

Palladium arsenide-antimonides from Itabira, Minas Gerais, Brazil

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SUMMARY. The arsenopalladinite concentrates from Itabira, Minas Gerais, Brazil, have been found to contain three arsenide-antimonides of palladium, namely arsenopalladinite, atheneite, and isomertieite. The second and third of these are new minerals.

Arsenopalladinite, redefined, is $\text{Pd}_3(\text{As,Sb})_2$ and triclinic with a 7.399, b 14.063, c 7.352 Å, α 92° 03', β 118° 57', γ 95° 54'. $Z = 6$. $D_{\text{meas}} = 10.4$, $D_{\text{calc}} = 10.46$. In reflected light arsenopalladinite is white with a yellowish creamy hue. The mineral shows complex polysynthetic twinning and is strongly anisotropic. Reflectance measurements at 470, 546, 589, and 650 nm respectively gave: in air, 46.67-48.86, 49.97-52.90, 52.82-54.96, and 55.61-57.72; in oil, 32.30-35.07, 37.12-39.40, 38.97-41.32, and 40.28-43.07. VHN_{100} 379-449, av. 407.

Atheneite, $(\text{Pd,Hg})_3\text{As}$, is hexagonal, space group $P6/mmm$ and cell dimensions a 6.798, c 3.483 Å. The strongest lines of the powder pattern are 2.423 vs (111), 2.246 vs (201), 1.371 s (212), 1.302 s (302), 1.259 s (321). $Z = 2$. $D_{\text{calc}} = 10.16$. In reflected light atheneite is white with a faint bluish tint compared to arsenopalladinite. Anisotropy distinct. Untwinned. Reflectivities for the two grains examined are: in air, 470 nm 47.51-54.75, 47.43-51.18; 546 nm 50.79-58.01, 51.36-54.36; 589 nm 53.13-61.01, 53.24-55.86; 650 nm 55.94-63.13, 54.76-56.77; in oil, 470 nm 30.03-43.67, 33.46-37.31; 546 nm 33.42-47.75, 37.64-41.07; 589 nm 35.80-49.04, 39.40-42.24; 650 nm 38.25-50.49, 41.07-42.85. VHN_{100} 419-442, av. 431.

Isomertieite, $(\text{Pd,Cu})_3(\text{Sb,As})_2$, is cubic, space group $Fd3m$, a 12.283 Å. The strongest lines of the powder pattern are 2.356 vs (333, 511), 2.167 vs (440), 0.8599 s (10.10.2, 14.2.2), 0.8206 s (12.8.4), 0.7996 s (10.10.6, 14.6.2), 0.7881 s (999, 11.11.1, 13.7.5, 15.3.3), 0.7801 s (12.10.2, 14.6.4). $Z = 16$. $D_{\text{calc}} = 10.33$. In reflected light isomertieite is a pale yellow colour. One grain was isotropic, three others displayed weak anisotropy. Untwinned. Reflectance measurements at 470, 546, 589, and 650 nm gave respectively: in air, 44.74-46.46, 52.23-53.25, 55.05-57.49, 56.97-62.03; in oil, 31.04-31.40, 38.42-38.90, 40.80-42.16, and 42.91-45.63. VHN_{100} 587-597, av. 592.

Quantitative colour values are also given, and the chemical and optical properties are compared with the related mineral, stibiopalladinite.

EARLY in 1934 Bernard Hall Sanders of Redruth, Cornwall, left for examination at the British Museum (Natural History) five mineral specimens he had acquired from Brazil. One of these, consisting of 4 g of residual concentrates from the gold washing at Itabira, Minas Gerais, aroused immediate interest since the preliminary analysis showed the major element to be palladium although an X-ray diffraction photograph did not correspond with any known palladium mineral. Sanders had blowpipe tests carried out on several portions of the concentrates and obtained an arsenic residue which led him to suggest that the mineral was a palladium arsenide. This was confirmed by chemical analyses made subsequently by M. H. Hey and, although the analyses showed a variable concentration of Pd, the formula Pd_3As was suggested for the mineral together with the name arsenopalladinite, thus linking it compositionally

with stibiopalladinite discovered a few years earlier at Potgietersrust, South Africa (Adam, 1927). Sanders was able to provide another 3 g of arsenopalladinite and the whole set of concentrates was registered as specimen no. BM 1934, 72.

Subsequently F. A. Bannister and then G. F. Claringbull studied the crystal structure of arsenopalladinite and a brief description of the mineral was eventually published (Claringbull and Hey, 1956 and 1957) giving the formula Pd_3As and hexagonal cell dimensions a 6.80 Å and c 3.48 Å. Conclusive evidence has emerged from the present investigation to show that there is more than one mineral in the concentrates and that the hexagonal cell dimensions were determined on a different mineral, atheneïte, from that on which the chemical analyses were made, arsenopalladinite. This is supported by R. J. Davis's later X-ray work on a triclinic phase in the concentrates, which we have shown to be near the composition of arsenopalladinite as originally published by Claringbull and Hey.

In this investigation the grains of the concentrates have been found to consist of three palladium arsenide-antimonides in varying quantity, the major phase being arsenopalladinite, followed by a number of grains resembling mertieite in composition (Desborough *et al.*, 1973) but with a different structure and optical properties, which we have named isomertieite, and finally a few grains of a new mineral, atheneïte (Pd, Hg) $_3\text{As}$. Two grains were also found of a palladium selenide, undoubtedly related to oosterboschite, and this is the subject of a separate communication. This paper is concerned with the three arsenide-antimonides namely, arsenopalladinite, atheneïte, and isomertieite and includes also the results of a comparative study of the related mineral stibiopalladinite.

The concentrates are of a rough dark-brown appearance often partially coated with native gold. The grain size generally varies between 0.15 and 0.75 mm although a small number of larger particles has been separated out. Only occasionally do these particles show traces of crystalline form.

In polished section the grain outlines of the four species are distinctive. Arsenopalladinite grains have a predominantly 'jig-saw piece' morphology with many embayments and promontories. They commonly have a corroded, and sometimes a serrated margin, with oriented parallel wedges and randomly oriented 'blebs' of oxide, coating and penetrating the grains. Two grains were partly coated with thin films of gold and gold alloy. Atheneïte grains also have embayed margins, but unlike arsenopalladinite their surfaces are neither serrated nor oxide coated. The isomertieite grains examined, some of which showed crystal boundaries, all had smooth, unembayed rims. Smooth margins are characteristic of the Potgietersrust stibiopalladinite grains, which most closely resemble atheneïte in that they also are embayed; however, the embayments are angular and most of the grains have many internal cavities, which are lacking in the three Itabira species. A peculiarity of these is that they all contain rounded subhedral (very rarely euhedral) inclusions of hematite.

