 67.09, Sb = 31.66, and Cu = 1.23. Thus the formula for Tweefontein stibiopalladinite is similar to that of mertieite (two grains of mertieite were reanalyzed for direct comparison of composi-

tion). In this connection, it is noteworthy that in the original description of stibiopalladinite, Adam (1927) reported values of 70.4 and 70.35 weight percent Pd for two determinations on a concentrate from Potgietersrust.

Comparison with Other Samples

Genkin (1968) investigated stibiopalladinite from the Noril'sk deposits and compared this with material from other localities by X-ray diffraction and reflectivity studies. One X-ray microanalyzer analysis of material from chalcopyrite veins indicated $\text{Pd}_{73}\text{Sb}_{25}$ (Borovskii *et al.*, 1959), but no statement is given regarding use of standards, detection limits, or precision of analysis. Genkin (1968) reported that microspectrographic analyses of crystalline grains of this stibiopalladinite show only Pd and Sb. X-ray diffraction data were presented by Genkin (1968, Table 17) for material identified as stibiopalladinite, as well as for two synthetic Pd-Sb phases. He recognized essentially two structural types and differentiated these on the basis of a strong line at 2.28–2.30 Å. The Noril'sk samples Pt-14, N-51, and Ramdohr's Potgietersrust, South Africa, sample exhibit this line, but the specimens of platinum concentrate (N-56) and Berry and Thompson's Potgietersrust sample do not. The sample of Berry and Thompson (1962, p. 32) is from the same specimen (USNM R6483) as that from which we obtained material for the electron microprobe analyses presented above and for the X-ray diffraction data presented in Table 2. We conclude that Genkin's (1968, Table 17) two groups of stibiopalladinite, recognized by him on the basis of X-ray diffraction data, are in fact identical to our chemical and X-ray diffraction distinction between mertieite — $\text{Pd}_5(\text{Sb,As})_2$ — and stibiopalladinite. In addition, it appears that the formula for stibiopalladinite corresponds more closely to Pd_5Sb_2 than to Pd_3Sb . Evidence of this is provided by our chemical data and by Genkin's diffraction data for the synthetic compound Pd_5Sb_2 (Genkin, 1968, Table 17, 5–4); the spacings of Genkin's synthetic Pd_5Sb_2 correspond closely to those of his stibiopalladinite N-56 and to those of Berry and Thompson's Tweefontein stibiopalladinite (1962, p. 32).

Similarities and Differences

There is no question that the structures of mertieite — $\text{Pd}_5(\text{Sb,As})_2$ — and stibiopalladinite — Pd_5

TABLE 3. OBSERVED AND CALCULATED INTERPLANAR SPACINGS FOR MERTIEITE (IN ANGSTROMS)

$d_{\text{obs.}}$ *	$d_{\text{calc.}}$ **	h k l
3.65	3.613	31.0
3.34	3.360	22.3
3.01	2.988	32.0
2.781	2.775	32.3
2.643	2.636	32.4
2.590	2.587	50.1
2.515	2.506	33.0
2.454	2.453	50.3, 42.1, 33.2
2.393	2.400	41.5
2.362	2.362	50.4
2.316	2.327	51.1
2.279	2.288	33.4
2.232	2.232	51.3
2.171	2.171	60.0
2.134	2.132	43.1, 60.2
2.078	2.077	52.1
2.017	2.016	60.4, 52.3
1.920	1.920	61.3
1.862	1.861	70.0, 53.0
1.814	1.816	61.5
1.798	1.800	62.1
1.574	1.575	72.2
1.491	1.491	55.2, 64.1
1.478	1.478	55.3, 64.2
1.453	1.453	73.2
1.433	1.435	90.2
1.413	1.414	73.4, 82.2
1.342	1.342	65.3, 91.3, 74.2
1.317	1.316	83.1, 83.2 ?
1.271	1.272	92.2, 10.0.4
1.253	1.253	66.0
1.223	1.223	84.2, 66.4
1.198	1.197	93.2
1.180	1.179	10.2.0
1.170	1.170	11.0.3
1.145	1.145	85.1, 11.0.5
1.103	1.103	10.3.1
1.089	-----	-----
1.081	1.080	12.0.2
1.061	1.060	95.0
1.054	1.055	95.2, 12.0.5
1.0407	1.0413	95.4, 86.5
1.0289	1.0291	86.6
1.0002	1.0018	13.0.0

* $d_{\text{obs.}}$ is averaged from Table 2.

