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PHASE RELATIONS IN THE SYSTEM Pd-Sb-Te

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ABSTRACT

Phase relations in the system Pd-Sb-Te were investigated at 1000°, 800°, and 600°C, using the sealed-capsule technique; the quenched products were studied by reflected light microscopy, X-ray diffraction, and electron-microprobe analysis. At 1000°C, the solid phases Pd, Pd₂₀Sb₇, Pd₈Sb₃, Pd₃₁Sb₁₂, and Pd₅Sb₂ are stable with a liquid phase that occupies most of the isothermal diagram. Additional solid phases at 800°C are: Pd₅Sb₃, PdSb, Pd₈Te₃, Pd₇Te₃, and a continuous Pd₂₀Te₇ - Pd₂₀Sb₇ solid solution. At 600°C, PdSb₂, Pd₁₇Te₄, Pd₉Te₄, PdTe, PdTe₂, Sb₂Te₃, and Sb and continuous PdSb - PdTe and PdTe - PdTe₂ solid solutions are stable. All the solid phases exhibit solid solution, mainly by substitution between Sb and Te to an extent that varies with temperature of formation. The maximum substitution (at. %) of Te for Sb in the Pd-Sb phases is: 44.3 in Pd₈Sb₃, 52.0 in Pd₃₁Sb₁₂, 46.2 in Pd₅Sb₂ at 800°C; 15.3 in Pd₅Sb₃, 68.3 in PdSb₂ at 600°C. The maximum substitution (at. %) of Sb for Te in the Pd-Te phases is 34.5 in Pd₈Te₃ at 800°C, and 41.6 in Pd₇Te₃, 5.2 in Pd₁₇Te₄, 12.4 in Pd₉Te₄, and 19.1 in PdTe₂ at 600°C. X-ray powder-diffraction data show the synthetic PdSb₂ phase to be cubic, probably with space group *P*₂13. Testibiopalladite, ideally PdSbTe, may be a member of the PdSb₂ - Pd(Sb_{0.32}Te_{0.68})₂ solid-solution series. Borovskite (Pd₃SbTe₄) has not been found in the synthetic system in the temperature range 1000 - 600°C.

Keywords: phase relations, system Pd-Sb-Te, phase diagrams, 1000°, 800°, 600°C, palladium minerals, solid solution.

SOMMAIRE

Nous avons étudié les relations de phases dans le système Pd-Sb-Te à 1000°, 800° et 600°C au moyen de tubes scellés; les produits de synthèse ont été étudiés en lumière réfléchie, par diffraction X, et par analyse à la microsonde électronique. A 1000°C, les phases solides Pd, Pd₂₀Sb₇, Pd₈Sb₃, Pd₃₁Sb₁₂ et Pd₅Sb₂ coexistent avec une phase liquide qui occupe la plupart du diagramme isothermal. A 800°C, les phases suivantes viennent s'ajouter aux précédentes: Pd₅Sb₃, PdSb, Pd₈Te₃, Pd₇Te₃, et une solution solide entre Pd₂₀Te₇ et Pd₂₀Sb₇. A 600°C, PdSb₂, Pd₁₇Te₄, Pd₉Te₄, PdTe, PdTe₂, Sb₂Te₃, Sb, et les solutions solides continues entre PdSb et PdTe et entre PdTe et PdTe₂ sont stables. Toutes ces phases sont en fait des solutions solides impliquant surtout une substitution (Sb,Te) qui dépend de la température. L'étendue maximale de la substitution du Te au Sb dans les phases à Pd-Sb (en %, base atomique) est 44.3 dans Pd₈Sb₃, 52.0 dans Pd₃₁Sb₁₂, 46.2 dans Pd₅Sb₂ à 800°C, et 15.3 dans Pd₅Sb₃ et 68.3 dans PdSb₂ à 600°C. L'étendue maximale de la substitution de Sb au Te dans les phases Pd-Te (en %) est 34.5 dans Pd₈Te₃ à 800°C, et 41.6 dans Pd₇Te₃, 5.2 dans Pd₁₇Te₄, 12.4 dans Pd₉Te₄, et 19.1 dans PdTe₂ à 600°C. Des données de diffraction X sur poudres montrent que le PdSb₂ synthétique est cubique, et correspond probablement au groupe spatial *P*₂13. La testibiopalladite, de formule idéale PdSbTe, pourrait appartenir à la solution solide PdSb₂ - Pd(Sb_{0.32}Te_{0.68})₂. Nous n'avons pas réussi à synthétiser la borovskite Pd₃SbTe₄ dans l'intervalle 1000 - 600°C.

(Traduit par la Rédaction)

Mots-clés: relations de phases, système Pd-Sb-Te, diagrammes de phase, minéraux de palladium, solution solide.

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INTRODUCTION

The phase relations in the system Pd-Sb-Te at 400°C were reported by El-Boragy & Schubert (1971). Their phase diagram, the only one for the system in the literature, shows equilibria among the phases known in the related binary systems. Later, phases and phase relations along the bounding binary joins were re-investigated by many investigators, as summarized below.