Chemical, optical, and X-ray examination of the concentrates

Grains of the concentrates were mounted in cold-setting epoxy resins and polished to the 1 μm stage using diamond abrasive on Hypocel paper laps with water as

lubricant. Engis machines were used for this and for the final polishing with MgO, lubricated with distilled water, on a cloth lap.

Electron microprobe analysis of a large number of the grains, using a Geoscan instrument, showed that the main elements present are palladium and arsenic together with a substantial amount of antimony in most of the grains. The few that did not contain antimony are invariably mercury bearing. The concentrates also contain a few grains of native gold, often intergrown with a palladium–mercury–gold alloy. Within the arsenopalladinite grains are two distinct types of grey inclusions, which were identified as hematite and palladium–mercury oxide. Quantitative analyses were made of the major phases relative to pure element standards (except mercury, for which cinnabar was used) at an accelerating voltage of 20 kV. After correcting the measured intensities for instrument dead time, the results were processed using the BM–IC–NPL computer programme (Mason *et al.*, 1969).

In the optical examination of the material, reflectance values in air and in Cargille A.D. oil were measured at 470, 546, 589, and 650 nm on 8 grains of arsenopalladinite, 2 grains of atheneite, and on 4 grains each of isomertieite and stibiopalladinite. In addition spectral reflectance data from 440–700 nm were obtained for one selected grain of arsenopalladinite. The equipment used was a Vickers–EEL spectral microphotometer with a continuous-band interference filter. A Carl Zeiss Co. calibrated tungsten carbide standard was used for all measurements as were a pair of Carl Zeiss $\times 8$ air and oil objectives. Primary and secondary glare corrections were applied.

VHN measurements were made with a 100 g load on all four minerals and, in addition, with a 50 g load on isomertieite and stibiopalladinite.

Arsenopalladinite comprises the major part of the concentrates and is closest in composition to the originally described mineral arsenopalladinite. The presence of over 5 % Sb probably accounts for the low totals in the earlier analyses. The thirteen grains analysed (Table I) show little variation in composition and from the mean analysis yield a formula $\text{Pd}_5(\text{As,Sb})_2$, which is significantly different¹ from the earlier derived formula of Pd_3As . The S.G. determined on about 20 mg of authenticated arsenopalladinite picked from a polished section is 10.4.

Arsenopalladinite grains, which varied in size from 0.3 to 1.8 mm, appeared in plane polarized light to be white, with a yellowish creamy hue. In two, intergrown, grains bireflectance was very weakly perceptible. Reflectance pleochroism was absent. The only difference when examined in oil was a slight change in colour to a purer white. The fifteen grains examined appeared to be monocrystalline in plane polarized light, but on introducing the analyser all but one of the grains were revealed as polycrystalline aggregates. Grain boundaries were simple curvilinear.

The most striking feature of the mineral is its complex polysynthetic twinning. Most, but not all, of the twin lamellae are straight parallel, with individual lamellae varying in width from 5 μm to 120 μm . It is strongly anisotropic, with very bright anisotropic tints. In air these show a colour sequence from red and golden browns, through blue

¹ The powder patterns for arsenopalladinite and synthetic Pd_3As_2 are not in agreement, and the name arsenopalladinite is reserved for triclinic $\text{Pd}_3(\text{As,Sb})_2$. This redefinition has been approved by the I.M.A. Commission.

to blue grey. With the analyser uncrossed by 1° the colours appear as pale yellows, blues and lilac pinks. These colours are enhanced in oil to give khaki brown, brown, purple brown (mauve), blue grey, and bright steel grey. The mineral does not extinguish in any position.

Nearly all the grains contain inclusions of subhedral to euhedral hematite, the grain size of which varies from 5 μm to 45 μm. A coating of a grey, low-reflecting (of the same order as hematite) mineral, which in crossed polars is strongly anisotropic, is frequently associated with the hematite. This phase also occurs as a superficial coating

TABLE I. *Electron probe analyses of palladium minerals*

Arsenopalladinite (13 grains)				Isomertieite (4 grains)		
	Range	Mean	Atomic ratios	Range	Mean	Atomic ratios
Pd	76.86–79.24	78.1	4.99	71.96–72.90	72.4	4.88
Cu	0.02–0.12	0.06	0.01	0.93–1.13	1.1	0.12
As	17.48–18.83	18.2	1.66	10.74–10.99	10.9	1.04
Sb	5.01–6.10	5.4	0.31	15.41–15.74	15.6	0.92
		101.8			100.0	

Atheneite				Stibiopalladinite (6 grains)			
	Grain 1	Atomic ratios	Grain 2	Atomic ratios	Range	Mean	Atomic ratios
Pd	66.0	2.66	65.6	2.64	66.56–67.12	66.9	4.80
Cu	0.1	0.01	0.1	0.01	1.56–1.94	1.7	0.20
Hg	14.9	0.32	16.1	0.34	—	—	—
Au	0.5	0.01	0.3	0.01	—	—	—
As	19.0	1.09	19.0	1.09	—	—	—
Sb	0.1	0.004	0.3	0.01	30.58–31.48	30.9	1.94
	100.6		101.4			99.5	

on the arsenopalladinite grains, which it replaced and penetrated in the form of oriented, parallel, wedge-like plates. In this form it replaced and defined the three microscopic partings, two of which are mutually perpendicular and the third oblique, in arsenopalladinite. It is proportionally a minor constituent, the analysis showing it to be a palladium–mercury oxide¹ (approx. 90 % PdO, 10 % HgO). Rounded quartz grains also occur within some of the arsenopalladinite grains.

Intergrowth of arsenopalladinite with the other species is uncommon. One intergrowth, and two two-phase compound grains were found. The arsenopalladinite in these polymineralic grains was untwinned. These grains will be noted in the descriptions of the minerals involved—atheneite and isomertieite.

Attempts to obtain X-ray powder data from arsenopalladinite showed that the

¹ This mineral, still under investigation, is probably a mercurian variety of the hitherto doubtful species palladinite, originally described from Gongo Socco mine, Minas Gerais, by Johnson and Lampadius (1837).

grains are malleable giving a weak and diffuse powder pattern. No improvement was effected by crushing the grains under liquid nitrogen. Using a Gandolfi camera patterns of similar quality were obtained, which we attribute to surface layers of other phases, which, like arsenopalladinite, are highly absorbing to X-rays and shield the centres of the grains.

