# PHASES AND PHASE RELATIONS IN THE SYSTEM Pd-Pt-Sn

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### ABSTRACT

Phase relations and phase compositions have been determined in the system Pd-Pt-Sn at 1000°C. There are no compounds that are exclusively ternary; all ternary phases are solid solutions that appear on one of the binary joins. The four ternary solid solutions observed at 1000°C in this study are (Pd,Pt,Sn) alloy and (Pd,Pt)<sub>3</sub>Sn (atokite-rustenburgite), both of which extend completely from pure Pd to pure Pt compounds, plus (Pt,Pd)Sn (niggliite) and a-(Pd,Pt)<sub>3</sub>Sn<sub>2</sub> (stannopalladinite), both of which have limited composition ranges. The a cell dimension of the cubic solid solution (Pd,Pt)<sub>a</sub> Sn varies between 3.967(2) and 4.018(2) Å for pure Pd and Pt end-members, respectively. For the hexagonal\_(Pt,Pd)Sn solid solution, a 4.014(2), c 5.436 (2) Å are observed over the composition range Pt1.04Sn to Pt0.84Pd0.20Sn. The cell dimensions for hexagonal  $c_{-}$  (Pd,Pt)<sub>3</sub>Sn<sub>2</sub> range from a 4.382 (4), c 5.658(4) Å to a 4.468(4), c 5.726(4) Å over the composition range Pd<sub>3.37</sub>Sn<sub>2</sub> to (Pd<sub>0.43</sub>Pt<sub>3.12</sub>)Sn<sub>2</sub>. Unitcell dimensions have been determined from X-ray powder patterns.

### SOMMAIRE

On a déterminé les relations entre les phases et la composition des phases dans le système Pd-Pt-Sn à 1000°C. Aucune des phases n'est exclusivement ternaire; chacune est liée à une solution solide binaire. Les quatre composés ternaires observés à 1000°C sont: (1) l'alliage (Pd,Pt,Sn) et (2) (Pd, Pt)<sub>3</sub>Sn (atokite-rustenbergite), qui forment des solutions solides complètes de Pd à Pt; (3) (Pt,Pd)Sn (niggliite) et (4)  $\alpha$ -(Pd,Pt)<sub>3</sub>Sn<sub>2</sub> (stannopalladinite), à solution solide limitée. Le paramètre réticulaire cubique a de la solution solide  $(Pd,Pt)_3Sn$  varie de 3.967(2) (terme Pd) à 4.018(2) Å (terme Pt). Dans la solution solide hexagonale (Pt,Pd)Sn, on observe a 4.104(2), c 5.436(2) Å pour les compositions entre Pt1.04Sn et Pt0.84Pd0.20Sn. La maille hexagonale de la phase  $\alpha$ -(Pd,Pt)<sub>3</sub>Sn<sub>2</sub> varie de *a* 4.382(4), *c* 5.658 (4) Å à *a* 4.468(4), *c* 5.726(4) Å entre les compositions Pd<sub>3.37</sub>Sn<sub>2</sub> et (Pd<sub>0.43</sub>Pt<sub>3.12</sub>)Sn<sub>2</sub>. Les dimensions de maille ont été déterminées aux rayons X par la méthode des poudres.

(Traduit par la Rédaction)

Mots-clés: palladium, platine, étain, relations entre les phases, atokite, rustenburgite, niggliite, stannopalladinite.

### INTRODUCTION

The list of minerals containing one or more of the platinum-group elements (PGE) has grown rapidly in recent years (Cabri 1972, 1976, 1981); so too have the reported assemblages of coexisting PGE minerals. Information concerning the genesis of PGE minerals and possibly of the associated rocks can, under certain conditions, be deciphered from the mineral assemblages. One essential piece of information in the deciphering process concerns the compositions and stable assemblages of coexisting phases under various conditions. This paper provides additional data for compounds and asse nblages in the system Pd-Pt-Sn, a system that bears upon the stabilities of five interesting PGE minerals.