For the system Pd-Sb, Pd₃Sb, first reported by Sander (1912) and shown in the Pd-Sb join of the Pd-Sb-Te diagram of El-Boragy & Schubert, was found to have a Pd:Sb ratio of 2.9:1 (Cabri *et al.* 1975), and its formula was revised to Pd₂₀Sb₇ (Wopersnow & Schubert 1977). The existence of Pd₂₀Sb₇, Pd₈Sb₃, Pd₃₁Sb₁₂, Pd₅Sb₂, Pd₅Sb₃, Pd₂Sb, PdSb and PdSb₂ was confirmed in the preliminary stages of this study.

For the phases in the system Pd-Te, the formula of the earlier-reported phases, Pd₄Te, Pd₃Te, and Pd₂Te, was revised to Pd₁₇Te₄ (Kim *et al.* 1990), Pd₂₀Te₇ (Wopersnow & Schubert 1977) and Pd₉Te₄ (Matković & Schubert 1978), respectively. The system also includes two new phases, Pd₈Te₃ (Cabri *et al.* 1979) and Pd₇Te₃ (Kim *et al.* 1990), which were not shown on the Pd-Te join of the Pd-Sb-Te diagram of El-Boragy & Schubert (1971). Kim *et al.* (1990) reported eight phases to exist in the system Pd-Te, namely: Pd₁₇Te₄, Pd₂₀Te₇, Pd₈Te₃, Pd₇Te₃, Pd₉Te₄, Pd₃Te₂, PdTe, and PdTe₂. Pd₅Te₂ of Grønvald & Røst (1956) was not found by Kim *et al.* (1990), who considered it a mixture of Pd₈Te₃ and Pd₇Te₃.

The phase relations in the system Sb-Te remain unclear. Hansen & Anderko (1958) reported only one intermediate phase, Sb₂Te₃, in the system. Later, Abrikosov *et al.* (1959) proposed two additional phases, β and γ, that exist in the range 0 - 60 at. % Te. Brown & Lewis (1962) suggested a phase (δ) with a homogeneity range from 11 to 60 at. % Te, and proposed that the β and γ phases of Abrikosov *et al.* may have been products of nonequilibrium. Kim & Chao (1990) reconfirmed the existence of Sb₂Te₃. Below 520°C, they also found a problematic phase, related to the δ phase of Brown & Lewis (1962), whose compositional limit on the Sb-rich side is 12 - 13 at. % Te, and is uncertain on the Te-side owing to failure in obtaining equilibrium assemblages.

The phase relations in the system Pd-Sb-Te merit re-investigation on the grounds that (1) the system is now known to include at least 17 binary phases, and (2) approximately 40% of those phases are known to have natural equivalents, and substitution between Sb and Te is common in them.

Because palladium antimonides and tellurides

are found in mineral assemblages of early crystallization from magma as well as in late-stage hydrothermal environments, the present investigation covers phase relations in the system Pd-Sb-Te at 1000, 800, and 600°C. According to the binary phase diagrams of Pd-Sb (Hansen & Anderko 1958, Wopersnow & Schubert 1977, Kim & Chao 1990), Pd-Te (Kim *et al.* 1990) and Sb-Te (Hansen & Anderko 1958, Abrikosov *et al.* 1959, Brown & Lewis 1962), only solid phases are stable below 400°C, implying that the ternary phase relations of the system Pd-Sb-Te below 400°C would be essentially the same as those at 400°C, as established by El-Boragy & Schubert (1971).

EXPERIMENTAL PROCEDURES

Starting materials were prepared from reagent-grade palladium, antimony and tellurium (all have 99.999% purity or better), and subsequently sealed in evacuated tubes of silica glass. The capsules were placed in a horizontal muffle furnace and heated at selected temperatures. To ensure homogeneity, most samples were opened, after initial heating, ground under acetone, pelletized and reloaded in the furnace for a further period of heating. The total heating period ranged from a few days to three months. Experimental runs were quenched by dropping the capsules in ice water.

Run products were studied by reflected light microscopy, X-ray powder diffraction and electron-microprobe analysis. X-ray-diffraction patterns were obtained with a 114.6-mm Gandolfi camera using Ni-filtered CuKα radiation. X-ray photographs were also taken in a Guinier-type focusing camera of 80-mm diameter with filtered CoKα radiation. Where accurate X-ray data were required for calculation of the cell dimensions, a Philips automated X-ray diffractometer was used. Compositions of individual phases were determined with a Cambridge MK5 and a JEOL 733 electron-microprobe analyzer using synthetic Pd-Te and Pd-Sb compounds and spectrographically pure Pd, Sb and Te elements as standards.

EXPERIMENTAL RESULTS

The experimental results, including starting bulk composition and compositions of phases identified are shown in Table 1, which is available through the Depository of Unpublished Data, CISTI, National Research Council, Ottawa, Ontario K1A 0S2. The interpretation of the experimental results at 1000, 800, and 600°C is presented diagrammatically in Figures 1, 2, and 3, respectively.

