

## On cooperite, braggite, and vysotskite<sup>1</sup>

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### Abstract

Detailed mineralogical analyses of cooperite, braggite, and vysotskite, together with phase equilibrium studies, reveal that, though there is no uncertainty regarding the identity of cooperite (PtS;  $P4_2/mmc$ ), one may consider braggite (Pt,Pd)S and vysotskite PdS to be nickeloan members of an isomorphous solid-solution series (Pd,Pt)S ( $P4_2/m$ ). The results also suggest that this solid-solution series (braggite series) may be subdivided by restricting the name vysotskite to those members with less than about 10 mole percent PtS. Cooperite and braggite can both form at magmatic temperatures of 1000°C or above, but vysotskite is only formed at submagmatic temperatures, possibly by crystallization from a residual immiscible sulfide-rich melt or by solid-state reaction.

### Introduction

Cooperite, braggite, and vysotskite are the only Pt–Pd sulfide minerals with ideal compositions in the system Pt–Pd–S. Cooperite is ideally PtS, braggite (Pd,Pt)S, and vysotskite PdS. All analyses, however, report the presence of significant amounts of Ni, so mineralogically they must be considered as being in the system Pt–Pd–Ni–S. We aim to clarify the nomenclature and to present new data on the compositions of the minerals. It is a pleasure to be able to do so in the Frondel-Hurlbut issue of *The American Mineralogist*, because these two distinguished mineralogists have clarified so many similarly confusing issues in the nomenclature of minerals.

Braggite and cooperite are both important platinum-group minerals (PG-minerals) and are known from many areas of the world; in the great Merensky Reef deposits of the Bushveld Igneous Complex in the Transvaal they are major ore minerals. Vysotskite has not so far been found in sufficient quantities to be considered an important ore mineral. First discovered in the Noril'sk deposits of the USSR and reported by Genkin and Zvyagintsev (1962), vysotskite

has since been reported, but not documented in detail, from the Stillwater Complex of Montana (Cabri and Laflamme, 1974) and the Lac des Isles deposit, Ontario (Cabri and Laflamme, 1976).

In this note we report new data on all three minerals from the Precambrian Stillwater Complex of Montana. Page *et al.* (1976) discussed the variations of PG-elements in the different mafic and ultramafic layers of the complex. In the layers identified by Page *et al.* as the Banded and Upper Zones we have identified, for the first time, the three minerals in the same deposit. The three minerals have not been found in contact so it is probable that the assemblage does not represent equilibrium, and its true significance can only be guessed at.

### Previous mineralogical studies

#### *Cooperite*

Cooperite was discovered in samples from the Bushveld by Cooper (1928) and named by Wagner (1929) following a suggestion by a Mr. Wartenweiller in a published discussion following presentation of Cooper's paper. Bannister and Hey (1932) determined the mineral to be tetragonal with  $a = 4.91$  and

<sup>1</sup> Minerals Research Program, Processing Contribution No. 88.

$c = 6.10\text{\AA}$ . Though they recognized that this was a  $c$  face-centered cell and that the true primitive cell was  $a = 3.47$ ,  $c = 6.10\text{\AA}$ , space group  $P4_2/mmc$ , they nevertheless used the centered cell in order to emphasize the relationship to the unit cell of platinum. Berry and Thompson (1962) reported a unit cell with  $a = 3.48$  and  $c = 6.11\text{\AA}$ ,  $Z = 2$ , in close agreement with the primitive cell of Bannister and Hey. In their powder pattern, however, they observed but could not index three lines at 2.81(2), 1.765(6), and 1.397A( $1/2$ ) respectively. Genkin (1968), reporting on cooperite from two different locations in the Noril'sk area, presented two new powder patterns. Neither pattern included the two weak lines (2.81 and 1.397A) of Berry and Thompson, suggesting they were probably due to impurity admixtures in the Berry and Thompson sample. Both of the Noril'sk sample patterns contained the strongest line reported by Berry and Thompson, observed at 1.763 and 1.770A respectively, thus strongly suggesting that it belongs to the pattern. The solution to the problem becomes apparent from the work of Grønvold *et al.* (1960), who studied synthetic PtS, for which they obtained a cell with  $a = 3.4700$  and  $c = 6.1096\text{\AA}$ . The Grønvold powder pattern contains a strong reflection at 1.754A, which is indexed as (103).

