THE SYSTEM Hg–Pt–Se AT 400°C: PHASE RELATIONS INVOLVING JACUTINGAITE

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Abstract

Phase relations within the system Hg–Pt–Se were studied experimentally in the temperature range 400–800°C using the technique of evacuated silica-glass tubes. In this system, one ternary phase, Pt_2HgSe_3, jacutingaite, was recently described from the Cauê iron-ore deposit, Minas Gerais, Brazil. At 400°C, the following assemblages are stable: $PtSe_2 + HgSe + (Se_L)$, $PtSe_2 + Pt_2HgSe_3 + HgSe$, $PtSe_2 + Pt_2HgSe_3 + Pt_5Se_4$, $Pt_2HgSe_3 + Pt_5Se_4 + (Pt)$, $Pt_2HgSe_3 + HgPt + (PtHg)_{ss}$, $Pt_2HgSe_3 + HgPt + Hg_2Pt$, $Pt_2HgSe_3 + Hg_2Pt + Hg_4Pt$, $Pt_2HgSe_3 + Hg_4Pt + HgSe$, and $Hg_4Pt + HgSe + (Hg_v)$. Below 250°C, the phase HgPt is not stable, and the low-temperature assemblage $Pt_2HgSe_3 + Hg_2Pt + (PtHg)_{ss}$ appears in the system. The amalgams Hg_2Pt and Hg_4Pt are likely to be found in nature.

Keywords: phase relations, Hg–Pt selenides, system Hg–Pt–Se, jacutingaite, Pt amalgams.

Introduction

Cabral *et al*. (2008) described the natural Hg–Pt selenide, Pt_2HgSe_3, from heavy-mineral concentrates recovered at the Cauê iron-ore deposit in the Itabira iron-ore district, Minas Gerais, Brazil. This phase occurs on an aggregate of potarite, PdHg, atheneite, $(Pd,Hg)_3As$, and hematite. With the support of documentation on synthetic Pt_2HgSe_3, Vymazalová *et al*. (2012) described this phase as a new mineral species and named this platinum mercury selenide *jacutingaite*. This description and the recognition of a seleniferous signature in the Pd–Pt-bearing auriferous mineralization in Brazil (Cabral & Lehmann 2007) made the phase relations within the system Hg–Pt–Se relevant from a mineralogical point of view. Hence we undertook to experimentally study the phase relations within this system, and now report our results.

Minerals in the System

In addition to native elements Hg, Pt and Se, four minerals have been described from the system: tiemannite (HgSe), sudovikovite ($PtSe_2$), luberoite (Pt_5Se_4), and the newly described ternary compound jacutingaite (Pt_2HgSe_3). This mineral and its name have been approved by the Commission on New Minerals, Nomenclature and Classification of the IMA (CNMNC 2010–078). No natural platinum amalgams have been found to date. Sudovikovite and jacutingaite were observed in hematite-rich auriferous veins at the Cauê iron-ore deposit, Itabira district (Kwitko *et al.* 2002, Cabral *et al.* 2008, Vymazalová *et al.* 2012).

Previous Experimental Results

Selected crystallographic data for phases in the systems Pt–Se, Hg–Se, Hg–Pt and Hg–Pt–Se are summarized in Table 1.

The system Pt–Se

The phase relations within the system Pt–Se were investigated in detail by Richter & Ipser (1994). Two stable phases were reported from the system: Pt_5Se_4 and $PtSe_2$, which melt congruently at 1070°C and 1245 ± 10°C, respectively.

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TABLE 1. CRYSTALLOGRAPHIC DATA FOR PHASES IN THE SYSTEM Hg–Pt–Se

Phase	Symmetry	Space group	Lattice parameters*		References
$PtSe_2$	hexagonal	$P\bar{3}m1$	a c	3.7278 5.0813	Grønvold et al. (1960)
Pt_5Se_4	monoclinic	$P2_1/c$	a b c β	6.584(5) 4.602(3) 11.10(1) 101.6(1)	Matkovic & Schubert (1977)
HgSe	cubic	$(F\bar{4}3m)$	a	6.08	Boctor & Kullerud (1986)
HgPt	tetragonal	$P4/mmm$	a c	4.2 3.82	Bauer et al. (1953)
Hg_2Pt	tetragonal	$P4/mmm$	a c	4.687 2.91	Bauer et al. (1953)
Hg_4Pt	cubic	$I432$	a	6.186	Bauer et al. (1953)
Pt_2HgSe_3	trigonal	$P\bar{3}m1$	a c	7.3477(2) 5.2955(1)	Vymazalová et al. (2012)

* Values of a, b, c in Å, β in degrees.