As part of a continuing X-ray single crystal study of a number of grains of arsenopalladinite, R. J. Davis reports that the mineral is triclinic, with cell dimensions a 7.399, b 14.063, c 7.352 Å, α 92° 03', β 118° 57', γ 95° 54', volume 663.4 Å³ with errors estimated at 0.004 Å, 2', and 1 Å³. Using this cell volume and the measured density, the unit cell of arsenopalladinite is found to contain six molecules of Pd₅(As,Sb)₂. The calculated S.G. is 10.46.

The name *atheneïte* is proposed for a mercury-rich palladium arsenide found among the concentrates. The name is in oblique reference to its palladium content, following the derivation of the word palladium from Pallas, the name of the Greek goddess, often referred to as Pallas Athēnē. The mineral and name have been approved by the Commission on New Minerals and Mineral Names of the International Mineralogical Association. About four grains were found during the investigation and the analyses of two of them are given in Table I. The formula of atheneïte is (Pd,Hg)₃As, which does not correspond with any known mineral, although this 3:1 Pd:As ratio has also been found for the tellurium-bearing palladium arsenide, vincentite, of Stumpfl and Tarkian (1974). The density of atheneïte (given by Claringbull and Hey, 1957) is 10.2, comparing very favourably with the calculated value of 10.16 based on two formula units per unit cell.

Three grains, the largest being 0.7 mm in diameter, were examined by reflected light. In plane polarized light, the separate grains of atheneïte appeared to be the same colour as arsenopalladinite. In the intergrown grain the atheneïte is just perceptibly faintly bluish by comparison; neither bireflectance nor reflectance pleochroism were visible to the eye in air; in oil, compared with arsenopalladinite, which remained white, atheneïte, in this single instance, displayed very weak reflectance pleochroism, with tints from pale yellow-white to a bluish-grey white.

The grains of atheneïte are monocrystalline and untwinned. Under crossed polars the mineral does not extinguish. It displays a range of bright anisotropic tints, from purple brown through light grey to a metallic dark grey. In oil the brightness of these colours is enhanced.

The intergrowth of arsenopalladinite with atheneïte consists of a rounded island of arsenopalladinite with an exsolved rim extending outwards into the atheneïte. In addition a compound grain of arsenopalladinite and atheneïte was discovered, the two phases showing a simple locking, curvilinear boundary. In common with all the Itabira species, rounded grains of hematite occur as inclusions. However, unlike arsenopalladinite, grain surface oxidation products and gold and gold alloy coatings are absent.

X-ray powder patterns were obtained for two grains of atheneïte using filtered Cu-radiation and an 11.46 cm diameter Gandolfi camera. The two patterns are identical, except for a small number of weak lines present in one film, found to be lines

TABLE II. X-ray powder data for athenette.
Hexagonal. Space group $P6/mmm$. a 6.798, c 3.483 Å

d_{calc}	d_{obs}	I	$hkil$	d_{calc}	d_{obs}	I	$hkil$
5.887	—	—	10 $\bar{1}$ 0	1.029	—	—	21 $\bar{3}$ 3
3.483	—	—	00 $\bar{0}$ 1	1.012	1.012	mw	51 $\bar{6}$ 1
3.399	—	—	11 $\bar{2}$ 0	0.9992	—	—	30 $\bar{3}$ 3
2.944	—	—	20 $\bar{2}$ 0	0.9812	—	—	60 $\bar{6}$ 0
2.433	2.423	vvs	11 $\bar{2}$ 1	0.9754	0.9750	vw	50 $\bar{5}$ 2
2.248	2.246	vs	20 $\bar{2}$ 1	0.9679	—	—	43 $\bar{7}$ 0
2.225	2.221	m	21 $\bar{3}$ 0	0.9587	—	—	22 $\bar{4}$ 3
1.962	1.958	w	30 $\bar{3}$ 0	0.9497	—	—	33 $\bar{6}$ 2
1.875	1.871	ms	21 $\bar{3}$ 1	0.9462	—	—	31 $\bar{4}$ 3
1.741	1.738	mw	0002	0.9444	0.9444	vw	60 $\bar{6}$ 1
1.710	1.708	vw	30 $\bar{3}$ 1	0.9427	0.9422	mw	52 $\bar{7}$ 0
1.700	—	—	22 $\bar{4}$ 0	0.9376	0.9364	w	42 $\bar{6}$ 2
1.670	—	—	10 $\bar{1}$ 2	0.9325	—	—	43 $\bar{7}$ 1
1.633	1.632	w	31 $\bar{4}$ 0	0.9115	—	—	40 $\bar{4}$ 3
1.550	—	—	11 $\bar{2}$ 2	0.9100	0.9094	w	52 $\bar{7}$ 1
1.527	1.526	vvw	22 $\bar{4}$ 1	0.9038	0.9030	mw	51 $\bar{6}$ 2
1.499	—	—	20 $\bar{2}$ 2	0.8978	—	—	61 $\bar{7}$ 0
1.478	1.477	mw	31 $\bar{4}$ 1	0.8804	0.8795	ms	32 $\bar{5}$ 3
1.472	—	—	40 $\bar{4}$ 0	0.8708	—	—	0004
1.371	1.371	s	21 $\bar{3}$ 2	0.8694	0.8692	vw	61 $\bar{7}$ 1
1.356	—	—	40 $\bar{4}$ 1	0.9614	0.8608	vw	{ 10 $\bar{1}$ 4
1.351	1.352	vw	32 $\bar{5}$ 0	0.8614			{ 41 $\bar{5}$ 3
1.303	1.302	s	30 $\bar{3}$ 2	0.8549	—	—	60 $\bar{6}$ 2
1.285	1.286	m	41 $\bar{5}$ 0	0.8497	0.8490	w	44 $\bar{8}$ 0
1.259	1.259	s	32 $\bar{5}$ 1	0.8460	—	—	43 $\bar{7}$ 2
1.216	1.215	vvw	22 $\bar{4}$ 2	0.8435	—	—	11 $\bar{2}$ 4
1.205	1.205	m	41 $\bar{5}$ 1	0.8410	—	—	70 $\bar{7}$ 0, 53 $\bar{8}$ 0
1.191	1.191	mw	31 $\bar{4}$ 2	0.8350	—	—	20 $\bar{2}$ 4
1.177	—	—	50 $\bar{5}$ 0	0.8290	0.8288	mw	52 $\bar{7}$ 2
1.161	—	—	0003	0.8267	0.8265	m	50 $\bar{5}$ 3
1.139	—	—	10 $\bar{1}$ 3	0.8255	0.8248	mw	44 $\bar{8}$ 1
1.133	1.134	vvw	33 $\bar{6}$ 0	0.8175	0.8168	vvw	{ 70 $\bar{7}$ 1, 53 $\bar{8}$ 1
1.124	1.124	vw	40 $\bar{4}$ 2	0.8164			{ 62 $\bar{8}$ 0
1.115	—	—	50 $\bar{5}$ 1	0.8109	0.8106	mw	{ 33 $\bar{6}$ 3
1.113	1.113	mw	42 $\bar{6}$ 0	0.8109			{ 21 $\bar{3}$ 4
1.099	1.098	mw	11 $\bar{2}$ 3	0.8033	0.8030	vvw	42 $\bar{6}$ 3
1.080	1.080	w	20 $\bar{2}$ 3	0.7980	0.7979	w	61 $\bar{7}$ 2
1.077	—	—	33 $\bar{6}$ 1	0.7959	0.7958	m	30 $\bar{3}$ 4
1.067	1.067	w	32 $\bar{5}$ 2	0.7949	0.7946	mw	62 $\bar{8}$ 1
1.060	1.059	w	{ 42 $\bar{6}$ 1	0.7818	0.7817	ms	51 $\bar{6}$ 3
1.057			{ 51 $\bar{6}$ 0	0.7798	0.7799	mw	71 $\bar{8}$ 0
1.034	1.034	ms	41 $\bar{5}$ 2	0.7750	—	—	22 $\bar{4}$ 4