Previous studies in the ternary system Pd–Pt– Sn have been restricted to 400°C and below, though each of the binary systems has been investigated over wide ranges of temperature. Minerals with compositions that fall in the system Pd–Pt–Sn are generally found in mafic and ultramafic igneous rocks or mineral deposits associated with such rocks. There is a possibility that the Pd–Pt–Sn minerals formed at magmatic temperatures or by reactions at near-magmatic temperatures. We therefore chose to extend the previous low-temperature studies by making our investigations of the system Pd–Pt–Sn at 1000°C.

### EXPERIMENTAL PROCEDURE

Experiments were carried out by weighing approximately 200 mg of spectographically pure palladium, platinum and tin in predetermined ratios into silica glass capsules. The loaded capsules were evacuated, sealed and heated to  $1250^{\circ}$ C to ensure homogenization of the charges through melting. The temperature was then reduced to  $1000^{\circ}$ C, and the charges were held for periods of 3 to 14 days. Tin-poor com-

Keywords: palladium, platinum, tin, phase relations, atokite, rustenburgite, niggliite, stannopalladinite.

Low-Temperature Assemblage	High-Temperature Assemblage	Reaction Temperature ( <sup>O</sup> C)	Remarks
(Pd,Sn) Alloy	melt	1552	17 mol % Sn at 1000°C. Cubic. Fm3m, $\alpha = 3.8898$ Å
Pd <sub>3+</sub> Sn			Not known, as a mineral. Tetragonal, Cu-Au-type, $a = 4.07$ , c = 3.73 Å
Pd <sub>3</sub> Sn	melt	1326	The mineral atokite. Cubic, $Cu_3Au$ -type, $Fm3m$ , $a = 3.967$ Å
Pd <sub>8</sub> Sn <sub>3</sub>			Not reported in the pure binary system. Ideal composition of palarstanide (Cabri & Laflamme 1981)
Pd <sub>2</sub> Sn	$Pd_3Sn + \alpha - Pd_3Sn_2$	820	The mineral paolovite. Orthorhombic, Ni <sub>2</sub> Si-type, a = 8.12, b = 5.65, c = 4.31 Å
∝-Pd3Sn2	melt	1287	The mineral stangpalladinite. Hexagonal, P6 $_3$ /mmc, a = 4.382, c = 5.658 Å
$\beta$ -Pd <sub>3</sub> Sn <sub>2</sub> + Pd <sub>2</sub> Sn	α-Pd Sn	475	
β-Pd₃Sn₂	α-Pd <sub>3</sub> Sn <sub>2</sub> + melt	900.	$\beta$ -Pd <sub>3</sub> Sn <sub>2</sub> is a superstructure of $\alpha$ -Pd <sub>3</sub> Sn <sub>2</sub> , $a_{\beta} = 2a_{\alpha}$ , $c_{\beta} = 3c_{\alpha}$
PdSn	β-Pd <sub>3</sub> Sn <sub>2</sub> + melt	810	PdSn is not known as a mineral. Orthorhombic, MnP-type, $\alpha$ = 6.12, $b$ = 6.31, $c$ = 3.86 Å
PdSn <sub>2</sub>	PdSn + melt	600	PdSn <sub>2</sub> is not known as a mineral. Quenched from melt it is monoclinic, distorted NiAs-type, $a = 6.18$ , $b = 3.93$ , $c = 6.38$ , $\beta = 88.5^{\circ}$ ; slowly cooled it is tetragonal, CuAl <sub>2</sub> -type, $a = 6.490$ , $c = 24.378$ Å
PdSn <sub>3</sub>	PdSn <sub>2</sub> + melt	345	PdSn <sub>3</sub> is not known as a mineral. Orthorhombic, Pcma or subgroup, $a$ = 6.47, $b$ = 6.50, $c$ = 17.2 Å
PdSn 4	PdSn <sub>3</sub> + melt	295	PdSn <sub>4</sub> is not known as a mineral. Orthorhombic, PtSn <sub>4</sub> -type, $a = 6.40$ , $b = 6.43$ , $c = 11.44$ Å

TABLE 1. PHASES AND MAJOR PHASE TRANSITIONS IN THE SYSTEM Pd-Sn AFTER ELLIOTT (1965) AND BERLINCOURT ET AL. (1981)

positions were held for longer reaction times. Reactions were rapid, and experiments were run longer than necessary to reduce the possibility that tiny metastable grains might be preserved by armoring. Charges were quenched in cold water, and the assemblages determined by examining the products using reflected light microscopy. Phase compositions were obtained by electron-microprobe analysis using pure elements as standards. Unit-cell dimensions were determined by X-ray powder diffraction with films using Ni-filtered Cu  $K\alpha$  radiation.