Cooperite makes up a significant fraction of the PG-minerals present in areas of the Bushveld Complex where the Merensky Reef is mined [e.g. 13.36 volume percent average from four areas in the Western Transvaal, Vermaak and Hendriks (1976); 10.3 volume percent at the Western Platinum mine, Brynard *et al.* (1976); and 25 volume percent at the Atok Platinum mine, Schweltnus *et al.* (1976)]. In spite of the significance of cooperite in the Merensky Reef, the only published microprobe analyses are those of Schweltnus *et al.* (1976) and Brynard *et al.* (1976), together with a single analysis by A. M. Clark reported by Cabri (1972). The five cooperite analyses of Schweltnus *et al.* (1976) are from samples from the eastern Bushveld, and they reveal a range of composition for Pd (by weight) from 0.15 to 5.78 percent and for Ni from 0.68 to 1.18 percent; the analyses also reveal Pb (1.14 to 1.35 percent) and Bi (0.41 to 0.71 percent). Six analyses of cooperite from the western Bushveld by Brynard *et al.* (1976) have a narrower range for Pd from 0.5 to 1.5 percent, with Ni ranging from 0.6 to 1.6 percent and traces of Rh.

### Braggite

Braggite was named by Bannister and Hey (1932) for a tetragonal mineral with  $a = 6.37$ ,  $c = 6.58\text{\AA}$ ,

space group  $P4_2/m$ ,  $Z = 8$ , and a composition approximating "... (Pt,Pd,Ni)S containing about 20 percent Pd and 5 percent Ni..." Braggite is even more abundant than cooperite in some mines of the Bushveld Complex. It averages 35.9 volume percent of the PG-minerals from four areas in the Western Transvaal (Vermaak and Hendriks, 1976) and 60 volume percent at the Atok Platinum mine in the eastern Bushveld (Schweltnus *et al.*, 1976).

The crystal structure of braggite was determined by Childs and Hall (1973) on a sample from the Potgietersrust district, Transvaal. They reported cell parameters of  $a = 6.380(1)$ ,  $c = 6.570(1)\text{\AA}$ ,  $Z = 8$ . Childs and Hall also proposed that 2 Pd atoms were "... the minimum requirement in the formation of the PdS (braggite or vysotskite) structure rather than the PtS (cooperite) structure." However, four of the six braggite analyses reported by Schweltnus *et al.* (1976) have less than two atoms of Pd per cell, thus casting considerable doubt on the Childs and Hall suggestion.

### Vysotskite

In 1962, Genkin and Zvyagintsev reported the mineral vysotskite, for which they indicated the formula (Pd,Ni)S, though they did not consider Ni to be an essential constituent. They found the mineral to be tetragonal with  $a = 6.371$  and  $c = 6.540\text{\AA}$ , and the powder pattern was very similar to that reported for braggite. The powder pattern was also very similar to that of synthetic PdS, for which Gaskell (1937) had reported  $a = 6.43(2)$  and  $c = 6.63(2)\text{\AA}$ , space group  $P4_2/m$ ,  $Z = 8$ . These data suggested strongly that braggite and vysotskite were members of an isomorphous series of which PdS was the end-member composition.

### Phases in the system Pt-Pd-S

The ternary phase relations for Pt-Pd-S at 1000°C were reported by Skinner *et al.* (1976). Those at 800°C have now been completed and are reported in Figure 1. No solid phases more sulfur-rich than PtS or PdS appear, thus we can confine discussion to the phase-volume PtS-PdS-Pd-Pt. Four phases appear: a continuous alloy from Pt to Pd, a liquid field located on the Pd-PdS join, and two sulfides. The first sulfide is a solid solution identical with cooperite extending from PtS, along the composition join toward PdS, to (Pt<sub>0.70</sub>Pd<sub>0.30</sub>)S at 1000°C and (Pt<sub>0.54</sub>Pd<sub>0.46</sub>)S at 800°C. The second is a phase identical in properties to braggite. At 1000°C the braggite-like phase ranges in composition from (Pd<sub>0.40</sub>Pt<sub>0.60</sub>)S

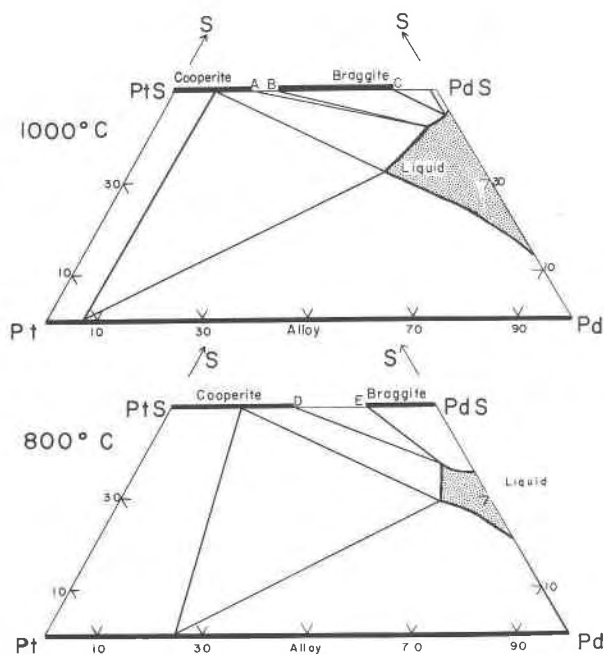


Fig. 1. Phase relations in the Pt-Pd-S system at 1000° and 800°C. The braggite solid solution at 800°C includes vysotskite. PtS: PdS, in atomic percent, for specific points are: A = 70:30; B = 60:40; C = 16:84; D = 54:46; E = 24:76.

to  $(\text{Pd}_{0.84}\text{Pt}_{0.16})\text{S}$ , but does not reach the composition PdS. PdS is stable below  $912 \pm 5^\circ\text{C}$ , and at 800°C the braggite-like solid solution ranges from PdS to  $(\text{Pd}_{0.76}\text{Pt}_{0.24})\text{S}$ .

