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The system Ag–Pd–Te: phase relations and mineral assemblages

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ABSTRACT

The phase equilibria in the system Ag–Pd–Te were studied by the technique of using an evacuated silica glass tube at 350° and 450°C. Five ternary phases were synthesized: sopcheite ($Pd_3Ag_4Te_4$), lukkulaisvaaraite ($Pd_{14}Ag_2Te_9$), telargpalite ($Pd_{2-x}Ag_{1+x}Te$) and the previously unknown phases $Pd_{7.5-x}Ag_{0.5+x}Te_3$ and $Pd_{2+x}Ag_{2-x}Te$. The synthetic telargpalite has a compositional range from 26 to 29 wt.% Ag, with the formula $Pd_{2-x}Ag_{1+x}Te$, where x varies from 0.09 to 0.22. The phase $Pd_{2+x}Ag_{2-x}Te$ has a compositional range from 34 to 35 wt.% Ag, where x varies from 0.18 to 0.24. The phase $Pd_{7.5-x}Ag_{0.5+x}Te_3$ forms a solid solution from 4 to 11 wt.% Ag, where x varies from 0.02 to 0.83. Phases $Pd_{20}Te_7$ and $Pd_{13}Te_3$ dissolve up to 3.5 and 2 wt.% Ag, respectively. Other binary palladium tellurides do not dissolve Ag. The phase $Pd_3Ag_4Te_4$, an analogue of the mineral sopcheite, forms a stable association with hessite and kotulskite it also coexists with lukkulaisvaaraite. Sopcheite is stable up to 383°C. Natural occurrences of hessite, kotulskite and lukkulaisvaaraite together in equilibrium indicate formation above this temperature. Phase relations defined the mineral assemblages that can be expected to occur in nature. The phase $Pd_{7.5-x}Ag_{0.5+x}Te_3$ potentially represents a new mineral; it will probably be found in association with lukkulaisvaaraite and telargpalite or telluropalladinite, among other platinum-group minerals. The phase $Pd_{2+x}Ag_{2-x}Te$ can be found in association with telargpalite. Mineral assemblages defined in this study can be expected in Cu-Ni-PGE mineral deposits, associated with mafic and ultramafic igneous rocks, particularly in mineralized zones with known silver-palladium tellurides.

KEYWORDS: Ag–Pd–Te system, Ag–Pd tellurides, phase relations, phase diagram, platinum-group minerals, sopcheite, lukkulaisvaaraite, telargpalite.

Introduction

THE system Ag–Pd–Te contains seven binary and three ternary minerals, including a recently described mineral, lukkulaisvaaraite (Vymazalová *et al.*, 2014). In addition, there are potential new minerals within the binary system Pd–Te (Vymazalová and Drábek, 2010). Also, unnamed phases with compositions in the system Ag–Pd–Te have been reported in the literature (Kovalenker *et al.*, 1972, Grokhovskaya *et al.*, 1992). The phase relations in the system Ag–Pd–Te are clearly of mineralogical interest. Nevertheless, only the phase relations along the binary subsystems are described in the literature, and the ternary system Ag–Pd–Te had not been experimentally studied. In this contribution, we present the phase relations in the system Ag–Pd–Te and predict possible stable assemblages under natural conditions; we explore the mineralogical implications of our findings.

Minerals

In addition to the native elements Ag, Pd and Te, the system Ag–Pd–Te comprises seven platinum-group

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minerals (PGM) and three Ag tellurides: kotulskite (PdTe), merenskyite ($PdTe_2$), telluropalladinite (Pd_9Te_4), keithconnite ($Pd_{3-x}Te$), empressite (AgTe), stützite ($Ag_{5-x}Te_3$), hessite (Ag_2Te), sopcheite ($Pd_3Ag_4Te_4$), telargpalite ($Pd_{2-x}Ag_{1+x}Te$) and the recently described lukkulaisvaaraite ($Pd_{14}Ag_2Te_9$). Minerals belonging to the system Ag–Pd–Te are summarized in Table 1 and plotted in Fig. 1.

In nature, minerals belonging to the system Ag–Pd–Te occur in various geological environments. The tellurides of palladium occur commonly in Cu-Ni-PGE mineral deposits, associated with mafic and ultramafic igneous rocks in the well-known complexes in Sudbury, Bushveld and Noril'sk, among many others. The tellurides of Pd can be also found in a less traditional environment for platinum-group minerals, e.g. porphyry copper deposits (Tarkian and Stribrny, 1999; Economou-Eliopoulos and Eliopoulos, 2000).

Palladium-silver tellurides were reported from Noril'sk (e.g. Kovalenker *et al*., 1972, 1974; Genkin *et al*. 1981; Sluzhenikin and Mokhov, 2015); the Lukkulaisvaara layered intrusion (e.g. Begizov and Batashev, 1978; Grokhovskaya *et al.*, 1992; Barkov *et al.*, 2001), and the Burakovsky layered complex (Grokhovskaya *et al*., 2005), in Karelia; the Monchegorsky magmatic layered complex (Orsoev *et al.*, 1982; Grokhovskaya *et al*., 2003), and the Volchetundra gabbro-anorthosite pluton (Chashchin and Petrov, 2013) and in the Fedorova-Pana intrusion (Tolstykh and Krivenko, 1996) in the Kola Peninsula, in Russia. They are also known from Sudbury (Cabri and Laflamme, 1976; Pentek *et al.,* 2008), the Coldwell Complex (Mulja and Mitchell, 1990; Watkinson and Jones, 1996), the Lac des Iles Complex in Ontario (Dunning *et al*., 1984), Mechanic Settlement pluton in southern New Brunswick (Grammatikopoulos *et al.*, 2007), in Canada and the Salt Chuck intrusion in Alaska (Watkinson and Melling, 1992).

Methods and Techniques

Experimental

Experiments were performed in evacuated and sealed silica glass tubes in horizontal tube furnaces following the method of Kullerud (1971). To prevent loss of material to the vapour phase during experiments, the free space in the tubes was reduced by placing closely fitting glass rods over the charge. Temperatures were measured with Pt-PtRh thermocouples and are accurate to within ±3°C. Charges of 100 to 300 mg were carefully weighed out from the pure elements. The starting chemicals used were Ag powder (Aldrich, 99.999% purity), a Te ingot (Aldrich, 99.999% purity) and Pd powder (Aldrich, 99.95% purity). The starting mixtures were first melted at 1000°C for three days. Then, the resulting run products were ground in an agate mortar under acetone and reheated to 350°C (for 130 days) and at 450°C (90 days). After heating, quenching occurred by dropping the capsules in cold water. Phases in the run products were characterized by powder X-ray diffraction (XRD), in polished sections examined in reflected light, and with electron-microprobe techniques. A detailed examination of run products with a reflected light microscope (according to optical properties and shape) was essential prior to carrying out the electron-microprobe analyses of studied phases in order to avoid the analysis of mixtures. The experimental products are fine grained and generally intergrown. The phases are difficult to distinguish in backscattered electron spectroscopy mode. Therefore, photographs in reflected light were made prior to electron microprobe analysis (EMPA) analyses.

X-ray diffraction and differential thermal analysis

First each experimental product was studied with powder XRD. The XRD data were collected on a PANalyticalX´Pert diffractometer using Co$K\alpha$ radiation and a BRUKER diffractometer (Cu$K\alpha$ radiation, graphite monochromator). The data were collected over the angular range from 10 to 145°2θ. The unit-cell parameters were calculated using the whole-profile pattern fitting method by means of the *FullProf* program (Rodríguez-Carvajal, 2006).

Selected experimental products were examined using differential thermal analysis (DTA). A test sample (70–100 mg) and reference material were placed in silica tubes and sealed under vacuum and heated using a R.M.I.-DTA 003 (Electronic Measuring Instruments, Czech Republic). The conditions of analysis were: rate of heating 10°C/minute, temperature range: 25–800°C, reference material: pure Al_2O_3. The temperature scale was calibrated using Sn, Zn, Pb and Al. The DTA output gave additional information on the samples with regard to phase transitions and melting.

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TABLE 1. Minerals in the system Ag–Pd–Te and their crystal structure data.

Mineral		Crystal structure data		Unit-cell parameters				Reference
			Space group	*a* (Å)	*b* (Å)	*c* (Å)	β (°)	
Empressite	AgTe	orthorombic	*Pmnm* or *Pmn**	8.90	20.07	4.62		1,2
		orthorombic	*Pmnb*	8.882	20.100	4.614		3
Hessite	Ag_2Te	monoclinic	$P2_1/c$	8.09	4.48	8.96	123.20	4
Keithconnite†	$Pd_{3-x}Te$ $0.14 < x < 0.43$	hexagonal	$R\bar{3}$	11.45		11.40		5
Kotulskite	PdTe	hexagonal	$P6_3/mmc$	4.19		5.67		6
Lukkulaisvaaraite	$Pd_{14}Ag_2Te_9$	tetragonal	$I4/m$	8.9599		11.822		7
Merenskyite	$PdTe_2$	hexagonal	$P\bar{3}m1$	4.023		5.113		8,5
Sopcheite	$Pd_3Ag_4Te_4$	orthorombic		9.645	7.906	11.04		9
Stützite	$Ag_{5-x}Te_3$ $x < 0.11$	hexagonal	$C6/mmm$	13.38		8.45		1,2
		hexagonal	$P6/mmm$	13.49		8.48		10
Telargpalite	$(Pd,Ag)_{3+x}Te$ or $(Pd,Ag)_{4+x}Te$	cubic		12.6 or 3.168				11
	$Pd_{2-x}Ag_{1+x}Te$ $0 < x < 0.3$							12
Telluropalladinite	Pd_9Te_4	monoclinic	$P2_1/c$	7.45	13.94	8.82	91.9	5

References: [1]Honea (1964), [2]Cabri (1965), [3]Bindi *et al.* (2004), [4]Frueh (1959), [5]Cabri *et al.* (1979), [6]Genkin *et al.* (1963), [7]Vymazalová *et al.* (2014), [8]Kingston (1965), [9]Orsoev *et al.* (1982), [10]Berry and Thompson (1962), [11]Kovalenker *et al.* (1974), [12]Barkov *et al.* (2001).

