



## Article

# The system Pd–Ag–S: phase relations and mineral assemblages

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### Abstract

Phase equilibria in the system Pd–Ag–S were studied using the silica-glass tube method at 400°C and 550°C. In the system we synthesised three ternary phases: coldwellite (Pd<sub>3</sub>Ag<sub>2</sub>S), kravtsovite (PdAg<sub>2</sub>S) and a new phase Pd<sub>13</sub>Ag<sub>3</sub>S<sub>4</sub>. At 400°C, coldwellite forms a stable association with vysotskite (PdS) and vasilite (Pd<sub>16</sub>S<sub>7</sub>); vysotskite and kravtsovite; phase Pd<sub>4</sub>S and a Ag–Pd alloy; it also coexists with a new phase Pd<sub>13</sub>Ag<sub>3</sub>S<sub>4</sub>. Kravtsovite is stable up to 507°C; the presence of kravtsovite in the mineral assemblage reflects its formation below this temperature. The occurrence of coldwellite, vysotskite and Ag<sub>2</sub>S together in equilibrium reflects the formation of this mineral assemblage above this temperature (507°C). Coldwellite is stable up to 940°C. Mineral assemblages defined in this study can be expected in Cu–Ni–PGE mineral deposits, associated with mafic and ultramafic igneous rocks, in particular in mineralisations with known silver–palladium sulfides.

**Keywords:** Pd–Ag–S system, phase relations, phase diagram, platinum-group minerals, coldwellite, kravtsovite, vysotskite, vasilite, phase Pd<sub>13</sub>Ag<sub>3</sub>S<sub>4</sub>

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### Introduction

The Pd–Ag–S system comprises three binary minerals: vysotskite (PdS), vasilite (Pd<sub>16</sub>S<sub>7</sub>), acanthite/argentite (Ag<sub>2</sub>S) and two ternary minerals: coldwellite (Pd<sub>3</sub>Ag<sub>2</sub>S) found in the Marathon Cu–PGE–Au deposit, Colwell Complex, Canada (McDonald *et al.*, 2015); and kravtsovite (PdAg<sub>2</sub>S) found in the Komsomolsky mine in the Talnakh deposit of the Noril'sk district, Russia (Vymazalová *et al.*, 2017). Minerals from the Pd–Ag–S system occur, in general, in Cu–Ni–PGE deposits associated with mafic and ultramafic rocks. Furthermore, the occurrences of unnamed phases with compositions that belong to the system Pd–Ag–S have also been reported in the literature, in particular from alluvial deposits related to mafic–ultramafic bedrock sources (e.g. Augé and Legendre 1992; Tolstykh *et al.*, 2009). Therefore, the phase relations within the Pd–Ag–S system are of mineralogical interest. Nevertheless, only the phase relations within the binary subsystems are described in the literature, and the ternary system Pd–Ag–S has not been studied experimentally up to now, only some preliminarily results reported by Vymazalová *et al.* (2015a). In this contribution, we present the phase relations in the Pd–Ag–S system and predict possible stable assemblages under natural conditions; we explore the mineralogical implications of our findings. The list of minerals belonging to the Pd–Ag–S system is summarised in Table 1.

### Previous experiments

#### The binary Pd–S system

The binary system Pd–S was evaluated by Okamoto (1992) based on the data of Matković *et al.* (1976) and Weibke and Laar (1935). The system comprises five intermediate phases: Pd<sub>4</sub>S, Pd<sub>3</sub>S (stable in the temperature interval from 555 to 635°C), Pd<sub>16</sub>S<sub>7</sub>, PdS and PdS<sub>2</sub>.

#### The binary systems Ag–Pd and Ag–S

Karakaya and Thompson (1988) reported complete solid solution for the Ag–Pd system. In the Ag–S system only one Ag<sub>2</sub>S phase exists with three polymorphic modifications ( $\alpha$ ,  $\beta$  and  $\gamma$ ) (Sharma and Chang, 1986).

#### The ternary system Pd–Ag–S

Phase relations in the ternary system Pd–Ag–S have not been studied to date. Nevertheless, Raub *et al.* (1954) studied experimentally the solubility of Pd in Ag<sub>2</sub>S in the temperature interval 700 to 900°C. El-Boragy and Schubert (1971) studied phases with  $\beta$ -Mn type structures and synthesised the phase denoted as 'Pd<sub>2</sub>AgS' at 550°C. Synthetic phases belonging to the Pd–Ag–S system are listed in Table 2.