Two conclusions can immediately be drawn from the synthesis studies. First, braggite and cooperite are not polymorphs, even though the Pd-rich limit of cooperite might slightly overlap the Pt-rich limit of braggite. Second, pure PdS, with powder patterns identical to vysotskite, is compositionally continuous with a phase identical in all X-ray properties with braggite. Clearly, therefore, the identity of braggite and vysotskite as minerals must rest on their composition ranges.

#### Analyses of PG-sulfide minerals

We had available to us samples of PG-minerals from the Stillwater Complex, the Rustenburg area of the Merensky Reef, Potgietersrust, and Lac des Isles. The Stillwater samples were collected in 1975 from the West Fork adit of the property worked by Johns-Manville Corporation (1, 2, 4) and supplemented by samples 5, 6 and 7 provided by the Corporation. Using local mine terminology, sample 1 came from the Bastard zone, which is a thin (2–6 in.) pyroxene

cumulate layer situated some 6 feet stratigraphically below the main olivine cumulate horizon (main marker) which contains large pyroxene oikocrysts; sample 2 came from the “dark anorthosite” which forms part of the ore horizon immediately above the main marker; and sample 4 came from an adjoining section of the same ore horizon, referred to as the “tri-colored anorthosite.” The three samples provided by the Corporation are located as follows: sample 5(1824-PP-20) is a sulfide concentrate milled and floated from a bulk sample taken from the West Fork adit. Sample 6(DDH 77-73-13) is from the Camp zone, located within the lower part of the Banded zone and 4.7 miles WNW along strike from the West Fork adit. Sample 7(789-T-1-1) is from a pyroxene cumulate layer in a trench in the southeast corner of claim Coors 8, located 6.5 miles WNW along strike from the adit.

The Lac des Isles vysotskite sample was discovered in a partly crushed drill core sample, P14-7, and the Rustenburg (MI9398) and Potgietersrust (MI9388) samples were PG-mineral concentrates from the Royal Ontario Museum collections.

The samples that needed crushing and concentration were processed as outlined by Cabri and Laflamme (1974). X-ray powder diffraction data were obtained by the film method using Gandolfi and Debye-Scherrer cameras. Film-shrinkage corrections were applied and the unit-cell parameters were refined by a least-squares computer program PARAM (Stewart *et al.*, 1972).

The compositions were determined using a Materials Analysis Company Model 400 electron probe microanalyzer, operated at 25 and 20 kV with a specimen current of about 0.03 microamperes. The following lines and synthetic standards were used:  $\text{PtL}\alpha(\text{Pt}_{0.7}\text{Pd}_{0.3}\text{S}$ ,  $\text{Pt}_2\text{Fe}$ ,  $\text{Pt}_3\text{Fe}$ ,  $\text{Pt}_5\text{Fe}_2$ );  $\text{PdL}\alpha(\text{Pt}_{0.7}\text{Pd}_{0.3}\text{S}$ , PdS, metal);  $\text{SK}\alpha(\text{Pt}_{0.7}\text{Pd}_{0.3}\text{S}$ , PdS);  $\text{CuK}\alpha(\text{Pt}_{1.0}\text{Fe}_{0.84}\text{Cu}_{0.16})$ ;  $\text{FeK}\alpha(\text{Pt}_3\text{Fe}$ ,  $\text{Pt}_5\text{Fe}_2$ ). Corrections to these X-ray data were applied with a modified version of the EMPADR VII computer program of Rucklidge and Gasparrini (1969).

#### Results

Fifty grains of Pt-Pd sulfides from the Stillwater samples were analyzed and the results are plotted in Figure 2. In addition, analyses of grains from the Rustenburg, Potgietersrust, and Lac des Isles samples are also plotted in Figure 2, together with analyses reported by Laputina and Genkin (1975), Brynard *et al.* (1976) and Schweltnus *et al.* (1976). Some analyses

are given in Table 1 while Table 2<sup>2</sup> lists all the analyses. A considerable number of grains were not homogeneous, especially grains of vysotskite and braggite. These are identified as filled circles with a HOM index >3 in Figure 2, and the range of variability between Pt and Pd, in particular, is demonstrated by the bars in Figure 3. A few grains were X-rayed to confirm identifications and to provide X-ray data.