†The synthetic phase $Pd_{20}Te_7$ is assigned as keithconnite in this study.

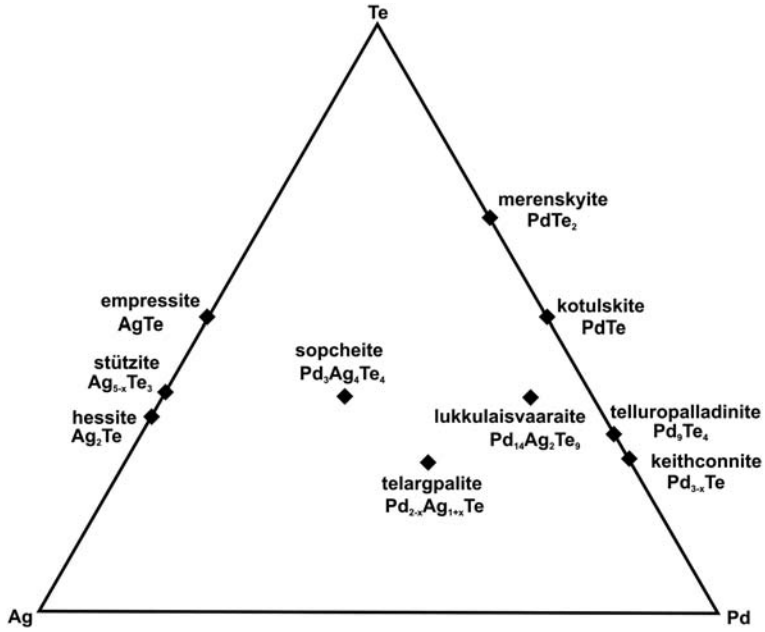


FIG. 1. Minerals in the system Ag–Pd–Te. Note that we assign the synthetic phase $Pd_{20}Te_7$ as keithconnite in this study.

Electron-microprobe analyses

Chemical analyses were performed with a CAMECA SX-100 electron probe microanalyser in a wavelength-dispersion mode using an electron beam focused to 1–2 μm. Pure elements were used as standards. Concentrations were quantified using Pd*L*α, Ag*L*β and Te*L*α (overlap correction on Pd*L*β) with an accelerating voltage of 15 keV and a beam current of 10 nA on the Faraday cup (with a count time 20 s on each element and 10 s on background). In a sample, compositional data were collected from several grains within a polished section and then averaged; MS Excel was used for the calculation of formulas and data evaluation.

Results and discussion

The system Ag–Pd–Te was studied at 350°C in detail, and representative experiments were performed at 450°C. Before tackling the ternary system, the binary phases were reinvestigated. The list of phases stable at 350°C and relevant crystallographic data are summarized in Table 2; a list of experimental runs with products are listed in Tables 3*a*, *b*. Experiments pertaining to the Pd–Te binary are plotted in the Pd–Te phase diagram (Fig. 2). Phase assemblages based on EPMA and powder XRD data are listed in Tables 3*a*, *b* and starting compositions are plotted in Fig. 3*a*. The isothermal section for 350°C is shown in Fig. 4*a*,*b*. At 350°C, the system contains five ternary compounds: $Pd_3Ag_4Te_4$ (sopcheite), $Pd_{14}Ag_2Te_9$ (lukkulaisvaaraite), $Pd_{2-x}Ag_{1+x}Te$ (telargpalite) with $0.09 < x < 0.22$, and new phases $Pd_{7.5-x}Ag_{0.5+x}Te_3$ with $0.02 < x < 0.83$ and $Pd_{2+x}Ag_{2-x}Te$ with $0.18 < x < 0.24$, summarized in Table 2. The EPMA data for the ternary phases studied are presented in Table 4.

Binary phases

The system Pd–Te

Binary Pd tellurides were investigated experimentally by, e.g. Medvedeva *et al.* (1961), Kim (1986), Kim *et al.* (1990), Chattopadhyay *et al.* (1986), Ipser and Schuster (1986), Kelm *et al.* (1990) and Vymazalová and Drábek (2010). However, there are still uncertainties with the Pd-rich phases (20–30 at.% Te), particularly concerning their stabilities and stoichiometry. We have performed new experiments in the system Pd–Te, focusing on phases $Pd_{20}Te_7$, Pd_8Te_3, Pd_7Te_3, Pd_9Te_4 at 350°C (Table 3*a*, Fig. 2). Owing to long-term kinetics, chemical similarity of phases $Pd_{20}Te_7$ and Pd_8Te_3, and Pd_7Te_3 and Pd_9Te_4, and some overlapping in

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TABLE 2. Synthetic phases in the system Ag–Pd–Te stable at 350°C and their crystal structure data.

Phase	Composition range Te (at.%)	Exp No	Composition	Crystal structure		Unit-cell parametrs				Primary reference
						a (Å)	*b* (Å)	*c* (Å)	β (°)	
$Pd_{13}Te_3$	18.4–19.4	228	$Pd_{13.05}Te_{2.95}$	cubic	$Fd\bar{3}m$	12.6761(5)				1*
$Pd_{20}Te_7$	25.6–27.4	265	$Pd_{20.01}Te_{6.99}$	rhombohedral	$R\bar{3}$	11.8205(2)		11.1669(2)		2*
		228	$Pd_{20.08}Te_{6.92}$			11.8261(6)		11.1523(6)		
		258	$Pd_{19.61}Te_{7.39}$			11.6210(2)		11.2647(3)		
Pd_9Te_4	30.9–31.5	261	$Pd_{8.91}Te_{4.09}$	monoclinic	$P2_1/c$	7.4496(3)	13.9295(5)	8.8315(4)	92.013(5)	3*
Pd_7Te_3	29.8–30.00	259	$Pd_{7.00}Te_{3.00}$	monoclinic		7.4394(6)	13.9209(8)	8.908(1)	92.25(1)	4,5*
Pd_3Te_2	40	264	$Pd_{3.00}Te_{2.00}$	orthorombic	*Cmcm*	3.8548(4)	12.681(1)	7.8988(8)		6*
PdTe	50.0–51.4	263	$Pd_{1.00}Te_{1.00}$	hexagonal	$P6_3/mmc$	4.1524(2)	4.1524(2)	5.6718(5)		7*
		17	$Pd_{0.98}Te_{1.02}$			4.1345(5)	4.1345(5)	5.6499(6)		
$PdTe_2$	66.7	262	$Pd_{1.00}Te_{2.00}$	hexagonal	$P\bar{3}m1$	4.0388(5)	4.0388(5)	5.1431(6)		8*
$Ag_{5-x}Te_3$	37.6–38.4	4	$Ag_{4.96}Te_{3.04}$	hexagonal	*P6/mmm*	13.460(1)		8.4597(8)		9,10*
Ag_2Te	33.3	5	$Ag_{2.00}Te_{1.00}$	monoclinic	$P2_1/c$	8.1637(7)	4.4687(4)	8.9747(6)	124.118(8)	11*
γ phase ($Ag_{1.9}Te$)	34.4–34.7[12]	29	$Ag_{1.90}Te_{1.00}$							12,10
$Pd_3Ag_4Te_4$		12	$Pd_{3.01}Ag_{3.91}Te_{4.08}$	orthorombic	*Cmca*	12.2226(8)	6.1480(4)	12.2398(8)		13
$Pd_{14}Ag_2Te_9$		47	$Pd_{13.95}Ag_{1.94}Te_{9.11}$	tetragonal	*I*4/*m*	8.9599(6)		11.822(1)		14
$Pd_{2-x}Ag_{1+x}Te$	$Pd_{1.91-1.78}Ag_{1.09-1.22}Te$	19	$Pd_{1.82}Ag_{1.21}Te_{0.97}$	tetragonal	?	5.9028(2)		9.638(2)		*
$Pd_{2+x}Ag_{2-x}Te$	$Pd_{2.18-2.24}Ag_{1.82-1.76}Te$	35	$Pd_{2.24}Ag_{1.78}Te_{0.98}$	hexagonal	?	4.621(3)		14.281(9)		*
$Pd_{7.5-x}Ag_{0.5+x}Te_3$	$Pd_{7.48-6.67}Ag_{0.52-1.33}Te_3$	49	$Pd_{7.06}Ag_{0.85}Te_{3.08}$	?						

References: [1]Janetzky and Harbrecht (2006), [2]Wopersnow and Schubert (1977), [3]Matkovic and Schubert (1978), [4]Kim (1986), [5]Kim *et al.* (1990), [6]Matkovic and Schubert (1977), [7]Thomassen (1929), [8]Groeneveld Meijer (1955), [9]Honea (1964), [10]Cabri (1965), [11]Schneider and Schultz (1991), [12]Kiukkola and Wagner (1957), [13]Laufek *et al.* (2013), [14]Vymazalová *et al.* (2014).
*Unit-cell parameters refined in this study.

XRD patterns, the existence of these phases was questioned or misinterpreted in some previous works.

