

THE SYSTEM Pd–Sn–Te AT 400°C AND MINERALOGICAL IMPLICATIONS. II. THE TERNARY PHASES

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ABSTRACT

The phase relations in the system Pd–Sn–Te were investigated with the evacuated silica tube method, and characterized by electron-microprobe analysis and powder X-ray diffraction. The experimental charges were weighed using pure elements or presynthesized binary phases. The isothermal section was investigated at 400°C. Our experiments revealed the existence of three ternary phases: Pd₆₇Sn₁₁Te₂₂, Pd₇₂Sn₁₆Te₁₂ and PdSnTe, unknown as minerals. Two previously reported ternary phases, “Pd₇₃Sn₁₀Te₁₇” and “Pd₇₁Sn₇Te₂₂”, were not identified in this work. The experiments presented have provided useful data concerning the ranges of solid solutions in the ternary system. The phase PdTe₂, analogue of merenskyite, dissolves up to 3.5 at.% Sn; the phase PdTe, analogue of kotulskite, dissolves up to 19 at.% Sn, and the phase Pd₂₀Te₇ dissolves up to 4 at.% Sn. The phase Pd₂Sn, analogue of paolovite, dissolves up to 4 at.% Te, and the phase Pd₃Sn, analogue of atokite, dissolves up to 0.5 at.% Te. At 400°C, the following assemblages were encountered: Sn(liq) + SnTe + PdSn₂, PdSn₂ + SnTe + PdSn, PdSn + SnTe + Pd₂₀Sn₁₃, SnTe + Te + PdTe₂, SnTe + Pd(Te,Sn)_{2ss} + PdSnTe, SnTe + Pd₂₀Sn₁₃ + PdSnTe, Pd₂₀Sn₁₃ + PdSnTe + Pd(Te,Sn)_{ss}, PdSnTe + Pd(Sn,Te)_{2ss} + Pd(Te,Sn)_{ss}, Pd₂₀Sn₁₃ + Pd₂(Sn,Te)_{ss} + Pd(Te,Sn)_{ss}, Pd₂(Sn,Te)_{ss} + PdTe + Pd₆₇Sn₁₁Te₂₂, PdTe + Pd₆₇Sn₁₁Te₂₂ + Pd₃Te₂, Pd₆₇Sn₁₁Te₂₂ + Pd₃Te₂ + Pd₉Te₄, Pd₆₇Sn₁₁Te₂₂ + Pd₉Te₄ + Pd₂₀Te₇, Pd₂(Sn,Te)_{ss} + Pd₆₇Sn₁₁Te₂₂ + Pd₇₂Sn₁₆Te₁₂, Pd₂(Sn,Te)_{ss} + Pd₇₃Sn₁₄Te₁₃ + Pd₃(Sn,Te)_{ss}, Pd₇₂Sn₁₆Te₁₂ + Pd₆₇Sn₁₁Te₂₂ + Pd₂₀(Te,Sn)_{7ss}, Pd₃(Sn,Te)_{ss} + Pd₇₂Sn₁₆Te₁₂ + Pd₂₀(Te,Sn)_{7ss}, Pd₃(Sn,Te)_{ss} + Pd₂₀(Te,Sn)_{7ss}, Pd₃(Sn,Te)_{ss} + Pd₁₇Te₄ and Pd₃Sn + Pd₁₇Te₄ + Pd.

Keywords: system Pd–Sn–Te, phase relations, phase diagram, palladium, tin, tellurium, platinum-group minerals.

SOMMAIRE

Nous avons étudié les relations de phases dans le système Pd–Sn–Te au moyen de tubes en silice évacués, et nous nous sommes servis de la diffraction X sur poudre et d’analyses avec une microsonde électronique pour en caractériser les produits. Les matériaux de départ étaient des mélanges d’éléments purs ou bien des phases binaires préalablement synthétisées. Nous avons étudié la section isothermale à 400°C. Nos expériences ont révélé l’existence de trois phases ternaires: Pd₆₇Sn₁₁Te₂₂, Pd₇₂Sn₁₆Te₁₂ et PdSnTe, méconnues comme minéraux. Deux phases ternaires déjà décrites dans la littérature, “Pd₇₃Sn₁₀Te₁₇” et “Pd₇₁Sn₇Te₂₂”, n’ont pas été confirmées. Les expériences présentées fournissent de l’information utile à propos de l’étendue des solutions solides dans le système ternaire. La phase PdTe₂, analogue de la merenskyite, peut dissoudre jusqu’à 3.5% Sn (pourcentage d’atomes); la phase PdTe, analogue de la kotulskite, dissout jusqu’à 19% Sn, et la phase Pd₂₀Te₇ dissout jusqu’à 4% Sn. La phase Pd₂Sn, analogue de la paolovite, dissout jusqu’à 4% Te, et la phase Pd₃Sn, analogue de l’atokite, dissout jusqu’à 0.5% Te. A 400°C, les assemblages suivants ont été rencontrés: Sn(liq) + SnTe + PdSn₂, PdSn₂ + SnTe + PdSn, PdSn + SnTe + Pd₂₀Sn₁₃, SnTe + Te + PdTe₂, SnTe + Pd(Te,Sn)_{2ss} + PdSnTe, SnTe + Pd₂₀Sn₁₃ + PdSnTe, Pd₂₀Sn₁₃ + PdSnTe + Pd(Te,Sn)_{ss}, PdSnTe + Pd(Sn,Te)_{2ss} + Pd(Te,Sn)_{ss}, Pd₂₀Sn₁₃ + Pd₂(Sn,Te)_{ss} + Pd(Te,Sn)_{ss}, Pd₂(Sn,Te)_{ss} + PdTe + Pd₆₇Sn₁₁Te₂₂, PdTe + Pd₆₇Sn₁₁Te₂₂ + Pd₃Te₂, Pd₆₇Sn₁₁Te₂₂ + Pd₃Te₂ + Pd₉Te₄, Pd₆₇Sn₁₁Te₂₂ + Pd₉Te₄ + Pd₂₀Te₇, Pd₂(Sn,Te)_{ss} + Pd₆₇Sn₁₁Te₂₂ + Pd₇₂Sn₁₆Te₁₂, Pd₂(Sn,Te)_{ss} + Pd₇₃Sn₁₄Te₁₃ + Pd₃(Sn,Te)_{ss}, Pd₇₂Sn₁₆Te₁₂ + Pd₆₇Sn₁₁Te₂₂ + Pd₂₀(Te,Sn)_{7ss}, Pd₃(Sn,Te)_{ss} + Pd₇₂Sn₁₆Te₁₂ + Pd₂₀(Te,Sn)_{7ss}, Pd₃(Sn,Te)_{ss} + Pd₂₀(Te,Sn)_{7ss}, Pd₃(Sn,Te)_{ss} + Pd₁₇Te₄ and Pd₃Sn + Pd₁₇Te₄ + Pd.