The isothermal section at 1000°C (Fig. 1) is characterized by the presence of palladium,

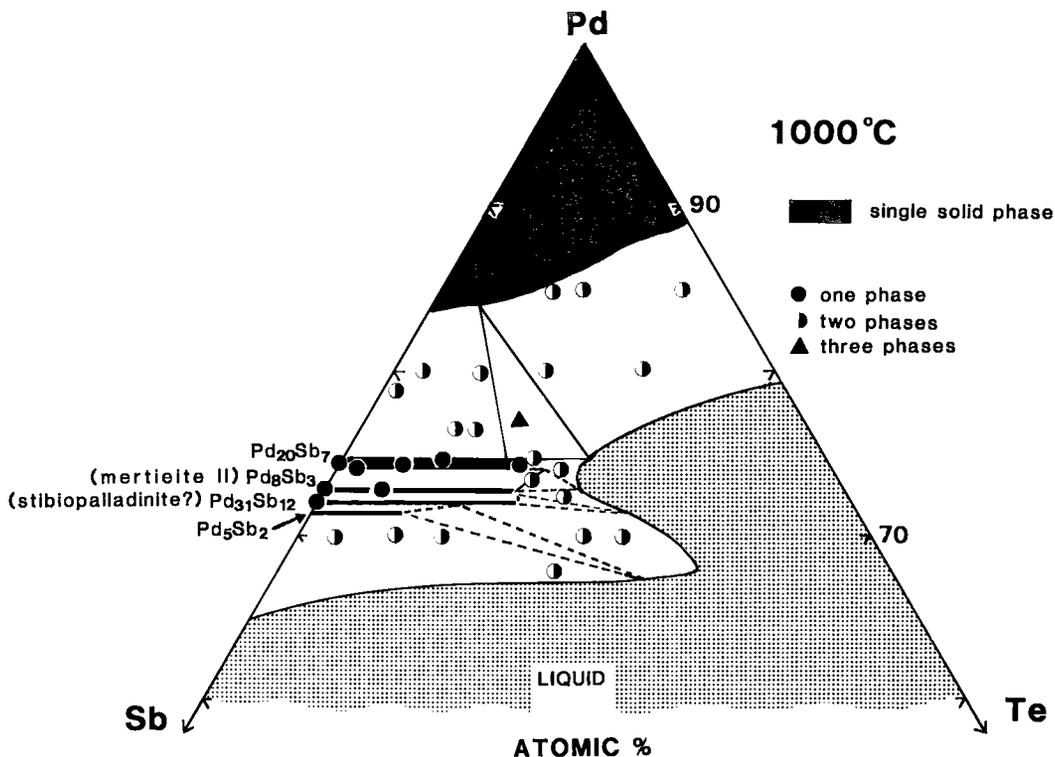


FIG. 1. Phase relations in the system Pd-Sb-Te at 1000°C. Boundaries of the 3-phase fields, postulated on the basis of the known tie-line of the neighboring 2-phase fields, are: $\text{Pd}_{20}\text{Sb}_7(\text{Pd}_{74.6}\text{Sb}_{15.1}\text{Te}_{10.9}) + \text{Pd}_8\text{Sb}_3(\text{Pd}_{72.3}\text{Sb}_{17.9}\text{Te}_{9.8}) + \text{liquid}$; $\text{Pd}_8\text{Sb}_3(\text{Pd}_{72.3}\text{Sb}_{17.9}\text{Te}_{9.8}) + \text{Pd}_{31}\text{Sb}_{12}(\text{Pd}_{72.1}\text{Sb}_{17.2}\text{Te}_{10.7}) + \text{liquid}$; and $\text{Pd}_{31}\text{Sb}_{12}(\text{Pd}_{72.0}\text{Sb}_{20.7}\text{Te}_{7.3}) + \text{Pd}_5\text{Sb}_2(\text{Pd}_{71.6}\text{Sb}_{23.7}\text{Te}_{4.7}) + \text{liquid}$.

$\text{Pd}_{20}\text{Sb}_7$, Pd_8Sb_3 , $\text{Pd}_{31}\text{Sb}_{12}$, Pd_5Sb_2 and a large field of liquid. Palladium contains up to 16.5 at.% Sb and 10.8 at.% Te in solid solution along the Pd-Sb and Pd-Te binary joins, respectively. The $\text{Pd}_{20}\text{Sb}_7$ phase has a homogeneity range of 24.6 to 26.0 at.% Sb. Tellurium substitution for Sb is 42 at.% in $\text{Pd}_{20}\text{Sb}_7$, 36–38 at.% in Pd_8Sb_3 , 38.3 at.% in $\text{Pd}_{31}\text{Sb}_{12}$ and 16.5 at.% in Pd_5Sb_2 . Boundaries of one three-phase assemblage are: Pd ($\text{Pd}_{0.84}\text{Sb}_{0.14}\text{Te}_{0.02}$) + $\text{Pd}_{20}\text{Sb}_7$ ($\text{Pd}_{20.17}\text{Sb}_{4.48}\text{Te}_{2.35}$) + liquid ($\text{Pd}_{0.74}\text{Sb}_{0.13}\text{Te}_{0.13}$). It is not possible to determine accurate boundaries of other invariant fields, because (i) compositions of the solid phases involved are very similar, (ii) the liquid phase coexisting with solid phases tends to separate into metastable phases during quenching, and (iii) $\text{Pd}_{31}\text{Sb}_{12}$ and the structurally related Pd_5Sb_2 are nearly identical in optical properties and X-ray powder-diffraction patterns.