The list of observed phases stable at 350°C, their chemical composition and crystallographic data are presented in Table 2. Figure 2 presents the Pd–Te phase diagram assessed by Okamoto (1992), indicating our findings at lower temperatures (350 and 450°C) (Tables 2,3). Okamoto (1992) evaluated previous studies in the system Pd–Te; he reported the Pd solvus lines to be contradictory, but considered data of Kim (1986) to be superior to those of Chattopadhyay *et al.* (1986) owing to longer annealing. He concluded that the solvus is tentative (dashed lines, Fig. 2). The phase $Pd_{17}Te_4$ (Kim, 1986; Kim *et al.,* 1990) is in fact the phase $Pd_{13}Te_3$ of Janetzky and Harbecht (2006), who also determined its crystal structure (Table 2). The run of starting composition '$Pd_{17}Te_4$' (exp. 266) and the run of starting composition '$Pd_{78}Te_{22}$' (exp. 228), (both heated for five months at 350°C) resulted in a two-phase assemblage: $Pd_{13}Te_3 + Pd_{20}Te_7$ (Table 3*a*). The phase Pd_8Te_3 was not confirmed to be stable at 350°C. This finding is in an agreement with the phase diagram proposed by Chattopadhyay *et al.* (1986), Ipser and Schuster (1986) and Okamoto (1992), who observed the phase Pd_8Te_3 above 563°C (Fig. 2). The phase $Pd_{20}Te_7$ forms a solid solution range from 25.6 to 27.4 at.% Te (from $Pd_{20.11}Te_{6.86}$ to $Pd_{19.61}Te_{7.39}$) at 350°C. It is worth noting the difference in the unit-cell parameters between endmembers of this solid solution (see Table 2); the difference in the *a* parameter reaches 0.2 Å. The phase Pd_7Te_3 (exp. 259, heated for one month at 350°C) was confirmed to be stable at 350°C. Although its XRD pattern and unit-cell parameters are very similar to the monoclinic phase Pd_9Te_4 (which is also very close chemically), it is not the endmember of a solid solution of the phase Pd_9Te_4, as we assumed in our previous study (Vymazalová and Drábek, 2010). The XRD data for the phase Pd_7Te_3 (exp. 259) at 350°C are in an agreement with the data proposed by Kim (1986) and Kim *et al.* (1990) for the phase Pd_7Te_3 at 600°C. At 350°C, we also observed the phase Pd_9Te_4 to be stable. However, according to Okamoto (1992), it appears at 472°C in the system. The XRD data for the phase Pd_9Te_4 (exp. 261) are in an agreement with those of Matkovic and Schubert (1978), Kim *et al*. (1990) and Cabri *et al.* (1979). Comparative experiments with the same starting composition as exp. 261 and 302 revealed the same results. We thus assume the phase Pd_9Te_4 to be stable at a lower temperature. Nevertheless, it is shown as dotted in Fig. 2, as the reaction responsible for its formation is unclear.

At 350°C, we observed the following stable binary phases: $Pd_{13}Te_3$, $Pd_{20}Te_7$, Pd_7Te_3, Pd_9Te_4, Pd_3Te_2, PdTe and $PdTe_2$. The products of the binary experiments were also heated at 450°C for one month and the products were examined by XRD. The results were found to be in accordance with the experimental products at 350°C. Within the ternary system, the phases $Pd_{20}Te_7$ and $Pd_{13}Te_3$ dissolve up to 3.5 and 2 wt.% Ag, respectively. Other binary Pd tellurides do not dissolve Ag.

Minerals belonging to the system Ag–Pd–Te are summarized in Table 1. In the binary system Pd–Te, there are four known minerals: kotulskite (PdTe), merenskyite ($PdTe_2$), telluropalladinite (Pd_9Te_4) and keithconnite ($Pd_{3-x}Te$). As the synthetic analogue of keithconnite is still ambiguous, we have investigated our synthetic phases in terms of similarity with keithconnite. The chemical composition of keithconnite best fits a synthetic analogue of $Pd_{20}Te_7$, particularly in view of a new observation on its solid-solution range from $Pd_{20.11}Te_{6.86}$ to $Pd_{19.61}Te_{7.39}$. Cabri *et al.* (1979) described keithconnite in a space group ($R\bar{3}$) with lattice parameters similar to those of the synthetic phase $Pd_{20}Te_7$ (Tables 1,2). Comparison of both diffraction patterns reveals similarities to a certain extent, although not structural identity (Kim, 1986). It cannot be excluded that a content of Sn (up. to 4.5 wt %) (or other elements like As or Bi) detected in a natural sample by Cabri *et al.* (1979) may have influenced its diffraction pattern. As the variation in keithconnite stoichiometry is in agreement with a range of composition of synthetic $Pd_{20}Te_7$, we tentatively quote the synthetic phase $Pd_{20}Te_7$ and keithconnite in this study. Nevertheless, definite proof of their identity requires better XRD data for the natural material.

The system Ag–Te

In the system Ag–Te, there are three binary phases stable at 350°C (Kracek *et al.* 1966): Ag_2Te, $Ag_{5-x}Te_3$ with $x < 0.11$, and γ phase (assigned as $Ag_{1.9}Te$). The Ag:Te ratio of the γ phase, originally proposed by Kiukkola and Wagner (1957) and confirmed by Cabri (1965) and Kracek *et al.* (1966), ranges from 1.88 to 1.91. According to Kracek *et al.* (1966), the high-temperature β polymorphs of phases Ag_2Te and $Ag_{5-x}Te_3$ are reversible but not quenchable. It has been confirmed in our experiments; we therefore only observed the low-temperature α varieties: Ag_2Te (monoclinic $P2_1/c$), the

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TABLE 3*a*. Results of selected experimental runs in the binary systems Pd–Te and Ag–Te.

Run no.	Starting composition (at.%) Pd	Ag	Te	Phase assemblages at 350°C
				Pd–Te
228	78		22	$Pd_{13.01}Te_{2.99}$ + keithconnite $Pd_{20.08}Te_{6.92}$
258	72.72		27.27	keithconnite $Pd_{19.61}Te_{7.39}$ + $Pd_{7.03}Te_{2.97}$
259	70		30	$Pd_{7.00}Te_{3.00}$
261	69.23		30.77	teluropalladinite $Pd_{8.91}Te_{4.09}$
262	33.33		66.67	merenskyite $Pd_{1.00}Te_{2.00}$
263	50		50	kotulskite $Pd_{1.00}Te_{1.00}$
264	60		40	$Pd_{3.00}Te_{2.00}$
265	74.07		25.93	keithconnite $Pd_{20.01}Te_{6.99}$
266	80.98		19.05	$Pd_{13.04}Te_{2.96}$ + keithconnite $Pd_{20.11}Te_{6.89}$
300	42		58	kotulskite $Pd_{0.98}Te_{1.02}$ + merenskyite $Pd_{1.03}Te_{1.97}$
300	42		58	kotulskite $Pd_{0.96}Te_{1.04}$ + merenskyite $Pd_{1.06}Te_{1.94}$**
301	55		45	kotulskite $Pd_{1.00}Te_{1.00}$ + $Pd_{2.92}Te_{2.08}$
302	65		35	teluropalladinite $Pd_{8.84}Te_{4.16}$ + $Pd_{2.96}Te_{2.04}$
				Ag–Te
4		62.5	37.5	stützite $Ag_{4.97}Te_{3.03}$
5		66.67	33.33	hessite $Ag_{2.00}Te_{1.00}$
6		50	50	stützite $Ag_{4.93}Te_{3.06}$ + Te
29		65.52	34.48	γ-phase $Ag_{1.90}Te_{1.00}$

**Run product at 450°C.

analogue of mineral hessite, and $Ag_{5-x}Te_3$ (hexagonal *P*6/*mmm*), the analogue of the mineral stützite at a temperature of 350°C. The mineral empressite (AgTe) is only stable below 200°C, and synthesis of the phase by direct combination of elements is not possible (Honea, 1964; Cabri, 1965). Our attempt (heating at 100°C for 11 months, exp. 6, Table 3*a*) to prepare the AgTe phase was also unsuccessful. Within the ternary system, only Ag_2Te dissolves up to 0.6 wt.% Pd; other Ag tellurides do not dissolve Pd.

In the system Ag–Te, there is also the phase $AgTe_3$ that only becomes stable above 0.4 GPa (Range *et al.*, 1982). Nevertheless a natural occurrence of $AgTe_3$ was reported recently from the Yangzhaiyu Au-deposit, Xiaoqinling region in China by Jian *et al.* (2014).

The system Ag–Pd

Ruer (1906) was reported by Karakaya and Thompson (1988) to have proposed a complete solid solution on the Ag–Pd binary. The Ag content of the (Ag,Pd) solid solutions is given in Tables 3*b*, *c*.

Ternary phases

Sopcheite ($Pd_3Ag_4Te_4$)

The phase $Pd_3Ag_4Te_4$, the analogue of the mineral sopcheite, forms stable associations with hessite and kotulskite. Such mineral assemblages are also known to occur in nature, e.g. in PGE mineralization in the Monchegorsky magmatic layered complex, Kola Peninsula (Grokhovskaya *et al.*, 2003), in the Lac des Iles complex, Ontario (Dunning *et al.,* 1984) or in the Salt Chuck intrusion, Alaska (Watkinson and Melling, 1992). Sopcheite also coexists with lukkulaisvaaraite and kotulskite (Fig. 5*a*). The upper stability-limit of sopcheite lies at 383°C, at which point it breaks down to Ag_2Te, $Pd_{14}Ag_2Te_9$ and PdTe. The presence of sopcheite in a mineral assemblage reflects its formation below this temperature. Table 4 summarizes the EMPA data for synthetic sopcheite. The crystal structure of synthetic sopcheite was defined by Laufek *et al.* (2013); it is orthorhombic, space group *Cmca*, with unit-cell parameters $a = 12.2226(8)$, $b = 6.1480(4)$ and $c = 12.2398(8)$ Å (Table 2).

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TABLE 3*b*. Results of selected experimental runs in the system Pd–Ag–Te at 350°C.