### The system Pd-Sn

Phase relations for the system Pd–Sn are summarized in Hansen & Anderko (1958), Elliott (1965) and Berlincourt *et al.* (1981). Eleven binary compounds are reported either as minerals, as phases in the synthetic system, or both; they are the alloy (Pd,Sn), Pd<sub>3</sub>+Sn, Pd<sub>3</sub>Sn, Pd<sub>8</sub>Sn<sub>3</sub>, Pd<sub>2</sub>Sn,  $\alpha$ - and  $\beta$ -Pd<sub>3</sub>Sn<sub>2</sub>, PdSn, PdSn<sub>2</sub>, PdSn<sub>3</sub> and PdSn<sub>4</sub>. Data concerning the structures and reactions temperatures of all the Pd–Sn compounds are presented in Table 1.

TABLE	2.	X-RAY	POWDER	DATA	FOR	SYNTHETIC	RUSTENBURGITES	(Pt <sub>3</sub> Sn)	and	ATOKITES	(Pd <sub>3</sub> Sn)*
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		S-4		 S-7		5-46		S-23			
hkl	a = I	4.018 A d meas.	a = I	4.008 A d meas.	a = I	3.993 Å d meas.	a = I	3.976 A d meas.	a = I	3.967 A d meas.	
111	10	2.279	10	2.272	10	2.256	10	2,228	10	2.210	
200	7	1.984	8	1.968	7	1.956	7	1.940	7	1.921	
220	8	1.401	7	1.399	7	1.392	7	1.382	8	1.365	
311	9	1.198	8	1.196	8	1.192	8	1.183	9	1.169	
222	4	1.148	4	1.146	4	1.142	5	1.134	4	1.124	
400	1	.998	2	. 996	1	.993	2	.987	1	.979	
311	7	.917	6	.916	8	.913	7	.907	7	.904	
420	7	.895	7	.893	8	.890	7	.885	7	.882	
422	6	.819	7	.817	9	.814	8	.811	6	.808	

\*Ni-filtered CuK, radiation ( $\lambda$  = 1.5405 Å), 57.3 mm camera, visual intensities. Calculated cell edges are corrected for absorption. Run compositions are listed in Table 4.

Low-Temperature Assemblage	High-Temperature Assemblage	Reaction Temperature ( <sup>O</sup> C)	Remarks			
(Pt,Sn) Alloy	melt	1773	12 mol % Sg at 1370°C, 8% at 1000°C. Cubic, Fm3m, $a = 3.923$ Å			
Pt <sub>3</sub> Sn	melt	∿1406	The mineral rustenburgite. Cubic, Cu <sub>3</sub> Au-type, Fm3m, $a$ = 4.018 Å			
PtSn	melt	∿1305	The mineral niggliite. Hexagonal, P6 $_3$ /mmc, NiAs-type, a = 4.104, c = 5.436 A			
Pt <sub>2</sub> Sn <sub>3</sub>	PtSn + melt	848	Pt <sub>2</sub> Sn <sub>3</sub> is not known as a minera]. Hexagonal, P6 /mmc, $\alpha$ = 4.334, $c$ = 12.960 Å			
PtSn <sub>2</sub>	$Pt_2Sn_3 + melt$	745	PtSn <sub>2</sub> is not known as a mineral. Cubic, CaF <sub>2</sub> -type $\alpha$ = 6.425 A			
PtSn 4	PtSn <sub>2</sub> + melt	∿522	PtSn <sub>4</sub> is not known as a minergl. Orthorhombic, $a = 6.338$ , $b = 6.419$ , $c = 11.357$ A			

TABLE 3. PHASES AND MAJOR PHASE TRANSITIONS IN THE SYSTEM Pt-Sn (AFTER HANSEN & ANDERKO 1958 AND BERLINCOURT ET AL. 1981)

Five of the phases,  $Pd_{3+}Sn$ , PdSn,  $PdSn_2$ ,  $PdSn_3$ and  $PdSn_4$ , are not known as minerals and were not observed in the present study.

