

## THE SYSTEM PtS–PdS–NiS BETWEEN 1200° AND 700°C

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### ABSTRACT

Results of experimental investigations in the dry system PtS–PdS–NiS between 1200° and 700°C are presented. The phases encountered in the experimental runs are synthetic cooperite [(Pt,Pd,Ni)S], synthetic braggite [(Pt,Pd,Ni)S], synthetic vysotskite [(Pd,Pt,Ni)S], quenched sulfide liquid, and Ni<sub>1-x</sub>S. Synthetic cooperite is stable to temperatures above 1200°C, whereas synthetic braggite is stable at temperatures below 1100°C, and synthetic vysotskite, below 1000°C. Below 900°C in the system PtS–PdS–NiS, Ni-saturated synthetic cooperite, braggite, and vysotskite coexist with Ni<sub>1-x</sub>S. At 900°C, only Ni-saturated, Pd-free synthetic cooperite coexists with Ni<sub>1-x</sub>S, and synthetic braggite and Pd-bearing synthetic cooperite coexist with a Pd–Ni–Pt sulfide melt. At temperatures ≥ 1000°C, Ni-saturated synthetic cooperite and braggite coexist with a Pd–Ni–Pt sulfide melt. In the experiments, there is a clearly defined miscibility-gap between cooperite and braggite, but no gap was observed between braggite and vysotskite. The Ni content of braggite and vysotskite with varying Pt:Pd ratio in a Ni-saturated environment is a function of temperature. A higher Ni content indicates a lower temperature of equilibration, and can be estimated using the following equation:  $T [^{\circ}\text{C}] = 998.07 (\pm 7.88) + 0.05 (\pm 0.02) \times \text{Pt}^2 - 4.24 (\pm 0.16) \times \text{Ni}^2$ . In cooperite, a similar relationship between the Ni content and the temperature of equilibration is applicable between 1200° and 900°C.

*Keywords:* system Pt–Pd–Ni–S, phase relations, experimental investigation, cooperite, braggite, vysotskite.

### SOMMAIRE

Nous présentons les résultats de nos expériences faites à sec sur le système PtS–PdS–NiS entre 1200° et 700°C. Les phases qui ont cristallisé au cours de ces expériences sont la cooperite synthétique [(Pt,Pd,Ni)S], la braggite synthétique [(Pt,Pd,Ni)S], la vysotskite synthétique [(Pd,Pt,Ni)S], un liquide sulfuré trempé, et le composé Ni<sub>1-x</sub>S. La cooperite synthétique demeure stable à une température au delà de 1200°C, tandis que la braggite synthétique est stable à une température inférieure à 1100°C, et la vysotskite synthétique, à une température inférieure à 1000°C. En dessous de 900°C dans le système PtS–PdS–NiS, cooperite, braggite, et vysotskite synthétiques saturées en Ni coexistent avec Ni<sub>1-x</sub>S. A 900°C, seule la cooperite synthétique dépourvue de Pd et saturée en Ni coexiste avec Ni<sub>1-x</sub>S, et la braggite et la cooperite palladifère synthétiques coexistent avec un liquide sulfuré Pd–Ni–Pt. A des températures ≥ 1000°C, la cooperite et la braggite synthétiques saturées en Ni coexistent avec un bain fondu sulfuré à Pd–Ni–Pt. Dans les expériences, il y a une lacune de miscibilité bien définie entre cooperite et braggite, mais aucune lacune n'a été observée entre braggite et vysotskite. Les teneurs en Ni de la braggite et de la vysotskite varient avec le rapport Pt:Pd dans un milieu saturé en Ni selon la température. Une teneur plus élevée de la concentration en Ni indique une température plus faible d'équilibration, comme l'indique l'équation:  $T [^{\circ}\text{C}] = 998.07 (\pm 7.88) + 0.05 (\pm 0.02) \times \text{Pt}^2 - 4.24 (\pm 0.16) \times \text{Ni}^2$ . Dans la cooperite, une relation semblable entre la teneur en Ni et la température d'équilibration s'appliquerait entre 1200° et 900°C.

(Traduit par la Rédaction)

*Mots-clés:* système Pt–Pd–Ni–S, relations de phases, étude expérimentale, cooperite, braggite, vysotskite.

### INTRODUCTION

The platinum-group minerals cooperite, braggite, and vysotskite have been described from a large variety of geological environments, including Alaskan-type complexes (Begizov *et al.* 1975, Johan *et al.* 1989), placer deposits, where cooperite and, less commonly, braggite occur as inclusions in Pt–Fe alloys (Augé & Legendre 1992, Cabri *et al.* 1996, Gornostayev *et al.*

1999, Tolstykh *et al.* 1999), in sulfur-poor mineralized horizons in layered intrusions (Grokhovskaya *et al.* 1992, Halkoaho *et al.* 1990, Kingston & El-Dosuky 1982, Kinloch 1982, Penberthy & Merkle 1999, Verryn & Merkle 1994, Volborth *et al.* 1986), and massive magmatic sulfide ores (Genkin & Evstigneeva 1986).

Virtually the complete range of Pt/Pd values between cooperite (ideally PtS) and vysotskite (ideally PdS) has been observed (Fig. 1). However, a clear miscibility-

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gap was observed by Cabri *et al.* (1978) and by Merkle & Verryn (1991) and Verryn & Merkle (1994) between coexisting cooperite and braggite from the Merensky Reef of the Bushveld Complex (Fig. 2). An evaluation of these minerals in the UG-2 of the Bushveld Complex, however, gives no indication of a miscibility gap between cooperite and braggite (Fig. 3). There is a subtle difference in the space group of cooperite and braggite; cooperite belongs to space group  $P4_2/mmc$ , braggite and vysotskite, to  $P4_2/m$  (Bannister & Hey 1932), which makes a miscibility gap plausible. As braggite and vysotskite, belonging to the same space group, form a solid solution, these two minerals are discussed together and are referred to as "braggite-vysotskite". In the tables and figures to be presented here, we have taken an arbitrary content of 10 mol.% PtS as the upper limit of vysotskite compositions, as discussed in Cabri *et al.* (1978). The question of the boundary is being re-evaluated (L.J. Cabri, pers. commun., 2001).