Run no.	Starting composition (at.%)			Phase assemblages at 350°C		
	Pd	Ag	Te			
7	20	40	40	hessite $Ag_{2.01}Te_{0.99}$	kotulskite $(Pd_{0.99}Ag_{0.01})_{\sum 2.00}Te_{1.00}$	
8	20	50	30	hessite $Ag_{2.02}Te_{0.98}$	telagpalite $Pd_{1.82}Ag_{1.21}Te_{0.98}$	
9	30	40	30	hessite $Ag_{2.01}Te_{0.99}$	lukkulaisvaaraite*	telargpalite $Pd_{1.84}Ag_{1.12}Te_{1.05}$
10	60	20	20	$Pd_{7.48}Ag_{0.59}Te_{2.93}$	keithconnite $(Pd,Ag)_{\sum 20}Te_{7\ ss}$*	Ag–Pd*
11	53	13	34	lukkulaisvaaraite $Pd_{13.96}Ag_{2.17}Te_{8.86}$	telargpalite $Pd_{1.82}Ag_{1.21}Te_{0.97}$	
12	27.27	36.36	36.36	sopcheite $Pd_{3.01}Ag_{3.91}Te_{4.08}$		
13	70	15	15	keithconnite $(Pd,Ag)_{\sum 20}Te_{7\ ss}$*	Ag–Pd (44 at.% Ag)*	$(Pd,Ag)_{\sum 13}Te_{3\ ss}$*
14	20	20	60	stützite $Ag_{4.98}Te_{3.02}$	merenskyite $Pd_{1.00}Te_{2.00}$	Te
16	20	60	20	hessite $Ag_{1.98}Te_{1.02}$	telargpalite $Pd_{1.82}Ag_{1.21}Te_{0.98}$	Ag–Pd (7 at.% Ag)
17	25	25	50	hessite $Ag_{2.00}Te_{1.00}$	merenskyite $Pd_{1.01}Te_{1.99}$	kotulskite $Pd_{0.98}Te_{1.02}$
18	54.55	9.09	36.36	lukkulaisvaaraite $Pd_{13.79}Ag_{2.10}Te_{9.11}$	kotulskite $(Pd_{1.00}Ag_{0.01})_{\sum 1.01}Te_{0.99}$	
19	45	30	25	telargpalite $Pd_{1.82}Ag_{1.21}Te_{0.97}$		
20	50	16.67	33.33	hessite $Ag_{1.99}Te_{1.01}$	lukkulaisvaaraite $Pd_{13.68}Ag_{2.25}Te_{9.08}$	telargpalite $Pd_{1.80}Ag_{1.20}Te_{1.00}$
21	40	20	40	sopcheite $Pd_{3.00}Ag_{3.96}Te_{4.03}$	lukkulaisvaaraite $Pd_{13.74}Ag_{2.17}Te_{9.09}$	kotulskite $(Pd_{1.00}Ag_{0.01})_{\sum 1.01}Te_{0.99}$
22	50	31.25	18.75	$Pd_{7.18}Ag_{0.81}Te_{3.01}$	$Pd_{2.22}Ag_{1.77}Te_{1.00}$	Ag–Pd (17 at.% Ag)
24	60	13.33	26.67	telargpalite $Pd_{1.87}Ag_{1.14}Te_{0.99}$	$Pd_{6.88}Ag_{1.06}Te_{3.06}$	
25	64.52	12.9	22.58	$Pd_{7.34}Ag_{0.67}Te_{2.99}$	keithconnite $(Pd_{19.10}Ag_{0.64})_{\sum 19.74}Te_{7.26}$	Ag–Pd (23 at.% Ag)
26	15	15	70	stützite $Ag_{4.92}Te_{3.08}$	merenskyite $Pd_{1.00}Te_{2.00}$	Te
27	40	40	20	telargpalite $Pd_{1.81}Ag_{1.22}Te_{0.97}$	Ag–Pd (16 at.% Ag)	
28	56.6	5.66	37.74	lukkulaisvaaraite $Pd_{14.03}Ag_{1.87}Te_{9.10}$	$Pd_{2.98}Te_{2.02}$	kotulskite $Pd_{1.00}Te_{1.00}$
30	50	10	40	sopcheite $Pd_{3.05}Ag_{3.93}Te_{4.02}$	lukkulaisvaaraite $Pd_{13.79}Ag_{2.16}Te_{9.05}$	kotulskite $Pd_{1.00}Te_{1.00}$
31	33.33	33.33	33.33	lukkulaisvaaraite $Pd_{13.79}Ag_{2.11}Te_{9.09}$	telargpalite $Pd_{1.80}Ag_{1.19}Te_{1.00}$	hessite $Ag_{1.99}Te_{1.01}$
32	57.14	7.14	35.71	lukkulaisvaaraite $Pd_{14.12}Ag_{1.79}Te_{9.09}$	telluropalladinite $Pd_{8.91}Te_{4.09}$	
34	56.25	12.5	31.25	lukkulaisvaaraite $Pd_{13.88}Ag_{2.09}Te_{9.03}$	telargpalite $Pd_{1.87}Ag_{1.14}Te_{1.00}$	$Pd_{6.68}Ag_{1.30}Te_{3.02}$
35	45	35	20	$Pd_{2.24}Ag_{1.78}Te_{0.98}$	$Pd_{7.11}Ag_{0.90}Te_{2.99}$	Ag–Pd (17 at.% Ag)
36	35.77	53.66	37.4	sopcheite $Pd_{3.04}Ag_{3.96}Te_{4.00}$	lukkulaisvaaraite $Pd_{13.79}Ag_{2.18}Te_{9.03}$	kotulskite $(Pd_{0.99}Ag_{0.01})_{\sum 1.00}Te_{1.00}$
37	47.5	27.5	25	telargpalite $Pd_{1.87}Ag_{1.14}Te_{1.00}$	$Pd_{6.69}Ag_{1.31}Te_{3.00}$	
38	42.5	32.5	25	telargpalite $Pd_{1.80}Ag_{1.21}Te_{0.99}$	hessite $(Ag_{1.98}Pd_{0.02})_{\sum 2.00}Te_{1.00}$	
39	45	33	22	telargpalite $Pd_{1.86}Ag_{1.18}Te_{0.96}$	$Pd_{2.18}Ag_{1.83}Te_{0.99}$	
40	48	30	22	telargpalite $Pd_{1.91}Ag_{1.09}Te_{1.00}$	$Pd_{7.08}Ag_{0.84}Te_{3.08}$	$Pd_{2.22}Ag_{1.78}Te_{1.00}$
42	68	10	22	keithconnite $(Pd_{19.68}Ag_{0.57})_{\sum 20.25}Te_{6.75}$	Ag–Pd (25 at.% Ag)	
43	75	3	22	$(Pd_{12.76}Ag_{0.30})_{\sum 13.06}Te_{2.94}$	keithconnite $(Pd_{20.07}Ag_{0.46})_{\sum 20.53}Te_{6.47}$	Ag–Pd*
45	66	4	30	$Pd_{7.15}Ag_{0.78}Te_{3.07}$	lukkulaisvaaraite $Pd_{13.95}Ag_{1.96}Te_{9.10}$	telluropalladinite $Pd_{8.93}Te_{4.07}$

46	44	36	20	$Pd_{2.18}Ag_{1.81}Te_{1.01}$	Ag–Pd (16 at.% Ag)
47	56	8	36	lukkulaisvaaraite $Pd_{13.95}Ag_{1.94}Te_{9.11}$	
48	60	12	28	lukkulaisvaaraite $Pd_{13.84}Ag_{2.07}Te_{9.10}$	$Pd_{6.71}Ag_{1.24}Te_{3.05}$
49	64	8	28	$Pd_{7.06}Ag_{0.85}Te_{3.08}$	
50	68	4	28	$Pd_{7.43}Ag_{0.51}Te_{3.06}$	telluropalladinite $Pd_{8.98}Te_{4.02}$
51	70	2	28	$Pd_{7.02}Te_{2.98}$	$Pd_{7.48}Ag_{0.47}Te_{3.05}$
52	46.5	28.5	25	telargpalite $Pd_{1.89}Ag_{1.10}Te_{1.01}$	
53	45.5	29.5	25	telargpalite $Pd_{1.81}Ag_{1.18}Te_{1.01}$	hessite*
54	58	14	28	lukkulaisvaaraite $Pd_{13.82}Ag_{1.96}Te_{9.22}$	$Pd_{6.67}Ag_{1.22}Te_{3.11}$
55	46	34	20	$Pd_{2.23}Ag_{1.77}Te_{1.00}$	$Pd_{7.15}Ag_{0.81}Te_{3.03}$
57	28	35	37	sopcheite $Pd_{2.99}Ag_{3.93}Te_{4.08}$	kotulskite $Pd_{1.00}Te_{1.00}$
58	27	36	37	sopcheite $Pd_{2.99}Ag_{3.94}Te_{4.07}$	telargpalite*
					Ag–Pd (17 at.% Ag)

*Results according to the XRD data.

Lukkulaisvaaraite ($Pd_{14}Ag_2Te_9$)

The compositional range for the phase $Pd_{14}Ag_2Te_9$ studied in the ternary system, the analogue of mineral lukkulaisvaaraite, is given in Table 4. Lukkulaisvaaraite coexists with kotulskite and sopcheite (Fig. 5*a*), hessite and sopcheite, telargpalite and hessite (Fig. 5*b*). Lukkulaisvaaraite, in association of telagpalite or kotulskite, has also been observed in nature (Grokhovskaya *et al.,* 1992; Barkov *et al.*, 2001; Vymazalová *et al.*, 2014). Lukkulaisvaaraite also forms stable associations with the phase Pd_3Te_2 and kotulskite, and with Pd_3Te_2 and telluropalladinite. It also coexists with a new phase, $Pd_{7.5-x}Ag_{0.5+x}Te_3$ and telargpalite, and with the phase $Pd_{7.5-x}Ag_{0.5+x}Te_3$ and telluropalladinite (Fig. 5*c*). Such associations (Fig. 4*a*,*b*) can be expected to occur in nature. Lukkulaisvaaraite is tetragonal, space group *I*4/*m*, with unit-cell parameters $a = 8.9599(6)$ and $c = 11.822(1)$ Å (Vymazalová *et al*., 2014) (Tables 1 and 2).