At 800°C, a few additional phases become stable (Fig. 2): Pd_5Sb_3 and PdSb on the Pd-Sb join, and $\text{Pd}_{20}\text{Te}_7$, Pd_8Te_3 and Pd_7Te_3 on the Pd-Te join.

There is a complete solid-solution between $\text{Pd}_{20}\text{Sb}_7$ and $\text{Pd}_{20}\text{Te}_7$, which are isostructural (Wopersnow & Schubert 1977). The palladium solid-solution field is determined by joining the solubility limits, 21 at.% Sb on the Pd-Sb join and 14.8 at.% Te on the Pd-Te join. Limits of tellurium substitution for Sb in Pd_8Sb_3 , $\text{Pd}_{31}\text{Sb}_{12}$, Pd_5Sb_2 , Pd_5Sb_3 and PdSb are 44.3, 52.0, 46.2, 4.5 and 4.0 at.%, respectively. Limits of antimony substitution for Te in Pd_8Te_3 and Pd_7Te_3 are 34.5 at.% and 36.3 at.%, respectively.

Phase relations in the areas between Pd_8Sb_3 and Pd_8Te_3 solid-solution end-members and between $\text{Pd}_{31}\text{Sb}_{12}$ and Pd_8Te_3 solid-solution end-members are not clear owing to difficulties in identification of the optically and compositionally similar phases.

In the isothermal section at 600°C (Fig. 3), more solid phases become stable, namely: PdSb_2 , $\text{Pd}_{17}\text{Te}_4$, Pd_9Te_4 , PdTe, PdTe_2 , Sb_2Te_3 , and Sb. The liquid fields exist only as thin strips near the three binary joins. Phase relations in the shaded areas in Figure 3 are not known because of the

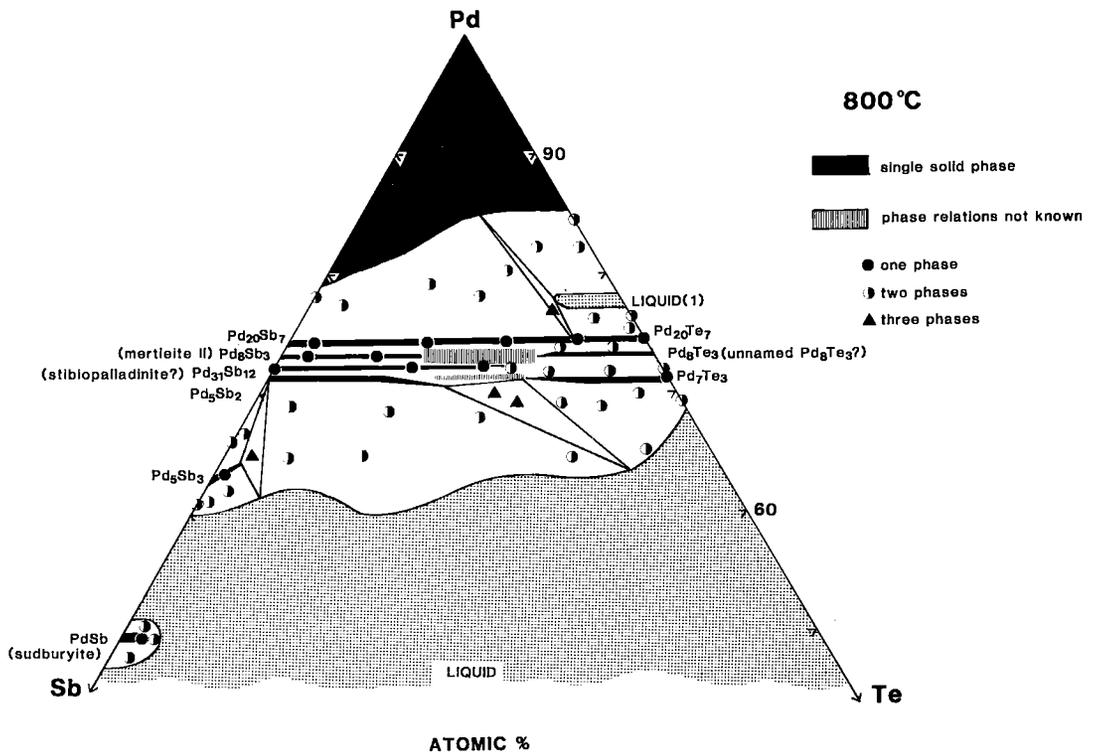


FIG. 2. Phase relations in the system Pd-Sb-Te at 800°C. Three 3-phase fields determined are: Pd(Pd_{84.6}Sb_{6.6}Te_{8.8}) + Pd₂₀(Te,Sb)₇(Pd_{73.6}Te_{21.8}Sb_{4.6}) + liquid(1); Pd₅Sb₂(Pd_{70.8}Sb_{15.7}Te_{13.5}) + Pd₇Te₃(Pd_{71.5}Sb_{10.3}Te_{18.4}) + liquid; and Pd₅Sb₂(Pd_{71.0}Sb_{28.7}Te_{0.3}) + Pd₅Sb₃(Pd_{64.4}Sb_{34.0}Te_{1.6}) + liquid.

