NEW DATA ON SOME PALLADIUM ARSENIDES AND ANTIMONIDES

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ABSTRACT

The Pd-As-Sb system contains many known compounds and to it several minerals have recently been ascribed. The poor x-ray powder diffraction characteristics of these minerals as well as the occurrence of structurally distinct, but compositionally very close phases, makes their characterization very difficult.

The following minerals were studied: stillwaterite, Pd_8As_3, a new mineral, hexagonal, with $a = 7.399(4)$, $c = 10.311(15)$Å, space group $P\bar{3}$ or $P3$; an unnamed Pd_5As_2 mineral, orthorhombic, with $a = 11.261(4)$, $b = 3.857(1)$, $c = 11.346(5)$Å; palladoarsenide, Pd_2As; unknown (Pd, Ni, As) and (Pd, Cu, As) minerals; sperrylite, $PtAs_2$; unnamed Pd_8Sb_3, with hexagonal axes $a = 7.565(1)$, $c = 43.207(3)$Å; and mertieite II, $Pd_8(Sb, As)_3$, with hexagonal axes $a = 7.546(2)$, $c = 43.18(1)$Å.

The results of some experiments in the Pd-As-Sb system are discussed with reference to minerals studied or reported in the literature.

RÉSUMÉ

Le système Pd-As-Sb continent plusieurs composés connus et plusieurs minéraux viennent récemment de lui être attribués. La caractérisation de ces minéraux est très difficile du fait des pauvres caractéristiques de la diffraction des poudres par rayons-X et de la présence de phases de composition très serrée et de structure différente.

*The mineral and name were approved by the Commission on New Minerals and Mineral Names, I.M.A.

Les minéraux suivants ont été étudiés: stillwaterite Pd_8As_3, un nouveau minéral hexagonal, avec $a = 7.399(4)$, $c = 10.311(15)$Å, de groupe spatial $P\bar{3}$ ou $P3$; un minéral innomé Pd_5As_2, orthorhombique avec $a = 11.261(4)$, $b = 3.857(1)$, $c = 11.346(5)$Å; palladoarsénide, Pd_2As; les minéraux inconnus (Pd, Ni, As) et (Pd, Cu, As); sperrylite, $PtAs_2$; le minéral innommé Pd_8Sb_3, avec des axes hexagonales $a = 7.565(1)$, $c = 43.207(3)$Å; et mertieite II, $Pd_8(Sb, As)_3$, avec des axes hexagonales $a = 7.546(2)$, $c = 43.18(1)$Å.

Les résultats de certaines expériences dans le système Pd-As-Sb sont discutés relativement aux minéraux étudiés ou rapportés dans les publications sur le sujet.

INTRODUCTION

This paper reports on an unnamed Pd_8Sb_3 mineral from Sudbury, Ontario, and on the platinum-group (PG) arsenides found in heavy-mineral concentrates from the Banded and Upper zones of Stillwater Complex, Montana. These zones consist of norites, gabbros and anorthosites. More detailed information on the geological and mineralogical literature of the Stillwater area is reviewed by Cabri & Laflamme (1974b). These authors described platinum-group native alloys from the same area and listed four PG-mineral groups: a) the native alloys; b) the tellurides; c) the sulphides; and d) the arsenides. The PG-arsenides reported here are the new mineral stillwaterite* (Pd_8As_3), palladoarsenide (Pd_2As), an unnamed Pd_5As_2 mineral, a (Pd,Ni,As) mineral, an ill-defined (Pd, Cu,As) mineral, and sperrylite ($PtAs_2$). Data for

TABLE 1. ELECTRON PROBE ANALYSES: RELATIVE COUNTING ERROR IN WEIGHT PER CENT AND HOMOGENEITY INDEX.

Mineral	Anal. No.	No. Spots	Pd CE*	HOM	Au CE	HOM	Hg CE	HOM	As CE	HOM	Sb CE	HOM	Sn CE	HOM
stl	1	5	0.41	1					0.14	0				
	2	5	0.40	0					0.14	1				
	3	6	0.40	1					0.14	8	0.04	31		
	4	7	0.40	1					0.14	1				
	5	7	0.40	1					0.12	1	0.05	1	0.04	2
	6	7	0.40	1					0.12	1	0.05	1	0.06	1
	7	8	0.41	1					0.13	1				
	8	7	0.40	1					0.12	1	0.05	1	0.06	1
	9	4	0.41	1					0.13	3				
	10	7	0.41	1					0.13	1				
	11	6	0.41	1					0.13	1				
	12	7	0.39	1					0.12	1			0.02	1
	13	9	0.39	1					0.12	1			0.08	1
Pd_5As_2	1	5	0.41	1	0.10	1	0.05	1	0.14	1				
	2	5	0.42	0					0.14	1				
	3	5	0.39	1	0.11	1	0.04	1	0.13	1				
	4	5	0.37	0	0.11	1	0.03	1	0.13	1				
	5	4	0.38	2	0.11	0	0.05	1	0.14	1				
Pd_2As	1	5	0.41	1					0.15	1				
	2	5	0.38	1					0.15	1				
mert.II	2	10	0.39	1					0.04	1	0.19	1		
	4	12	0.36	1					0.04	1	0.15	1		

*CE= $\sqrt{\frac{N}{n}}$ where N=total counts and n=no. of spots; reported in weight per cent. This relative counting error may be considered to correspond to the standard deviation (σ).

an unnamed $Pd_2(As,Bi)$ mineral will be reported at a later date.

New data are also presented for mertieite II from Goodnews Bay, Alaska, and for preliminary experiments in the Pd-As-Sb system.

MATERIALS AND METHOD OF INVESTIGATION

The PG minerals from the Stillwater Complex, characterized in this work, came from the same samples previously described by Cabri & Laflamme (1974b) as well as from other similar samples. The concentrates, polished sections, reflectance, micro-indentation hardness, and x-ray powder data were all obtained by methods described previously. The unnamed Pd_8Sb_3 mineral from Sudbury was obtained from a sample labelled "Copper Cliff Concentrate" after handpicking grains under a binocular microscope. The mertieite was obtained from the U.S. National Museum, Smithsonian Institution (NMNH #132499).

Compositions were determined with the same electron probe and operating conditions using the following x-ray lines and (synthetic standards): $PdL\alpha$, $AsK\alpha$ (Pd_5As_2, Pd_8As_3, and $Pd_8As_{1.49}Sb_{0.51}$); $HgL\alpha$ (Pd_3HgTe_3); $PtL\alpha$, $SnL\alpha$ (PtSn); $PdL\alpha$, $SbL\alpha$ ($Pd_{2.9}Sb$, Pd_8Sb_3); $CuK\alpha$ ($Pd_{4.85}Cu_{0.15}Sb_2$); $SbL\alpha$, $AuL\alpha$, $CuK\alpha$, $NiK\alpha$, $AgL\alpha$, $TeL\alpha$, and $BiL\alpha$ (pure metals). Synthetic Pd_5As_2 had to be freshly polished before use because it tarnishes, even when carbon coated.

Corrections to these x-ray data were applied using the EMPADR VII computer program of Rucklidge & Gasparrini (1969). The homogeneity of the analyzed minerals was determined from the homogeneity index built into the program by use of the relation $HOM=\sigma/\sqrt{N/n}$ after Boyd et al. (1969), where σ = standard deviation of a set of counts, N = mean of the number of counts and n = number of readings in a set. Therefore the HOM is a measure of the observed vs. the variance predicted from counting statistics. A HOM >3 is equivalent to >3σ in observed variance and thus such samples are non-homogeneous. In most cases HOM was less than 3 (Table I) and these are considered homogeneous grains.

PLATINUM-GROUP ARSENIDES AND ANTIMONIDES

The PG-arsenides found in our studies of Stillwater Complex samples are mainly of palladium, only one being the platinum di-arsenide (sperrylite). These palladium arsenides are characterized by either having numerous minor-element substitutions for Pd (by Pt, Au, Cu, Hg) or for As (by Sn, Sb, Te, Bi), but they sometimes occur as pure Pd-As minerals, within the detection limits of the electron probe for such elements. The optical, physical and chemical properties, as far as these were determined, will be described separately for each arsenide.

Our studies of Sudbury-area PG-minerals have revealed only one PG-arsenide, sperrylite. We have found more variety among the PG-antimonides but, in contrast to the one platinum arsenide, they are all palladium minerals: unnamed Pd_8Sb_3 (Cabri & Laflamme 1974c), un-named Pd(Sb,Bi,Te) (Cabri *et al.* 1973) and sudburyite, PdSb (Cabri & Laflamme 1974a).