The remaining phases either are observed as minerals or are polymorphs of minerals. However, three of the phases, Pd<sub>2</sub>Sn, Pd<sub>8</sub>Sn<sub>3</sub> and  $\beta$ -Pd<sub>3</sub>Sn<sub>2</sub>, are not stable at 1000°C and so were not studied in the present investigation. Pd2Sn corresponds to the mineral paolovite (Table 1). Its optical properties are reported to be similar to those of  $\alpha$ -Pd<sub>3</sub>Sn<sub>2</sub>. Pd<sub>8</sub>Sn<sub>3</sub> is postulated by Cabri (1981) to represent the ideal composition of the mineral palarstanide (V. D. Begizov, pers. written comm. to L. J. Cabri, 1979). The composition of palarstanide reported by Cabri & Laflamme (1981) is (Pd7.46 Pt0.29 Au0.12 Cu0.09) x=7.96 (Sn1.41 As1.10 Sb0.41 Pb0.12)  $\Sigma = 3.04$ . Pd<sub>8</sub>Sn<sub>3</sub> has not been observed in the pure Pd-Sn system, and may in fact require other elements such as As to exist. Palarstanide is hexagonal with a 6.784, c 14.80 Å (Cabri 1981). The phase  $\beta$ -Pd<sub>3</sub>Sn<sub>2</sub> is the lowtemperature polymorph of Pd<sub>3</sub>Sn<sub>2</sub> and hence of the mineral stannopalladinite;  $\beta$ -Pd<sub>3</sub>Sn<sub>2</sub> is hexagonal  $P6_3/mmc$ , and it has a superstructure derived from  $\alpha$ -Pd<sub>3</sub>Sn<sub>2</sub> ( $a_{\beta} = 2a_{\alpha}, c_{\beta} = 3c_{\alpha}$ : Nowotny et al. 1946). The optical properties of  $\alpha$ - and  $\beta$ -Pd<sub>3</sub>Sn<sub>2</sub> are reported to be essentially identical (Malevskiy et al. 1978).

 $\alpha$ -Pd<sub>3</sub>Sn<sub>2</sub> corresponds to the mineral stannopalladinite. It is hexagonal, space group P6<sub>3</sub>/ mmc, with a 4.382, c 5.658 Å. The composition ranges from Pd<sub>3.39</sub>Sn<sub>2</sub> to Pd<sub>3.37</sub>Sn<sub>2</sub> at 1000°C, a somewhat larger composition range than is reported for  $\beta$ -Pd<sub>3</sub>Sn<sub>2</sub>. The phase is bireflectant from light pink to pinkish brown and anisotropic from lilac-red to grey blue.

The alloy (Pd,Sn) corresponds to the mineral palladium. It is cubic, space group Fm3m, with a cell edge of 3.8898 Å for pure palladium and 3.955 Å for a Sn-saturated alloy (Malevskiy *et al.* 1978). The compositional limit of the alloy at 1000°C is 17 mol. % Sn. The phase has a high reflectance on the polished surface, is isotropic and white to light cream in color.

Pd<sub>3</sub>Sn corresponds to the mineral atokite



FIG. 1. Phase relations in the system Pd-Pt-Sn at 400°C, after Berlincourt *et al.* (1981). Stippled regions are one-phase compositional fields. The shaded area was not investigated.

(Table 2). No evidence of a primitive cubic cell, as mentioned by Malevskiy *et al.* (1978) and Berlincourt *et al.* (1981), was detected in the X-ray-diffraction patterns. The composition of the phase ranges from  $Pd_{3.28}Sn$  to  $Pd_{2.85}Sn$  at 1000°C. On the polished surface, the phase has a high reflectance, is isotropic and light cream to cream in color.