from hematite, PdO, gold or potarite, and Pd_{2.65}As. The second film contains only one extra line at 2.67 Å, still not fully explained. The films could be indexed using the hexagonal $P6/mmm$ cell given by Claringbull and Hey (1957) for arsenopalladinite. Fully indexed powder data are given in Table II and from high-angle extrapolation graphs cell dimensions a 6.798 ± 1 and c 3.483 ± 1 Å were obtained.

Isomertieite. A number of grains in the concentrates were found to be much richer in antimony than is arsenopalladinite and the analyses of four such grains are given in Table I. The individual grains show no significant variation in composition and the analyses are very close to the mineral mertieite recently described by Desborough *et al.* (1973) from Goodnews Bay, Alaska. They ascribed a general formula of $(\text{Pd}, \text{Cu})_{5+x}(\text{Sb}, \text{As})_{2-x}$ to the mineral, with x between 0.1 and 0.2. However, the grains of our mineral do not show such a departure from stoichiometry and, with an arsenic concentration a little higher than the Goodnews Bay mertieite, give a general formula $(\text{Pd}, \text{Cu})_5(\text{Sb}, \text{As})_2$ with $\text{As} \approx \text{Sb}$.

The five grains of isomertieite examined by reflected light varied from 0.4 to 0.8 mm in size. In plane polarized light the mineral is a pale yellow-white colour. Bireflectance and reflectance pleochroism are not detectable by eye, either in air or in oil. By comparison with arsenopalladinite in one compound grain, isomertieite is noticeably yellower. In oil this difference is enhanced so that isomertieite appears pale yellow compared with the blue/grey-white arsenopalladinite.

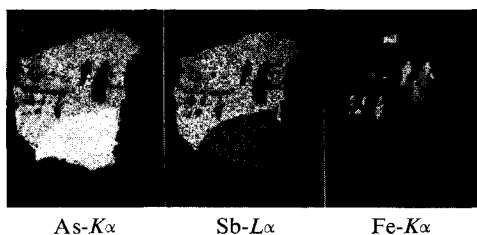


FIG. 1. X-ray scanning photographs of a compound grain of isomertieite and arsenopalladinite ($\times 90$) with hematite inclusions in the isomertieite.

The grains are monocrystalline, un-twinned, and under crossed polars do not extinguish. Anisotropic tints are, in air, shades of dull brown; in oil these colours are brightened. One grain retained a constant brown tint on rotation. Conoscopic examination confirmed that this section is uniaxial. It is also the only grain of isomertieite examined that extinguishes in monochromatic light.

The compound grain previously referred to consists of about 70 % isomertieite and 30 % arsenopalladinite in the plane of the section (fig. 1). This grain is noteworthy in that the isomertieite alone contains the hematite inclusions.

X-ray powder films of two isomertieite grains on a Gandolfi camera gave identical patterns, which could be indexed on a face-centred cubic unit cell, with systematic absences suggesting a space group $Fd\bar{3}$ or $Fd\bar{3}m$. High-angle extrapolation graphs gave the cell dimension $a = 12.283 \pm 1 \text{ \AA}$ and fully indexed powder data are given in Table III (single crystal photographs by R. J. Davis now confirm these results and the space group $Fd\bar{3}m$). The S.G. of isomertieite could not be determined directly owing to the small amount of material available, but, since there was no significant difference in S.G. between the bulk concentrates and hand-picked arsenopalladinite grains it has been assumed to have a similar S.G. to arsenopalladinite. Using the values $D = 10.2$ and the above cubic cell dimension the unit cell of isomertieite is found to contain sixteen molecules of $(\text{Pd}, \text{Cu})_5(\text{Sb}, \text{As})_2$, in keeping with its face-centred cubic structure. The calculated S.G. is 10.33 .

That three of the grains are optically anisotropic contradicts the conclusion from X-ray studies that the mineral is cubic. Explanation of this discrepancy must, however, await the findings of an X-ray structure analysis.