The scatter around a perfect linear relationship between Pt and Pd is caused by rather large variations in

Ni content, especially in material from layered intrusions (Tables 1, 2). Concentrations of other elements are typically rather low (Daltry & Wilson 1997), but depend on coexisting minerals. The variation in the Pt/Pd values of this group of minerals can be attributed to intrinsic differences in Pt/Pd values of silicate melts and immiscible sulfide melts from which the Pt-Pd sulfides formed, fractionation processes, variations in temperature, and changes in sulfur fugacity. The reasons for variation in Ni content are less obvious. We originally presumed (Verryn & Merkle 1994) that in the Merensky Reef and the UG-2 of the Bushveld Complex, distinct trends of substitution of Pd + Ni for Pt exist for braggite-vysotskite coexisting with pentlandite and millerite. A substantial broadening of the database led to the conclusion that the compositional variations in the two assemblages overlap, which suggests that the implied temperature dependence of Ni-uptake in cooperite and braggite-vysotskite may indeed be the controlling factor.

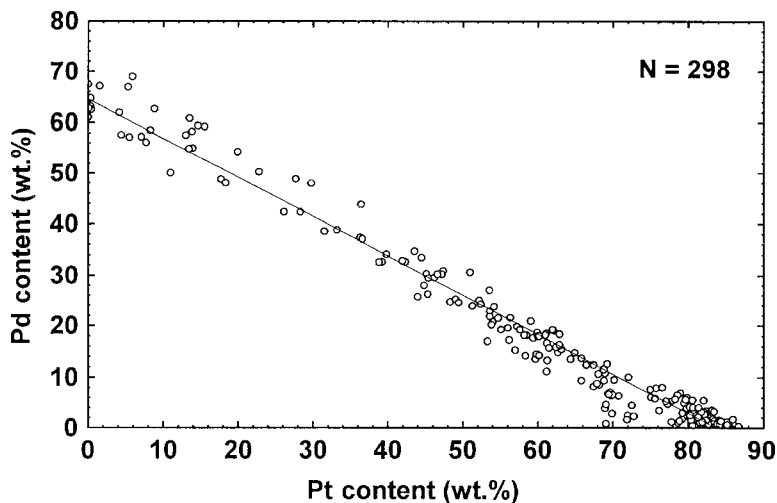


FIG. 1. Pt content versus Pd content in cooperite, braggite, and vysotskite. The analytical data were taken from the literature (Augé *et al.* 1998, Bannister & Hey 1932, Barkov *et al.* 1995, Bowles 2000, Brynard *et al.* 1976, Cabri *et al.* 1978, 1996, Coghill & Wilson 1993, Corriveau & Laflamme 1990, Cowden *et al.* 1990, Criddle & Stanley 1985, Distler *et al.* 1999, Genkin & Evstigneeva 1986, Genkin & Zvyagintsev 1962, Halkoaho 1989, Johan *et al.* 1989, Kingston & El-Dosuky 1982, Laputina & Genkin 1975, Legendre & Augé 1992, Mitrofanov *et al.* 1998, Mostert *et al.* 1982, Rudashevsky *et al.* 1995, Schwellnus *et al.* 1976, Shcheka *et al.* 1991, Tarkian 1987, Todd *et al.* 1982, Tolstykh & Krivenko 1997, Tolstykh *et al.* 1999, Toma & Murphy 1978, Volborth *et al.* 1986, Vuorelainen *et al.* 1982, Watkinson & Dunning 1979, Weiser & Schmidt-Thomé 1993). The solid line indicates the best linear fit.

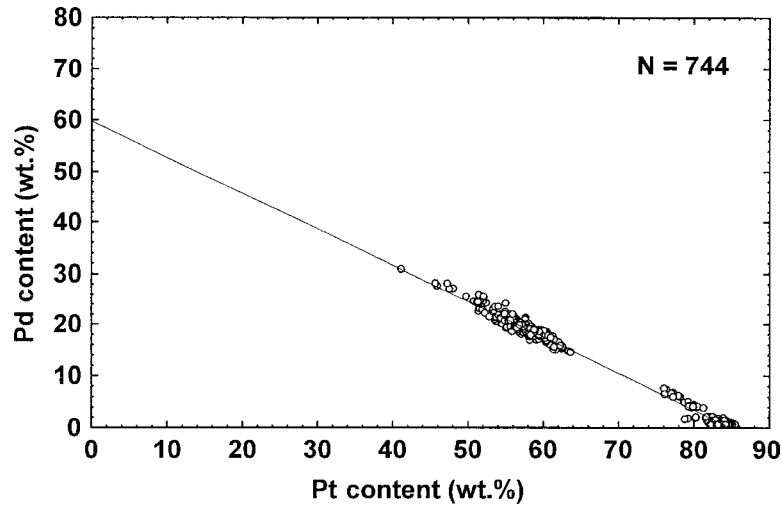


FIG. 2. Pt content *versus* Pd content in cooperite, braggite, and vysotskite from the Merensky Reef of the Bushveld Complex. The solid line indicates the best linear fit.

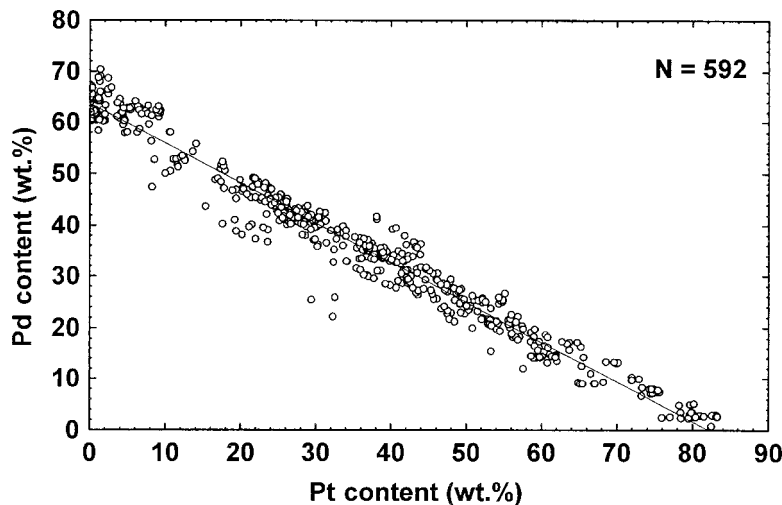


FIG. 3. Pt content *versus* Pd content in cooperite, braggite, and vysotskite from the UG-2 Chromitite of the Bushveld Complex. The solid line indicates the best linear fit.