### The system Pt-Sn

Phase relations for the system Pt-Sn were summarized by Hansen & Anderko (1958) and, more recently, by Berlincourt *et al.* (1981). Six binary compounds are reported, a (Pt,Sn) alloy, Pt<sub>3</sub>Sn, PtSn, Pt<sub>2</sub>Sn<sub>3</sub>, PtSn<sub>2</sub> and PtSn<sub>4</sub>, but only the first three correspond to minerals and

Bi	ulk Com	positio	n (At.	%)	
Sample	Pt	Pd	Sn	Phases Present	Composition (mol. %)
S-1	34 1	0.0	65.0	[ + no	
6.2	40.2	0.0	50.0	Ling	119 - 51.16 Ft, 40.56 51
5-2	40.2	0.0	59.0	ng + L	ng = 50.9% Pt, 49.1% Sn
5-3	49.7	0.0	50.3	ng	ng = 49.8% Pt, 50.2% Sn
S-4	74.6	0.0	25.4	(rs-at)	(rs-at) = 74.5% Pt. 25.5% Sn
S-5	70.6	20.2	9.2	A + (rs-at)	A = 72.2% Pt, 19.8% Pd, 8.0% Sn (rs-at) = 54.7% Pt, 23.3% Pd, 22.0% Sn
S-6	65.1	15.8	19.1	(rs-at) + A	(rs.at) = 60.7% Pt, 17.9% Pd, 21.4% Sn A = 90.7% Pt, 2.2% Pd, 7.1% Sn
S-7	60.2	14.9	24.9	(rs-at)	
S-8	56.3	11.7	32.0	st + (rs-at)	st = 52.7% Pt, 12.3% Pd, 35.0% Sn (rs-at) = 67.8% Pt, 6.5% Pd, 25.7% Sn
S-9	48.5	13.5	38.0	st	
S-10	40.4	9.5	50 1	ng + 1	ng = 42 2% Pt 8 8% Pd 40 0% Sp
5-11	31 0	7 7	60 4	1.4.00	$n_0 = A0.0\% \text{ D} + 3.0\% \text{ D} + A0.2\% \text{ Cm}$
S_12	29.2	6.0	64 0	L + 119	ny - 49.06 PL, 2.08 PU, 40.28 Sh
C 12	20.2	0.3	04.9	L	
2-12	25.2	5.7	69.1	Ļ	
S-14 a	13.8	12.7	73.5	L	
b	19.6	21.1	59.3	L	
S-15	22.4	22.7	54.9	1 + nq + st	
S-16	24.8	25.2	50.0	1 + s + n q	nn = 41.0%  D+ 10.1%  D- 49.0%  Sm
S-17	30.6	29.7	39.7	st + ng	st = 24.9% Pt, 38.4% Pd, 36.7% Sn
S-18	36.0	33.7	30.3	st + (rs-at)	ng = 42.0% Pt, 31.0% Pd, 48.0% Sn st = 34.8% Pt, 35.0% Pd, 30.2% Sn (rs-at) = 49.2% Pt. 27.0% Pd. 23.8% Sn
S-19	40.8	39.3	19.9	(rs-at) + A	·····
S-20	45.4	45.1	9.5	A A	
5-21	17 3	73 1	0.6	A	
C 22	17.6	64 2	10.0		
5-22	17.0	04.2	10.2	(rs-at) + A	(rs-at) = 17.0% Pt, 61.2% Pd, 21.8% Sn A = 17.1% Pt, 68.9% Pd, 14.0% Sn
5-23	14.8	60.9	24.3	(rs-at)	
5-24	13.5	56.8	29.7	st + (rs-at)	st = 10.4% Pt, 56.8% Pd, 32.8% Sn (rs-at) = 20.0% Pt, 56.0% Pd, 24.0% Sn
S-25	13.2	52.1	34.7	st	st = 13.1% Pt, 52.0% Pd, 34.9% Sn
S-26	12.5	44.4	43.1	L + st	st = 15.9% Pt. 46.1% Pd. 38.0% Sn
S-27	10.6	45.8	43.6	l. + st	
S-28	9.6	40.0	50.4	1	
5-29	8.8	36 8	54 4	1	
5-30	0.0	60 1	20.0		at CO. ON B.1. 07 00 0
5-30	0.0	00.1	39.9	St + L	st = 62.8% Pa, 37.2% Sn
3-31	0.0	00.8	33.2	St	st = 66.9% Pd, 33.1% Sn
5-32	0.0	74.9	25.1	(rs-at)	(rs-at) = 75.0% Pd, 25.0% Sn
S-33	0.0	55.8	44.2	L	
S-34	85.0	15.0	0.0	A	
S35	15.1	84.9	0.0	A	
S~36	49.8	50.2	0.0	A	
S-37	54.5	9.0	36.5	st + ng	st = 53.8% Pt, 9.8% Pd, 36.4% Sn
S-38	32.5	32.1	35.4	s†	ing control of Lion Ing TTION DI
5_30	45 0	0.0	45 2	30	
5-35	95.0	20.0	40.2	ng + st	
5-40	25.1	30.0	44.9	st + L + ng	st = 24.8% Pt, 38.4% Pd, 36.8% Sn ng = 42.0% Pt, 9.8% Pd, 48.2% Sn
5-41	49./	9.8	40.5	st + ng	
5-42	25.1	39.8	35.1	st	st = 24.9% Pt, 39.9% Pd, 35.2% Sn
S-43	52.9	24.1	23.0	st + (rs-at)	st = 41.0% Pt, 24.3% Pd, 34.7% Sn (rs-at) = 58.2% Pt, 17.0% Pd, 24.8% Sn
S-44	40.1	19.6	40.3	st + ng	•
S-45	66.5	0.0	33.5	(rs-at) + ng	(rs-at) = 73.5% Pt, 26.5% Sn ng = 55.5% Pt, 44.5% Sn
S-46	33.1	43.5	23.4	(rs-at)	
S-47	41.4	40.6	18.0	Á + (rs-at)	
S-48	57.8	5.5	36.7	(rs-at) + nq + st	
5-49	62.5	4 8	32 7	$(re_at) + na + et$	
- т <i>э</i>	JE.J	7.0	JL . /	יוש∽מנ/ דווא ד Σנ	