It is apparent that cooperite approaches an ideal Ni-free composition more closely than do braggite and vysotskite, and no difficulty or uncertainty clouds its identity. From analyses to date, it appears that braggite and vysotskite contain a minimum of about 10 mole percent Ni replacing the other metals. The spread shown by these analyses, when plotted in the PdS–PtS–NiS composition triangle (Fig. 3), highlights the problem concerning the nomenclature of vysotskite–braggite.

Both braggite and vysotskite were named without specification of compositional ranges, prior to knowledge of phase relations in the Pt–Pd–S system, and prior to the extensive microprobe analyses now available from a wide range of samples. It has generally come to be accepted that braggite is (Pt,Pd,Ni)S (*P4<sub>2</sub>/m* space group), with a composition between the compositional end-members PdS and PtS. It is interesting to note, however, that the average composition

<sup>2</sup> A copy of Table 2 is available as Document AM-78-077 from the Business Office, Mineralogical Society of America, 1909 K Street N.W., Washington, D. C. 20006. Please remit \$1.00 in advance for the microfiche.

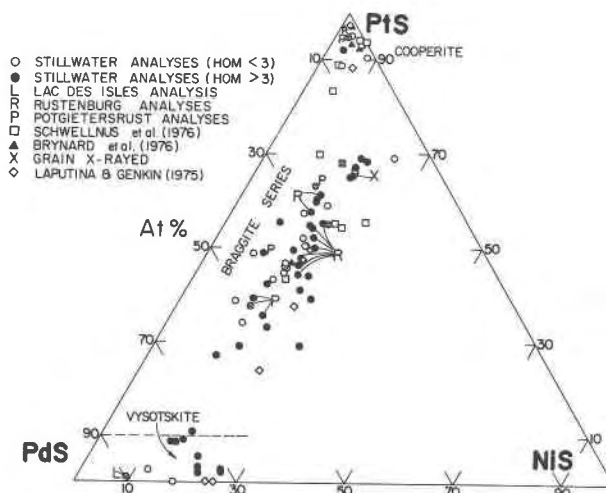


Fig. 2. Cooperite, braggite, and vysotskite analyses plotted in the PtS–PdS–NiS composition triangle.

from *in situ* analyses for 19 homogeneous grains is very close to that given by Bannister and Hey (1932). The data plotted in Figure 2, despite the uncertainties shown in Figure 3, do suggest compositional groupings which might be used to clarify the nomenclature of braggite and vysotskite.

Vysotskites are, as defined by Genkin and Zvyagintsev, (Pd,Ni)S compounds. All analyzed samples contain a small amount of Pt as well, but in naturally occurring samples a distinct break separates vysotskites from braggites (Fig. 2). Thus, vysotskites can be defined as all members of the braggite solid solution series containing less than 10 mole percent PtS.

Table 1. Electron probe analyses of cooperite, braggite, and vysotskite

	Weight percent				Total	Atomic proportions				
	Pt	Pd	Ni	S		Pt	Pd	Ni	ΣM	S
<b>Cooperite</b>										
High Pt	85.8	0.77	0.50	14.1	101.17	0.98	0.02	0.02	1.02	0.98
Low Pt	71.8	4.0	7.3	17.3	100.4	0.69	0.07	0.23	0.99	1.01
AVE(14 anal.)	83.5	1.4	1.2	14.5	100.6	0.94	0.03	0.04	1.01	0.99
Grain C*	83.5	1.4	0.64	14.2	99.74	0.96	0.03	0.02	1.01	0.99
<b>Braggite</b>										
High Pt	68.1	8.5	5.6	16.7	98.9	0.67	0.15	0.18	1.00	1.00
Low Pt	40.9	33.9	5.1	19.6	99.5	0.34	0.52	0.14	1.00	1.00
AVE(19 anal.)	56.4	20.3	5.1	18.2	100.0	0.51	0.34	0.15	1.00	1.00
Grain H*	64.6	13.5	3.9	17.1	99.1	0.63	0.24	0.12	0.99	1.01
<b>Vysotskite</b>										
High Pd (Gr. 6)*	2.0	69.5	3.9	23.7	99.1	0.01	0.89	0.09	0.99	1.01
Low Pd	4.3	65.7	5.3	23.7	99.0	0.03	0.84	0.12	0.99	1.01
AVE(3 anal.)	2.2	67.6	5.9	24.1	99.8	0.02	0.85	0.13	1.00	1.00

\*Grain X-rayed; Bi, Pb sought for but not detected. Analyses used in averaging had HOM ≤ 3.