The system Hg–Se

A phase diagram was presented by Sharma et al. (1992). Only one binary phase, α-HgSe, is stable in the system. It melts congruently at 799°C. At high pressures, α-HgSe converts to β-HgSe (>7.5 kbar, Kafalas et al. 1962).

The system Hg–Pt

Phase relations within the system Hg–Pt according to Guminsky (1990, 1992) are shown in Figure 1. According to this author, the phases $HgPt_4$ and Hg_2Pt are stable between room temperature and 424°C and 436°C, respectively, in the system. The compound HgPt is a high-temperature phase, stable in the temperature interval 250–471°C. Below 250°C, the assemblage Hg_2Pt + Pt becomes stable (Guminsky 1990). The solubility of Hg in Pt up to 250°C is low (0.2–1 at.% Hg). Above 250°C, the solubility increases progressively with temperature up to 18.5 at.% Hg at 450°C (Jangg & Lugscheider 1973). Ionashiro & Fertonani (2002) studied the reaction of mercury with platinum–rhodium alloy and documented in the reaction products two intermetallic compounds, Hg_4Pt and Hg_2Pt.

The system Hg–Pt–Se

Phase relations within the system Hg–Pt–Se have not been studied to date. However, Vymazalová et al. (2012) described in a companion paper the ternary mineral jacutingaite (Pt_2HgSe_3) in detail.

EXPERIMENTAL TECHNIQUES

Fifty-six charges 50–300 mg in weight were synthesized from mercury (Lachema, 99.999% purity), fine wire platinum (Safina, Czech Republic, 99.9% purity), and selenium (Aldrich, 99.999% purity). Starting materials were sealed in evacuated silica-glass tubes and heated in horizontal tube furnaces. The temperatures were measured with Pt–PtRh thermocouples and are accurate to ±3°C. High vapor-pressure over the mercury amalgams limited the temperature range that we could use. For this reason, most experiments were conducted at 400°C. We allowed several weeks for equilibrium to be approached. During most of the runs, the charges were repeatedly reground (2–3 times) under acetone and reheated to the target temperature. After the completion of the runs, the tubes were quenched in ice water. The reaction products were examined by X-ray powder diffraction, reflected-light microscopy, and with an electron microprobe. For analytical work, a CAMECA SX100 microprobe equipped with crystal spectrometers was used. Wavelengths used were Se$L\alpha$, Pt$M\alpha$ and Hg$M\alpha$. We used elemental Se and Pt, and cinnabar as standards. The excitation voltage was 15 kV, with a sample current of 10 nA. We used a beam 1–2 μm across.

EXPERIMENTAL RESULTS

Experiments were conducted in the temperature range 400°–800°C. A few experiments in the binary system Hg–Pt were performed to check phase relations

reported in the literature. The details of relevant experiments are given in Table 2.

The system Pt–Hg

According to our experiments, the phase HgPt is unquenchable. In the run products of experiments quenched from 400°C, we identified only a mixture of Pt and Hg_2Pt. The Hg_2Pt is stoichiometric, and Pt contains 18.06 at.% Hg. This concentration corresponds well with the solubility of Hg in Pt at higher temperatures reported in the literature (Jangg & Lugscheider 1973).

The system Hg–Pt–Se

On the basis of literature data for the binary subsystems and on our experiments within the ternary system, an isothermal condensed phase-diagram for the temperature 400°C is presented in Figure 2. The ternary phase Pt_2HgSe_3, analogue to jacutingaite, is the

dominant compound of the system; it is stoichiometric. In the run products, the phase Pt_2HgSe_3 forms platelets with a visible cleavage (Fig. 3). With the exception of native Se and Hg, the phase Pt_2HgSe_3 forms stable assemblages with all phases in the system. On the basis of our experiments and literature data (particularly for the binary system Hg–Pt) at 400°C, the following univariant assemblages are stable in the system: $PtSe_2$ + HgSe + (Se_L), $PtSe_2$ + Pt_2HgSe_3 + HgSe, $PtSe_2$ + Pt_2HgSe_3 + Pt_5Se_4, Pt_2HgSe_3 + Pt_5Se_4 + (Pt), Pt_2HgSe_3 + HgPt + $(PtHg)_{ss}$, Pt_2HgSe_3 + HgPt + Hg_2Pt, Pt_2HgSe_3 + Hg_2Pt + Hg_4Pt, Pt_2HgSe_3 + Hg_4Pt + HgSe and Hg_4Pt + HgSe + (Hg_v). Note that the subscript "ss" indicates solid solution, "v" vapor, and "L" liquid.