TABLE 4. RESULTS OF EXPERIMENTS PERFORMED IN THE SYSTEM Pt-Pd-Sn AT 1000°C \*

\*Compositions of phases, where reported, were determined by electron-microprobe analysis. Abbreviations: A = (Pd,Pt,Sn) alloy, L = Liquid, ng = niggliite, (rs-at) = rustenburgiteatokite solid solution, st = stannopalladinite. exist at 1000°C (Table 3). The phases  $Pt_2Sn_3$ ,  $PtSn_2$  and  $PtSn_4$  were not observed in our studies.

The alloy (Pt,Sn) corresponds to the mineral stanniferous platinum. At 1000°C, platinum coexisting with Pt<sub>8</sub>Sn contains 8 mol. % Sn in solid solution. The alloy is cubic, with the same space group as pure platinum, Fm3m. The alloy has a high reflectance on the polished surface, though not so high as that of pure platinum; it is white to light cream in color and isotropic.

Pt<sub>s</sub>Sn is the ideal composition for the mineral rustenburgite. The compound is cubic with a Cu<sub>3</sub>Au-type structure, space group Fm3m and a cell edge of 4.018 Å. X-ray powder-diffraction data (Table 2) do not reveal any evidence of a primitive unit-cell, a possibility mentioned by Berlincourt *et al.* (1981). The phase has a composition range about Pt<sub>s</sub>Sn from Pt<sub>3.55</sub>Sn to Pt<sub>2.85</sub>Sn at 1000°. It has a high reflectance, is isotropic and under reflected light is light cream in color.

PtSn is the ideal composition for the mineral niggliite (Table 3). The composition of the phase ranges from  $Pt_{1.94}Sn$  to  $Pt_{1.26}Sn$  at 1000°C. It is highly bireflectant on a polished surface, with colors ranging from light pink to pale cobalt blue, and strongly anisotropic from pink to dark cobalt blue (Cabri & Harris 1972).