Mertieite II from Goodnews Bay district, Alaska, was also studied to compare with the Sudbury and Stillwater palladium arsenides and antimonides.
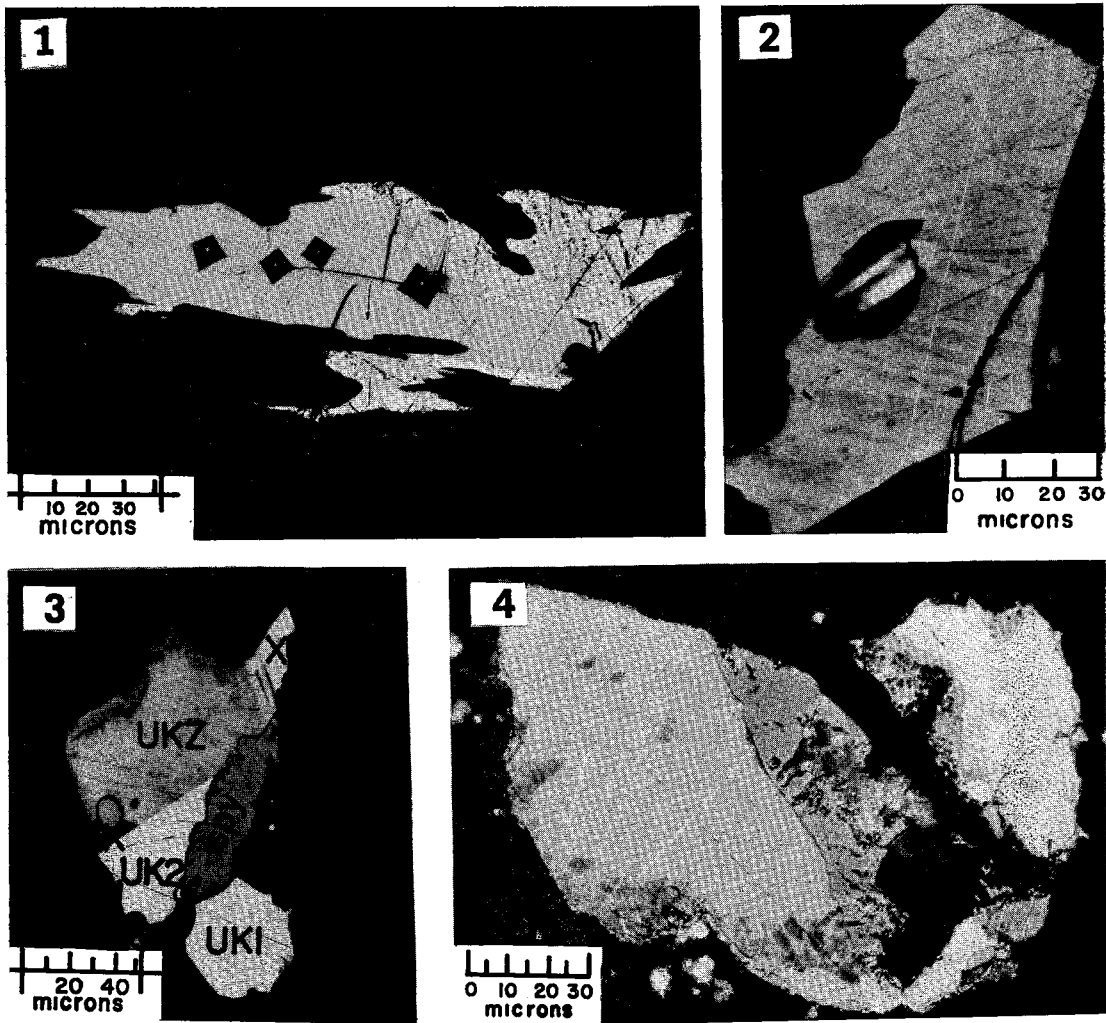

FIG. 1. Photomicrograph of a stillwaterite grain (grey) associated with native gold. (Anal. No. 1, Table 2, R.O.M. No. M33559).

FIG. 2. Photomicrograph showing twinning in stillwaterite.

FIG. 3. Photomicrograph illustrating a complex multimineralic assemblage. UKI = Au-bearing unnamed Pd_5As_2, UK2 = palladoarsenide, UKZ = unnamed Pd_5As_2, spy = sperrylite, cp = chalcopyrite, x = unknown. Partly crossed nicols.

FIG. 4. Photomicrograph with a complex assemblage: kotulskite (white) in contact with unknown (Pd,Ni, As) mineral (which itself contains a hole). The largest light grey area is palladoarsenide with some intergrowths of unknown (Pd,Cu,As) mineral (dark grey) and an elongate inclusion of another unknown mineral only visible under x-nicols (gr. 8, Anal. 2, Table 4).
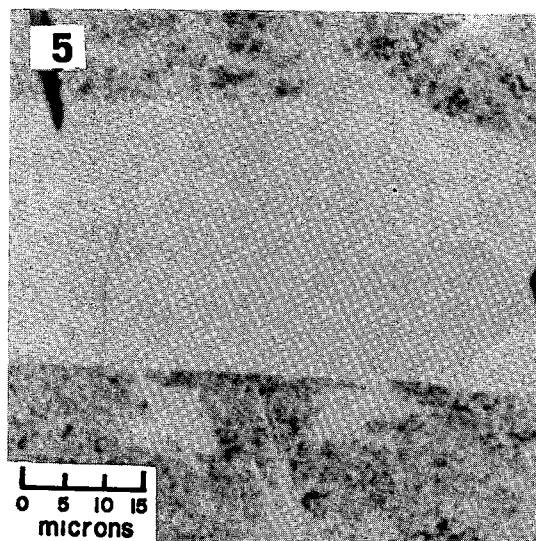
FIG. 5. Photomicrograph showing a sperrylite inclusion in a lamella of unnamed Pd_5As_2 which occurs in a matrix of intergrowths of unknown (Pd,Cu,As)+unnamed Pd_5As_2 (gr. 12, Anal. 4, Table 4).

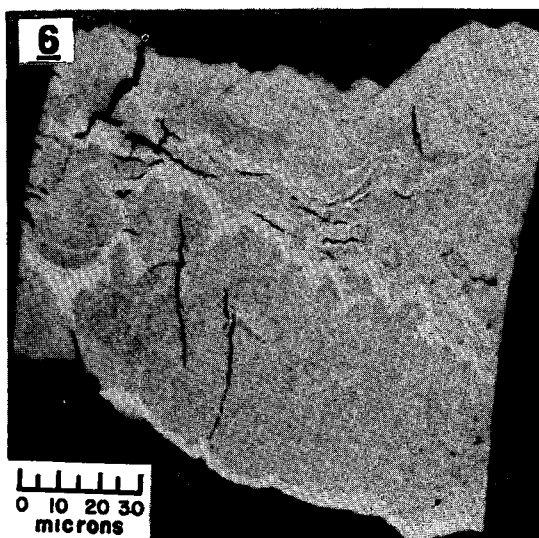FIG. 6. Photomicrograph illustrating the banded or colloform textures developed by unknown (Pd,Cu, As) mineral (dark grey) with unnamed Pd_5As_2.

ARSENIDES FROM THE STILLWATER COMPLEX

Stillwaterite

Thirteen grains of stillwaterite were studied and type material is preserved at the Royal Ontario Museum, Toronto, (M33559) and at the U.S. National Museum, Washington, D.C. (NMNH #132500). The mineral occurs as small anhedral grains, 40×75 to 120×265 microns. Closely associated minerals are gold, other palladium arsenides, and silicates (Fig. 1). The mineral is named after the Stillwater Complex.

Under reflected light, in air, the mineral is light creamy grey, shows no bireflectance, and is weakly anisotropic with colour effects from dark grey to brownish grey. Under oil immersion the anisotropy is distinct, with brownish black colours and a blue to yellow-brown tinge. One grain was twinned (Fig. 2). Reflectance measurements in air with a silicon standard (mean of four grains) are: 470nm 51.6, 52.7; 546nm 52.5, 53.2; 589nm 53.1, 53.7; 650nm 54.4, 55.0%. Micro-indentation hardness measurements gave VHN_{30} = 384 (360-416) for seven indentations measured on two grains.

Quantitative electron probe analyses on thirteen grains showed the mineral to be $Pd_8(As,Sb,Te,Sn,Bi)_3$ (Table 2), corresponding to an ideal end-member of Pd_8As_3 and to the phase $Pd_{2.65}As$

synthesized by Saini et al. (1964a). All grains except one (Anal. 3, Table 1) proved to be homogeneous and stoichiometric within analytical error. The range of Pd/As from 7.84/3.00 to 8.13/3.00 in Table 2 is considered reasonable for electron probe analyses of such materials.

Single-crystal precession studies show that stillwaterite is hexagonal. The symmetry of the diffraction spots indicated Laue group $\bar{3}$ and the extinction conditions gave $P\bar{3}$ or $P3$ as possible space groups. The cell dimensions of grain 3 (Table 2), determined from an x-ray diffraction powder film using a Gandolfi camera, are a = 7.399(4), c = 10.311(15) Å, and correspond well with those of synthetic Pd_8As_3: a = 7.426(4), c = 10.316(7) Å (Debye-Scherrer camera, Table 3). Both powder patterns are very similar to the unindexed pattern for $Pd_{2.65}As$ reported by Saini et al. (1964a), though there is not exact correspondence between all the reflections for stillwaterite and synthetic Pd_8As_3. For example, the (030) and (114) reflections are not resolved for stillwaterite, but are for synthetic Pd_8As_3. This is ascribed to a better Debye-Scherrer pattern being obtained from annealed material in contrast to the poorer Gandolfi x-ray pattern of natural material. A Gandolfi x-ray pattern of a stillwaterite grain with the lowest analyzed As content (Anal. No. 13) is similar to that shown in Table 3. This grain has

$a = 7.39(1)$, $c = 10.30(1)$Å, and though its diffraction pattern was generally weaker, some reflections were resolved better; e.g. (030) and (114) were resolved, though not with the same intensities as for synthetic Pd_8As_3. The calculated densities for stillwaterite and synthetic Pd_8As_3, based on three formula units per unit cell, are 10.96 and 10.88 g/cm³, respectively. The measured density for synthetic Pd_8As_3 is 10.4 g/cm³.

Unnamed Pd_5As_2

Several grains of a palladium arsenide were found which have compositions very close to Pd_5As_2, but some contain minor amounts of Au, Hg, Pt and Cu replacing Pd, and Sn replacing As (Table 4). This mineral was never found as free grains and occurred in three associations: with palladoarsenide, sperrylite and chalcopyrite; with stillwaterite; and with an ill-defined tarnished palladium arsenide, with or without sperrylite. The last association (without sperrylite) is probably the most common, but the nature of the intergrowth and of the tarnished mineral itself (described below) did not permit many reliable analyses.

The unnamed Pd_5As_2 mineral in reflected light appeared pale cream to cream-coloured in air, and in oil. No bireflectance was observed in air, but in oil immersion this varied from nil to very weak. Anisotropism in air varied from distinct (or moderate) to strong, with colours varying from grey (or dull grey) to black (or brownish black). The anisotropism and colours were similar under oil immersion. Two further qualitative observations are relevant: a) the presence of Au (e.g., in grain UKI vs. UKZ) increases the reflectance and bireflectance; this was very marked in the association with palladoarsenide (Fig. 3), where the Au-bearing Pd_5As_2 (UKI) was considered from optical observations to be the same mineral as the palladoarsenide (UK2) but different from the Au-free Pd_5As_2 (UKZ) prior to analysis; b) the unnamed Pd_5As_2 (anal. 5, Table 4) is more reflectant and anisotropic than the stillwaterite (anal. 4, Table 2) to which it is attached.