Because Ni appears to be the most important cation besides Pt and Pd in this group of minerals, we decided to investigate the system PtS–PdS–NiS experimentally. In order to avoid confusion with naturally occurring cooperite, braggite and vysotskite (Nickel 1995), the synthetic equivalents are indicated as “cooperite”, “braggite”, and “vysotskite” throughout this communication.

#### RELATED EXPERIMENTAL INVESTIGATIONS

The system Pd–Ni–S was investigated by Karup-Møller & Makovicky (1993) up to 900°C, and the system Ni–NiS–PtS–Pt, by Gulyaniitskaya *et al.* (1979). Experimental investigations by Skinner *et al.* (1976) at 1000°C and Cabri *et al.* (1978) at 800°C concentrated on the PtS–PdS join; these authors did not explore the

TABLE 1. CONCENTRATIONS OF ADDITIONAL CATIONS IN Pt-Pd SULFIDES, AS RECORDED IN THE LITERATURE

	mean	standard deviation (1σ)	minimum	maximum	N
<b>Braggite from placer deposits*</b>					
Cu wt.%	0.55	0.73	0.14	2.55	10
Fe	0.43	0.35	0.05	1.18	9
Ir	1.54	2.39	0.16	6.45	7
Ni	0.82	0.78	0.06	2.97	12
Os	0.35	0.22	0.15	0.87	9
Rh	2.19	4.63	0.2	12.63	7
Ru	0.41	0.06	0.35	0.47	3
<b>Braggite from layered intrusions</b>					
Ag	0.3	0.13	0.07	0.43	7
Bi	0.53	0.26	0.06	0.9	7
Cu	0.26	0.24	0.07	0.7	6
Fe	0.37	0.7	0.01	4.14	43
Ni	6.24	2.8	0.47	16.6	118
Pb	0.9	0.13	0.74	1.11	6
Rh	0.19	0.12	0.07	0.3	3
<b>Cooperite from placer deposits*</b>					
As	0.1	0.02	0.08	0.12	3
Cu	0.67	0.88	0.03	2.75	11
Fe	0.4	0.47	0.1	2.14	25
Ir	0.58	0.85	0.08	4.18	34
Ni	0.3	0.24	0.01	0.99	28
Os	0.34	0.09	0.08	0.085	55
Rh	0.92	1.58	0.13	6	15
Ru	0.25	0.23	0.04	0.5	3
<b>Cooperite from ophiolite complexes</b>					
Cr	1.47	0.63	0.86	2.11	3
Fe	0.92	0.63	0.52	1.65	3
Ir	0.24	0.14	0.09	0.36	3
Ni	0.58	0.39	0.07	1	4
<b>Cooperite from Alaskan-type intrusions</b>					
Cu	0.08	0.07	0.02	0.2	6
Fe	0.32	0.22	0.05	0.64	7
Ni	0.13	0.08	0.03	0.25	7
Rh	0.17	0.11	0.05	0.35	12
Ru	0.06	0.03	0.03	0.11	5
<b>Cooperite from layered intrusions</b>					
Bi	0.78	0.74	0.12	2.39	7
Cu	0.32	0.3	0.1	0.7	6
Fe	0.81	0.77	0.05	2.64	19
Ir	1.84	1.06	0.62	2.5	3
Ni	1.01	1.24	0.1	7.6	63
Pb	1.27	0.08	1.14	1.35	5
Rh	0.18	0.19	0.03	0.5	7

The sources of this compilation are listed in caption of Figure 1. N: number of observations. \*Considered to be derived from Alaskan-type intrusions and ophiolite complexes. Mainly present as inclusions in Pt-Fe alloy.

possible influence of Ni on thermal stabilities and miscibility ranges of minerals in the system.

The system Pd-Fe-Ni-S was investigated by Makovicky *et al.* (1990) and Makovicky & Karup-Møller (1995); the influence of Pt, however, has not been assessed.

TABLE 2. CONCENTRATIONS OF ADDITIONAL CATIONS IN Pt-Pd SULFIDES FROM THE MERENSKY REEF AND THE UG-2 CHROMITITE OF THE BUSHVELD COMPLEX

	mean	standard deviation (1σ)	minimum	maximum	N
<b>Cooperite from the Merensky Reef</b>					
As wt.%	0.11	0.04	0.06	0.22	62
Co	0.04	0.01	0.02	0.07	76
Cu	0.18	0.23	0.03	1.4	147
Fe	0.19	0.35	0.02	2.13	154
Ni	0.61	0.1	0.28	1.1	432
Rh	0.24	0.18	0.12	0.95	29
<b>Braggite from the Merensky Reef</b>					
Cu	0.11	0.16	0.03	1.09	75
Fe	0.17	0.25	0.024	1.7	62
Ni	4.92	0.64	3.412	6.61	312
<b>Cooperite from the UG-2 chromitite</b>					
Co	0.03	0.02	0.01	0.08	18
Cu	0.1	0.16	0.01	0.86	31
Fe	0.74	0.63	0.01	3.01	44
Ni	2.17	2.34	0.53	8.6	44
Rh	0.26	0.11	0.11	0.51	28
<b>Braggite-vysotskite from the UG-2 chromitite</b>					
Co	0.02	0.02	0.01	0.1	136
Cu	0.16	0.24	0.01	2.52	469
Fe	0.49	0.51	0.01	5.66	548
Ni	7.37	2.81	0.28	18.14	548
Rh	0.16	0.26	0.01	2.69	237

Only values above the lower limit of detection are considered. N: number of observations.