Mots-clés: système Pd–Sn–Te, relations de phases, diagramme de phases, palladium, étain, tellure, minéraux du groupe du platine.

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INTRODUCTION

The system Pd–Sn–Te contains several important platinum-group minerals, such as kotulskite (PdTe), merenskyite (PdTe₂), telluropalladinite (Pd₉Te₄), atokite (Pd₃Sn) and paolovite (Pd₂Sn), as summarized in Cabri (2002). Furthermore, several unnamed mixtures or phases with compositions that plot within the system Pd–Sn–Te have been reported by Balabonin *et al.* (2000) and Li & Naldrett (1993), among others. Surprisingly, no ternary phase has been described as a mineral, even though binary phases commonly occur in nature together. The discovery of a Pd–Sn telluride in nature should be expected. As only phase relations within the three binary subsystems are known, the phase relations in the condensed Pd–Sn–Te system were investigated. In this contribution, we determine the phase relations in the Pd–Sn–Te system at 400°C, and therefore predict the stable assemblages under natural conditions. Information concerning the genesis of PGE minerals and possibly of associated rocks can, under certain conditions, be deciphered from the mineral assemblages.

BACKGROUND INFORMATION

The binary subsystems of the system Pd–Sn–Te were re-investigated prior to the experimental work in the ternary system. The results are summarized in the first part of this “back-to-back” contribution (Vymazalová & Drábek 2010). The binary systems Pd–Te, Pd–Sn and Sn–Te were also evaluated in works by Okamoto (1992), Massalski (1990), and Sharma & Chang (1986), respectively.

In the marginal binary systems, the following binary phases were confirmed to be stable at 400°C: Pd₁₇Te₄, Pd₂₀Te₇, Pd₉Te₄, Pd₃Te₂, PdTe, PdTe₂, Pd₃Sn, Pd₂Sn, Pd₂₀Sn₁₃, PdSn, PdSn₂, and SnTe. Phase relations in the ternary Pd–Sn–Te system have not been studied so far, and a phase diagram of the system is not available in the literature. However, El-Boragy & Schubert (1971) reported the existence of two ternary palladium-rich phases, Pd₇₃Sn₁₀Te₁₇ and Pd₇₁Sn₇Te₂₂. Furthermore, Savilov *et al.* (2005) synthesized and described the crystal structure and electronic structure of modulated Pd_{7-δ}SnTe₂ (0.3 ≤ δ ≤ 0.8).

According to previous experimental studies of systems with PGE, summarized by Makovicky (2002) and Berlincourt *et al.* (1981), Pd-bearing platinum-group minerals, particularly those containing As, Bi, Sn and Te, form under postmagmatic conditions, at lower temperatures. Furthermore, Evstigneeva & Nekrasov (1980) proved experimentally that palladium intermetallic compounds formed in the systems Pd–Sn–HCl and Pd–Sn–Cu–HCl from hydrothermal chloride solutions at temperatures of 300° to 400°C.

In this study, an investigation in the system Pd–Sn–Te was carried out at 400°C, as we believe that

minerals in the system Pd–Sn–Te form close to this temperature. Some experiments were carried out also at 600° and 800°C.

METHODS AND TECHNIQUES

Experimental

The experimental method is described in the first part of this joint contribution (Vymazalová & Drábek 2010). The run products are extremely fine-grained, commonly form intimate intergrowths, and thus cause certain difficulties in evaluation. Therefore, a significant number of experiments were repeated, even several times. Only selected representative runs are listed in Table 1. The experimental products were investigated by X-ray-diffraction analysis, in polished sections examined in reflected light, and with electron-microprobe techniques.

X-ray-diffraction analysis

Data on the experimental products was collected using a Philips X’Pert MPD X-ray diffraction (XRD) system with a vertical goniometer PW3020 in the Bragg–Brentano reflecting geometry, used with copper radiation (40 kV and 40 mA), a secondary graphite monochromator, and a proportional counter to collect the X-ray powder data. Powder patterns were collected in the range from 10 to 140°2θ CuKα, with step size of 0.02°2θ CuKα and exposures of 10 seconds per step (for a detailed study of the phases) and in the range from 10 to 75°2θ CuKα with step size of 0.1°2θ CuKα and exposures of two seconds per step (for the basic identification of phases and preliminary X-ray results). The data obtained were evaluated using X-ray powder-diffraction software BEDE ZDS – System version 4.00 (Ondruš 2000). The whole profile-fitting method (WPPF) was applied to calculate unit-cell parameters from powder data. We employed the program FULLPROF (Rodríguez-Carvajal 2001) for our calculations.

Electron-probe micro-analysis

Chemical analyses were performed with a Cameca SX–100 electron microprobe using wavelength-dispersion mode and a focused beam (size 1–2 μm). The accelerating voltage was set to 15 keV, and the beam current was 10 nA. The samples were analyzed using PdLα, SnLα, and TeLα. Pure metals (Pd, Sn, and Te) were used as primary standards. The results of the analyses are given in Table 1; in order to simplify the orientation of the experiments performed in the phase diagram, the results of analyses were recalculated as at.%. Compositional data were collected for several different grains within the polished section (at a minimum, n = 4) and then averaged.