A poor x-ray powder diffraction pattern was obtained (Table 5), and indexed on an ortho-

TABLE 2. ELECTRON PROBE ANALYSES OF STILLWATERITE

No.	Gr. no., size in µm associated minerals	weight per cent							atomic proportions*					
		Pd	As	Sb	Te	Sn	Bi	Total	Pd	As	Sb	Te	Sn	Bi
1	gr. 2, 70x200, +Au+si	79.2	20.7	n.d.	n.d.	n.d.	--	99.9	8.09	3.00	--	--	--	--
2	gr. 3**, 110x135	79.0	21.2	n.d.	n.d.	n.d.	--	100.2	7.88	3.00	--	--	--	--
3	gr.4, 60x115 +si	78.5	19.7	1.4	0.33	n.d.	--	99.93	7.99	2.85	0.12	0.03	--	--
4	gr.9, 65x110 +Pd$_5$As$_2$+si	78.9	21.0	n.d.	n.d.	n.d.	--	99.9	7.94	3.00	--	--	--	--
5	gr.4¦ 135x170 +incl.?	76.8	17.8	2.7	n.d.	1.5	0.24	99.04	7.92	2.62	0.24	--	0.13	0.01
6	gr.5, 110x190 +Pd$_2$(As,Bi)	76.7	17.3	2.8	n.d.	2.3	n.d.	99.1	7.88	2.53	0.25	--	0.22	--
7	gr.6, 120x265	79.1	20.8	n.d.	n.d.	n.d.	n.d.	99.9	8.05	3.00	--	--	--	--
8	gr.7, 80x190 +si	77.5	17.2	3.1	n.d.	2.3	n.d.	100.1	8.01	2.52	0.27	--	0.21	--
9	gr.9¦ 135x145 +?	78.8	20.5	n.d.	n.d.	n.d.	n.d.	99.3	8.13	3.00	--	--	--	--
10	gr.10, 80x120	78.8	20.6	n.d.	n.d.	n.d.	n.d.	99.4	8.07	3.00	--	--	--	--
11	gr.11, 60x90	78.5	20.6	n.d.	n.d.	n.d.	n.d.	99.1	8.05	3.00	--	--	--	--
12	gr.UM, 65x65 +si	78.3†	17.3	0.7	1.1	3.0	1.3	101.7	7.95	2.50	0.06	0.10	0.27	0.07
13	gr.9F**, 60x185 +si	76.2	17.0	1.6	0.30	3.8	n.d.	98.9	7.84	2.49	0.14	0.02	0.35	--

* Sum of As+Sb+Te+Sn+Bi = 3.00, ** Grain x-rayed - see Table 3, † (Pd+Pt), Pt = 0.08 wt.%

n.b. - 1. n.d. = element sought for, but not detected. 2. other elements sought for, but not detected: Au,Ag,Cu,Pt,Ni for all analyses. Analyses Nos. 1-4 also Hg sought for, but not detected.

Abbreviations used in this and subsequent tables: Au = gold, si = silicate, Pd$_5$As$_2$= unnamed Pd$_5$As$_2$, incl. ? or ? = unknown inclusion, Pd$_2$(As,Bi) = unnamed Pd$_2$(As,Bi), spy = sperrylite, cp = chalcopyrite, Pd$_2$As = palladoarsenide, tarnished ? = unknown (Pd,Cu,As) mineral, stl = stillwaterite, (Pd,Ni,As) = unknown (Pd,Ni,As) mineral, kot = kotulskite, ca = calcite, pol = polarite ?, Fe-S = undetermined Fe sulphide.

TABLE 3. X-RAY POWDER DATA FOR STILLWATERITE AND SYNTHETIC Pd_8As_3

Stillwaterite: a 7.399 (4), c 10.311 (15)
Pd_8As_3 Synthetic: a 7.426 (4), c 10.316 (7)

Stillwaterite I	d_{meas}	d_{calc}	hkl	Pd_8As_3 I	d_{meas}	d_{calc}
		3.204	020	1	3.22	3.215
		3.006	112	3	3.013	3.013
3	2.700	2.721	022	3	2.727	2.728
2	2.521	2.518	113	3	2.522	2.522
		2.422	120	2	2.434	2.431
8	2.355	2.357	121	10	2.360	2.366
½	2.189	2.192	122	5	2.205	2.198
		2.136	030		2.144	2.144
10	2.115	2.115	114	8	2.126	2.118
3B	1.991	1.980	123	4	1.988	1.985
1	1.818	1.820	221	3	1.826	1.827
1	1.747	1.751	131	4	1.760	1.757
		1.718	006	½	1.718	1.719
		1.680	132	2	1.688	1.685
		1.659	016	1	1.665	1.661
		1.628	223	2	1.635	1.633
		1.582	041	½	1.586	1.588
		1.558	116	½	1.563	1.560
		1.530	042	½	1.532	1.535
2	1.511	1.503	224	3	1.508	1.507
½	1.465	1.463	134	2B	1.469	1.467
½	1.434	1.435	017	½	1.443	1.436
		1.414	232	½	1.421	1.418
½	1.403	1.401	126	2	1.401	1.404
5	1.351	1.351	233	5	1.357	1.356
		1.295	143	1	1.300	1.299
1	1.264	1.263	018	2B	1.263	1.264
		1.244	052	½	1.242	1.247
½	1.231	1.233	330	2B	1.234	1.237
		1.224	331	3	1.222	1.229
2B	1.201	1.203	241	4	1.208	1.207
2	1.159	1.160	333	3B	1.162	1.164

Stillwaterite I	d_{meas}	d_{calc}	hkl	Pd_8As_3 I	d_{meas}	d_{calc}
		1.152	227	1	1.152	1.154
½	1.138	1.137	128	1	1.138	1.139
½	1.060	1.058	335	1	1.061	1.061
1	1.043	1.043	138	1	1.048	1.045
		1.031	0010	½	1.032	1.031
½	1.019	1.021	251	½	1.025	1.025
½	1.003	1.002	336	½	1.001	1.004
1	0.9765	0.9772	160	½B	0.9778	0.9805
2	0.9493	0.9483	065	3B	0.9527	0.9512
		0.9381	345	1	0.9404	0.9409
		0.9118	351	½	0.9152	0.9151
½	0.9034	0.9036	239	1	0.9060	0.9052
		0.8862	149	4	0.8885	0.8877
4	0.8858	0.8830	165	4	0.8858	0.8858
1	0.8757	0.8757	262	1B	0.8785	0.8788
1	0.8660	0.8670	0410	2	0.8683	0.8682
		0.8633	263	½	0.8622	0.8633
½B	0.8559	0.8569	347	2	0.8588	0.8591
		0.8459	171	½	0.8487	0.8489
2B	0.8458	0.8441	2310	1	0.8457	0.8454
		0.8419	257	½B	0.8433	0.8441
½	0.8313	0.8299	1410	½	0.8323	0.8312
		0.8178	451	½	0.8205	0.8208
		0.8161	265	½	0.8183	0.8186
1	0.8100	0.8102	452	3	0.8128	0.8131
½	0.8050	0.8048	361	3	0.8066	0.8078
½	0.8013	0.8010	080	2	0.8023	0.8039
2	0.7999	0.7976	362	4	0.8000	0.8004
		0.7972	0312	2	0.7979	0.7979
½	0.7944	0.7915	082	2	0.7943	0.7943
½	0.7905	0.7904	2311	1	0.7907	0.7915
½	0.7866	0.7859	363	½	0.7885	0.7886
		0.7849	175	1	0.7874	0.7874
2	0.7818	0.7818	454	½	0.7848	0.7844
		0.7801	083	3B	0.7825	0.7828

rhombic cell with $a = 11.261(4)$, $b = 3.857(1)$, $c = 11.346(5)$Å. The symmetry and approximate cell parameters were determined by examining the crystal with a precession camera. The x-ray powder diffraction pattern and the symmetry are in contrast to that of synthetic Pd_5As_2. The powder data for Pd_5As_2 were indexed on a hexagonal cell with $a = 7.318(1)$, $c = 27.524(1)$Å. The a-dimension and the hexagonal symmetry were confirmed by precession camera study, but the c-dimension could not be defined more precisely other than determination that it is a multiple of ~13.7Å. Several attempts to produce perfect single crystals using a Bridgeman technique modified for small samples were unsuccessful.

TABLE 4. ELECTRON PROBE ANALYSES OF Pd_5As_2 AND PALLADOARSENIDE

UNNAMED Pd_5As_2

Anal. No.	gr.no., size in μm, associated minerals	Pd	Pt	Au	Hg	Cu	As	Sn	Sb	Te	Bi	Total	Pd	Pt	Au	Hg	Cu	Σ	As	Sn	Σ
1	gr.UK1, 30x30, +spy+cp+Pd8As3+si	70.1	0.24	6.8	2.7	0.21	21.2	--	--	n.d.	--	101.25	4.66	<.01	0.24	0.09	0.02	5.01	2.00	--	2.00
2	gr.UK2*, 45x75, +spy+cp+Pd2As+si	79.0	n.d.	n.d.	n.d.	n.d.	22.2	--	--	n.d.	--	101.2	5.02	--	--	--	--	5.02	2.00	--	2.00
3	gr.7, 55x100,** +tarnished?	68.4	n.d.	7.4	2.3	0.13	21.0	0.31	n.d.	n.d.	--	99.54	4.54	--	0.27	0.08	0.01	4.90	1.98	0.02	2.00
4	gr.12, 25x50, +spy+tarnished?	68.6	n.d.	7.8	1.3	0.09	20.8	0.26	n.d.	n.d.	n.d.	98.85	4.60	--	0.29	0.05	0.01	4.95	1.99	0.01	2.00
5	Gr.9, 25x30** +stl+si	68.0	n.d.	6.9	2.5	n.d.	20.6	n.d.	n.d.	n.d.	--	98.00	4.65	--	0.26	0.09	--	5.00	2.00	--	2.00

* grain x-rayed   ** Ni also n.d.