Below 250°C, the phase HgPt no longer is stable, assemblages Pt_2HgSe_3 + Hg_2Pt + HgPt and Pt_2HgSe_3 + HgPt + $(PtHg)_{ss}$ disappear from the system, and a new assemblage, Pt_2HgSe_3 + Hg_2Pt + $(PtHg)_{ss}$ appears. The phase HgPt was not detected among the products of any runs below 250°C.
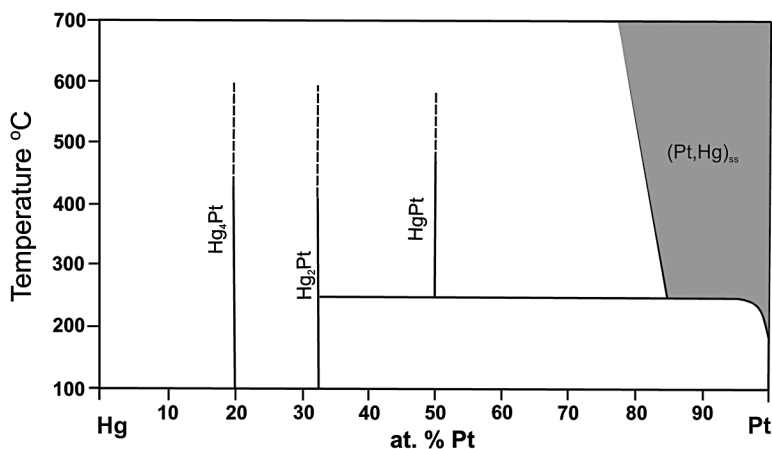

FIG. 1. A schematic phase-diagram of the system Hg–Pt after Guminski (1992). The subscript "ss" indicates solid solution.

TABLE 2. KEY EXPERIMENTS IN THE SYSTEM Pt–Hg–Se

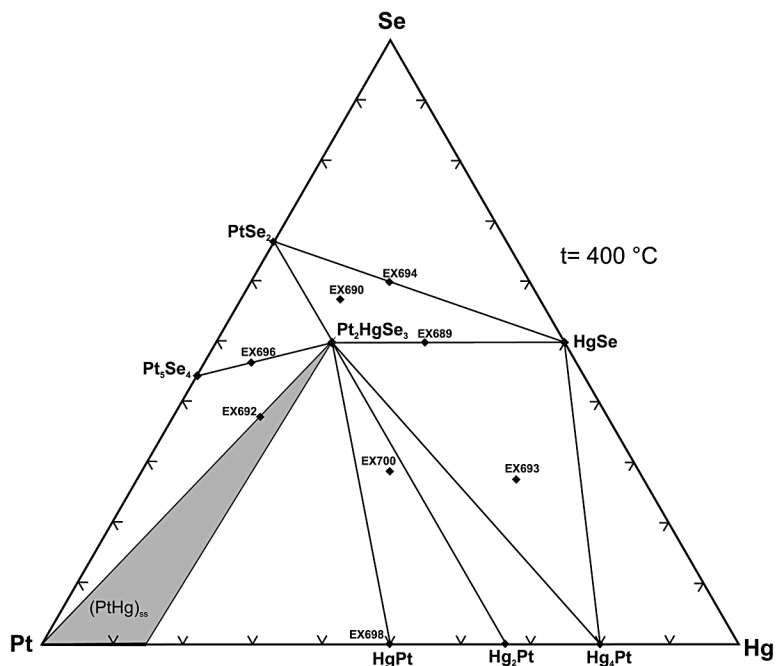| Run No.	Starting mixes, at. %		T°C	Time, hours	Run products
	Pt	Hg			
EX689	20	30	400	96	Pt_2HgSe_3 + HgSe
EX690	28.57	14.29	400	96	Pt_2HgSe_3 + $PtSe_2$ + HgSe
EX692	50	12.5	800	96	Pt_2HgSe_3 + (Pt)
EX693	18.18	54.54	400	70	Pt_2HgSe_3 + Hg_4Pt + HgSe
EX694	20	20	400	70	$PtSe_2$ + HgSe
EX696	46.67	6.67	800	29	Pt_2HgSe_3 + Pt_5Se_4
EX698	50	50	450	394	Hg_2Pt + $(PtHg)_{ss}$ (18.06 at.% Hg)
EX700	35.51	35.71	450	65	Pt_2HgSe_3 + Hg_2Pt + $(PtHg)_{ss}$