TABLE 1. RESULTS OF REPRESENTATIVE EXPERIMENTAL RUNS IN THE SYSTEM Pd-Sn-Te AT 400°C

Run No.	Starting material	Initial composition (at.%)			Time hrs	Phase assemblages produced at 400°C	Electron-microprobe data (at.%)			
		Pd	Sn	Te			Phase	Pd	Sn	Te
11	5Pd+Sn+3Te	55.55	11.11	33.33	360	PdTe + Pd ₂ (Sn,Te)	PdTe	51.8	0.1	48.1
							Pd ₂ (Sn,Te)	66.4	29.7	3.9
14	0.5SnTe+Pd ₃ Te ₂	50	8.33	41.67	528	Pd(Te,Sn) + Pd ₂ (Sn,Te)	Pd(Te,Sn)	50.2	8.0	41.8
18	Pd+3Sn+Te	20	60	20	1776	PdSn ₂ + SnTe	PdSn ₂	33.2	66.8	0.0
							SnTe	0.0	49.8	50.1
19	Pd+Sn+0.5Te	40	40	20	1752	Pd ₂₀ Sn ₁₃ + SnTe + C	C	34.0	31.6	34.4
							Pd ₂₀ Sn ₁₃	59.6	39.5	0.8
20	2Pd+Sn+0.5Te	57.14	28.57	14.29	1752	Pd ₂₀ Sn ₁₃ + Pd(Te,Sn) + Pd ₂ (Sn,Te)				
30	73Pd+16Sn+13Te	71.57	15.69	12.74	2784	B + traces Pd ₃ Sn	B	72.0	16.2	11.7
							Pd ₃ Sn	75.7	24.3	0.0
31	7Pd+4Sn+Te	58.33	33.33	8.33	1920	Pd ₂₀ Sn ₁₃ + Pd(Te,Sn)	Pd ₂₀ Sn ₁₃	61.7	38.3	0.0
32	3Pd+Sn+2Te	50	16.67	33.33	840	Pd(Te,Sn) + Pd ₂ (Sn,Te)	Pd(Te,Sn)	49.7	15.9	34.4
39	5Pd+Sn+2Te	62.5	12.5	25	1032	Pd ₂ (Sn,Te) + A + PdTe	A	68.1	10.9	21.0
							Pd ₂ (Sn,Te)	66.8	29.7	3.6
43	14Pd+5Sn+1Te	70	25	5	1032	Pd ₂ (Sn,Te) + B + (Pd ₃ Sn?)	B	71.8	16.6	11.5
							Pd ₂ (Sn,Te)	66.3	29.8	3.9
45	3Pd+2Sn+2.5Te	40	26.67	33.33	560	Pd ₂₀ Sn ₁₃ + C + Pd(Te,Sn)	C	34.0	31.0	35.1
							Pd ₂₀ Sn ₁₃	60.1	0.7	39.3
							Pd(Te,Sn)	47.5	19.2	33.3
46	SnTe+2Pd	50	25	25		Pd ₂₀ Sn ₁₃ + Pd(Te,Sn) + C	Pd(Te,Sn)	45.5	19.4	35.1
48	11Pd+1Sn+6Te	61.11	5.56	33.33	1680	A + Pd ₃ Te ₂ + PdTe	A	66.5	10.5	23.1
55	18Pd+8Sn+2.58Te	62.98	27.99	9.03	528	Pd ₂ (Sn,Te) + Pd(Te,Sn)				
56	39Pd+6Sn+5Te	78	12	10	1680	Pd ₃ Sn + Pd ₁₇ Te ₄ (?)	Pd ₁₇ Te ₄	81.3	0.0	18.7
58	68Pd+15Sn+17Te	68	15	17	864	Pd ₂ (Sn,Te) + B + A	A	67.6	10.7	21.6
							B	71.7	16.8	11.5
							Pd ₂ (Sn,Te)	67.3	28.6	4.0
59	68Pd+5Sn+27Te	68	5	27	864	A + Pd ₉ Te ₄ + (Pd ₃ Te ₂ ?)				
69	Pd+Sn+2Te	25	25	50	528	SnTe + Pd(Te,Sn) ₂ + C	C	33.9	30.8	35.3
80	3Pd+2Sn+Te	50	33.33	16.67	648	Pd ₂₀ Sn ₁₃ + C + Pd(Te,Sn)				
85	7Pd+10Te+33Sn	35	50	15	664	PdSn + SnTe				
87	7Pd+1Sn+2Te	70	10	20	664	A + B + Pd ₂₀ (Te,Sn) ₇	A	67.2	10.9	21.9
							B	72.1	15.5	12.4
							Pd ₂₀ (Te,Sn) ₇	73.7	3.9	22.4
88	Pd+0.4Sn+2Te	29.41	11.76	58.82	688	SnTe + Pd(Te,Sn) ₂ + C	Pd(Te,Sn) ₂	33.4	3.3	63.3
89	37Pd+10Sn+3Te	74	20	6	912	Pd ₃ Sn + B + Pd ₂₀ (Te,Sn) ₇	Pd ₃ Sn	75.3	24.2	0.5
							B	72.0	15.8	12.3
90	15Pd+Sn+4Te	75	5	20	1680	Pd ₃ Sn + Pd ₂₀ (Te,Sn) ₇ + Pd ₁₇ Te ₄ (?)	Pd ₃ Sn	74.9	24.6	0.5
							Pd ₂₀ (Te,Sn) ₇	73.3	4.1	22.6
91	8.6Pd+Sn+10.4Te	43	5	52	688	Pd(Te,Sn) + Pd(Te,Sn) ₂	Pd(Te,Sn) ₂	33.5	2.9	63.6
							Pd(Te,Sn)	48.8	6.6	44.6
93	33Pd+7Sn+60Te	33	7	60	520	C + Pd(Te,Sn) ₂	Pd(Te,Sn) ₂	33.3	3.5	63.2
104	22.9Pd+9.7Sn+17.4Te	45.8	19.4	34.8	2904	Pd(Te,Sn) + C				
107	14Pd+1Sn+5Te	70	5	25	2784	A + Pd ₉ Te ₄ + Pd ₂₀ Te ₇				
108	7Pd+4Sn+9Te	35	20	45	2784	C + Pd(Te,Sn) ₂ + Pd(Te,Sn)				
111	6Pd+Sn+2Te	66.67	11.11	22.22	2784	A (Pd ₆₇ Sn ₁₁ Te ₂₂)	A	67.2	11.0	21.8
112	71Pd+7Sn+22Te	71	7	22	1752	A + B + Pd ₂₀ (Te,Sn) ₇	A	66.7	11.4	21.9
							B	72.1	15.6	12.3
							Pd ₂₀ (Te,Sn) ₇	74.1	3.6	22.3
113	73Pd+10Sn+17Te	73	10	17	1752	Pd ₃ Sn + B + Pd ₂₀ (Te,Sn) ₇	B	72.1	16.1	11.9
							Pd ₃ Sn	75.1	24.5	0.4
							Pd ₂₀ (Te,Sn) ₇	74.2	3.8	22.0
122	74Pd+13Sn+13Te	74	13	13	2112	Pd ₃ Sn + B + Pd ₂₀ (Te,Sn) ₇	B	71.8	16.2	12.1
							Pd ₂₀ (Te,Sn) ₇	73.4	3.9	22.7
123	SnTe+2PdTe	33.33	16.67	50	1008	C + Pd(Te,Sn) ₂				
135	67Pd+11Sn+22Te	67	11	22	1720	A	A	67.4	10.6	22.0
136	34Pd+31Sn+35Te	34	31	35	1720	C + traces Pd ₂₀ Sn ₁₃	C	33.3	31.1	35.6
137	72Pd+16Sn+12Te	72	16	12	1720	B + traces Pd ₃ Sn	B	71.7	15.0	13.3
							Pd ₃ Sn	74.6	24.8	0.6
138	68Pd+10Sn+22Te	68	10	22	1720	A + Pd ₂₀ (Te,Sn) ₇	A	67.6	10.7	21.8
611	PdTe+Sn	33.33	33.33	33.33	1728	C (+ traces SnTe, Pd ₃₀ Sn ₁₃)	C	33.8	32.5	33.6
612	Pd+SnTe	33.33	33.33	33.33	1728	C (+ traces SnTe)	C	34.1	31.9	34.1