### Methods and techniques

#### Experimental

Experiments were performed in evacuated and sealed silica-glass tubes in horizontal tube furnaces. To prevent loss of material to the vapour phase during experiments, the free space in the

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**Table 1.** Minerals in the system Pd–Ag–S and their crystal-structure data.

Mineral	Crystal-structure data			Unit-cell parameters				References
	System	Space group		<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	$\beta$ (°)	
Coldwellite	Pd <sub>3</sub> Ag <sub>2</sub> S	cubic	<i>P4<sub>3</sub>32</i>	7.247				McDonald et al. (2015)
Kravtsovite	PdAg <sub>2</sub> S	orthorhombic	<i>Cmcm</i>	7.9835	5.9265	5.7451		Vymazalová et al. (2017)
Vasilite	Pd <sub>16</sub> S <sub>7</sub>	cubic	<i>I43m</i>	8.922				Anatsov (1990)
Vysotskite	PdS	tetragonal	<i>P4<sub>2</sub>/m</i>	6.368		6.562		Genkin and Zvyagintsev (1962), Cabri et al. (1978)
Acanthite	Ag <sub>2</sub> S	monoclinic	<i>2/m</i>	4.229	6.931	7.962	99.61	Emmons et al. (1926)
Argentite*	Ag <sub>2</sub> S	cubic	<i>Im3m</i>	4.89				Emmons et al. (1926)

\*The high-temperature form of Ag<sub>2</sub>S, stable over 177°C.

tubes was reduced by placing closely fitting glass rods over the charge. Charges of 100 to 300 mg were weighed out carefully from the native elements. We used, as starting chemicals, silver powder (Aldrich Chem. Co., 99.9999% purity), sulfur flakes (Aldrich Chem. Co., 99.999% purity) and palladium powder (Aldrich Chem. Co., 99.95% purity). The starting mixtures were heated up slowly to 300°C until all the sulfur was reacted, then the mixture was annealed at 800°C. The resulting run products were ground in an agate mortar under acetone and reheated to 400°C (for 110 days), and at 550°C (for 80 days). After heating, quenching occurred by dropping the capsules in cold water. Phases in the run products were characterised by powder X-ray diffraction; in polished sections examined in reflected light; and with electron-microprobe techniques. A list of representative experimental runs (starting material and products) is given in Table 3.

### X-ray diffraction analysis

Each experimental product was primarily studied with powder X-ray diffraction (XRD) using PANalytical X'Pert (CoK $\alpha$  radiation) and Bruker D8 Advance (CuK $\alpha$  radiation, secondary graphite monochromator) diffractometers. The data were collected in the angular range from 10 to 145°2 $\theta$ . The unit-cell parameters were calculated using the whole-profile pattern fitting method using *FullProf* (Rodríguez-Carvajal, 2006).

### Electron-microprobe analyses

Chemical analyses were performed with a CAMECA SX-100 electron probe microanalyser (EPMA) in wavelength-dispersion mode using an electron beam focussed to 1–2  $\mu$ m. Pure elements were used as standards. Concentrations were quantified on the

AgL $\alpha$ , PdL $\alpha$  and SK $\alpha$  (overlap correction PdL<sub>b1</sub>) with an accelerating voltage of 15 keV, and a beam current of 10 nA. The standards used were pure silver, palladium and sphalerite. In a sample, compositional data were collected from several grains within a polished section (minimum: *n* = 5) and then averaged. The EPMA data of the studied phases are presented in Table 4.

### Results and discussion

The system Pd–Ag–S was studied at 400°C and 550°C. Phase assemblages based on EPMA and powder XRD data, are listed in Table 3. The isothermal sections for 400°C and 550°C are shown in Figs 1 and 2, respectively. At 400°C, the system contains three ternary compounds: Pd<sub>3</sub>Ag<sub>2</sub>S (coldwellite), PdAg<sub>2</sub>S (kravtsovite) and Pd<sub>13</sub>Ag<sub>3</sub>S<sub>4</sub>. At 550°C, the only one ternary phase Pd<sub>3</sub>Ag<sub>2</sub>S (an analogue of mineral coldwellite) is stable in the system.