** calculated for pseudo-hexagonal cell for which $a = 15.04$, $c = 22.41$ Å.

Sb_2 — have some atomic arrangement in common. This can be deduced from the presence of a 1.56–1.59 Å line of medium intensity as shown in Table 2 and also by Genkin (1968, Table 17), as well as from the presence of the 2.17–2.20 Å and 2.25–2.28 Å lines, all of which are present in mertieite and stibiopalladinite. The 2.23 Å line of mertieite readily distinguishes the two minerals (Table 2). It is also

TABLE 4. OBSERVED AND CALCULATED INTERPLANAR SPACINGS OF STIBIOPALLADINITE (IN ANGSTROMS)

$d_{\text{obs.}}^*$	$d_{\text{calc.}}^{**}$	$\frac{h}{k} \frac{l}{1}$
3.88	3.860	311
3.50	3.526	321
3.35	3.354	023,312
3.13	3.131	410
2.95	2.945	420
2.84	2.840	004
2.78	2.782	014,104
2.55	2.548	500,214,342
2.48	2.471	034
2.40	2.403	520,441
2.33	2.335	260,314
2.270	2.271	005
2.194	2.192	450
2.015	2.013	072,621
1.954	1.953	533
1.880	1.880	080
1.860	1.860	180
1.820	1.816	206,710,372
1.791	1.791	470,155,273
1.577	1.576	811
1.507	1.507	0·10·0,822
1.480	1.480	490,760,555
1.427	1.426	057,705
1.385	1.386	208
1.359	1.361	4·10·0
1.335	1.334	086
1.316	1.316	706,690
1.282	1.282	058,10·0·0

[Remaining 15 lines not indexed]

* $d_{\text{obs.}}$ taken from pattern B, Table 2.** Calculated for orthorhombic(?) cell for which $\underline{a} = 12.80$; $\underline{b} = 15.04$; $\underline{c} = 11.36 \text{ \AA}$.

of interest that the value of the other strong line (2.27 Å) for the stibiopalladinite in Table 2 is not in good agreement with the value of 2.25 Å given for the same specimen by Berry and Thompson (1962, p. 32). The gross similarity but distinctive difference in the structure of mertieite and stibiopalladinite is confirmed by precession photographs.

The powder data for stibiopalladinite USNM R6483 can be indexed (Table 4) on a primitive orthorhombic cell which compares closely to the pseudo-hexagonal mertieite cell:

Stibiopalladinite

$$\begin{aligned} a &= 12.80 \text{ \AA} \\ b &= 15.04 \text{ \AA} \\ c &= 11.36 \text{ \AA} \\ v &= 2,186.9 \text{ \AA}^3 \end{aligned}$$

Mertieite

$$\begin{aligned} a \cos 30^\circ &= 13.02 \text{ \AA} \\ b &= 15.04 \text{ \AA} \\ c &= 22.41 \text{ \AA} \\ v &= 4,388.3 \text{ \AA}^3 \end{aligned}$$

No attempt was made to determine a hexagonal cell for stibiopalladinite because the optical data exclude hexagonal symmetry and because an orthorhombic cell seemed more likely from comparison of the powder data of stibiopalladinite and mertieite. Nor was an attempt made to vary b for stibiopalladinite in order to achieve a closer fit between the cells of the two minerals. If the provisional primitive orthorhombic cell is indeed the true cell, the space group of stibiopalladinite is uniquely determined as $P2_212$. (All orders of reflections are represented except for $0k0$, which has $k = 2n$.) An unequivocal determination of the space group and unit cell cannot be made from our single-crystal fragments.

The provisional cell edges of stibiopalladinite USNM R6483 differ substantially from $a_0, b_0, c_0 = 2.8, 5.2, 4.6 \text{ \AA}$ reported for stibiopalladinite by Ramdohr (1969, p. 413).

Synthesis of Palladium Compounds

High purity metals, certified to contain less than 50 parts per million (ppm) of metals as impurities, were utilized in attempts to synthesize compounds composed of Pd and Sb; Pd, Sb, and As; Pd, Sb, and Cu; Pd, Sb, Cu, and As; and Pd_3Sn_2 . Each compound was weighed to the desired proportion of metals, sealed in a silica tube evacuated to less than 20 microns pressure, melted in a hydrogen-oxygen flame, and either quenched from a melt or annealed in a furnace after melting. A major objective of this effort was directed at synthesis of compounds corresponding to Pd_3Sb , $\text{Pd}_3(\text{Sb,As})$, $\text{Pd}_3(\text{Sb,Cu})$, or $\text{Pd}_3(\text{Sb,As,Cu})$, because Pd_3Sb was the formula given for stibiopalladinite by Adam (1927). We were unable to obtain a stable phase corresponding to Pd_3Sb or $\text{Pd}_3(\text{Sb,As,Cu})$ despite many attempts. Previous investigators of the Pd-Sb system have not recognized a Pd_3Sb phase as one which crystallizes with fixed composition (Hansen and Anderko, 1958; Pratt *et al.*, 1968). Furthermore, configuration of the Pd-Sb diagram (Hansen and Anderko, 1958, Fig. 610) indicates that crystallization of Pd_3Sb from a liquid would require quenching at a temperature of 1200°C , which is geologically unreasonable.