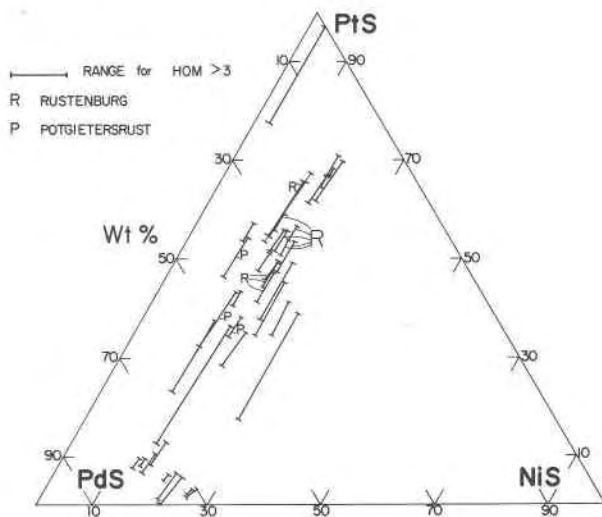


Fig. 3. Cooperite, braggite, and vysotskite analyses with HOM > 3 are plotted in the PtS-PdS-NiS composition triangle to show the range of inhomogeneity, mainly between Pt and Pd.

Braggite would then refer to all compounds in the series with a PtS content in excess of 10 mole percent.

The reason for two compositional groups in a continuous solid solution series is an interesting point, and a possible answer is suggested by the phase relations in Figure 1. Braggites formed at magmatic temperatures of 1000°C or above must all contain 16 mole percent PtS or more, because phases containing lower Pt contents are not stable (Skinner *et al.*, 1976). However, as temperatures decline, a sulfide melt can remain stable down to almost 600°C, and, as pointed out by Skinner *et al.* (1976), this melt probably plays an important role in the crystallization sequence of

PG-minerals. One of the phases that will crystallize from the cooling sulfide melt is a braggite-series mineral. As the temperature drops, the braggite mineral will be increasingly Pd-rich and will, in fact, fall in the vysotskite composition range. Thus, we suggest that most braggites are probably formed at high, magmatic temperatures, while all vysotskites are formed at sub-magmatic temperatures. Unless an early-formed braggite grain happens, by chance, to be adjacent to a late-formed vysotskite grain and thereby able to become homogenized, we should expect to observe separate compositional populations of braggite and vysotskite, even if the two should be found to coexist in the same rock.

#### Crystal chemistry

The cooperite X-ray powder diffraction pattern (Table 3) is free of the extraneous lines observed by some previous workers and is also the first X-ray pattern reported from an analyzed grain of cooperite. The braggite X-ray powder diffraction pattern (Table 4) has better resolution than the pattern listed in PDF 9-421 [*e.g.* the (102) and (210) reflections are resolved]. The vysotskite X-ray powder diffraction pattern is compared to that of Genkin and Zvyagintsev (1962) which has four bracketed unindexed reflections (Table 5), presumed to be beta. The considerably higher intensity for the (200) reflection for the Noril'sk sample is probably due to its enhancement by the beta for the (210). Unit cells and other physical data are listed in Table 6, the space group assignments for cooperite and vysotskite having been confirmed by single crystal examination with a precession camera in this study. The cooperite cell dimensions are very close to those reported by Grøn-vold *et al.* (1960) for synthetic PtS. Braggite cell dimensions compare favourably with those reported by Childs and Hall (1973) for a grain with a similar composition. Except for some differences in intensities, the powder pattern for vysotskite is the same as that reported for Genkin and Zvyagintsev's (1962) in PDF 15-151, though the calculated *c*-dimension in Table 6 is a little longer than that given by Genkin and Zvyagintsev. These data show that, while it is possible to distinguish cooperite from braggite, it is impossible to differentiate between braggite and vysotskite by X-ray methods, because substitution of Pt for Pd leads only to very small shifts in cell edges in the braggite-vysotskite cell structure.

Childs and Hall (1973) inferred the structure of braggite from Gaskell's (1937) determination of the structure of PdS. They tested five different configura-

Table 3. X-ray powder diffraction data of cooperite

<i>I</i>	<i>d</i> <sub>meas</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>	<i>I</i>	<i>d</i> <sub>meas</sub>	<i>d</i> <sub>calc</sub>	<i>hkl</i>
3	3.45	3.46	010	4	1.030	1.031	132
3	3.051	3.052	002	$\frac{1}{2}$	1.018	1.017	006
10	3.013	3.013	011	1	1.004	1.004	033
6	2.450	2.450	110	2	0.9592	0.9591	125
2	2.290	2.290	012	1	0.9557	0.9554	224
8	1.911	1.910	112	1	0.9496	0.9494	231
6	1.753	1.754	013	1	0.9397	0.9397	116
5	1.732	1.732	020	1	0.8901	0.8901	134
3	1.526	1.526	004	1	0.8771	0.8774	026
7	1.507	1.507	022	$\frac{1}{2}$	0.8691	0.8690	233
3	1.295	1.295	114	2	0.8664	0.8663	040
5	1.231	1.232	123	1	0.8456	0.8457	017
1	1.224	1.225	220	1	0.8390	0.8391	035
2	1.150	1.151	015	3	0.8327	0.8326	141
3	1.144	1.145	024	2	0.7893	0.7890	332
3	1.137	1.137	222	1	0.7828	0.7827	226
2	1.096	1.096	130	4	0.7770	0.7768	143
				4	0.7750	0.7749	240

114.6 mm Debye Scherrer camera, Ni-filtered Cu radiation,  $\lambda = 1.5405$ . ROM M 19388, gr. C in Table 1, from Potgietersrust.