same difficulties in identification of the phases in the quenched products. In addition to Pd₂₀Sb₇ - Pd₂₀Te₇, there is one more complete solid-solution: PdSb - PdTe (hexagonal, *P6₃/mmc*). The PdSb - PdTe solid solution shows a slight depletion in Pd (approximately 1 at.%) on the Te-rich side. The PdSb - PdTe solid solution is stable to at least 670°C and may persist to the melting temperature of PdTe at 746°C, as measured by Ipsier & Schuster (1986). The cell parameters of the Pd₂₀Sb₇ - Pd₂₀Te₇ and PdSb - PdTe solid solutions (Tables 2, 3) show good linear correlations with Te content. Run products with bulk compositions Pd₄₀Sb₅Te₅₅ (run 1037), Pd₃₉Sb₁₀Te₅₁ (run 1068), and Pd_{37.4}Sb_{12.6}Te_{50.0} (run 1082), quenched from 600°C, yielded a "perthitic" intergrowth of PdTe and PdTe₂ solid solutions. The texture strongly indicates that the phases in the intergrowths are exsolution products from an originally homogeneous solid-solution, and supports the interpretation of Kim *et al.* (1990) that there is a complete solid-solution between PdTe (NiAs-type structure) and PdTe₂ [Cd(OH)₂-

type structure]. The solid solution is apparently not quenchable, and exsolution occurs somewhere below 600°C. This two-phase exsolution area is shown in Figure 3 (shaded). Fine intergrowths of the mineral analogue of PdTe (kotulskite) and PdTe₂ (merenskyite) have been observed in deposits in the Stillwater Complex, Montana (Cabri & Pickwick 1974) and the Merensky Reef, South Africa (Kingston 1966).

PdSb₂ shows an extensive solid-solution from pure PdSb₂ to Pd(Sb_{0.32}Te_{0.68})₂, but does not form a complete solid-solution with the structurally different PdTe₂. A similar extension of the PdSb₂ - Pd(Te,Sb)₂ solid-solution also was observed at 400°C (El-Boragy & Schubert 1971). PdSb₂ was reported to have a pyrite structure, with an *a* parameter of 6.439 Å (Thomassen 1928), 6.4584(5) Å (Furuseth *et al.* 1965), and 6.460 Å (Pratt *et al.* 1968). However, X-ray powder data, obtained by powder diffractogram as well as by Guinier and Gandolfi camera methods with approximately 6-8 hour exposure time, consistently reveal a very weak