TABLE 1 (cont'd). RESULTS OF REPRESENTATIVE EXPERIMENTAL RUNS IN THE SYSTEM Pd–Sn–Te AT 400°C

Run No.	Starting material	Initial composition (at.%)			Time hrs	Phase assemblages produced at 400°C	Electron-microprobe data (at.%)			
		Pd	Sn	Te			Phase	Pd	Sn	Te
613	PdSn+1.5Te	28.57	28.57	42.86	1728	SnTe + Pd(Te,Sn) ₂ + C	C	33.3	32.2	34.5
							SnTe	0.1	49.0	50.9
615	1.5PdTe+Sn	37.5	25	37.5	1728	Pd(Te,Sn)+ C + Pd(Te,Sn) ₂	C	33.4	1.5	65.1
							Pd(Te,Sn) ₂	33.6	32.5	33.9
617	PdTe+1.3Sn	30.30	39.39	30.30	1728	Pd ₂₀ Sn ₁₃ + SnTe + C	C	33.7	0.3	66.0
							Pd ₂₀ Sn ₁₃	33.7	32.6	33.6
619	1.5Pd+SnTe	42.86	28.57	28.57	1728	Pd ₂₀ Sn ₁₃ + C + Pd(Te,Sn)	C	59.3	40.4	0.3
							SnTe	0.0	49.0	50.9
652	4PdSn+PdTe	50	40	10	1728	Pd ₂₀ Sn ₁₃ + SnTe + C	C	33.8	31.6	34.6
							Pd ₂₀ Sn ₁₃	61.3	38.0	0.7
653	2PdTe+Sn	40	20	40	1728	Pd(Te,Sn)+ C + Pd(Te,Sn) ₂	Pd(Te,Sn)	47.6	19.3	33.2
							C	33.9	32.2	33.9
654	2.5PdTe+Sn	41.67	16.67	41.67	1728	Pd(Te,Sn)+ C + Pd(Te,Sn) ₂	Pd(Te,Sn) ₂	33.8	0.3	65.9
							C	47.8	18.5	33.8
655	PdSn+3PdTe	50	12.5	37.5	1728	Pd(Te,Sn) + Pd ₂ (Sn,Te)	C	34.3	31.3	34.4
							Pd(Te,Sn) ₂	33.6	0.9	65.5
							Pd(Te,Sn)	47.2	18.3	34.5
							Pd(Te,Sn)	49.4	12.0	38.6
							Pd ₂ (Sn,Te)	66.3	30.6	3.2

Abbreviation: A: ternary phase Pd₆₇Sn₁₁Te₂₂, B: ternary phase Pd₇₂Sn₁₆Te₁₂, C: ternary phase PdSnTe, ss: solid solution.

Differential thermal analysis

Selected experimental products were examined using differential thermal analysis (DTA). A test sample (100–150 mg) and reference material were placed into specially shaped silica tubes (Kullerud 1971), sealed under vacuum conditions and heated using a Derivatograph Q-1500 (Faculty of Science, Charles University). The conditions of analysis were: rate of heating: 2.5°C/minute, temperature range: 20 to 900°C, reference material: pure tin with an index temperature of 231°C (melting point of Sn). The temperature scale was calibrated using the temperature of melting for Sn (231°C), Zn (420°C), Al (660°C) and the phase transition of SiO₂ (573°C). The DTA output gave additional information on the samples with regard to phase transitions and melting. The recorded thermal effects, which were interpreted on the basis of prior knowledge of the phase relations under investigation, were verified experimentally.

EXPERIMENTAL RESULTS AND DISCUSSION

Only relevant results (selected from a total of 160 runs) are given in Table 1 and plotted in Figure 1. On the basis of experiments performed and background information on binary systems, the 400°C “condensed” isothermal section (stable assemblages coexisting with a vapor phase are not shown) for the system Pd–Sn–Te is presented in Figure 1. Back-scattered electron images of