Table 4. X-ray powder diffraction data of braggite

<i>I</i>	<i>d</i> meas	<i>d</i> calc	<i>hkl</i>	<i>I</i>	<i>d</i> meas	<i>d</i> calc	<i>hkl</i>
3	4.55	4.56	101	5	1.393	1.397	412
5	3.71	3.71	111	1	1.374	1.374	233
3	3.28	3.28	002	1	1.362	1.364	332
3	3.18	3.18	200	1	1.270	1.273	500
9	2.914	2.916	102	1	1.259	1.261	413
10	2.848	2.847	210	1	1.249	1.250	501
5	2.649	2.651	112	1	1.236	1.237	333
8	2.610	2.612	211	1	1.226	1.226	151
4	2.148	2.150	212	1	1.210	1.212	025
3	2.066	2.068	103	1	1.200	1.202	234
3	2.015	2.019	301	3B	1.191	1.191	125
7	1.921	1.924	311	3B	1.185	1.187	052
1	1.854	1.856	222	2B	1.165	1.167	152
4	1.799	1.802	203	3	1.141	1.142	044
3	1.780	1.782	302	2	1.124	1.124	144
4	1.764	1.766	230	3	1.094	1.093	006
5	1.731	1.735	213	1	1.085	1.084	153
6	1.714	1.716	312	1	1.079	1.078	106
1	1.705	1.705	231	3B	1.061	1.063	116
5	1.638	1.640	004	1B	1.052	1.053	235
3	1.589	1.591	400	1	1.045	1.047	061
5	1.542	1.544	410	1	1.039	1.040	253
2	1.499	1.500	330	4	1.033	1.034	026
1	1.479	1.481	133	1/2B	1.000	1.000	145
1	1.460	1.463	331	1	0.9874	0.9879	335
5	1.420	1.421	124	1	0.9643	0.9649	245

114.6 mm Debye Scherrer camera, Ni-filtered Cu radiation, λ = 1.5405; B = Broad. ROM M 19388, gr. H in Table 1, from Potgietersrust. Additional 23 reflections are not recorded.

tions of metal ordering for an ideal composition of Pt<sub>5</sub>Pd<sub>2</sub>NiS<sub>8</sub>. Their conclusions that a minimum of two Pd atoms were required, and that the Pd atoms preferentially occupy the 2(*d*) positions in space group P4<sub>2</sub>/*m* while Pt and Ni were disordered over the 2(*e*) and 4(*j*) positions, were made partly on the basis of crystallographic considerations (e.g. *R* values, isotropic temperature factors, etc.). The limited information available at the time of Childs and Hall's study on the compositional range of braggite had a bearing on the selection of the different ordering models tested. Our analytical results suggest that the proposals regarding the minimum number of Pd atoms and the exclusive replacement of Pt by Ni need to be re-examined. These proposals cannot both be true at the same time because the most Pt-rich compositions have formulae approximately (Pt,Ni)<sub>0.9</sub>Pd<sub>0.1</sub>S, resulting in only 0.8 Pd atoms per unit cell. If one assumes that all the Ni replaces Pd only, the resultant formula approximates Pt<sub>0.7</sub>(Pd,Ni)<sub>0.3</sub>S, corresponding very nicely to the Pt-rich limit found by Skinner *et al.* (1976) at 1000°C in the Pt-Pd-S system. It is, however, more likely that the formula for the Pt-rich limit of braggite may approximate (Pt,Ni)<sub>0.75</sub>(Pd,Ni)<sub>0.25</sub>S, a formula which would fit the analytical, phase equilibrium, and structural requirements for a minimum of 2 Pd atoms/unit cell. Though this possibility is attractive, Childs and Hall

point out that this would also require additional disordered replacement of the Pt positions by Pd. This can only be confirmed by further crystal structure investigation of different ordering models.