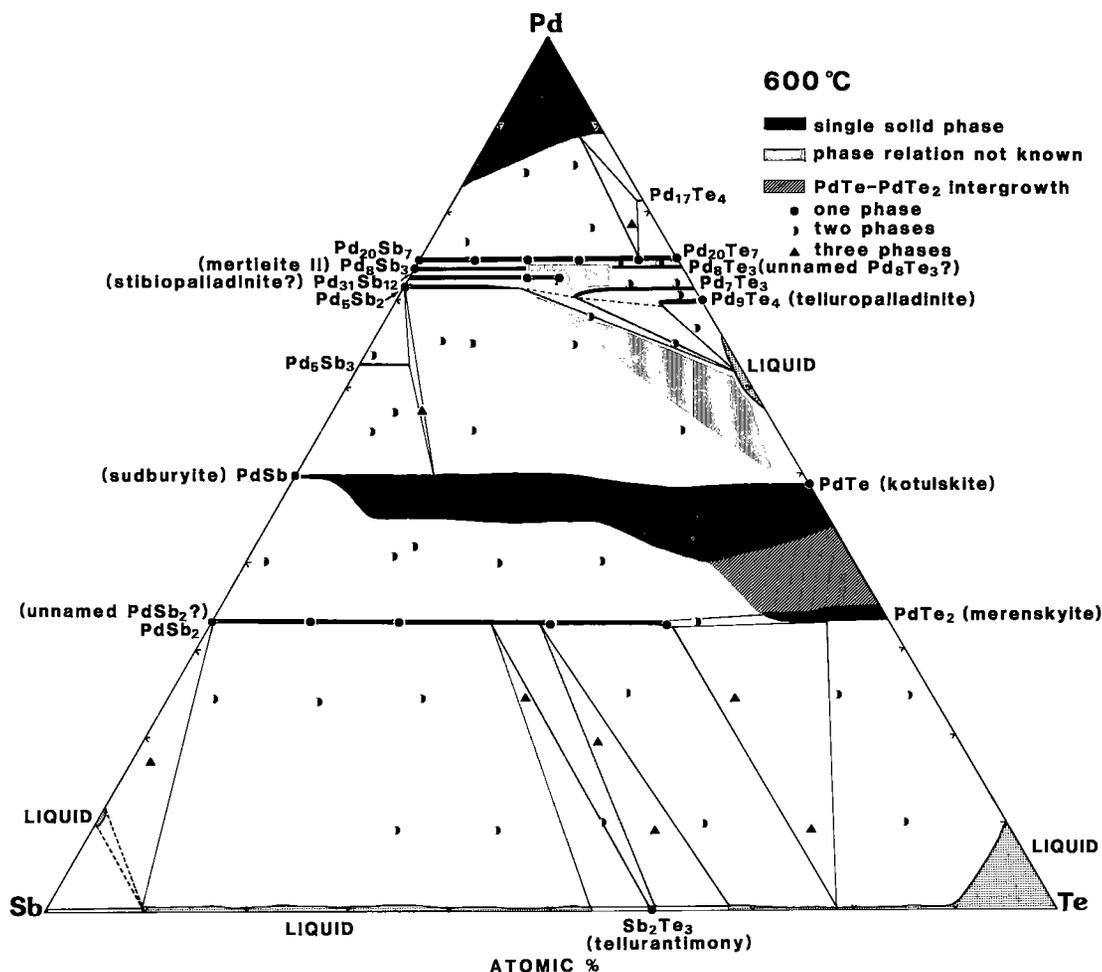


Fig. 3. Phase relations in the system Pd-Sb-Te at 600°C. Five 3-phase assemblages determined are: Pd(Pd₈₉Te₈Sb₃) + Pd₁₇Te₄(Pd₈₁Te₁₈Sb₁) + Pd₂₀(Te,Sb)(Pd_{74.3}Te₂₂Sb_{3.7}); Pd₅Sb₂(Pd_{69.8}Sb_{29.8}Te_{0.4}) + Pd₅Sb₃(Pd_{62.2}Sb_{32.0}Te_{5.8}) + Pd(Sb,Te)(Pd_{49.6}Sb_{36.0}Te_{14.4}); PdTe₂(Pd_{33.4}Te_{60.1}Sb_{6.5} + PdSb₂(Pd_{33.1}Te_{45.7}Sb_{21.2}) + liquid (76.8 at.% Te); PdSb₂(Pd_{32.9}Sb_{34.8}Te_{32.3}) + Sb₂Te₃(Sb_{40.4}Te_{59.6}) + liquid (68 at.% Te); and PdSb₂(Pd_{33.5}Sb_{39.2}Te_{27.3}) + Sb₂Te₃(Sb_{40.4}Te_{59.6}) + liquid (54 at.% Te).

reflection, with a d of 2.035 Å, which can be indexed as 310. The 310 reflection is prohibited in the $Pa3$ pyrite structure but is consistent with a $P2_13$ ullmannite (NiSbS) structure. The refined a parameter [6.4626(3) Å] for PdSb₂ synthesized at 600°C in this study is in good agreement with 6.460 Å given by Pratt *et al.* (1968). The X-ray powder patterns of single-phase products (runs 1010, 1011, 1012, and 1012A) on the PdSb₂-Pd(Te_{0.68}Sb_{0.32})₂ solid-solution also reveal a weak 310 reflection, indicating the absence of structural break in the solid solution. Figure 4 shows a positive correlation of the cell dimension of the PdSb₂ solid solution with Te content.

All the phases, except for Pd₁₇Te₄, Sb₂Te₃, and Sb, exhibit extensive solid-solution. Palladium contains 17 at.% Sb on the Pd-Sb join and 11 at.% Te on the Pd-Te join. Pd₅Sb₂, Pd₅Sb₃ and PdSb₂ contain as much as 39.8, 15.3, and 68.3 at.% Te, respectively, in substitution for Sb. The extent of antimony substitution for Te in Pd₁₇Te₄, Pd₇Te₃, Pd₉Te₄ and PdTe₂ is 5.2, 41.6, 12.4, and 19.1 at.%, respectively.

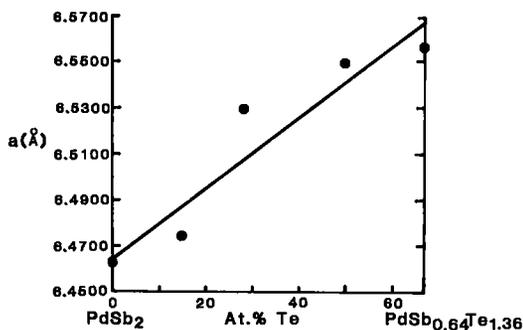
The Pd-Sb-Te phase diagram at 400°C proposed by El-Boragy & Schubert (1971) shows some similarities to that of this study at 600°C (Fig. 3), especially for the 33.3 - 100 at.% Pd region, although the designation of some phases on the