### Binary phases

The following binary phases are stable at 400°C: Pd<sub>4</sub>S, Pd<sub>16</sub>S<sub>7</sub>, PdS and PdS<sub>2</sub>. The phase Pd<sub>4</sub>S incorporates up to 2.7 wt.% of Ag and phase Pd<sub>16</sub>S<sub>7</sub>, an analogue of the mineral vasilite, incorporates up to 1.3 wt.% of Ag.

The  $\beta$  polymorph (cubic) of phase Ag<sub>2</sub>S, the analogue of the mineral argentite, is unquenchable and reverses to its  $\alpha$  variety Ag<sub>2</sub>S (monoclinic), the analogue of the mineral acanthite. The phase Ag<sub>2</sub>S does not incorporate Pd.

### Ternary phases

#### Coldwellite Pd<sub>3</sub>Ag<sub>2</sub>S

The phase Pd<sub>3</sub>Ag<sub>2</sub>S, the analogue of the mineral coldwellite, forms a stable association with vysotskite and vasilite, vysotskite

**Table 2.** Synthetic phases in the system Pd–Ag–S and their crystal-structure data.

Phase	Experiment No.	Composition (at.%)			Crystal structure		Unit-cell parameters			Primary reference
		Pd	Ag	S	System	Space group	<i>a</i> (Å)	<i>b</i> (Å)	<i>c</i> (Å)	
PdS <sub>2</sub>	5	33.33		66.67	orthorhombic	<i>Pbca</i>	5.460	5.541	7.531	Grønvold and Rost (1957)
PdS	4	50		20	tetragonal	<i>P4<sub>2</sub>/m</i>	6.43		6.63	Gaskell (1937)
Pd <sub>16</sub> S <sub>7</sub>	3	69.6		30.4	cubic	<i>I43m</i>	8.9539			Matković et al. (1976)
Pd <sub>3</sub> S*	2	75		25	orthorhombic	<i>Ama2</i>	6.088	5.374	7.453	Rost and Vestersjoe (1968)
Pd <sub>4</sub> S	1	80		20	tetragonal	<i>Fm3m</i>	5.1147		5.5903	Grønvold and Rost (1962)
$\alpha$ -Ag <sub>2</sub> S**	6		66.67	33.33	monoclinic	<i>P2<sub>1</sub>/n</i>	4.23	6.91	7.87 $\beta$ 99°	Sharma and Chang (1986)
Pd <sub>3</sub> Ag <sub>2</sub> S	14	50	16.67	33.33	cubic	<i>P4<sub>3</sub>32</i>	7.2400(1)			This study
PdAg <sub>2</sub> S	13	25	50	25	orthorhombic	<i>Cmcm</i>	7.983	5.926	5.745	Vymazalová et al. (2017)
Pd <sub>13</sub> Ag <sub>3</sub> S <sub>4</sub>	18	65	15	20	unknown (pseudocubic)				subcell <i>a</i> = 7.236 Å	This study

\*Stable in the temperature interval from 555 to 635°C; \*\*Ag<sub>2</sub>S exists in three allotropic forms ( $\alpha$ -Ag<sub>2</sub>S,  $\beta$ -Ag<sub>2</sub>S and  $\gamma$ -Ag<sub>2</sub>S).