*Mineral associations*

Though the three minerals occur in the Stillwater samples, they were not observed to coexist. Cooperite Pt<sub>0.98</sub>Pd<sub>0.01</sub>Ni<sub>0.02</sub>S<sub>0.99</sub> and braggite Pd<sub>0.50</sub>Pt<sub>0.38</sub>Ni<sub>0.10</sub>S<sub>1.02</sub> were found coexisting in only one sample (No. 4). Cooperite and also braggite occurred as contiguous grains in the Rustenburg samples, but microanalyses revealed very little compositional variation in the coexisting mineral pairs, though the compositions of

Table 5. X-ray powder diffraction data of vysotskite

LAC DES ISLES*				NORIL'SK**			
<i>I</i>	<i>d</i> meas.	<i>d</i> calc.	<i>hkl</i>	<i>I</i>	<i>d</i> meas.	<i>d</i> calc.	<i>hkl</i>
			111	4	3.74	3.718	
<1	3.19	3.184	200	5	(3.22)		
				5***	3.16	3.194	
				2	(2.93)		
9	2.914	2.914	102	10	2.91	2.915	
10	2.846	2.848	210	10	2.86	2.851	
7	2.650	2.652	112	7	2.64	2.647	
8	2.612	2.612	211	8	2.61	2.617	
				2	(2.39)		
6	2.150	2.150	212	6	2.15	2.148	
				3	(2.06)		
3	2.020	2.020	301	3	2.02	2.021	
7	1.857	1.856	222	7	1.859	1.855	
2	1.804	1.803	203	4	1.801	1.801	
1	1.782	1.782	302	3	1.781	1.782	
2	1.765	1.766	230	3	1.766	1.768	
3	1.736	1.735	213	6	1.732	1.731	
5	1.716	1.716	312	8	1.717	1.716	
6	1.640	1.641	004	5	1.636	1.635	
5	1.593	1.592	400	4	1.594	1.594	
1	1.544	1.544	410	3	1.543	1.546	
1/2	1.523	1.523	033	2	1.509	1.505	
1	1.463	1.463	331	2	1.463	1.466	
4	1.422	1.422	124	6	1.419	1.418	
5	1.397	1.397	412	6	1.396	1.397	
			323	1	1.374	1.373	
1/2	1.274	1.274	500	3	1.273	1.275	
1/2	1.260	1.262	413	2	1.260	1.261	
1	1.250	1.250	501	2	1.252	1.252	
1	1.238	1.238	333	2	1.237	1.237	
			511	2	1.227	1.228	
1	1.213	1.213	025	3	1.209	1.209	
2	1.202	1.202	234	4	1.198	1.200	
4	1.187	1.187	052	8	1.185	1.187	
3	1.165	1.167	152	3	1.165	1.167	
7	1.142	1.142	044	7	1.138	1.141	
6	1.124	1.124	144	6	1.121	1.123	
1	1.115	1.116	035	2	1.111	1.113	
1	1.100	1.101	053	2	1.098	1.100	
2B <sup>†</sup>	1.094	1.094	006	3	1.088	1.089	
1	1.083	1.084	153	3	1.080	1.084	
			106	6	1.071	1.074	
6	1.064	1.063	116	3	1.058	1.059	
3	1.046	1.047	061	3	1.047	1.049	
			610	3	1.044	1.048	
6B	1.040	1.040	253				
			611	9	1.031	1.034	
1	1.021	1.021	126	2	1.015	1.017	
1	1.013	1.012	045				
			620	4	1.006	1.008	
4B	1.001	1.001	145	2	1.001 <sup>††</sup>	1.005	
			540	5	0.993	0.990	
2B	0.9878	0.9880	335				

\*Sample P14-7, gr. 6, 57.3 mm Gandolfi, Mn-filtered Fe radiation, λ = 1.93597  
 \*\*Genkin & Zvyagintsev (1962), Fe radiation, 57.3 mm camera. \*\*\*Probably enhanced by beta contribution of (210)  
 †Broad, ††Published as (504)

Table 6. Physical data for the Pt-Pd sulfide minerals

Mineral	Composition	Space Group	Cell Dimensions Å		Cell vol. Å <sup>3</sup>		Z	V/Z	Dx gcm <sup>-3</sup>
			a	c	Å <sup>3</sup>	Å <sup>3</sup>			
cooperite <sup>1</sup>	Pt <sub>0.96</sub> Pd <sub>0.03</sub> Ni <sub>0.02</sub> S <sub>0.99</sub>	P4 <sub>2</sub> /mmc	3.465(3)	6.104(3)	73.286	2	36.643	10.123	
braggite <sup>2</sup>	Pt <sub>0.63</sub> Pd <sub>0.24</sub> Ni <sub>0.12</sub> S <sub>1.01</sub>	P4 <sub>2</sub> /m	6.367(3)	6.561(6)	265.974	8	33.246	9.383	
vysotskite <sup>3</sup>	Pd <sub>0.89</sub> Pt <sub>0.01</sub> Ni <sub>0.09</sub> S <sub>1.01</sub>	P4 <sub>2</sub> /m	6.368(3)	6.562(3)	266.098	8	33.262	6.705	