## EXPERIMENTAL PROCEDURES

All experiments were conducted under dry conditions following standard procedures in evacuated silica glass capsules (Kullerud 1971, Moh & Taylor 1971). Charges of 200–300 mg each were prepared using chemically pure (purity of ≥99.99%) fine powders of platinum, palladium, nickel, and sulfur and sealed under a vacuum of  $\sim 2 \times 10^{-5}$  bar. The contents of Pt, Pd, and Ni in the experimental charges were varied in such a manner that saturation in Ni was achieved in most experiments. Although we are aware of the effects of variable S content (Verryn & Merkle 1996, Verryn 2000), here we report only on initial sulfur contents of 50 atomic %. In order to avoid introduction of oxygen into the charges due to surface oxidation from exposure to the atmosphere, Ni was reduced before use. It was not found necessary to reduce Pt and Pd, because oxidation of natural PGE alloys is extremely slow (Westland 1981).

An excess of sulfur can cause experimental difficulties in dry sulfide research. Sulfur vapor pressures are not known very accurately (Nell 1987), but to avoid failure of the glass containers due to high vapor pres-

tures of sulfur, the charges were pre-reacted at 700–850°C for 3–6 weeks. This pre-reaction treatment gives the sulfur enough time to react with metals at a temperature where the sulfur pressure is low enough not to cause failure of the glass tubes. After pre-reaction, the samples were quenched in air to avoid unnecessary strain on the silica glass.

After pre-reaction, charges were placed for tempering at 1200° and 1100°C into the furnace directly at the required temperature. Charges intended for tempering at 900° to 700°C were heated up to a higher temperature than required (1200°C) for ~8 hours in order to achieve quick homogenization in the melt stage and then slowly cooled down to the required temperature.

The charges were reacted at the relevant temperatures between 5 (at 1200°C) and 85 (at 700°C) days. The experimental charges were quenched in water. It is very difficult to predict the time required to achieve equilibrium. We rejected experiments where the compositional heterogeneities exceeded the analytical uncertainty.

#### ANALYTICAL TECHNIQUES

Polished sections of quenched products of each completed experiment were studied by reflected light microscopy. The compositional variation of the products was determined by electron-microprobe analysis on a JEOL 733 microprobe in wavelength-dispersion mode. The accelerating potential was 20 kV, and the beam current,  $5 \times 10^{-8}$  A. Between 50 and 100 spot analyses were taken on “cooperite”, “braggite”, “vysotskite”, and  $\text{Ni}_{1-x}\text{S}$  in each sample where present. We used synthetic PdS ( $L\alpha$  line) for Pd, the  $K\alpha$  line on the same standard for S, synthetic  $\text{Pt}_{0.7}\text{Pd}_{0.3}\text{S}$  ( $L\alpha$  line) for Pt, and synthetic NiS ( $K\alpha$  line) for Ni. Detection limits are 0.09 wt.% for Pt and for Pd and 0.02 wt.% for Ni. Maximum analytical uncertainties determined at the  $3\sigma$  level according to Kaiser & Specker (1956) are 0.85 wt.% for Pt, 0.76 wt.% for Pd, 0.84 wt.% for Ni, and 0.65 wt.% for S. The solidified melt was analyzed using a defocused beam (about 50  $\mu\text{m}$  in diameter) or by scanning multiple preselected areas at low magnifications (depending on the size of the area occupied by melt), using the same standards as for the solid phases. Counting times were 50 seconds at the peak positions and 25 seconds at symmetrically disposed background positions.

#### THE PHASES ENCOUNTERED

The phases encountered in the polished sections of the experimental runs are “cooperite” [(Pt,Pd,Ni)S], “braggite”[(Pt,Pd,Ni)S], “vysotskite” [(Pd,Pt,Ni)S], quenched sulfide liquid, and  $\text{Ni}_{1-x}\text{S}$ . As discussed above, cooperite and braggite are separated by a miscibility gap, braggite and vysotskite, belonging to the same space-group, form a solid solution.

#### RESULTS

Arithmetic means of the results of spot analyses (wt.%), including standard deviations at the  $1\sigma$  level, were calculated for each phase in each experiment. Atomic proportions were calculated from these means, and their standard deviations are taken from the calculations of the mean of all the analyses recalculated to atomic proportions (Table 3). Phase relations for each temperature are presented in Figure 4. The diagrams are presented in cation proportions rather than as PtS–PdS–NiS, as the melt in some cases contains less than 50 at.% sulfur. Tie lines represent the exact compositions of the experimental runs as indicated in Table 3.

##### Phase relations at 1200°C

At 1200°C, the two phases recognized are “cooperite” and a melt. The PdS–NiS join is occupied by a melt with a maximum solubility of 19.0 at.% Pt along the PtS–NiS join and of 16.5 at.% Pt along the PtS–PdS join. Toward the central portion of the melt field, along the PdS–NiS join, the Pt content increases to a maximum of 22.4 at.% Pt. The maximum solubility of Ni in ideal, Pd-free “cooperite” coexisting with a Pd-free melt along the PtS–NiS join is 1.5 at.%. The Pd content limit in Ni-free “cooperite” coexisting with a Ni-free melt at 1200°C is 6.3 at.%. The Ni content in “cooperite” at 1200°C decreases slightly with increasing Pd content.