Fig. 2. Phase relations in the system Hg–Pt–Se (at.%) at 400°C. Starting compositions of key experiments are shown by diamonds, and details of experimental conditions appear in Table 2. The two-phase field is shown in grey. Subscript "ss" indicates solid solution.
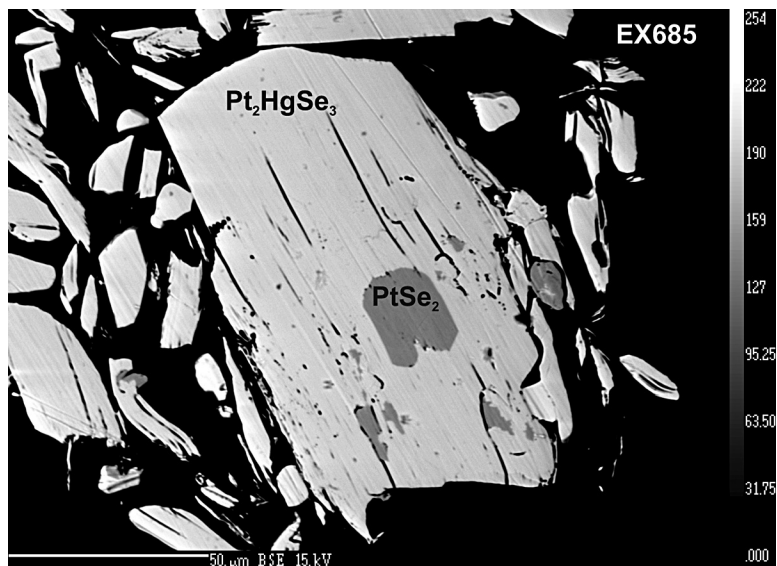

Fig. 3. Back-scattered electron microphotograph of Pt_2HgSe_3 (light) and $PtSe_2$ (dark inclusions) grown at 400°C (run EX685). Scale bar (50 μm) appears at lower left.

Optical Characteristic of Selected Phases

Optical properties of HgSe (tiemannite), $PtSe_2$ (sudovikovite), Pt_5Se_4 (luberoite) and Pt_2HgSe_3 (jacutingaite) are described in the literature. However, optical properties of Hg_2Pt and Hg_4Pt have not been reported yet. As these phases may occur in nature, we present their optical properties.

Hg_2Pt

In reflected light, the phase Hg_2Pt is tan with a pinkish tinge, has strong anisotropism with pinkish brown to dark lilac blue, and strong bireflectance, pleochroic from dark pinkish tan to lilac blue.

Hg_4Pt

In reflected light, the phase Hg_4Pt is pale yellow-white and isotropic.

Discussion and Conclusions

Our experiments show that jacutingaite (Pt_2HgSe_3) forms stable assemblages with the Pt selenides sudovikovite ($PtSe_2$) and luberoite (Pt_5Se_4), and with tiemannite (HgSe). The phase HgPt is stable above 250°C and is unquenchable. Therefore, the assemblage HgPt + Pt is not stable at lower temperatures. Only the phases Hg_2Pt or Hg_4Pt + $(HgPt)_{ss}$ can be expected in low-temperature assemblages where native Pt and Hg occur together. This is likely the case of the Hg-rich palladiferous Pt found in supergene Pt–Pd aggregates at Córrego Bom Sucesso (Cabral et al. 2006), but the assemblage still needs a proper characterization by X-ray diffraction.

Although our experiments have been applied to localities in Minas Gerais, they are applicable to any oxidized ore-forming systems in which hematite is the main Fe mineral. This is because S:Se ratios of <1 occur where reduced Se predominates over reduced sulfur in fluids within the stability field of hematite (e.g., Goldschmidt & Hefter 1933, Simon et al. 1997). The hematite-bearing selenide veins of Tilkerode, Germany, are good examples (e.g., Tischendorf 1959). Tilkerode is the type locality of tischendorfite, $Pd_8Hg_3Se_9$, which coexists with tiemannite (Stanley et al. 2002). The coexistence of tischendorfite and tiemannite seems to be the Pd analogue of the jacutingaite–tiemannite assemblage found in the system Hg–Pt–Se studied here.

Acknowledgements

References

Bauer, E., Nowotny, H. & Stempfl, A. (1953): Röntgenographische Untersuchungen im System: Platin – Quecksilber. *Monatsh. Chem.* **84**, 211-212.