Telargpalite ($Pd_{2-x}Ag_{1+x}Te$)

Telargpalite was described from the Oktyabr mine in Noril'sk by Kovalenker *et al.* (1974), who suggested two possible formulae: $(Pd,Ag,Bi,Pb)_{4+x}Te$ and $(Pd,Ag)_3(Te,Bi,Pb)$. According to Begizov and Batashev (1978), Grokhovskaya *et al.* (1992) and Barkov *et al.* (2001), telargpalite from the Lukkulaisvaara intrusion has the atomic ratio (Pd + Ag): (Te + Bi + Pb) ≈ 3, with limited Ag-for-Pd substitution. Tolstykh and Krivenko (1996) also assumed the stoichiometry 3:1 for telargpalite from the Fedorova-Pana intrusion in the Kola Peninsula. Barkov *et al*. (2001) proposed the formula of telargpalite $Pd_{2-x}Ag_{1+x}$(Te, Bi, Pb), where $0 < x < 0.3$. The chemical composition of synthetic telargpalite was studied in detail. The experimental results (see Table 4) are consistent with a very limited Ag-for-Pd substitution, confirming the formula as proposed by Barkov *et al.* (2001), $Pd_{2-x}Ag_{1+x}Te$, where x varies from 0.09 to 0.22 (from 26 to 29 wt.% Ag). The existence of a distinct phase with an atomic ratio 4 : 1 of (Pd + Ag) : Te, the phase $Pd_{2+x}Ag_{2-x}Te$, was also confirmed experimentally (Fig. 4*a*). Telargpalite coexists with the phase $Pd_{2+x}Ag_{2-x}Te$. The incorporation of Bi and Pb, which occurs in natural samples, should be assigned to the Te site instead of the (Pd,Ag) site.

The crystal structure of telargpalite has not yet been determined. Considering the formula of telargpalite $(Pd,Ag,Bi,Pb)_{4+x}Te$, Kovalenker *et al.* (1974) observed the similarity of XRD data for telargpalite and the synthetic phase Pd_4Te (Grønvold

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TABLE 3*c*. Results of selected experimental runs in the system Pd–Ag–Te at 450°C.

Run no.	Starting composition (at.%)			Phase assemblages at 450°C		
	Pd	Ag	Te			
9	30	40	30	hessite $(Ag_{1.99}Pd_{0.01})_{\sum 2.00}Te_{1.00}$	lukkulaisvaaraite*	telargpalite $Pd_{1.82}Ag_{1.04}Te_{1.15}$
23	73.91	17.39	8.7	$(Pd_{12.76}Ag_{0.33})_{\sum 13.07}Te_{2.91}$	Ag–Pd (69 at.% Ag)	
34	56.25	12.5	31.25	lukkulaisvaaraite $Pd_{13.84}Ag_{2.16}Te_{9.00}$	telargpalite $Pd_{1.73}Ag_{1.09}Te_{1.18}$	$Pd_{6.72}Ag_{1.27}Te_{3.01}$
35	45	35	20	$Pd_{2.18}Ag_{1.83}Te_{1.00}$	$Pd_{6.95}Ag_{1.03}Te_{3.02}$	Ag–Pd (17 at.% Ag)
36	35.77	53.66	37.4	hessite $Ag_{2.00}Te_{1.00}$	lukkulaisvaaraite $Pd_{13.77}Ag_{2.20}Te_{9.03}$	kotulskite $(Pd_{0.99}Ag_{0.02})_{\sum 1.01}Te_{0.99}$
37	47.5	27.5	25	telargpalite $Pd_{1.85}Ag_{1.17}Te_{0.98}$	$Pd_{6.58}Ag_{1.42}Te_{3.00}$	
38	42.5	32.5	25	telargpalite $Pd_{1.79}Ag_{1.24}Te_{0.98}$	hessite $(Ag_{1.99}Pd_{0.01})_{\sum 2.00}Te_{1.00}$	
41	56	22	22	$Pd_{2.29}Ag_{1.73}Te_{0.98}$	$Pd_{7.62}Ag_{0.48}Te_{2.90}$	Ag–Pd (17 at.% Ag)
42	68	10	22	keithconnite $(Pd_{19.75}Ag_{0.63})_{\sum 20.38}Te_{6.68}$	Ag–Pd (25 at.% Ag)	
50	68	4	28	$Pd_{7.43}Ag_{0.50}Te_{3.07}$	$Pd_{7.01}Te_{2.99}$	
246	10	80	10	hessite*	Ag–Pd*	telargpalite*
245	33	57	10	$Pd_{2+x}Ag_{2-x}Te_{1\ ss}$*	$Pd_{7.5-x}Ag_{0.5+x}Te_{3\ ss}$*	Ag–Pd*
259	55	15	30	lukkulaisvaaraite $Pd_{13.99}Ag_{1.98}Te_{9.03}$	telargpalite $Pd_{1.82}Ag_{1.14}Te_{1.04}$	$Pd_{6.62}Ag_{1.15}Te_{3.03}$
260	55	5	40	lukkulaisvaaraite $Pd_{14.12}Ag_{1.85}Te_{9.03}$	$Pd_{3.00}Te_{2.00}$	kotulskite $Pd_{1.01}Te_{0.99}$
270	25	25	50	hessite $Ag_{2.00}Te_{1.00}$	merenskyite $Pd_{1.01}Te_{1.99}$	kotulskite $Pd_{0.96}Te_{1.04}$
271	40	20	40	hessite $Ag_{2.00}Te_{1.00}$	lukkulaisvaaraite $Pd_{13.92}Ag_{2.07}Te_{9.00}$	kotulskite $(Pd_{1.00}Ag_{0.01})_{\sum 1.01}Te_{0.99}$
272	35	35	30	hessite $Ag_{2.00}Te_{1.00}$	telargpalite $Pd_{1.80}Ag_{1.10}Te_{1.10}$	lukkulaisvaaraite*
273	30	30	40	hessite $Ag_{2.00}Te_{1.00}$	lukkulaisvaaraite $Pd_{13.75}Ag_{2.23}Te_{9.01}$	kotulskite $(Pd_{1.00}Ag_{0.01})_{\sum 1.01}Te_{0.99}$
274	75	5	20	keithconnite $(Pd_{19.82}Ag_{0.86})_{\sum 20.68}Te_{6.32}$	$(Pd_{12.76}Ag_{0.30})_{\sum 13.06}Te_{2.94}$	Ag–Pd (44 at.%Ag)
275	70	10	20	keithconnite $(Pd_{19.58}Ag_{0.95})_{\sum 20.53}Te_{6.47}$	$(Pd,Ag)_{\sum 13}Te_{3\ ss}$*	Ag–Pd (44 at.%Ag)

*Results according to the XRD data.

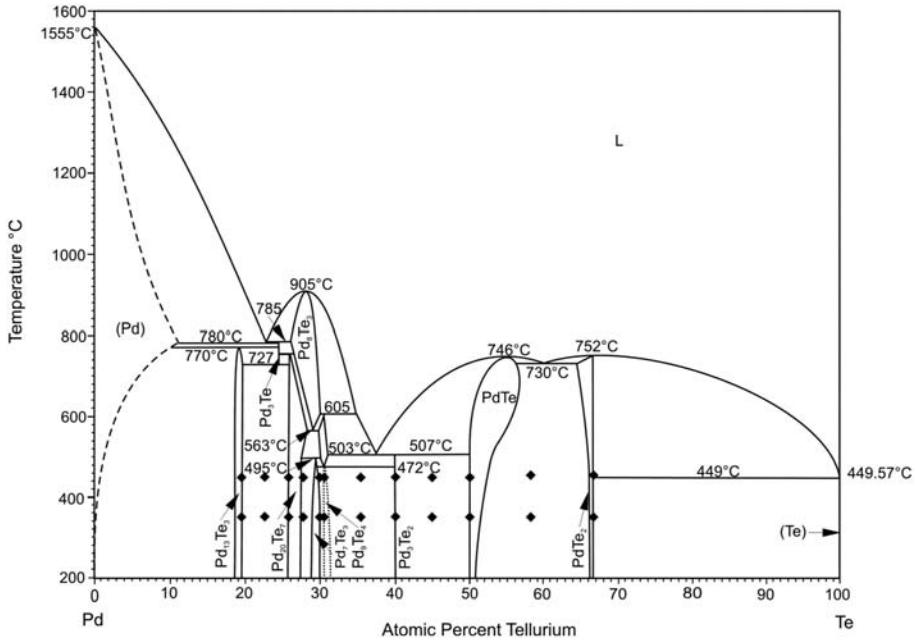


FIG. 2. Phase diagram of the binary system Pd–Te, redrawn from Okamoto (1992), showing our experimental results at lower temperature. Experiments are marked with a diamond, initial compositions and phase assemblages in experimental products are given in Table 3*a*. We assume the phase Pd_9Te_4 to be stable at lower temperature. However, it is shown as a dotted line, as the reaction responsible for its formation is unclear. The Pd line of the solvus is tentative (dashed lines, Okamoto, 1992).

and Rost, 1956). Considering the alternative formula $(Pd,Ag)_3(Te,Bi,Pb)$, Kovalenker *et al.* (1974) suggested a possible structural relation with the mineral zvyagintsevite (Pd_3Pb). However, they were not able to index all the reflections with any of the structural models. The most intense reflections in the XRD pattern of synthetic telargpalite (run 19, Table 5) can be indexed with a cubic cell, $a = 4.1714(2)$ Å (i.e. by analogy with zvyagintsevite). However, many weak reflections remain unindexed. Tripling the unit cell to $a = 12.513(1)$ Å improved the indexing, but it is still not sufficient to cover all observed diffraction maxima. The observed XRD data can be indexed satisfactorily with a tetragonal cell, $a = 5.8942(2)$ Å and $c = 9.625(2)$ Å (Table 5). A more detailed crystallographic study, including crystal-structure determination of this mineral, is needed to resolve this question.