PALLADOARSENIDE

Anal. No.	gr.no., size in μm, associated minerals	Pd	Pt	Au	Hg	Cu	As	Sn	Sb	Te	Bi	Total	Pd	Pt	Au	Hg	Cu	Σ	As	Sb	Te	Σ
1	gr.UK2, 30x30, +spy+cp+Pd5As2+si	74.0	0.10	0.11	n.d.	0.34	24.4	n.d.	--	1.3	--	100.25	2.07	<.01	<.01	--	0.01	2.08	0.97	--	0.03	1.00
2	gr.8, 65x110 +(Pd,Ni,As)+kot	73.1	n.d.	n.d.	n.d.	n.d.	25.0	n.d.	0.64	0.59	--	99.33	2.00	--	--	--	--	2.00	0.97	0.015	0.015	1.00

n.b. Ni & Ag also sought for, but not detected

Palladoarsenide

The mineral palladoarsenide, described by Begizov *et al.* (1974), was discovered in the "veinlet-disseminated" pentlandite-chalcopyrite ores in the footwall "excontact" of the northwestern side of the Talnakh intrusion. The mineral is equivalent to the low-temperature polymorph of Pd_2As, synthesized and described by Saini *et al.* (1964a).

Two grains of palladoarsenide were found closely associated with other minerals such as sperrylite, chalcopyrite, unnamed Pd_5As_2, (Pd, Ni,As), kotulskite, gold, and silicates. The grains were too small and intergrown for removal and confirmation by *x*-ray diffraction. The electron probe analyses (Table 4) and optical properties suggest that the grains are palladoarsenide. The analyses show that minor quantities of Pt, Cu or Au may substitute for Pd, whereas minor Sb or Te may substitute for As. The four analyses of Talnakh palladoarsenide reported by Begizov *et al.* (1974) showed minor substitution of only Au and Ag for Pd; however, the totals are between 1.2 and 2.2 wt % less than 100%.

Unknown (Pd,Ni,As) mineral

One grain of this mineral was observed in a complex intergrowth with kotulskite, the unnamed (Pd,Cu,As) mineral, and palladoarsenide (Fig. 4). The mineral was too small for complete characterization and appeared light yellow to greyish under reflected light in oil immersion. It is either isotropic or weakly anisotropic, and analysis gave: Pd 48.6, Ni 17.4, As 32.7, Te 0.38 — total 99.08 wt %. This analysis suggests a formula of $(Pd,Ni)_2(As,Te)$ or PdNi(As, Te), but these formulae must be considered very tentative because of the limited data available.

Unknown (Pd,Cu,As) mineral

Several grains of this mineral were found in one of the concentrates and were nearly always closely associated with the unnamed Pd_5As_2 mineral. The mineral appears to be an alteration product or a secondary mineral and it had a pitted or intergrowth texture with a dull grey colour under reflected light (Fig. 5). It also frequently exhibited a banded or colloform texture with the unnamed Pd_5As_2 mineral (Fig. 6) and tarnished with time and exposure to air. Although these physical and textural properties made electron probe analysis unreliable, it was possible to determine that Pd was the major element with Cu and As in minor and nearly equal quantities by weight.

TABLE 5. X-RAY POWDER DATA FOR UNNAMED Pd_5As_2

I	d_{meas}	hkl	d_{calc}	I	d_{meas}	hkl	d_{calc}
	a 11.261 (4)		*b* 3.857 (1)		*c* 11.345 (5)		
4	3.565	301	3.563	<1	1.473	711	1.472
10	3.066	211	3.064	<1	1.410	108	1.408
6	2.778	212	2.776	1	1.363	523	1.366
2	2.702	013	2.701	<1	1.334	621	1.336
1	2.613	311	2.617	1	1.297	218	1.295
3	2.528	402	2.522	1	1.222	902	1.222
5	2.433	312	2.431	<1	1.166	912	1.165
3	2.241	114	2.239	1	1.145	904	1.145
8	2.119	214	2.117	<1	1.111	531	1.111
9	1.947	510	1.945	<1	1.089	823	1.089
1B	1.878	121	1.878	<1B	1.050	129	1.050
3	1.804	122	1.802	<1B	1.011	923	1.011
2	1.735	315	1.734	<1	0.9938	634	0.9936
3	1.698	123	1.698	<1	0.9419	61.10	0.9417
<1	1.639	322	1.642	<1	0.9295	827	0.9309
<1	1.602	514	1.604	<1	0.9102	144	0.9101*
1	1.539	613	1.541	9	0.7770	745	0.7772

Pattern obtained with 57.3 mm Gandolfi camera using Cu, Ni-filtered radiation.
* six additional weak reflections not reported. Cell refinement using 28 reflections.

Sperrylite

Sperrylite is a common mineral in many platinum-bearing deposits and its presence in the Stillwater samples is not unexpected. There are, however, few electron probe analyses of sperrylite in the literature, most of the analytical information on the mineral having been obtained by bulk chemical methods. Table 6 lists seven analyses of Stillwater sperrylite; it is noteworthy that two analyses contain minor quantities of rhodium, and that the rhodium is not homogeneously distributed. This occurrence of rhodium is in addition to its presence in the platinum alloys (Cabri & Laflamme, 1974b).

NEW MINERAL (?) FROM SUDBURY

Unnamed Pd₈Sb₃

A single grain, $190 \times 300 \mu m$, found in a sample of "Copper Cliff Concentrate" from the Sudbury area, gave electron probe results identical to the synthetic standard Pd_8Sb_3. Under the binocular microscope the mineral appeared metallic with a pinkish cast, and in polished

TABLE 6. ELECTRON PROBE ANALYSES OF SPERRYLITE

Anal. No.	Size in µm, associated minerals	Pt	Rh	As	Total	Pt	Rh	Σ	As
		weight per cent				atomic proportions			
1	55x110,cp	57.0	n.d.	42.6	99.6	1.00	-	1.00	1.95
2	110x165	56.7	n.d.	43.0	99.7	1.00	-	1.00	1.98
3	110x110, si+tarnished?	55.6	0.56 (.22-1.28)	43.0	99.16	0.98	0.02	1.00	1.98
4	110x165	56.5	n.d.	43.1	99.6	1.00	-	1.00	1.99
5	82x165 si,	55.9	0.39 (.11-1.07)	43.3	99.59	0.99	0.01	1.00	1.99
6	60x165, si	56.8	n.d.	43.5	100.3	1.00	-	1.00	1.99
7	100x200 Fe-S	57.0	n.d.	42.3	99.3	1.00	-	1.00	1.93

Sb,Sn, and Cu not detected.

section under reflected light, it had a pale cream to white colour in air and in oil immersion. No bireflectance was observed and it was moderately anisotropic (reddish brown to light grey) in air. Under oil immersion the anisotropism was slightly stronger but the colours were the same.

Reflectance measurements were made using a silicon standard on the mineral and on synthetic Pd_8Sb_3. These were for the mineral (average of four separate measurements) at 470nm 47.7, 52.2; 546nm 49.7, 53.5; 589nm 50.9, 54.6; 650nm 52.6, 56.4% and for the synthetic Pd_8Sb_3 (average of measurements on three grains) at 470nm 50.3, 52.1; 546nm 52.2, 54.0; 589nm 53.2, 55.1; 650nm 54.6, 55.8%. Ten micro-indentation hardness measurements were made on the synthetic Pd_8Sb_3 and gave VHN_{50} = 516 (501-545).

The x-ray diffraction pattern of unnamed Pd_8Sb_3 was indexed as hexagonal with $a = 7.565(1)$, $c = 43.207(3)$ Å with a rhombohedral lattice. The powder pattern is compared with that of mertieite II and synthetic Pd_8Sb_3 in Table 7. The calculated density is 11.32 g/cm^3, based on $Z = 12$.

RE-ANALYSIS OF MERTIEITE

Mertieite II

Two of the four mertieite grains analyzed by Desborough et al. (1973), and referred to them as Group II, were re-analyzed by us using different synthetic standards (Table 8). These new analyses show very small differences in weight per cent to those reported by Desborough and co-workers but, nevertheless, these result in significant differences in stoichiometry. Our analyses indicate that mertieite II is stoichio-

TABLE 7. X-RAY POWDER DATA FOR MERTIEITE II AND SYNTHETIC AND NATURAL Pd_8Sb_3

Left group cell parameters — MERTIEITE II*: a 7.546 (2), c 43.18 (1); Pd₈Sb₃ Synthetic**: a 7.601 (1), c 42.904 (1); Unnamed Pd₈Sb₃***: a 7.565 (1), c 43.207 (3)