##### Phase relations at 1100°C

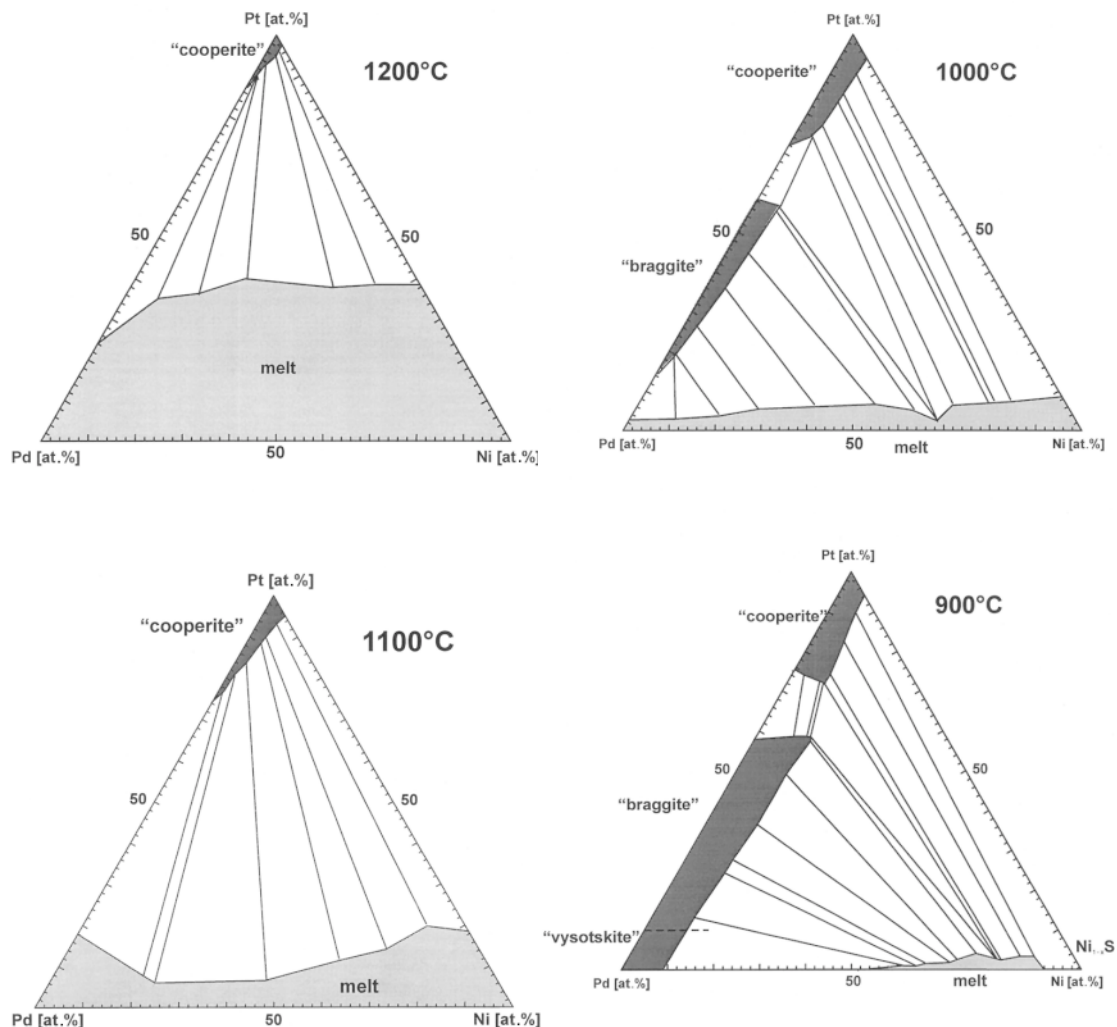
The two phases observed at 1100°C are “cooperite” and a melt. Compared to the phase relations at 1200°C, the compositional field of the melt is reduced and that of “cooperite” is enlarged (Fig. 4).

The PdS–NiS join is occupied by a melt with a maximum solubility of 9.0 at.% Pt along the PtS–NiS join as well as along the PtS–PdS join. Contrary to the observations at 1200°C, the Pt content decreases slightly to a minimum of 3.5 at.% Pt toward the central portion of the melt field along the PdS–NiS join at 1100°C. The maximum solubility of Ni in ideal, Pd-free “cooperite” coexisting with Pd-free melt along the PtS–NiS join is 2.7 at.%. The limit in Pd content in Ni-free “cooperite” coexisting with Ni-free melt at 1100°C lies at 12.8 at.%.

##### Phase relations at 1000°C

At 1000°C, the compositional field of the melt is reduced further with respect to that at 1100°C. In addition to “cooperite” and melt, a third phase corresponding to “braggite” appears.

The maximum solubility of Pt in the melt along the PtS–PdS join is 1.1 at.%, which increases with increasing Ni content in the melt to a maximum of 4.0 at.% Pt along the PtS–NiS join. In the region where the melt



coexists with “cooperite” and “braggite” (*i.e.*, where all three phases coexist), however, the Pt content in melt declines to a minimum of 0.7 at.% (Fig. 4). The maximum solubility of Ni in ideal, Pd-free “cooperite” coexisting with Pd-free melt along the PtS–NiS join is 3.3 at.%. The Pd content in Ni-free “cooperite” coexisting with Ni-free “braggite” at 1000°C is 13.7 at.%, whereas the Pt content in Ni-free “cooperite” coexisting with Ni-free “cooperite” is 29.0 at.%. The Ni content in both “cooperite” and “braggite” decreases with increasing Pd content, but is higher in “braggite” than in “cooperite”.

#### Phase relations at 900°C

At 900°C, the compositional field of the melt is reduced much further compared to that at 1000°C, especially on the Pd-rich side of the PdS–NiS join. The

compositional field of “braggite–vysotskite” stretches down to the PdS–NiS join.  $\text{Ni}_{1-x}\text{S}$  appears as another stable phase at this temperature. At 900°C, analytical totals lower than 97.0 wt.% were accepted for the solidified melt of some experiments, owing to its porosity. The Pt-free “vysotskite” that coexists with Pt-free melt contains a maximum of 4.3 at.% Ni. Pd-free “cooperite” containing a maximum of 3.1 at.% Ni coexists with  $\text{Ni}_{1-x}\text{S}$ , with a maximum solubility of 0.3 at.% Pt along the PtS–NiS join. Pt-free  $\text{Ni}_{1-x}\text{S}$  contains 0.6 at.% Pd where it coexists with a melt containing 6.7 at.% Pd (Karup-Møller & Makovicky 1993).