TABLE III. X-ray powder data for isomertieite. Cubic. Space group $Fd\bar{3}m$. a 12.283 Å

d_{calc}	d_{obs}	I	hkl	d_{calc}	d_{obs}	I	hkl
7.092	—	—	111	1.053	—	—	866, 10.6.0
4.343	—	—	220	1.042	—	—	973, 11.3.3
3.703	—	—	311	1.038	1.038	m	10.6.2
3.546	—	—	222	1.024	1.024	vvw	884, 12.0.0
3.071	—	—	400	1.013	1.012	vw	777, 11.5.1
2.818	—	—	331	0.9963	0.9958	ms	10.6.4, 12.2.2
2.507	2.502	vw	422	0.9866	—	—	975, 11.5.3
2.364	2.356	vs	333, 511	0.9711	0.9712	mw	12.4.0
2.172	2.167	vvs	440	0.9621	0.9622	w	991
2.076	—	—	531	0.9591	—	—	886, 12.4.2
2.047	2.044	vw	442	0.9477	—	—	10.8.2
1.942	1.940	vvw	620	0.9393	—	—	993, 11.5.5, 13.1.1, 11.7.1
1.873	1.874	vvw	533	0.9366	0.9364	vw	10.6.6
1.852	1.846	w	622	0.9259	—	—	12.4.4
1.772	—	—	444	0.9181	0.9179	m	977, 11.7.3, 13.3.1
1.720	1.724	vw	711, 551	0.9155	—	—	10.8.4
1.641	—	—	642	0.9055	0.9054	m	12.6.2
1.599	1.597	mw	731, 553	0.8982	0.8979	m	13.3.3, 995
1.535	1.533	ms	800	0.8864	0.8863	vvw	888
1.501	—	—	733	0.8796	0.8795	ms	11.7.5, 13.5.1
1.490	—	—	820, 644	0.8774	—	—	12.6.4
1.448	1.446	m	822, 660	0.8685	0.8684	ms	10.8.6, 10.10.0
1.418	1.418	mw	555, 751	0.8623	—	—	11.9.1, 13.5.3
1.409	1.409	mw	662	0.8600	0.8599	s	10.10.2, 14.2.2
1.373	—	—	840	0.8517	0.8519	vvw	12.8.0
1.348	—	—	911, 753	0.8456	0.8454	vw	997, 11.9.3
1.340	1.340	mw	842	0.8436	—	—	12.8.2
1.309	—	—	664	0.8357	0.8356	w	10.10.4, 12.6.6, 14.4.2
1.288	1.287	m	931	0.8300	0.8300	ms	11.7.7, 13.5.5, 13.7.1
1.254	1.253	ms	844	0.8207	0.8206	s	12.8.4
1.234	1.234	m	755, 933, 771	0.8152	0.8154	m	11.9.5, 13.7.3, 15.1.1
1.204	1.204	vw	10.2.0, 862	0.8135	—	—	10.8.8, 14.4.4
1.187	1.188	ms	773, 951	0.8064	0.8065	w	14.6.0
1.182	1.182	m	666, 10.2.2	0.8013	—	—	15.3.1
1.145	1.145	vvw	953	0.7996	0.7996	s	10.10.6, 14.6.2
1.140	—	—	864	0.7880	0.7881	s	999, 11.11.1, 13.7.5, 15.3.3
1.121	—	—	10.4.2	0.7863	—	—	12.8.6
1.108	1.106	vvw	11.1.1, 775	0.7800	0.7801	s	12.10.2, 14.6.4
1.086	1.086	m	880	0.7753	0.7754	m	11.9.7, 11.11.3, 15.5.1
1.073	—	—	955, 11.3.1, 971	—	—	—	—
1.069	1.070	vw	882, 10.4.4	—	—	—	—

Mertieite gives a different powder pattern from isomertieite (Desborough *et al.*, 1973), which the authors have indexed on a pseudohexagonal cell with a 15.04 Å and c 22.41 Å. Therefore, despite their chemical similarity, mertieite and isomertieite have different structures. The powder pattern of mertieite is much closer to the published pattern for stibiopalladinite than to that of isomertieite. The name isomertieite has been approved by the Commission on New Minerals and Mineral Names, I.M.A.

Stibiopalladinite. Since antimony was found as a major component of both arsenopalladinite and isomertieite from Itabira, it was therefore appropriate to combine the study with an examination of stibiopalladinite (supposedly Pd_3Sb). Six grains of the concentrates from Potgietersrust (Specimen no. BM. 1930,952) were polished and analysed in the same way as the arsenopalladinite concentrates. The analyses (Table I) show little variation between individual grains and the mean value suggests a general formula of $(\text{Pd,Cu})_5\text{Sb}_2$. These analyses are very close indeed to the analyses recently published by Desborough *et al.* (1973) on material from the same locality.

Optically ten Potgietersrust grains were examined and found to be monomineralic with no associated inclusions or coatings. In plane polarized light they do not display bireflectance or reflectance pleochroism. Their colour is white. Arsenopalladinite in comparison has a blue hue. Anisotropy varies in different grains from weak to distinct, colour effects being from reddish brown to bright grey. Relative to the Itabira species anisotropy is much stronger than that of mertieite, weaker than in some atheneite, and weaker than in all arsenopalladinite. In oil three of the grains display anisotropic tints in various shades of brown, the other seven showing colours varying from yellow brown, through dark iron grey to light brownish grey.

X-ray powder patterns of stibiopalladinite (Desborough *et al.*, 1973, and Genkin, 1968, Table 17, p. 68) have not yet been indexed. Although a study of the structure of stibiopalladinite is beyond the scope of the present investigation, it is obviously required in view of the similarities between the patterns of stibiopalladinite and mertieite.

Quantitative reflectance and VHN properties

Measurement of $R\%$ on all the grains were made at positions of maximum and minimum reflectance. It should be noted that all the values quoted represent minima and maxima for unoriented grains, and that these measurements cannot be taken as absolute R_g and R_p , or R_o and R_e values.

The tabulated data (Table IV) for arsenopalladinite, isomertieite, and stibiopalladinite show, in the first column, the mean reflectance values for their respective maximum and minimum reflectances. In the second column the extreme maxima and minima, derived from all the separate grain measurements, are shown. These data are included to demonstrate how remarkably consistent individual grain values are relative to their calculated means. The maximum measured bireflectance is that measured from the grain that was most strongly bireflectant for the species. The tabulated data for atheneite are slightly different. This results from the fact that only two grains of the species were available for measurement and the individual values were therefore recorded.