hkl	MERTIEITE II* I	d_{meas}	d_{calc}	Pd₈Sb₃ Synthetic** I	d_{meas}	d_{calc}	Unnamed Pd₈Sb₃*** I	d_{meas}	d_{calc}	hkl	MERTIEITE II I	d_{meas}	d_{calc}	Pd₈Sb₃ Synthetic I	d_{meas}	d_{calc}	Unnamed Pd₈Sb₃ I	d_{meas}	d_{calc}
116				<1	3.?4	3.356				4022	3	1.257	1.256	<1	1.258	1.257	4B	1.258	1.258
024				<1	3.14	3.147				2032	<1	1.249	1.247	2	1.244	1.242			
0114				2B	2.788	2.778				336							1	1.238	1.241
0210	<1	2.596	2.605	2	2.609	2.611				4118	7	1.226	1.226	6	1.230	1.230			
211	2	2.468	2.466	4	2.480	2.484	1	2.476	2.472	339							<1	1.217	1.219
214	1	2.407	2.407	2	2.425	2.424	2	2.414	2.414	5014				2	1.209	1.209			
125				2	2.385	2.389	4	2.369	2.369	3030	7	1.200	1.200	3B	1.197	1.198	4	1.205	1.202
1115	10	2.286	2.288	9	2.281	2.285	8	2.293	2.291	3312	1	1.188	1.187				1	1.198	1.190
2014	3	2.247	2.243	3	2.243	2.243	7B	2.238	2.246	511				3	1.182	1.182			
300	9	2.177	2.178	10	2.191	2.194				1328							<1	1.178	1.176
2110	1	2.148	2.144	1	2.147	2.152	1	2.144	2.148	155	<1	1.163	1.163						
1211				1	2.096	2.097				517	<1	1.154	1.153				2B	1.158	1.156
0216				<1	2.074	2.079				4214	<1	1.146	1.146	1	1.151	1.152	1	1.150	1.149
1118	5	2.022	2.024	4	2.015	2.019	4B	2.025	2.026	5110	<1	1.134	1.132	1	1.141	1.141	1	1.134	1.135
1214	3	1.930	1.928	4	1.929	1.931	2	1.930	1.931	4028				<1	1.122	1.121			
1022	3	1.874	1.879	1	1.866	1.869	1	1.883	1.881	1235				2	1.102	1.099	<1	1.104	1.105
131				2	1.826	1.824				600				3	1.094	1.097	3	1.091	1.091
226	<1B	1.825	1.825				<1	1.829	1.829	3132	<1	1.082	1.082	3	1.081	1.081	2	1.080	1.083
2020				<1	1.796	1.797				345							<1	1.070	1.070
315	<1	1.773	1.773				<1	1.779	1.778	2329	<1	1.056	1.056				3	1.058	1.058
137	<1	1.736	1.739							253	3	1.043	1.044	3B	1.051	1.051	2	1.048	1.046
1220				<1B	1.622	1.624				526				<1	1.041	1.042			
2215	4	1.577	1.577	5	1.582	1.582	3B	1.577	1.580	1238				<1	1.027	1.028			
2122				<1	1.533	1.535				4130				<1	1.013	1.013			
321	4	1.496	1.498	2	1.508	1.509				161				2	1.004	1.004			
2218	1	1.483	1.483	4	1.485	1.486	2	1.485	1.485	1523				<1	0.9983	0.9987			
327	<1	1.458	1.457	1	1.465	1.466				2515				2B	0.9885	0.9892			
0414				<1	1.450	1.450				6111	<1	0.9678	0.9659	2B	0.9721	0.9723			
0030	4	1.439	1.439	4	1.429	1.430	<1	1.446	1.440	2518	<1	0.9583	0.9591	3	0.9637	0.9641			
3210	3	1.413	1.416				3	1.420	1.419	443				3B	0.9483	0.9482			
2311				1B	1.406	1.408	2	1.404	1.404	440	<1	0.9436	0.9432						
2314	3	1.345	1.348	4	1.354	1.354	1	1.351	1.351	446	6	0.9355	0.9352	1	0.9419	0.9420	3B	0.9356	0.9376
1130				3	1.337	1.338				535	2	0.9283	0.9282						
0132	<1	1.318	1.321	3	1.315	1.314				2431				4	0.9254	0.9253			
2317							<1	1.293	1.293	1529	1	0.9227	0.9217				1	0.9237	0.9234
1415	4	1.278	1.278	5	1.283	1.283	1	1.279	1.280	1436	2	0.9192	0.9179	2	0.9172	0.9173	<1	0.9193	0.9192
330				5	1.267	1.267				4232	2	0.9113	0.9110	2	0.9118	0.9120	3	0.9119	0.9125
										4040	<1	0.9010	0.9006	3	0.8992	0.8987			

*   Grain 6B (Table 8) 24 additional high angle reflections not reported; cell refinement using 42 reflections. Pattern obtained with 114.6 mm Gandolfi camera using Cu, Ni-filtered radiation.

** 31 additional high angle reflections not reported; cell refinement using 53 reflections. Cu, Ni-filtered radiation with 114.6 mm Debye - Scherrer type camera.

*** From Sudbury, Ontario. 14 additional high angle reflections not reported; cell refinement using 34 reflections. Pattern obtained with 114.6 mm Gandolfi camera using Cu, Ni filtered radiation.

TABLE 8. ELECTRON PROBE ANALYSES OF MERTIEITE II.

No.	Gr. No., size in μm	Pd	Cu	Sb	As	Total	Pd	Sb	As	
1	gr.6B**, 120x280	71.6	n.d.	25.9	2.9	100.4	8.03	2.54	0.46	(1)
2	gr.6B**	71.4	n.d.	25.9	2.9	100.2	8.01	2.54	0.46	(2)
3	gr.6B***	72.5	<0.1	25.0	2.8	100.3	8.42	2.54	0.46	(3)
4	gr.7, 80x220	71.7	n.d.	25.9	2.9	100.5	8.04	2.54	0.46	(1)
5	gr.7***	73.0	<0.1	25.0	2.8	100.8	8.48	2.54	0.46	(3)

The column header row reads: weight per cent (Pd Cu Sb As Total) and atomic proportions* (Pd Sb As).

*sum of Sb+As = 3.00, **grain x-rayed, n.d. = not detected
***Detailed data given to Smithsonian Institution
(1) X-ray lines and standards used: PdLα, SbLα (synth.Pd$_{2.9}$Sb), AsKα (synth. Pd$_{5.0}$As$_{1.49}$Sb$_{.51}$), CuKα (synth.Pd$_{4.85}$Cu$_{.15}$Sb$_{2.0}$)
(2) X-ray lines and standards used: PdLα, SbLα (synth. Pd$_8$Sb$_3$), AsKα (synth.Pd$_{5.0}$As$_{1.49}$Sb$_{.51}$).
(3) Desborough et al. (1973)***

metric Pd$_8$(Sb,As)$_3$ rather than having the more general formula of (Pd,Cu)$_{5+x}$(Sb,As)$_{2-x}$ proposed earlier.

The x-ray diffraction pattern (Table 7) of grain 6B has been indexed on a rhombohedral cell with hexagonal axes of $a = 7.546(2)$, $c = 43.18(1)$Å. This unit cell was determined by single-crystal precession photographs of a fragment of grain 6B and was confirmed in a more comprehensive x-ray structure investigation currently in progress. This unit cell may be related to the earlier proposal of Desborough et al. (1973) that the mineral was pseudohexagonal, possibly monoclinic, with pseudohexagonal $a' = 15.04$, $c' = 22.41$Å by the relationship $a' \simeq 2a$ and $c' \simeq \frac{1}{2}c$. The density of mertieite II was calculated using our hexagonal parameters and an idealized Sb:As ratio of 5:1, indicated from the structure studies, which suggest a special position for the As atoms. This density, based on $Z = 12$, is 11.2 g/cm³.

SYNTHESIS EXPERIMENTS

Synthesis experiments had to be performed because of the complexity of the minerals encountered in this study, as well as the necessity of having synthetic standards of similar compositions for x-ray and electron probe standards. Limited experiments were made by reacting high-purity elements in evacuated silica-glass tubes. The charges were examined periodically and the contents were subjected to various grinding, pelletizing and annealing operations. It was also discovered that phase relations in the Pb-Sb system were not known sufficiently well and there were even less published data on the Pd-As-Sb system.

The Pd-Sb system

The Pd-Sb phase diagram reviewed by Hansen & Anderko (1958) contains the following phases: (Pd,Sb) solid solution, Pd$_3$Sb, Pd$_5$Sb$_3$ (stable between 550 and 845°C), PdSb, PdSb$_2$ and Sb. Pratt et al. (1968) extended the (Pd,Sb) solid-solution field to 17 at. % Sb with no temperature dependence at 800-1000°C. El-Boragy et al. (1970) reported the presence of Pd$_5$Sb$_2$ ($P6_3cm$ with $a = 7.60_6$, $c = 13.86_3$Å), and a structurally related phase Pd$_{5+}$Sb$_{2-}$ ($a = 7.6_{13}$, $c = 42.3_{40}$Å) but no mention was made of Pd$_8$Sb$_3$ reported earlier by Schubert et al. (1953). El-Boragy & Schubert (1971) presented new data on the system between Pd$_3$Sb and Pd$_5$Sb$_2$ at 500 to 800°C. Four phases were reported, each with a solid-solution field: Pd$_3$Sb, Pd$_8$Sb$_3$, Pd$_{5+}$Sb$_{2-}$, and Pd$_5$Sb$_2$. They stated that the structures of both Pd$_8$Sb$_3$ and Pd$_{5+}$Sb$_{2-}$ are unique, but that both structures are related to that of Pd$_5$Sb$_2$.

A few syntheses were made at 600 and 700°C between 25 and 40 at. % Sb. At 700°C Pd$_3$Sb is not stoichiometric, the composition being nearer to Pd$_{2.9}$Sb. Pd$_8$Sb$_3$ and Pd$_5$Sb$_2$ were synthesized as homogeneous phases at 700°C. Pd$_8$Sb$_3$ was indexed as rhombohedral with hexagonal axes of $a = 7.60(1)$, and $c = 42.904(1)$Å (Table 7), in good agreement with the cell dimensions of El-Boragy & Schubert (1971): $a = 7.57_9$, $c = 42.80_3$Å. The calculated density of Pd$_8$Sb$_3$ is 11.29 g/cm³ using our cell dimensions with $Z = 12$. Attempts to synthesize Pd$_5$Sb$_3$ at 700 and 600°C, and at 700°C for other closely-related compositions, were not successful in that two- and three-phase assemblages were obtained. Electron probe analysis suggested that one of these phases may have a stoichiometry close to Pd$_7$Sb$_4$ but this area of study was not pursued further.

The Pd-As system

Saini et al. (1964a) reported intermediate phases in the Pd-As system: PdAs$_2$, Pd$_2$As (α and β), Pd$_5$As$_2$, Pd$_{2.65}$As, Pd$_3$As, and Pd$_5$As. Their data are similar to those of Raub & Webb (1963) except for a reported Pd$_7$As phase which may be Pd$_5$As or the Pd$_6$As reported by El-Boragy & Schubert (1971). The polytypism reported by Saini et al. (1964b) for Pd$_5$As$_2$ is discussed below.