**Table 3.** Representative experimental runs, starting material and run products (based on XRD and EPMA data).

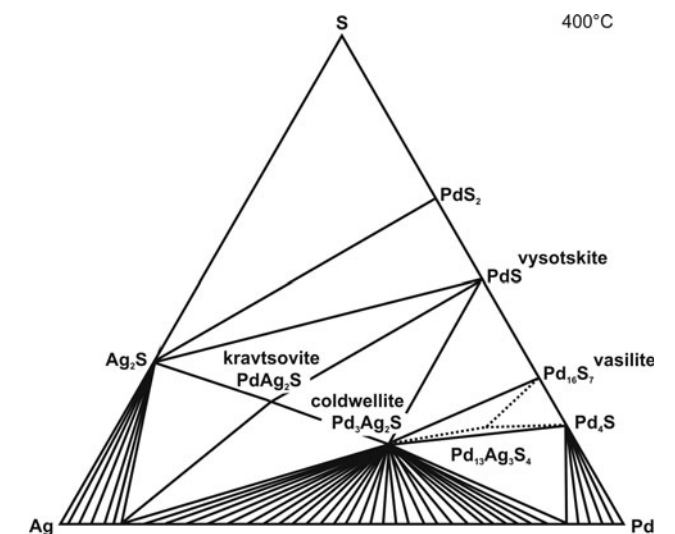
Run No.	Starting composition (at.%)			Phase assemblages at 400°C			Phase assemblages at 550°C		
	Pd	Ag	S						
S7	25	25	50	Ag <sub>2</sub> S	PdS <sub>2</sub>	PdS	Ag <sub>2</sub> S	PdS <sub>2</sub>	PdS
S8	40	20	40	PdAg <sub>2</sub> S	PdS		Ag <sub>2</sub> S	PdS	Pd <sub>3</sub> Ag <sub>2</sub> S
S9	30	40	30	PdAg <sub>2</sub> S	PdS		Ag <sub>2</sub> S	PdS	Pd <sub>3</sub> Ag <sub>2</sub> S
S10	50	25	25	Pd <sub>3</sub> Ag <sub>2</sub> S	PdS		Pd <sub>3</sub> Ag <sub>2</sub> S	PdS	
S11	40	40	20	PdAg <sub>2</sub> S	Pd <sub>3</sub> Ag <sub>2</sub> S		Pd <sub>3</sub> Ag <sub>2</sub> S	Ag <sub>2</sub> S	
S12	15	15	70	Ag <sub>2</sub> S	PdS <sub>2</sub>	S <sub>I</sub>	Ag <sub>2</sub> S	PdS <sub>2</sub>	S <sub>I</sub>
S13	25	50	25	PdAg <sub>2</sub> S			Pd <sub>3</sub> Ag <sub>2</sub> S	Ag <sub>2</sub> S	PdS
S14	50	33.33	16.67	Pd <sub>3</sub> Ag <sub>2</sub> S			Pd <sub>3</sub> Ag <sub>2</sub> S		
S15	60	20	20	Pd <sub>3</sub> Ag <sub>2</sub> S	Pd <sub>16</sub> S <sub>7</sub>	Pd <sub>13</sub> Ag <sub>3</sub> S <sub>4</sub>	Pd <sub>3</sub> Ag <sub>2</sub> S	Pd <sub>16</sub> S <sub>7</sub>	Pd <sub>4</sub> S
S16	25	60	15	PdAg <sub>2</sub> S	Pd <sub>3</sub> Ag <sub>2</sub> S	Ag-Pd alloy	Ag <sub>2</sub> S	Pd <sub>3</sub> Ag <sub>2</sub> S	Ag-Pd alloy
S17	70	15	15	Pd <sub>3</sub> Ag <sub>2</sub> S	Pd <sub>4</sub> S	Ag-Pd alloy	Pd <sub>3</sub> Ag <sub>2</sub> S	Pd <sub>4</sub> S	Ag-Pd alloy
S18	65	15	20	Pd <sub>13</sub> Ag <sub>3</sub> S <sub>4</sub>	Pd <sub>3</sub> Ag <sub>2</sub> S	Pd <sub>16</sub> S <sub>7</sub>	Pd <sub>3</sub> Ag <sub>2</sub> S	Pd <sub>16</sub> S <sub>7</sub>	Pd <sub>4</sub> S