TABLE 2. CELL DIMENSION OF THE Pd₂₀(Sb,Te)₇ SOLID-SOLUTION SERIES

Run No.	Composition (at.%)			Temperature (°C)	Cell parameters	
	Pd	Sb	Te		a (Å)	c (Å)
1052	74.4	25.6		600	11.717(3)	11.011(8)
1048	74.2	15.2	10.6	600	11.754(2)	11.061(3)
1049	74.1	10.1	15.8	600	11.765(2)	11.094(2)
1050	74.0	5.1	20.9	600	11.779(1)	11.135(4)
1051	74.3		25.7	600	11.797(3)	11.150(4)

TABLE 3. CELL DIMENSION OF THE Pd(Sb,Te) SOLID-SOLUTION SERIES

Run No.	Composition (at.%)			Temperature (°C)	Cell parameters	
	Pd	Sb	Te		a (Å)	c (Å)
1001	50.0	50.0		600	4.0753(4)	5.5910(5)
1004	50.0	40.0	10.0	600	4.0955(4)	5.6015(6)
1005	49.4	24.9	25.7	600	4.1152(1)	5.6186(2)
1006	48.7	11.7	39.6	600	4.1293(2)	5.6357(3)
1002	48.6		51.4	600	4.130(3)	5.661(5)

FIG. 4. Cell dimension versus composition of PdSb₂ solid solution.

Pd-Te join of their diagram differs from ours.

Pd-Sb-Te MINERALS IN RELATION TO SYNTHETIC PHASES

Many of the synthetic phases in the system occur in nature. These are Pd₉Te₄ (telluropalladinite), PdTe (kotulskite), PdTe₂ (merenskyite), Pd₈Sb₃ (mertieite II), PdSb (sudburyite), and Sb₂Te₃ (tellurantimony). Physical properties and X-ray powder data of these synthetic phases correspond very well with those of the natural minerals.

The X-ray powder pattern of Pd₃₁Sb₁₂ (Table 4) synthesized in this study is very similar to that of Pd₅₊Sb₂₋ (later revised to Pd₃₁Sb₁₂) of El-Boragy

et al. (1970) and that of the stibiopalladinite from Potgietersrust, South Africa (Cabri & Chen 1976). The parameters of the hexagonal cell of stibiopalladinite, established by single-crystal X-ray diffraction, are *a* 7.598(2), *c* 28.112(9) Å (Cabri & Chen 1976). The X-ray pattern of Pd₅₊Sb₂₋ of El-Boragy *et al.* (1970), which contains additional weak lines, must be indexed on a larger hexagonal cell with *a* 7.6006(1), *c* 41.945(8) Å. The X-ray powder pattern of Pd₃₁Sb₁₂ from this study, however, may be indexed on both cells. Thus, the mineral stibiopalladinite and the synthetic phase Pd₃₁Sb₁₂ of El-Boragy *et al.* (1970) and of this study are, clearly, structurally related, but their true relationship can only be established by further single-crystal study of the synthetic material.

Telargpalite [(Pd,Ag)₄₊Te], cubic with an *a* of 12.60(2) Å, from Oktyabr deposit, U.S.S.R. (Kovalenker *et al.* 1974), was considered by Berlincourt *et al.* (1981) as the natural equivalent of the synthetic Pd₄Te phase of Grønvold & Røst (1956). Although Pd₄Te (presently proposed to be Pd₁₇Te₄; Kim *et al.* 1990) also is cubic, with an *a* of 12.67 Å, its powder pattern is not identical with that of telargpalite.

The Pd:Te ratio in keithconnite, Pd_{3-x}Te (0.14 < *x* < 0.43), from the Stillwater Complex, Montana, was reported to be between 2.571 and 2.714, that is, between Pd₂₀Te₇ and Pd₇Te₃ (Cabri *et al.* 1979). Although the X-ray powder pattern of keithconnite is vaguely similar to that of Pd₂₀Te₇, a phase identical to keithconnite has not been found in this study.

TABLE 4. X-RAY POWDER-DIFFRACTION DATA FOR SYNTHETIC Pd₃₁Sb₁₂

hkl	d _{calc.}	d _{obs.}	I
113	3.495	3.495	2
116	3.338	3.337	4
1·0·12	3.087	3.084	2
206	2.977	2.976	3
0·1·14	2.726	2.734	1
1·1·12	2.572	2.571	2
211	2.483	2.481	6
213	2.449	2.448	15
2·0·12	2.396	2.395	19
216	2.343	2.344	6
1·1·15	2.252	2.251	85
030	2.194	2.193	100
2·1·12	2.026	2.026	8
1·1·18	1.986	1.986	11
1·2·14	1.914	1.914	1
2·0·18	1.902	1.901	1
0·3·12	1.858	1.858	5
226	1.833	1.834	1
227	1.811	1.811	2
0·0·24	1.747	1.748	1
1·0·24	1.689	1.691	1
2·2·12	1.669	1.669	1
3·0·14	1.597	1.598	1
323	1.501	1.502	2
2·2·18	1.472	1.473	3
3·1·18	1.437	1.437	2
2·1·24	1.430	1.430	3
0·0·30	1.398	1.399	5
3·2·12	1.386	1.387	7
4·0·17	1.369	1.368	1
3·2·14	1.348	1.349	1
4·0·19	1.319	1.319	2
502	1.313	1.313	3
504	1.306	1.304	1
4·1·14	1.295	1.296	1
2·0·30	1.2868	1.2873	1
4·1·15	1.2776	1.2789	10
3·0·27	1.2679	1.2685	8
331	1.2662	1.2660	4
4·1·17	1.2413	1.2408	2
0·0·34	1.2336	1.2332	3
426	1.2247	1.2241	6
0·0·35	1.1984	1.1994	1
4·2·10	1.1926	1.1923	2
512	1.1803	1.1804	6

Plus many more lines.