selected experimental runs representing the phase associations are shown in Figure 2. At 400°C, the following nineteen univariant assemblages were found to be stable; the subscript “ss” indicates a solid solution: (Sn(liq) + SnTe + PdSn₂, PdSn₂ + SnTe + PdSn, PdSn + SnTe + Pd₂₀Sn₁₃, SnTe + Te + PdTe₂, SnTe + Pd(Te,Sn)_{2ss} + PdSnTe, SnTe + Pd₂₀Sn₁₃ + PdSnTe, Pd₂₀Sn₁₃ + PdSnTe + Pd(Te,Sn)_{ss}, PdSnTe + Pd(Sn,Te)_{2ss} + Pd(Te,Sn)_{ss}, Pd₂₀Sn₁₃ + Pd₂(Sn,Te)_{ss} + Pd(Te,Sn)_{ss}, Pd₂(Sn,Te)_{ss} + PdTe + Pd₆₇Sn₁₁Te₂₂, PdTe + Pd₆₇Sn₁₁Te₂₂ + Pd₃Te₂, Pd₆₇Sn₁₁Te₂₂ + Pd₃Te₂ + Pd₆Te₄, Pd₆₇Sn₁₁Te₂₂ + Pd₆Te₄ + Pd₂₀Te₇, Pd₂(Sn,Te)_{ss} + Pd₆₇Sn₁₁Te₂₂ + Pd₇₃Sn₁₄Te₁₃, Pd₂(Sn,Te)_{ss} + Pd₇₃Sn₁₄Te₁₃ + Pd₃(Sn,Te)_{ss}, Pd₇₃Sn₁₄Te₁₃ + Pd₆₇Sn₁₁Te₂₂ + Pd₂₀(Te,Sn)_{7ss}, Pd₃(Sn,Te)_{ss} + Pd₇₃Sn₁₄Te₁₃ + Pd₂₀(Te,Sn)_{7ss}, Pd₃(Sn,Te)_{ss} + Pd₂₀(Te,Sn)_{7ss} + Pd₁₇Te₄, Pd₃Sn + Pd₁₇Te₄ + Pd.

Binary phases unknown as minerals coexist with phases that do occur naturally. These associations can be expected to occur in nature. For example, SnTe coexists with merenskyite, Pd₃Te₂ with kotulskite and telluropalladinite, Pd₂₀Te₇ with telluropalladinite, and Pd₂₀Sn₁₃ with paolovite and kotulskite.

This study proved the existence of five ternary solid-solutions in which tin substitutes for tellurium. The ranges of solid solutions are depicted in Figure 1, and the data are given in Table 1. The phase PdTe, analogue of kotulskite, dissolves up to 19 at.% Sn; the phase PdTe₂, analogue of merenskyite, dissolves up to 3.5 at.% Sn; the phase Pd₂₀Te₇ dissolves up to 4 at.% Sn. Palladium–tin phases form limited solid-solutions;

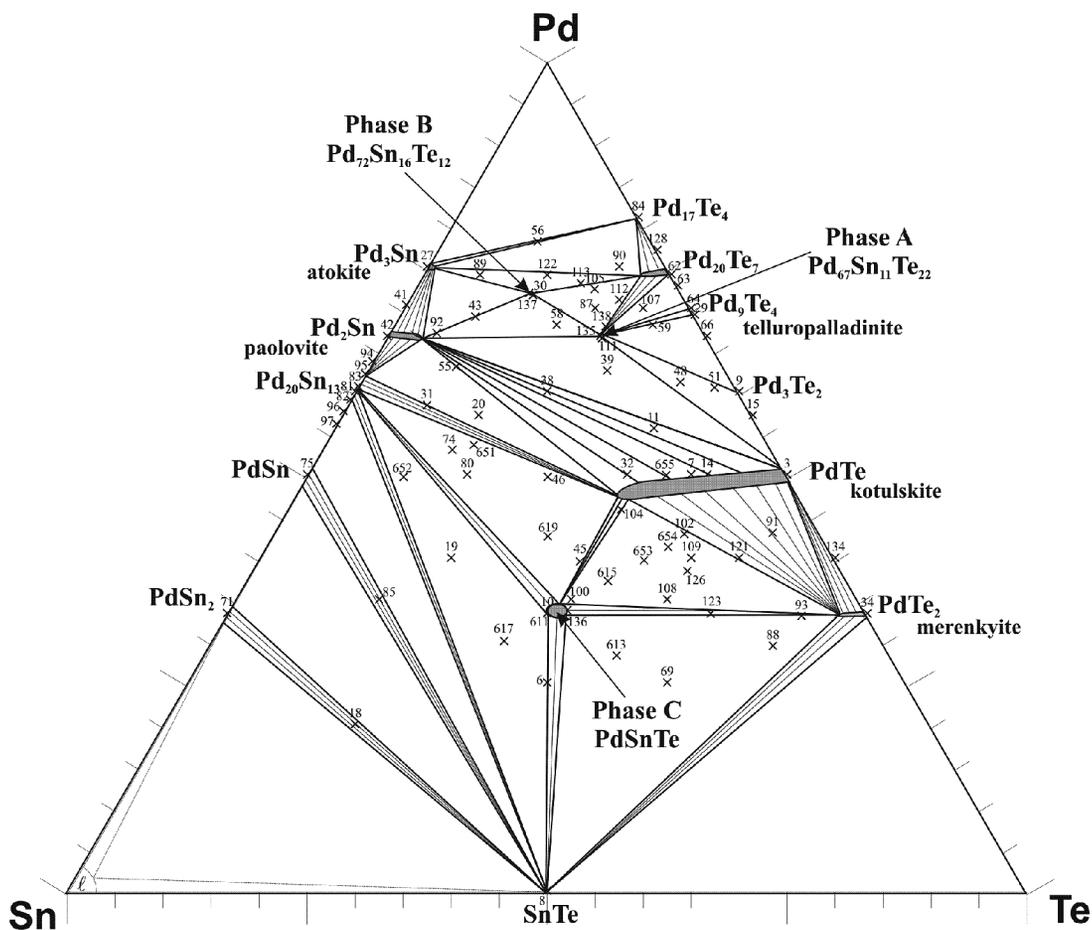


FIG. 1. Isothermal section of the ternary phase diagram of the system Pd–Sn–Te at 400°C and plot of representative experimental runs, according to the initial composition of experimental charges (at.%) (Table 1). Experiments performed in the corresponding binary systems are listed in the companion paper (Vymazalová & Drábek 2010).