**Table 4.** EPMA results for the phases studied\*.

Phase	Run No.	wt.%				apfu		
		Ag	Pd	S	Total	Ag	Pd	S
Pd <sub>4</sub> S	S1	0	93.47	6.31	99.78	0	4.08	0.92
	S2	0	90.77	8.97	99.73	0	4.09	0.91
	S17	2.69	89.39	6.59	98.67	0.12	3.92	0.96
	S18	0.14	92.93	6.63	99.69	0.01	4.04	0.96
Pd <sub>3</sub> S	S2 <sub>600</sub>	0.34	90.91	9.25	100.50	0.01	2.98	1.01
	Pd <sub>16</sub> S <sub>7</sub>	S2	0	88.94	10.77	99.71	0	16.41
PdS	S3	0	88.77	10.84	99.61	0	16.37	6.63
	S4	0	88.93	10.63	99.55	0	16.47	6.53
	S15	1.31	87.00	11.46	99.77	0.23	15.84	6.92
	S4	0	77.58	21.71	99.29	0	1.04	0.96
	S5	0	77.59	22.01	99.60	0	1.03	0.97
	S7	0.28	77.33	22.65	100.27	0	1.01	0.98
	S8	0.06	77.27	22.64	99.98	0	1.01	0.99
	S9	0.84	77.10	21.76	99.69	0.01	1.03	0.96
	S10	0.00	77.83	22.16	99.99	0	1.03	0.97
	PdS <sub>2</sub>	S7	0.20	62.90	36.11	99.21	0	1.03
Ag <sub>2</sub> S	S6	85.45	0	13.64	99.09	1.95	0	1.05
	S7	85.24	0.01	13.99	99.25	1.93	0	1.07
PdAg <sub>2</sub> S	S8	60.42	30.91	8.83	100.16	1.99	1.03	0.98
	S9	60.69	31.18	8.83	100.70	1.99	1.04	0.97
	S10	60.33	31.48	8.69	100.50	1.99	1.05	0.96
	S11	59.88	31.49	8.79	100.16	1.97	1.05	0.97
	S13	60.42	30.98	8.70	100.11	2.00	1.04	0.97
	S16	59.97	30.44	8.92	99.34	1.98	1.02	0.99
	S9	38.42	57.06	5.50	100.98	2.01	3.02	0.97
Pd <sub>3</sub> Ag <sub>2</sub> S	S11	38.20	56.98	5.33	100.52	2.01	3.04	0.94
	S14	37.55	57.13	5.29	99.97	1.99	3.07	0.94
	S15	36.73	57.33	5.56	99.62	1.94	3.07	0.99
	S17	34.72	58.80	5.54	99.06	1.84	3.17	0.99
	S16	37.81	56.02	5.46	99.29	2.01	3.02	0.98
Pd <sub>13</sub> Ag <sub>3</sub> S <sub>4</sub>	S18	37.10	58.34	5.43	100.87	1.94	3.10	0.96
	S15	17.54	75.16	6.94	99.65	3.00	13.01	3.99
	S18	17.16	76.07	6.62	99.85	2.94	13.23	3.82
Ag-Pd alloy	S17	32.07	67.42	0.06	99.55	0.64	1.36	0.00
	S16	88.56	11.03	0.17	99.76	1.77	0.22	0.01

\*Compositional data were collected from several grains within a polished section (n = 5) and then averaged. Run products are quenched at 400°C, for S2 (phase Pd<sub>3</sub>S) at 600°C.

and kravtsovite, ternary phase Pd<sub>13</sub>Ag<sub>3</sub>S<sub>4</sub> and Pd<sub>4</sub>S, and a Ag-Pd alloy (Fig. 3). The XRD data for Pd<sub>3</sub>Ag<sub>2</sub>S at 400°C are in an agreement with the crystal-structure data determined by McDonald *et al.* (2015) for natural Pd<sub>3</sub>Ag<sub>2</sub>S (Tables 1 and 2). The phase is stable up to 940°C (Raub *et al.*, 1954). In the study of El-Boragy and Schubert (1971) the phase ‘Pd<sub>2</sub>AgS’ is assumed to have a β-Mn type structure. However the phase ‘Pd<sub>2</sub>AgS’



**Fig. 1.** Isothermal section of the phase diagram of the ternary system Pd-Ag-S system at 400°C.

synthesised at 550°C by El-Boragy and Schubert (1971) is in fact the phase Pd<sub>3</sub>Ag<sub>2</sub>S. The phase ‘Pd<sub>2</sub>AgS’ is not stable at 550°C (Fig. 2).

Coldwellite was discovered in a heavy-mineral concentrate from the Marathon Cu-PGE-Au deposit, Coldwell Complex, Ontario in Canada (McDonald *et al.*, 2015) and also reported by Ames *et al.* (2017) and Good *et al.* (2017) from the same deposit. Prior to full characterisation of coldwellite by McDonald *et al.* (2015), a mineral with the same composition was also reported by Seversen and Hauck (2003) from the Birch Lake deposit, Duluth complex, Minnesota in USA and by Subbotin *et al.* (2012) from the Federova-Pana layered intrusion, Kola Peninsula in Russia.