Fig. 2, a plot of reflectance against wavelength, has been drawn to illustrate the spectral dispersion of reflectivity of the four species and their measured mean bireflectances (with the exception of atheneite for which, again, individual grain values are shown). The figure shows that the difference in optical properties of the four species is sufficient for them to be used diagnostically. Atheneite in one grain displays enormous bireflectance, an effect which is nearly doubled in oil. These R_{max} and R_{min} curves for this highly reflecting mineral run virtually parallel, which, to some extent,

TABLE IV. Reflectivity data

λ (nm)	Atheneite															
	Air						Oil									
	R_1	R_2	R_1	R_2	$(R_1 + R_2)/2$		Maximum bireflectance		R_1	R_2	R_1	R_2	$(R_1 + R_2)/2$		Maximum bireflectance	
	Grain 1		Grain 2		Grain 1	Grain 2	Grain 1	Grain 2	Grain 1		Grain 2		Grain 1	Grain 2	Grain 1	Grain 2
470	47.51	54.75	47.43	51.18	51.13	49.30	7.24	3.75	30.03	43.67	33.46	37.31	36.85	35.38	13.64	3.85
546	50.79	58.01	51.36	54.36	54.40	52.86	7.22	3.00	33.42	47.75	37.64	41.07	40.48	39.36	14.33	3.43
589	53.13	61.01	53.24	55.86	57.07	54.55	7.88	2.62	35.80	49.04	39.04	42.24	42.42	40.82	13.24	2.84
650	55.94	63.13	54.76	56.77	59.54	55.76	7.19	2.01	38.25	50.49	41.07	42.85	44.37	41.96	12.24	1.78
	Air						Oil									
	R_1	R_2	R_1	R_2	$(R_1 + R_2)/2$		Maximum measured bireflectance		R_1	R_2	R_1	R_2	$(R_1 + R_2)/2$		Maximum measured bireflectance	
	Mean (1)		Min.	Max.	from (1)				Mean (2)		Min.	Max.	from (2)			
<i>Arsenopalladinite</i>																
470	47.08	48.48	46.67	48.86	47.78		1.77		32.81	34.48	32.30	35.07	33.44			2.51
546	51.24	52.35	49.97	52.90	51.79		1.39		37.65	39.00	37.12	39.40	38.32			2.28
589	53.61	54.39	52.82	54.96	54.00		1.18		39.65	40.69	38.97	41.32	40.17			2.35
650	55.92	56.65	55.61	57.72	56.28		1.15		40.84	42.44	40.28	43.07	41.64			2.78
<i>Isomertieite</i>																
470	45.23	45.66	44.74	46.46	45.44		0.73		31.09	31.37	31.04	31.40	31.23			0.33
546	52.67	52.88	52.23	53.25	52.77		0.34		38.50	38.86	38.42	38.90	38.68			0.50
589	55.82	55.93	55.05	57.49	55.87		0.81		41.46	41.69	40.80	42.16	41.57			0.69
650	58.80	58.82	56.97	62.03	58.51		0.63		43.93	44.17	42.91	45.63	44.05			0.68
<i>Stibiopalladinite</i>																
470	47.62	49.22	47.41	49.57	48.21		2.33		34.56	36.08	34.06	36.24	35.32			2.18
546	52.90	54.02	52.83	54.51	53.46		1.67		39.60	40.32	39.20	40.51	39.96			1.31
589	55.35	56.12	55.28	56.31	55.73		0.96		41.70	42.02	41.70	42.06	41.86			0.35
650	58.43*	58.30	57.82	59.07	58.36		0.64		44.91	44.97	43.93	46.02	44.94			1.44

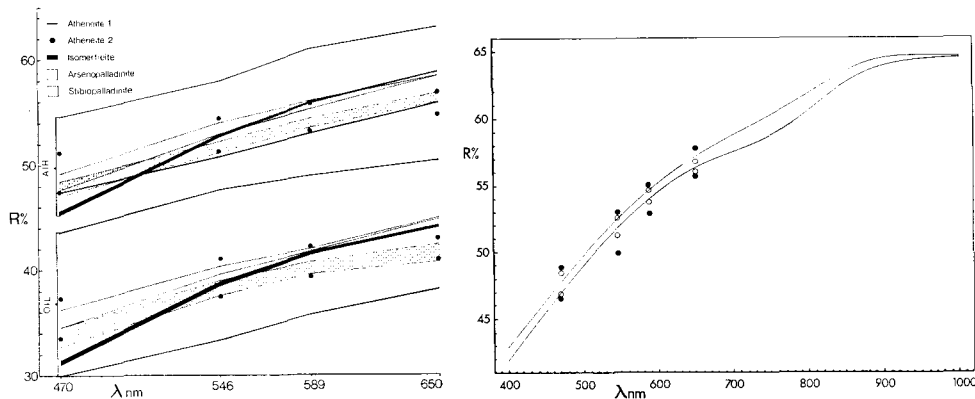
The mean values were derived from measurements of 8 grains of arsenopalladinite and 4 each of isomertieite and stibiopalladinite.

The maximum and minimum columns of R_1 and R_2 refer to the extreme values for the species taken from separate grains.

* A change of sign of bireflectance was observed in 3 grains of stibiopalladinite.

explains the lack of perceptible bireflectance. Yet it is doubtful whether this explains such an absence in oil where there was a measured difference of the order of 13 %.

By comparison, arsenopalladinite's bireflectance is low, and in air there is a detectable reduction in this from the blue to the red end of the spectrum. This is not the case in oil where its bireflectance is at a maximum in the red. Stibiopalladinite shows a similar, but more pronounced reduction in bireflectance from blue to red. The smallest bireflectance is that of isomertieite. The measured bireflectance for the three



FIGS. 2 and 3: FIG. 2 (left). Spectral dispersion and reflectance graphs derived from Table IV. FIG. 3 (right). Spectral dispersion of reflectance for arsenopalladinite in the visible and near infra-red spectral region. The black dots are the extreme R_1 and R_2 values and the circles are the mean values for R_1 and R_2 for the eight grains measured by A. J. C. (Table IV). The dispersion curves are those obtained from the grain measured by A. L. S. (Table V).

anisotropic grains is outside the limit of measurement error. The fourth, uniaxial grain, of course, lacks any bireflectance. Isomertieite is more strongly reflecting at the red end of the spectrum, which, in part, explains its stronger yellow coloration relative to arsenopalladinite. Reflectance measurements were made with Zeiss equipment on one grain of arsenopalladinite in the visible and near infra-red spectrum by A. Lopez-Soler¹ (Table V). These measurements were made partly to establish, by comparison, the accuracy of the visible light measurements made in the two laboratories. Fig. 3 demonstrates that, within this spectral region, the consistency of the values obtained is very satisfactory.