The phase $Pd_{7.5-x}Ag_{0.5+x}Te_3$

The ternary phase $Pd_{7.5-x}Ag_{0.5+x}Te_3$, with $0.02 < x < 0.83$, forms a broad solid-solution from 4 to 11 wt.% Ag (Table 4). Silver substitutes for Pd in the $Pd_{7.5-x}Ag_{0.5+x}Te_3$ structure with an almost constant content of Te (Table 4).

A phase of similar chemical composition (of size 10 μm), was observed in association with kotulskite, moncheite, telargpalite and tulameenite by Grokhovskaya *et al.* (1992) in the Lukkulaisvaara intrusion. The natural sample (although based on only one analysis) almost corresponds to the synthetic endmember $Pd_{7.43}Ag_{0.51}Te_{3.05}$ (run 50, Table 4) of the solid solution. The natural mineral assemblage corresponds with the experimentally determined phase relations. The phase forms stable associations with telargpalite and lukkulaisvaaraite, lukkulaisvaaraite and telluropalladinite (Fig. 5*c*), telargpalite and $Pd_{2+x}Ag_{2-x}Te$ (Fig. 4*d*), $Pd_{2+x}Ag_{2-x}Te$ and Ag–Pd alloy. It also coexists with keithconnite ($Pd_{20}Te_7$) and Pd_7Te_3. Those associations (Fig. 4*a,b*) and the phase $Pd_{7.5-x}Ag_{0.5+x}Te_3$ as a new mineral species can be expected to occur in nature.

The crystal structure of $Pd_{7.5-x}Ag_{0.5+x}Te_3$ is unknown and requires further examination. The XRD data show a certain resemblance to those for Pd_5Sb_2 (Cabri and Chen, 1976); however, no satisfactory agreement was obtained in a Rietveld

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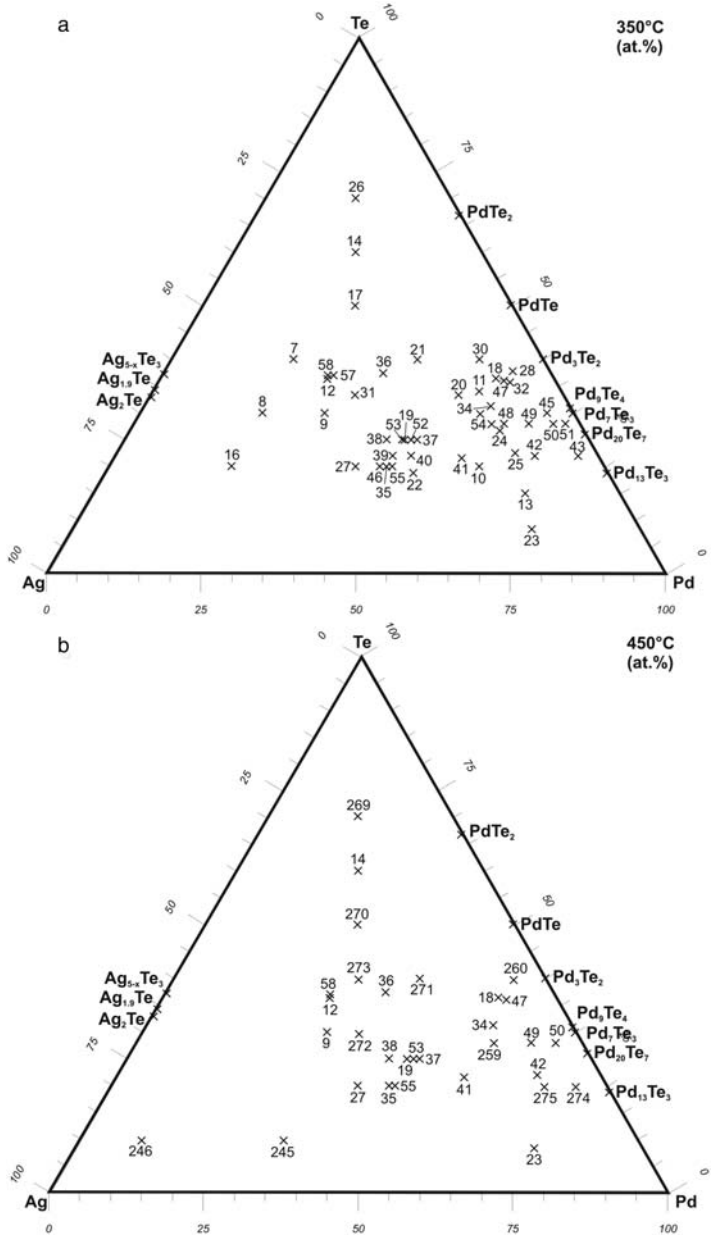


FIG. 3. Experimental starting compositions (in at.%) in the ternary phase diagram. Experiments are marked with numbers (*a*) at 350°C (*b*) at 450°C. Initial compositions and phase assemblages in experimental products are given in Tables 3*a*, *b*, *c*.

fit. Attempts to index the XRD data using the Pd_8Sb_3 (El-Boragy *et al.*, 1970) and $Pd_{20}Te_7$ (Wopersnow and Schubert, 1977) structure models have also been made, but none of them have been successful. The strongest ten lines of the observed XRD pattern [*d* in Å (I)] are: 3.0145(13), 2.6527(14), 2.4757 (27), 2.3825(8), 2.3413(47), 2.2577(38), 2.2061 (100), 2.1967(68), 2.1454(10), 1.9256(24).

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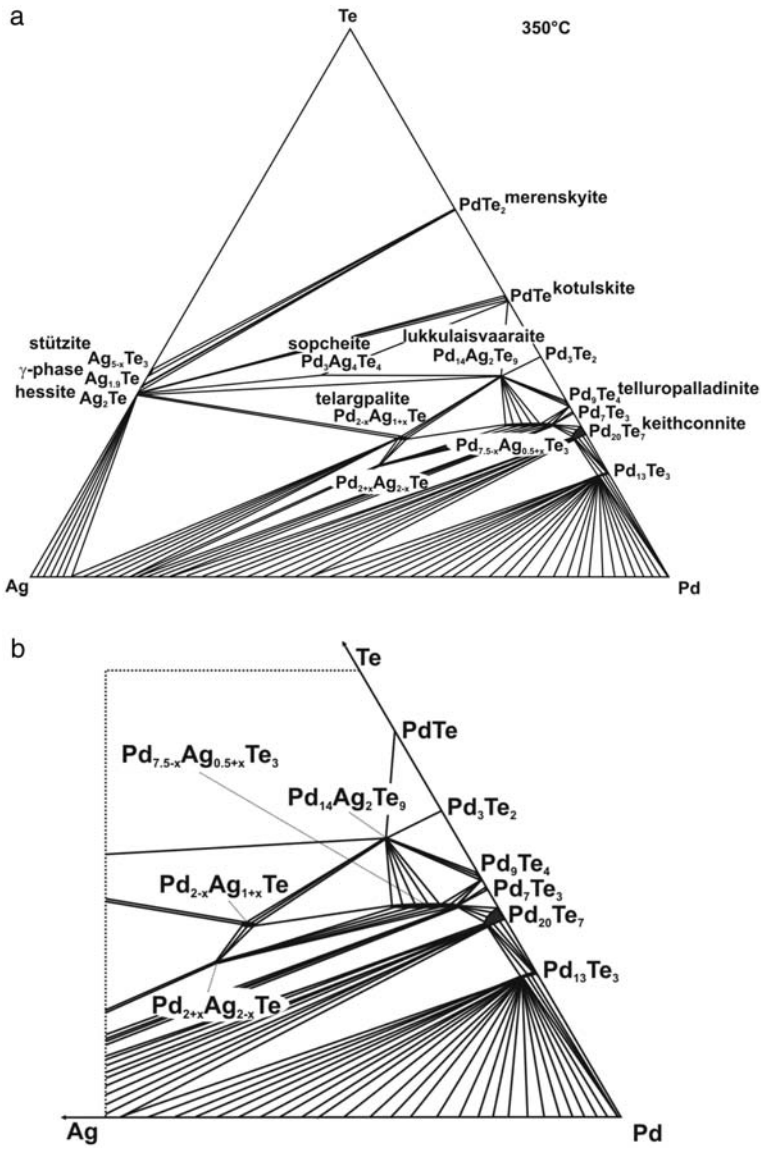


FIG. 4. (*a*) Isothermal section through the ternary system Ag–Pd–Te system at 350°C. (*b*) The detail of the Pd-rich corner.

The phase $Pd_{2+x}Ag_{2-x}Te$

Our experimental study proved the existence of a phase with the atomic ratio (Pd + Ag): Te ≈ 4, i.e., $Pd_{2+x}Ag_{2-x}Te$, where x is from 0.18 to 0.24 (Table 4). A phase with the same atomic ratio of (Pd + Ag): Te (4:1) was observed by Kovalenker *et al.* (1972) in the Noril'sk ores, and the existence of the phase was also suggested by Evstigneeva and Trubkin (2006). The phase $Pd_{2+x}Ag_{2-x}Te$ forms a stable association with telargpalite and Ag–Pd alloy, and also coexists with the phase $Pd_{7.5-x}Ag_{0.5+x}Te_3$ (Fig. 5*d*). In the sample of Kovalenker *et al.* (1972), the phase '$(Pd,Ag)_{\sum 4}Te$' replaces kotulskite. This is in agreement with the phase relations elucidated here, where kotulskite is not in equilibrium with $Pd_{2+x}Ag_{2-x}Te$. The phase $Pd_{2+x}Ag_{2-x}Te$ can be expected to be described as a new mineral species. It should be sought in the Noril'sk ores. The XRD

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TABLE 4. EMPA data of synthetic ternary phases in the system Ag–Pd–Te (at 350°C).