We have successfully synthesized homogeneous single phases for the following compositions: Pd$_3$As, Pd$_8$As$_3$ (the Pd$_{2.65}$As above), Pd$_5$As$_2$, and Pd$_2$As.

The Pd-As-Sb system

There are very little data in the literature on this ternary system. Furuseth et al. (1967) reported a complete solid-solution between PdAs$_2$ and PdSb$_2$ at 600°C. Desborough et al. (1973)

made some preliminary synthesis experiments but these produced results which were either too finely crystalline or too inhomogeneous for single-crystal x-ray diffraction studies.

We have limited our experiments in the ternary system to a series of five compositions along the Pd_5As_2 - Pd_5Sb_2 join, shown as triangles in Figure 7. The charges were prepared by combining weighed quantities of previously-synthesized Pd_5As_2 and Pd_5Sb_2 in silica tubes which were evacuated, sealed and heated at 710°C. Table 9 gives the elemental weighed amounts for Pd_5As_2 and Pd_5Sb_2 and the weighed quantities of Pd_5As_2 and Pd_5Sb_2 for the five compositions, as well as their respective atomic proportions. The charges were quenched, ground and pelletized and re-annealed after periods of

4, 65, and 56 days. A final annealing period of two years and four months completed these experiments. The charges were examined by ore microscopy, electron probe, and x-ray diffraction. Single-phase homogeneous products were obtained for $Pd_5As_{1.49}Sb_{0.51}$ and for $Pd_5Sb_{1.94}As_{0.06}$. The intermediate compositions, however, consisted principally of large homogeneous grains with compositions near the bulk composition of the weighed-in components, but with a few intergranular areas containing a fine-grained multiphase mixture which must have been liquid at the annealing temperature. These intergranular areas were analyzed and their approximate bulk compositions are plotted as an x in Figure 7 with a dotted line leading to the bulk composition of the initial charge.
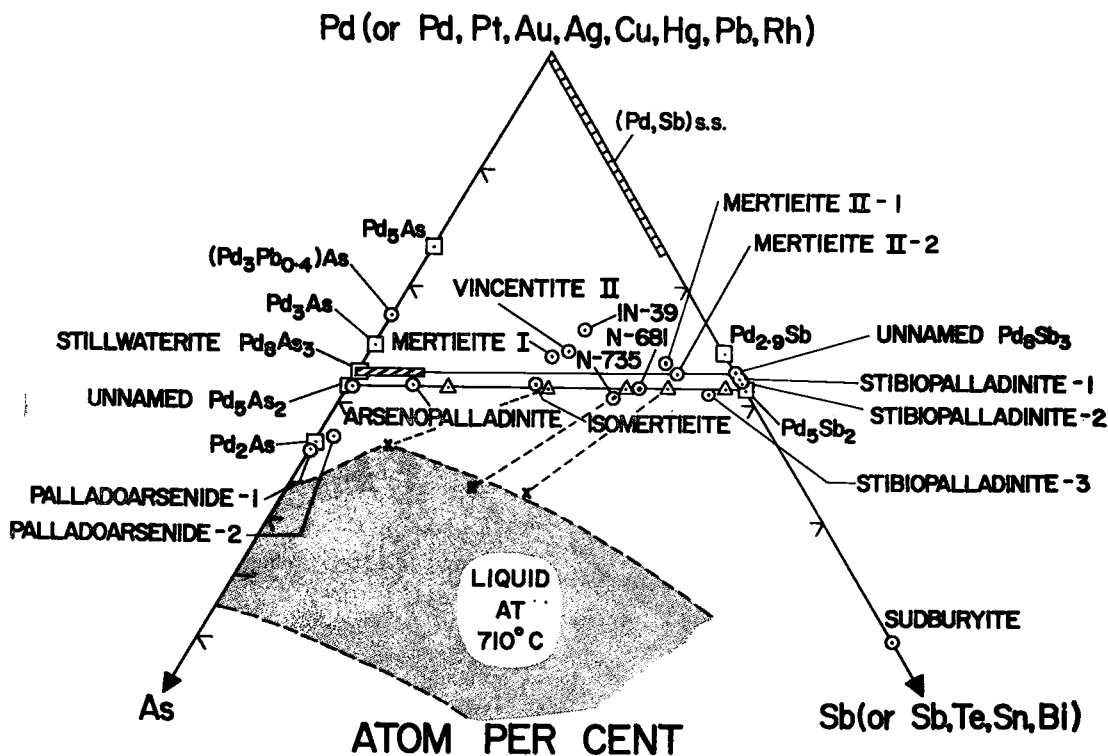
FIG. 7. The palladium-rich part of the Pd-As-Sb composition diagram. Squares refer to known synthetic compounds in the Pd-As and Pd-Sb binaries, and triangles represent bulk compositions of syntheses at 710°C in this study. Dashed lines extending from three triangles represent (at the cross) the analyzed composition of the minor phase(s), interpreted as being liquid at 710°C, which were used to estimate the extent of the liquid field at that temperature. The (Pd,Sb) and stillwaterite solid-solution fields are shown as hatching. Compositions of all natural phases (except stillwaterite) are indicated by circles: (Pd₃Pb₀.₄)As (Genkin 1968); unnamed Pd₅As₂, palladoarsenide-2, mertieite II-2, (this study); arsenopalladinite, stibiopalladinite-2, isomertieite (Clark *et al.* 1974); unnamed Pd₈Sb₃ (Cabri & Laflamme 1974); mertieite II-1, stibiopalladinite-1 (Desborough *et al.* 1973); vincentite II (Stumpfl & Tarkian 1974); In-39, N-375, and N-681 are "mertieites" of Razin & Dubakina (1974); stibiopalladinite-3 (Tarkian & Stumpfl 1975). The minerals of Yu *et al.* (1974), discussed with Pd₃As, are not shown in this Figure.

TABLE 9. COMPOSITIONS AND CRYSTALLOGRAPHY OF QUENCHED PHASES SYNTHESIZED AT 710°C ALONG THE Pd_5As_2-Pd_5Sb_2 JOIN

| | | weight per cent | | | atomic proportions | | | diffraction | sub-cell dimensions Å | | n† |
Pd_5As_2	Pd_5Sb_2	Pd	As	Sb	Pd	As	Sb	symbol	$a=a'$	c'	
100.0	–	78.03	21.07	–	5.00	2.00	–	–	7.318(1)	13.762(1)	?
72.0	28.0	75.39	15.82	8.79	5.00	1.49	0.51	P6/*c*	7.385(2)	13.793(6)	3
46.8	53.2	73.01	10.28	16.71	5.00	1.00	1.00	P6/*c*	7.468(2)	13.916(4)	3
27.4	72.6	71.18	6.01	22.81	5.00	0.60	1.40	R**	7.531(3)	14.075(6)	6
17.4	82.6	70.24	3.81	25.95	5.00	0.39	1.61	P6/*c*	7.556(1)	13.99 (1)	9
2.6	97.4	68.85	0.57	30.58	5.00	0.06	1.94	P6/*c*	7.595(1)	13.880(4)	1
–	100.0	68.60	–	31.40	5.00	–	2.00	–	7.603(1)	13.853(4)	1

† True $c = n \times c'$

These results are interpreted as indicating that, at 710°C, the liquid field in the Pd-As binary extends into the Pd-As-Sb ternary. The presence of quenched liquid in the three charges with intermediate compositions may have resulted either from a deviation from 5:2 stoichiometry or from weighing errors in the synthesis of the original As and Sb end members.

The large homogeneous grains in the five synthetic products along the Pd_5As_2-Pd_5Sb_2 join gave sharp x-ray diffraction patterns which were studied by the precession method, using MoKα and CuKα radiations. The good diffraction characteristics of these grains are thought to be the result of the 28-month annealing period at 710°C. The c-dimensions and extinction conditions were determined in some cases with the aid of enlarged photographic prints of single-crystal films. The cell parameters obtained by the single-crystal method were refined using the powder diffraction data. The results are listed in Table 9.

$Pd_5As_{1.49}Sb_{0.51}$, Pd_5AsSb, $Pd_5As_{0.39}Sb_{1.61}$ and $Pd_5As_{0.06}Sb_{1.94}$ show the same diffraction aspect, P6/*c*, corresponding to space groups $P6_3/mcm$, $P6_3cm$ or $P\bar{6}c2$, whereas $Pd_5As_{0.6}Sb_{1.4}$ is R** corresponding to $R\bar{3}m$, R3m or R32. The extinction conditions for Pd_5As_2 were not determined due to the poor crystallinity of the synthetic phase, which had not been subjected to the long annealing period of the intermediate compositions. All the phases, however, possess a common sub-cell with $a' \sim 7.4$, $c' \sim 13.9$Å, and a more pronounced sub-cell with $a'' = \frac{1}{3}a'$, $c'' = \frac{1}{2}c'$, similar to those of Pd_5As_2 reported by Saini et al. (1964b). The true cells have $a = a'$ and $c = n \times c'$ as shown in Table 9. Saini et al. (1964b) reported that Pd_5As_2 showed polytypism with $a = 7.31(1)$ and c-values of 10.34, 13.70, 27.48 and 96.2Å, corresponding to a basic repeat distance of 3.43Å along the c-axis. The c-dimensions observed in the present study can also be expressed in terms of ~ 3.5Å. The cell dimensions generally increase with increasing Sb content in the structure, varying from $a' = 7.32$ and $c' = 13.76$Å for Pd_5As_2 to $a' = 7.60$ and $c' = 13.85$Å for Pd_5Sb_2, except that the c'-dimension of $Pd_5As_{0.6}Sb_{1.4}$, which has rhombohedral symmetry, is somewhat larger.