The present synthetic studies suggest that if As or Cu is available, either or both will become incorporated in the Pd-Sb compound. In general, copper and arsenic apparently substitute for antimony, according to simultaneous analysis of Cu and Sb or As and Sb on the electron microprobe. However, analysis of one synthetic phase — $\text{Pd}_{59.7}\text{Sb}_{27.5}\text{Cu}_{10.5}\text{As}_{3.7}$ in wt percent — indicates Cu substitution for Pd, with the resulting formula $(\text{Pd}_{4.0}\text{Cu}_{1.0})(\text{Sb}_{1.7}\text{As}_{0.3})$.

All the single synthetic compounds were either too finely crystalline or too inhomogeneous for single-crystal X-ray diffraction studies. The two-product synthetic compounds were very intimately intergrown, precluding X-ray diffraction study of each separately.

One charge with a bulk composition of $\text{Pd}_{70.69}\text{Sb}_{23.27}\text{As}_{6.04}$ wt percent yielded an inhomogeneous product with a composition of $\text{Pd}_{70.3-73.8}\text{Sb}_{19.8-25.8}\text{As}_{4.0-0.7}$ wt percent. This material exhibits the major X-ray powder lines shown by natural mertieite (Table 1). Simultaneous microprobe analysis of Pd, Sb, and As on this synthetic product shows substitution between As and Sb; results of more than 40 analyses demonstrate that although the product is somewhat inhomogeneous, each point analysis corresponds to the formula $\text{Pd}_5(\text{Sb,As})_2$. Furthermore, the range in Pd, Sb, and As content of this inhomogeneous synthetic product corresponds remarkably well to that shown for the various grains of natural mertieite presented in Table 1.

Of four additional synthetic compounds of Pd and Sb combined with Cu and/or As, all have a 2.20–2.23 Å strong line, 1.56–1.57 Å and 1.27 Å lines, and other lines in common. These data seem to corroborate the conclusion that there is some basic atomic arrangement common to this group of compounds. The arrangement is apparently controlled by appropriate substitution of As for Sb, Cu for Sb, and in one case, Cu for Pd. However, thermal history is obviously a very important aspect, and thus, except for the synthetic product showing the X-ray powder pattern which corresponds to mertieite (Table 1), direct comparisons with natural minerals should be avoided.

Note added in proof: El-Boragy, Bhan, and Schubert (1970, *Jour. Less-Common Metals* **22**, 445–458) determined by single-crystal work that the synthetic compound $\text{Pd}_{71.5}\text{Sb}_{28.5}$, or $\text{Pd}_{5+0.20}\text{Sb}_{2-0.20}$, at 760°C has what they term the Pd_5Sb_2

type of structure, $P6_3cm$, $a = 7.60_6$, $c = 13.86_3$ Å. The compositionally similar compound $\text{Pd}_{72.0}\text{Sb}_{28.0}$, or $\text{Pd}_{5+0.22}\text{Sb}_{2-0.22}$, at 500°C gives a different powder pattern—one indicating a superlattice whose symmetry is slightly lower than $P6_3cm$. The cell edges of the second compound are $a = 7.6_{13}$, $c = 42.2_{40}$ Å. They consider the structure of the second compound (their “ $\text{Pd}_{5+}\text{Sb}_{2-}$ ”) to be a variant of the structure of the first—a part of the same phase bundle. Though one is inclined to regard the structural difference as the result of ordering at lower temperature, the authors state that the difference is due to the slight change in composition. The recalculated powder data of the two compounds are not identical with those of mertieite, of the synthetic analogue of mertieite, or of stibiopalladinite, though the three strongest reflections of synthetic $\text{Pd}_{72.0}\text{Sb}_{28.0}$ (d 2.265, 2.199, 1.579 Å) do match those of our stibiopalladinite (d 2.272, 2.194, 1.578 Å). We can only echo the interpretation of El-Boragy *et al.*: for the minerals, as well as for the related synthetic compounds near Pd_5Sb_2 , small changes in composition may be attended by substantial variations or changes in structure.

Acknowledgments

We are grateful to John B. Mertie, Jr., and the Goodnews Bay Mining Company for providing the material for study. We thank John White, U.S. National Museum, for providing us with stibiopalladinite, and Michael Fleischer, U.S. Geological Survey, for translating part of Genkin's Noril'sk monograph.

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Manuscript received December 13, 1968; accepted for publication, September 6, 1972.