Boctor, N.Z. & Kullerud, G. (1986): Mercury selenide stoichiometry and phase relations in the mercury–selenium system. *J. Solid State Chem.* **62**, 177-183.

Cabral, A.R., Beaudoin, G., Kwitko, R., Lehmann, B., Polônia, J.C. & Choquette, M. (2006): Platinum–palladium nuggets and mercury-rich palladiferous platinum from Serro, Minas Gerais, Brazil. *Can. Mineral.* **44**, 385-397.

Cabral, A.R., Galbiatti, H.F., Kwitko-Ribeiro, R. & Lehmann, B. (2008): Platinum enrichment at low temperatures and related microstructures, with examples of hongshiite (PtCu) and empirical "Pt_2HgSe_3" from Itabira, Minas Gerais, Brazil. *Terra Nova* **20**, 32-37.

Cabral, A.R. & Lehmann, B. (2007): Seleniferous minerals of palladium and platinum from ouro preto-bearing mineralisation in Brazil. *Ore Geol. Rev.* **32**, 681-688.

Goldschmidt, V.M. & Hefter, O. (1933): Zur Geochemie des Selens. *Nachrichten von der Gesellschaft der Wissenschaften zu Göttingen, Mathematisch-Physikalische Klass*, 245-252.

Grønvold, F., Haraldson, H. & Kjekshus, A. (1960): On the sulfides, selenides, and tellurides of platinum. *Acta Chem. Scand.* **14**, 1879-1893.

Guminski, C. (1990): The Hg–Pt (mercury–platinum) system. *Bull. Alloy Phase Diagram* **11**, 26-32.

Guminski, C. (1992): Hg–Pt (mercury–platinum). *In* Binary Alloy Phase Diagrams (2nd edition, T.B. Massalski, ed.). ASM International, Materials Park, Ohio (2154-2755).

Ionashiro, E.Y. & Fertonani, F.L. (2002): Thermogravimetry (TG) applied to the study of the reaction of mercury with platinum–rhodium alloy. *Thermochim. Acta* **383**, 153-160.

JANGG, G. & LUGSCHEIDER, E. (1973): Die Löslichkeit von Quecksilber in verschiedenen Metallen. *Monatsh. Chem.* **104**, 1269-1275.

KAFALAS, J.A., GATOS, H.C., LAVINE, M.C. & BANUS, M.D. (1962): High pressure phase transition in mercury selenide. *J. Phys. Chem. Solids* **23**, 1541-1544.

KWITKO, R., CABRAL, A.R., LEHMANN, B., LAFLAMME, J.H.G., CABRI, L.J., CRIDDLE, A.J. & GALBIATTI, H.F. (2002): Hongshiite (PtCu) from itabirite-hosted Au–Pd–Pt mineralization (*jacutinga*), Itabira district, Minas Gerais, Brazil. *Can. Mineral.* **40**, 711-723.

MATKOVIC, P. & SCHUBERT. J. (1977): Kristallstruktur von Pt_5Se_4. *J. Less-Common Metals* **55**, 185-190.

RICHTER, K.V. & IPSER, H. (1994): Transition metal–chalcogen systems. XI. The platinum–selenium phase diagram. *J. Phase Equilibria* **15**, 165-170.

SHARMA, R.C., CHANG, Y.A. & GUMINSKI, C. (1992): The Hg–Se system. *J. Phase Equilibria* **13**, 663- 671.

SIMON, G., KESLER, S.E. & ESSENE, E.J. (1997): Phase relations among selenides, sulfides, tellurides, and oxides. II. Applications to selenide-bearing ore deposits. *Econ. Geol.* **92**, 468-484.

STANLEY, C.J., CRIDDLE, A.J., FÖRSTER, H.-J. & ROBERTS, A.C. (2002): Tischendorfite, $Pd_8Hg_3Se_9$, a new mineral species from Tilkerode, Harz Mountains, Germany. *Can. Mineral.* **40**, 739-745.

TISCHENDORF, G. (1959): Zur Genesis einiger Selenidvorkommen, insbesondere von Tilkerode im Harz. *Freib. Forsch.* H. **C69**, 1-168.

VYMAZALOVÁ, A., LAUFEK, F., DRÁBEK, M., CABRAL, A.R., HALODA, J., SIDORINOVÁ, T., LEHMANN, B., GALBIATTI, H. F. & DRAHOKOUPIL, J. (2012): Jacutingaite, Pt_2HgSe_3, a new platinum- group mineral from the Cauê iron-ore deposit, Itabira district, Minas Gerais, Brazil. *Can. Mineral.* **50**,