The close relationships of these phases are apparent in their x-ray powder-diffraction patterns. The powder-diffraction patterns of Pd_5As_2 are poorly defined but are essentially similar to those given by Saini et al. (1964b). The powder data for $Pd_5As_{0.06}Sb_{1.94}$ are similar to those of Pd_5Sb_2 and the latter confirm the results given by El-Boragy et al. (1970). The powder data for Pd_5AsSb and $Pd_5As_{1.49}Sb_{0.51}$ are similar to each other, whereas those of $Pd_5As_{0.6}Sb_{1.4}$ are different, especially in d-values less than 1.4Å. The strong lines with similar d-values for all five intermediate phases can be indexed with the same indices using the common sub-cell (a', c'), except for a few lines in the $Pd_5As_{0.6}Sb_{1.4}$ pattern due to the different symmetry.

The products heated at 710°C, after grinding, were subsequently annealed at 325°C. These annealed and quenched products gave different x-ray powder patterns to those of the corresponding 710°C products, indicating some changes had taken place and that this system is even more complex at lower temperatures.

DISCUSSION

Minerals reported in the literature, as well as those found in this study, which belong to the Pd-As-Sb system, have been plotted in Figure 7 together with some synthetic compositions. Minor quantities of Pt, Au, Ag, Cu, Hg, Rh and/or Pb, when present, have been calculated as Pd and minor quantities of Te, Sn, and/or Bi have been calculated as Sb. Inspection of Figure 7 reveals a considerable number of minerals, not all of which have clearly identifiable synthetic equivalents. A statement of our understanding, at present, of each of these minerals and synthetic phases is pertinent.

Pd₅As and (Pd,Sb) s.s.

These phases are not known as mineral species.

$(Pd_3Pb_{0.4})As$

An incompletely characterized mineral reported by Genkin (1968) which may be related to Pd_3As, or to vincentite of Stumpfl & Tarkian (1974), or to some of the $(Pd,Pb)_3(As,Te,Bi)$ minerals reported by Kovalenker et al. (1972).

Pd_3As

A phase well-known in the synthetic Pd-As system for which tetragonal symmetry has been reported (Saini et al. 1964a), but for which no mineralogical equivalent has yet been clearly identified. Yu et al. (1974), however, have described Pd_3As and $Pd_3(As,Sb)$ from mafic-ultramafic rocks in China. They proposed the name guanglinite for Pd_3As and reported the mineral to have orthorhombic symmetry though their powder data are closely related to synthetic tetragonal Pd_3As.

Stillwaterite

Ideal end-member Pd_8As_3 and equivalent to synthetic Pd_8As_3 which may contain minor quantities of Sb, Te, Sn, Bi to the extent shown in Figure 7. The individual stillwaterite analyses are plotted on a more expanded scale in Figure 8. The small deviations from the 8:3 stoichiometry (cf. also Table 2) are considered to be largely analytical.
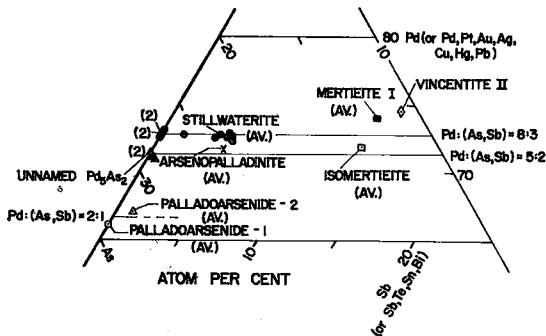
FIG. 8. A more detailed area of the Pd-As-Sb composition diagram (Fig. 7) showing individual stillwaterite analyses (black circles) with respect to the line defining 8:3 stoichiometry. The straight line from the word STILLWATERITE locates the average value for the 13 analyses and (2) refers to two grains with identical analyses. Also shown are the locations of the analyses (black triangles) of the unnamed Pd_5As_2 and of palladoarsenide-2 (open triangle), both of this study. The other minerals plotted are from analyses reported in the literature as detailed in the legend for Fig. 7.

Unnamed Pd_5As_2

The unnamed Pd_5As_2 phase may be considered a new mineral. It is felt, however, that this mineral should not be named until type arsenopalladinite has been re-examined. The fact that syntheses of Pd_5As_2 did not produce single crystals, but a phase whose x-ray diffraction pattern may be indexed as hexagonal (in contrast to the orthorhombic symmetry of the mineral), is not unique because several minerals have yet to be synthesized or have polymorphs which have not been synthesized.

Palladoarsenide

Palladoarsenide is equivalent to the low-temperature polymorph of synthetic Pd_2As as originally defined by Begizov et al. (1974). The very slight deviations from the 2:1 stoichiometry in the original analyses, as well as in ours, may be due to analytical errors.

Arsenopalladinite

Arsenopalladinite was redefined by Clark et al. (1974) as $Pd_5(As,Sb)_2$ and triclinic with $a = 7.399$, $b = 14.063$, $c = 7.352$Å, $\alpha = 92°03'$, $\beta = 118°57'$, $\gamma = 95°54'$. Thirteen grains were analyzed with the results reported as the mean values and range. Though the mean value is very close to the 5:2 stoichiometry (Fig. 8), it is not possible to ascertain the exact range for the individual analyses from the published data. If one takes the maximum Pd with the minimum Cu, As, and Sb values reported, the resulting hypothetical analysis is more Pd-rich than stillwaterite, suggesting either an overlap with the 8:3 stoichiometry or the possibility that some analyses represent hard-to-detect two-phase intergrowths. The lack of a published powder pattern because of the poor x-ray diffraction characteristics of the mineral also makes further comparison to stillwaterite impossible at this time. This comparison may be possible on completion of a re-examination of arsenopalladinite (A. M. Clark, personal comm., 1975).

Isomertieite

The new mineral isomertieite was described by Clark et al. (1974) as $(Pd,Cu)_5(Sb,As)_2$ with As $\simeq$ Sb, cubic, space group $Fd3m$, $a = 12.283(1)$Å. However, the mineral was weakly anisotropic in reflected light, only one grain being isotropic. The synthetic compound whose composition is close to that of isomertieite in Figure 7 is strongly anisotropic under reflected

light. The average composition of isomertieite from published data is plotted in Figure 8; the composition appears to lie between a 5:2 and an 8:3 stoichiometry.

Mertieite

The new mineral mertieite was described by Desborough *et al.* (1973) as occurring in two compositional groups (Group I and Group II), with a best approximation for the mertieite formula being $(Pd,Cu)_{5+x}(Sb,As)_{2-x}$, where $x = 0.1-0.2$. They suggested that mertieite is pseudo-hexagonal, possibly monoclinic, with pseudo-hexagonal $a = 15.04$, $c = 22.41$Å. The average analyses reported for mertieite I and mertieite II are plotted in Figure 7, whereas the very small differences obtained by our re-analysis of mertieite II (*cf.* Table 8) suggest an 8:3 stoichiometry. The completion of a crystal-structure analysis of mertieite II, currently underway in our laboratories, should provide additional information on the mineral.

Razin & Dubakina (1974) reported an analysis of mertieite from Ingali (In-39) to which they assigned an ideal formula $(Pd,Cu)_{3+x}$ (Sb,As), and two analyses of mertieite from Noril'sk (N-735 and N-681), for which the ideal formula $(Pd,Ag)_{5-x}(Sb,As)_2$ was proposed. These analyses are shown on Figure 7 and they do, indeed, lie in two groups. The Ingali mineral is nearer mertieite I whereas the two Noril'sk minerals appear to have stoichiometries closer to 5:2 than the 8:3 of mertieite II. If the Noril'sk minerals have, indeed, a 5:2 stoichiometry, their relationship to stibiopalladinite, rather than to mertieite II, should be carefully evaluated. Razin & Dubakina (1974) pointed out the similarity of x-ray powder diffraction patterns of their mertieite samples to those of Desborough *et al.* (1973) and to stibiopalladinite. It is most important, therefore, that a re-examination be made by single-crystal methods.

Vincentite

Vincentite was described as a new mineral by Stumpfl & Tarkian (1974) with a proposed general formula of $(Pd,Pt)_3(As,Sb,Te)$ and the
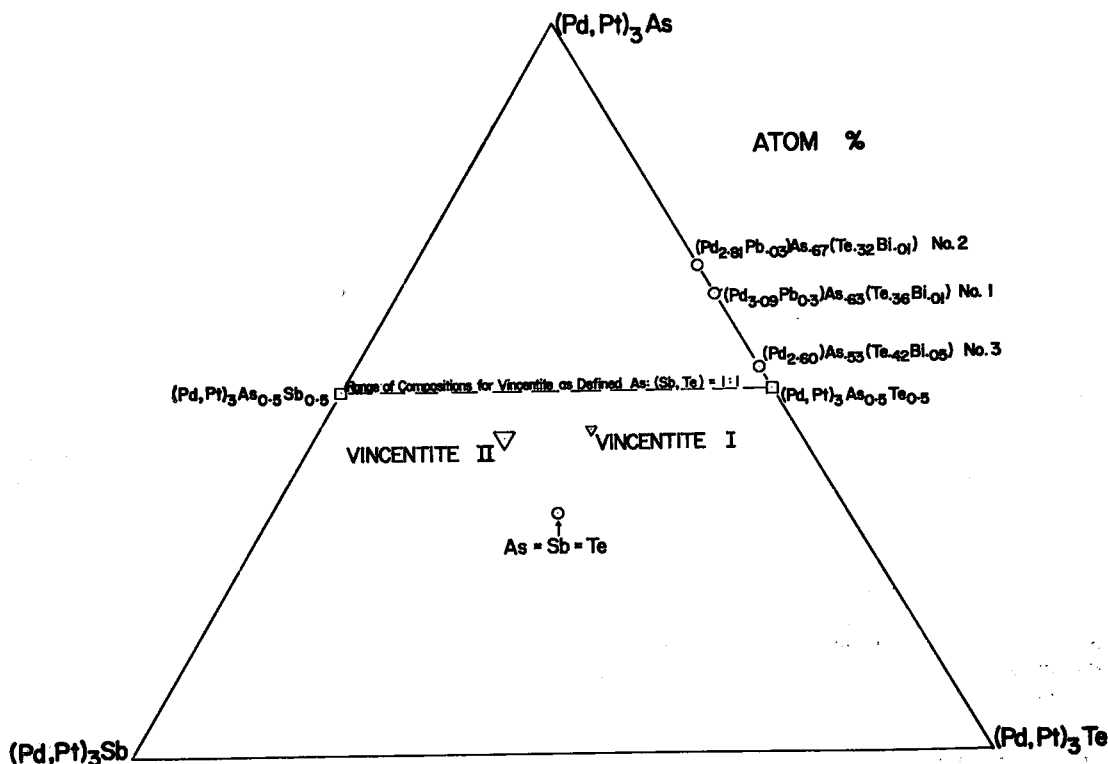