The field of the solidified melt does not span across the entire PdS–NiS join as it does at the higher temperatures. The Ni content of the melt varies between 25.8 and 43.3 at.%. Similar to the observation at 1000°C, the Pt content of the melt declines where it coexists with

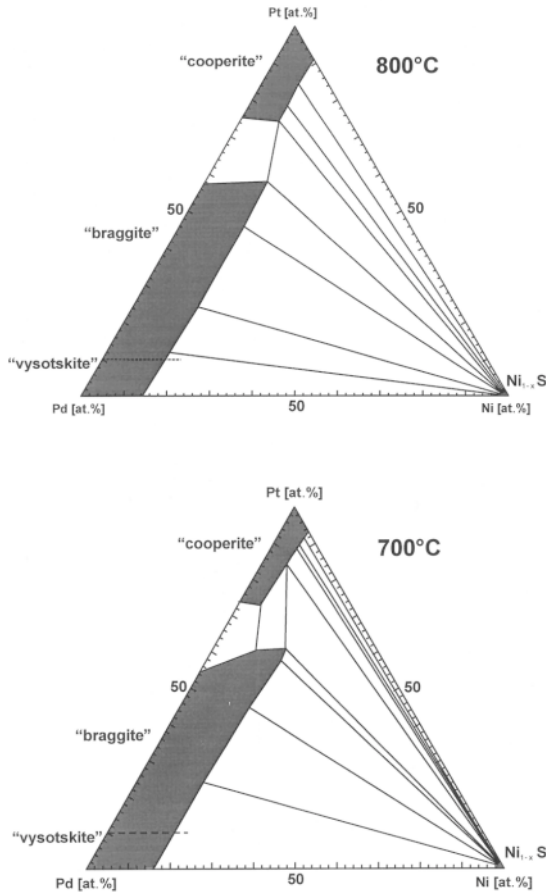


FIG. 4. Phase relations in the system PtS–PdS–NiS in cation proportions at 1200°, 1100°, 1000°, 900°, 800°, and 700°C (the stippled line indicates the border between “braggite” and “vysotskite”).

“cooperite” and “braggite” (*i.e.*, where all three phases coexist) (Fig. 4). The Ni content of “cooperite” increases with increasing Pd content, whereas the Ni content decreases in “braggite–vysotskite” with increasing Pd content. The Ni content is higher in “braggite–vysotskite” than in “cooperite”.

#### Phase relations at 800°C

At 800°C, no melt phase is present, and “cooperite”, “braggite”, and “vysotskite” that formed under Ni-saturated conditions all coexist with  $\text{Ni}_{1-x}\text{S}$ . In general, two charges with constant Pt:Pd ratio but varying Ni content (25 and 10 at.%) were prepared. Nickel seems to act as a “flux” at this temperature, because in the experiments with low Ni content in the charges, the

quenched products in some cases displayed some degree of heterogeneity.

The  $\text{Ni}_{1-x}\text{S}$  that coexists with Pt-free “vysotskite” and Pd-free “cooperite” contains a maximum of 1.7 at.% Pd and 0.2 at.% Pt, respectively. Maximum solubility of Ni in Pd-free “cooperite” along the PtS–NiS join is 4.5 at.%. The Pd-limit in Ni-free “cooperite” coexisting with Ni-free “braggite” at 800°C is 12.6 at.%.

The Ni content of both “cooperite” and “braggite–vysotskite” in a Ni-saturated environment remains fairly constant. The Ni content ranges from 4.0 to 4.5 at.% Ni in “cooperite” and between 6.9 and 7.5 at.% Ni in “braggite–vysotskite”. These levels are slightly higher than at 900°C. In both mineral groups, there is a slight decline in Ni content with increasing Pd content (Fig. 4).

#### Phase relations at 700°C

At 700°C, the “cooperite”, “braggite”, and “vysotskite” that formed in a Ni-saturated environment coexist with  $\text{Ni}_{1-x}\text{S}$ . The  $\text{Ni}_{1-x}\text{S}$  that coexists with Pt-free “vysotskite” and Pd-free “cooperite” contains a maximum of 1.0 at.% Pd and 0.1 at.% Pt, respectively. Maximum solubility of Ni in Pd-free “cooperite” along the PtS–NiS join is 3.7 at.%. The Pd limit in Ni-free “cooperite” coexisting with Ni-free “braggite” at 700°C is 13.1 at.%. The Ni content in both “cooperite” and “braggite–vysotskite” formed in a Ni-saturated environment remains fairly constant, ranging from 3.07 (Pd-free) to 3.7 at.% Ni in the former and between 8.1 (Pt-free) and 8.7 at.% Ni in the latter. The Ni content in “braggite–vysotskite” is slightly greater than that at 800°C, whereas the Ni content of “cooperite” is slightly lower than that at 800°C. In both mineral groups, there is a slight decline in Ni content with increasing Pd content.

The phase relations of coexisting “cooperite” and “braggite” at 700°C are somewhat different than those at 800°C. At 700°C, “cooperite” coexisting with “braggite” synthesized under slightly Ni-undersaturated conditions (implying that they do not coexist with  $\text{Ni}_{1-x}\text{S}$ ) contains significantly higher amounts of Pd (13.1 at.% Pd) than that formed under Ni-saturated conditions (5.3 at.% Pd).

#### TRENDS IN Ni CONTENT

As already shown by Makovicky *et al.* (1990) and Makovicky & Karup-Møller (1995) for the system Fe–Ni–Pd–S and by Karup-Møller & Makovicky (1993) for the system Pd–Ni–S, solubility of Ni in “cooperite”, “braggite”, and “vysotskite” with varying Pt:Pd ratios in a Ni-saturated environment is a function of temperature, *i.e.*, a lower temperature of equilibration permits a higher Ni content. The mineral compositions, especially their Ni contents, thus have the potential to indicate at which stage of development of the ore deposit these phases crystallized, were exsolved, or underwent overprinting by fluids.