Vickers Hardness Numbers for the four species offer an added means of identification. The four minerals are, in order of increasing hardness, arsenopalladinite, atheneite, isomertieite, and stibiopalladinite. The indentations were, in all species, perfect in form, and only in atheneite was fracturing encountered. Fractured indentations were not measured. In addition to the use of a 100 g load, one of 50 g was used for stibiopalladinite and isomertieite to enable a direct comparison with Leonard's

¹ A. Lopez-Soler's measurements were made at the Departamento de Cristalografía Mineralogía y Mineralotecnía, Universidad de Barcelona, Barcelona-7 (Spain).

data (in Desborough *et al.*, 1973). Contrary to expectation the values obtained were slightly lower at this load than at the 100 g load. Our data (Table VI) are in good agreement with Leonard's for stibiopalladinite, the difference being that our specimens show a lower bireflectance and have a shorter range of VHN.

TABLE V. Reflectance percentage values for one grain of arsenopalladinite (measured by A. Lopez-Soler)

λ nm	R_1	R_2	λ nm	R_1	R_2	λ nm	R_1	R_2	λ nm	R_1	R_2
400	41.9	42.9	550	52.1	52.8	700	57.6	58.8	850	62.7	63.6
410	42.7	43.7	560	52.6	53.4	710	57.7	59.1	860	63.1	63.9
420	43.6	44.4	570	53.2	53.8	720	57.9	59.3	870	63.5	64.1
430	44.3	45.1	580	53.7	54.3	730	58.2	59.5	880	63.7	64.4
440	44.9	45.7	590	54.1	54.8	740	58.4	59.8	890	64.0	64.5
450	45.5	46.4	600	54.7	55.1	750	58.7	60.2	900	64.1	64.6
460	46.2	47.1	610	55.1	55.6	760	59.0	60.5	910	64.2	64.6
470	46.9	47.7	620	55.5	56.1	770	59.3	60.8	920	64.3	64.6
480	47.6	48.4	630	55.8	56.4	780	59.7	61.1	930	64.3	64.6
490	48.3	49.1	640	56.2	56.8	790	60.1	61.4	940	64.4	64.7
500	49.0	49.7	650	56.4	57.3	800	60.5	61.8	950	64.5	64.7
510	49.6	50.3	660	56.6	57.7	810	60.9	62.2	960	64.5	64.7
520	50.3	51.0	670	56.9	57.9	820	61.3	62.6	970	64.6	64.7
530	50.9	51.7	680	57.1	58.2	830	61.8	62.9	980	64.6	64.7
540	51.5	52.3	690	57.3	58.5	840	62.3	63.2	990	64.6	64.7
									1000	64.6	64.7

TABLE VI. VHN data for the four minerals

	Atheneite	Arsenopalladinite	Isomertieite		Stibiopalladinite	
	HV ₁₀₀	HV ₁₀₀	HV ₁₀₀	HV ₅₀	HV ₁₀₀	HV ₅₀
Number of grains measured	2	10	4	2	4	2
Number of indentations	15	50	20	10	40	10
Average V.H.N.	431	407	592	591	610	605
Range of V.H.N.	419-42	379-449	587-97	585-98	603-17	585-625

As a way of deciding the most rapid means of identifying a mineral from this group, Fig. 4 was drawn. Based on the Bowie and Taylor (1958) construction, it incorporates the VHN data as the horizontal axis and $R\%$ as the vertical axis. It differs in that, since so few data are to be plotted, it is possible to include $R\%$ values for the four standard wavelengths. The $R\%$ and VHN values intersect at their respective means and the co-ordinates extend from such a point to the extreme of the measured values. To isolate the individual plots the extreme points are connected to form a quadrilateral. It can be seen from this construction that the four species are most easily differentiated

by measurements of $R\%$ at 470 nm together with VHN measurements (since minimum overlap occurs at this wavelength).

Quantitative colour values (Table VII) were derived from a graphical extrapolation of the data shown in Table IV by means of the selected ordinate method described by Hardy (1936, pp. 49–54). The application of this technique to opaque minerals was described by Piller (1966) and more recently by Htein and Phillips (1973).

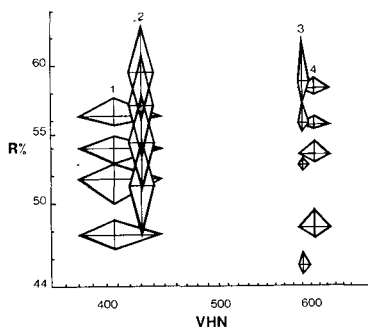


FIG. 4. Plots of reflectivity ($R\%$) against VHN. 1 arsenopalladinite, 2 atheneite, 3 isomertieite, 4 stibiopalladinite. The quadrilaterals for each species are aligned on the vertical axis representing its average VHN. Each vertical group of four quadrilaterals represents in ascending order the range of $R\%$ values for the species for the wavelengths 470 nm, 546 nm, 589 nm, and 650 nm.

Direct comparison of observed with calculated colour is impossible since the observations were made with an unfiltered tungsten halogen source, of colour temperature 3300 °K, and the Colour Values were calculated for an illuminant (ICI. C) having a colour temperature of 6750 °K. Nevertheless the observed and calculated colour sense is in general agreement.

In air the saturation or excitation purity P_e of all four species was low, which was in keeping with their observed near-whiteness. Also, the most noticeably yellow mineral isomertieite had relatively the highest saturation. The P_e levels for different vibration directions for the various species were very nearly uniform. This, together with the near constancy of the dominant wavelength for arsenopalladinite, atheneite 2, and

isomertieite explains the absence of reflectance pleochroism. In atheneite 1 and stibiopalladinite this absence is perhaps explained by the lack of accommodation of the eye to high visual brightness when this is accompanied by very low colour saturation levels.

In oil, the P_e as expected was generally increased. The observed enhancement of hue for isomertieite is thus accounted for not as a change in hue, but as an effect of increased saturation. The whiteness of stibiopalladinite is explained by its low saturation levels. Atheneite's and arsenopalladinite's weak colour effects also arise from the low saturation levels. The anomalous lack of observed reflectance pleochroism and bireflectance in atheneite 1 was, unfortunately, impossible to check as the grain had been used for an X-ray Gandolfi mount.