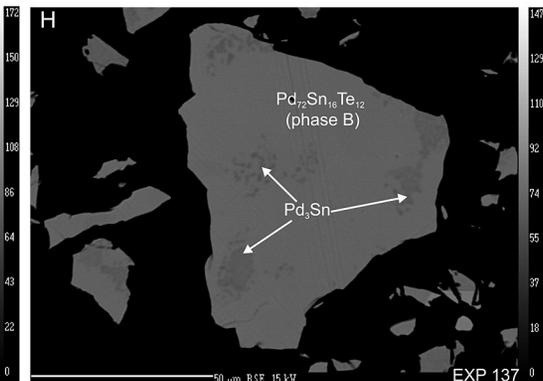
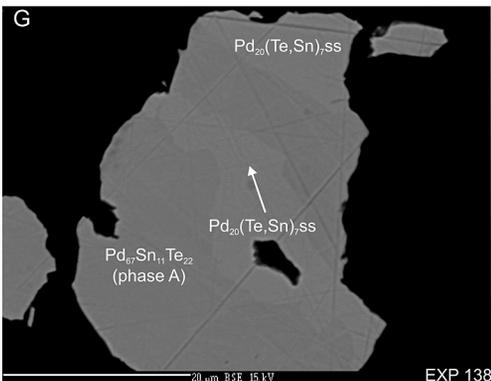
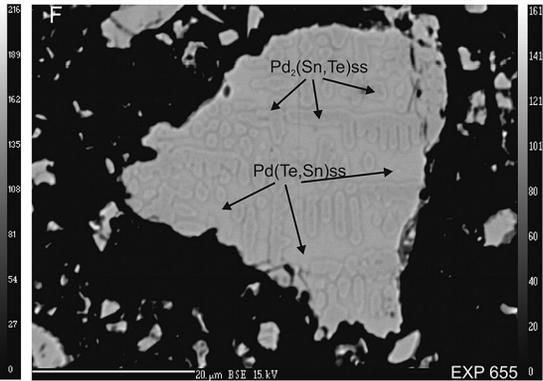
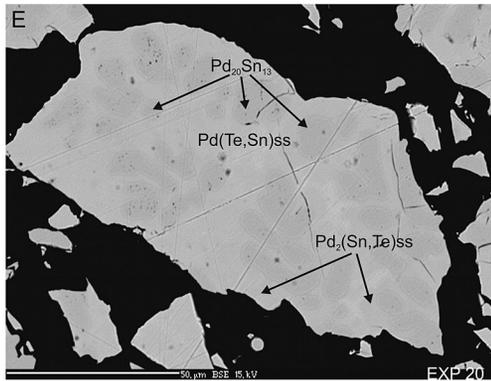
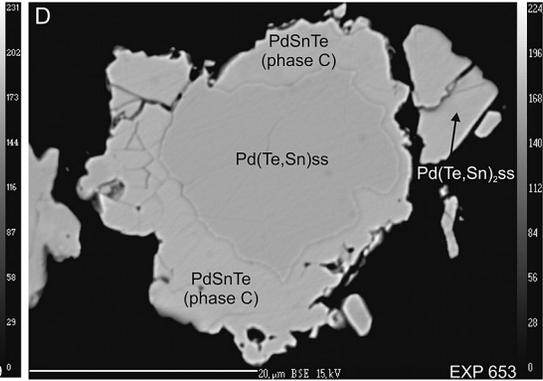
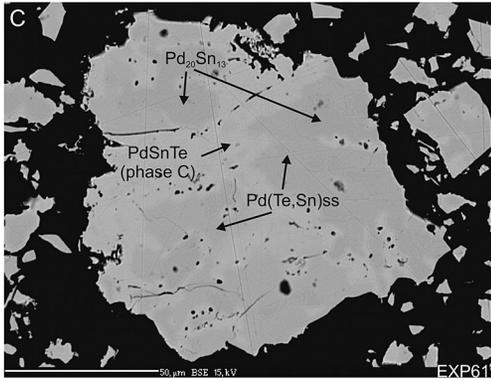
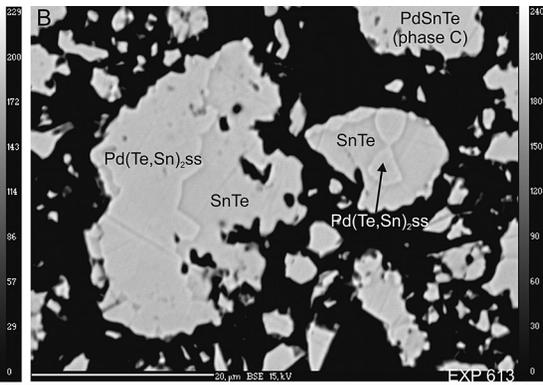
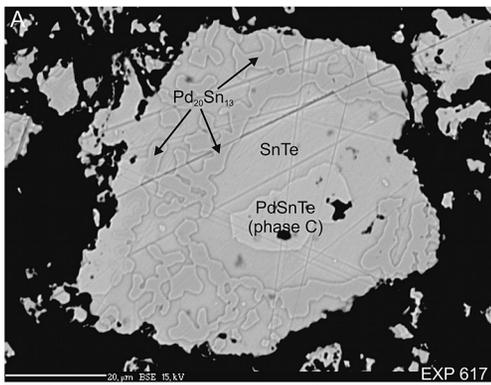
the phase Pd₃Sn, analogue of atokite, dissolves up to 0.5 at.% Te, and the phase Pd₂Sn, analogue of paolovite, dissolves up to 4 at.% Te. The ternary phases Pd₇₃Sn₁₀Te₁₇ and Pd₇₁Sn₇Te₂₂, reported by El-Boragy & Schubert (1971), were not identified in this work. The experiments with the corresponding initial composition (runs 112 and 113, Table 1) resulted in a three-phase mixture (see Fig. 1). Observations by El-Boragy & Schubert (1971) could reflect the initial composition that did not react properly owing to the short time of heating.

A large number of experiments were performed, particularly in the compositional range Pd₂₀Sn₁₃ – PdTe – PdTe₂ – PdSnTe. The experimental products are extremely fine-grained, and the phases are intimately intergrown with each other. Therefore, it is very difficult to distinguish and analyze the separate phases. In addition,

it seems that the phase Pd₂₀Sn₁₃ has exsolved in some cases during the cooling (even very rapid) in the field of PdSnTe (phase C) – PdTe₂ – Pd(Te,Sn)_{ss}. This problem caused some uncertainties in the evaluation of experimental products in this range. Therefore, the related experiments were repeated several times. The tielines Pd₂₀Sn₁₃ – Pd(Te,Sn)_{ss}, Pd(Te,Sn)_{ss} – PdTe₂, and PdSnTe (phase C) – Pd(Te,Sn)_{ss} seem to be confirmed (Table 1).