## The system Pd-Pt

The only binary phase is the alloy (Pd,Pt) which has a continuous composition range from Pd to Pt. The phase is cubic, space group Fm3m.

# The system Pd-Pt-Sn

Published data for the system Pd-Pt-Sn are summarized by Berlincourt *et al.* (1981). Previous studies were restricted to the Sn-poor section of the ternary system and resulted in a  $400^{\circ}$ C isothermal section (Fig. 1; Malevskiy *et al.* 1978) and a room-temperature section (Mihálik *et al.* 1975).

The ternary phase relations determined for  $1000^{\circ}$ C are presented in Table 4 and Figure 2. There are no compounds that are exclusively ternary; all ternary phases are solid solutions that appear on one of the binary joins. The four ternary solid solutions observed at  $1000^{\circ}$ C are the alloy (Pd,Pt,Sn) and (Pd,Pt)<sub>3</sub>Sn, both of which extend completely from pure Pd to pure Pt compounds, plus (Pt,Pd)Sn and  $\alpha$ -



FIG. 2. Phase relations in the system Pd-Pt-Sn at 1000°C; x: bulk compositions investigated by electron-microprobe analysis.

 $(Pd,Pt)_{a}Sn_{a}$ , both of which have limited composition ranges.

The (Pd,Pt,Sn) alloys extend over a composition range of  $Pt_{0.92}Sn_{0.08}$  to  $Pd_{0.83}Sn_{0.17}$ . Our observations approximate the composition ranges reported by Mihálik *et al.* (1975) and Malevskiy *et al.* (1978), which suggests that the composition field for the alloy remains virtually unchanged from near room temperature to 1000°C.

The phase  $(Pd,Pt)_{s}Sn$  has a complete solid solution at 1000°C and also, according to Mihálik *et al.* (1975), at room temperature. At all temperatures of mineralogical interest, therefore, atokite and rustenburgite are completely miscible. Available unit-cell data for the phases in the solid-solution series that have a (Pd,Pt)/Sn ratio of 3 are listed in Table 5 and shown in Figure 3.

The (Pt,Pd)Sn solid solution (nigliite) extends to (Pt<sub>0.84</sub>Pd<sub>0.20</sub>)Sn at 1000°C, but the shape of the composition field is complex (Fig. 2). The substitution limit of Pd for Pt at 1000°C is less than it is at 400°C (Pt<sub>0.62</sub>Pd<sub>0.28</sub>Sn, reported by Malevskiy *et al.* 1978), suggesting that the large field of liquid centred on the Sn apex (Fig. 2) is restricting the composition field. Unit-cell dimensions for phases prepared in this study and for those described in previous publications are listed in Table 6.

 $\alpha$ -(Pd,Pt)<sub>3</sub>Sn<sub>2</sub> has a broad composition field, reaching a Pt-rich limit of (Pd<sub>0.48</sub>Pt<sub>8.12</sub>)Sn<sub>2</sub> at 1000°C. As temperature drops, the composition field shrinks towards the Pd–Sn binary join, reaching (Pd<sub>1.5</sub>,Pt<sub>1.5</sub>)Sn<sub>2</sub> at 400°C, re-

		Mol. %			8	
Sample	Pt	Pd	Sn	X Pt <sub>3</sub> Sn	a	Source
S-32	0.0	75.0	25.0	0.0	3.967	this study <sup>†</sup>
S-23	14.8	60.9	24.3	0.196	3.976	this study
S-46	33.1	43.5	23.4	0.432	3.993	this study
S-7	60.2	14.9	24.9	0.802	4.008	this study
S-4	74.5	0.0	25.5	1.0	4.018	this study
PdaSn	0.0	75.0	25.0	0.0	3.965	Malevskiy et al. (1978)
Pt <sub>2</sub> Sn	75.0	0.0	25.0	1.0	4,005	Malevskiv et al. (1978)
Pt <sub>2</sub> Sn	75.0	0.0	25.0	1.0	4.01	Kosovinc et al. (1969)
rustenburgite	39.8	38.6	21.6	0.508	3.991	Mihalik et al. (1975)
atokite	30.2	48.6	21.2	0.383	3,991	Mihâlik et al. (1975)
rustenburgite						
Pd <sub>1.13</sub> Pt <sub>1.81</sub> Cu. atokite	12N1.09Fe.	<sub>01</sub> Bi <sub>.07</sub> Sn		0.616	3.995	Malevskiy et al. (1978)
Pd2.29Pt.72Cu.1	1Ni.04Au.0	<sub>4</sub> Rh <sub>.02</sub> Sb.	<sub>02</sub> Pb <sub>.09</sub> Sn	0.239	3.987	Malevskiy et al. (1978)