Comparison with other minerals and synthetic compounds

Arsenopalladinite. The palladium–arsenic system has been investigated by Saini *et al.* (1964a) who found seven distinct phases ranging from PdAs_2 to Pd_5As . The mineral vincentite (Stumpfl and Tarkian, 1974) has similar cell dimensions and general chemical formula to synthetic Pd_3As . It is notable, however, that the three minerals described in this paper do not correspond to any synthetic equivalents in the Pd–As system. Synthetic Pd_5As_2 was found by Saini to be extremely malleable and difficult

to powder, giving a rather complex powder pattern. The same general properties applied to the mineral arsenopalladinite. The difficulty of indexing the powder pattern of synthetic Pd_5As_2 was overcome by Saini in a later paper (Saini *et al.*, 1964b) when, by single crystal studies, they established that it exhibits polytypism with an *a* cell

TABLE VII. *Quantitative colour values*

	Air					Oil					
	<i>x</i>	<i>y</i>	λ_D	$P_e\%$	<i>Y</i>	<i>x</i>	<i>y</i>	λ_D	$P_e\%$	<i>Y</i>	
Arseno- palladinite	R ₁	0.3244	0.3286	580	8.7	51.75	0.3297	0.3359	578	10.2	37.78
	R ₂	0.3230	0.3276	580	8.3	52.76	0.3279	0.3337	578	9.8	39.11
Atheneïte 2	R ₁	0.3233	0.3278	579	8.1	51.63	0.3275	0.3394	574	10.4	38.57
	R ₂	0.3192	0.3252	578	7.4	54.54	0.3227	0.3475	566	10.9	43.22
Atheneïte 1	R ₁	0.3232	0.3256	583	8.0	51.28	0.3302	0.3371	577	10.4	34.51
	R ₂	0.3144	0.3290	565	7.3	58.89	0.3160	0.3523	558	10.6	50.75
Isomertieite	R ₁	0.3327	0.3382	578	11.0	53.13	0.3405	0.3470	578	13.2	38.80
	R ₂	0.3319	0.3376	578	10.7	53.28	0.3400	0.3471	577	13.2	39.16
Stibio- palladinite	R ₁	0.3189	0.3350	568	8.7	53.35	0.3207	0.3247	580	7.5	39.94
	R ₂	0.3242	0.3296	578	8.6	54.33	0.3276	0.3319	579	9.5	40.61

The values are all relative to the ICI illuminant C having a colour temperature of 6750 °K. *Y* is the visual brightness, *x* and *y* the rectangular chromaticity co-ordinates. The dominant wavelength λ_D and the excitation purity $P_e\%$ (the 2-dimensional colour space co-ordinates) were derived from the *x* and *y* values plotted on Hardy's (1936) chromaticity diagram (chart 13, p. 75).

dimension of 7.31 Å and *c* values of 13.7, 10.34, 27.48, and 96.2 Å on different crystals corresponding to a single layer repeat distance of 3.43 Å along the *c* axis. The first of these cells has hexagonal and the other three trigonal symmetry. However, the unit cell of arsenopalladinite, being triclinic, does not resemble the synthetic material, the difference undoubtedly being the consequence of considerable antimony occupying arsenic lattice sites.

The spectral reflectance characteristics of arsenopalladinite distinguish it from all but vincentite. The shape of the curves of dispersion of reflectance of a lead-bearing palladium arsenide (Genkin, 1968, Table 18, p. 71) are virtually identical with those of arsenopalladinite. However, its reflectance values are consistently lower. Genkin's reflectance data for this unnamed mineral $(\text{Pd,Pb})_3\text{As}$, were included erroneously in Cabri's (1972, p. 15) tabulation of the platinum group minerals as arsenopalladinite. Chemically, this mineral must be considered suspect because of the difficulty in obtaining reliable microprobe analyses of substances containing both lead and arsenic, due to their overlapping *L* α and *K* α lines. Qualitatively, arsenopalladinite, with its strong anisotropy and polysynthetic twinning, differs from the untwinned, weakly anisotropic vincentite and lead-bearing palladium arsenide. VHN data is not available for the latter, but vincentite with its HV₁₅ of 494 is appreciably harder than arsenopalladinite (HV₁₀₀ of 407).

Atheneïte. Before the discovery of atheneïte, the only platinum group mineral

containing mercury as a major component was the palladium alloy, potarite, PdHg. Optically the only known mineral similar to atheneïte is plumbopalladinite, Pd₃Pb₂ (Genkin *et al.*, 1970). It is strongly bireflectant. Cabri's summary tabulation (1972, p. 18) of Genkin's data for grains of variable chemical composition (1970, p. 65) takes the extreme maxima and minima of these different grains. The 'bireflectance' derived from these extremes diminishes from 6 % at 460 nm to 2.8 % at 660 nm. Atheneïte 2, which is less strongly bireflectant and has a lower over-all reflectance, diminishes from 3.8 % at 470 nm to 2 % at 650 nm. Atheneïte 1 is different, its bireflectance remaining nearly constant at about 7 % from the blue to the red end of the spectrum. The reflectance curves of plumbopalladinite and atheneïte are not identical, but they are similar enough to be confusing. Both minerals are strongly anisotropic, the anisotropic tints differing from plumbopalladinite's orange and dark brown to atheneïte's purply brown, light and dark grey. Atheneïte's range of VHN, 419–42, falls within the range of plumbopalladinite, 394–461, but its average value is slightly higher at 431 (plumbopalladinite 422).

Isomertieite. The chemical similarity between isomertieite and mertieite has already been noted. The spectral dispersion of reflectance of isomertieite is virtually identical with that of the minimum reflectance curve of mertieite (Desborough *et al.*, 1973). It is readily distinguished from mertieite, which is bireflectant and distinctly anisotropic, in that it is only weakly anisotropic and slightly bireflectant. Isomertieite is somewhat harder than mertieite, HV₅₀ averaging 591 and 578 respectively.

Stibiopalladinite. Both isomertieite and mertieite are softer than stibiopalladinite for which Leonard (in Desborough *et al.*, 1973) obtained an average HV₅₀ of 607. Our determination yielded HV₅₀ of 605. Stibiopalladinite of this investigation is considerably less bireflectant than that described by Desborough (*loc. cit.*), despite the remarkable similarity in the electron probe analyses. Our bireflectance values, however, all fall within the range quoted for their specimens. Qualitatively, stibiopalladinite BM. 1930, 952 from Potgietersrust matches Genkin's (1968, p. 65) description of stibiopalladinite from the same (type) locality and both differ from Desborough's Tweefontein specimen. The Potgietersrust material, being uniformly white (Genkin, *loc. cit.*, detected a pale-rose tint), displayed neither reflectance pleochroism nor the yellow colour of the Tweefontein mineral.

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