		Wt.%				Atoms per formula unit		
Run no.	*n*	Pd	Ag	Te	Total	Pd	Ag	Te
				sopcheite $Pd_3Ag_4Te_4$				
12	4	25.36	33.44	41.28	100.08	3.01	3.91	4.08
18	2	25.17	33.35	41.42	99.94	2.99	3.91	4.10
21	4	25.31	33.83	40.76	99.90	3.00	3.96	4.03
30	6	25.72	33.58	40.68	99.97	3.05	3.93	4.02
36	3	25.89	34.15	40.80	100.85	3.04	3.96	4.00
57	3	25.23	33.61	41.21	100.05	2.99	3.93	4.08
58	5	25.34	33.59	40.92	99.85	2.99	3.94	4.07
				lukkulaaisvaraite $Pd_{14}Ag_2Te_9$				
11	3	51.55	8.14	39.24	98.93	13.96	2.17	8.86
18	7	50.99	7.87	40.40	99.26	13.79	2.10	9.11
20	4	50.96	8.49	40.56	100.00	13.68	2.25	9.08
21	4	51.15	8.17	40.60	99.92	13.74	2.17	9.09
28	4	52.33	7.08	40.71	100.11	14.03	1.87	9.10
30	6	51.43	8.18	40.48	100.10	13.79	2.16	9.05
31	5	51.12	7.94	40.42	99.48	13.79	2.11	9.09
32	4	52.43	6.74	40.47	99.64	14.12	1.79	9.09
34	4	51.79	7.91	40.42	100.12	13.88	2.09	9.03
36	4	51.53	8.27	40.48	100.28	13.79	2.18	9.03
45	2	51.65	7.34	40.41	99.40	13.95	1.96	9.10
47	4	52.22	7.35	40.91	100.47	13.95	1.94	9.11
48	4	51.99	7.87	40.98	100.84	13.84	2.07	9.10
54	5	50.92	7.32	40.70	98.94	13.82	1.96	9.22
				$Pd_{2+x}Ag_{2-x}Te$				
22	6	42.57	34.45	23.03	100.05	2.22	1.77	1.00
35	5	43.20	34.76	22.80	100.76	2.24	1.78	0.98
39	5	41.78	35.68	22.76	100.22	2.18	1.83	0.99
40	4	42.29	34.46	22.97	99.72	2.22	1.78	1.00
46	8	41.95	35.26	23.17	100.38	2.18	1.81	1.01
55	8	42.66	34.34	22.92	99.92	2.23	1.77	1.00
				telargpalite $Pd_{2-x}Ag_{1+x}Te$				
8	4	43.15	29.11	27.82	100.08	1.82	1.21	0.98
9	8	43.45	26.80	29.69	99.94	1.84	1.12	1.05
11	4	42.93	28.86	27.59	99.38	1.82	1.21	0.97
19	4	42.85	28.89	27.36	99.10	1.82	1.21	0.97
20	6	42.55	28.73	28.53	99.80	1.80	1.20	1.01
24	4	44.49	27.56	28.37	100.41	1.87	1.14	0.99
27	4	43.05	29.48	27.72	100.25	1.81	1.22	0.97
31	4	42.46	28.49	28.34	99.29	1.80	1.19	1.00
34	4	44.66	27.56	28.55	100.78	1.87	1.14	1.00
37	4	44.39	27.38	28.37	100.14	1.87	1.14	1.00
38	5	42.97	29.40	28.23	100.61	1.80	1.21	0.99
39	4	44.16	28.33	27.43	99.92	1.86	1.18	0.96
40	4	45.19	26.17	28.44	99.81	1.91	1.09	1.00
52	4	44.57	26.32	28.59	99.47	1.89	1.10	1.01
53	4	42.52	28.16	28.63	99.31	1.81	1.18	1.01

(continued)

data of synthetic $Pd_{2+x}Ag_{2-x}Te$ (run 35) were tentatively indexed with a hexagonal cell, with lattice parameters $a = 4.621(3)$ and $c = 14.281(9)$ Å (Table 5). The crystal structure is unknown.

Possible associations

Phase relations defined the mineral assemblages that can be expected to occur in nature. The

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TABLE 4. (*contd*.)

Run no.	*n*	Wt.%				Atoms per formula unit		
		Pd	Ag	Te	Total	Pd	Ag	Te
				$Pd_{7.5-x}Ag_{0.5+x}Te_3$				
10	4	64.20	5.13	30.11	99.44	7.48	0.59	2.93
22	1	62.14	7.11	31.30	100.54	7.18	0.81	3.01
24	7	59.04	9.25	31.50	99.79	6.88	1.06	3.06
25	5	63.59	5.90	31.03	100.51	7.34	0.67	2.99
34	5	57.78	11.41	31.28	100.46	6.68	1.30	3.02
37	4	57.73	11.49	31.09	100.31	6.69	1.31	3.00
40	5	59.99	7.22	31.23	98.43	7.08	0.84	3.08
45	4	60.66	6.71	31.17	98.54	7.15	0.78	3.07
48	5	58.01	10.86	31.65	100.51	6.71	1.24	3.05
49	5	60.41	7.41	31.62	99.43	7.06	0.85	3.08
50	7	63.86	4.42	31.52	99.80	7.43	0.51	3.06
54	6	56.51	10.47	31.58	98.56	6.67	1.22	3.11
55	2	61.52	7.09	31.28	99.89	7.15	0.81	3.03

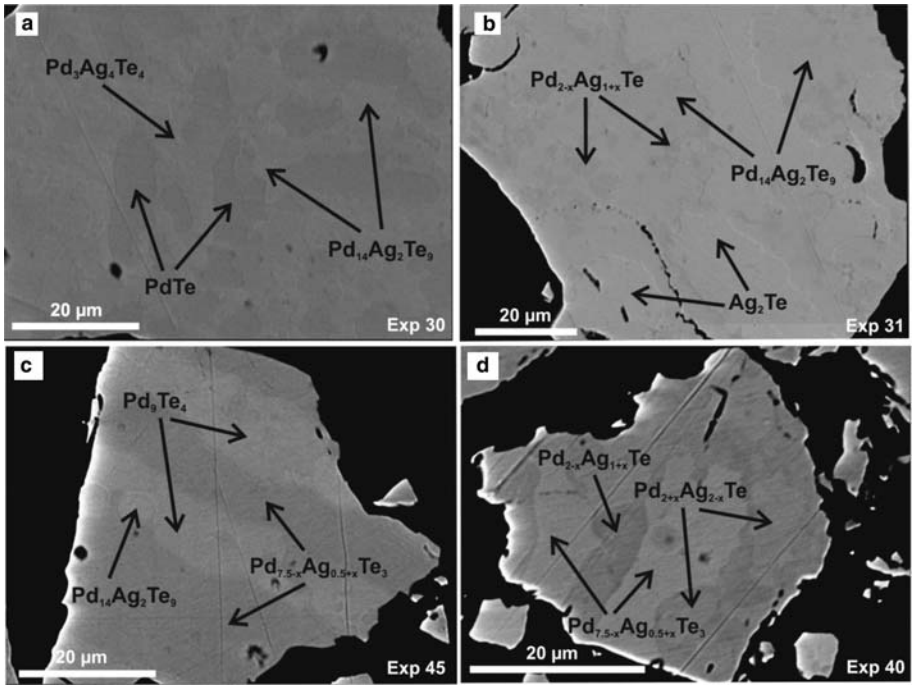


FIG. 5. Backscattered electron images illustrating the assemblages of: (*a*) sopcheite ($Pd_3Ag_4Te_4$) + lukkulaaisvaraite ($Pd_{14}Ag_2Te_9$) + kotulskite (PdTe) (run 30); (*b*) telargpalite ($Pd_{2-x}Ag_{1+x}Te$) + lukkulaaisvaraite ($Pd_{14}Ag_2Te_9$) + hessite (Ag_2Te) (run 31); (*c*) lukkulaaisvaraite ($Pd_{14}Ag_2Te_9$) + telluropalladinite (Pd_9Te_4) + ($Pd_{7.5-x}Ag_{0.5+x}Te_3$) (run 45); and (*d*) telagpalite ($Pd_{2-x}Ag_{1+x}Te$) + ($Pd_{7.5-x}Ag_{0.5+x}Te_3$) + $Pd_{2+x}Ag_{2-x}Te$ (run 40).

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TABLE 5. Tentative indexing of the synthetic phases $Pd_{2-x}Ag_{1+x}Te$, Exp 19 (in a tetragonal cell) and $Pd_{2+x}Ag_{2-x}Te$, Exp 35 (in a hexagonal cell), first twenty lines (Co$K\alpha$ radiation).