Run 3066 (Pd_{72.0}Sb_{28.0}), quenched from 800°C. Automated diffractometer, CuK α radiation (λ 1.54059 Å). Indices based on a hexagonal cell a 7.6006(9), c 41.945(8) Å.

Cabri (1981) reported an unnamed Pd₈Te₃ mineral in heavy-mineral concentrates from the Stillwater Complex, Montana. The X-ray powder pattern of the unnamed Pd₈Te₃ mineral is, however, not identical to either of the two synthetic forms of Pd₈Te₃ (Kim *et al.* 1990), although it bears some similarity to the X-ray powder pattern of the lower-temperature form quenched from 500°C.

Another unnamed mineral, with the composition PdSb₂, was reported by Graham (1978) from the Nairne pyrite deposit, South Australia. The mineral is optically isotropic and is probably the natural equivalent of the synthetic PdSb₂ phase. However, there are insufficient data on the natural phase to substantiate its identity with synthetic PdSb₂.

The mineral testibiopalladite from China (P.M.M.R.G. 1974, Fleischer *et al.* 1976) was given a chemical formula of Pd(Sb,Bi)Te based on the assumption that Bi substitutes for Sb. The formula of testibiopalladite was later idealized to PdSbTe

(Cabri 1981), which implies that the mineral is an ordered 1:1:1 compound. The structure of testibiopalladite was considered to be of Pa3 pyrite type, but later corrected to P2₁3 ullmannite type by analogy to michenerite (Institute of Geochemistry, Chinese Academy of Science 1981). The X-ray powder pattern of a phase with PdSbTe composition, synthesized at 600°C (run 1012), compares well with that of testibiopalladite given by P.M.M.R.G. (1974). The cell dimension *a* of the synthetic PdSbTe is 6.5483 Å, close to the value of 6.533 Å reported by Hulliger (1963) but smaller than the value (6.557–6.581 Å) reported for the natural phases (P.M.M.R.G. 1974). The larger cell parameter of the natural phases is probably due to the presence of Ni and Bi in the mineral. From the phase diagram at 600°C (Fig. 3), it is clear that PdSbTe is a member of the PdSb₂ – PdTe(Sb_{0.64}Te_{0.36}) solid solution and not an ordered 1:1:1 compound. Consequently, the definition of testibiopalladite should perhaps be modified to cover the Te-rich members of the PdSb₂ – PdTe(Sb,Te) solid solution. The ideal formula of testibiopalladite may then be written as PdTe(Sb,Te), with the general formula PdTe(Sb,Te,Bi), because up to 0.5 atom of Bi has been found to substitute for Sb or Te in the (Sb,Te) site in natural phases (Institute of Geochemistry, Chinese Academy of Science 1981).

The mineral borovskite (Yalovoi *et al.* 1973, Fleischer 1974) has an ideal composition of Pd₃SbTe₄. However, an ordered compound of this composition has not been found in the temperature range investigated here. An attempt to synthesize borovskite at 600°C from the bulk composition Pd_{37.4}Sb_{12.6}Te_{50.0} (run 1082) yielded fine intergrowths of PdTe solid solution (Pd_{40.8}Te_{44.5}Sb_{14.7}) and PdTe₂ solid solution (Pd_{34.1}Te_{53.3}Sb_{12.6}) in approximately a 1 to 1 ratio. The composition of borovskite is, therefore, either unquenchable or unstable in the pure system. The presence of Pt in substitution for Pd and of Bi in substitution for Sb and Te may have played an important role in stabilizing the mineral.

Natural analogues of the PdSb – PdTe solid solution are demonstrated by the assemblages found by Watkinson & Hak (pers. comm., 1989) in sulfide-rich ores from the Expo Ungava deposit, Quebec, the Shebandowan deposit, Ontario, and the Birchtree deposit, Manitoba. The composition of sudburyite and kotulskite grains in these assemblages ranges from (Pd_{0.92}Ni_{0.05}Fe_{0.01}Co_{0.01})(Sb_{0.82}As_{0.09}Bi_{0.08}Te_{0.01}S_{0.01}) to (Pd_{0.89}Fe_{0.03})(Te_{0.61}Sb_{0.27}Bi_{0.15}As_{0.04})Σ1.07, and thus covers a large portion of the PdSb – PdTe solid solution. As synthetic PdSb shows very limited solid-solution, up to Pd₅₀Sb₄₈Te₂ at 800°C, the mineral as-

semblages in these deposits must have been formed at a lower temperature, perhaps below 746°C, the melting temperature of PdTe, as determined by Ipser & Schuster (1986).

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