TABLE 5. UNIT-CELL DIMENSIONS OF SYNTHETIC AND NATURAL RUSTENBURGITES AND ATOKITES

 $^{\dagger}$  The average standard error associated with the cell edges measured in this study is  $_{\pm}$  0.002 Å.



FIG. 3. Change in unit-cell dimensions of  $Pd_3Sn-Pt_3$ Sn as a function of platinum concentration. The triangles represent data from natural atokite and rustenburgite (see Table 5 for data).

flecting the appearance of Pd<sub>2</sub>Sn at 820°C in the system Pd–Sn. The influence of composition on unit-cell edges of phases in the composition field of  $\alpha$ -(Pd,Pt)<sub>8</sub>Sn<sub>2</sub> is described in Table 7. Cell-dimension data are plotted in Figure 4.

The minerals most likely to provide useful data concerning the genesis of PGE minerals are those that show the largest changes in composition: niggliite, stannopalladinite and paolovite. In particular, the assemblage niggliite + stannopalladinite + rustenburgite is very interesting because the compositions of three extensive, temperature-sensitive solid solutions are involved.

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TABLE 6. UNIT-CELL DIMENSIONS FOR SYNTHETIC AND NATURAL NIGGLIITES

		Mo1. %				
Sample	Pt	Pd	Sn	a	c	Source
S-3	49.8	0.0	50.2	4.104	5.436	this study <sup>†</sup>
S-10	42.2	8.8	49.0	4.104	5.436	this study
PtSn	50.0	0.0	50.0	4.111	5.439	Hansen & Anderko (1958)
PtSn	50.0	0.0	50.0	4.100	5.432	Cabri & Harris (1972)
PtSn	50.0	0.0	50.0	4.101	5.440	Harris et al. (1968)
nigaliite	Pt <sub>1 o</sub> B	i nasSb	Sn es	4.106	5.438	Cabri & Harris (1972)
niggliite	Pt <sub>1.0</sub> B	1_0 45Sb	17Sn 79	4.106	5.438	Cabri & Harris (1972)

 $^\dagger$  The average standard error associated with the cell edges measured in this study is  $\pm$  0.002 Å.

TABLE 7. UNIT-CELL DIMENSIONS FOR SYNTHETIC STANNOPALLADINITES

		Mol.%			-		
Sample	Pt	Pđ	Sn	Pt Pt + Pd	a	c	Source
S-30 S-25 S-38 S-9 Pd <sub>3</sub> Sn <sub>2</sub> Pd <sub>3</sub> Sn <sub>2</sub> Pd <sub>3</sub> Sn <sub>2</sub>	0.0 13.1 32.5 48.5 0.0 0.0 0.0	62.8 52.0 32.1 13.5 64.0 58.5 60.0	37.0 34.9 35.4 38.0 36.0 41.5 40.0	0.0 0.201 0.503 0.782 0.0 0.0 0.0	4.382 4.408 4.435 4.468 4.399 4.388 4.390	5.658 5.678 5.699 5.726 5.666 5.645 5.655	this study <sup>†</sup> this study this study this study Hansen & Anderko (1958) Hansen & Anderko (1958) Nowotny <i>et al.</i> (1946)

 $^\dagger$  The average standard error associated with the cell edges measured in this study is  $\pm$  0.004 Å.



FIG. 4. Change in unit-cell dimensions of  $\alpha$ -Pd<sub>3</sub> Sn<sub>2</sub> as a function of platinum concentration (see Table 7 for data).

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