$Pd_{2-x}Ag_{1+x}Te$						$Pd_{2+x}Ag_{2-x}Te$					
h	*k*	*k*	d_{obs}	d_{calc}	I_{obs}	*h*	*k*	*l*	d_{obs}	d_{calc}	I_{obs}
0	0	1	9.6593	9.639	2	0	1	0	4.0038	4.0018	1
0	1	0	5.9099	5.9029	3	0	1	3	3.0656	3.0633	3
1	1	1	3.831	3.8303	1	0	1	4	2.6652	2.6642	2
0	0	3	3.2125	3.213	4	0	1	5	2.3239	2.3249	83
0	0	4	2.4093	2.4098	100	1	1	0	2.3092	2.3104	100
1	0	4	2.2304	2.231	2	1	1	3	2.0787	2.0786	12
2	0	3	2.1732	2.1736	4	0	0	7	2.0415	2.0402	13
1	1	4	2.0866	2.0869	40	0	2	2	1.9271	1.9267	4
0	3	0	1.9674	1.9677	5	1	1	6	1.6581	1.6578	4
0	0	5	1.9276	1.9278	3	0	2	5	1.6377	1.6388	15
1	0	5	1.8324	1.8326	3	0	1	8	1.6309	1.6303	7
1	2	4	1.7796	1.7798	2	0	2	6	1.5322	1.5316	2
1	1	5	1.7501	1.7502	1	1	2	1	1.5044	1.5041	2
3	0	3	1.6779	1.678	2	1	2	2	1.4795	1.4797	2
3	1	4	1.4757	1.4757	17	0	1	9	1.4741	1.4751	8
2	2	5	1.4162	1.4161	1	0	2	7	1.4276	1.4285	5
1	1	7	1.3078	1.3077	2	0	1	10	1.3455	1.345	5
3	3	3	1.2768	1.2768	1	0	2	8	1.3324	1.3321	25
4	0	4	1.2585	1.2585	16	1	2	6	1.2769	1.2766	1
4	1	4	1.2309	1.2309	1	1	2	8	1.1538	1.154	8

following assemblages of unknown phases with minerals can be expected (Fig. 4):

Pd_3Te_2 + kotulskite (PdTe)
+ lukkulaisvaaraite ($Pd_{14}Ag_2Te_9$);
Pd_3Te_2 + telluropalladinite (Pd_9Te_4)
+ lukkulaisvaaraite ($Pd_{14}Ag_2Te_9$);
$Pd_{7.5-x}Ag_{0.5+x}Te_3$ + lukkulaisvaaraite ($Pd_{14}Ag_2Te_9$)
+ telluropalladinite (Pd_9Te_4);
$Pd_{7.5-x}Ag_{0.5+x}Te_3$ + telluropalladinite (Pd_9Te_4)
+ Pd_7Te_3;
$Pd_{7.5-x}Ag_{0.5+x}Te_3$ + keithconnite ($Pd_{20}Te_7$)+Pd_7Te_3;
$Pd_{7.5-x}Ag_{0.5+x}Te_3$ + keithconnite ($Pd_{20}Te_7$)
+ Ag–Pd alloy;
$Pd_{7.5-x}Ag_{0.5+x}Te_3$ + lukkulaisvaaraite ($Pd_{14}Ag_2Te_9$)
+ telargpalite ($Pd_{2-x}Ag_{1+x}Te$);
$Pd_{2+x}Ag_{2-x}Te$ + telargpalite ($Pd_{2-x}Ag_{1+x}Te$)
+ $Pd_{7.5-x}Ag_{0.5+x}Te_3$;
$Pd_{2+x}Ag_{2-x}Te$ + telargpalite ($Pd_{2-x}Ag_{1+x}Te$)
+ Ag–Pd alloy;
$Pd_{2+x}Ag_{2-x}Te$ + $Pd_{7.5-x}Ag_{0.5+x}Te_3$ + Ag–Pd alloy

The isothermal section for 450°C is shown in Fig. 6. Phase assemblages based on EPMA and powder XRD data are listed in Table 3*c*. The starting compositions are plotted in Fig. 3*b*. Phase relations are similar to those for 350°C; however, at this temperature the phases $Pd_3Ag_4Te_4$ (stability limit: 383°C, this study) and $Ag_{5-x}Te_3$ (stability limit: 420°C, Kracek *et al.*, 1966) are no longer stable, and a liquid appears (48 at.% Ag, Kracek *et al.*, 1966). Subsequently, the following assemblages

sopcheite ($Pd_3Ag_4Te_4$) + hessite (Ag_2Te)
+ kotulskite (PdTe);
sopcheite ($Pd_3Ag_4Te_4$) + kotulskite (PdTe)
+ lukkulaisvaaraite ($Pd_{14}Ag_2Te_9$);
sopcheite ($Pd_3Ag_4Te_4$) + hessite (Ag_2Te)
+ lukkulaisvaaraite ($Pd_{14}Ag_2Te_9$);
γ-phase ($Ag_{1.9}Te$) + stützite ($Ag_{5-x}Te_3$)
+ merenskyite ($PdTe_2$);
stützite ($Ag_{5-x}Te_3$) + merenskyite ($PdTe_2$) + Te

disappear from the system, and new assemblages, hessite (Ag_2Te) + kotulskite (PdTe) + lukkulaisvaaraite ($Pd_{14}Ag_2Te_9$) and γ phase ($Ag_{1.9}Te$) + merenskyite ($PdTe_2$) + *L* appear in the system at 450°C. Natural occurrences of the three minerals

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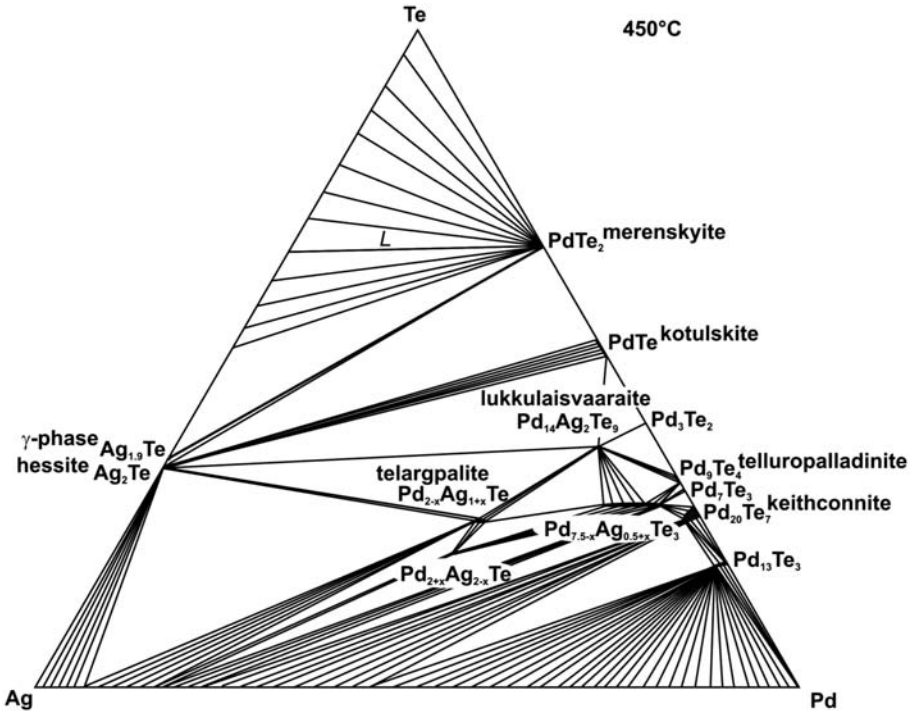


FIG. 6. Isothermal section through the ternary system Ag–Pd–Te at 450°C.

hessite, kotulskite and lukkulaisvaaraite together at equilibrium can reflect the formation of the mineral assemblage above 383°C.

Conclusions and implications

We have elucidated phase relations in the system Ag–Pd–Te at 350°C and 450°C. Five ternary phases were found to be stable in the system at 350°C: sopcheite ($Pd_3Ag_4Te_4$), lukkulaisvaaraite ($Pd_{14}Ag_2Te_9$), telargpalite ($Pd_{2-x}Ag_{1+x}Te$ $0.09 < x < 0.22$) and new phases $Pd_{7.5-x}Ag_{0.5+x}Te_3$ $0.02 < x < 0.83$ and $Pd_{2+x}Ag_{2-x}Te$ $0.18 < x < 0.24$.

Sopcheite forms a stable association with hessite and kotulskite; it also coexists with lukkulaisvaaraite. Sopcheite is stable up to 383°C. The presence of sopcheite in mineral assemblages reflects its formation below this temperature. On the contrary, the association of hessite, kotulskite and lukkulaisvaaraite together at equilibrium reflects its formation above this temperature.

Synthetic telargpalite shows a very limited extent of Ag-for-Pd substitution, with a formula $Pd_{2-x}Ag_{1+x}Te$, where x varies from 0.09 to 0.22 (from 26 to 29 wt.% Ag). The ternary phase $Pd_{7.5-x}Ag_{0.5+x}Te_3$ forms a solid solution with a range from 4 to 11 wt.% Ag. The phases $Pd_{20}Te_7$ and $Pd_{13}Te_3$ dissolve up to 3.5 and 2 wt.% Ag, respectively. Other binary palladium tellurides do not dissolve Ag.

The phase relations define the mineral assemblages that can be expected to occur in nature. The ternary phases $Pd_{7.5-x}Ag_{0.5+x}Te_3$ and $Pd_{2+x}Ag_{2-x}Te$ can be expected to be described as new mineral species. The phase $Pd_{7.5-x}Ag_{0.5+x}Te_3$ can be found in association with lukkulaisvaaraite and telargpalite or telluropalladinite, among other platinum-group minerals. The phase $Pd_{2+x}Ag_{2-x}Te$ can be found in association with telargpalite. The binary phase Pd_3Te_2, as yet unknown as a mineral, can be expected in association with lukkulaisvaaraite and kotulskite or telluropalladinite.

Mineral assemblages defined in this study can be expected in magmatic Cu-Ni-PGE mineral deposits, associated with mafic and ultramafic igneous rocks. Particular targets are those associations where Pd-Ag tellurides are known to occur, as in deposits in the Kola Peninsula, Karelia or Noril'sk in Russia, and the Coldwell Complex, the Lac des Iles Complex or Sudbury in Canada.

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