*Kravtsovite PdAg<sub>2</sub>S*

The ternary phase PdAg<sub>2</sub>S, an analogue of the mineral kravtsovite, is orthorhombic, has space group (Cmcm) and unit-cell parameters a = 7.983, b = 5.926 and c = 5.745 Å (Vymazalová *et al.*, 2017). The phase is isostructural with the phase Na<sub>2</sub>AuBi (Kim *et al.*, 2010) forming the zigzag chains of [S-Pd-S-Pd].

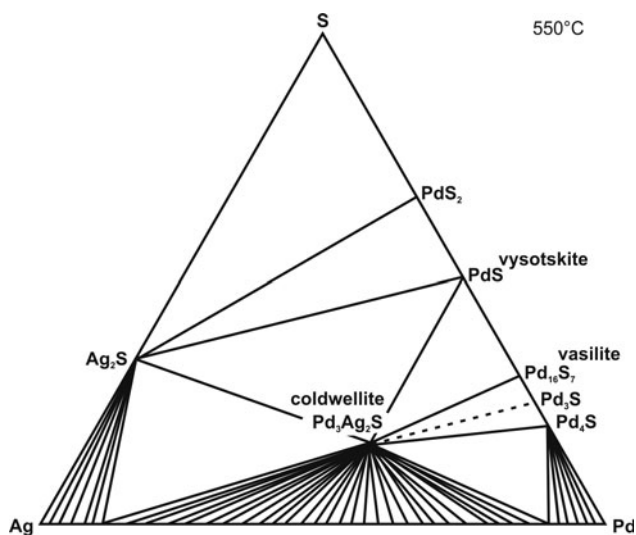


Fig. 2. Isothermal section of the phase diagram of the ternary system Pd-Ag-S system at 550°C.

Kravtsovite forms a stable association with  $\text{Ag}_2\text{S}$  and vysotskite; vysotskite and coldwellite; and it also coexists with a Ag-Pd alloy (Fig. 3a). Kravtsovite is stable up to 507°C.

Kravtsovite was found in the same specimen as the holotype for recently described minerals thalhammerite ( $\text{Pd}_9\text{Ag}_2\text{Bi}_2\text{S}_4$ , Vymazalová *et al.*, 2018) and vymazalováite ( $\text{Pd}_3\text{Bi}_2\text{S}_2$ , Sluzhenikin *et al.*, 2018). The sample came from the vein-disseminated pyrite-chalcopyrite-galena ore characterised by lack of Ni minerals, high galena content and Pt-Pd-Ag bearing minerals, in an association of pyrite and chalcopyrite (Talnakh deposit, Noril'sk district, Sluzhenikin, 2011; Sluzhenikin and Mokhov, 2015). Kravtsovite was also found in the W Horizon in the Marathon Cu-Pd deposit (Ames *et al.*, 2017).

#### The phase $\text{Pd}_{13}\text{Ag}_3\text{S}_4$

In the Pd-Ag-S system we observed a new phase  $\text{Pd}_{13}\text{Ag}_3\text{S}_4$  that coexists with coldwellite and vasilite (Fig. 3b); coldwellite and phase  $\text{Pd}_4\text{S}$ ; vasilite and phase  $\text{Pd}_4\text{S}$  at 400°C, but is not stable at 550°C. However, we were unable to synthesise the pure phase. All attempts to prepare the pure phase resulted in a mixture containing the phase  $\text{Pd}_{13}\text{Ag}_3\text{S}_4$  and other phases