TABLE 3 (continued). MEAN (ARITHMETIC) COMPOSITIONS OF PHASES IN THE SYSTEM PtS-PdS-NiS AT 1200, 1100, 1000, 900, 800, AND 700°C

Sample	Phase		Pt	Pd	Ni	S	TOTAL	Sample	Phase		Pt	Pd	Ni	S	TOTAL
SV708	"Cpr"	w	71.35 (0.64)	11.64 (0.43)	1.62 (0.08)	16.36 (0.23)	100.96	SV712	"Cpr"	w	82.95 (0.85)	1.04 (0.39)	1.86 (0.16)	14.41 (0.50)	100.26
		a	36.10 (0.56)	10.80 (0.34)	2.72 (0.14)	50.38 (0.35)	N=20			a	46.41 (1.06)	1.07 (0.40)	3.46 (0.43)	49.06 (1.02)	N=37
		"Brg"	w	62.89 (0.19)	16.67 (0.32)	3.38 (0.16)	17.86 (0.10)	100.86		Ni <sub>1-x</sub> S	w	0.43 (0.10)	0.29 (0.14)	64.55 (0.75)	36.02 (0.57)
SV710	"Cpr"	a	29.47 (0.10)	14.33 (0.29)	5.26 (0.24)	50.94 (0.22)	N=12		a	0.10 (0.04)	0.12 (0.06)	49.35 (0.67)	50.43 (0.64)	N=9	
		w	81.56 (0.55)	2.41 (0.43)	1.90 (0.16)	14.83 (0.36)	100.69	SV713	"Brg"	w	30.36 (0.75)	41.56 (0.55)	6.59 (0.12)	21.80 (0.38)	99.92
	a	44.68 (0.62)	2.42 (0.43)	3.46 (0.33)	49.44 (0.83)	N=40	a	11.99 (0.34)		29.68 (0.34)	7.27 (0.17)	51.06 (0.43)	N=13		
	Ni <sub>1-x</sub> S	w	0.31 (0.09)	0.56 (0.13)	63.35 (0.44)	36.25 (0.62)	100.48		Ni <sub>1-x</sub> S	w	0.06 (0.03)	1.44 (0.10)	62.63 (0.33)	36.73 (0.33)	100.86
SV711	"Cpr"	a	0.07 (0.02)	0.24 (0.06)	48.68 (0.47)	51.01 (0.50)	N=23		a	0.01 (0.01)	0.61 (0.04)	47.92 (0.25)	51.46 (0.22)	N=23	
		w	82.20 (0.81)	1.73 (0.46)	1.80 (0.16)	14.49 (0.43)	100.21	SV716	"Vsk"	w	0	68.48 (0.36)	7.35 (0.24)	24.66 (0.12)	100.49
	a	45.79 (0.87)	1.77 (0.48)	3.33 (0.27)	49.11 (0.91)	N=29	a	0		41.85 (0.18)	8.14 (0.25)	50.01 (0.16)	N=25		
	Ni <sub>1-x</sub> S	w	0.42 (0.10)	0.50 (0.11)	63.35 (0.87)	35.95 (0.65)	100.21		Ni <sub>1-x</sub> S	w	0	2.33 (0.17)	61.32 (0.71)	36.54 (0.16)	100.19
	a	0.10 (0.03)	0.21 (0.05)	48.89 (0.69)	50.80 (0.70)	N=21		a	0	0.99 (0.08)	47.35 (0.21)	51.66 (0.17)	N=4		

Compositions are quoted in weight % (w) and atom % (a). Values in parenthesis show the standard deviation at the 1 $\sigma$  level. Symbols: N: number of analyses carried out in each case; "Cpr": "cooperite", "Brg": "braggite", "Vsk": "vysotskite".

Between 1200° and 1000°C, the Ni content of "cooperite" increases with decreasing temperature at constant Pt contents of the "cooperite". The Ni content also increases with increasing Pt content at each temperature. In "cooperite" formed at 900°C, however, the Ni content decreases with increasing Pd content. In "cooperite" formed at 700°C, the Ni content is lower than that at 800°C, but still higher than that at 1000°C (Fig. 5).

Owing to this complex relationship between the Ni content and the temperature of synthesis of "cooperite", no mathematical model was derived to describe a relationship between the composition of phases and temperature. To estimate the temperature of formation or equilibration of cooperite from natural occurrences, Figure 5 may be used as an indicator. This method is, however, only applicable in areas of Figure 5 where there is no overlap of regression lines.

In "braggite-vysotskite", a higher Ni content indicates a lower temperature of equilibration (Fig. 6). In order to deduce a relationship between temperature of formation and composition of "braggite" and "vysotskite", all the compositions of "braggite" and "vysotskite" not coexisting with "cooperite" obtained in this study in a Ni-saturated environment between 1000° and 700°C were statistically evaluated. After testing various relationships between the temperature of formation of "braggite-vysotskite" and the Pt, Pd, and Ni content (using the temperature of formation as the dependent variable and Pt, Pd, and Ni content as independent variables) in a forward stepwise multiple-regression analysis, a quadratic relationship (eq. 1) led to the highest R<sup>2</sup> values, as presented in Table 4.

In Table 4, we show that the squared Ni content of "braggite" may be used alone in the prediction of the temperature of formation or equilibration. Adding either the squared Pt or the squared Pd content to the equa-

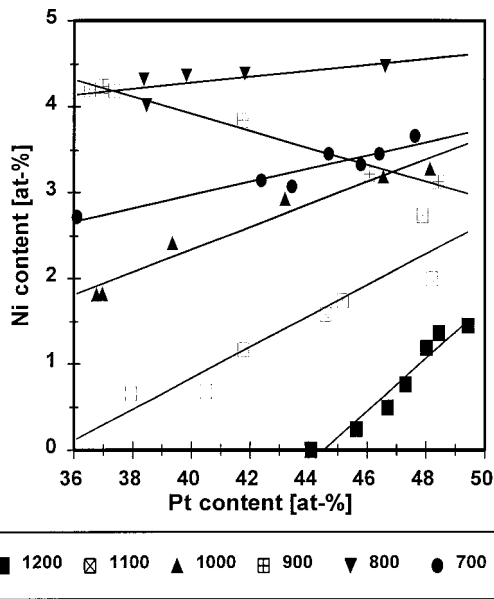


FIG. 5. Ni content versus Pt content in "cooperite" in at.% formed between 1200° and 700°C in a Ni-saturated environment. The solid lines show the best linear fits of the data for the various temperatures (°C) indicated in the legend.