Ternary phases

This study revealed the existence of three ternary phases in the system: Pd₆₇Sn₁₁Te₂₂, Pd₇₂Sn₁₆Te₁₂ and PdSnTe, denoted as A, B and C, respectively. From the phase diagram (Fig. 1), it is apparent that the ternary phases coexist with phases known to exist as minerals



in this system. For example, PdSnTe coexists with merenskyite and kotulskite; Pd₆₇Sn₁₁Te₂₂ forms a stable assemblage with kotulskite and paolovite, and coexists with telluropalladinite. In addition, Pd₇₂Sn₁₆Te₁₂ forms a stable assemblage with paolovite and atokite. These associations can be expected to occur in nature.

Phase A, ideally Pd₆₇Sn₁₁Te₂₂, forms a narrow solid-solution. The Pd content varies in the range 66.5–68.1 at.%, the Sn content varies between 10.5 and 11.4 at.%, and the Te content varies in the range 21.0–23.1 at.% (Table 1). In reflected light, phase A is creamy with a pinkish tint. It is distinctly to strongly anisotropic (grey to blue to orange brown).

The X-ray powder-diffraction data for phase A (Pd₆₇Sn₁₁Te₂₂) are in an accordance with the structural model proposed by Savič *et al.* (2005) for modulated Pd_{7-δ}SnTe₂ (0.3 ≤ δ ≤ 0.8), which is tetragonal, space group *I4/mmm*, and *a* = 4.001(2), *c* = 20.929(3) Å. In this study, the parameters *a* = 4.006(1), *c* = 20.8121(4) Å were calculated for the average structure of the A phase.

The upper stability limit of phase A lies at ~596°C, where it melts incongruently to the high-temperature polymorph of the B phase and PdTe. A quench from 800°C (run 111, 552 hrs) resulted in a mixture of a high-temperature modification of phase B and PdTe (electron-microprobe and X-ray powder-diffraction data).

Phase B, ideally Pd₇₂Sn₁₆Te₁₂, forms a limited solid-solution at 400°C. The Pd content varies between 71.7 and 72.2 at.%, the Sn content, between 15.0 and 16.8 at.%, and the Te content, in the range 11.5 and 13.3 at.% (Table 1). In reflected light, phase B is white with a distinct anisotropy (bluish grey to brown).

The observed *d* values (and relative intensities) of phase B (run 30) at 400°C are given in Table 2. Our evaluation of the X-ray powder-diffraction data, in terms of crystal-structure determination and peak indexing, was not successful. The crystal structure assumed by El-Boragy & Schubert (1971) for

Pd₇₃Te₁₀Te₁₇, isotypic with Pd₈Sb₃, could not be applied to phase B (quenched at 400°C). Self-indexing did not succeed. Some difficulties in evaluation of the X-ray data for phase B may have been caused by the presence of Pd₃Sn in the sample.

Phase B undergoes a phase transformation at ~753°C and does not melt up to ~900°C. The X-ray powder-diffraction data of phase B quenched from 800°C (552 hrs) confirm the existence of a high-temperature polymorph. The high-temperature modification of phase B has a hexagonal cell, with space group *P6₃cm*, *a* = 7.6456(3), *c* = 13.9575(9) Å (Laufek *et al.* 2007).

Phase C, ideally PdSnTe, actually varies in the ranges 33.3–34.3 at.% Pd, 30.8–32.6 at.% Sn and 33.6–35.6 at.% Te (Table 1).

In reflected light, phase C is grey with a yellowish tint, is markedly birefractant (light to dark grey) and weakly anisotropic (from grey to brownish grey).

The crystal structure of PdSnTe was determined by Laufek *et al.* (2009); it is orthorhombic, space group *Pbca*, with unit-cell parameters *a* = 6.5687(2), *b* = 6.6028(2), and *c* = 12.8849(4) Å. Phase C breaks down at 588°C to SnTe, Pd₂₀Sn₁₃ and Pd(Te,Sn)_{ss}.

TABLE 2. X-RAY POWDER-DIFFRACTION DATA (OBSERVED) FOR THE B PHASE, QUENCHED FROM 400°C (run 30)

<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>	<i>d</i> (Å)	<i>I</i>
10.42	7	1.9486	9	1.2755	16
5.21	5	1.9298	10	1.2726	6
3.92	2	1.8879	13	1.2632	6
3.68	3	1.8668	14	1.2513	5
3.59	5	1.8274	6	1.2457	5
3.47	8	1.8203	5	1.2359	8
3.35	8	1.7779	5	1.2281	9
3.14	3	1.7373	17	1.2245	7
3.09	3	1.7128	8	1.2185	13
2.988	5	1.6789	3	1.2155	7
2.892	9	1.6713	3	1.2124	7
2.837	9	1.6546	1	1.1991	37
2.784	5	1.6494	1	1.1959	2
2.727	9	1.6309	2	1.1893	15
2.693	11	1.6048	4	1.187	15
2.606	8	1.5777	17	1.1845	2
2.564	8	1.5696	16	1.1482	21
2.489	30	1.5293	2	1.1449	14
2.466	19	1.5227	4	1.1384	12
2.444	17	1.5103	4	1.1357	1
2.424	48	1.5052	1	1.1343	8
2.398	18	1.4751	11	1.1269	5
2.354	11	1.4409	26	1.1243	1
2.294	100	1.4202	25	1.1029	7
2.272	62	1.406	35	1.0938	5
2.252	76	1.3877	21	1.0832	4
2.206	69	1.3834	17	1.0679	3
2.186	48	1.3665	2	1.0595	3
2.128	30	1.3426	4	1.0579	5
2.084	48	1.3283	5	1.0559	5
2.021	33	1.3154	9	1.0498	5
2.002	36	1.3097	13	1.0469	4
1.9877	94	1.2833	17	1.0391	3

FIG. 2. Back-scattered electron images of selected products of experiments showing the phase relations and associations. (A) Ternary phase C, ideally PdSnTe, in association with Pd₂₀Sn₁₃ and SnTe, run 617. (B) Phase C in association with SnTe and Pd(Te,Sn)_{2ss}, run 613. (C) Phase C in association with Pd₂₀Sn₁₃ and Pd(Te,Sn)_{ss}, run 619. (D) Phase C in association with Pd(Te,Sn)_{ss} and Pd(Te,Sn)_{2ss}, run 653. (E) Fine intergrowths of Pd₂₀Sn₁₃, Pd₂(Sn,Te)_{ss} and Pd(Te,Sn)_{ss}, run 20. (F) Solid solutions Pd(Te,Sn) and Pd(Te,Sn)₂, run 655. (G) Ternary phase A, ideally Pd₆₇Sn₁₁Te₂₂, and Pd₂₀(Te,Sn)_{7ss}, run 138. (H) Ternary phase B, ideally Pd₇₂Sn₁₆Te₁₂, and with admixtures Pd₃Sn, run 137. For detailed characterization of runs, see Table 1 and Figure 1; ss: solid solution.