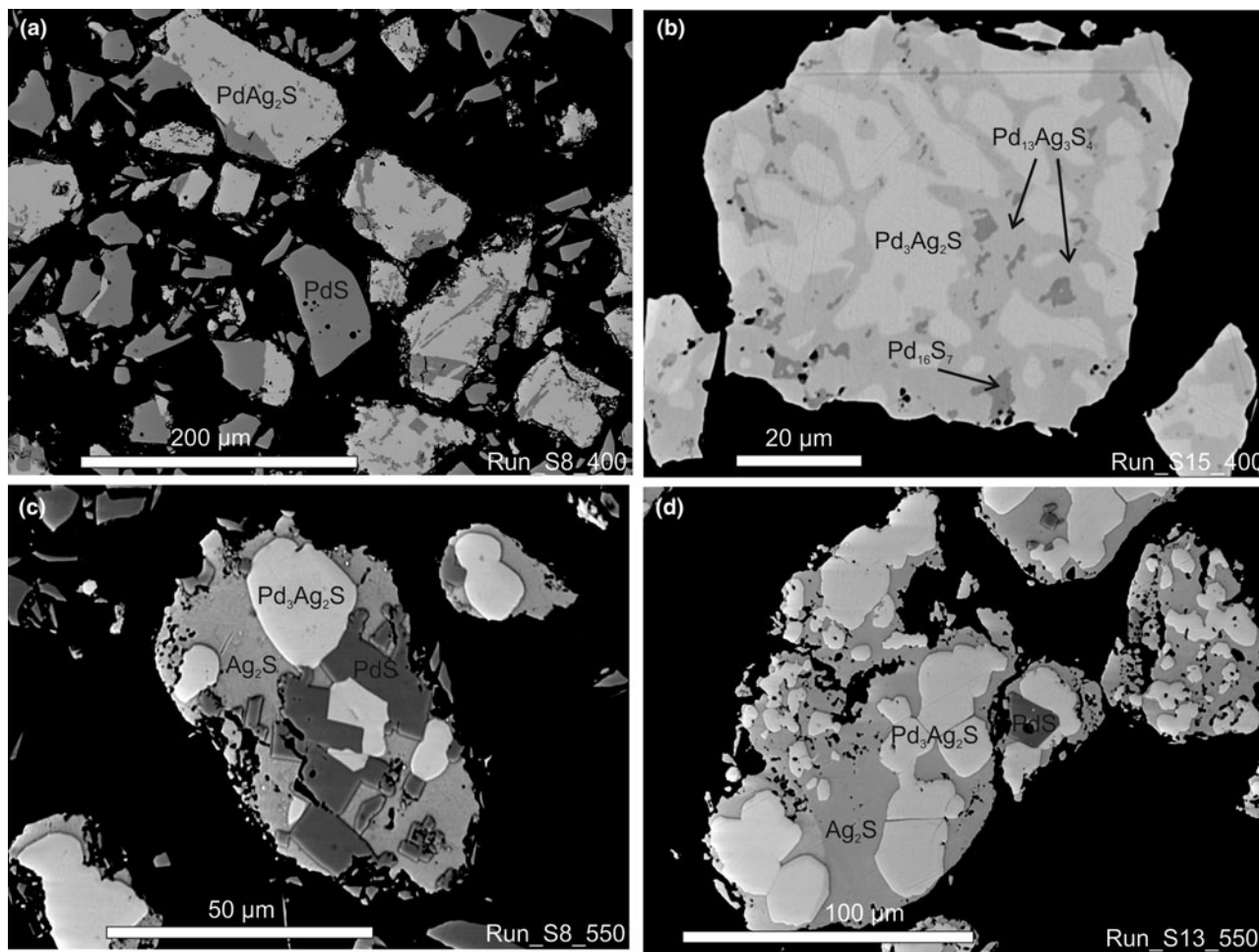


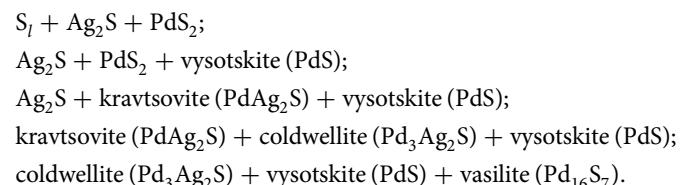
Fig. 3. Back-scattered electron images illustrating the assemblages: (a) kravtsovite ( $\text{PdAg}_2\text{S}$ ) +  $\text{PdS}$ , Run S8, 400°C; (b) coldwellite ( $\text{Pd}_3\text{Ag}_2\text{S}$ ) + vasilite ( $\text{Pd}_{16}\text{S}_7$ ) + phase  $\text{Pd}_{13}\text{Ag}_3\text{S}_4$ , Run S15, 400°C; (c) coldwellite ( $\text{Pd}_3\text{Ag}_2\text{S}$ ) +  $\text{Ag}_2\text{S}$  + vysotskite ( $\text{PdS}$ ), Run S8, 550°C; and (d) coldwellite ( $\text{Pd}_3\text{Ag}_2\text{S}$ ) +  $\text{Ag}_2\text{S}$  + vysotskite ( $\text{PdS}$ ), Run S13, 550°C.