FIG. 9. Some minerals reported in the $(Pd,Pt)_3Sb$—$(Pd,Pt)_3Te$—$(Pd,Pt)_3As$ composition diagram. Analyses No. 1, 2 & 3 refer to the $(Pd,Pb)_3(As,Te,Bi)$ mineral reported by Kovalenker *et al.* (1972). Vincentite I and II represent the two analyses reported by Stumpfl & Tarkian (1974). On this diagram $(Pd,Pb)_3As$ of Genkin (1968) would lie on the apex of the triangle.

specific compositional requirements that Pd > Pt *and* that As:(Sb+Te) $\simeq$ 1:1. This proposed compositional range requires that the name vincentite be applied to minerals with compositions between (and including) the end-members $(Pd,Pt)_3As_{0.5}Sb_{0.5}$ to $(Pd,Pt)_3As_{0.5}Te_{0.5}$ as shown in Figure 9. The proposed compositional range for vincentite is rather unusual as it represents a presumed solid-solution series, each end-member of which lies at the mid-point of systems whose own phase relations are unknown. One of the two published vincentite analyses (referred to here as vincentite II) may also be plotted on a Pd-As-Sb diagram by substituting Te for Sb (Figure 7) where it lies between mertieite II and mertieite (In-39). Fleischer (1974) has noted that vincentite needs further study, especially single-crystal work and synthesis.

Stibiopalladinite

Stibiopalladinite was formerly thought to be Pd_3Sb, but recent analyses (Desborough *et al.* 1973 and Clark *et al.* 1974) on material from the Potgietersrust district of South Africa suggest a stoichiometry closer to Pd_5Sb_2. The average values obtained from seven and six grains by these authors, respectively, are plotted in Figure 7. Neither analysis is precisely Pd_5Sb_2, and both lie between Pd_5Sb_2 and Pd_8Sb_3. El-Boragy *et al.* (1970) reported another phase, $Pd_{5+}Sb_{2-}$, structurally related to Pd_5Sb_2, but still considered a unique phase in the Pd-Sb system. El-Boragy & Schubert (1971) detailed the boundaries of the solid-solution field of this phase between 500 and 800°C. Tarkian & Stumpfl (1975) reported a stibiopalladinite analysis from the Driekop mine which is more As-rich and plots slightly under the Pd_5Sb_2-Pd_5As_2 line in Figure 7. We have recalculated their analysis (from their Table 8) as $(Pd_{4.68}Cu_{.16}Pt_{.06})_{\Sigma=4.90}Sb_{1.82}As_{.18}$. It is therefore essential that type stibiopalladinite be re-examined in great detail, preferably by re-analysis with good synthetic standards whose compositions are close to that of the mineral, as well as by a detailed *x*-ray analysis, especially by single-crystal methods. The latter is most important because, as discussed by Razin & Dubakina (1974), stibiopalladinite is also structurally related to "mertieite" and to a mineral described as $Pd_{5+x}(Sn,As,Sb)_3$.

Unnamed Pd_8Sb_3

The close similarity of the powder patterns and unit cells of mertieite II, synthetic Pd_8Sb_3, and unnamed Pd_8Sb_3 (Table 7) strongly suggest that all these have the same structure. Some differences in intensities for certain reflections among the three patterns may be due either to the effects of As substitution for Sb, or to systematic intensity errors because of incomplete powder diffraction by the Gandolfi camera. Should further work confirm the suggested structural similarity, re-definition of mertieite II will be necessary together with Pd_8Sb_3 as ideal end-member. It would also be helpful if mertieite I were re-examined in the light of these new findings.

Unknown (Pd,Cu,As) mineral

This mineral is too poorly characterized to warrant showing its location in the Pd-As-Sb composition diagram.

REFERENCES

BEGIZOV, V. D., MESHCHANKINA, V. I. & DUBAKINA, L. S. (1974): Palladoarsenide, Pd_2As, a new natural palladium arsenide from the copper-nickel ores of the Oktyabr deposits. *Zapiski Vses Mineralog. Obshch.* 103, 104-107.

BOYD, F. R., FINGER, L. W. & CHAYES, F. (1969): Computer reduction of electron probe data. *Carnegie Inst. Washington,* Year Book 67, 210-215.

CABRI, L. J., HARRIS, D. C. & GAIT, R. I. (1973): Michenerite (PdBiTe) redefined and froodite (PdBi₂) confirmed from the Sudbury area. *Can. Mineral.* 11, 903-912.

———— & LAFLAMME, J. H. G. (1974a): Sudburyite, a new palladium-antimony mineral from Sudbury, Ontario. *Can. Mineral.* 12, 275-279.

———— (1974b): Rhodium, platinum, and gold alloys from the Stillwater Complex. *Can. Mineral.* 12, 399-403.

———— (1974c): Mineralogical investigations of the platinum-group elements in the Sudbury-area deposits — a preliminary report. *Can. Mineral.* 12, 429.

CLARK, A. M., CRIDDLE, A. J. & FEJER, E. E. (1974): Palladium arsenide-antimonides from Itabira, Minas Gerais, Brazil. *Mineral. Mag.* 39, 528-543.

DESBOROUGH, G. A., FINNEY, J. J. & LEONARD, B. F. (1973): Mertieite, a new palladium mineral from Goodnews Bay, Alaska. *Amer. Mineral.* 58, 1-10.

EL-BORAGY, M., BHAN, S. & SCHUBERT, K. (1970): Crystal structure of Pd_5Sb_2, Ni_5As_2 and some variants. *J. Less-Common Metals* 22, 445-458 (in German).

———— & SCHUBERT, K. (1971): On some variants of the NiAs family in mixtures of palladium with B-elements. *Z. Metallkde.* 62, 314-323 (in German).

FLEISCHER, M. (1974): New mineral names. *Amer. Mineral.* 59, 1330-1332.

FURUSETH, S., SELTE, K. & KJEKSHUS, A. (1967): On the solid solubility and structural properties of $PdAs_{2-x}Sb_x$, $PtP_{2-x}As_x$, $PtP_{2-x}Sb_x$, $PtP_{2-x}Bi_x$, $PtAs_{2-x}Sb_x$, $PtAs_{2-x}Bi_x$, $PtSb_{2-x}Bi_x$, $Pd_{1-m}Pt_mAs_2$, $Pd_{1-m}Pt_mSb_2$, $Pd_{1-m}Au_mSb_2$ and $Pt_{1-m}Au_mSb_2$. *Acta Chem. Scand.* 21, 527-536.

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. Mestorozh., Petrogr. Mineral. Geokhim.*, 106 pp. (in Russian).

HANSEN, M. & ANDERKO, K. P. (1958): *Constitution of Binary Alloys.* McGraw Hill, New York. 1305 pp.

KOVALENKER, V. A., LAPUTINA, I. P., VYAL'SOV, L. N,. GENKIN, A. D. & EVSTIGNEEVA, T. L. (1972): Tellurium minerals in copper-nickel sulphide ores at Talnakh and Oktyabr' (Noril'sk district). *Internat. Geol. Rev.* 15, 1284-1294.

PRATT, J. N., MYLES, K. M., DARBY, J. B. &

MUELLER, M. H. (1968): X-ray studies of palladium-cadmium and palladium-antimony alloy. *J. Less-Common Metals* 14, 427-433.

RAUB, C. J. & WEBB, G. W. (1963): An investigation of the phase-diagram palladium-arsenic in connection with superconductivity. *J. Less-Common Metals* 5, 271-277.

RAZIN, L. V. & DUBAKINA, L. S. (1974): The first finds of palladium arsenoantimonides and arseno-stannides in platinum ore deposits of the Soviet Union. *Zapiski Vses Mineralog. Obshch.* 103, 582-594 (in Russian).

RUCKLIDGE, J. C. & GASPARRINI, E. L. (1969): Electron microprobe analytical data reduction. EMPADR VII. *Dept. Geol. Univ. Toronto.*

SAINI, G. S., CALVERT, L. D., HEYDING, R. D. & TAYLOR, J. B. (1964a): Arsenides of transition metals. *Can. J. Chem.* 42, 620-629.

———— ———— & TAYLOR, J. B. (1964b): Compounds of the type M_5X_2: Pd_5As_2, Ni_5Si_2, and Ni_5P_2. *Can. J. Chem.* 42, 1511-1517.

SCHUBERT, K., ANDERKO, K., KLUGE, M., BEESKOW, H., ILSCHNER, DÖRRE, E. & ESSLINGER, P. (1953): Structure of the alloy phases Cu_2Te, $CuTe$, Cu_3Sb, $InTe$, Bi_2Se_3, Pd_5Sb_3, and Pd_5Bi_3. *Naturwiss.* 40, 269.

STUMPFL, E. F. & TARKIAN, M. (1974): Vincentite, a new palladium mineral from south-east Borneo. *Mineral. Mag.* 39, 525-527.

TARKIAN, M. & STUMPFL, E. F. (1975): Platinum mineralogy at the Driekop mine, South Africa. *Mineralium Deposita* 10, 71-75.

YU TSU-HSIANG, LIN CHU-JEN, CHAO PAO, FANG CHING-SUNG & HUANG CHI-SHUN (1974): A preliminary study of some new minerals of the platinum-group and another associated new one in platinum-bearing intrusions in a region in China. *Acta Geol. Sinica* 2, 202-218 (in Chinese, English abstract).