CONCLUSIONS

1. The experiments performed allowed us to specify the phase relations in the ternary system Pd–Sn–Te at 400°C. The experiments also provided useful data concerning the ranges of solid solutions.

2. Three ternary phases were identified in the system: phase A: Pd₆₇Sn₁₁Te₂₂, phase B: Pd₇₂Sn₁₆Te₁₂, and phase C: PdSnTe. Phase B has low- and high-temperature polymorphs.

3. The existence of ternary phases with the compositions “Pd₇₃Sn₁₀Te₁₇” and “Pd₇₁Sn₇Te₂₂” suggested by El-Boragy & Schubert (1971) was not confirmed.

4. The binary (Pd₁₇Te₄, Pd₂₀Te₇, Pd₈Te₃, Pd₃Te₂, Pd₂₀Sn₁₃, PdSn, PdSn₂, and SnTe) and ternary (Pd₆₇Sn₁₁Te₂₂, Pd₇₃Te₁₄Te₁₃ and PdSnTe) phases of the system can be expected to occur in nature in close association with known Pd tellurides or Pd–Sn alloys. In particular, the presence of natural Pd–Sn and Pd–Te minerals (like atokite, paolovite, kotulskite, merenkyite and telluropalladinite) raises the probability of discovering Pd–Sn tellurides as minerals in nature.

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REFERENCES

- BALABONIN, N.L., KORCHAGIN, A.U., SUBBOTIN, V.V., NEDAROVSKY, YU.N., KARPOV, S.M., PAKHOMOVSKY YA.A. & SAVCHENKO E.Y. (2000): Platinum-group minerals and new data on mineralization of the Fedorovo–Pansky massif (Kola Peninsula, Russia). *Vestnik MGU* **3**(2), 179–204 (in Russian).
- BERLINCOURT, L.E., HUMMEL, H.H. & SKINNER, B.J. (1981): Phases and phase relations of the platinum-group elements. *In* Platinum Group Elements: Mineralogy, Geology, Recovery (L.J. Cabri, ed.). *Can. Inst. Mining Metall., Spec. Vol.* **23**, 19–45.
- CABRI, L.J. (2002): The platinum-group minerals. *In* The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements (L.J. Cabri, ed.). *Can. Inst. Mining Metall., Spec. Vol.* **54**, 13–129.
- EL-BORAGY, M. & SCHUBERT, K. (1971): Über einige Varianten der NiAs-Familie in Mischungen des Palladiums mit B-Elementen. *Z. Metallkd.* **62**, 314–323.
- EVSTIGNEEVA, T.L. & NEKRASOV, I.Y. (1980): Conditions of phase synthesis and phase relations in the systems Pd₃Sn–Cu₃Sn and Pd–Sn–Cu–HCl. *In* Sketches of Physico-chemical Petrology **10** (V.A. Zharikov & V.A. Fed'kin, eds.). Nauka, Moscow, Russia (20–35; in Russian).
- KULLERUD, G. (1971): Experimental techniques in dry sulfide research. *In* Research Techniques for High Pressure and High Temperature (G.C. Ulmer, ed.). Springer-Verlag, New York, N.Y. (288–315).
- LAUFEK, F., VYMAZALOVÁ, A., NAVRÁTIL, J., DRÁBEK, M., PLÁŠIL, J. & PLECHÁČEK, T. (2009): Synthesis and crystal structure of PdSnTe. *J. Alloys Compounds* **468**, 69–72.
- LAUFEK, F., VYMAZALOVÁ, A. & PLÁŠIL, J. (2007): Crystal structure and powder diffraction pattern of high-temperature modification of Pd₇₃Sn₁₄Te₁₃. *J. Powder Diffraction* **22**, 334–339.
- LI, CHUSI & NALDRETT, A.J. (1993): Platinum-group minerals from the Deep Copper zone of the Strathcona deposit, Sudbury, Ontario. *Can. Mineral.* **31**, 31–44.
- MAKOVICKY, E. (2002): Ternary and quaternary phase systems with PGE. *In* The Geology, Geochemistry, Mineralogy and Mineral Beneficiation of Platinum-Group Elements (L.J. Cabri, ed.). *Can. Inst. Mining Metall., Spec. Vol.* **54**, 131–175.
- MASSALSKI, T.B. (1990): *Binary Alloy Phase Diagrams* **3** (2nd ed.). ASM International, Materials Park, Ohio (3049–3051).
- OKAMOTO, H. (1992): The Pd–Te system (palladium – tellurium). *J. Phase Equilibria* **13**, 73–78.
- ONDRUŠ, P. (2000): ZDS – *Software for Analysis of X-Ray Powder Diffraction Patterns*. ZDS Systems Inc., Prague, Czech Republic.
- RODRIGUEZ-CARVAJAL, J. (2001): FULLPROF.2k Rietveld, Profile Matching & Integrated Intensities Refinement of X-ray and/or Neutron Data (powder and/or single-crystal). Laboratoire Léon Brillouin, Centre d'Études de Saclay, Gif-sur-Yvette Cedex, France. [ftp://charybde.saclay.cea.fr/pub/divers/fullp](http://charybde.saclay.cea.fr/pub/divers/fullp).
- SAVILOV, S.V., KUZNETSOV A.N., POPOVKIN, B.A., KHRUSTALEV, V.N., SIMON, P., GETZSCHMANN, J., DOERT, T. & RUCK, M. (2005): Synthesis, crystal structure and electronic structure of modulated Pd_{7–8}SnTe₂. *Z. Anorg. Chem.* **631**, 293–301.
- SHARMA, R.C. & CHANG, Y.A. (1986): The Sn–Te (tin–tellurium) system. *Bull. Alloy Phase Diagrams* **7**, 72–80.
- VYMAZALOVÁ, A. & DRÁBEK, M. (2010): The system Pd–Sn–Te at 400°C and mineralogical implications. I. The binary phases. *Can. Mineral.* **48**, 1041–1050.

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