tion improves the coefficient of determination slightly. Using the squared Pt and the squared Pd content together with the squared Ni content in an equation does not improve the R<sup>2</sup> value, as they complement each other. The equation (at the 95% confidence level) to express the incorporation of Ni and Pt (in at.%) in "braggite" is:

$$\text{Temperature [}^\circ\text{C]} = 998.07 (\pm 7.88) + 0.05 (\pm 0.02) \times \text{Pt}^2 - 4.24 (\pm 0.16) \times \text{Ni}^2 \quad (1)$$

The coefficient of determination using the Ni and Pt content (non-squared) in a linear equation is 0.9205. A

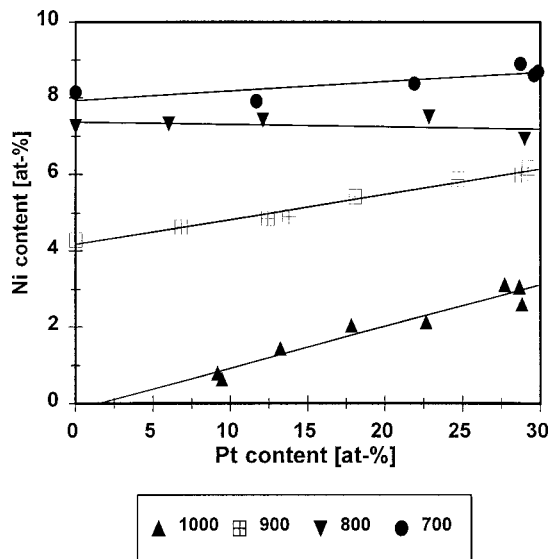


FIG. 6. Ni content *versus* Pt content in “braggite–vysotskite” in at.% formed between 1000° and 700°C in a Ni-saturated environment. The solid lines show the best linear fits of the data for the various temperatures (°C) indicated in the legend.

plot of the predicted temperature of formation *versus* the observed temperature of formation using the equation above is shown in Figure 7.

#### APPLICABILITY AND LIMITATIONS

We have shown that the solubilities of Ni in “cooperite”, “braggite”, and “vysotskite” are sensitive to temperature and the nature of coexisting phases. However, the Ni content in natural cooperite, braggite, and vysotskite also is considered to be a function of the activity of nickel sulfide in the system and, therefore, of the phase association in which these minerals occur. Estimations of temperature of formation or equilibration based on the experimental phase diagrams can be affected by the Ni:Fe ratio in the base-metal sulfide assemblage. Makovicky *et al.* (1990) and Makovicky &

TABLE 4. COEFFICIENT OF DETERMINATION ( $R^2$ ) AS A FUNCTION OF QUADRATIC VARIABLES USED IN A FORWARD STEPWISE MULTIPLE REGRESSION ANALYSIS WITH TEMPERATURE OF SYNTHESIS AS THE DEPENDENT VARIABLE

Variables in equation	$R^2$
$\text{Ni}^2$	0.9621
$\text{Ni}^2, \text{Pt}^2$	0.9753
$\text{Ni}^2, \text{Pd}^2$	0.9753
$\text{Ni}^2, \text{Pt}^2, \text{Pd}^2$	0.9753

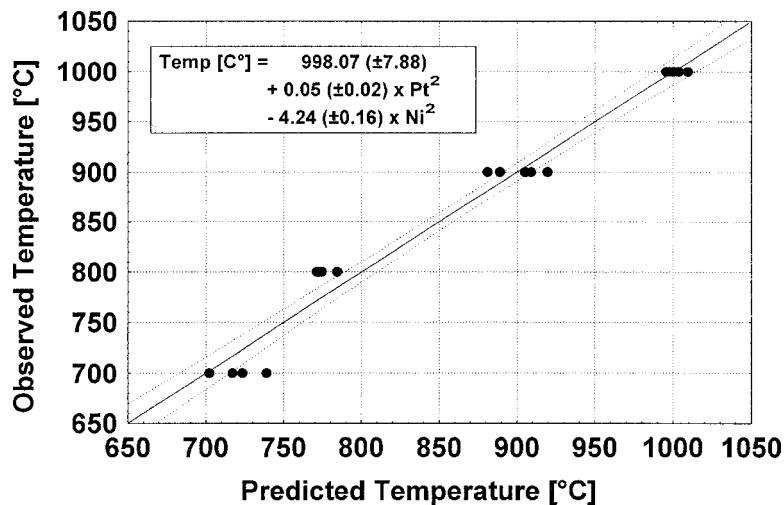


FIG. 7. Predicted *versus* observed temperature of synthesis (°C) for “braggite” and “vysotskite” not coexisting with “cooperite”, formed in a Ni-saturated environment between 1000° and 700°C, according to the quadratic equation shown. The solid line indicates the best fit, and the stippled line, the 95% confidence interval.

Karup-Møller (1995) showed experimentally that the Fe content in the monosulfide solid-solution and in the melt associated with "vysotskite" influences the maximum solubility of Ni in the "vysotskite". The higher the Fe content of the system at a constant temperature, the lower is the Ni content in the "vysotskite". The influence of other base metals like Co and Cu is not yet fully understood.

Assuming that the incorporation of Pt into PdS (*i.e.*, natural braggite) does not change the general observations in the behavior of Ni and Fe as discussed above, the following points concerning the applicability of our experimental results emerge:

(i) The temperature of formation or equilibration of cooperite occurring in a Ni-saturated environment can be estimated using Figure 5.

(ii) If there is saturation in Ni, the temperature of formation or equilibration of braggite and vysotskite can be estimated between 1000° and 700°C.

(iii) Temperatures of formation or equilibration of cooperite, braggite, and vysotskite formed in an environment saturated in Fe ± (Cu) ± (Co) cannot be estimated using the data produced in this study. The maximum Ni content in cooperite, braggite, and vysotskite may be lowered by the presence of Fe, as demonstrated by Makovicky & Karup-Møller (1995) and Makovicky *et al.* (1990). If no elements other than Ni and Fe play a role in the compositional variation, the estimated temperatures invariably give the maximum temperature of formation.

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