(e.g. Pd<sub>3</sub>Ag<sub>2</sub>S, Pd<sub>16</sub>S<sub>7</sub> or Pd<sub>4</sub>S). Therefore, the phase is depicted tentatively in the phase diagram (Fig. 1).

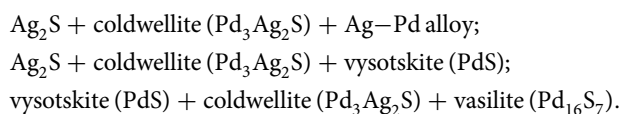
The most intensive peaks in XRD patterns of this phase can be indexed by a cubic cell with  $a = 7.236 \text{ \AA}$  though several weak peaks remained unindexed. Attempts to index all peaks attributed to the phase Pd<sub>13</sub>Ag<sub>3</sub>S<sub>4</sub> remained unsuccessful. The above-mentioned cubic subcell suggests a possible structural relationship of this phase to coldwellite. However, Rietveld refinement using a coldwellite-like structure model yielded an unacceptable fit. Even various attempts to refine the occupancy parameters in a coldwellite structure model of Pd<sub>13</sub>Ag<sub>3</sub>S<sub>4</sub> phase did not result in satisfactory agreement factors.

### Phase relations

Phase relations confirmed the stable mineral assemblages that are known to occur in nature, in addition they can also explain the mineral sequences of formation and define the mineral assemblages that can be expected to occur in Nature. The following assemblages of unknown phases with minerals can be expected (Fig. 1):



At 550°C only one ternary phase, coldwellite (Pd<sub>3</sub>Ag<sub>2</sub>S) is stable (Fig. 2). Coldwellite coexists with palladium sulfides PdS, and Pd<sub>16</sub>S<sub>7</sub>. The binary phase Pd<sub>3</sub>S appears in the system at 555°C (Matković *et al.*, 1976). Subsequently the following assemblages become stable 550°C:



The occurrence of coldwellite, Ag<sub>2</sub>S and vysotskite together in equilibrium reflects the formation of the mineral assemblage above the temperature 507°C.

In comparison with other Ag–Pd chalcogenides, there are no analogues or isostructural ternary phases in the systems Pd–Ag–Se and Pd–Ag–Te (Vymazalová *et al.*, 2014, 2015b, respectively).

### Conclusions and implications

We have determined phase relations in the system Pd–Ag–S at 400°C and 550°C. Three ternary phases were observed in the system at 400°C: Pd<sub>3</sub>Ag<sub>2</sub>S (coldwellite), PdAg<sub>2</sub>S (kravtsovite) and phase Pd<sub>13</sub>Ag<sub>3</sub>S<sub>4</sub>. At 550°C only one ternary phase Pd<sub>3</sub>Ag<sub>2</sub>S (coldwellite) is stable.

Coldwellite, at 400°C forms a stable association with vysotskite and vasilite, coexists with ternary phase Pd<sub>13</sub>Ag<sub>3</sub>S<sub>4</sub> and Pd<sub>4</sub>S, and also coexists with kravtsovite and a Ag–Pd alloy. Kravtsovite is stable up to 507°C; the presence of kravtsovite in the mineral assemblage reflects its formation below this temperature. In contrast, the occurrence of coldwellite, vysotskite and Ag<sub>2</sub>S together

in equilibrium reflects the formation of a mineral assemblage above 507°C. Coldwellite is stable up to 940°C and may occur at high-temperature assemblages at natural conditions.

Mineral assemblages defined in this study can be expected in Cu–Ni–PGE mineral deposits, associated with mafic and ultramafic igneous rocks and in particular in those mineralisations where Pd–Ag sulfides are known to occur such as deposits in Noril'sk–Talnakh in Russia and the Marathon deposit in the Coldwell Alkaline Complex in Canada.

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