1. Potgietersrust, ROM M19388, gr.C; 2. Potgietersrust, ROM M19388, gr.H; 3. Lac des Isles, P14-7, gr.6.

the braggites were significantly different to the Stillwater sample. Cooperite ranged from Pt<sub>0.97</sub>Pd<sub>0.02</sub>Ni<sub>0.02</sub>S<sub>0.99</sub> to Pt<sub>0.98</sub>Pd<sub>0.01</sub>Ni<sub>0.02</sub>S<sub>0.99</sub> and braggite from Pt<sub>0.50</sub>Pd<sub>0.34</sub>Ni<sub>0.15</sub>S<sub>1.01</sub> to Pt<sub>0.57</sub>Pd<sub>0.28</sub>Ni<sub>0.14</sub>S<sub>1.01</sub>. The significance of this cannot be assessed without further detailed sampling and mineralogical studies.

The occurrence of Pt-Fe alloy with cooperite or braggite was not uncommon in the Stillwater samples. These assemblages were further examined because Skinner *et al.* (1976) found that cooperite + isoferroplatinum + pyrrhotite was a stable assemblage in the Pt-Fe-S ternary at 1000°C. The Pt-Fe alloy grains coexisting with cooperite and braggite (Figs. 4, 5) were analyzed and, in all cases, were found to have compositions within the isoferroplatinum field reported by Cabri and Feather (1975), in good agreement with the synthetic work of Skinner *et al.* (1976). Typical compositions ranged from Pt<sub>2.92</sub>(Fe<sub>1.05</sub>Ni<sub>0.02</sub>Cu<sub>0.01</sub>) to Pt<sub>2.76</sub>Pd<sub>0.07</sub>(Fe<sub>1.09</sub>Ni<sub>0.06</sub>Cu<sub>0.02</sub>). The fifteen grains analyzed were too small (from less than 5 × 5 μm to about 30 × 80 μm) to extract for X-ray diffraction in order to determine whether the Pt-Fe alloy was primitive cubic isoferroplatinum or face-centered cubic ferroan platinum.

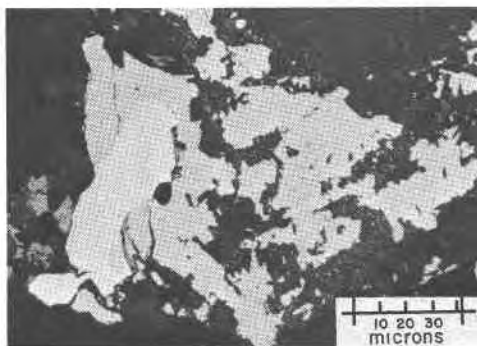


Fig. 4. Pt-Fe alloy inclusion (white) in braggite (light grey)-silicate intergrowth. The 10 μm long inclusion in Pt-Fe is pentlandite. Sample 1824-PP-20, Stillwater Complex.

## Conclusions

The composition ranges and mineral assemblages of the PG-sulfide minerals agree reasonably well with data obtained from equilibrium phase studies. The data suggest that in layered intrusive rocks, both cooperite and braggite can be formed at magmatic temperatures of 1000°C or above, while vysotskite is only formed at sub-magmatic temperatures and probably arises by crystallization from a residual immiscible sulfide-rich melt that separated from the parent magma.

We conclude that Ni is not an essential element in the formation of cooperite, braggite, or vysotskite, because each of the phases can be prepared, Ni-free, in the laboratory. Presumably the high Ni-contents reflect the origin of the three minerals as phases formed in mafic or ultramafic igneous rocks rich in Ni. Should any of the minerals be formed in other kinds of geological environments, where Ni was not readily available or was already tied up in other minerals and removed from reaction, we suggest that Ni-free or at least Ni-poor braggite, vysotskite, and cooperite could be expected.

Finally, we conclude that braggite and vysotskite are simply compositional variants of the same phase,

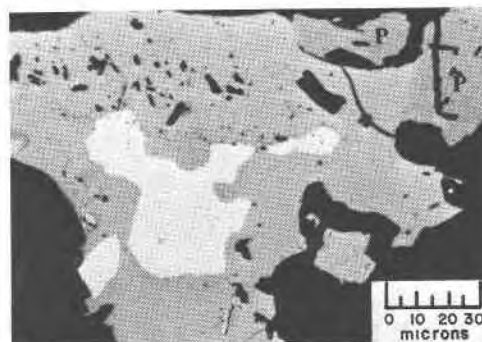


Fig. 5. Pt-Fe alloy included in braggite coexisting with pyrrhotite (upper right, P). Sample 2, Stillwater Complex.

(Pd,Pt,Ni)S, of which the end-member composition, PdS, has not been found in nature. We suggest that the family of minerals be called the braggite series and that all compositions containing less than 10 mole percent PtS be called vysotskite.

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